Center for
Materials Science

Inorganic Materials Division

Technical Activities 1984

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Materials Science

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Dr. Thomas D. Coyle, Chief
Mr. Samuel J. Schneider,
Deputy Chief

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INORGANIC MATERIALS DIVISION

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ABSTRACT

This report is a summary of the 1984 research activities of the Inorganic Materials Division, Center for Materials Science, National Bureau of Standards. It includes descriptive information on the work (in progress) carried out through the five technical tasks of the Division:

High Temperature Materials Chemistry for Processing and Durability

Ceramic Processing and Characterization

Glass and Optical Materials

Materials Processing and Durability Chemistry

Mechanical Properties of Ceramics

It also provides auxiliary information important to Division research such as recent publications and invited talks, professional/standard committee activities, and industrial/academic interactions.

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INTRODUCTION

INORGANIC MATERIALS DIVISION (420)

Thomas D. Coyle, Chief
Samuel J. Schneider, Deputy Chief
Lillian L. Ware, Secretary
Mary J. Nestor, Secretary

The mission of the Inorganic Materials Division is to provide industry, government agencies, and scientific organizations with data, measurement methods, standards, reference materials, and fundamental concepts related to the processing, structure, chemistry, physical properties, and performance of ceramics, glasses, and other inorganic materials. The Division pursues studies of inorganic materials to foster their safe, efficient, and economical use, and to address national concerns for productivity, critical materials, and environmental quality.

Advanced ceramic materials currently account for a four billion dollar market worldwide in electronic, dielectric, structural, and other applications. Prospective new applications such as ceramic components for high-temperature, fuel-efficient heat engines offer the prospect of greatly expanded market opportunities for the US ceramic industry. The major roadblocks to expanded high-technology applications of advanced ceramic materials are their inherently brittle nature and the inability of current technology to produce consistently defect-free ceramic components with acceptable service life and reproducible properties. The key to improved reliability of ceramics is the elimination of property limiting microstructural defects, and the approach to defect-free microstructure is improved understanding and control of processing.

During Fiscal Year 1984, the Inorganic Materials Division emphasized research underlying ceramic processing and performance in response to the needs of industry and other government agencies for basic data and concepts supporting advanced ceramics technology. New or expanded programs have been developed in ceramic phase diagrams, ceramic powder processing, characterization of microstructure evolution during processing, non-destructive evaluation of green state ceramics, and the mechanical properties of ceramics under service conditions. In addition, the Division has maintained programs in other areas of materials processing and performance, including unique activities in biocorrosion and bioprocessing of materials and high temperature friction and wear of advanced ceramic materials.

Critically evaluated reference data required for processing and use of inorganic materials is an important Division output. The Phase Diagrams for Ceramists Data Center compiles, evaluates, and disseminates ceramic phase diagrams in close cooperation with the American Ceramic Society (ACerS). Under a recently-concluded formal agreement between NBS and ACerS, these organizations work jointly, under NBS technical leadership, to provide timely evaluated phase diagram information to the ceramic community. The Division emphasizes work on phase diagram modeling, improved thermochemical evaluation techniques for phase diagrams, and the development of a computerized ceramic phase diagram data base. ACerS has initiated a major development program to generate support from industry to improve the scope and currency of phase diagram compilations and to provide expanded phase diagram dissemination services such as on-line availability of phase diagram information. This program is closely integrated with the activities of the NBS/American Society for Metals Alloy Phase Diagram Data Center to ensure efficient use of resources in areas of common concern such as the development of computer graphics.

A somewhat similar cooperative program with the Joint Committee on Powder Diffraction Standards/International Centre for Diffraction Data (JCPDS/ICDD) provides standard x-ray powder patterns and develops new methods for quantitative x-ray diffraction analysis, profile analysis, and powder characterization. Under this program, a nine-person group of Research Associates, supported by JCPDS/ICDD, works at NBS under the technical direction of a Division staff member, to provide this standard x-ray data.

Other joint activities with the private sector take the form of Research Associate or Guest Worker programs as well as individual scientific collaborations. These provide for continuing interchange with industry and for effective transfer of NBS-developed measurement methodology and may be illustrated by the following examples: A Research Associate program has been established with Cummins Engines for high-temperature mechanical properties evaluations of structural ceramics; a similar program with Mobil Oil has led to development of methods to identify and measure arsenic compounds in shale oil, critical to protecting process catalysts in this area of synthetic fuel technology. A cooperative program with Bell Laboratories and the Reactor Division is investigating the structural chemistry characteristics of fast ion conductor materials. A program with Bell Laboratories and Alpha Industries is studying process-property relationships in microwave dielectric ceramics. We are collaborating with manufacturers such as Cummins Engines and General Motors to evaluate the friction and wear properties of ceramics for advanced heat engine applications. Cooperative programs involving more than a dozen companies in the petroleum industry have established a basis for quality control assessments of lubricants and their oxidation stability.

The Division also maintains strong contacts with the academic community. It is closely associated with the recently established industry-academic ceramic processing centers at MIT and Rutgers University and funds selected research programs such as a project at the University of Maryland in sol-gel process chemistry. Distinguished faculty members from MIT, Ohio State, Northwestern, and the University of Minnesota have spent varying periods of time working in the Division's laboratories during the past year.

Joint programs with other government agencies provide data and measurement methods required by those agencies in support of their mission. Our ceramics programs provide data on the chemical, mechanical, and tribological performance of structural ceramics for the Department of Energy, and phase equilibria data related to high energy propulsion systems for the Department of Defense. The Mechanical Properties Group assists the Department of Defense by developing methods to predict performance of advanced ceramics in heat engine applications, and by providing data on contact damage and environmental effects on crack growth in ceramics. Our Glass group provides tailored glasses and optical data for DOE applications in laser fusion research and data to support DoD needs for thin-film optical materials. Other research programs are supporting a major development of new antifoulant coating technology by the Navy and providing to the US Postal Service a detailed understanding of the mechanisms of stamp phosphor deterioration.

The development and production of Standard Reference Materials (SRM) and Reference Materials (RM) is another major Division activity. Overall, the Division has responsibility for over 100 different SRMs and RMs. These cover a diverse variety and include standards for qualitative and quantitative x-ray diffraction analysis, property standards for control of processing in the glass industry, and compositional standards for particulate and surface analysis. Currently, some 25 new SRMs are under development to meet new and demonstrated user needs in areas such as particle size measurements, glass property determinations, compositional analysis, and lubricant chemical characterization.

The research activities of the Division, and its recent accomplishments, are described in the following pages. For management purposes, the technical program is divided into five task areas, as follows:

Task 15415—HIGH TEMPERATURE MATERIALS CHEMISTRY FOR PROCESSING AND DURABILITY. Investigates the thermodynamic and kinetic behavior of materials in high-temperature/high-pressure (gaseous) process and service environments. Phase equilibria of ceramic and glass systems are determined through modeling and experiment. The Phase Diagrams for Ceramists Data Center, included in this task, compiles and evaluates ceramic phase diagrams in cooperation with the American Ceramic Society.

Task 15416—CERAMIC PROCESSING AND CHARACTERIZATION. Investigates chemical and physical processes important to producing reliable and durable ceramic materials. Emphasis is given to establishing the controlling parameters affecting microstructure and property evolution at all stages of the ceramic processing cycle from powders to fully densified bodies. Activities include advanced powder synthesis techniques, powder and compact characterization, and structural chemistry of ceramic materials. X-ray SRMs and standard powder patterns, developed in cooperation with JCPDS/ICDD, are produced in this task.

Task 15417—GLASS AND OPTICAL MATERIALS. Investigates processes involved in synthesis, forming, and uses of glasses and optical materials, including thin films. Activities include development of SRMs needed by the glass industry and others, such as those for viscosity, resistivity, dielectric constant, thermal expansion, and chemical composition; optical properties of glass; and process structure-property relationships in thin films of glasses and ceramics.

Task 15418—MATERIALS PROCESSING AND DURABILITY CHEMISTRY. Investigates chemically and biologically mediated processes affecting processing and durability of inorganic materials. Activities currently include research in microbial corrosion of metals, bioprocessing of metals, and combined chemical and mechanical factors in friction and wear, including the tribology of high-performance ceramics.

Task 15419--MECHANICAL PROPERTIES OF CERAMICS. Investigates processes affecting the structural reliability and performance of ceramics and glass at ambient and high temperatures and in aggressive environments. Theoretical and experimental work is directed to understanding of fracture and deformation mechanisms and their relationships to microstructure.

RESEARCH STAFF

Blackburn, Douglas H.	•Special glass formulations •Glass processing •Glass standards for microprobe analysis
Blair, William R.	•Ultratrace metals speciation •Biotransformations of metals •Environmental durability of coatings
Blendell, John	•Ceramic processing •Sintering •Diffusion controlled processes •Activation analysis
Block, Stanley	•Properties, structure and polymorphism of materials at pressure •Ultra high pressure properties •Crystallography and pressure phase relations of ceramics •Generation/measurement of high pressures
Bonnell, David W.	•High temperature-pressure mass spectrometry •Computer modeling •Vapor transport •Levitation calorimetry
Brinckman, Frederick E.	•Environmental metal transport •Materials durability (predictors) •Organometallic chemistry •Biological mediation of surface chemistry •Ultratrace metal speciation
Burton, Benjamin	•Calculation of phase diagrams
Cellarosi, Mario J.	•Glass SRM development •Glass standards for manufacture and use •Glass property measurements
Chuang, Tze-Jer	•Ceramics •Diffusional crack growth •Finite element analysis •Creep theory
Chuck, Leon	•High temperature mechanics •Scanning electron microscopy •Acoustic monitoring of cracks

Coblenz, William S.	●Ceramic processing ●Sintering (theory and experiment) ●Covalently bonded ceramics ●Sol-gel chemistry
Cook, Lawrence P.	●Phase equilibria of ceramics (modeling & experiment) ●Phase diagrams for ceramists (data center) ●Electron microscopy ●Thermodynamics
Coyle, Thomas D.	●Inorganic and organometallic chemistry ●Chemistry of materials processing and durability ●Organometallic chemistry of ceramic precursor materials
Dragoo, Alan L.	●Chemical bonds in solids ●Corrosion of structural ceramics ●Ceramic powder synthesis ●Covalent ceramics
Farabaugh, Edward N.	●Thin film deposition and analysis ●X-ray diffraction analysis ●Scanning electron microscopy ●Surface analysis
Feldman, Albert	●Optical materials ●Thin films ●Solid state physics ●Photoelasticity and thermo-optics ●Guided waves
Frase, Katharine G.	●Ionic conductivity ●Ceramic powder synthesis and processing ●Neutron scattering
Frederikse, Hans	●Electrical and mass transport in solids ●Electrical conductivity ●Depth profiling (Rutherford backscattering)
Freiman, Stephen W.	●Ceramics and glasses ●Fracture mechanics ●Mechanical properties, environmental effects
Fuller, Edwin R.	●Atomistic models of fracture ●Fracture mechanics of ceramics ●Fracture, environment-assisted ●Mechanical properties at high temperature ●Nondestructive evaluation

Gates, Richard	•Friction and wear of materials •Wear mechanisms and analysis •Engine condition monitoring •Ferrography
Grabner, Ludwig H.	•Optical properties •Testing and Measurements •Spectroscopy
Haller, Wolfgang K.	•Glass properties, manufacture and use •Structure of glass •Sol-Gel processes •Fine (small) particles
Hastie, John W.	•High temperature chemistry of ceramics •Ceramic phase equilibria, solution models •High temperature-pressure mass spectrometry •Chemistry of combustion
Hockey, Bernard	•Ceramics •Deformation and wear •Scanning and transmission electron microscopy
Hsu, Stephen M.	•Tribology •Oxidation mechanisms of organic mixtures •Lubrication and wear mechanisms •Molecular structural effects on friction •High temperature ceramic wear
Hubbard, Camden R.	•Crystallite size and residual stress •Quantitative x-ray diffraction methods •X-ray diffraction standard reference materials •Reference powder patterns (JCPDS Research Associateship)
Iverson, Warren P.	•Biocorrosion of metals •Microbial extraction/uptake of metals •Ceramic and stone biodeterioration
Jewett, Kenneth L.	•Organometallic speciation •Oxidation kinetics •Analysis of organic mixtures •SRM research
Krause, Ralph J.	•Chemical equilibria •High pressure-high temperature testing •Vapor pressure measurements •Refractories

Ku, Chia-Soon	●Oxidation kinetics ●Friction and wear test development ●Modeling of reaction systems
Lawn, Brian R.	●Structural reliability ●Fracture mechanics ●Contact phenomena ●Erosion and wear
Lockhart, Thomas	●Highfield NMR (multinuclear) ●Organometallic transformations ●Metal centered materials reactions (rates and pathways)
McDaniel, Clyde	●Ceramics ●Creep ●X-ray diffraction
Millet, Jean Marc	●Phase equilibria ●Ceramic powder synthesis ●Sol-gel processes
Minor, Dennis B.	●Ceramic composites ●High temperature ceramic synthesis ●Analytical SEM of ceramics
Munro, Ronald G.	●Theory and modeling ●Tribology ●Molecular dynamics of phase stability ●Temperature modeling of ceramic pairs
Olson, Gregory	●Metals biotransformation ●Bioprocessing industrial materials ●Epifluorescence microscopy imaging ●Surface modification and bioadhesion
Ondik, Helen M.	●Phase diagrams for ceramists data center ●Materials properties for coal conversion ●Data compilation systems
Parks, Edwin J.	●Macromolecular organometallic chemistry ●Bioactive polymers ●Ultratrace metal speciation ●Controlled-release polymers ●Metallo-organic synthesis
Pei, Patrick	●Separation of complex organic mixtures ●Trace organic compound identification ●Differential scanning calorimetry
Perloff, Alvin	●XRD standard reference materials ●Processing of ceramic powders ●X-ray structural analysis

Piermarini, Gasper J.	●Pressure/temperature effects on ceramic materials ●Generation/measurement of high pressures ●Physical and structural properties of materials at high pressures and temperatures ●X-ray diffraction, phase relations, optical measurements
Plante, Ernest R.	●High temperature chemistry of ceramics ●Knudsen effusion mass spectrometry ●Vaporization thermodynamics
Rhyne, Kay V.	●Ceramics ●Small angle neutron scattering ●Nondestructive analysis
Ritter, Joseph J.	●Synthetic inorganic chemistry ●Ceramic powders from organometallic precursors ●Ceramic powders from gas phase, solution and precipitation reactions
Robbins, Carl R.	●Fine ceramic particulate properties and characterization ●Spray drying; powder preparation ●Quantitative microscopy and x-ray diffraction ●NDE of ceramics
Roberts, D. Ellis	●Mechanical testing ●Erosion and wear
Roth, Robert S.	●Crystal chemistry of ceramic materials ●Phase equilibria ●Dielectric and ionic conducting ceramics ●Phase diagrams for ceramists data center
Sanders, David M.	●Thin film production, characterization, and properties ●Amorphous and crystalline inorganic films ●Glass vapor pressure ●Diffusion
Schenck, Peter K.	●Laser spectroscopy ●Temperature measurement ●Computer graphics
Schneider, Samuel J.	●Ceramic processing ●Structural ceramics and composites ●Phase equilibria ●High temperature measurements ●Ceramics for energy applications

Tighe, Nancy J.	●Ceramics ●Creep at high temperatures ●Mechanical properties, high temperature ●Scanning and transmission electron microscopy
White, Grady S.	●Ceramics and glass ●Nondestructive evaluation ●Subcritical crack growth
Wiederhorn, Sheldon M.	●Ceramics ●Erosion ●Fracture processes ●Mechanical properties at high temperature and pressures

TECHNICAL ACTIVITIES

HIGH TEMPERATURE MATERIALS CHEMISTRY FOR PROCESSING AND DURABILITY
Task 15415

New technologies, such as those based on materials processing, refractory materials durability, nuclear waste management, and more efficient fossil fuel combustion require for process optimization, monitoring, and test method development, a quantitative understanding of high temperature phase equilibria and chemical reaction pathways. The objective of this task is to provide a general high temperature chemistry measurement science base for advanced/substitute/conventional materials processing (e.g., ceramic, glass, steel) and service behavior in extreme environments (e.g., hot corrosion, slagging, and defense applications). This objective is accomplished through: development of new or improved experimental methods, their application to determination of basic data and new concepts, modeling of ceramic/metal gas-liquid-solid equilibria, and critical evaluation and compilation of ceramic phase equilibrium diagrams. The latter activity results in the periodic publication of Phase Diagrams for Ceramists (PDFC). These volumes currently emphasize systems containing oxides, sulfides, sulfates, halides, C- and N- containing compounds, and involve solid, liquid, and gaseous species. Future volumes will, in addition, include compound semi-conductors, nitrides, borides and carbides; thus providing a comprehensive coverage of all non-metallic ceramic/inorganic systems.

Molecular-specific experimental methodologies and theoretical modeling tools are being developed and applied to the determination of basic thermochemical and kinetic data and chemical mechanisms for interactions of ceramics, and glasses with aggressive gaseous high temperature processing and service environments. These methods primarily emphasize the identification of molecular species, together with accurate measurement and model predictions of their concentration, spatial, and temporal distribution in high temperature vapors and gases, and in the presence of complex solid or liquid phases. The related *in situ* measurement problems of temperature and flow (gas phase) are also addressed by this task. In support of phase diagram determinations, and for completion of thermodynamic cycles in gas-solid-liquid equilibria, the characterization of condensed phase composition and structure is achieved by x-ray diffraction, electron microscopy, and electron spectroscopy for chemical analysis (ESCA). The work of this task is described here under five subtasks: (1) Phase Diagrams for Ceramists Data Center; (2) Vapor Transport Thermochemistry; (3) Characterization of High Temperature Gaseous Environments in Processing and Service; (4) Data Center on Materials and Components for Fossil Energy Applications; and (5) High Temperature Thermophysical Properties.

The results of this work are used by industry and other government agencies for (a) performance predictions and test method development in new high technology applications such as coal-combustion and conversion and advanced propulsion systems, and (b) to support materials processing at high temperatures including chemical vapor deposited coatings, and ceramic, glass, and metals processing. In addition to base program support, the task addresses other NBS program and other agency needs, including those of the Office of Standard Reference Data (OSRD) and Department of Energy (phase diagram evaluation/compilation), Army Research Office (ARO) (alkali chemistry in flames), NASA (levitation calorimetry of liquid tungsten), DuPont-DOE Savannah River (vaporization of nuclear waste glass), Office of Naval Research (ONR) (phase equilibria for stored chemical energy propulsion), Bell Laboratories (glass optical fiber processing), Air Force Office of Scientific Research (AFOSR) (laser-materials interaction mechanisms), Defense Nuclear Agency (DNA) (boron nitride-composite vaporization), and DOE-Laramie (data book on materials for fossil energy). An expanded effort in the Phase Diagrams for Ceramists activity is expected in FY85 with new support (Research Associates) arising from the American Ceramic Society (ACerS) through Industrial-Government sources.

FY84 Significant Accomplishments:

- In preparation for the NBS-ACerS five year expansion program for a ceramic phase diagram data center, novel procedures were developed and implemented for computer storage and retrieval of bibliographic files (in collaboration with C. Messina, OSRD) and for diagram digitization, computer editing, topographical manipulation and preparation of production-quality ceramic phase diagrams.

- Three books were published: Vol V of "Phase Diagrams for Ceramists", containing critically evaluated halide, sulfide, oxynitride, aqueous, and ceramic-gas systems; a cumulative index of phase diagrams published in vols I-V; and a supplemental volume on "Construction Materials for Coal Conversion--Performance and Properties Data". The former two publications represent a major output of the NBS-ACerS Ceramic Phase Diagram data center and the latter was sponsored by DOE and represents an evaluated compilation of data provided by DOE materials research contractor's reports.

- New phase equilibria models were developed and applied to high-order oxide systems and binary alkali halide mixtures. For oxide systems, the model is predictive, requiring no prior phase diagram or thermodynamic mixing data. The model has been validated for systems containing solids and liquids of Li_2O, Na_2O, K_2O, CaO, MgO, Al_2O_3, FeO, Fe_2O_3, Fe_3O_4 and SiO_2. For halide mixtures, A. Pelton of McGill Univ. has applied a coupled thermodynamic data--phase diagram analysis to the optimization of existing binary phase diagrams.

- New phase equilibria data were obtained for the Li_2O-Al_2O_3 system which is important in chemical propulsion systems. Experimentally this is a very difficult system to determine owing to the high melting temperatures, reactivity with container materials, and slow equilibration kinetics. The multifaceted experimental and modeling approach used classical (DTA/TGA/X-Ray diffraction) phase equilibria methods in addition to Knudsen effusion mass spectrometry and the predictive multicomponent solution mixing model.

- A new experimental technique was developed, laser-induced vaporization mass spectrometry, for determination of time-resolved molecular-level mechanisms of very high temperature, (> 4300°C) high pressure (> 1 atm) vapor plume formation from refractory materials.

The method was applied to graphite and BN refractory materials, providing new mechanistic details on the vaporization kinetics of these materials.

- Existing rules and approximations for converting raw mass spectral ion intensities to absolute concentration (partial pressure) data were critically tested and found to be seriously inaccurate. In particular, the cardinal assumption of ionization cross section (σ)--temperature independence was found to be unreliable. Also, σ-additivity and energy-scaling approximations were found to be less accurate than previously believed. During the past year, members of this task group have played a lead role in conducting a national (AAMS) workshop and initiating an international (IUPAC) study on these problems.

Phase Diagrams for Ceramists Data Center
Subtask 1 of Task 15415

J. W. Hastie, L. P. Cook, H. M. Ondik, M. A. Clevinger, D. McKenna, M. Lukens, P. K. Schenck and R. Roth

NBS has a well-established role in the critical evaluation, compilation, and dissemination of ceramic phase diagrams. This is a joint activity with the American Ceramic Society (ACerS). The work is closely coupled with current needs, as identified by NBS and an ACerS advisory committee. Recent activity in this area has been expanded in response to the increased complexity and quantity of new phase diagrams, together with an expanded dependence by industry and others on critically evaluated diagrams and related thermodynamic data. According to the terms of the recently signed agreement between NBS and ACerS and the associated five year expansion plan, resources for an expanded phase diagram data base activity will be provided jointly by Industry, NBS, and other Government agencies, together with international participation. The basic objectives of the plan are to:

- improve the literature currency of the published phase diagram volumes from 7 to 2 yr;
- expand systems-coverage to include carbide, nitride, boride and compound semi-conductor and other systems, resulting in a comprehensive data base for all ceramic/inorganic phase diagrams; this expansion will more than triple the number of diagrams evaluated to date (past 50 yrs) over the next 5 yr period;
- computerize the collection, evaluation, and dissemination procedures to the maximum extent possible;
- enhance the utility and reliability of the phase diagrams through research developments in modeling, thermochemical optimization, computer graphics, and data base management.

The expansion plan is scheduled to begin in 1985 provided the ACerS fund-raising activity, currently in progress, remains on schedule. During the past fiscal year, significant progress has been made in the computerization of the bibliographic, graphic and thermochemical modeling functions of the Data Center, as indicated by the following discussion.

Key elements of current data center activities include: (a) Evaluation and Production, leading to publication by ACerS of the Phase Diagrams for Ceramists (PDFC) book series; (b) Data Base Development, with emphasis on computer control; (c) Modeling/Optimization, in support of the critical evaluation activity; (d) Experimental, to maintain evaluative competence, improve measurement techniques, and to be responsive to specialized needs for new phase diagram data. Other task activities have also been focused on the needs of the Data Center, particularly in support of the modeling and experimental functions. In addition, the Contributing Editor program (with academic, industrial, and international experts) has been expanded and also includes, for selected systems, coupled thermodynamic--phase diagram model evaluations. Coordination of new Data Center plans with those of the ASM-NBS alloy Data Center (located in the Metallurgy Division) and the Society of Plastic Engineers-National Bureau of Standards (SPE-NBS) polymer (Polymer Division) counterparts has also been implemented. These combined NBS phase diagram Data Center activities and plans are detailed in the CMS report Phase Diagrams in Materials Science.

(a) Evaluation/Production. A major Data Center output is the publication of PDFC books, beginning with Vol. I in 1964, with the most recent Vol. V being published during the past year. These volumes contain critically evaluated phase diagrams together with commentary and bibliographic information. This latest volume, edited by R. S. Roth, T. Negas, and L. P. Cook, contains 663 new diagrams of halides, halides with other substances (especially metals and oxides), sulfides, oxycarbides and oxynitrides, aqueous systems, systems with CO_2, and ceramic-gas (primarily C-O-H) systems.

Considerable progress has also been made in the preparation of Volume VI (oxides and oxygen-containing systems) and Volume VII (halides and sulfides) for which about 8000 phase diagrams are being considered for possible inclusion. Approximately 75 percent of the literature for Volumes VI/VII is in the critical evaluation process and an anticipated completion date for Volume VI is 1986. The cutoff for inclusion of literature in these volumes is January, 1983 (Chemical Abstracts date), with the result that the bulk of literature through 1982 will be covered. Volume VII will be the first to contain thermochemically optimized phase diagrams. These diagrams will represent computer-drawn "best-fits" to available phase diagram and thermochemical data, for alkali halide systems, and will include experimental data points for comparison along with a detailed thermochemical critique. The first series of thermochemically optimized diagrams for inclusion in the new volumes has been prepared under contract with Prof. A. Pelton of Ecole Polytechnique, and Thermofact, Ltd., both in Montreal, Canada. To date, about 24 binary molten salt systems have been optimized.

(b) Data Base Development. A major objective of the Data Center, central to the NBS-ACerS five year plan, is to convert to full computer control the manual operations previously used for the preparation and production of phase diagram compilations. The data base organization necessary to achieve this objective is basically as follows: (1) a bibliographic file containing primary bibliographic information as well as chemical descriptors and keywords; (2) a file of graphical data containing the phase diagrams in both unedited and edited or optimized versions; (3) a file of experimental critiques (text subfile); (4) a file of optimized Gibbs energy functions to be used for computer calculation of the phase diagram, and a thermochemical critique (text subfile). At present it is planned to utilize existing thermochemical data bases, rather than to develop an independent thermochemical data base. However it may be necessary to create specialized data files for some systems, especially those containing solutions as there is no central source of data on ceramic solution activities. Also, a software file will be developed, containing programs designed to provide links among the other four files, manipulate their data, and produce phase diagram outputs. An important component of this software file will be programs for the calculation of phase diagrams, modeling, optimization, extrapolation, and prediction.

Significant progress has been achieved in the past year in software and protocol development for the first two files, bibliographic and graphical. The bibliographic file system, developed in collaboration with the Office of Standard Reference Data (C. Messina), is near completion and is being used to prepare Vol. VI of PDFC. About 30% of Vol. VI material has been entered into the computer file, to date. The file is fully transportable (all ASCII characters). Other special features include totally variable record length, with easy updating and editing. Each reference has 48 data items associated with it - this number can be expanded if necessary. Data items include bibliographic reference information but also data on the phase diagrams which will allow cross-linkage to the graphical phase diagram file.

A very efficient prototype graphics system has been developed and tested on representative binary and ternary ceramic phase diagrams. In FY 85, with ACerS Research Associate support, the refined system will be applied to the digitization, computer storage, editing, and camera ready production of diagrams for Vol VI and future volumes of PDFC. The micro computer-based graphics work station consists of a 16/32 bit micro computer with 1.1 MByte memory (HP9836), a high resolution digitizer, graphics plotter, 14.6 MByte Winchester disc drive, dual 1.1 MByte floppy disc drives, thermal printer, and color graphics printer. The prototype software, developed in FY 83, has been translated into extended basic and made more versatile and useable with minimal training. The main thrust of this software expansion has been to increase the dynamic editing powers once a figure has been entered via the digitizer, keyboard, or from an external data link.

Also during the past FY, a trial set of over 50 binary oxide phase diagrams has been entered into the data base, an example of which is given in figure 1. These diagrams were digitized from copies of the original "as published figures" (see fig. 1-A) together with additional data from the text of the papers, such as eutectic coordinates. The goal of this activity, in addition to reproducing the diagrams, was to develop an accurate data base from which details of the systems could be derived. In many cases, this has required substantial editing of the literature figures to remove drafting errors. To facilitate curve shifting and diagram enlargement, algorithms have been added to the dynamic editing package of the software. These algorithms allow the operator to enlarge and edit any section of the diagram, with real-time computer screen monitoring. The operator normally only edits the end points of curves (phase boundaries) and, on command, the computer shifts the curve to these points preserving the curve's shape. This algorithm, alone, reduces the time to edit most curves by at least 70%. In addition, figure labels can be edited and moved in real time on the computer screen. Another major refinement in the program is that it provides a "best initial guess" to operator queries, such as axis locations and range, which can then be approved or altered.

In addition to the development of the graphics programs and data base for use in production of future volumes, computer linkage with other data bases has been demonstrated. The PDFC Data Center graphics work station has been sucessfully linked with other NBS computers via the NBS network as well as external computers via "Telenet". These computer links are shown in figure 2. Via these links a data file from the AMS/NBS Alloy Data Center computer was transferred to the PDFC facility for plotting, and vice-versa. In support of the NACE/NBS Corrosion Data Center, programs were developed for generating color-coded Pourbaix diagrams on the PDFC facility. These algorithms will be transferred to the Corrosion Data Center (Metallurgy Division) in the future.

Computer programs have been developed for generating three dimensional (3D) representations of ternary systems which can be rotated or represented as stereo pairs, as shown in Figure 3. Algorithms for generating 2D-sections of the 3D-data base of the ternary prism are under development. In these 2D-sections, one component is fixed and the binary diagram of the other two components is derived from the 3D-data base. Alternatively, the ratio of two components may be fixed and the binary diagram derived. Examples of these two types of section, using the data of figure 3, are shown in Figure 4.

(c) Modeling/Optimization. Computer modeling of ceramic phase diagrams can enhance or "optimize" experimental phase diagrams, particularly when coupled with associated thermochemical data such as mixing enthalpies, compound Gibbs energies of formation, and solution activities. Development of computer models is essential to the long range goal of computer-aided critical evaluation and production of ceramic phase diagrams. At the present time two groups within the Division contribute to this effort, in addition to three non-NBS specialists. These activities focus on: (1) application of cluster variation methods for the prediction of solid phase transitions (B. Burton, NBS), (2) the development of new solution models for phase diagram optimization and prediction (this Task), (3) incorporation and testing of NBS-developed solution models, and others, into existing computer codes for phase diagram optimization, (K. Spear, Penn State), (4) application of the THERMFACT computer code, with its extended regular solution model, to phase diagram optimization for relatively simple molten salt systems, and (5) development of a thermodynamic data base for complex oxide systems, for use with the SOLGASMIX (Erickson, Sweden) and other computer codes applicable to phase equilibria predictive modeling (W. Horton). Description of the first activity is given elsewhere in this report and the present discussion deals with progress on the solution modeling problem.

In principle, phase boundaries and thermodynamic functions such as Gibbs energy are interrelated. However, specification of a single phase-boundary-point on the liquidus curve of a phase diagram requires both temperature and composition to be fixed. For the complete thermodynamic construction of a phase diagram the Gibbs energy of each phase is required as a function of temperature and composition. Such analytical expressions can be derived provided a solution model is assumed, which essentially is a thermodynamic relationship between activities (or apparent mole fractions) and nominal mole fractions for the mixture components. Well-known examples of solution models include, ideal, regular, and the molecular-level associated liquid or clustering models. Models of this type have been useful for coupled thermodynamic--phase diagram optimization analysis of select binary alloy and molten salt systems. However, for typical ceramic systems the available models do not appear to be applicable owing to the substantial thermochemical interactions that occur on mixing. Development of new strong-interaction solution models for ceramic systems is therefore needed. In addition to allowing for thermochemical optimization of experimental phase diagrams, such models also form the basis for converting phase diagram information to useful vapor pressure data and vice-versa. Also, in some cases, such as the ideal mixing of complex components (IMCC) model developed under this Task, phase diagram predictions appear feasible for systems where no experimental phase equilibria data exists.

During the past year, a successful model has been developed for prediction of solution activities and vapor pressures in binary and higher order systems containing compounds (solid and liquid) of Li_2O, Na_2O, K_2O, CaO, MgO, Al_2O_3, SiO_2, FeO, Fe_2O_3, and Fe_3O_4. This model has a thermodynamic basis and does not rely on an assumed molecular structure of the liquid phase, or on experimental information such as mixing thermochemistry. The ability of the model to predict (as distinct from optimize) solution thermodynamic properties for highly non-ideal complex oxide mixtures is shown by the example of figure 5. Here, the model activity data have been converted to partial pressures for comparison with our experimental Knudsen effusion mass spectrometry results (obtained under subtask 2). The model components which control the properties of this glass system are listed in table 1. Note that the liquid entities are formal thermodynamic components and should not be considered as molecular species. Also, components containing three or four cations are significant (see table 1). This is in marked contrast with the model behavior of most alloy and molten salt systems where components with more than two cations present have for not been required for good model behavior.

The model has attracted considerable interest in industrial and other laboratories for diverse applications. The computer program and model data base are already in use, by DOE-Morgantown for predictions of slag/coal mineral behavior in coal conversion technology, and by the University of Tennessee Space Institute for modeling MHD slag thermochemistry. Also, the following establishments have expressed an interest in utilizing the computer program, data base, and related material: DuPont-Wilmington (glass-metal wetting); A. Cooper-Case Western Reserve (diffusion in glass); DuPont-Savannah River (nuclear waste processing); PPG-Pittsburgh (fluoride glass volatility in fiber production); CSIRO-Sydney (fluidized bed coal-slagging); New South Wales Electricity Comm.-Australia (steam plant design for high slagging coals); St. Gobain-France (glass processing); and Oak Ridge National Laboratory (MHD slag thermochemistry). Also, Dr. N. Christensen of F. L. Smith and Company (Denmark) has pointed out that this modeling activity is important to the prediction of corrosive alkali vapor transport and deposition in cement processing.

In principle the model should also permit calculation of phase diagrams and this aspect is under investigation. As an example, part of the $Li_2O-Al_2O_3$ phase diagram shown in figure 6 was obtained using this modeling approach. One should stress, however, that the viability and reliability of this model requires continued experimental testing as additional components are added to the database. Thus this modeling effort is closely coupled with experimental determinations of solution activities and phase equilibria [see item (d) below].

(d) Experimental. Experimental research performed in support of the Data Center program includes both classical determination of phase diagrams (i.e., direct phase identification) and indirect measurement based on Gibbs energy relationships. In the latter case use is made of vapor pressure measurement using unique NBS facilities, as discussed under Subtask 2. These thermochemical measurements of phase equilibria are particularly useful for testing solution models under development for phase diagram optimization and prediction, as discusssed above under item (c).

During the past year, a new project has been initiated in response to basic data needs of the Office of Naval Research (ONR) and Garrett Corporation for development of stored chemical energy propulsion systems. The system of interest is based on the exothermic reaction of a Li/Al alloy with H_2O (steam) to yield $Li_2O-Al_2O_3$ phases and H_2 (to be burned for additional thermal energy). Phase equilibrium data, needed for process design by Garrett, are virtually unknown for this system. This is an exceptionally complex system and a concerted experimental and theoretical effort is underway combining the expertise of three Groups within Division 420. Current effort is focused on a determination of phase equilibria in the system $Li_2O-Al_2O_3$. In addition to the 1:1 compound of principal interest, $LiAlO_2$, solid state and melting relationships involving this compound and Li_2O, Li_5AlO_4, Li_3AlO_3, $LiAl_5O_8$, and Al_2O_3 are under investigation. This activity is closely coordinated with measurement of vapor pressures by thermogravimetric analysis and Knudsen effusion mass spectrometry.

The $Li_2O-Al_2O_3$, system is an exceptionally difficult one for experimental phase equilibria determination. At high alumina compositions the melting temperatures are in excess of those obtainable by conventional platinum resistance furnaces and containers. This has necessitated the use of a tungsten furnace and sealed molybdenum containers. Also, for high Li_2O concentrations inert atmospheres are required for sample preparations. Results obtained to date also indicate slow reaction rates, leading to possible non-equilibrium phases. A preliminary phase diagram is shown in figure 6. Also indicated are the various techniques used for different regions of the diagram.

Vapor Transport Thermochemistry
Subtask 2 of Task 15415

J. W. Hastie, E. R. Plante, D. W. Bonnell, P. K. Schenck, A. B. Sessoms, M. Wilke

This subtask develops and applies new or improved measurement techniques to the molecular-level analysis of vaporization processes for high temperature solids (e.g., ceramics) and melts (e.g., coal slags, glasses, and salts) in process atmospheres containing reducing, oxidizing carbonated, halogenated, sulfated, hydrous, and other reactive components. These environments are characterized by extremes of temperature (typically 10 - 5000 K), gas pressure (10^{-6} - 10^{2} atm), chemical reactivity, and phase complexity. The conditions and data obtained are generic to high temperature process environments, and particularly those where hot corrosion and high temperature oxidation are material-limiting factors. For example, in the developing technology of pressurized fluidized bed combustion (PFBC), removal of coal and dolomite-derived alkali (Na and K-containing species) impurities to a gas stream concentration level below 0.02 ppm is necessary to control hot corrosion of turbine blades in PFBC. NBS participation, at DOE's request, in the DOE-Morgantown Energy Technology Center research and development program on particulate and alkali control in coal combustion process streams, has provided for close interaction and technology transfer with industrial participants, particularly General Electric , Westinghouse, the Electric Power Research Institute, Exxon, and a number of relatively small air pollution technology companies. NBS expertise in this area has also led to a recent request, and a formal collaborative program, by the DuPont Atomic Energy Division for NBS to carry out vapor transport measurements over simulated nuclear waste glass materials. These data are urgently required for the design of process conditions to isolate nuclear waste in glass materials.

In cooperative work with other federal agencies, the recent measurement focus has been on ceramic, coal slag, and glass systems in atmospheres typical of coal gasifiers (CG), magnetohydrodynamic (MHD) electric generators, and pressurized fluidized bed combustors. Other cooperative projects involve oxides in reducing atmospheres (Navy-Garrett), BN-SiO_2 composites in very high temperature--low pressure oxidizing atmospheres (Defense Nuclear Agency), graphitic materials in low pressure neutral atmospheres (Air Force), and GeO_2-SiO_2 fiber optic glasses in neutral atmospheres (Bell Laboratories). These extreme conditions have required continued development of the transpiration (TMS) and modulated molecular beam Knudsen effusion (KMS) mass spectrometric techniques. In addition, a new technique was developed, laser-induced vaporization mass spectrometry (LVMS), for time-resolved analysis of vapor plumes over refractory materials. The fundamental basis of high temperature mass spectrometry is also being re-evaluated under this subtask. Standard procedures for converting mass spectral ion intensities to absolute concentrations (partial pressures) have been found to be less-accurate than previously believed.

Complementary efforts in data-base (solution activities, species Gibbs energies,...) acquisition and computer modeling also constitute an integral part of this extreme-environment characterization effort. For most of the coal conversion and combustion systems of interest, the chemical state of alkali metal-containing species represents a pervasive theme in our understanding of the high temperature processes and of materials durability problems (e.g., in CG and PFBC). Examples of recent experimental and modeling activities pertinent to these problems are summarized below.

(a) Alkali Control in Combustion Atmospheres. Dolomitic limestone is used for sulfur retention in fluidized bed combustors. However, alkali impurities in the limestone, together with the neutralizing effect of this basic material on alkali-containing coal mineral impurities (e.g., illite), can lead to excessive alkali vapor transport and corrosion of downstream components. To determine whether alkali vaporization from dolomite itself will exceed the tolerance (to hot corrosion) limits for turbine gas streams vapor pressure data have been obtained for a representative dolomite sample. At the temperatures expected of PFBC operation (> 1200 K) the alkali (Na + K) pressure was found to exceed the turbine tolerance limit of 0.02 ppm (1.5 x 10^{-7} atm). In order to extend the applicability of the laboratory measurements to process conditions, and to other dolomitic compositions, a predictive thermodynamic model has been developed. The basis for the model is the IMCC approximation discussed under subtask 1. Good agreement between model and experimental Na and K partial pressure-temperature data was obtained for the SRM 88a dolomitic limestone. Predicted data for a Tymochtee dolomite, for which no experimental data exist, are given in Table 2. Note that under a typical PFBC temperature of 1200 K, the predicted alkali pressure exceeds the tolerance limit of 1.5 x 10^{-7} atm. A copy of the model data base and multicomponent equilibrium computer code has been delivered to DOE-Morgantown for general-purpose predictions of alkali vapor transport and retention in coal conversion systems.

Even higher alkali pressures are likely in the combustor, than those indicated by the phase equilibrium model data of Table 2, for instance. This results from the interaction of dolomite with alkali-containing coal minerals, and with the H_2O and HCl gases present, to yield volatile hydroxide and halide species KOH, NaOH, KCl and NaCl. Thermodynamic computer models are in increasing usage by process design engineers for the prediction of the likely concentration of these species. However, the thermodynamic data base for KOH is particularly suspect owing to the widely disparate literature data. Using the TMS method we have obtained new, accurate thermodynamic data, including Gibbs energies, enthalpies, and entropies of formation, for the vapor species KOH, $(KOH)_2$ and KO_2. Figure 7 shows data for KOH in comparison with the literature.

(b) Nuclear Waste Glass Processing. Industrial and DOE plans for nuclear waste storage require the waste to be incorporated into a borosilicate glass. Vapor pressure data are needed for these glass-waste forms in order to optimize the process conditions (e.g., temperature, composition) and minimize losses of radionuclides by vapor transport during the high temperature mixing processing of the wastes. The primary objective of the present study was to define the vaporization thermodynamics of a simulated nuclear waste borosilicate glass, containing non-radioactive isotopes, as prepared by DuPont-Savannah River. Also, measurements of partial pressures for each vapor species allowed thermodynamic activities and related partial molar functions to be derived. Such basic data are pertinent to the development of thermodynamic models of other nuclear waste properties such as leaching and storage durability. Special emphasis is being given to vapor species containing the following elements which in actual nuclear waste form are highly radioactive: Cs, Sr, Ru, and Re--added as a technetium simulant.

In the past FY, experimental work was completed on the vaporization of a synthetic processed glass sample. The data have provided important source-term information for an Engineering Department (DuPont-Savannah River) off-gas model. Following this successful study, DuPont has recently requested NBS to undertake a systematic research study of the earlier stages of the glass-forming process. Emphasis is on the extent and mechanism for release of Cs during the initial mixing/fusion of nuclear waste "sludge" and glass frit materials.

(c) Stored Chemical Energy Propulsion. Knudsen-effusion mass spectrometric measurements of species partial pressures and solution activities have been initiated in support of the recently implemented project on phase equilibria in the Li_2O-Al_2O_3 system (see Subtask 1). The results will allow for phase diagram construction using both the classical and Gibbs energy approaches. Also, the activity data, obtained as a function of temperature and composition, will aid in developing thermodynamic models of the heterogeneous reactions involving H_2O and H_2. An interim phase diagram has been constructed from the mass spectrometric data obtained to date, together with the results of other techniques as indicated in figure 6 (see also Subtask 1). Measurements of the Li and O_2 partial pressures were made over the $LiAlO_2$-$LiAl_5O_8$ and $LiAl_5O_8$-Al_2O_3 phase systems as a function of temperature and composition. However, the results were not reproducible with temperature and it appears likely that the following effects are present: surface depletion of the vaporizing phase and; an order-disorder transformation in $LiAl_5O_8$ at 1300 °C accompanied by a large volume change which disturbs the layers blocking the vaporization reaction. Owing to the surprisingly slow kinetics for the vaporization process, no indication of whether $LiAlO_2$ and $LiAl_5O_8$ exist as line compounds or exhibit homogeneity ranges could be determined from the vaporization measurements. However, the constant ratio of Li^+/O_2^+ observed indicates that the vaporization process involves only the removal of Li_2O as Li(g) and O_2(g). Other vapor species, Li_2O and LiO, were present at less than 1% of the total vapor pressure.

(d) Laser-Induced Vaporization Mass Spectrometry. Degradation of materials by high powered lasers is important in, for example, the design of laser fusion processes, laser welding, laser processing of ceramics, and in the durability of refractories in defense and space applications. In addition, the use of lasers as point heat-sources has provided high temperature materials scientists with a means of characterizing materials phase transformations at very high temperatures under essentially containerless conditions. In response to a request from the Air Force Office of Scientific Research, NBS has undertaken fundamental studies of laser ablation phenomena, with initial emphasis on graphitic materials. The determination of spacecraft survivability in laser ablative situations is dependent on the mechanisms of smoke and aerosol formation from high temperature vapors. Fundamental understanding of these processes requires a molecular level description of the vaporization/condensation process.

Figure 8 shows a schematic of the apparatus developed for this study. A very high pumping speed is maintained in the sample chamber to simulate the environment of near-earth orbit conditions. Use of a Nd/YAG laser with nanosecond pulse duration, and collection of mass spectral signals as a function of time provides a dynamic picture of the laser-induced vaporization process. The apparatus also allows for multiple shots in a single location thereby simulting cratering and ablation processes. Techniques for laser beam-sample surface angle dependence are being developed to isolate laser/plume interaction processes. Temperature, molecular weight and other information is convoluted in the time resolved mass spectral profile (e.g. see figure 9). Graphite vaporizes as polymeric C_n (n=1-7, or higher) molecules, whose relative pressures are a function of temperature. In addition, the species time of flight (between the surface and mass spectrometer) depends on the square root of mass, as shown in figure 10. Experiments on spectroscopic grade graphite show that this technique is capable of attaining temperatures up to 4200 K, that the heating process is approximately equilibrium, and that measured distributions of C_n polymer species are the expected equilibrium values. Spacecraft survivability depends on such distributions as interference with the laser beam and surface cooling is expected to be greatest with atomic vaporization. Carbides (e.g. TaC) are predicted to yield markedly more monomer, and survey studies of TaC are in progress.

(e) Reentry Window Materials, Thermal Stability. Ceramic microwave transmission windows on atmospheric reentry space vehicles suffer from a communications blackout due to increasing electronic conductivity in the window and, possibly, in the boundary layer. In support of defense needs (DNA) for basic data and mechanistic understanding of the thermal and electrical degradation processes involved, mass spectrometric measurements have been undertaken on BN and BN-silica composite materials. Special mass spectrometric techniques were developed, or modified, to carry out these measurements. A modulated molecular beam Knudsen effusion mass spectrometric technique was utilized for quantitative vapor species concentration measurements over a BN-SiO_2 composite at 1500 to 1900 K and 10^{-7} to 10^{-4} atm. For high temperature measurements, a laser vaporization-mass spectrometer system was developed and applied to thermochemical analysis of high purity hot-pressed BN at 2900 K and ~ 1.0 atm. The principal conclusions from these studies are as follows.

The BN/SiO_2 composite vaporizes at a lower temperature than either BN or SiO_2 via the synergistic reaction:

$$2BN(c) + 3SiO_2(c) = 3SiO(g) + N_2 + B_2O_3(g).$$

At higher temperatures, the N_2 pressure tends to be controlled by the reaction:

$$BN(c) = 0.5\ N_2 + B(c).$$

Under pulse-laser heating conditions, BN (Boralloy) vaporization is controlled by several competing processes, in decreasing order of significance:

$$
\begin{aligned}
BN(c) &= B(\ell) + 0.5\ N_2 \\
BN(c) &= BN(g) \\
2B(\ell) &= B_2(g) \\
B_2O_3(c) &= BO(g) + BO_2(g).
\end{aligned}
$$

At the high gas pressures generated (~ 1 atm), the vapor plume exhibited adiabatic free-jet expansion properties such as translational cooling. The measured vapor species partial pressures were consistent with a surface equilibrium model for a fixed stoichiometry of $B/N_2 = 0.5$.

Future research should address the effects of varying laser power, surface morphology and surface temperature on BN vaporization. Extension of the laser mass spectrometric studies to BN-SiO_2 and other microwave window materials is needed. Also, the effects of atmospheric impurities (O_2, N_2, H_2O) on these high temperature processes should be examined by the two mass spectrometric methods.

(f) Reexamination of the Fundamental Basis for Converting Mass Spectral Data to Thermodynamic Functions. Much of the literature high temperature vapor pressure data, and the thermodynamic functions derived there-from (activities, ΔG, ΔH, ΔS, K_p), are based on certain fundamental relationships between mass spectral ion intensities and partial pressures. These maxims of high temperature mass spectrometry are: (1) the total and partial ionization cross sections (σ) are temperature independent, (2) unknown molecular ionization cross sections (σ) can be approximated by a summation (or some constant empirical fraction of the sum) of the known atomic ionization cross sections, (3) σ values, at ionizing electron energies (E) less than the maximum cross section values [E (max)] can be obtained from σ (max) by a scaling law based on the energy interval $E-A_i$, where A_i is the appearance potential for species i. Evidence of the recent international concern about the reliability of these long standing maxims is given by the appointment by IUPAC commission II-3, on High temperature and Solid State Chemistry, of a task group to study this question. Dr. J. W. Hastie is the U. S. representative of this international task group. Within the U.S., the American Association for Mass Spectrometry and Allied Topics recently requested NBS to organize a workshop (San Antonio, May 1984) on the same subject and Dr. D. Bonnell chaired this activity.

The development of Transpiration Mass Spectrometry (TMS) under this task several years ago has provided NBS with a unique tool to critically examine the three mentioned assumptions regarding cross section behavior. A particular advantage of TMS for this application is the wide temperature range allowed by the cooling effect of an adiabatically expanded high pressure gas--allowing for a critical test of maxim (1). Also, the use of a permanent gas as a carrier of vapor species provides a means of obtaining σ values using the carrier gas as a reference--allowing for a test of maxims (2) and (3).

Results obtained to date indicate the following. Maxim (1) has been shown to be in serious error for the alkali halides, but other test species such as KOH and As_4O_6 did not exhibit an anomalous dependence of σ on T. A molecular potential energy model has been developed to explain the observed behavior for the alkali halides. Measurement of σ for a variety of high temperature species has indicated errors in the atomic additivity maxim (2) typically of the order of 30% but with deviations as great as 500%. These errors translate to similar errors in partial pressure, which are usually believed to be accurate to 30% or better. With regard to maxim (3), errors as great as 500% were indicated for the As_4O_6 species. These results are cause for considerable concern regarding the accuracy of data derived from high temperature mass spectrometry, such as that given in the widely used JANAF Thermochemical Tables. Further experimental and new theoretical work is clearly warranted.

Characterization of High Temperature Gaseous Environments in Processing and Service

Subtask 3 of Task 15415

P. K. Schenck, J. W. Hastie, and D. W. Bonnell

Objectives of this Subtask are to develop and optimize measurement techniques for characterizing high temperature gaseous environments, including flames and laser induced plasmas, and to apply the methodology to mechanistic studies of materials processing and performance in those environments. Current research is directed at the base program goals in improved measurement methods in addition to specialized OA needs. Other Agency problems currently under investigation include: laser vaporization molecular-level mechanisms of graphitic and BN refractory materials [see Subtask 2, items (d) and (e)] for AFOSR and DNA, and the mechanistic action of alkalies (K) in suppressing secondary flash in miltary applications, for ARO. During the past FY, new or improved experimental methods were developed in support of these studies. These techniques basically rely on laser excitation of electronic states in atoms and molecules and on thermal effects. The effect of enhanced thermal ionization of laser excited atoms (the optogalvanic effect or laser enhanced ionization) is used to modify the neutral/ion ratio from which species flow velocity and diffusion parameters are determined. For solids or liquids, the laser energy is rapidly converted to heat which can be spatially and temporally controlled over a wide range of temperature.

In collaboration with the Center for Analytical Chemistry, modeling and experimental studies have continued through FY84 on the collection mechanism of ions and electrons from laser enhanced ionization (LEI). Maximum sensitivity is obtained when a water cooled probe is inserted in the flame to collect the signal produced by electrons and ions formed by LEI using pulsed lasers. This sensitivity is explained by the near unity collection efficiency possible if the laser beam producing the electrons and ions is within the cathode sheath formed by the background flame ions around the probe (held at a negative potential with respect to the burner body or anode). The reason for this effect has been verified using a computer model for the behavior of the charge distribution in the flame.

In separate studies a new IR dye has been obtained which can be pumped by the blue line of argon ion lasers. This new dye is being used to replace the krypton ion laser pumped IR dye which proved troublesome in continuing work on mapping the potassium atom concentrations in normal and inhibited K-seeded flames. In addition a new ultrasonic aspiration system has been tested for seeding burners with alkali metal atoms. This type of aspiration system dramatically reduces the amount of water aspirated into a flame compared to standard techniques while increasing the metal atom density in the flame. The IR dye laser will allow us to monitor K concentrations either by absorption or LEI (to the ppb level). Temperatures in the base (non-seeded) flames were measured earlier by optical techniques, such as Raman and line reversal, and similar determinations are planned for the seeded flames. Efforts are underway to couple these optical experiments with the high pressure sampling mass spectrometer (HPMS) for simultaneous measurements of temperature and species concentration.

Preliminary time-resolved laser vaporization mass spectroscopy tests made on carbon (graphite) and boron nitride refractory materials started last fiscal year have been analyzed to obtain plume temperatures and absolute species concentrations from the experimental data. The goal of this program is to characterize, by optical and mass spectroscopic techniques, the molecular processes occurring in the plasmas resulting from surface ablation by high powered pulsed and continuous lasers. In order to facilitate and expand these studies a 200mJ Nd-YAG pulsed laser system is being installed. The output pulses of this laser will be piped into the HPMS facility which is being prepared for computer automation. The sample's position inside the chamber of the HPMS (see fig. 8) will be controlled by a laboratory automation computer to assure that the laser ablates from a fresh portion of the surface during the experiments. In addition, the time resolved signals from the mass spectrometer will be stored (see fig. 9) for later analysis of plume temperature and species concentrations.

In support of the new NBS Laser Processing Laboratory for ceramic materials, a design has been prepared for potential diagnostic techniques, including optical and mass spectrometric. Planned for the facility are real-time spectrographic (species) and pyroelectric (temperature) measurements during the laser processing. Other techniques involving laser diagnostics will be studied for their applicability in laser processing research.

Data Center on Materials and Components for Fossil Energy Applications

Subtask 4 of Task 15415

H. M. Ondik, B. W. Christ[1]

Fracture and Deformation Division (430)

The Fossil Energy Materials and Components project supports DOE Fossil Energy R&D needs by providing a central source of evaluated data on the properties and performance of materials and components in fossil energy systems. Particular emphasis is given to corrosion, erosion, and mechanical property data for metals and ceramics tested under coal conversion conditions. Materials properties and testing performance data are evaluated and compiled for construction materials intended for coal conversion use. The primary source of data is the library of DOE materials research contractor's reports. In addition, materials and components plant performance data were evaluated and compiled by the staff of the Fracture and Deformation Division (430) from reports of materials and component failures submitted to DOE on a voluntary basis by the various coal conversion pilot plants. These two data sets are combined in the form of a periodically updated book, Construction Materials for Coal Conversion--Performance and Properties Data, NBS Special Publication 642, first published in September 1982 (826 pages). A second book, issue date December 1983, has been published as NBS Special Publication 642, Supplement 1 (774 pages). The books are produced as sets of pages numbered such that sections of the book are independent and can be updated and revised readily. By February 1984, the Government Printing Office had sold over four hundred copies of the first book. Announcements for the Supplement volume were circulated in March 1984 and as of May 1984 over forty copies had been sold. The Inorganic Materials Division has responsibility for compilation of the basic set of data and also the analysis and discussion of the refractories information. The Fracture and Deformation Division (B. W. Christ and others) has responsibility for analysis of the metals and alloys data, as well as for the discussion of component failures which were largely concerned with metal components.

The first issue of the book focused on plant materials data for coal gasification, as this form of coal conversion provided the largest body of materials data. The Supplement, the second book in a projected three-volume series, not only updated the SP 642 data for materials for coal gasification use but expanded coverage to include materials data for coal liquefaction and direct combustion. The data include information gained in practical plant experience, as well as the results of the materials research and testing programs. The books deals with the information in the context of ten separate component areas of coal conversion plants. The data applicable for a component area are summarized and discussed under that heading. The detailed results of the research and testing programs are included in a separate section which is divided into four parts covering the major performance and properties investigated in these programs. These four sections are headed:

(1) Corrosion Effects, Chemical Reactions, and Phase Changes;
(2) Erosion, Erosion/Corrosion, and Abrasion Effects;
(3) Mechanical Properties Testing; and
(4) Physical Properties Testing.

Each of these sections is divided into subsections for alloys, ceramic refractories, and where such data exist, for coatings. A detailed index to the book lists the materials covered grouped by type. For metals, typical categories are stainless steels, cobalt based alloys, carbon steels, etc. For refractories, the groupings first list the industrial categories--bricks, castables, etc.--and then the composition. For each material, the various properties are given for which data appear in the book, followed by the section reference and page. The index allows for location of testing and properties data for specific materials.

Current activity is focussed on the preparation of the second supplementary volume. Supplement 1, containing chiefly alloy information, brought the data set for alloys up to date as of December 31, 1982. The second supplement which will deal chiefly with refractories will bring that data set up-to-date as of December 31, 1983, and will complete the overall Data Center objectives.

High Temperature Thermophysical Properties
Subtask 5 of Task 15415

D. W. Bonnell

A joint experimental effort between NBS, Rice University, and the General Electric Company's Space Systems Division (GE), has been in progress for several years. This effort, with the support of the NASA Materials Processing in Space program, focuses on technique development and application to thermophysical property measurement, including heats of fusion, heat capacities, and enthalpy increment functions for extremely refractory materials. High temperature heats of fusion, enthalpy functions and heat capacities (Cp) are essentially all estimated by the Tamman rule for third row transition metals, and are largely unknown for most other refractories with melting points above 2000 K. Theory has no predictive capability for these data, particularly at phase transitions, e.g. the change in Cp, solid to liquid, or the value of Cp near the melting point. This effort utilizes electromagnetic levitation for containerless support of the refractory metal, coupled with auxiliary heating, such as the GE electron beam gun system to provide extra energy for melting. A conventional isoperibol drop-type calorimeter has been modified to accept samples dropped from the levitation region to measure their heat content.

The newly developed (GE) imaging optical pyrometer was completed, tested, and calibrated under in-service operating conditions. This unit has the capability for two color operation, with the alternate colors sampled at a rate of the order of a few hertz. The system appears to be a reasonable prototype with a major improvement in stablity of operation. Special techniques were developed to connect the temperature scale of the pyrometer to that of the standard lamp. A new, tighter coil design was tested with major improvement in holding ability and stable levitation. Successful coupling of this levitation coil and the electron-beam heat source proved more difficult than anticipated, with the result that a controlled tungsten melt has not yet been achieved. Tests were conducted with tantalum, with melting being easily achieved. However, Ta is much more sensitive to outgas contamination, and additional studies are needed to eliminate this effect.

A major recent effort has been the preparation of a chapter on Levitation Calorimety in collaboration with workers at Rice. This chapter represents a comprehensive review of the subject of electromagnetic levitation and thermophysical property measurement, the first such effort since the early 1960's.

Table 1

Composition and Model Components in SRM-621 Glass

Input Composition (mole %)

Na_2O (12.54), K_2O (1.30), CaO (11.68), MgO (0.41), Al_2O_3 (1.66), SiO_2 (72.41).

Significant components (liquid) at 1400 K[a]

$Na_2Si_2O_5$
Na_2SiO_3
$NaAlSi_3O_8$
$KCaAlSi_2O_7$*
$K_2Si_4O_9$
$K_2Si_2O_5$
SiO_2
$CaSiO_3$
$CaO\cdot MgO\cdot 2SiO_2$
$Al_2O_3\cdot CaO\cdot 4SiO_2$*
Ca_2SiO_4

Insignificant components (liquid and solid) at 1400 K[b]

Al_2O_3
K_2O
Na_2O
CaO
MgO
K_2SiO_3
$KAlO_2$
$KAlSiO_4$
$KAlSi_2O_6$
$3Al_2O_3\cdot 2SiO_2$
$K_2O\cdot 9Al_2O_3$
$CaO\cdot Al_2O_3$
$2CaO\cdot MgO\cdot 2SiO_2$
$Al_2O_3\cdot CaO\cdot 2SiO_2$
$Al_2O_3\cdot 2CaO\cdot SiO_2$
$12CaO\cdot 7Al_2O_3$

---

[a] Significant components are those having $> 10^{-4}$ mole fraction (X*) concentration as predicted by the computer model.

[b] Insignificant components are those considered in the model but calculated to be present at $< 10^{-4}$ mole fraction (X*).

Table 2

Model Prediction of Alkali Vapor Pressures and Phase Equilibria for Tymochtee Dolomite at 1800 K

Input elemental composition-calcined (mole %)

Ca (43.6), Mg (40.5), Si (11.1), Al (9.0), K (0.32), Na (0.08)

Phase distribution of component oxides (mole %)

	CaO	MgO	Al_2O_3	SiO_2	K_2O	Na_2O
Solid phase	48.2	48.2	--	1.15	--	--
Liquid phase	1.15	0.12	0.25	0.83	0.14	3.9×10^{-4}

Phase composition (mole %)

Solid MgO (49.7), CaO (48.4), $3CaO \cdot MgO \cdot 2SiO_2$ (0.64).
Total Liquid (1.1)
Gas (0.09)

Major liquid components (mole fraction, X*)[a]

Ca_2SiO_4 0.33, $KCaAlSi_2O_7$ 0.246, MgO 0.134, CaO 0.108,
$Ca_2Al_2SiO_7$ 0.07, $KAlO_2$ 0.046, $CaAl_2O_4$ 0.045, $CaSiO_3$ 0.017

Alkali liquid components (mole fraction, X*)[a]

$KCaAlSi_2O_7$ 2.46×10^{-1}, $KAlO_2$ 4.59×10^{-2}, K_2SiO_3 7.5×10^{-4}
$KAlSiO_4$ 4.74×10^{-4}, Na_2SiO_3 4.12×10^{-4}, $NaAlSiO_4$ 1.04×10^{-4}

Alkali partial pressures (atm)

	Na	K
1800 K	4.84×10^{-4}	1.25×10^{-3}
1200 K	2.94×10^{-7}	1.43×10^{-6}

Note: log P vs T^{-1} linearity can be used to extrapolate to other temperatures.

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[a] Significant components are those having > 10^{-4} mole fraction (X^*) concentration as predicted by the computer model.

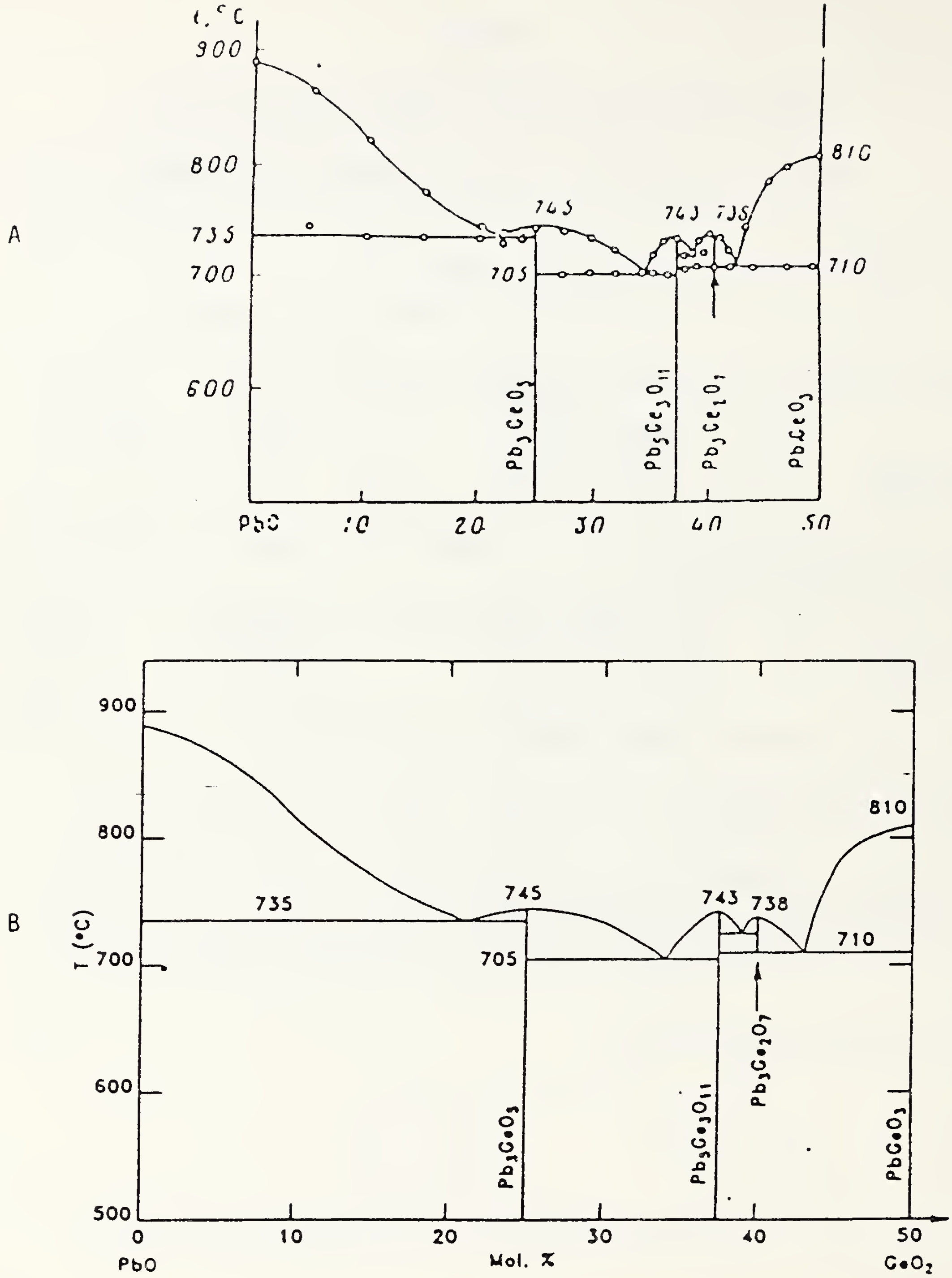

Figure 1. Example of literature (A) and digitized (B) phase diagrams.

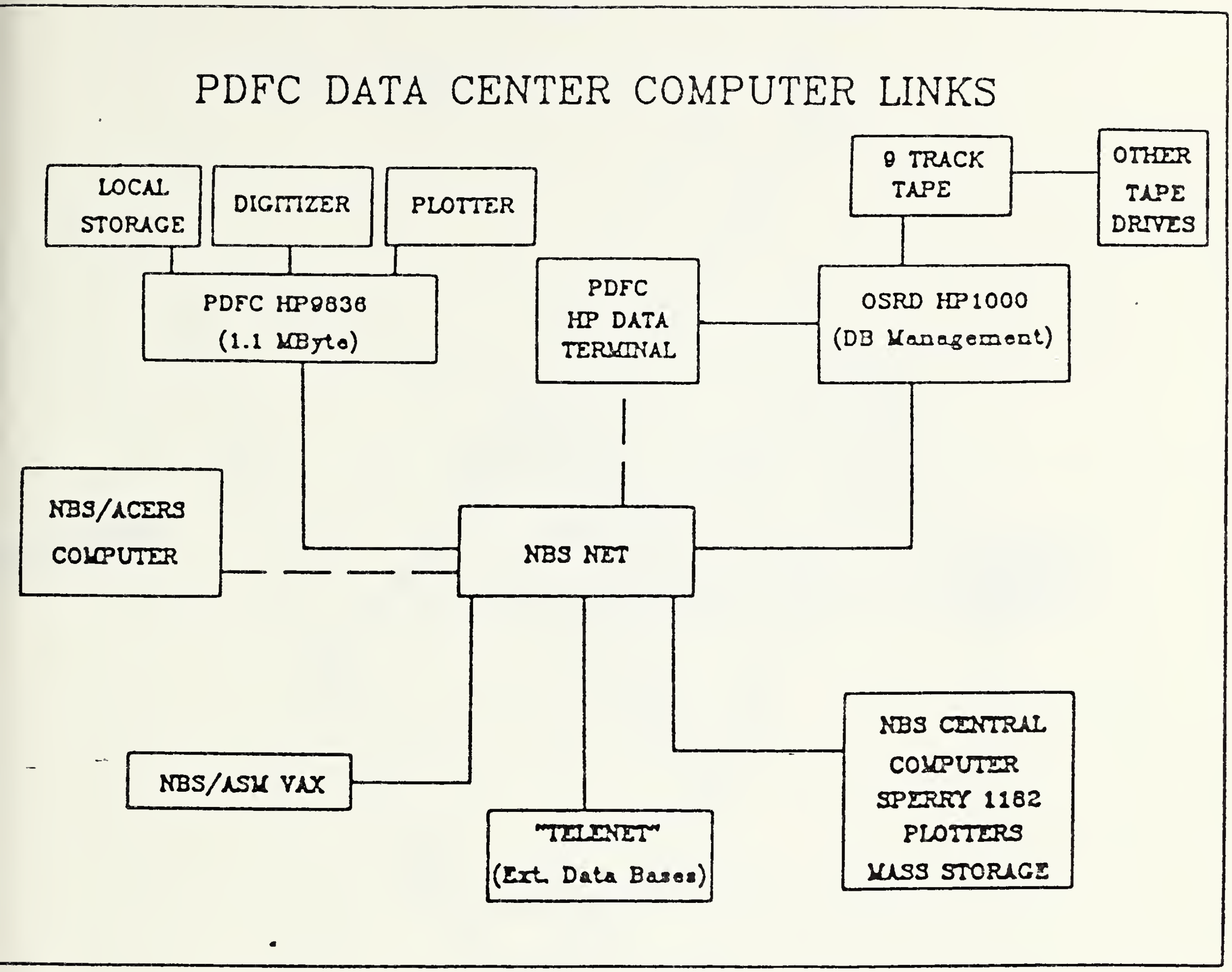

Figure 2. Existing and planned (---) computer links between the PDFC Data Center and other data bases and computer facilities.

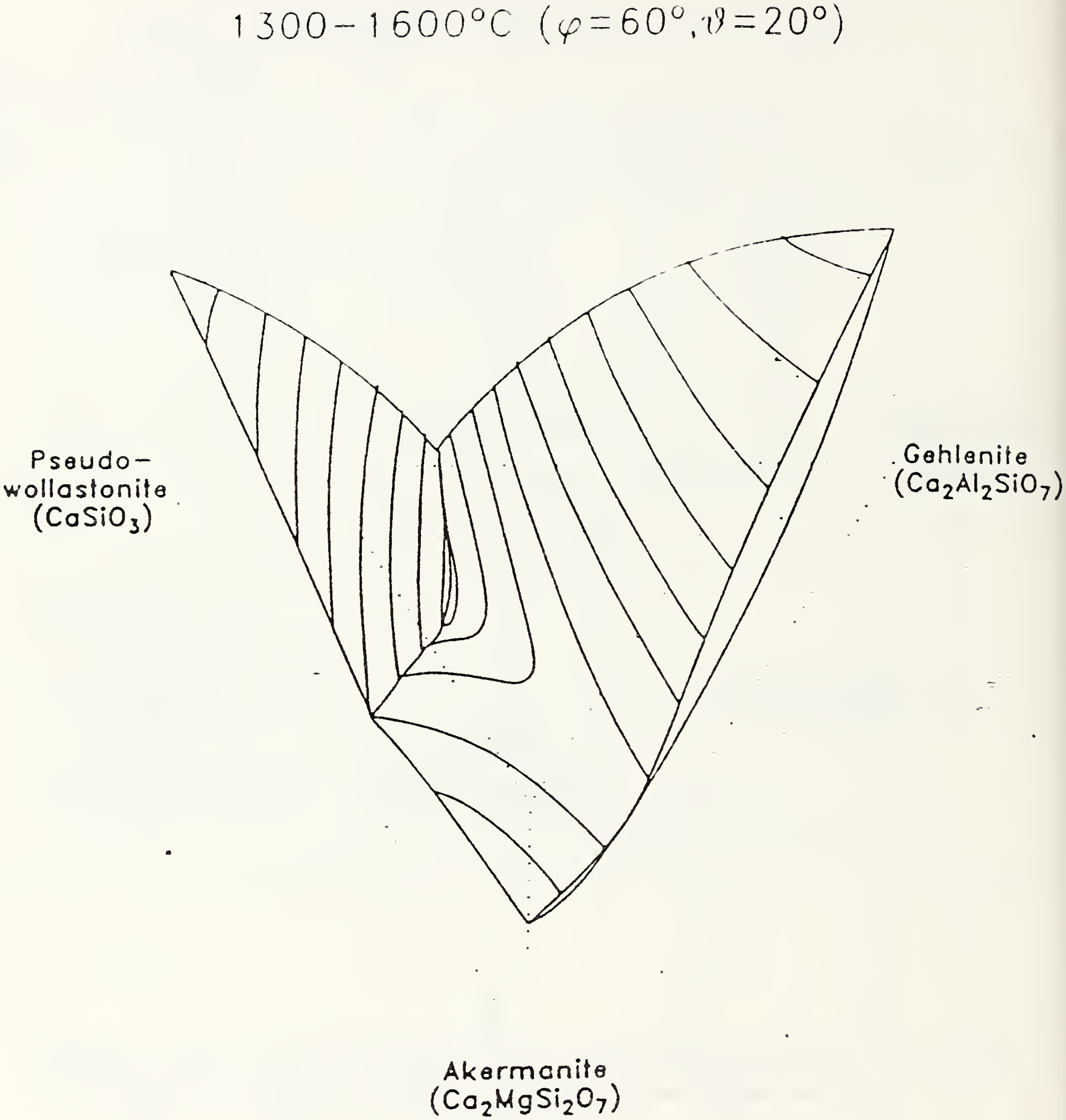

Figure 3. Computer generated 3D representation of a ternary phase diagram.

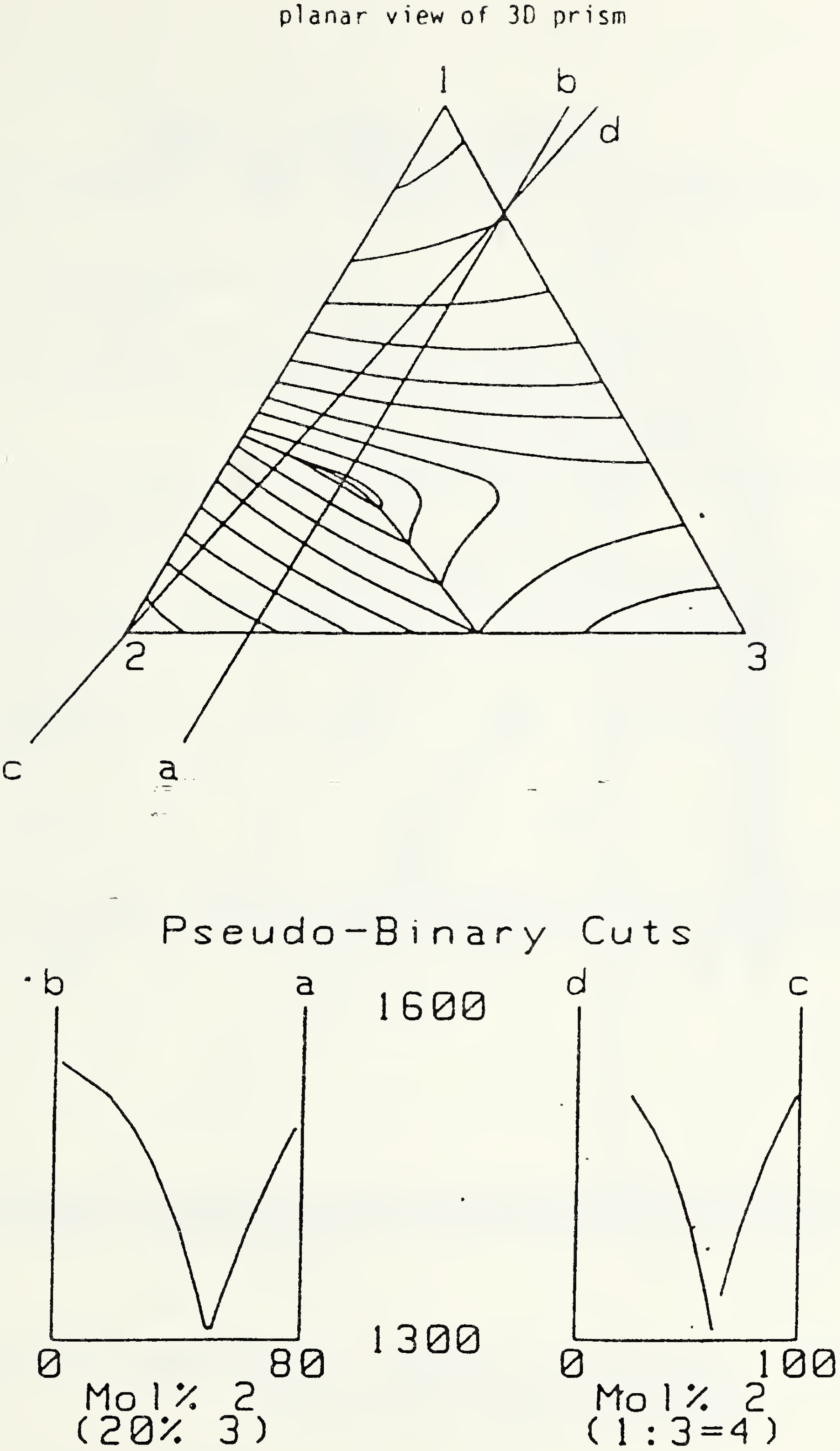

Figure 4. Computer generated pseudo-binary sections of a ternary phase diagram (same system as in fig. 3; 1 is gehlenite, 2 pseudo-wollastonite, 3 akermanite).

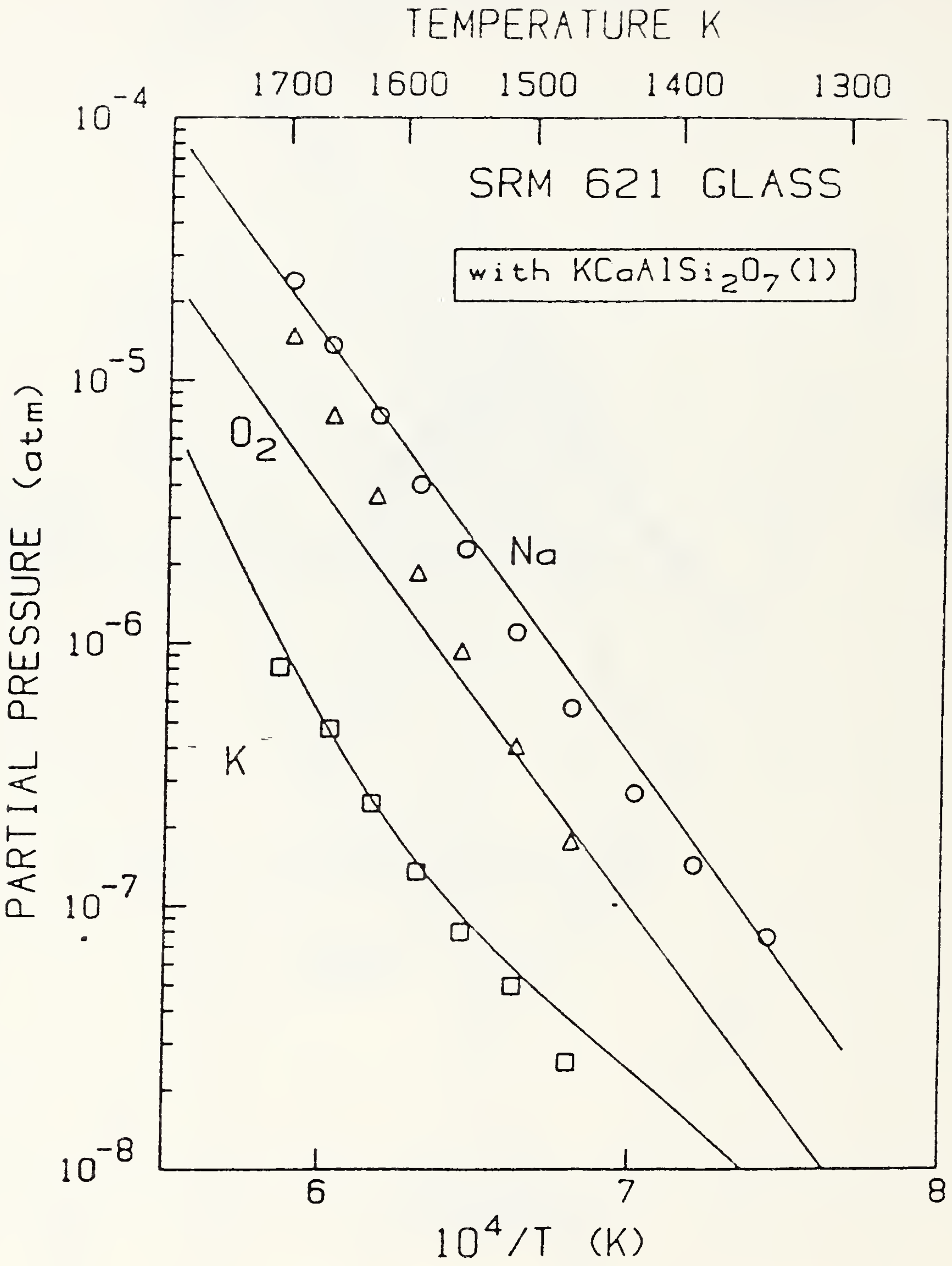

Figure 5. Comparison of predictive computer model (solid curves) with experiment (symbol data points).

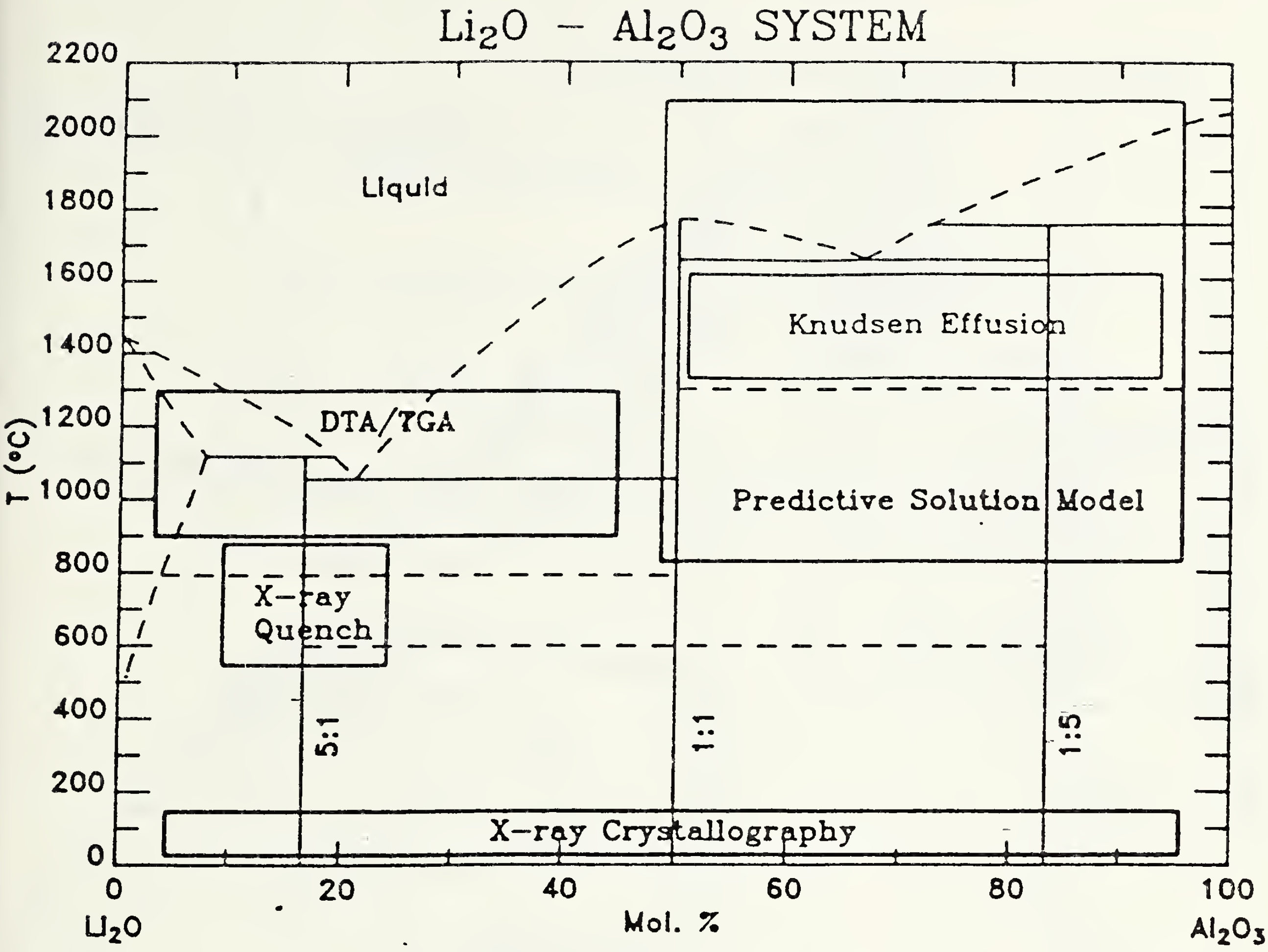

Figure 6. Preliminary Li_2O-Al_2O_3 phase diagram based on the experimental and modeling studies indicated for the applicable regions.

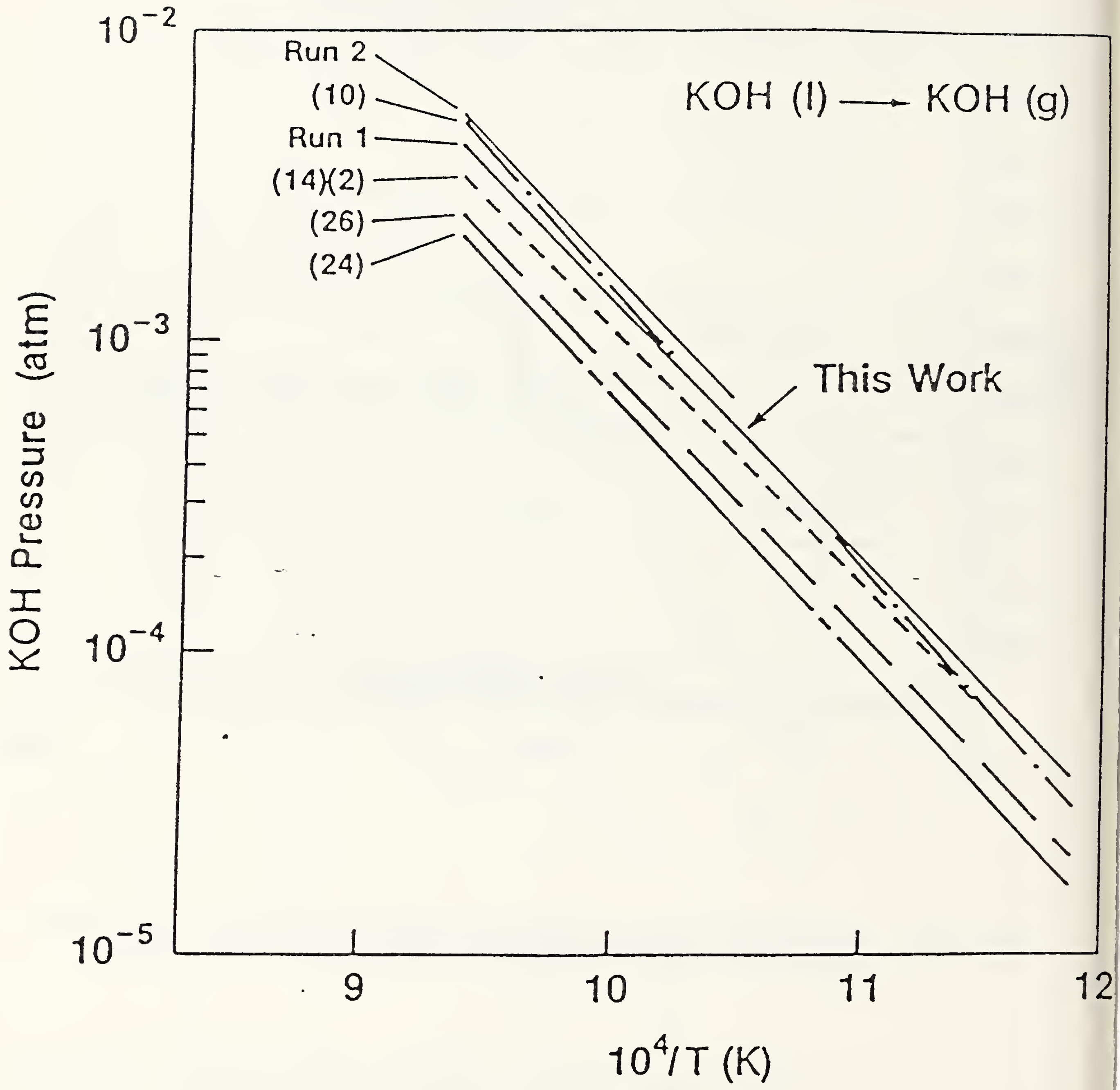

Figure 7. Comparison of KOH partial pressure data with literature curves. The short-dash curve [labelled (14)(2)] represents the JANAF literature evaluation.

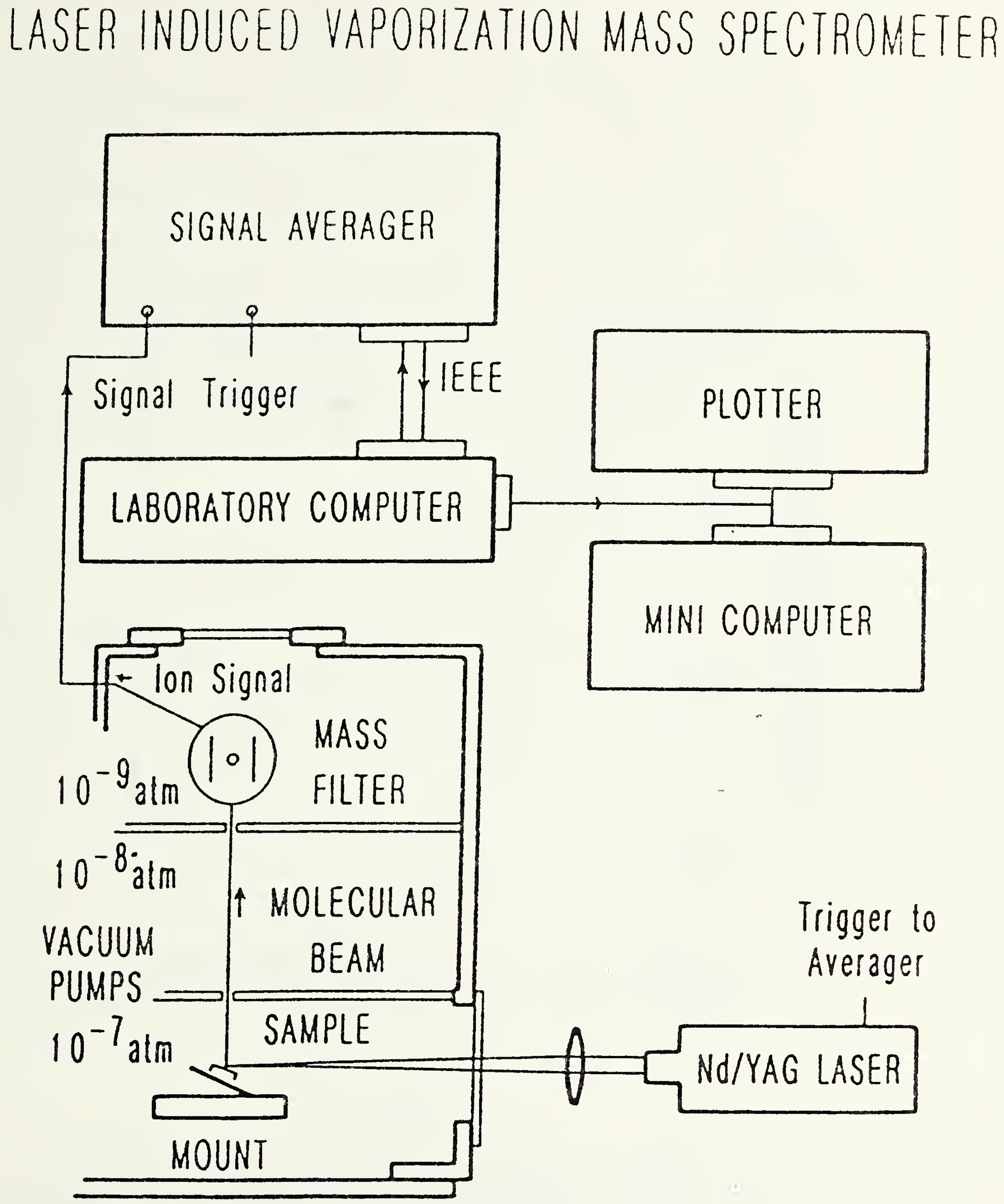

Figure 8. Schematic of laser-induced vaporization mass spectrometric facility.

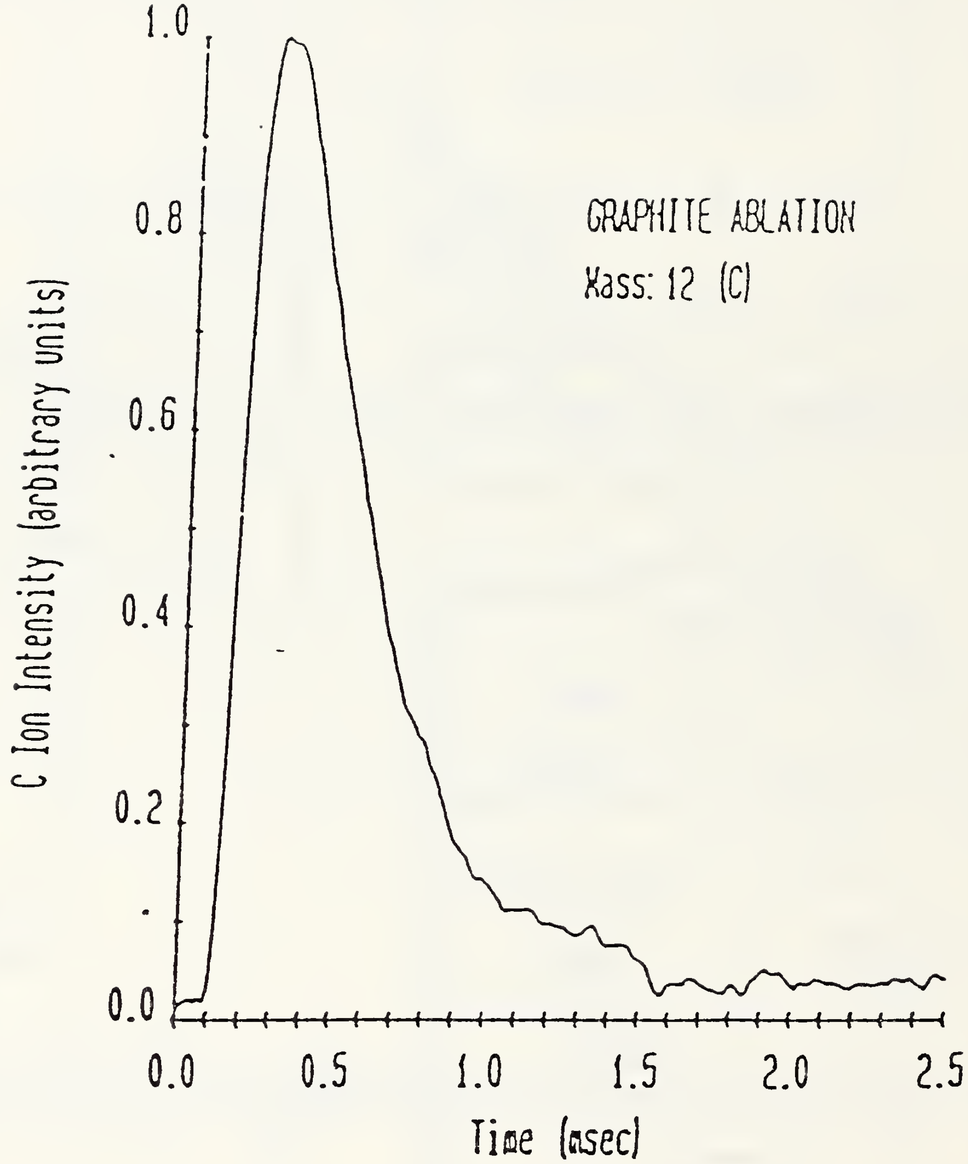

Figure 9. Time resolved profile of C^+ (C atom precursor) produced by laser-induced vaporization mass spectrometry of graphite at 4200 K and 1 atm.

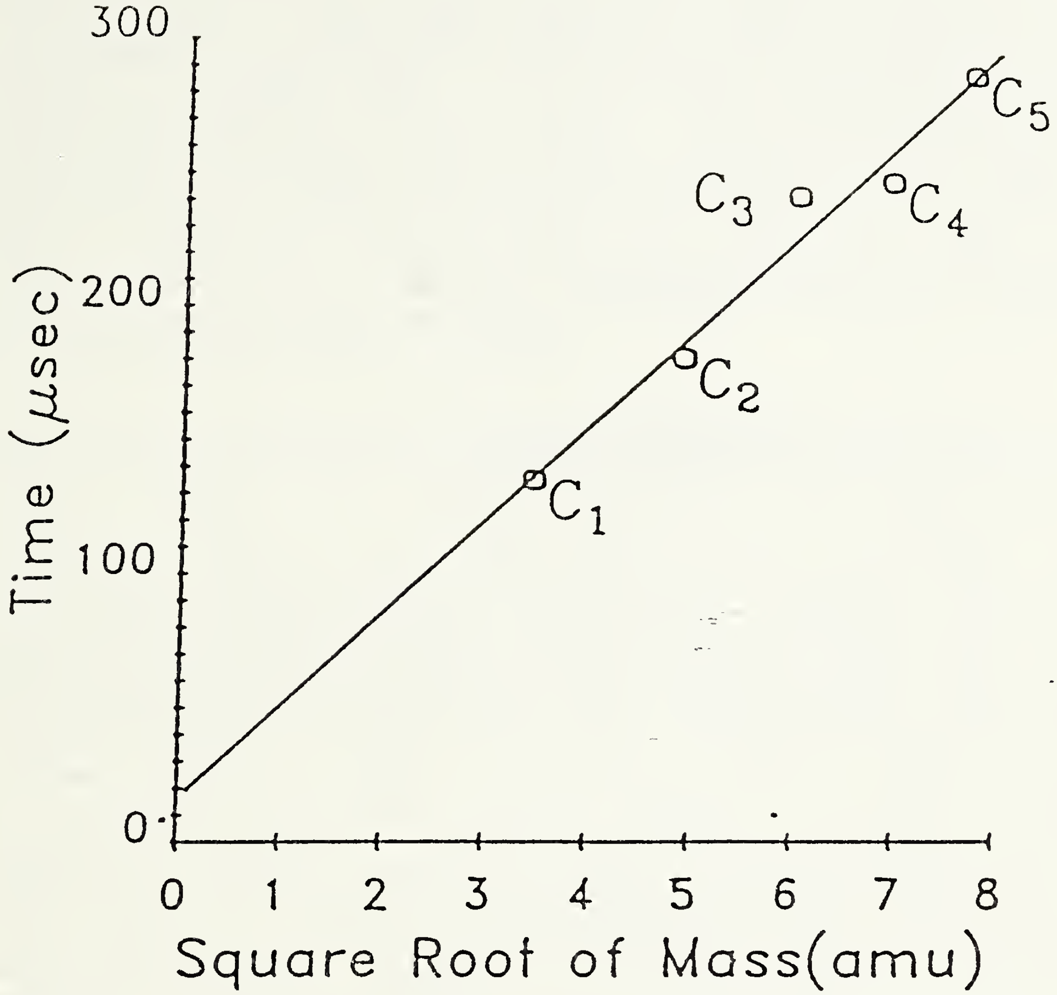

Figure 10. Dependence of C_n^+ (n=1 to 5) ion arrival time on molecular weight in the laser vaporized graphite system.

CERAMIC PROCESSING AND CHARACTERIZATION
Task 15416

Ceramics possess special property and functional characteristics that make them the preferred or only material for a host of applications in the basic industries and in the developing high technology areas such as electronics, heat engines, optical communication systems, advanced cutting tools and sensors. Even though ceramics can exhibit exceptional properties, industrial development and commercialization of new and improved products is inhibited because of the inability to manufacture ceramics on a high volume basis in a reliable manner. Unreliable manufacture leads to inconsistent performance and over design requirements which limit full exploitation of the useful and needed set of ceramic property characteristics. The technical difficulties associated with ceramic reliability are directly related to the need for improved processing as property limiting defects are introduced in the early processing stages and are propagated through each step so that they serve as origins for degraded properties and unreliable performance in service.

This task is concerned with Ceramic Processing Science and has major objectives to develop theory, concepts, measurement methodology, standards and data important to the advancement by industry of improved and reliable ceramics. Emphasis is on advanced (technical) ceramics such as dielectric and structural non-oxide materials, but activities relate also to the more conventional ceramics (e.g., refractories) as processing science is a key facet needed for the improvement of all types of ceramics. The Ceramic Processing and Characterization task is a coupled activity which integrates investigations on specific processing aspects with allied property/performance activities carried out in other Division tasks and through cooperative arrangements with universities, industry and other government agencies. Figure 1 schematically shows the integrated nature of the Division's ceramics program and indicates the breath and scope of the ceramic processing and characterization work. All major processing elements are included from powder synthesis to microstructure development. Significant work is underway on multicomponent ceramic powder synthesis using advanced precursor techniques (e.g., alkoxides, organometallics, decomposition routes). Coupled to the synthesis effort are companion phase equilibria investigations which define reaction pathways and establish the phase assemblages necessary for property achievement. Allied with this work are investigations devoted to sintering science and controlled microstructure development of NBS synthesized and conditioned powders. Combined with the processing oriented projects are companion characterization investigations, which encompass a full range of techniques, including complete electron microscopy, quantitative x-ray diffraction, NDE, Rutherford Back Scattering (RBS), neutron diffraction and small angle neutron scattering, and importantly powder measurements. The powder characterization facility has "clean room" (class 100) stations and a full-range of state-of-the-art measurement devices for submicron particle generation, size distribution, surface areas, porosity, etc. These characterization facilities in combination with an extensive assortment of processing laboratories (chemical precursors; laser processing; compaction and densification-isostatic and hot pressing, HIP; pressureless sintering, etc.) provide a unique set of experimental capabilities to carry out task objectives.

Through formal and informal scientific collaborations task activities are carried out in concert with leading groups in and external to NBS. Under a program established with the Joint Committee for X-Ray Powder Diffraction (JCPDS), research associates, with technical guidance by NBS, provide critical evaluation of published powder diffraction data, develop a numerical data base and provide "standard" powder patterns on selected materials. Research on the crystallographic characterization of ionic materials is being carried out with Bell Laboratories using neutron diffraction. In a joint program with Bell Labs, Trans Tech, University of Pennsylvania and Arizona State University investigations are underway to provide the basis for development of important dielectric ceramics for microwave applications. Collaborative work with Westinghouse Research Laboratories relates to the characterization of powder produced by the sol gel process. Joint work with MIT on sintering is underway and investigations on toughening mechanisms are being studied with Ohio State University. In a newly initiated activity with Martin Marietta Laboratories and Johns Hopkins University work will focus on powder properties and related surface science of non-oxide ceramic materials as well as on NDE characterization methods. These collaborative programs result in a comprehensive processing program which involves not only NBS staff but also three postdoctoral appointments, seven guest workers and nine Research Associates.

Financial support to carry out task research is derived from direct NBS appropriations and from other NBS offices (Office of Standard Reference Materials and Office of Nondestructive Evaluation). In addition partial support was provided by various divisions of the Department of Energy and the Department of Defense. For the purposes of this report major research activities of the Ceramic Processing and Characterization Task are summarized by the following subtask areas:

1. Powder Synthesis and Densification

2. Phase Equilibria and Structural Chemistry

3. Characterization and Properties

Each of these subtask areas are described in greater detail in following pages through the description of specific projects and their technical progress. The processing oriented task was established less than two years ago and yet many positive contributions to ceramic processing science are evident. For this fiscal year the most noteworthy include:

FY84 Significant Accomplishments

- A novel, low-temperature synthetic route to hard, wear-resistant ceramics is under development. A modified Wurtz-Fittig-reaction scheme is used to generate TiB_2 and SiC precursors at 150 °C. The precursors are converted to crystalline TiB_2 and SiC at 700 °C.

- Titania "rich" barium titanate precursors for $BaTi_5O_{11}$, $Ba_2Ti_9O_{21}$ and $BaTi_4O_9$ compounds having special dielectric properties, have been synthesized at low temperature by the controlled hydrolysis of barium-titanium alkoxide mixture. The amorphous precursors are converted to single-phase crystalline materials by calcining between 700 and

1100 °C. The nature of the products obtained in calcination is related to the synthesis parameters employed during precursor preparation. A "metastable" phase diagram based on these synthetically prepared materials has been constructed.

- Phase equilibria in ternary systems involving BaO and TiO_2 were investigated in order to attempt to find compositions amenable to producing dense ceramics by liquid phase sintering and to find alternative ways to synthesize the barium polytitanates at low temperatures. $Ba_2Ti_9O_{20}$ can be sintered at ~ 1000 °C with about two mole percent B_2O_3 to form specimens single phase to x-ray diffraction. It was found that a ternary compatability triangle exists at ~ 850 °C with $Ba_2Ti_9O_{20}$-$Ba_3V_2O_8$-$Ba_2V_2O_7$. Thus, fine grained single phase powder of $Ba_2Ti_9O_{20}$ can be synthesized by heating appropriate mixtures of $BaTiO_3$ and barium vanadates at 800 °C to 850 °C and dissolving the vanadate phases in dilute HCl.

- Research quantities of ZrO_2 doped TiO_2 powders with particle sizes from 4 to 0.2 µm have been prepared from controlled hydrolyses of Ti and Zr alkoxides in a flow-through reactor. The results of preliminary evaluations of these materials by scientists in the Center for Analytical Chemistry indicate that the powders will be useful as standards for microprobe analyses.

- Because of its fast ion conduction properties, β"-alumina ceramics have wide application as sensors or in fuel cells. Precursor powders have been prepared by the hydrolysis of mixed alkoxide solutions which crystallize to form mixed β/β"-alumina at 1100 °C, 400 °C below conventional methods. The tractability and tendency to form β- or β"-alumina preferentially can be controlled by the hydrolysis conditions.

- In collaboration with Dr. Peter Davies of Univ. of Pennsylvania, high resolution electron microscope lattice images were made of various BaO-TiO_2 phases prepared at NBS and from several industrial sources. All specimens of $BaTi_4O_9$, $Ba_2Ti_9O_{20}$ and $BaTi_5O_{11}$ showed an extremely large number of extended defects. These defects have been interpreted as being due to polytypic phases in each case. The distribution of polytypic defects causes incommensurate diffraction and leads to a modulated electron diffraction pattern. These extended defects apparently are at least partially responsible for the variability of the high Q values at gigahertz frequency found for these specimens.

- Phase transformations in zirconia have been used to produce toughened ceramics. This advance is based in part on information gained from its phase diagram. The pressure-temperature phase diagram of zirconia has been determined in the region up to 30.0 GPa and to 700 °C. The monoclinic form (M) transforms to a tetragonal phase (T') which is different, but related, to the high temperature tetragonal form (T). The transformation pressure varies from 2.8 to 4.2 GPa at room temperature depending on the history of the crystal and on increasing or decreasing pressure. The triple point, M-T-T', coordinates vary depending on direction of temperature and pressure with a range of P = 2.26 GPa, T = 596 °C; and P = 1.76 GPa, T = 535 °C with the former being the most probable values. The T' phase transforms to the high temperature T form at 596 °C and is essentially pressure independent. The T' form also transforms to an orthorhombic form at about 20.0 GPa at room temperature.

- A bond deformation model (BDM) has been developed of interactions in rocksalt structure compounds. The model established a phenomenological representation of central and many-body short-range interactions in these compounds.

- The fraction of the driving force during grain growth in sintering associated with chemical unmixing of a segregated solute has been estimated and can be significant. The effect is largest for small grain sizes and so may be important in stabilizing microcrystalline materials, narrowing grain size ditributions during grain growth and in inhibiting break away grain growth.

- SRM 1878, Respirable Quartz, was certified for weight percent quartz. This SRM will assist industry in a frequently required analysis. A major advance in quantitative x-ray powder diffraction methods was developed in order to determine accurate and precise values for the weight percent quartz.

- NBS in collaboration with the JCPDS-International Centre for Diffraction Data designed, wrote and tested a data entry, data evaluation, and data base building program. A multi-year test involving over 30,000 data base entries has been successfully completed, and the system has been transferred to the ICDD. Using the system, the ICDD with NBS assistance has reevaluated over half of the 42,000 entry Powder Diffraction File, the most widely used numerical data base in the world.

Powder Synthesis and Densification
Subtask 1 of Task 15416

J. Blendell, W. Coblenz, L. Domingues[1], K. Frase, J. Millet[2], D. Minor, T. Negas[1], J. Ritter, C. Robbins, S. Schneider

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[2] Guest Worker, Claude Bernard University Lyon I

Synthesis of Titania "Rich" Barium Titanate Powders From Alkoxides

Titania "rich" barium titanates have attractive dielectric properties for microwave applications, but are difficult to synthesize by conventional high temperature solid state reactions. This investigation explored alternate low-temperature solution routes to single phase titania-rich compounds. The syntheses of the barium titanate precursors were effected through the controlled hydrolyses of mixed barium and titanium alkoxides at ~ 80 °C. The initially amorphous materials were crystallized by calcining at temperatures in excess of 700 °C. Initial problems in establishing accurate Ba/Ti ratios during the mixing of the Ba and Ti alkoxides have been resolved through improved analytical procedures. Precursors for $BaTi_5O_{11}$ and $Ba_2Ti_9O_{21}$ have been produced in 10 to 20 gram amounts. These amounts are sufficient for initial ceramic pellet fabrication studies. Several distinct intermediate stages in the course of the syntheses reactions have been identified. Preliminary studies indicate that the behavior of the precursor is dependent upon the intermediate stage selected for hydrolysis and upon the pH of the hydrolysis system. Thus, for example it is possible to generate a barium titanate precursor which will yield $Ba_2Ti_9O_{21}$ upon heating at only 1100 °C whereas normally this phase does not appear until 1300 °C is reached.

This work has shown that the hydrolysis of mixed solutions of barium and titanium alkoxides can yield precursors which afford single-phase barium titanate materials upon calcination. There is a definite relationship between the development of an intermediate stage and the nature of the precursor derived from the hydrolysis at that stage. Precursors generated from a given Ba/Ti composition may yield a single phase product, a multiphase product or show anomalous phase-temperature relationships, depending upon the manipulations of the synthesis chemistry. Future work will involve: (1) Investigations into the structural relationships in the intermediate stages with the precursors generated therefrom, (2) studies on the incorporation, during the synthesis stage, of small amounts of other elements such as boron or vanadium to act as sintering aids for the final ceramic powder, (3) studies on the control of particle morphology based on advanced flow reactor technology being developed in an allied project.

Synthetic Methods for β"-Alumina

Sodium β"-alumina is a sodium fast ion conductor with wide applications in sensors and fuel cells. The β"-alumina structure can also accommodate and conduct other mono- and divalent ions and protons. Conventional preparative techniques require temperatures in excess of 1550 °C to transform and sinter ceramic sodium β"-alumina. This work has focused on the applications of low temperature synthetic methods to the preparation of β"-alumina precursor powders.

A variety of precipitation methods were tested. The most successful of these is the controlled hydrolysis of the mixed alkoxide. The amorphous hydroxide powder is calcined at 750 °C and crystallized at 1100 to 1400 °C, and characterized at various stages using x-ray diffraction, sedimentation and neutron activation analysis (NAA). The particle size distribution and powder tractability can be controlled through the hydrolysis conditions; the parameters involved include the temperature and duration of refluxing the alkoxide, stirring efficiency and the pH of the hydrolysis medium. Under optimum conditions, fine, mono-dispersed (0.2 to 0.4 microns) powders can be produced.

As in other low temperature syntheses, in the sodium β"-alumina system a relationship between the precursor "structure" and the subsequent crystallization reaction can be discerned. There is also evidence that changes in the phase diagram of the ternary Na-Al-Mg system are indicated for materials produced by these low temperature methods. Further experiments in these two areas are underway.

Accurate compositional analysis of β"-alumina is complicated by the presence of sodium, magnesium and aluminum simultaneously. A non-destructive analytical method using Neutron Activation Analysis is in the process of being refined in collaboration with Dick Lindstrom of the Center for

Analytical Chemistry. In addition to the further exploration of the interesting trends noted above, plans for future research include the characterization of sintered compacts of these powders.

A Novel Synthetic Route to Hard, Wear-resistant Ceramics

This work explored the chemistry of low-temperature routes to hard ceramics such as TiB_2, SiC and B_4C, as an alternate to the high temperature procedures now employed. The Wurtz-Fittig-reaction, sometimes employed in organic syntheses to couple aromatic and aliphatic halides was adapted for use in inorganic synthesis. For example $TiCl_4$, BCl_3 and Na were reacted in heptane at 150 °C to produce a TiB_2 precursor at ~ 750 °C in an argon atmosphere. A silicon carbide precursor was generated in a similar fashion from $SiCl_4$, CCl_4 and Na. Preliminary free energy estimates for the proposed reactions $TiCl_4 + 2BCl_3 + 10Na \rightarrow TiB_2 + 10NaCl$ and $SiCl_4 + CCl_4 + 8Na \rightarrow SiC + 8NaCl$ suggested a substantial bias towards the indicated products. However, in practice, the reactions proceed rather slowly and the resultant precursor is most probably an intermetallic material of indefinite structure. X-ray diffraction studies on the precursors indicated that they were amorphous. The mechanism for precursor formation is speculative at this stage but may involve a coupling of the two metals as a first step. For example:

$$BCl_3 + TiCl_4 + 2Na \rightarrow \underset{(I)}{Cl_2B\text{-}TiCl_3} + 2NaCl$$

Intermediate (I) can undergo further couplings with like moieties or with BCl_3 or $TiCl_4$ to produce large Ti-B clusters, i.e., the precursor. Heating this precursor to ~ 700 °C resulted in atomic rearrangements leading to crystal formation. The SiC precursor undergoes this change with considerable violence at ~ 600 °C. Both TiB_2 and SiC have been identified by XRD after heat treatment of the respective precursors.

Future studies on the reaction kinetics and mechanisms will be undertaken. The kinetic effects of using reagents with more labile halogens (e.g., $SiBr_4$ in lieu of $SiCl_4$), other solvent systems, etc., will be examined as well as the utility of alternative coupling agents such as Na-K or Na-Hg. Wurtz-Fittig-reactions are believed to occur through the formation of a organosodium intermediate, i.e., $RX + Na \rightarrow Na\ R + X$. The mechanism for the inorganic systems mentioned may be analogous or it may involve free radicals. An understanding of the reaction mechanisms and kinetics may permit optimization of the process, with control of product purity and product structure.

Submicron Ceramic Particles for Microprobe Analyses Standards

This work involved the synthesis of micron and submicron particles with a homogeneous distribution of heavy metals such as Zr, Hg, Pb and U, for application as calibration standards needed in microprobe techniques. The controlled hydrolyses of mixture of metal alkoxides was used as the primary synthetic technique. The reactions were conducted in an advanced flow-through reactor of commercial design to control particle size and morphology. Prototype materials were synthesized with two to three percent ZrO_2 in a matrix of TiO_2. These materials were evaluated for stability under microprobe conditions; elemental homogeneity, particle size and dispersion. Four samples were prepared with respective average particle sizes (Sedigraph measurement) of 4, 3, 1, and 0.2 µm. Initial evaluations by J. Small/D. Newbury, Center for Analytical Chemistry, indicated the following: (1) the materials are well behaved under the analysis conditions existing in the microprobe instrumentation, (2) the Zr distribution in the TiO_2 matrix appears reasonably homogeneous, (3) particle sizes and particle dispersions, particularly for this 0.2 µm material are satisfactory. Preliminary conclusions drawn from the work indicates that doped ceramic precursor materials have considerable potential for development into standards for microprobe measurements. Future work will include the synthetic chemistry required to introduce other elements such as U, Pb and Hg into a TiO_2 matrix. The flow reactor parameters will be adjusted to yield optimum particle size and dispersion.

Possible Transition Toughening in Enstatite--Cordierite Ceramics

Martensitic transitions in $MgSiO_3$ (enstatite) and Ca_2SiO_3 might possibly be utilized to toughen ceramics in a manner similar to the utilization of the martensitic transition in partially stabilized zirconia-yttria solid solutions. Ceramics composed essentially of $Mg_2Al_4Si_5O_{18}$ cordierite solid solutions have considerable utility as insulators in both high voltage electrical components and as substrates in computer chip technology. As enstatite, $MgSiO_3$, is in equilibrium with cordierite, it was decided to examine devitrified glasses and other precursor synthesized ceramic specimens of two-phase mixtures in the system $MgO-Al_2O_3-SiO_2$. Preliminary experiments at NBS in collaboration with Dr. C. Semler of Ohio State University showed that protoenstatite reverted to clinoenstatite upon surface grinding and that peculiar orientation effects also appeared in both phases on surface grinding.

However, these orientations proved to be inherent in the glass/ceramic devitrification process. The occurence or non-occurence of the martensitic transition to clinoenstatite does not appear to cause toughened ceramics in this system and it appears that the volume change required as protoenstatite transforms to clinoenstatite does not result in a toughening mechanism.

Sol-Gel Synthesis of Magnesium Aluminosilicates

Compositions in the $MgO-Al_2O_3-SiO_2$ system are candidates for use as semiconductor substrates due to their potentially low dielectric constants and high strengths. They also have applications in heat exchangers. Two different sol-gel processing procedures have been investigated for the preparation of cordierite and two phase cordierite-enstatite mixtures.

In the first process: aluminum sec-butoxide $[Al(C_4H_9O)_3]$ is added to a solution of partially hydrolyzed TEOS $[Si(C_2H_5O)_4]$. Magnesium acetate tetrahydrate $[Mg(C_2H_3O_2)_2 \cdot 4H_2O]$ is next added to the polymer sol. The final step is the co-hydrolysis of the mixed sol. The second process method was developed to avoid the use of the magnesium acetate since it was discovered that the acetate anion is trapped in the gel structure and high temperatures are required to burn it out. Magnesium and aluminum ethoxide are first dissolved and reacted to form a mixed alkoxide in solution. The mixed alkoxide is next reacted with a partially hydrolyzed solution of TEOS to form a polymeric sol which is hydrolyzed. In each process the nature and quantity of solvent, reaction temperatures and quantity of water used for hydrolysis have been controlled to give gels which are homogeneous on the molecular level.

Thermal treatments up to 700 °C have been used to convert the gels to glasses. Thermal analysis (DTA and TGA), infrared spectroscopy and x-ray diffraction were used to characterize the evolution from gel-to-glass-to-crystalline phases. For gels which have been dried at 200 °C, DTA and TGA measurements show an additional weight loss of 16 wt % and 14 wt % for processes one and two, respectively. For the first process, the weight loss occurs in two stages at 400 °C and 500 °C. IR spectroscopy indicates that the first stage corresponds to loss of the alkyl groups while the second, more exothermic stage involves loss of the acetyl groups. For the second process method the weight loss occurs in one step with a broad exotherm at about 300 °C. Crystallization of glasses with the composition of cordierite begins in both cases between 850 and 900 °C. Stuffed beta quartz solid solutions (containing Mg^{2+} and Al^{3+}) are the first crystalline phases to appear followed by cordierite.

Green State Ceramics

Proven reproducibility and reliability of ceramic components are needs that can be accomplished only by a combination of processing controls and NDE procedures together with a fundamental understanding of how defects arise and evolve within the processing cycle. This program focuses on the early stages of ceramic processing, the "green state", which consists of an assemblage of particulates loosely consolidated by forming methods and often containing binders, moisture, and other additives that normally are "burned out" during a preliminary calcination step. The green part, therefore, constitutes a reservoir of accumulated processing flaws and imperfections (voids, pressure or particle packing heterogeneities, fissures, agglomerates, inclusions, etc.) that persist and/or generate new defects during subsequent processing. Ideally, characterization and rejection of parts should begin at this stage, but virtually no work has been done on the properties of green compacts. Reliable methods to detect and relate initial flaws to final structural imperfections, therefore, have not been demonstrated.

Research consists of the following related elements:

(a) processing of green ceramics containing flaws of controlled size and distribution;

(b) characterization of these compacts through final microstructural evolution, primarily by microscopy and small angle neutron scattering (SANS); and

(c) evaluation of potential NDE methods cross-correlated with characterization measurements.

The cooperative program established last year between NBS and Argonne National Laboratory (ANL) has been continued. Within this program, ANL is conducting exploratory NDE measurements (ultrasonic, microfocus radiography, NMR) measurements on both the green and fully densified compacts prepared and characterized by NBS. At NBS, very promising NDE results have been obtained on the same group of specimens by SANS (see Mechanical Properties Section). This approach permits correlation of NDE methods with results obtained from measurements by microscopy, mercury porosimetry, surface analysis, image analysis, fracture mechanics and others.

Work continued on the spinel ($MgAl_2O_4$) green ceramics. Specimen sets have been prepared containing 0, 2 and 20 percent volume fractions of hard spinel agglomerates that serve as known and controlled amounts of flaws, with a median diameter of 2.5 µm. A second class of green compacts for NDE study consists of Al_2O_3 samples prepared by die pressing. Agglomerate size and strength is controlled by slugging and granulating high purity deagglomerated powders. It had been necessary to add a binder to the powder to permit increasing the pressing pressure from 5 kpsi to 30 kpsi without endcapping, and to permit examination of pressing pressures both above and below the slugging pressure. A binder/plasticizer combination has been added (by spray drying) such that the glass transition temperature of the binder is below room temperature.

A new cooperative NDE program has been established between Johns Hopkins University and NBS to evaluate these specimens ultrasonically.

Sintering Science

Sintering is a general term for the collection of processes which take place on heating a powder compact. For crystalline materials heated to temperatures below which any liquid phase appears, the possible mechanisms which contribute to a reduction in surface area are lattice diffusion, grain boundary diffusion, surface diffusion and vapor phase transport. Both lattice and grain boundary diffusion transport matter from grain boundaries to internal pores resulting in shrinkage as well as surface area reduction and these mechanisms are termed shrinkage mechanisms. In contrast, surface diffusion and vapor phase transport rearrange matter within pores due to local variations in surface curvature. This results in surface area reduction without shrinkage and these mechanisms are therefore termed coarsening mechanisms. Initial, intermediate and final stage sintering models have been developed over the last thirty years to quantify sintering kinetics during the microstructure evolution from porous bodies to dense material. In a multicomponent body the dominant sintering mechanism is rate limited by the slowest species over its fastest path. Sintering aids or dopants are added to change the relative mass transport coefficients and thus the microstructure development. Much of the science of sintering is concerned with determining the mechanism by which a sintering aid acts. The complexity involved in sintering is evident when one considers that for a simple oxide (two species) with the four mechanism considered, we have eight transport coefficients which can be changed by the addition of a dopant. Dopants also may have an important influence on grain boundary and pore mobility during final stage sintering. It must also be realized that the relative contributions of the various mechanisms generally changes with temperature and with microstructure evolution at a given temperature. Particle size and packing in the green compact provide the boundary conditions from which subsequent microstructures evolve.

A two fold approach is being taken to further our understanding of sintering. On the theoretical side, we continued to develop and refine models to describe the competition between mechanisms and their combined effect on microstructure evolution. Models which predict the effect of dopants on the various mass transport paths are also being developed since the mass transport data base alone is rarely sufficient to predict sintering behavior. The second approach is experimental and involves the effect of joint chemical and curvature driving forces on sintering and grain growth. A full range of equipment has been assembled to characterize the sintering process from starting powder to dense sintered bodies. Equipment is in place to measure particle size/agglomerate size distributions, surface area (BET), pore size distribution and to perform quantitative image analysis.

Differences in surface or grain boundary curvature provide the local driving forces for mass transport during sintering or grain growth, respectively. These driving forces are generally small when compared to driving forces associated with chemical reactions. It is therefore of interest to study the influence of joint driving forces on microstructure development since real systems may exhibit greater or lesser degrees of chemical equilibria during densification and grain growth.

The case of a spherical shrinking grain shedding segregated solute into the lattice has been examined. The increase in free energy associated with chemical unmixing must be less than the decrease in free energy associated with the decrease in grain boundary area. The ratio, F, of the free energy of chemical unmixing to the decrease in free energy associated with reduction of grain boundary area is:

$$F = \frac{\Gamma}{\nu_{G.B.}} \kappa T \left[\frac{C_s + \frac{2\Gamma}{r}}{C_s} \right]$$

where Γ = Gibbs excess (moles/cm^2)
C_s = concentration of solute in bulk (moles/cm^2)
$\nu_{G.B.}$ = Grain Boundary Energy (J/cm^2)
κ = boltzman constant = 1.38×10^{-23} J/atom-°K
T = absolute temperature (°K)
r = grain radius (cm)

The magnitude of F is large, and therefore the free energy of unmixing term is important, for small C_s, large Γ and small grain size. The effect may be important in narrowing grain size distributions and in stabilizing microcrystalline materials. Future experiments to investigate grain growth with joint chemical curvature driving forces are planned on material combinations such as NiO with MgO.

Crystallization of Sol-Gel Glasses

Many ceramics have been produced by sol-gel techniques at lower temperatures than is possible with conventional powder processing. However, the crystallization process is difficult to control to achieve the proper crystalline phase assemblage. Controlled nucleation was used in an effort to make crystalline quartz via sol-gel techniques, to produce a tough transparent ceramic that may substitute for glass in high performance applications. High density polycrystalline quartz has only been produced under hydrothermal conditions. When powders are sintered in air at high temperature cristobalite forms, while at low temperature no densification occurs. Dense SiO_2 glasses can be made by sol-gel processing and if the desired phase can be nucleated it would be possible to produce polycrystalline quartz. Nuclei were introduced during sol-gel processing of SiO_2 glass and the samples were heat treated to cause the nuclei to grow. Initial experiments have been unsuccessful due to homogeneous nucleation of other phases (cristobalite, tridymite) at the temperature required to densify the glass. In collaboration with John Blum (Rutgers U.) different techniques of producing the sol-gel glasses will be investigated and nucleation and growth of the quartz phase will be studied.

Densification of Titania "Rich" Barium Titanates

Recent investigations in the $BaO-TiO_2$ system by R. Roth have shown the existence of several new low temperature phases. These phases, which cannot be produced by conventional processing techniques, require novel powder production techniques as have been developed by J. Ritter. One of these new phases, $BaTi_5O_{11}$, is predicted to have excellent dielectric properties. Extrapolation from the lower Ti containing phases predicts a temperature independent dielectric constant and low loss at microwave frequencies. However, this phase is not stable above 1150 °C but it can be retained metastably at 1200 °C for short times (< 1 hr).

Dense samples (> 99 percent of theor.) have been produced. The powders were calcined (700 °C, 1 week), isostatically pressed (400 MPa/60,000 psi) and sintered (1150 to 1200 °C, 15 to 30 min). The initial powder particle size has been measured by sedimentation and the final grain size has been determined by SEM examination of the sintered samples. Preliminary measurements of the dielectric properties (H. O'Bryan, Bell Laboratories) have indicated that phase stability is of critical importance. If excess Ti is present, the samples have a large loss. Wet chemical analysis of Ba compounds is not accurate enough for determining the phase chemistry of these materials. Thus the Ba/Ti ratio has been measured using gamma-ray spectroscopy (activation analysis). This involved making standards for Ba and Ti and then developing a standard for $BaTi_5O_{11}$ with R. Fleming of the Center for Analytical Chemistry.

Sintering of Silicon Oxynitride Ceramics

The incorporation of boron into silicon oxynitride structures has been largely a subject for speculation. Boron is used as a sintering aid in the densification of SiC ceramics but has received little attention in the case of Si_3N_4 and oxynitride ceramics. Estimates of the strain associated with the substitution of B for Si suggests that substitution of some B into the structure could be achieved if B could be forced to enter a tetrahedral coordination with N rather than the trigonal coordination which is found in hexagonal BN.

Consideration of the Si-Y-O-N and Si-Al-O-N systems suggests that B might substitute more readily into Si-Y-O-N phases than the Si-Al-O-N phases. The Si-Y-O-N phases are expected to be favored (1) because the somewhat higher ionicity of Y than of Al suggests that charge transfer to B atoms may occur to promote the necessary tetrahedral coordination of the B; and (2) because the occurrence of compounds such as the N-melilites in the Si-Y-O-N system are expected to be more tolerant of strains associated with B substitution than are the phases of the Si-Al-O-N system.

Fabrication of silicon oxynitride ceramics containing various amounts of Al_2O_3, B_2O_3 and Y_2O_3 has been undertaken. Results show that either Al_2O_3 or B_2O_3 separately improve the densification of N-melilite ($Y_2O_3:Si_3N_4$) at 1650 °C; but when added together, melting and precipitation of hexagonal BN is observed at this temperature. Techniques are being investigated to produce a transparent, fully dense oxynitride ceramic with a nominal N-melilite composition.

Phase Equilibria and Structural Chemistry
Subtask 2 of Task 15416

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The System $BaO-TiO_2$

Several of the compounds in the high titania portion of the $BaO-TiO_2$ system have properties which make them useful as dielectric components in several microwave applications such as 4 gigahertz relays for cellular telephones and phased array radar components. The compounds used commercially for these applications include $BaTi_4O_9$ (1:4) and, $Ba_2Ti_9O_{20}$ (2:9). The compound $BaTi_5O_{11}$ (1:5) has been postulated to have similar properties but had never previously been prepared as a single phase sintered ceramic. The properties of interest include a high dielectric constant (20 to 50) a very high Q (the reciprocal of the dielectric loss) and a very low τ_K (temperature coefficient of the dielectric constant) as well as a low Tf or changes in the temperature coefficient of the resonance frequency of the dielectric constant. Of all of these properties the very high Q at gigahertz frequencies is the most desirable for all microwave applications and the most difficult to obtain and to optimize. This study has been undertaken in an effort to understand the factors which affect high Q properties of these materials at microwave frequencies.

Amorphous coprecipitated powders, prepared by hydrolyses of mixed Ba and Ti ethoxides, were heat treated at various times and temperature to determine the apparent phase relations in the $BaO-TiO_2$ system. The results are not necessarily completely interpretable in terms of lowest free energy phase equilibria. Indeed, these results are highly dependent upon the degree of polymerization which is allowed to take place in the mixed ethoxide solutions. A phase "equilibrium" diagram for highly polymerized solution precursors has been constructed and is shown in figure 2. The major "non-equilibrium" features of this diagram are the occurrence of only the 1:2 and 1:5 phases at 700 °C and the extended existence of the 1:5 phase up to about 1200 °C. The 2:9 phase is not found in these mixtures until the 1:5 compound begins to decompose. However, the 2:9 phase can be found to occur at 1100 °C or below if the ethoxide mixtures are hydrolyzed immediately after mixing.

It was found that coprecipitated specimens of $BaTi_5O_{11}$ could be formed into sintered ceramic specimens with about 99 percent theoretical density. The powder was first calcined for extended periods (25 to 100 hours) at 700 °C to form a crystallized ultra fine grained product (~ 100 Å grain size) free from alcohol or other carbon impurities. Pellets of the desired size were die pressed and then iso-pressed to remove extraneous pores. These pellets were then fast fired from ~ 700 °C to 1200 °C (in ~ 10 min.) held for half an hour and removed from the furnace. High density specimens were invariably attained by this technique. A sample of precipitated powder was sent to Dr. H. O'Bryan of AT&T Bell Telephone Laboratories for analysis of physical properties. Using other modifications of this basic sintering technique he prepared specimens of somewhat lower density and found physical properties somewhat similar to those of the 1:4 and 2:9 ceramics.

Ternary Systems Containing BaO and TiO_2

In order to obtain a larger temperature range for examination of $BaTi_4O_9$, $Ba_2Ti_9O_{29}$ and $BaTi_5O_{11}$, further experimental studies have been attempted to discover ways to extend their stable or metastable existence. Additions of ZrO_2 to $BaTi_5O_{11}$ seem to slow down the kinetics of the high temperature decomposition and further studies are contemplated. However, attempts to add a low melting third component to encourage grain growth at lower temperatures (B_2O_3, V_2O_5 and MoO_3) all show that the 1:5 phase decomposes more readily at temperatures between about 900 and 1000 °C. These components, however, do make it feasible to examine larger grain size equilibrated specimens of 2:9 and 1:4. For instance, both 1:4 and 2:9 are in equilibrium with $BaTiB_2O_6$ (dolomite structure) which melts at about 1050° and form apparently "single phase" dense ceramics with about two percent B_2O_3 at ~ 1000 °C.

Phase equilibria studies in the system $BaO-TiO_2-V_2O_5$ were the most revealing. The system $BaTiO_3-BaV_2O_6$ (1:1) is not binary; instead the join is crossed by equilibrium tie lines between the polytitanates and $Ba_3V_2O_8$ (3:1) and $Ba_2V_2O_7$ (2:1). In addition, a ternary compound was found of the composition $Ba_3TiV_4O_{15}$, which is orthorhombic; $\underline{a} = 32.427$, $\underline{b} = 7.701$, $\underline{c} = 5.556$ Å. The other compound in the barium vanadate system, $Ba_3V_4O_{13}$, was found in equilibrium only with the ternary phase and the 1:1 and 2:1 vanadates. Rutile (TiO_2) was found to form a tie line with $Ba_2V_2O_7$ but not with $Ba_3V_2O_8$. Instead, a three phase triangle was found to exist composed of $Ba_2Ti_9O_{20}$ and both $Ba_3V_2O_8$ and $Ba_2V_2O_7$. This ternary equilibria can be established by heating $BaTiO_3$ with either BaV_2O_6 or V_2O_5 in the appropriate composition range at temperatures as low as 800 °C. Convenient compositions are $2BaTiO_3$:$1BaV_2O_6$ and $3BaTiO_3$:$1V_2O_5$. A 100 gm batch of the former was prepared by heating at 850 °C for 18 hours. The batch was then treated with dilute HCl and carefully washed and decanted. The resulting product of 27.2 grams, better than 95 percent theoretical yield, was found by x-ray diffraction to be single phase $Ba_2Ti_9O_{11}$. These x-ray patterns are similar in most, but not all details, to the specimens calcined at ~ 1000 °C or higher. These heat treatments of the vanadium synthesized $Ba_2Ti_9O_{20}$ specimens are currently being examined by HREM to determine if any relationship exists between the heat treatment and the two polytypes. The join $BaTi_5O_{11}$-$Ba_2V_2O_7$ appears to exist at very low temperatures but decomposes to $Ba_2Ti_9O_{11}$-$Ba_2V_2O_7$-TiO_2 before 900 °C. The join 1:4-$Ba_3V_2O_8$ exists at all temperatures in the solid state above about 900 °C. A large batch of low temperature calcined $BaTi_4O_9$ is currently being prepared in the same manner as was done for $Ba_2Ti_9O_{20}$ in order to examine the thermodynamic relationship between the two $BaTi_4O_9$ polytypes.

The System Li_2O-Al_2O_3

This system, important in chemical propulsion systems, can be naturally divided into two parts, $LiAlO_2$-Al_2O_3 and Li_2O-$LiAlO_2$. The high Al_2O_3 portion is a refractory system with melting points all above 1600 °C and with little or no problems related to hydration by atmospheric moisture. The high Li_2O portion is the opposite, with melting beginning near 1000 °C and must be protected from atmospheric moisture at all times. The high alumina portion of the system contained the spinel-like compound $LiAl_5O_8$, which melts incongruently at about 1750 ± 20 °C. The eutectic between $LiAlO_2$ and $LiAl_5O_8$ was found to occur at about 1650 ± 20 °C near the 1:2 composition.

A large batch of $LiAl_5O_8$ was prepared for neutron diffraction analysis by the Rietveld technique in order to test for Li/Al site ordering in the spinel structure. The specimen was quickly cooled from about 1600 °C and should have represented the high temperature order/disorder state. The neutron diffraction pattern, unlike the corresponding x-ray pattern, showed many peaks which could not be attributed to the phase $LiAl_5O_8$ characterized by the cell parameter $a = 7.9036$ Å, nor to either $LiAlO_2$ or Al_2O_3. The "spurious" peaks can be indexed on the basis of a primitive cell with parameter $a = 8.09$ Å. Their origin is, as yet, not known. These "spurious" peaks were eliminated from the pattern and the structure of $LiAl_5O_8$ was refined by the Rietveld method. The results show that the structure is similar to $LiFe_5O_8$ and the structural formula can be written as $Al_8(Li_4Al_{12})O_{32}$ involving a 1:3 ordering of the cations in the octahedral sites. There is no sign of Li^+ in tetrahedral sites.

Six compositions were prepared in the high Li_2O portion of the system by dry mixing of Li_2O and precalcined $LiAlO_2$. Small portions of these specimens were sealed in Pt tubes and quenched in air from various temperatures between 700° and 1050 °C.

Care was taken to protect the specimens from atmospheric moisture during handling and characterization before and after heating. Most specimens showed only a small amount of LiOH which probably formed during the x-ray exposure, as this technique requires exposure to atmosphere for a few seconds. However, the results of these heat treatments are very inconclusive. Compositions containing 95 and 90 percent Li_2O show only Li_2O and $LiAlO_2$ or melted material. Compositions between 85 and 55 percent Li_2O show inconclusive results for the phase transition between α and β Li_5AlO_4. Apparently this transition cannot be reproducibly quenched from any given temperature although both phases were never found to exist in the same diffraction pattern. Further work is needed to characterize this transition.

The P-T Phase Diagram of Zirconia

Zirconia (ZrO_2) is currently a very important major component of modern ceramic materials. Since the discovery of the phenomenon of transformation toughening, a process which significantly improves the mechanical properties of the ceramic by the presence of a denser metastable phase in the matrix, it has become increasingly important to develop a clearer understanding of the pressure-temperature phase diagram of ZrO_2. Despite the many studies reported for the zirconia system as a function of pressure and temperature, the phase diagram and structures of the high pressure phases are poorly understood, primarily because in situ measurements under hydrostatic conditions are lacking. Thus, this project is concerned with the determination of the phase diagram and structures of the zirconia system as a function of pressure and temperature.

The stability fields of the several different phases of zirconia were determined by detecting the phase transformations in single crystals as a function of pressure and temperature through optical polarizing microscopy. The observations were made in both hydrostatic and nonhydrostatic conditions in a diamond anvil pressure cell (DAC), designed especially for high temperature use. In these experiments the DAC was heated externally with a high-power miniature resistance coil heating element. With this heating arrangement, temperatures, measured with a chromel-alumel thermocouple, were accurate to within 5 °C for temperatures below 300 °C and to within 10 °C in the 600 °C range. The precision in the temperature measurement was 2 °C over the entire range.

Pressures were measured by the ruby fluorescence method with the appropriate corrections for the temperature dependence of the R-lines included. As the high accuracy of this method of pressure measurement is limited to temperatures below about 300 °C, the pressures at higher temperatures were estimated, assuming that the values measured at 300 °C did not change significantly on heating the cell to higher temperatures.

To identify the structure of the various phases of zirconia, x-ray powder diffraction studies were made in the DAC by the energy dispersive technique at room temperature. A methanol-ethanol-water mixture (16:3:1 by volume, respectively) was used as the pressure transmitting medium to provide a hydrostatic environment up to 14.4 GPa and to temperatures up to 450 °C. Above this temperature this ternary mixture decomposes and cannot be used. A substitute pressure transmitting medium, polydimethylsiloxane can be used successfully to 650 °C before it too begins to decompose.

The revised portion of the zirconia phase diagram determined in this work, is shown in figure 3. The previously reported diagram by Becquillon and Susse is depicted by the heavy solid lines, while the new results are shown as the broken lines along with their associated data points. One of the main features of the new results is that the monoclinic phase (M) transforms to a tetragonal II structure (T') which is different from the high temperature tetragonal I structure (T) by having lower symmetry (from $P4_2/nmc$ to possibly $P4$) and an a axis which is the √2 times the a-axis of the high temperature tetragonal I phase. Because of a similarity in cell constants, this high pressure phase is very likely the tetragonal T' phase reported by Heuer and also by Brandon.

The M-T' transition pressure depends on the history of the crystal. For temperatures below 300 °C the M-T' phase boundary was crossed at a constant temperature by varying only the pressure. The solid squares in figure 3 are data points for the transformation when it occurs for the first time in a "virgin" crystal with increasing pressure. Those points are at higher pressures than the corresponding ones after the crystal has been subjected to several transformation cycles (open diamond data points in Fig. 3.). The lowering of the transformation pressure may be due to an increase in the number of defects in the crystal as a result of the cycling of the transformation. The defects can be considered as nucleation sites for initiating the transition, thus the increased number of these defects favors the occurrence of the phase transformation. The points representing the reverse transformation, T'-M, (open circles in Fig. 3), occur at lower pressures indicating a hysteresis effect that appears to be independent of temperature. The transformation takes place rapidly with some cracks developing in the crystal. After cycling through the transformation several times, bands of strias are formed which are probably the result of twinning. This effect together with the apparent temperature independence of the hysteresis and the rapidity with which the transformation takes place, suggests that a diffusionless martensitic-type transformation is involved. The broken lines represent least-squares fits of straight lines to the data points. The higher pressure broken line represents the M-T' transformation on increasing pressure, and the lower pressure broken line the T'-M transition on decreasing pressure. One can assume that the equilibrium phase boundary for the M-T' transition lies somewhere intermediate to these two extremes.

The T'-T phase boundary was crossed at constant pressure while changing the temperature. The solid diamonds represent the transformation on increasing temperature, and the solid circles, the reverse. Here also a rapid transformation and pronounced hysteresis were observed. The broken lines are least-squares fits to the data. They intersect at a triple point whose exact location is not well determined because of the uncertainty in locating the true position of the equilibrium phase boundaries. The intersection of lines determined by increasing pressure and increasing temperature give a triple point of 2.2 GPa and 596 °C. The corresponding values for the decreasing variables are 1.7 GPa and 535 °C. The former are probably closer to the equilibrium value.

Upon increasing pressure at room temperature, the tetragonal T' phase was observed to be stable up to about 20 GPa, at which point a new transformation takes place. The new high pressure phase is the same one first reported by Liu, having the cotunnite structure after zirconia had been subjected to pressures higher than 20 GPa and temperatures of 1000 °C. However, in that report it was noted that the phase could be retained at atmospheric pressure, whereas in the present experiments a nearly complete reverse transition to the original monoclinic phase was observed on release of pressure.

A program has been initiated to retain the T' form at atmospheric conditions in order to determine the retrieved material's mechanical properties as a toughening agent comparable to the high temperature tetragonal form.

Tetragonal Zirconia

The physical properties of CeO_2 stabilized tetragonal zirconia are similar to, but slightly different from, the partially stabilized zirconia found in the Y_2O_3-ZrO_2 system. In order to better understand these properties, both thermodynamic and mechanical, it would be desirable to study single crystals. However, such crystals cannot be prepared by the standard skull growth techniques because, at the melting point (~ 2700 °C for 18 percent Ce) CeO_2 is at least partially reduced in air or even O_2 to Ce_2O_3. Attempts were made to flux grow single crystals using either Bi_2O_3 or PbF_2. Other common fluxes using either V_2O_5 or MoO_3 would only result in rapid formation of Ce^{+3} ions. Single crystals of both ZrO_2 and CeO_2 have been grown from both Bi_2O_3 and PbF_2, however, the 18 to 20 percent CeO_2 tetragonal solid solutions merely decompose to their respective end members in both fluxes, as well as under hydrothermal conditions. Apparently the tetragonal solid solution is not stable at temperatures between 700 to 1200 °C under these flux conditions.

In an effort to find another system where single crystals of tetragonal zirconia can be synthesized, studies were conducted on the system ZrO_2-$YTaO_4$ and flux reactions of the resultant solid solutions. Tetragonal ZrO_2 solid solutions can be prepared at about 15 mol % $YTaO_4$. The extent of the tetragonal phase field has not yet been established but the amount of tetragonal vs. monoclinic ZrO_2 (usually about 90/10) is dependent on the heat treatment and presumably on the grain size and stress relationships of the grains in a ceramic pellet. Preliminary experiments with Li-molybdate indicate some success but considerable decomposition occurs at low temperatures. Further experiments will be conducted to attempt crystal growth at higher temperatures and to establish the thermodynamic and mechanical properties of the solid solutions in this system.

Extended Defects in Barium Titanates Ceramic Dielectric Materials

Specimens of $BaO:TiO_2$ 1:4, 2:9 and 1:5 prepared by heat treatment of coprecipitated powders were provided to Dr. Peter Davies of the University of Pennsylvania for examination by high resolution electron microscope lattice images (HREM-LI). Other sintered ceramic specimens having 1:4 and 2:9 compositions prepared by AT&T Bell Labs and by L. Domingues of Trans Tech, Div. of Alpha Industries were also transmitted to Dr. Davies. These two companies are the only U.S. industrial sources of these microwave ceramic components. Electron microscope examinations were conducted at the University of Pennsylvania utilizing a Phillips 400 microscope capable of about 3.5 Å resolution.

A higher resolution (JEOL 200CX) microscope was utilized at the NSF regional facility of high resolution microscopy at Arizona State University. The highest resolution, however, was obtained utilizing the new NBS microscope (Phillips 430) with the cooperation of L. Ives of the Metallurgy Division.

All of the specimens examined from the NBS alkoxide precursor preparations as well as both industrial sources and from all three compounds ($BaTi_4O_9$, $Ba_2Ti_9O_{20}$ and $BaTi_5O_{11}$) show a very large number of extended defects. These defects seem to be intrinsic to these three phases. As yet, we have not established whether or not a relationship exists between the number and extent of the defects and the experimental heat treatments and corresponding physical properties. It seems to be self evident, however, that these extended defects are in a large part responsible for the high Q values (3000 to 10,000) at gigahertz frequencies. For instance, the previously examined specimens of $BaNd_2Ti_5O_{14}$ which show similar properties at kilohertz frequencies have normal Q values (20 to 30) at gigahertz frequencies. This compound and other titanates with similar properties show no sign of such intrinsic extended defects, although $Ba(Zn,Ta)O_3$ and $Zr(Ti,Sn)O_4$ which are also utilized at microwave frequencies probably show extended defects due to order/disorder phase transitions.

The high resolution electron microscope lattice images (HREM-LI) of the 1:4, 2:9 and 1:5 compounds have all been interpreted as showing that each of these phases has a second polymorph of the same composition and similar structure with lower symmetry than the previously postulated structure. In each case the two polymorphs seem to exhibit a polytypic relationship coexisting with coherent integrowths in all the high temperature heat treatments examined. As has been done with other polytypic transitions (SiC, ZnS) it may be postulated that some second order thermodynamic relationship exists and/or a third or higher order continuous transition occurs. As with such other more well known polytypes the theory is more easily established than the experimental confirmation. No such transition has been proven for other polytypes.

Structurally, the new polytypes of the three compounds have not been proven as no single crystals of such phases have yet been prepared. However, from the electron diffraction patterns and the high resolution lattice images their structures may easily be postulated. The 2:9 compound has been previously shown to be triclinic, space group P1, with a six-layer structure composed of hexagonally close packed, oxygen ions with Ti in octahedral intersticies and two Ba ions substituting for three absent oxygen ions. The alternate polytype is that of a three layer structural repeat with the other three symmetry related layers missing. Such a polytype has the lowest possible symmetry of P1 and requires two Ti-octahedra to share a single face per unit cell. The <u>b</u> axis of the P1 polytype of 89.5° is then found to be 79.2° in both the lattice image and an ideal model of close packed ions. The $BaTi_5O_{11}$ compound also has a six-layer structure of similar Ti-octahedra but with a one-for-one substitution of Ba and oxygen and monolinic symmetry. Adjacent layers of either the 2nd and 3rd or 5th and 6th can coherently intergrow with a slip of one octahedra along the "c" direction resulting in two Ti-octahedra sharing a common face per unit cell and triclinic symmetry. Such a shift can only occur between two adjacent layers in which at least one does not contain a Ba^{+2} ion. The compound $BaTi_4O_9$ has been shown to be orthorhombic with infinitely extended double rows of double Ti-octahedral sharing only corners and edges. The structure is repeated, by a process known as "chemical twinning", twice each unit cell. The Ba ion occurs in a 10-fold coordinated hole formed by this chemical-twinning which results in a mirror image of the rows every 1/2 unit cell. However, if the "chemical-twinning" process does not occur a new polytype would be formed with Ba in an 8 to 12 fold coordinated site. Such a structure is found for $Na_2Ti_4O_9$ which is actually non-stoichiometric as the site is too small for two full Na^{+1} ions. This new monoclinic polytype of $BaTi_9O_{11}$ is found in the HREM-LI. It should be noted that each of the new polytypes has lower symmetry than the original, occurs in coherent integrowth with the previously reported structure, is present to some degree in all examined specimens and has an as yet unexplained thermodynamic relationship to the originals.

Cluster Variation (CVM) Models and Theory of Phase Diagrams

The Cluster Variation Method (CVM) is one approach currently under investigation to model and predict phase relations and structures of ceramic oxide systems. The CVM forms a hierarchical set of approximate solutions for Ising-model type problems; in which the free energy is approximated as a function of the energies, and probabilities of occurrence, of all possible configurations of some small cluster of atoms. Because the CVM includes considerations of short range order (SRO) and space group symmetry, which are absent from regular-type solution models, it yields results which are both quantitatively and qualitatively superior.

CVM analysis of the antiferromagnetic-paramagnetic transitions in Cr_2O_3 and α-Fe_2O_3 illustrate the quantitative improvement obtained with CVM, relative to a mean field (MF) approximation; and since the antiferromagnetic transition is analogus to an order-disorder transition these results are generally applicable to order-disorder and cluttering transitions. In the Cr_2O_3 case for example, the Neel temperature (T_N) calculated by a MF-approximation is 1.3 times the experimental value (1.3 T_{EXP}), but for CVM approximations with 4- and 6-atom clusters the results are 0.9684 T_{EXP} and 0.9651 T_{EXP}, respectively. For α-Fe_2O_3 the MF-result is 1.4 T_{EXP} and the 4- and 6-atom cluster approximations yield 1.21 T_{EXP} and 1.17 T_{EXP}, respectively. Clearly, the CVM results represent a dramatic improvement relative to the MF.

Theoretical calculations of the Fe_2O_3-$FeTiO_3$ phase diagram have also been performed in a pseudoternary CVM approximation which includes both chemical and magnetic interactions. Inclusion of the magnetic degree of freedom produces a more realistic treatment of the configurational entropy, and therefore a much improved value for the stabilization of $FeTiO_3$, due to cation ordering. Also, it is predicted that magnetic ordering has a dramatic effect on the compositions of coexisting Fe_2O_3-rich and $FeTiO_3$-rich solutions at low temperatures, a prediction for which there is strongly suggestive evidence in mineral samples (Fig. 4).

Current work includes the modeling of systems which feature coupled substitutions in a variety of geometries. An example of a coupled substitution is $Mg^{++} + Na^{+}$ for $Al^{+++} + []^{\circ}$ ($[]^{\circ}$ = a vacancy) in sodium β-alumina. Typically, coupled substitutions lead to ordering and/or clustering on distinct but interacting sublattices, and this ordering can affect physical properties. For example, disordering of Na^+ and []° in sodium β-alumina promotes ionic conductivity; but preliminary results indicate that ordering of Al^{+++} and Mg^{++} in the spinel block will promote ordering of Na^+ and []° and therefore suppress ionic conductivity.

Computer Simulation of Crystal Structures and Properties

A cooperative program has been established between NBS (R. S. Roth and B. Burton), University College, London (C.R.A. Catlow and A.N.C. Cormack) and University of Pennsylvania (P. Davies) to apply computer simulation of crystal structures to the elucidation of the structure and properties of the Ba-polytitanates. At University College the investigators utilize minimum potential energy functions to yield optimum bond lengths and angles for any given composition and structure. Elastic and dielectric properties can be calculated and coherent interfaces and properties in ceramic systems can be modeled. This is currently being done for the 1:4, 2:9 and 1:5 phases and polytypes as well as $BaNd_2Ti_5O_4$ and $Nd_2Ti_9O_{24}$. At the same time, the relevant structure and property data are being examined with Dr. M. Zocchi (University of Milano, Italy) Dr. D. Kolar, University of Ljubljana, Yugoslavia and Dr. A. Olsen, University of Oslo, Norway as well as Dr. H. O'Bryan, Bell Labs and L. Domingues, Trans Tech. At NBS the Cowley-Moody multislice program, as developed and updated at Arizona State, is being utilized to interpret the lattice images obtained by P. Davies of the Ba-polytitanates and other ceramic specimens. Dr. Burton has also written a program for graphic display of the atomic positions of these various structures utilizing known atomic radii to simulate the high resolution lattice images. These graphically displayed structures can be rotated at will to illustrate the structure in three dimensions from any orientation and has proven invaluable in interpreting the lattice images obtained from variously oriented crystals.

Bond Deformation Models

Many binary compounds crystallize in the cubic structure of NaCl (rocksalt). In addition to the well-known alkali halides (e.g., NaCl) and the alkaline earth oxides, (e.g., MgO) the list includes some transition metal oxides (e.g., NiO), some sulfides (e.g., PbS) and heavier chalcogenides, many nitrides and heavier pnictides of the lanthanide series (e.g., LaN), alkali hydrides and some transition metal carbides (e.g., NbC) and nitrides (e.g., TiN). Bonding in these compounds ranges from ionic to covalent to metallic. Thus, a wide range of properties exist. For example, GdN has a melting point of 2900 °C, whereas the rare earth phosphides begin to dissociate around 400 °C. TiC and TiN are very hard and are used for cutting tools whereas the alkali halides are moderately soft. MgO is a good insulator, whereas the sulfides generally are small gap semiconductors with interesting properties for infrared applications.

During the past year a phenomenological description of short-range, central and many-bodied interactions in rocksalt-structure compounds was published. The formal problem was developed in what was termed the "bond-deformation model (BDM)" and applied to compounds which exhibit predominantly ionic bonding. Currently, this work is being extended to include the electronic polarization of ions (or atoms) within the BDM description. It is expected that the BDM model can be applied to compounds with other than ionic bonding and that it can be used to correlate and to estimate mechanical, dielectric, optical and optico-mechanical properties. Data are being collected for other compounds so that the model can be tested further.

Phase Transition and Compression of $LiNbO_3$

Lithium niobate ($LiNbO_3$) has been the subject of a considerable amount of study stimulated mostly by its important technological applications. Its remarkable piezoelectric and optical properties have found important uses in many fields including nonlinear optics, ultrasonics and integrated optics technologies.

Recently, Stanton and Graham, motivated by the possible use of $LiNbO_3$ as a piezoelectric gauge in shock wave experiments, studied its behavior under shock loads up to 44 GPa. Their results showed a number of unusual features, including an abnormally large pressure derivative of the bulk modulus interpreted as resulting from localized heating due to heterogeneous yielding of $LiNbO_3$ under shock load. Evidence for a phase transformation was reported but was not confirmed in a subsequent shock wave experiment up to 19 GPa.

The high pressure x-ray study and optical observations were carried out at room temperature with a diamond anvil cell and the pressures were measured by the shift of the ruby fluorescence line. X-ray powder diffraction measurements were performed by the energy dispersive method using an intrinsic germanium detector at a fixed 2θ angle of 9.5°.

Figure 5 shows the pressure dependence of the c/a ratio and the volume change up to 25 GPa. Despite some scatter in the points at the higher pressures which can be attributed to nonhydrostatic effects, there is no indication of a phase transformation up to 25 GPa. At about 30 GPa, several new peaks were observed in the x-ray powder pattern indicating the appearance of a new high pressure phase. At 35 GPa the transformation was complete. Because these pressures are far higher than the hydrostatic limit for the pressure transmitting medium used, the resulting broadening of the diffraction peaks precluded an unambiguous identification of the structure of this new phase. However, all the observed reflections can be indexed on the basis of a cubic unit cell with a = 6.78 Å.

In order to better characterize this phase transformation, single crystal fragments of $LiNbO_3$ were also studied by optical polarizing microscopy in the diamond cell. At pressures up to 25 GPa the sample was clear and transparent. As the pressure increased further, a dark opaque region spread over the sample which covered two-thirds of the sample at 30 GPa and the whole sample at 34 GPa. These observations are in good agreement with the results of the x-ray diffraction measurements. The opaque appearance of the new high pressure phase could be due to a conductive or semiconductive state similar to that found for GaP and ZnS in earlier high pressure experiments. Upon release of pressure, the reverse transformation to the transparent state was observed at 10 GPa. The reversibility of the transformation was also confirmed by x-ray diffraction measurements.

It is not altogether clear that the transformation described here at about 30 GPa corresponds to the one reported earlier by Stanton and Graham, beginning at 13.9 GPa and not completed to 44 GPa under shock loading. Because of the transient character of shock waves and the localized heating effect found in shock loaded $LiNbO_3$, it is not suprising that those results are not consistent with the results obtained by the present static method. The heating effect could result in crossing the transformation kinetic barrier at lower pressures in shock wave experiments. It could also cause the transition to occur at lower pressures if the slope of the phase boundary in the P-T plane is negative. This work was suggested and partially supported by D. Dandekar of Watertown Arsenal.

Structural Studies of Amorphous V_2O_5-Nb_2O_5 Glasses

The structure of amorphous V_2O_5 was examined by Dr. J. Galy of CNRS Toulouse utilizing newly developed large angle x-ray scattering techniques. A seminar by Dr. Galy last year at NBS resulted in a collaborative study with R. S. Roth on a series of amorphous specimens of V_2O_5-Nb_2O_5 compositions. A series of glasses from 5 to 35 mole percent Nb_2O_5 were prepared by D. Cronin (formerly NBS) and D. Blackburn of the Division's Glass Group and transmitted to Dr. Galy in Toulouse. The results clearly show the influence of the known crystal chemistry of niobia on the amorphous structure of V_2O_5. The amount of V^{+4} ions and the resultant change in the semiconducting properties of these amorphous glasses are directly related to the temperature needed to prepare the higher and higher niobia content compositions.

Characterization and Properties

Subtask 3 of Task 15416

S. Block, A. Dragoo, J. da Jornada[1], H. P. R. Frederikse, C. Hubbard, A. Perloff, G. Piermarini

[1] Guest Worker, Universidade Federal do Rio Grande do Sul (UFRGS) and CNPq

X-ray Powder Diffraction

Quantitative x-ray powder diffraction (QXRD) is of major importance to many industries, including fine ceramics and structural ceramics, which require characterization of materials at each stage in processing in order to achieve the desired properties and performance. QXRD is often the only method available for determination of the concentration of phases in materials. Unfortunately, QXRD methods are traditionally time consuming, without standardization of procedures, and of low accuracy. These limitations have hindered industries' ability to fully characterize solid phase materials.

In the last few years, NBS has explored many of the limitations and has proposed methods to overcome or reduce most of them. These developments include: spray drying to achieve random orientation; automated data collection with optimizing algorithms to reduce experimental time and increase accuracy; Standard Reference Material 674 (set of five phases) for calibration and analysis; and data analysis software for standardizing procedures, incorporating auxiliary data for improved accuracy, and for testing for systematic errors. Fifteen copies of the NBS*QUANT84 program package have been distributed. The accompanying documentation to this program package has been used as the text for three national workshops on QXRD.

This system has now been revised and expanded following the development and testing of a new QXRD procedure for determination of amorphous content. This procedure is sensitive to low concentrations of an amorphous phase (approximately 2 to 20 wt%) present in a crystalline matrix. The method may prove invaluable in the phase characterization of glass/ceramic composites, polycrystalline dielectric substrates such as cordierite $[(Mg,Fe)_2Al_4Si_5O_{18}]$, and structural ceramics such as SiC and Si_3N_4.

The theoretical basis of the procedure is the addition of analyte (spiking) method of QXRD. The spiking phase is an amorphous material of composition similar to the analyte phase. This approach circumvents the need for a 100 percent crystalline reference material--a need which is virtually impossible to satisfy. Since the net intensity of amorphous scattering must be determined, the background scattering intensity must be measured. In the certification of SRM 1878, Respirable Quartz Powder, a large grain (> 10 µm) polycrystalline quartz powder obtained from an optical grade quartz crystal was used to define the background.

To assess the precision of the procedure three independent amorphous "halo" regions were selected. Intensity measurements for the three regions for the original sample and spiked samples yielded curves as shown in figure 6. Each of the three curves closely fit the expected straight line slope. The common intercept at $y = -0.043$ (4.3 wt%) indicates that no systematic errors as a function of 2θ are present and that the estimated standard deviation is about 0.5 wt%.

The accuracy of the modified spiking technique was explored by a direct determination of percent crystalline quartz using hot phosphoric acid washing and calculated reference intensity ratios. These methods yielded values of 99 and 98 wt % with an uncertainty of nearly 5 wt%. The modified spiking technique gave 4.5 wt% amorphous based on repetitive measures plus an assessment of probable errors. From this value, SRM 1878 was certified as 95.5 wt% crystalline quartz.

The respirable quartz SRM, whose development was partially sponsored by NIOSH, will be widely used by industry for determination of the respirable quartz content in the work place. The SRM can also be used by the ceramics industry for calibration of QXRD methods for quartz.

The same methods are now being applied to the certification of a cristobalite respirable powder SRM.

The determination of crystallite size and residual stress in ceramic materials is more challenging than in many metal systems due to a much smaller deformation for a given applied force. Thus the resulting line broadening is far less than in many metals, and hence the requirements for accuracy of measurement are significantly increased. Certification of a crystallite size SRM is our first effort in this field. Bulk quantities of MgO, previously selected for this SRM, have not shown the stability exhibited by previously prepared samples. Yttria stabilized zirconia is now being evaluated.

Based on this work a collaborative effort between Prof. J. Stewart, University of Maryland and Dr. B. Morosin, Sandia Laboratory, has begun. Samples that will be analyzed for residual stress are shock loaded α-Al_2O_3 and TiC. Samples will be provided by Sandia, measurements will be performed at NBS by Prof. Stewart and graduate students, and analysis will be performed using modifications of NBS's program for determining residual stress and crystallite size.

Powder Diffraction Data

Identification of each crystalline phase in solid phase raw materials, intermediates and final products by x-ray powder diffraction (XRD) measurements and search of the Powder Diffraction File (PDF) is heavily used in mining, ceramics, metals and other industrial segments of the economy. NBS assures that measurement methods and essential reference data are available through advancing automated measurement methods, developing computer data analysis procedures, producing Standard Reference Materials, and collaborating with the JCPDS-International Centre for Diffraction Data (ICDD) on improving this internationally used reference pattern file, the PDF.

A joint program between the ICDD and NBS to produce very accurate standard reference powder patterns has been in operation successfully since 1952. The published reference patterns are recognized world-wide for accuracy and reliability. In December 1983, this joint program was renewed and expanded to include development of methods for computer aided data evaluation and computer readable data base building.

The ICDD supports nine Industrial Research Associates at the Gaithersburg site. Dr. W. Wong-Ng[1] is the newest staff addition to the technical staff. She transferred from her post as Critical Review Scientist at ICDD headquarters to gain experience in experimental aspects of XRD while continuing the critical review of PDF sets 1-32. The NBS-ICDD program has four objectives: production of reference patterns; critical review of sets 1-32; editorial evaluation of new data; and collaboration with the ICDD Technical Committee, Subcommittees and Task Groups.

The primary objective of the ICDD-NBS program is to produce very accurate x-ray powder diffraction reference patterns. For the last two and a half years an automated diffractometer has been routinely used for data collection. This digital data is then processed with an extensive software system which is connected by a data file. Accuracy in 2θ meas-

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[1] JCPDS/ICDD Research Associates:

Marlene Morris	Eloise Evans
Donna Gladhill	Howard McMurdie
Mary Mrose	Boris Paretzkin
Harry Parker	Carolyn Wingo
Winnie Wong-Ng	

urements is typically ± 0.005° compared with ± 0.02° for the strip chart recording procedures previously used. Intensities of the reference patterns are also accurately recorded. NBS Monograph 25, Section 21, published in October 1983, contains 92 experimental patterns (an increase of 27 patterns from Section 20). Over three fourths of the phases are classified as common phases. For the first time, each report in the Monograph was produced directly from the AIDS computer data base thereby eliminating the need for extensive proof reading and the potential for typographic error. Submission of these reference patterns to the PDF is by magnetic tape.

While reference patterns from the collaborative ICDD-NBS program are of high accuracy, the majority of patterns in the reference file are not. Since accuracy of the reference pattern is very important in phase identification a five-year project was initiated in 1981. The goals are to develop computer assisted evaluation procedures to critically evaluate the entire PDF and to build a master data base was initiated in 1981. Dr. C. R. Hubbard, as ICDD Data Base Chairman, designed and tested the system at NBS in collaboration with members of the Industrial Research Associates (IRA). On June 1984 the system was turned over to the ICDD. Substantial progress has been achieved to date on the critical review of the 38,000 patterns in series 1-32. The numerical review is expected to be completed by June 1985 by ICDD staff at NBS and headquarters with technical guidance from NBS.

Neutron Diffraction Crystallographic Analyses

An ongoing collaborative program utilizing Rietveld analyses of powder neutron diffraction patterns has continued on the elucidation of various alkali containing structures of oxide phases of general interest for their possible ionic conductivity. Dr. M. Zocchi of the University of Milan and Dr. A. Santoro of the Reactor Division have collaborated with R. S. Roth on the examination of the white spinel-like phase in the system Li_2O-TiO_2 and the spinel-like phase in the system $Li_2O-Al_2O_3$. These can now be structurally compared to the Li-inserted phases examined by Drs. R. J. Cava of AT&T Bell Telephone Labs and Roth and Santoro of NBS. Dr. Cava and Murphy of Bell Labs have also been examining some alkali containing pyrochlores formed by ion exchange of the alkali in this phase. It was indeed found that the position of the alkali ion deviated from the center of the structural cavity in direct proportion to its ionic radii, if great care was taken to exclude H_2O or other anionic impurities. However, peculiar effects were found for the smaller ions, attributed to as yet poorly understood impurity contamination. These alkali pyrochlore structure determinations can be correlated with the work of R. Catlow, F. Beech, and Santoro and Roth on the defect Pb^{+2} pyrochlore $Pb_{1.5}Ta_2O_{6.5}$. Additional studies at CNRS, Grenoble with Santoro, Roth and A. McHale were conducted on NBS specimens of $ZrTiO_4$, $Zr_5Ti_7O_{32}$ (0.5 percent Y_2O_3) and $FeNb_2O_6$, columbite, to compare the coordination and order/disorder of these similar phases.

Structural Ceramics

Silicon carbide ceramics are stable at high temperatures, maintain high strength to 1200 °C and are protected from reaction in oxidizing environments to 1500 °C by a dense, coherent oxide layer. However, at low oxygen partial pressures and high temperatures the protecting oxide coating can be lost by volatilization of SiO or by chemical attack of other reactants. In this work reactions of silicon carbide ceramics with various reactive gases are being investigated.

The initial and principal motivation for this work has been the potential use of silicon carbide as a structural ceramic in advanced fossil fuel-fired power plants. Consequently, the reactions of silicon carbide with components of combustion gases are of interest. Sulfur dioxide, which is one of those components has been the subject of further study. Sulfur dioxide was shown during the previous year to enhance the attack of N_2 on SiC under nonoxidizing conditions. This year, the protective effect of an initial oxide layer has been examined with focus on the reactivity of SO_2-containing and SO_2-free atmospheres. At oxygen partial pressures of 10^{-3} to 10^{-4} atm., some nitridation of oxide-free silicon carbide is observed for both N_2 and N_2/SO_2 gases. However, in the case of SiC with an initial oxide coating, disappearance of this coating was observed in the case of reaction with N_2/SO_2 but not in the case of N_2.

Thermal Decomposition Kinetics of High Energy Materials

A Fourier transform infrared (FTIR) microscopic method has been developed for obtaining kinetic data as a function of pressure and temperature. The method, which is widely applicable to kinetic measurements, in general, employs a diamond anvil high pressure cell with heating capability in conjunction with a FTIR spectrometer modified with an on-axis Cassegrain-type beam condenser. Time-dependent absorption spectra have been obtained for the thermal decomposition of 1,3,5-Trinitrohexahydro-1,3,5-Triazine (RDX) as a function of temperature and pressure. The results indicate that the thermal decomposition of RDX follows complex kinetics, but it appears that the decomposition rate decreases with increasing pressure. Furthermore, the results indicate that decomposition takes place in RDX prior to melting by as much as 25 °C below the melting point. Two different rate mechanisms are involved in thermal decomposition of RDX. One, which is the slower rate, is for the solid, and the other, which is the faster rate, is for the liquid. Work is continuing to confirm these preliminary results.

Boron Nitride

The high temperature electrical and dielectric properties of hexagonal boron nitride were investigated to assess its potential as a microwave window material in re-entry vehicle communication systems. This project has been completed. Electrical resistivity measurements up to 2400 °C (H. P. R. Frederikse and A. L. Dragoo) were performed on hot-pressed and on pyrolytic BN samples and also on composite specimens consisting of BN fibers impregnated with silica (34 and 50 percent SiO_2). Agreement between the results on various specimens was good; these data confirm that at high temperatures BN is an intrinsic semiconductor with an energy gap of 6.2 ± 0.4 eV (at $T = 0$ K). Extrapolation to 3333 K shows resistivity values between 5 and 25 ohm cm.

An analysis of the response of BN to microwave radiation (A. H. Kahn, Metallurgy Division) indicates that at high temperatures the thermal excitation of electrons to conduction states causes the material to have metal-like reflectivity. Using resistivity values of 1 to 10 ohm-cm for the hot surface layer, it was found that the microwave reflectivity exceeded 90 percent. The calculated transmissivity and absorptivity were of the order of a few percent, and showed interference oscillations with window thickness characteristic of standing waves in the cool region of the window.

Rutherford Back Scattering for Depth Profiling

During the past year the Rutherford Back Scattering Facility has been completed [H. P. R. Frederikse in cooperation with A. O. Wasson of the Center for Radiation Physics]. A beam line has been constructed equipped with the appropriate focusing devices, collimators, beamstops and gate valves. Mono-energetic ions (H or He ions) of 1 to 4 MeV from the NBS Van de Graaff accelerator can be targeted on samples located in the center of a 1 foot diameter vacuum chamber. A turbomolecular pump underneath this chamber helps to keep the entire system at pressures of (1 to 5) X 10^{-6} Torr. A manipulator with several modes of rotation and translation makes it possible to accurately position the samples with respect to the incoming ion beam. Part of the back scattered ions are intercepted, recorded and energy separated by a solid state detector. A multichannel analyzer counts these events and the signals are collected, stored and further analyzed by a microprocessor/computer. Preliminary measurements were performed on two kinds of samples: (1) a 3000 A zirconia film covered with 500 A Cr_2O_3, and (2) a multiple Cr-Ni sandwich (SRM, obtained from J. Fine, Surface Science Division). These measurements indicate that the system works satisfactorily and that the resolution approaches the resolution of the detector (14 keV).

High Temperature, Pressure Gauge for the Diamond Anvil Cell

The diamond anvil pressure cell (DAC) is being used extensively as a powerful and reliable instrument for quantitative studies in many fields of high pressure research. One of the main reasons for its high popularity is the existence, since 1972, of a simple, rapid and precise method for pressure measurement, based on the pressure dependence of the sharp ruby fluorescence R-lines. The ruby fluorescence method, however, suffers severe limitations when used at high temperatures due to the broadening and resultant decrease in intensity of the R-line fluorescence peaks. Its practical use is limited to temperatures below about 300 °C.

A new method was developed for pressure measurement in the DAC (or any other pressure vessel with optical access), based on an optical interferometric pressure gauge, especially usable at high temperatures. The new technique is particularly useful for the investigation of pressure-temperature phase diagrams in materials where phase transformations can be detected by optical means.

In this method the pressure is measured by the shift in the channel spectrum of a miniature Fabry-Perot etalon interferometer which is placed inside the sample chamber of a diamond cell. The gauge consists of a thin plate of a transparent crystal with parallel faces covered by semi-transparent reflecting films. The interference pattern for white light traversing the gauge perpendicular to its parallel faces will show periodic maxima in intensity at certain wavelengths.

One gauge was fabricated from a $ZnWO_4$ single crystal. This material was selected because thin, stiff sheets are easily obtainable by cleavage in the 010 plane. The gauge consisted of a parallelepiped about 100 µm long, cut from sheets approximately 50 µm thick and coated on both sides with an aluminum film, 25 nm thick.

Calibration of the $ZnWO_4$ gauge to 4.6 GPa at room temperature was done against the ruby fluorescence shift, and the results showed a decrease in λ_m with pressure in a consistent and reproducible way. For this particular gauge and for $\lambda_m(o) = 697$ nm, the gauge function was well reproduced by a second degree polynomial:

$$g(p) = A*P+B*P^2$$

with coefficients:

$$A = -(1.95 \pm 0.03) * 10^{-3}/\mathrm{GPa}$$

and

$$B = (5.7 \pm 0.7) * 10^{-5}/\mathrm{GPa}^2$$

For this case the modulus of the rate of change of λ_m with pressure at $P = 0$, $|d\lambda_m/dp|$, is 1.36 nm/GPa. This is nearly four times greater than the ruby fluorescence line shift with pressure (0.36 nm/GPa). The line-width (FWHM) obtained in the gauge experiment is about 0.7 nm, which is about the same as the line-width of the ruby fluorescence. Consequently, the etalon method is, in principle, four times as precise as the ruby method. Yet, the line-width obtained by the etalon experiment can be even further reduced by eliminating the cleavage steps in the gauge surfaces through improved fine polishing techniques.

As a function of temperature the gauge performed well with the spectra being nearly the same up to 720 K. Above this temperature the interference peaks became progressively broader and the background intensity increased significantly because of the deterioration of the aluminum coatings. However, this is not the limiting temperature, because materials with higher melting points and greater chemical inertness than aluminum can be used as reflecting coatings.

The comparatively strong pressure dependence of the peak positions, together with a reasonable peak width, indicates that this etalon method is potentially more precise and, with proper calibration, more accurate than the ruby fluorescence method, with the additional advantage of not being restricted to low temperatures. The precision can be increased further by selecting materials with a higher $|d\lambda/dp|$ and by reducing the peak widths through improvements in the gauge's fabrication. It is also important to note that this new etalon method, as outlined here, has an added advantage in that it can be used for accurate measurements of the pressure dependence of solid materials.

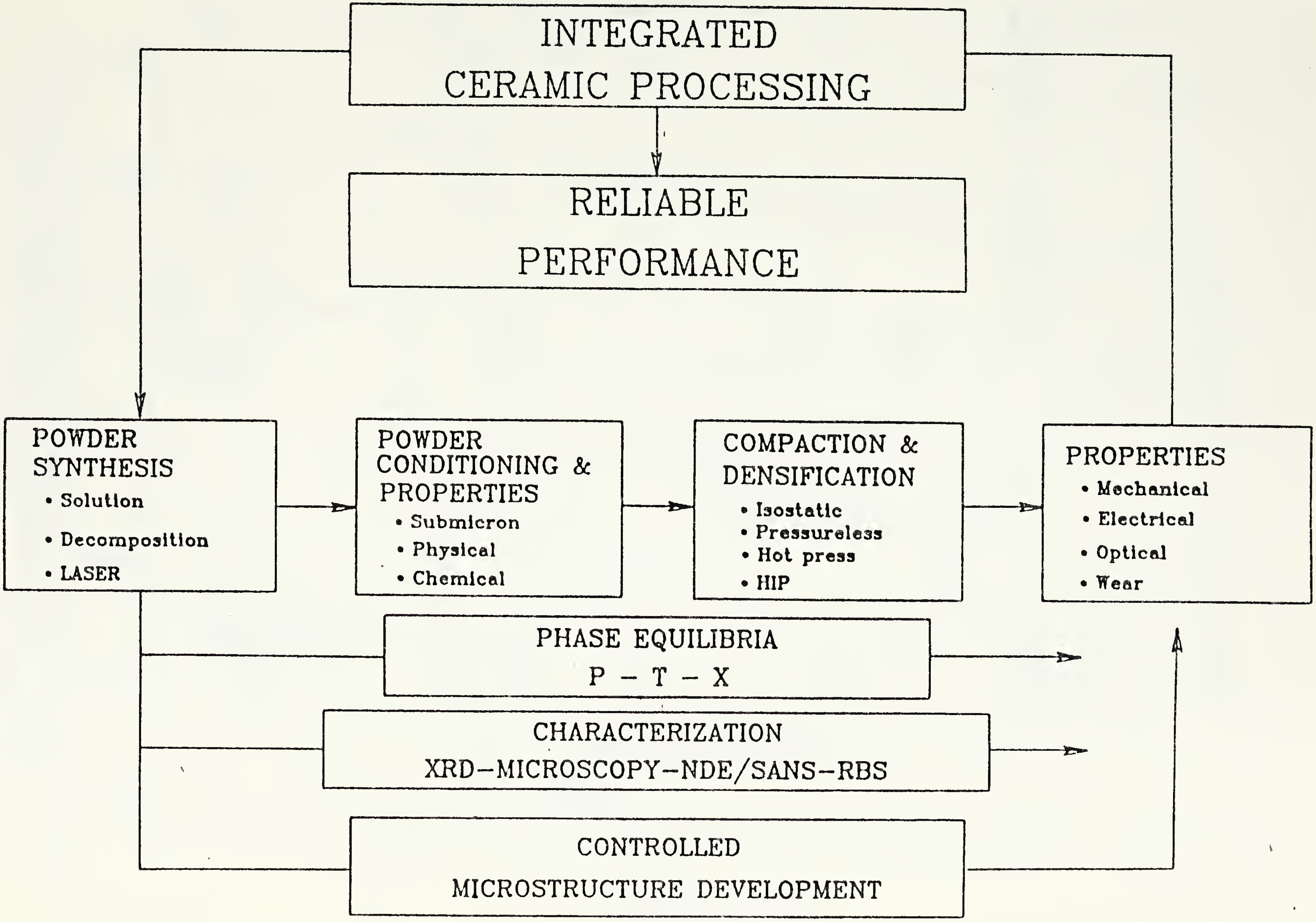

Figure 1. Integrated Ceramics Program.

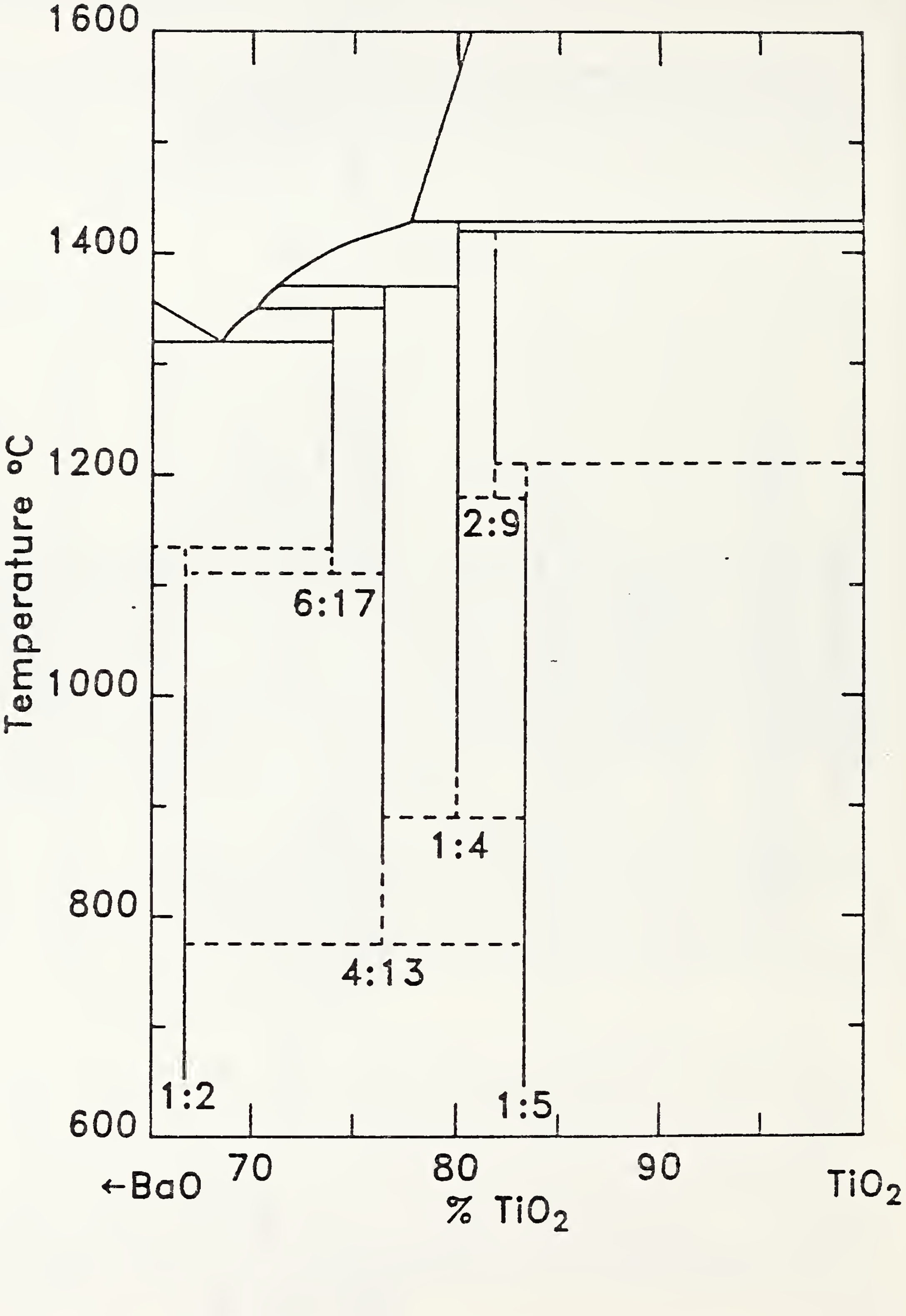

Figure 2. Phase "Equilibrium" Diagram for the System BaO-TiO_2 showing results of heat treatments of highly polymerized alkoxide precursors.

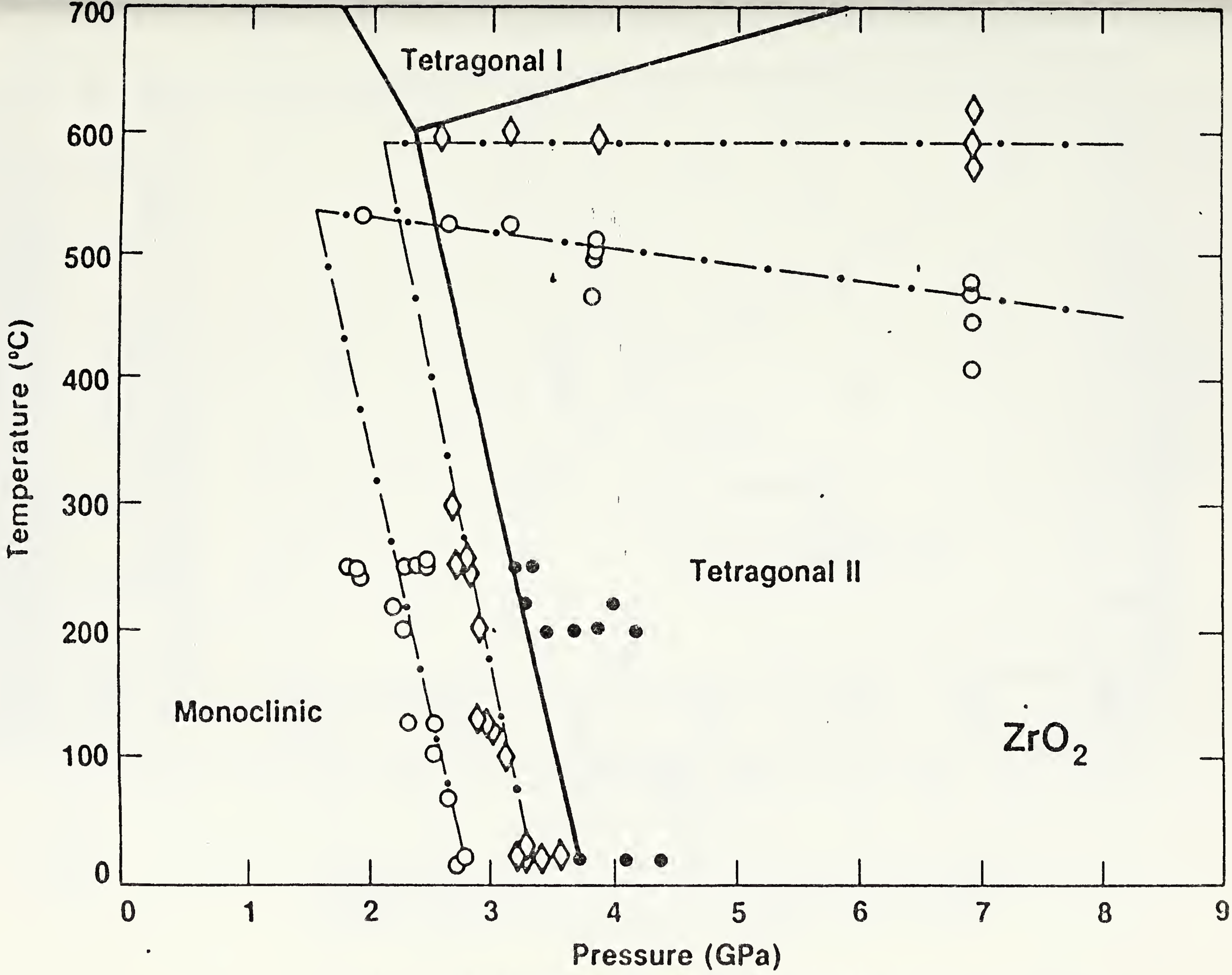

Figure 3. The revised phase diagram of zirconia in the region up to 700 °C and 9 GPa. The solid lines refer to previously published data and the dot-dash lines are the present results.

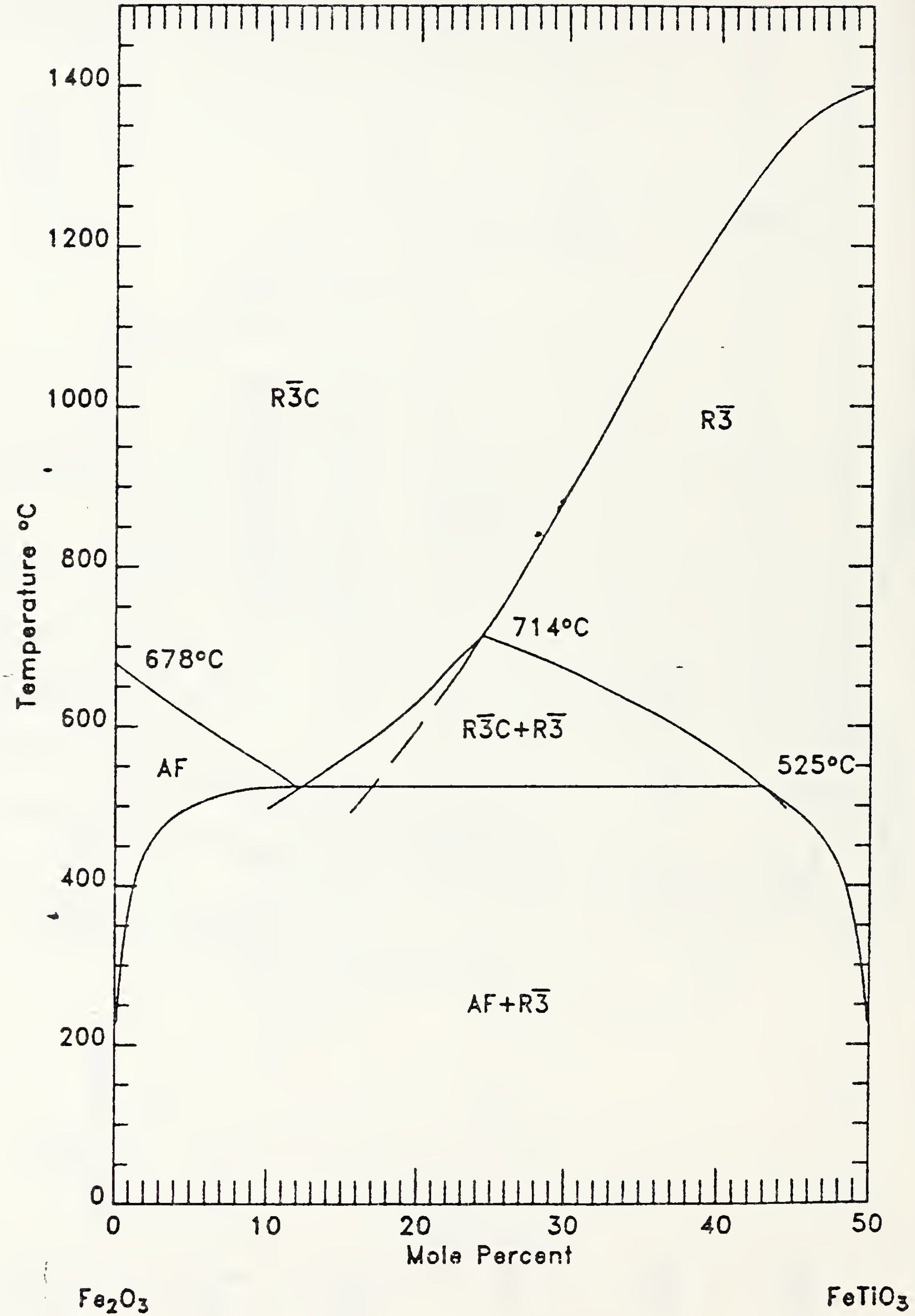

Figure 4. Theoretical phase diagram for the system Fe_2O_3-$FeTiO_3$: $R\bar{3}C$ is the space group of the disordered corundum structure phase; R3 is for the chemically ordered ilmenite structure phase; AF indicates the antiferromagnetically ordered phase.

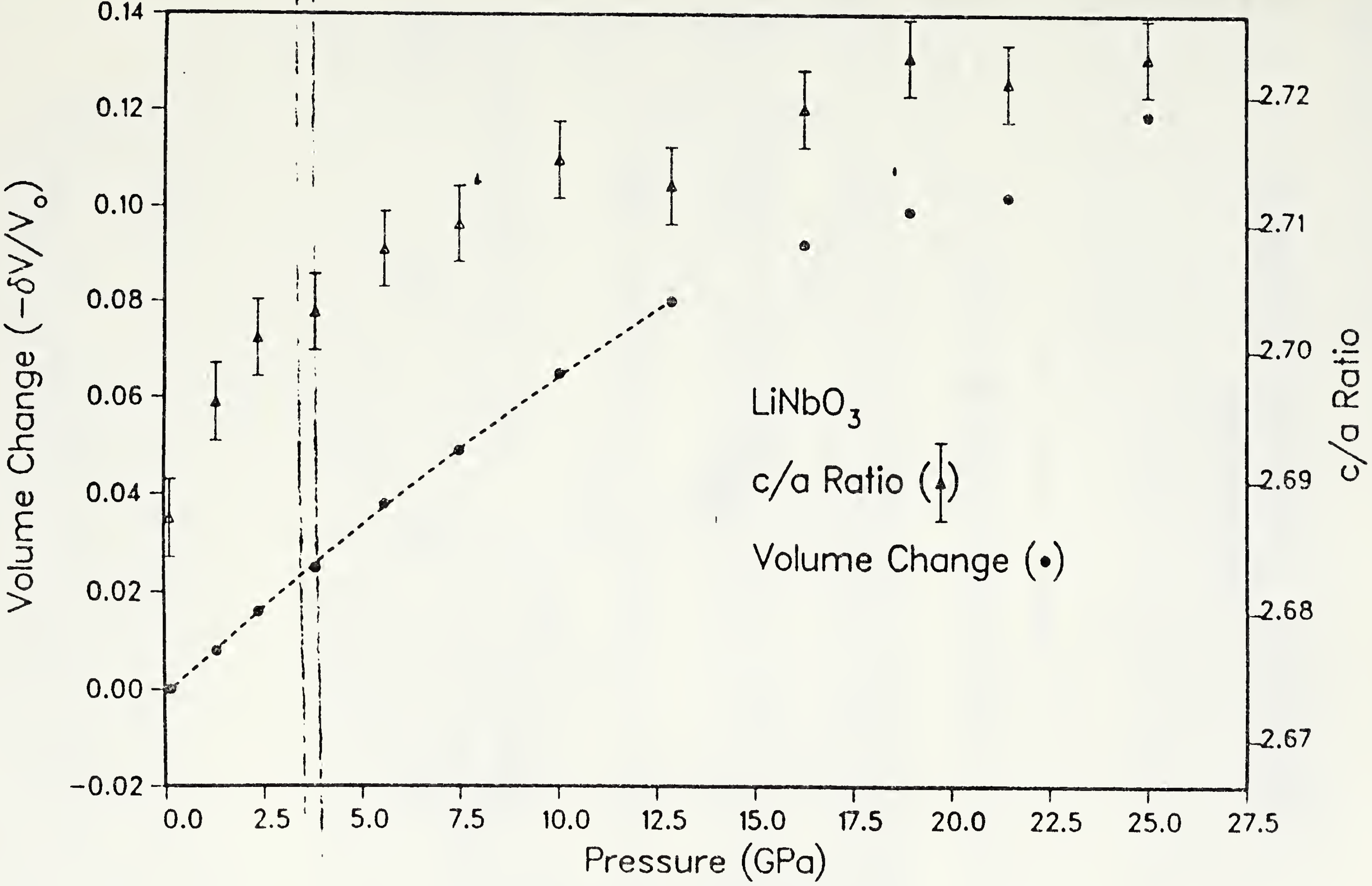

Figure 5. Volume change, relative to its value at 0.15 GPa (circles) and c/a ratio (triangles) as a function of pressure. The dashed line represents a least-squares fit by the Birch-Murnaghan equation of state in the hydrostatic region.

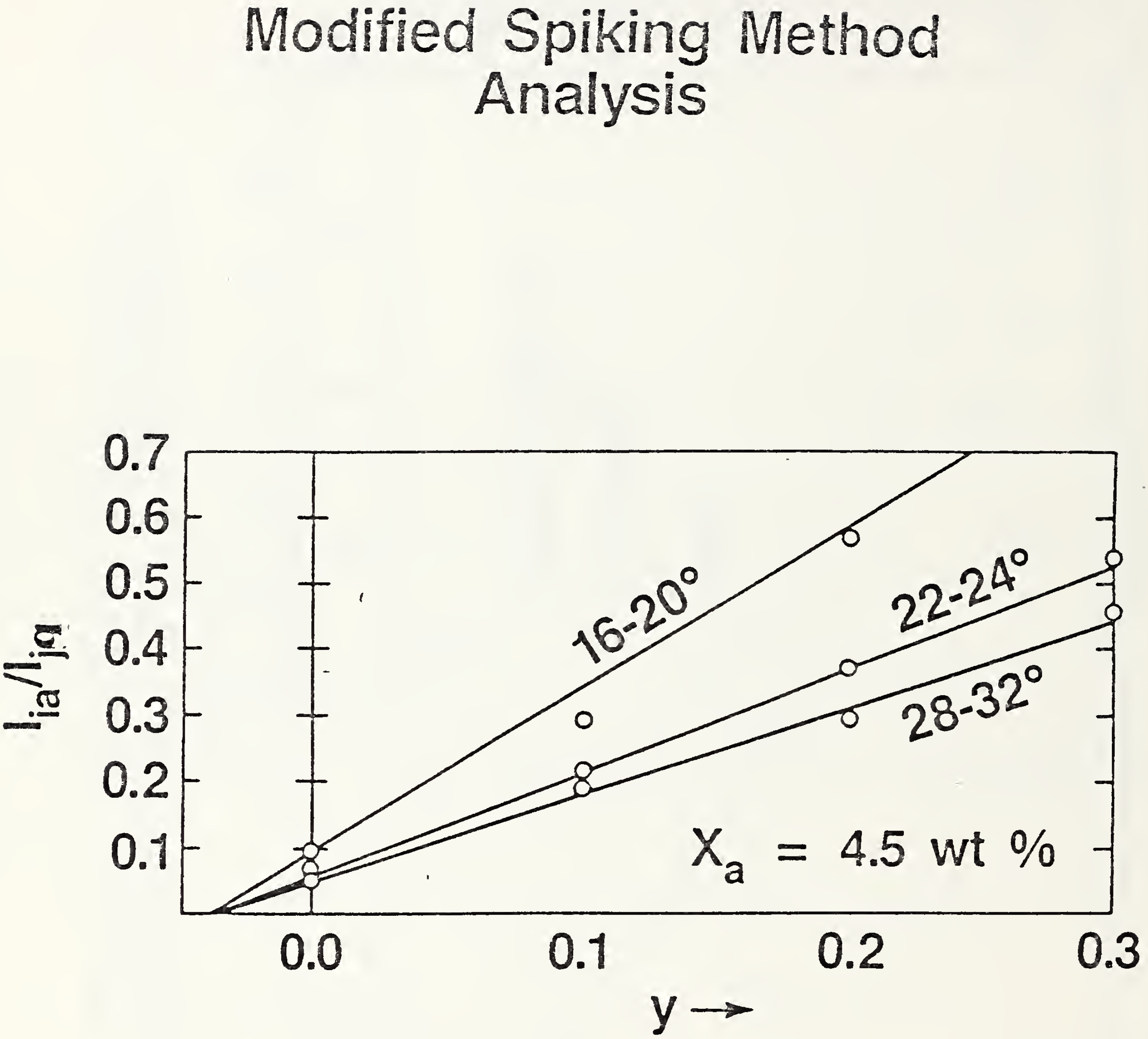

Figure 6. The net diffracted intensity of three regions of the amorphous "halo" (I_{ia}) were recorded as a function of grams amorphous silica added per gram sample (y). A quartz diffraction line intensity (I_{jq}) is used as a reference. The common intercept yields the weight percent amorphous silica in the respirable quartz sample.

GLASS AND OPTICAL MATERIALS

Task 15417

The objectives of this task focus on the development of scientific concepts, measurement technology, scientific data base, standard reference materials, and materials characterization as they relate to the material glass and to optical materials. Because certain military and civilian uses of glass products are of specific interest to the government, the NBS has a long-standing expertise in this field. This expertise is being used by government agencies and industrial producers and users of glass and accounts for a large number of technical requests from these groups as well as for a number of collaborative programs with other government agencies.

For the purpose of this report, the work has been divided into three subtasks:

Subtask 1. The Physics and Chemistry of Glass addresses such fundamental factors as glass formation, melt viscosity, devitrification, ionic bonding and adhesion to polymers.

Subtask 2. Thin Films address the measurement of thin film structure and optical properties as they relate to such advanced applications as integrated optics, optical coatings, corrosion, barrier layers, and optical sensors.

Subtask 3. Standards Activities relate to the development of glass standards for the glass industry, glasses for analytical standards, standard fluorescent specimens for the U.S. Postal Service, and materials for nuclear waste research.

Collaborative work with universities, guest workers and Research Associates has been a source for stimulating scientific exchange as well as scientific manpower.

Several of the listed activities were joint programs with other agencies, universities and other parts of NBS. Outside financial support for research projects was received from: Lawrence Livermore National Laboratory for laser glass developments and piezo-optic studies, Naval Research Laboratory for work on fluoride glass optical films; NBS Office of Standard Reference Materials for SRM development; Department of Defense for development of small particle standards; Department of Energy for assistance in developing and procurement of nuclear waste leachability materials; U.S. Postal Service for evaluation and development of fluorescence standards; Air Force Office of Scientific Research for thin film structure studies.

FY84 Significant Accomplishments:

- The extended fine structure of the oxygen K-edge in the electron energy loss spectrum taken from thin amorphous SiO_2 films has been obtained. Films prepared from evaporation of SiO_2 with and without oxygen, and evaporation of Si with oxygen were studied. The results showed that there was a close relationship between the O-Si bondlength and the stoichiometry of the SiO_2.

- ESCA (Electron Spectroscopy for Chemical Analysis) has been used to determine the presence of oxygen in heavy metal fluoride glasses which had been prepared by the Naval Research Laboratory. By analyzing the spectra taken from these glasses before and after ion sputtering, it was demonstrated that the glasses could be ranked according to their oxygen and carbon contents, Zr-F and Zr-O bonds distinguished, and very small oxygen concentrations detected. ESCA was proven to be very useful tool in the analysis of these fluoride glasses.

- In cooperation with the Metallurgy Division Staff, an ESCA determination of the valence state of Cr in Co-Cr-Mo alloy commonly used in permanent surgical implants was accomplished. The corrosion resistance of the Co-Cr-Mo alloy is due to an adherent oxide film composed mainly of chromium oxide. It was shown that the valence state of the Cr in this film was +3 rather than +6. This is important because it has been shown that Cr in the +6 state is potentially more harmful to cells in the human body than +3 Cr.

- Thin films in the ZrO_2-Y_2O_3 system formed by e-beam evaporation were shown not to form an amorphous film at any point in the composition field as determined by x-ray diffraction. This is a markedly different behavior than has been observed in the systems ZrO_2-SiO_2 and ZrO_2-MgO. Addition of Y_2O_3 to the ZrO_2 did, however, apparently produce a 100 percent stabilized tetragonal ZrO_2 phase. This stabilization has been seen and reported previously in the ZrO_2-SiO_2 and ZrO-MgO mixed films. In addition, excellent agreement was found between film compositions determined by comparison of ESCA spectra of films and of quenched materials and film compositions calculated from thickness measurements obtained from quartz crystal monitors used during deposition.

- Thin films of Ag and Pd were e-beam evaporated onto highly perfect single crystal Cu (111) and (220) surfaces. The Cu substrate and deposited film were then examined by x-ray topography at NBS and at the Cornell High Energy Synchrotron. Indentation sites could be imaged in the Cu substrate but not in the overlaying metal film. However, the film could be imaged without detail over its extent, with the thickest film (10,000Å) diffracting as if it were an epitaxial crystalline film.

- A method of analysis has been developed for determining, unambiguously, the fringe orders in the channel spectra of transparent thin films. The method of channel spectra is important for determining the dispersive properties of thin films. A criterion has been derived which shows that the method is applicable when the film thickness is less than a material-dependent critical value.

- Two hundred twenty-five kilograms of glass were shipped from NBS to the Materials Characterization Center at Battelle Pacific Northwest Laboratory. NBS research identified this material for the study of leaching mechanisms and interactions of nuclear wastes in repository environments. NBS carried out measurements that verified compliance with specifications for homogeneity and chemical composition.

- Specifications were issued for a glass to replace viscosity SRM 710 which has run out of stock. Candidate soda lime glasses were evaluated and one thousand kilograms of high homogeneity optical grade glass were obtained by NBS through a donation from a glass company. This material when characterized will replace the similar glass SRM 710 which is an important standard because of its role in research and manufacturing.

- Under the leadership of NBS two standard specifications were prepared for inclusion in the ASTM Book of Standards on Glass. One specification covers flat glass for general architectural uses and mirrors, and glass for the control of light transmission, heat and or solar radiation. The other document covers heat strengthed glass. Both specifications will be used by the glass industry and other users of glass including military and other government procurement interests.

Physics and Chemistry of Glass

Subtask 1 of Task 15417

D. Blackburn, M. Cellarosi, E. Farabaugh, A. Feldman, L. Grabner, W. Haller, D. Kaufman, B. Schoening

Bonding Studies in Silica

Because of the current wide use of silicon and SiO_2 in both semiconductor and optical devices, the study of amorphous silicon oxide films was undertaken. Using a TEM and an electron energy loss spectrometer, the extended energy loss fine structure (EXELFS) above the oxygen K-edge in the electron energy loss spectrum (EELS) was obtained from various silicon oxide films. These films were made by e-beam evaporation from a SiO_2 source with and without a partial pressure of O_2, and by e-beam evaporation from a Si source in the presence of an O_2 partial pressure. ESCA (Electron Spectroscopy for Chemical Analysis) spectra were also obtained from each film immediately after deposition before removing from the vacuum chamber and transfer to the TEM.

Analysis of the EXELFS spectra yields O-Si and O-O nearest neighbor distances and also O-Si-O bond angles for these films. Preliminary results of the analysis together with the results of the examination of the ESCA spectra suggest that the films fall into two groups. One group of films are those formed by the evaporation of Si in the presence of O_2. These films departed furthest from stoichiometry and have the largest (1.68A) O-Si bondlength. The other group is comprised of those films formed by evaporation from SiO_2 with and without O_2 partial pressures during deposition. These films are still deficient in O_2 ($\sim SiO_{1.2}$) and possess O-Si bondlengths intermediate between 1.68A and that of the crystalline quartz reference material, 1.61A. The results to date tend to show a close relationship between the measured O-Si bondlength and the stoichiometry of the film.

Working with A. J. Forty, (Dept. of Physics, University of Warwick) G. Danko and G. Long (NBS) the analysis will be further refined and models corresponding to measured O-Si, O-O and O-Si-O bond angles proposed.

In Situ Characterization of the Interface Region of Glass Reinforced Composites

The assistance of the Glass and Optical Materials Group to work on a project sponsored by the Army Research Office (ARO) has been requested to characterize the interfacial region between glass fibers and resins used to form composite structures. Knowledge about this interfacial region is important for minimizing structure failure.

It is known that the evanescent field of a guided electromagnetic wave is confined very closely to the interface region. Bruno Fanconi and Francis Wang of the Polymers Division, the principal investigators of the project, have proposed to examine the interfacial region by dissolving an organic dye in a resin and monitoring the fluorescence induced by the evanescent field of a guided light beam propagating in a glass fiber embedded in the resin. The expertise on guided waves that has been developed within the Glass Group is being used to assist in developing the experimental tools required for these experiments.

Two approaches are being used. The first approach utilizes a fiber embedded in an epoxy resin containing a dye. Preliminary experiments utilizing rhodamine B as the dye have been made. Because of the high index value of the resin (refractive index, n = 1.576) commercial glass fibers were unavailable for the experiments. Thus, it was necessary for us to prepare our own fibers; a fiber was drawn from a sample of SRM 711 (n = 1.618).

First, we propagated 488nm radiation from an argon-ion laser down a fiber embedded in epoxy. The output end of the fiber was focused onto the entrance slit of a monochromator. It was necessary to insert a long pass filter prior to the monochromator entrance slit to eliminate unwanted laser radiation, however the filter is made of a glass that is known to fluoresce. A scan of wavelengths indicated the presence of the fluorescent band of the filter, but we were unable to detect the dye fluorescence. However, if we focused a length of a side of the fiber embedded in the epoxy on the entrance slit, then the dye fluorescence showed up very clearly. Because of the large amount of scattered radiation emanating from the fiber, it is not yet clear what fraction of the detected fluorescence originated from the interfacial region.

As a control experiment, dye dissolved in dichlorobenzene was used instead of the epoxy. In this case a fiber with a lower nominal index was drawn (n = 1.55) for the experiment. At first no laser radiation could be guided down the fiber because the fiber index was slightly lower than the index of the dye solution. Therefore, isopropanol was added to the solution until laser radiation was observed to exit the fiber. In this case the dye fluorescence spectrum was observed to exit from the fiber end. The second approach will utilize a planar guided wave apparatus with epoxy placed on top of a thin film waveguide. At present, parts are on order for construction of the apparatus.

Oxygen in Heavy Metal Fluoride Glasses Using ESCA

Heavy metal fluoride glasses promise decreased transmission losses compared to silica based glasses because they transmit at longer wavelengths with decreased intrinsic Rayleigh scattering. Fluoride glasses now in production exhibit losses due to the presence of oxygen containing impurities. In this work, which was concluded this reporting period, the ESCA (Electron Spectroscopy for Chemical Analysis) technique was used to characterize various fluoride glasses of known compositions prepared at the Naval Research Laboratory.

Since the ESCA method is a surface technique, the preparation of the surface is of prime importance. A final surface preparation protocol was formulated and consisted of breaking the glass outside of the analysis chamber, mounting it on a special holder which exposed only the fractured glass surface to the spectrometer, and in situ, ion cleaning with 3.5 kV Ar ions.

Spectra were recorded from the specimens "as received" and after each period of cleaning. When identical spectra were recorded after repeated ion cleanings, the cleaning was terminated and the last spectrum was considered to be typical of that glass. Only narrow regions centered on the Ba, F_{1s}, F auger, O_{1s}, $Zr_{3d3/2}$ and C_{1s} (the constitutients of the glasses) were recorded so as to collect the maximum amount of data in the minimum time. Ratios of peak heights were used to characterize the glasses. Several important results were obtained from this work. It was shown that the ESCA technique could rank the glasses as to their oxygen content, even when a low oxygen content BaF_2 single crystal was studied. This ranking showed that glass T1, a cladding glass, possessed the highest oxygen content. It also possessed the lowest carbon content.

Following the C_{1s} peak indicated that surface carbon, in the form of hydrocarbon, was present in all cases. The carbon content was reduced by ion cleaning. As the ion cleaning proceeds the C_{1s} peak shifts to a value more characteristic of C-C bonds. This suggests free carbon, originating from the starting materials or contamination during melting, may exist dissolved in the glass.

The $Zr_{3d3/2}$ peak also changed upon ion sputtering. At the surface one peak is observed, thought to be characteristic of ZrO_2. As sputtering proceeds a second peak develops which is likely due to Zr associated with a fluoride environment.

Thus, the ESCA technique has demonstrated that glasses can be ranked according to oxygen and carbon content and suggests the chemical bonding of the Zr and carbon. It can detect low levels of oxygen and distinguish between the binding of Zr to F and O. It has proven to be an extremely useful tool to study these fluoride glasses.

Thin Films

Subtask 2 of Task 15417

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Thin Films for Integrated Optics

The development of low-loss optical fibers has triggered a new technology in which optical fibers are now being used in place of traditional electronic and microwave communication links. However, the signal processing before and after the optical transmission is still done electronically, which limits the ultimate frequency responsivity of the system. The full realization of the advantages of optical communications requires the development of means for direct processing of the optical signal and this new technology is integrated optics. The role of the Glass and Optical Materials Group in this area is:

1. Research to support the development of new low-loss thin film materials of potential application in integrated optics.
2. The fabrication of planar waveguides with carefully controlled mode structures for minimizing coupling losses due to mode mismatch between integrated optical components.

3. The search for new materials and thin film structures that show enhanced nonlinear optical coefficients with the view toward applications in integrated optics.
4 The development of consensus standards, in cooperation with industry and government, for characterizing and evaluating materials for integrated optics.

Optical scatter is an important mechanism for loss in optical waveguides. Work has continued this year on optical scatter measurements in thin films.

In the previous year it was shown that a film of ZrO_2 mixed with SiO_2 showed significantly less optical scatter than a pure ZrO_2 film. This year we have measured the effect of compositional variation of coevaporated $ZrO_2:SiO_2$ thin films on optical scatter. The scatter profiles of five mixed component thin films evaporated onto fused silica substrates have been measured. The apparatus and the experimental procedure for the measurements were described the previous year.

Table 1 summarizes the properties of the thin film specimens.

Table 1. Parameters of Mixed $ZrO_2:SiO_2$ Thin Films

Specimen #	%ZrO_2	%SiO_2	Scatter	Thickness t(um)	n
428	100	0	8.2×10^{-4}	1.13	1.92
430	82	18	2.3×10^{-4}	0.95	2.04
431	63	37	4.8×10^{-5}	0.65	1.98
438	39	61	1.9×10^{-4}	0.69	1.79
439	23	77	7.9×10^{-5}	0.72	1.65
substrate		100	6.3×10^{-6}		

The films were prepared by coevaporation of ZrO_2 and SiO_2 from independent electron beam sources in the thin film facility. The compositions of the films (by volume) were estimated from thicknesses determined by quartz crystal thickness monitors that measured independently the output of the separate electron beam sources. The total hemispherical scatter was measured as described previously; it represents the fraction of incident optical radiation back-scattered into a hemisphere but excluding a cone with full angle of 5.5 deg. about the specimen normal. The values presented are the smallest measured on each specimen.

Specimen thicknesses were measured by T. Vorgurger and C. Giauque of the Micro and Optical Technology Group by means of a diamond stylus surface profiling instrument. Refractive indices were computed from channel spectra measurements of optic path and from the thickness values.

Several observations can be made from the table: (1) All films show significantly greater scatter than the fused silica substrate. (2) The scatter is observed to generally decrease with the addition of SiO_2, however, at an intermediate composition the scattering shows an increase. It is known from earlier work that the mixed films are amorphous as determined by x-ray diffraction, whereas the pure ZrO_2 films are polycrystalline with a large surface roughness and a high pore density; thus, it is reasonable to expect the scattering of the mixed films to be less. However, the reason for the nonmonotonic behavior of scattering with composition is not yet evident. Other measurements on mixed films deposited on microscope slides appear to confirm this nonmonotonic behavior. (3) The refractive index as a function of composition appears to first increase with the addition of SiO_2, and then it subsequently decreases. The initial increase is unexpected because SiO_2, which has a lower intrinsic refractive index than ZrO_2, is expected to lower the refractive index of the mixed films. One possible explanation is that the porosity of the mixed films is lower than the porosity of the pure ZrO_2 films.

In order to answer some of the questions that have arisen, additional studies have begun. Measurements have been started to study film porosity by measuring the effect of water uptake from the atmosphere on the refractive indices of the films. In particular, we have found that the refractive index of a pure ZrO_2 films can increase by as much as 5 percent when removed from the deposition chamber and allowed to stand in the laboratory. Depending on the model of computing refractive index in mixed systems, the porosity to account for such a change would be in the range 10 to 40 percent. The method of channel spectra was used in these measurements.

During this work a method of analysis was developed for determining unambiguously the fringe order in the channel spectrum of a thin film. The question of fringe order has always been a problem in the analysis of channel spectra. As used here, the channel spectrum consists of a series of oscillations observed in the transmission spectrum when a thin film specimen is placed in a scanning spectrophotometer. Each oscillation corresponds to a change of one order of interference within the specimen. It was found that the order can be determined if the thickness of the film is less than a critical value equal to minus one-half the reciprocal dispersion of the thin film material. Dispersion data for 33 optical materials shows that the critical thickness exceeds 10 μm, a value that greatly exceeds thin film thicknesses in many applications.

Another possible explanation for the nonmonotonic dependence of optical scatter on the SiO_2 content of the mixed films is that the scatter depends on optic path within the specimen. For example, if the scatter comes from the bulk of the film, the scatter would be expected to increase monotonically with thickness. A series of measurements has been started to determine the effect of optic path on optical scattering. For this purpose, wedged films have been prepared in the thin film facility. Special apparatus was constructed for the deposition of wedged films. This consists of a movable shutter within the deposition chamber coupled to a programmable stepping motor located outside the deposition chamber.

Scattering measurements were made on a wedged film of pure ZrO_2; simultaneously, the specular reflectance was monitored. A curious result occurred. Although the optic scatter for thickness less than one optic fringe showed no particular correlation with the reflectance signal, the optic scatter for thickness between one and two optic fringes showed a very strong correlation with the reflectance signal. A close examination of the film in white light indicated that the film contained both a clear area and a clouded area. Scattering from the clear area showed no correlation with the specular reflectance but scattering from the clouded area did show the correlation. Theories of scattering from rough surfaces are being studied to explain the effect.

Several improvements have been made on the experimental apparatus related to the thin film program. Deposition controllers have been installed on the film deposition facility. Stabilization of the deposition rate at the set point is now greatly improved over prior manual deposition rate control.

The total hemispherical scatter apparatus has been interfaced with a computer. The specimen position is controlled by two stepping motors and up to 16 voltages can be read. Currently we are building a computer controlled variable attenuator which will permit almost complete automation of the experimental procedure allowing for three orders of dynamic range in the measurement of scatter signals.

Deformation in Thin Metallic Films

Properties of thin films are different from their bulk properties. One of the important characteristics to be measured is the plastic deformation occuring from Knoop indentation in a thin film. To do this, films of Ag and Pd were e-beam evaporated onto highly perfect single crystal Cu (111) and (220) surfaces. The substrate and film were then examined by x-ray topography at NBS using a rotating anode source and at the Cornell High Energy Synchrotron Source (CHESS). The topography was carried out by R. Dobbyn of the Metallurgy Division.

The Cu substrates were Ar ion sputtered until ESCA spectra revealed the removal of surface oxygen and carbon. Ag films of 500 Å, 1,000 Å and 10,000 Å and Pd films of 1,000 Å and 10,000 Å were then evaporated onto the substrate surface.

X-ray topography taken in the Bragg geometry of the substrate and film showed that sharp images of the indents made with loads from 5 to 20g could be seen in the substrate through the 500 Å films. As the film thickness increases, the sharpness of the images decreases with the 10,000 Å film allowing only a very fuzzy image around the indentation site.

The films themselves could be imaged both by the NBS rotating anode source and using the higher intensity CHESS. The thick film (10,000 Å) diffracts as if it were an epitaxial crystalline film with (111) planes parallel to the film's surface. However, broad rocking curves suggest a highly strained film of not as high perfection as originally thought. The extent of the epitaxy varies from substrate to substrate, sometimes covering only 40 to 50 percent of the substrate, the remaining film being of a different orientation. Thinner films, although behaving similarly, do not have the diffracted intensity of the 10,000 Å film. The highly strained nature of the films is a possible explanation for the inability to image the indent in the film itself. Both Pd and Ag films exhibit the same diffracting and growth properties. The major result of this work thus far is that a film can be produced with a high degree of epitaxy. Future work will involve the production of films and substrates in which the hardness indent can be seen.

Mixed Films in the ZrO_2-Y_2O_3 System

The activities of this work, initiated in this reporting period, involved: (1) extension of previous work on mixed films (ZrO_2-SiO_2) to a different system (ZrO_2-Y_2O_3), and (2) in cooperation with MIT (J. Marc Lihrmann) use of the ESCA analysis of quenched material in the ZrO-Y_2O_3 system as standards to check the composition of e-beam formed films.

Films in the ZrO_2-Y_2O_3 system were made using our e-beam coevaporation deposition system. Each film was characterized by x-ray diffraction and by ESCA measurement over the C_{1s}, O_{1s}, $Zr_{3d3/2}$ and $Y_{3d3/2}$ peaks. Film compositions covered the complete field from 100 percent ZrO_2 to 100 percent Y_2O_3.

As already known, the 100 percent ZrO_2 film possessed both the tetragonal and monoclinic phases. The 100 percent Y_2O_3 film showed lines of the bcc cubic cell. An addition of a second material, Y_2O_3, to the host ZrO_2 by coevaporation resulted in a single phase tetragonal ZrO_2 film. Examination of the x-ray diffraction patterns of this mixed film system revealed that there was a progressive and regular shift of the peaks with the addition of Y_2O_3, indicative of extensive solid solutions. There were no amorphous films identified in the system, a result different from that found in the systems ZrO_2-SiO_2 and ZrO_2-MgO.

From the ESCA spectra from these films the atomic percent of O, Y, and Zr can be calculated. This provides a data point which can characterize the composition of the films.

Specimens of known ZrO_2-Y_2O_3 compositions were made at MIT by mixing known amounts of starting materials, laser melting them and rapidly quenching them on a chilled anvil. These rapidly solidified materials were then used as a control base for the ESCA measurements. X-ray diffraction patterns taken from these quenched specimens revealed that despite very high cooling rates (10^6 to 10^7 °C/sec) all of the phases present were crystalline with no glassy or amorphous phase present.

ESCA spectra were collected from the quenched specimens in the same manner as from the evaporated films. Atomic percent of O, Y and Zr were calculated from the known compositions and also from the ESCA spectra. A plot was made of $Y_{at}/Y_{at} + Z_{at}$ (from quenched material) vs. $Y_{at}/Y_{at} + Z_{at}$ (from ESCA). Using this plot, $Y_{at}/Y_{at} + Zr_{at}$ data points from the ESCA patterns from evaporated films can be located and the composition of the film read on the other axis. It was found that there was excellent agreement between the film composition as determined using the ESCA peak, and that calculated from quartz crystal thickness data.

Work is continuing and is addressing the problems of preferred orientation in the e-beam films, grain size measurements, models for stabilization of tetragonal ZrO_2 and the nature of the defect structure which may be generated uniquely in this ZrO_2-Y_2O_3 system.

Surface Analysis of Surgical Implant Materials

Co-Cr-Mo is the most commonly used alloy for permanent surgical implants. Corrosion resistance of this implant is obviously very critical, for when metal ions are released into the body from the implants, there exists the possibility of irritation, allergic reaction and possible loss of the use of the implant.

The corrosion resistance of the Co-Cr-Mo alloy is due to the adherent oxide film composed mainly of chromium oxide. Chromium in the +6 valence state has been shown to be more harmful to cells than the +3 valence state. The ESCA application of our surface analysis system was used in cooperation with the Metallurgy Division staff (A. Van Orden) to determine the valence state of the Cr and to characterize the protective surface film. These surface films were produced by exposure to air and by anodic polarization. ESCA measurements were made before and after polarization.

The determination of the valence state of Cr was made by studying the Cr doublet which is found in the region 660 to 680 eV (K.E.). Standards for +3 (Cr_2O_3) and +6 ($K_2Cr_2O_7$) were used so that comparisons could be made when the implant material was examined. All peaks were calibrated with respect to the C_{1s} peak. The results of a series of spectra revealed that the valence state of the film in each case was +3 rather than +6, suggesting that the less harmful valence state is present.

Use of Thin Films in High Pressure Measurement

The shift in the ruby fluorescence line with applied pressure is routinely used as a pressure gauge in high pressure research using the diamond anvil cell. However, its effectiveness diminishes at temperatures of 600°K and above, because of line broadening and attendant intensity decrease. A new gauge which can be employed at temperatures above 600°K utilizes a miniature Fabry-Perot interferometer inside the diamond cell.

The essential part of the interferometer is a thin plate of transparent material coated on each face by a 95 percent reflecting metallic film. Initially, cover glasses with 200 Å, 250 Å, 300 Å and 350 Å thick Al films were tested by Division 420's high pressure Group (J. daJornada, S. Block & G. Piermarini). It was demonstrated that enhanced signal to noise ratios and higher quality channel spectra when e-beam films were used instead of sputter coated material. Of the various film thicknesses, 250 Å films gave the best spectra and all subsequent coatings were of that thickness.

The final design of the gauge employed plates of single crystal $ZnWO_4$ approximately 50 μm thick. On each face, 250 Å thick Al films were deposited using e-beam evaporation techniques. The results of this work indicates that the new pressure gauge has the potential for being more precise and, after careful calibration, more accurate than the ruby fluorescence method plus the ability to operate over a wide temperature range.

Standards Activities
Subtask 3 of Task 15417

D. Blackburn, M. Cellarosi, D. Kauffman

Glass High Temperature Resistivity SRM

ASTM Committee C-14 on Glass and Glass Products lists the development of this standard as a priority.

Accurate melt resistivity data are used in glass melting operations to match power transfer, and to minimize energy usage at maximum production. The trend in the glass industry shows that electrical energy is becoming more effective and economical than conventional fuels because it yields increased production, with lower rejection rates. In electric melting there are also significant cost savings resulting from longer furnace campaigns and reduced pollution emissions. The standard will help also in the design of advanced melting processes.

NBS is cooperating with five industrial laboratories in comparison measurements to generate a standard and related measurement methodology. An important result of this project will be a measurement system and SRMs for the combined determination of resistivity and viscosity.

Viscosity SRM

NBS Glass Viscosity SRMs are important in glass research and manufacture. Viscosity and temperature data are used in research, manufacturing, and in advanced technical application such as sealing of glass-to-glass and glass to other materials.

NBS Viscosity SRM 710 (soda-lime-silica glass) with sales running about 50 units per year, is now out of stock. Activities are in progress to replace this standard.

Specifications for candidate replacement glass were written and submitted to potential vendors. Two companies have responded and evaluation of their material as candidate for replacement of SRM 710 was carried out.

Approximately 1000 kg of high homogeneity glass has been donated to NBS by one of the companies. Acceptance/homogeneity studies to verify that specifications have been met are in progress. This work includes statistical sample selection, preparation of specimens, measurements of refractive index, stress birefringence, bubble content, striae grade and inclusion counts. Interlaboratory comparison measurements will be carried out at NBS in collaboration with industrial laboratories and ASTM Committee C-14 on Glass and Glass Products.

Other SRM Development Activities for the Glass Industry

Thermal Expansion Standard - The glass industry needs a soda-lime-silica glass thermal expansion standard which has an expansivity coefficient of ~ 9 x 10^{-6}/°C. NBS does not have an SRM in this range. Several candidates have been evaluated as candidate SRM but have shown unacceptable thermal history effects.

A search for other glasses is continuing. If a suitable material is not found, a supply of soda-lime glass (Kimble R-6) which has already passed homogeneity testing will be used with a prescribed thermal cycle.

High Alumina Glass Sand Standard - Interlaboratory testing on chemical analysis was carried out. Data from five laboratories were analyzed. There is some concern about the homogeniety of the material -- a mixture of quartz and feldspar. Moisture values have fluctuated. Analysis will be recalculated and reported on an ignited basis.

Soft Borosilicate Glass for Analytical Standard - Results from six cooperating labs were compiled and analyzed. Data is under review for certification.

Glass for Ferrous/Ferric Ratio Analytical Standard - Consensus procedures for wet chemical analysis of ferrous iron (0.05 percent) and higher iron (0.15 percent) glasses were written and distributed to participating laboratories. Results are under review. Since a considerable amount of effort is involved in doing the analyses, consideration is given to the total reduced species instead of the specific ferrous iron value.

Glass Density Standards - Densities of three glasses (Borosilicate, soda-lime and lead silica) were determined by the NBS. Data and sample requirements are currently under review for applicability of Standards in buoyancy and sink-float comparative methods.

Thermal Conductivity - Economics and availability factors are being considered for two candidate materials: (a) glass-ceramic, C-9606 and (b) "black" basalt glass.

Borate Ore - Ore was finely ground, screened and blended. Material was distributed and data were received from two of six cooperating labs.

Multicomponent Glass - Analytical Standard - Data were received from three of six participating labs. This glass may also serve as a standard for toxic metal release. Lead and cadmium components are of particular interest in the USA and European Community.

Fused Quartz Annealing Point and Strain Point - Interlaboratory comparison measurements are near completion. Data will be analyzed by the NBS.

Nuclear Waste Leachability Research Material

During the year the NBS assisted the Materials Characterization Center (MCC) at Batelle Pacific Northwest Laboratories in the procurement of a glass for use as a research material in chemical durability testing plans related to the U.S. Nuclear Waste Disposal Program.

The NBS carried out research, evaluation and identification of a candidate glass. NBS also issued procurement specifications and carried out measurements that verified compliance with specifications for chemical composition and homogeneity. Measurements included chemical analysis of constituents, refractive index, striae grading, stress birefringence, bubble content, and inclusions count.

Two special melts of glass were found by NBS to meet all specifications. All glass was shipped to the MCC for use in the study of the mechanisms of leaching and interactions in repository environments.

Development of X-Ray Fluorescence Standards

In cooperation with the Center for Analytical Chemistry, work has continued on the development of thin glass films for the calibration of X-ray fluorescence spectrometers. This work has produced a number of NBS and EPA internal standards and now a glass, consisting of (wt%) SiO_2 40, TiO_2 10, ZnO 10, Fe_2O_3 10, K_2O 10 and PbO 20 is being issued as SRM 1833, " Thin Glass Film On Polycarbonate for X-Ray Fluorescence Spectrometry". This standard was prepared by focused ion beam sputtering of the glass onto polycarbonate substrates. The film is a continuous layer approximately 0.55 µm thick and 47 mm in diameter.

Previous efforts to develop a sulfur standard by additions of sulfates to oxide glass systems failed to retain sufficient sulfur in the sputtered films. However, arsenic sulfide glass gave excellent sputtered films which are surprisingly durable and show considerable promise as a future SRM for sulfur. Other chalcogenide glasses may be explored for sputtering in the development of standards for Hg, Se, Te and other elements which can be added only in limited amounts to oxide glass.

Thin film SRM's for analytical Electron Microscopy

A series of thin films of glasses prepared by ion beam sputtering of a bulk glass target is being developed to serve as standards for thin film analysis techniques such as analytical electron microscopy and laser microprobe mass analysis. The films prepared have been shown to be homogeneous on a nanometer scale and to have a constant thickness which can be selected in the range 10nm to 500nm. For AEM analysis, one composition prepared from SRM 470 (K-411 bulk glass) has been given initial characterization to be issued as an SRM in FY85.

Particle Samples of Glass

An extensive series of glasses have been prepared in particle form by grinding to form irregularly shaped particles with dimensions on the micrometer scale. An on-going project will convert these irregular particles into spherical particles which can serve as standards for microanalysis, including:

1. New Standards for analytical electron microscopy:
   - -- Heavy element glasses (for L and M x-ray line calibration).
   - -- Stoichiometric glass composition for oxygen content.

2. Particle standards:
   - -- Isotopic standard particles.
   - -- Sub-micrometer spherical particle standards.

Luminescence Standards for Automatic Postal Canceling Machines

As part of the modernization of the U.S. Postal Services, smart mail handling machines will be used. A class of such machines recognizes various luminescence markers incorporated in stamps in order to trigger certain responses by the equipment. The U.S. Postal Service has asked the National Bureau of Standards to develop go/no-go standards which simulate luminescence marked postage stamps which are calibrated for their luminescence value wavelength and decay time, are stable and durable. Glass and ceramics are favored for durability, stability and ability to be cleaned. Since the standards should, at the same time, be nonbreakable and have the dimensions of postage stamps, a composite material had been chosen for this purpose. This material consisted of squares of steel sheet, coated with glass (enamel) layers. To simplify surface preparation of the steel sheets and to overcome possible melting problems pre-enameled sheets were obtained commercially and overcoated with glass layers into which luminescent elements were incorporated. Europium and manganese-doped zinc orthosilicate were used to produce red and green luminescence, respectively. Six different intensities of red and green were produced and two hundred standards of each were delivered to the Post Office.

MATERIALS PROCESSING AND DURABILITY CHEMISTRY
Task 15418

The objectives of this task are to provide data, measurement methods, and mechanistic understanding of chemically and biologically mediated processes that affect the processing and performance of inorganic materials. In this broad context, the experimental work of this task includes investigations of microbial corrosion, bioprocessing of materials, chemistry related to the environmental impact of the use of inorganic materials in service, and the processes related to friction and wear of materials. The work of the task is carried out under two subtasks, one dealing with chemical and biotransformations of materials, and one emphasizing tribology.

The chemical and biotransformations subtask has focused in FY 84 on developing an improved understanding of the mechanisms of microbial corrosion to provide field methods for detecting and controlling this economically important mode of materials degradation; on fundamental research in support of innovative new antifoulant coating technology being developed by the US Navy; and on research into the properties and performance of phosphor materials of interest to the U.S. Postal Service.

The tribology subtask has continued investigations of chemical processes related to friction and wear of materials and has developed major new thrusts in the area of tribological properties of advanced ceramic materials for applications such as adiabatic diesel and turbine engines, in cooperation with industry and other government agencies.

FY84 Significant Accomplishments

- Improved methods have been developed for the extraction and ultratrace chemical speciation of butyltin compounds in seawater and are being used to measure transformation of butyltin biocides by resistant microorganisms from the Chesapeake Bay. These measurement methods, are critical for valid organotin biocide environmental fate models affecting their widespread use by the Navy and future decisions controlling industrial biocides design.

- The first world-wide comparison of methods for the determination and speciation of organotin compounds is underway with distribution of a stabilized aqueous ppm solution of tributyltin ion to 22 government, 13 university, and 11 industrial laboratories. Returned data will undergo statistical analysis at NBS for evaluation of the accuracy of the analytical methods employed. Study results will establish a basis for preparation of a speciated organotin SRM, critically needed in an expanding commercial field where the materials performance of organotin compounds is governed entirely by the molecular configuration of the organotin molecule.

- A general method for predicting both important physico-chemical and bioactivity properties of organotins has been developed which employs a stereochemically sensitive topological application of commercially important tin molecules' total surface areas. Input data required involve only independent bonding parameters.

Computer-generated surface areas for tin and other organometallic materials are demonstrated also to predict solubilities, interfacial partition coefficients, and gas or liquid chromatographic retention.

- A new application of high-field ^{119}Sn solution NMR to probe the molecular topology of organotin compounds has been demonstrated. The spin coupling [$^{2}J(^{119}Sn-^{117}Sn)$] through oxygen in hexaorganodistannoxanes is extremely sensitive to changes in the organic ligand due to the influence of the ligand on the size of the Sn-O-Sn bond angle. Spin coupling in distannoxanes is also extremely sensitive to solvent effects, and an explanation at the level of specific molecular interactions has been proposed.

- A new flame photometric detection method for methyl iodide was developed and used to demonstrate a potential route to MeI biogenesis in the environment. These investigations supported our development of a general model for endo- and exo-cellular methylation of elements and minerals solubilization important to environmental and biotechnological metals cycling and biomining.

- The Advanced Power Systems Division of the Electric Power Research Institute has requested and is funding our evaluation of key coal molecular structural features for selection of promising microorganisms/enzymes potentially capable of industrial coal upgrading and liquefaction. Proof of concept laboratory experiments for microbial coal upgrading are underway to help define for EPRI the commercial feasibility of coal processing biotechnology.

- The first systematic investigation of spin coupling in solid-state NMR has been carried out on a number of organotin compounds. In these magic angle spinning ^{13}C NMR experiments, signal multiplicity and the magnitude of the spin coupling [$^{1}J(^{13}C-^{117,119}Sn)$] has been found to arise from subtle structural parameters. The method has been applied successfully to polycrystalline and even amorphous organotin polymers and presages a method for characterizing ceramic sol-gel precursors.

- An electrochemical noise technique for the detection of anaerobic biological corrosion has been tested in the field. Preliminary results indicate that it may be promising for locating areas of on-going anaerobic corrosion on underground steel pipelines which could then be more efficiently cathodically protected to eliminate current multi-million dollar costs per annum.

- High temperature ceramics wear facility -- The design for the first experimental facility for the study of ceramic wear mechanisms at controlled temperatures up to 1500 °C has been completed and construction is underway. The apparatus allows specimen configurations with a ball sliding on a flat plate or a flat disk. Both unidirectional and reciprocating motions have been included.

- Production of a chlorine SRM completed--EPA regulations on hazardous wastes now include the amount of polychlorinated bi-phenyl (PCB) in used oil. The new regulation makes it imperative that a standard reference material for PCB or chlorine analysis be available. Production of a chlorine SRM was completed. Certification was achieved using neutron activation analysis and x-ray fluorescence.

- Effects of temperature on the wear of ceramics studies--An idealized model of a four-ball wear tester has been developed to compute the evolution and distribution of temperatures as a function of the thermal conductivity of the material being tested. A significant dependence on thermal conductivity was found. Comparison with experimental wear data showed an apparent correlation between the wear rates and the contact temperatures.

- GPC-FTIR-GFAA system installed--A Fourier transform infrared spectroscopy (FTIR) has been installed as a detector in the state-of-the-art lubricating film analysis system. The system consists of a liquid chromatograph coupled with a graphite furnace atomic absorption and is capable of measuring nanogram of organometallic compounds produced in the wear contact.

Chemical and Biotransformations in Materials Processing and Durability

Subtask 1 of Task 15418

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This subtask seeks to elucidate the fundamental role of chemical and biological processes in novel or improved materials processing, use, recycling, and performance. Interdisciplinary expertise in inorganic chemistry and microbiology is applied to investigate both synthesis or finishing and in-service performance of specialty and large-volume materials, providing a reliable basis for development of strategies for production control, performance design and evaluation, and selection for minimal adverse environmental impacts. Inorganic and ceramic materials of concern to CMS and its clients commonly incorporate metals and metalloids in processing or in performance environments. Consequently, ultratrace chemical speciation and imaging of materials' tell-tale transformation intermediates keyed on diagnostic elements is crucial to establishing reliable molecular structure-activity predictors for their formation, recovery, or finishing, and therefore remains a continuing activity of this subtask. Such unique NBS measurement capabilities, coupled with our interdisciplinary materials science expertise, increasingly attract a variety of OA and industrial research support and guest workers directed toward investigating major national materials problems requiring advanced scientific concepts, measurements, and data bases.

Primary Materials Bioprocessing

Microbial processes for metals and fuels beneficiation are receiving serious industrial and federal attention as novel cost effective alternatives to conventional raw materials processing. Optimization of such microbial processes through genetic engineering has been advocated. However, prerequisite basic information on microbial enzymatic and nonenzymatic transformations of metals and fossil including data on factors affecting bioprocessing rates or monitoring and product quality is limited.

Coal bioliquefaction. The U.S. electric power industry has a keen interest in advanced concepts for domestic coal upgrading (desulfurization, demetalation, liquefaction). The Electric Power Research Institute (EPRI), recognizing the need for an interdisciplinary feasibility study for measuring and evaluating chemical and biological factors in coal bioprocessing, has recently provided support to 1) critically evaluate the international literature on microbial coal upgrading, and 2) design and perform laboratory research demonstrating the feasibility of microbial processes for improving coal quality prior to its combustion.

We found that most world literature on coal upgrading by microorganisms concerns biodesulfurization. A large number of investigators have studied the removal of organic and inorganic sulfur from coal, chiefly by acidophilic bacteria including *Thiobacillus ferrooxidans*, *T. thiooxidans*, and *Sulfolobus acidocaldarius* which is also a thermophile. These bacteria obtain energy by oxidizing reduced iron or sulfur compounds in coal, resulting in sulfur and metals solubilization and release.

Much less research has been done on bioliquefaction of coal. Here we are evaluating literature on biodegradation of molecules structurally related to coal. For example, some lignin-degrading fungi have been reported to liquefy lignite coal. Structure-activity relationships also described elsewhere in this report can allow us to predict and test organisms which attack key molecular structures such as disulfide, ether and alkyl cross-linkages resulting in liquefaction of coal. Microbial coal processing experiments are drawing on fuels characterization expertise from the Tribochemistry Group in this Division to evaluate product fuel quality.

Such low-energy biological processes for coal upgrading are attractive alternatives to current energy-intensive liquefaction and desulfurization treatments. This new technology could allow for greater utilization of domestic energy reserves by permitting oil burning electric power plants to use coal liquid products without costly retrofitting and would significantly cut costly sulfur and metals emissions to the atmosphere.

Metals bioextraction. The biological processing and recovery of critical metals is also an area of expanding industrial interest. Already, nearly one-fourth of U.S. copper production comes from microbially assisted hydrometallurgical processing of ores, and efforts are under way world-wide to determine other metals and ores amenable to bioprocessing. In last year's report, we described the solubilization of metals and metal sulfides by a biogenic metabolite, methyl iodide. We have extended this work to show that ternary metal sulfide ores (FeAsS, Cu_3AsS_4) are also solubilized by MeI. A summary of reactions is shown in Fig. 1a. This research has formed a part of our contribution to the NBS steel industry initiative. Because of the industrial potential, we are involved in patent procedures with the General Counsel for DOC for the use of methyl iodide for metal ore solubilization and we are conducting larger scale, longer term leaching experiments.

Bioprocessing of coals and ores exposes container, pump, and pipeline materials to powerful biogenic corrosive agents. Even stainless steels are susceptible to deterioration under such stressed conditions. Development of resistant materials such as advanced ceramics will be critical to industrial process development. Evaluation of resistant container materials in bioprocessing of strategic metals is a central area of research interest developed in discussions and interactions with the Office of Naval Research. They are now considering a major research proposal from our group along these lines.

MeI-metal reactions may also be significant in environmental cycling of metallic materials, yet very little is known about MeI biogenesis and occurrence in sediments. It is ubiquitous in the marine aquatic environment at ng/L concentrations but can be at µg/L concentrations in areas of high marine algal productivity. A metabolite of marine macroalgae, β-dimethylpropiothetin (DMPT), has been reported to produce methylated sulfur compounds. We found that DMPT in the presence of KI produces methyl iodide allowing us to propose a general model for endo-and exocellular methylation of elements by algae in the marine environment (Fig. 1b). We also found that Chesapeake Bay phytoplankton apparently produce DMPT, as evidenced by the production of dimethylsulfide when cells are treated with base. Thus a substantial, previously undescribed pathway for environmental metal methylation may exist in estuarine waters.

These studies may enable us to predict methylation of metals to toxic forms in certain environmental situations, which will help us to anticipate potential problems in metal-containing materials use, hazardous waste disposal, and environmental fate. The U.S. Navy, for example, which is partially supporting our studies, has strong interests in environmental fate and transformations of tin related to its fleet organotin antifouling program. In longer range considerations, we, along with other NBS units, are discussing with DOD representatives general disposal of military hazardous materials by bioprocessing.

In-Service Materials Performance Monitoring/Evaluation: Organotins

Deployment of selected organotins in commercial and military materials as polymer stabilizers, antifoulants, and agricultural biocides, has achieved a world-wide scale with sustained, rapid growth. As the production and use of organotin compounds has expanded, so has international concern for their impact on the environment.

Our long history of research into chemical and biotransformations of organometallic materials and our advances in ultratrace metal speciation and measurement methodology has resulted previously in collaborations with many U.S. Navy laboratories. Currently, at the request of the Office of Naval Research and with their sponsorship, we are conducting research on the environmental fate and mechanisms of degradation of organotin compounds. We have been requested to apply our unique interdisciplinary understanding of molecular speciation and microbiological transformation of metals to gain an insight into the environmental pathways, repositories, and cycles of organotin compounds. Inherent in this request is the support for development of advanced measurement and speciation methodology presently unavailable in the scientific community.

The U.S. Navy intends to implement organotin-based antifoulant paints for the nation's fleet. Triorganotin biocides are demonstrated to sustain paint performance for years at sea, saving hundreds of millions of dollars annually in fuel costs and increasing strategic preparedness by reducing drydock time. However, the toxicity to estuarine or harbor aquatic life of leached tributyltin (TBT), the primary biocide incorporated in first generation antifouling paints, has raised Navy concerns over its use. The environmental fate and food chain bioaccumulation of tributyltin is unknown, preventing development of models for its persistence in nature. Consequently, quantitation of butyltin species in seawater, sediments, and tissues at ultratrace environmental levels employing improved measurement methodology is required.

Improved Organotin Molecular Characterization. Very substantial improvements in both organic solvent extraction efficiency and graphite furnace atomic absorption (GFAA) detection levels have been achieved for the quantitation of organotin species in seawater. Both tributyltin and dibutyltin are extracted quantitatively by toluene from spiked samples of seawater. Monobutyltin, more hydrophilic and less readily extracted, can be recovered with near 100% efficiency by extraction when a complexing agent such as tropolone is added to the toluene extractant. Signal enhancement for GFAA (15-fold) is effected by adding ammonium dichromate to either aqueous or organic solutions of organotin, and supplemented by use of L'vov furnace tubes (Fig. 2a). These complementary techniques are approximately additive and allow detection limits of 0.1 ng or 0.2 ppb tin in seawater (Fig 2b), a concentration below that at which tributyltin adversely affects sensitive marine organisms.

Improvement in the speciation and detection of the tetra-, tri-, di-, and monobutyltin series of compounds by our previously described element selective gas chromatography-flame photometric detector system has recently been accomplished. Optimization of column parameters and sample treatment now enable us in a single run to speciate all of the above compounds at nanogram levels in solvent extracts (Fig. 2c).

SRM Development: International Measurement and Speciation Methods Comparison. Analytical methods have proliferated for determination and speciation of organotin compounds in environmental samples, but reliable data that can be compared between widely separated laboratories and field sampling locations is lacking. With Office of Naval Research sponsorship, we have begun an international comparison of organotin measurement methods. A stable aqueous tributyltin containing research sample has been prepared chromatographically and distributed to more than 45 laboratories world-wide; recipients include industrial, academic and government research laboratories. The research sample may be analyzed for total tin as well as speciated, with the results returned to NBS for statistical analysis and evaluation of the accuracy of the method employed. This methods intercomparison is the first attempt to evaluate the intercomparability of the various analytical methods being employed on an international level for a major metal commodity totally dependent on its molecular form for its function. The results of this study will help establish the basis for eventual organotin SRM production and will allow recommendation of specific organotin measurement methodologies with the precision and accuracy required for comparison of analytical data internationally.

Epifluorescence Microscopy Detection and Imaging of Organotins. We also developed and demonstrated a flow injection analysis technique with a microbore HPLC-epifluorescence microscopy system for detection of fluorescent complexes of inorganic tin(IV) and organotins at pg (fmole) levels (Fig. 2d). We have used 3-hydroxyflavone- (λ_i=365nm, λ_e=453nm) and morin-tin complexes (λ_i=420nm, λ_e=500nm) in flow injection mode with our UV epifluorescence microscope that is equipped with a photometer-monochromator system for fluorescent tin detection. Surveyed were $Me_{1-3}Sn$, $Bu_{1-3}Sn$, Ph_3Sn and inorganic tin-ligand complexes. Detection limits for tin varies with its chemical species, but are lowest with inorganic tin(IV), $MeSn^{3+}$, and $BuSn^{3+}$ (detection limits 5, 27, 130 pg, respectively) using flavonol. The technique is showing great promise as a sensitive, selective microbore HPLC solution flow detector as well as for the in vivo characterization of biological tin and other metals uptake and transformations at the cellular level.

We have also begun microbiological studies, supported by the above speciation methods, to determine if the environmental persistence of tributyltin species in commercial use is controlled by microorganisms as a means of detoxification or as a substrate. Populations of estuarine microorganisms appear to be quite sensitive to tributyltin, with the majority of the aerobic, heterotrophic population being sensitive to 1.0 mg/L tin as TBT, and >99% of the population is sensitive to 10.0 mg/L. The resistant organisms are being analyzed for TBT degradation. Additionally, microorganisms resistant to other butyltin species have been isolated. All of these TBT resistant isolates will be incubated with some candidate second generation biocides to determine their resistance and potential for degradation of these compounds. We have already developed structure-activity correlations for a series of organotin compounds for predicting toxicity.

Molecular Structure-Activity (SA) Predictors of Materials Properties. It is recognized that the basic molecular architecture conferred by long-lived tin-carbon covalent bonding dictates rates and modes of chemical and biological action which is the basis for the multi-million dollar tin biocide market. Heretofore, no basic theoretical means were available to quantitatively assess the effect of the shape or number of carbon atoms, or organic groups bonded to tin, on physico-chemical and biological properties.

In past annual reports we have described preliminary SA work that exploits our progress in ultratrace molecular speciation of bioactive organometal species in aquatic service environments. This unique background has permitted concurrent efforts to test related chemical and biological effects of other critical materials directly measurable in terms of molecular topologies, e.g., bonding parameters and conformation. During FY84, in collaboration with colleagues at the Naval Bioscience Laboratory (NBL), University of California, we successfully extended our measurement methods in concert with previously described computational procedures using bonding data, to define the first predictors of organometal toxicity based upon completely independent molecular structure data.

Moreover, our correlations are general and probably can be applied to solution properties of most organometals, such as their aqueous solubility (Fig. 3a), their chromatographic retention, and their n-octanol-water partition coefficients which are highly valuable for estimating bioconcentration. In Table 1 are summarized linear correlations for a number of important materials properties with their corresponding total surface area values computed from independent molecular bonding data, all of which are in accord with the relationship

$$\ln(\text{PROPERTY}) = m\,(\text{TSA}) + \text{constant},$$

where m is the slope of the regression line.

Figure 3b illustrates computer-generated ORTEP drawings from our PROPHET program which employs bond distances, bond angles, and Van der Waal radii from known or estimated structures to calculate "total surface area" (TSA) in $Å^2$. TSA is among several topological descriptors which are extremely sensitive to subtle conformational changes produced by local molecular or solvent environments. This is suggested for the two most likely chemical forms (tetra- or penta-coordinate) shown for the commercial tri-n-butyltin biocide cation dissolved at low concentrations in seawater. With this approach we are now extending the TSA predictor to quantitative evaluations of organotin toxicity for second generation materials of urgent concern to the U.S. Navy and industry.

At NBL, an important marine target organism, the Mud Crab larvae, Rhithropanopeus harrisii, was exposed at sub-acute concentrations in fresh seawater to a large series of triorganotin biocides, representative of all those in commercial use. Resultant averages of replicate LD50 (survival) data (in nM), were subsequently correlated with NBS TSA values computed from handbook bond data to give the excellent results indicated by Figure 3c and in Table 1. Also in the table are collected several other linear correlations from microbial uptake or algal growth inhibition data for organotins elsewhere reported which suggest the power of our structure-activity technique. These results show that both physicochemical and biological activities in aqueous media are predicted for organotins based upon specific molecular structural features. Of even greater scientific and practical interest will be the extension of the method to predictions of physico-chemical and biological properties of other metal-containing materials relevant to NBS and its clients.

Non-Destructive Measurement and Methods Development: Molecular Characterization of Ceramic Precursors

Fundamental investigations of organotins by NMR spectroscopy in support of DOD projects have led to the development of new measurement methodologies. Hexaorganodistannoxanes are widely employed as selective biocides and catalysts by industry. Nevertheless, very few direct methods for establishing the presence of the Sn-O-Sn linkage in these molecules have been developed. We have investigated a number of distannoxanes by high-field solution NMR and found that the Sn-Sn spin-spin coupling through oxygen is a simple, unambiguous, and diagnostic structural probe for these compounds. A preliminary correlation of the magnitude of the spin coupling with molecular topology has been made. A striking influence of solvent on the spin coupling has been observed for several of the compounds (Fig. 4a); detailed study of this effect indicates that electron acceptor solvents, especially those which can hydrogen-bond, stabilize the partial negative charge on oxygen. This interaction may lead to a solvent-induced decrease in the Sn-O-Sn bond angle. Implications of this work extend beyond organotin molecules to other metal oxides such as homogeneous organometallic catalysts and ceramic precursors. A collaboration with General Electric Corporate Research and Development is underway to obtain additional X-ray structural information for distannoxanes with interesting solution NMR properties.

In collaboration with the Center for Fire Research, an investigation of the solid state NMR of organotin compounds also has been initiated. We have obtained the first high-resolution solid state spectra in which $^{13}C-^{117,119}Sn$ spin coupling has been detected (Fig. 4b). These studies, carried out with a large number of organotin compounds, represent the only systematic investigation of various structural parameters on spin coupling in the solid state. Indeed, other reports of spin coupling in the solid state are rare. The method promises to reveal the dependence of NMR parameters on molecular structure with a precision previously unavailable. This development also presents a new and extremely powerful non-destructive method for determining the bonding in amorphous, solid organometals which are unsuited for X-ray analysis; as one example, we have successfully obtained spin coupling-resolved spectra of dimethyltin oxide, an amorphous organotin polymer.

The extension of these methods to sol-gel solutions and green ceramics is being actively pursued with the Ceramic Processing, and Characterization Group.

Materials Durability: Laboratory and Field Monitoring of Biocorrosion

It has been estimated by the NBS/Battelle Study that in 1975 the national cost of corrosion of pipelines alone was 158 million dollars. For many years, the exterior corrosion of underground pipelines by anaerobic sulfate-reducing bacteria has been recognized as an important cause of this corrosion. In England, for example, it has been estimated that at least 50 per cent of failures were due to bacterial corrosion. It is highly probable that there could be as many, if not more, reportable cases of bacterial corrosion failures of pipelines in the U. S. were it not for the fact that these failures are not recognized or detected by many pipeline operators.

Presently there are no available techniques which can accurately determine the location on the exterior surface of underground steel pipelines where sulfate-reducing bacteria are actively causing corrosion. Location of these areas and the ability to institute cathodic protection measures would provide major cost savings to industry and reduce the danger to human life.

Our long-term studies conducted for ONR on anaerobic biological corrosion have indicated that a highly volatile phosphorus compound produced by sulfate-reducing bacteria appears to be the corrosive agent. This phosphorus compound appears to be produced by the bacterial reduction of phosphates, phosphites and hypophosphites. Sulfate reducing bacteria which lack this capability appear to be non-corrosive. Hydrogen sulfide, also produced by these bacteria, appears to inhibit corrosion at neutral pH values by forming a partial protective sulfidic film which is highly diagnostic of the status of anaerobic surface corrosion. It is believed that corrosion occurs when this film of iron sulfide (Fig. 5a) breaks allowing the diagnostic corrosive phosphorus compound to come into active contact with the steel. Preliminary laboratory evidence at NBS has indicated that when this film of iron sulfide breaks down, rapid potential fluctuations (electrochemical noise) are produced in the steel. A simple technique to detect this electrochemical noise had already been developed.

An opportunity to test this technique in the field came as a result of a recent serious rupture of a gas pipeline in West Virginia, due to bacterial corrosion, which caused 9 injuries in an ensuing fire. Through the concern and interest of the gas pipeline safety section of the Public Service Commission of West Virginia as well as a number of gas pipeline transmission companies (including Columbia Gas Transmission Company, Consolidated Gas Supply Corporation, Tennessee Gas Transmission Company and the Cabot Corporation) a 1,600 foot section of 20-inch pipeline was made available for field study by NBS. This pipeline was in an area where bacterial corrosion had already caused a number of failures.

The technique previously developed at NBS for the laboratory detection of electrochemical noise was employed in the field with the assistance of a guest worker from the Department of Transportation (responsible agency for U.S. pipeline safety). After the pipeline was located, electrical connections were made to the pipeline at four points. A platinum electrode was placed in the soil above the pipeline and moved at 25 ft. intervals along the pipeline. Electrochemical noise from one area of possible anaerobic corrosion is indicated in Fig. 5b. The recorder tracings 25 ft. on either side of this area indicated little if any electrochemical noise.

Figure 5c depicts a system in use for simulating anaerobic pipeline corrosion in the laboratory. The soil is replaced by a nutrient agar medium. Corrosion rates and potential (pipe to soil potential and redox potential) measurements are also made in addition to electrochemical noise measurements. Refinements of the apparatus will permit us to directly monitor volatile phosphorus-containing metabolites during microbial growth to relate their production at the molecular level with electrical field test parameters.

It remains for these very preliminary observations to correlate this electrochemical noise with action areas and biochemical mechanisms of biological corrosion. Upon establishment of this relationship, this nondestructive technique would be most useful in locating areas of biological pipeline corrosion in the field and applying prompt corrective measures (cathodic protection) before a major disaster occurs.

Materials Processing and Durability Chemistry
Subtask 2 of Task 15418

Ceramic Tribology

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Advanced ceramics have the potential for many structural applications in which tribological considerations are important and often crucial. High heat resistance (engine parts, heat exchanges, exhaust nozzles), hardness and wear resistance (bearings, cutting tools), low thermal conductivity (coatings), and light weight (engines) are some of the more important characteristics (applications). The most prominent feature of these applications is the occurrence of high temperature. It may be noted, for example, that some ceramics can be operated at 1400 °C while the best superalloys are limited to about 1100 °C. Data on the tribological properties are scarce or nonexistent in this high temperature regime.

The Tribology group of the Inorganic Materials Division has developed a program to meet the challenges in high temperature tribology. The program includes measurements and modeling of a four-ball wear tester, a high temperature wear facility, high temperature vapor phase lubrication, and studies on ceramic coatings.

The interpretation of friction and wear measurements of ceramic on ceramic in a device such as the four-ball wear tester is dependent upon the understanding of temperature effects. This is true, for example, in the study of lubrication mechanisms, a new project supported by the Office of Basic Energy Science of the Department of Energy. A theoretical study of the evolution and distribution of temperature in an idealized model of a four-ball wear tester under dynamic contacting conditions has been developed. In a four-ball apparatus, one ball spins at a constant angular velocity while in frictional contact with three stationary balls. Experimentally, the rotating ball especially in the case for ceramic contacts, exhibits more wear than the stationary balls. The theoretical results show that the temperature distribution has a significant dependence on thermal conductivity. This result is important because for some ceramics, the thermal conductivity is lower than in steel. Fig. 6 shows a comparison of calculated temperatures and measured wear rates for a range of thermal conductivities. The figure suggests that wear results for ceramics are much more dependent on frictional heating than metal systems. Hence, the interpretation of ceramic wear data is more complex than it is for metal contacts.

Design and construction of unique friction and wear testers for operation at temperatures up to 1500 °C has begun. This temperature range was unprecedented in the design and operation of wear testers. Major considerations were the dimensional and the mechanical stabilities of the high temperature structural components. These componenets were required to support significant thermally induced stresses arising from the large temperature gradients. Especially important was the heater-specimen holder interface. The material requirements were satisfied through the use of advanced ceramic components. The apparatus has been designed to include specimen configurations in the forms of a ball sliding on a flat plate and a ball or pin sliding on a flat disk. Both unidirectional and reciprocating motions are allowed. Thus, for example, both the sliding contact between a cam and tappet and the wear of piston liners or rings can be studied. The facility, scheduled to be operational early in FY 85, will provide the first experimental facility to study the wear mechanisms of ceramics under slow sliding and with externally controlled temperatures up to 1500 °C.

Lubrication of ceramic materials at high temperatures will require new developments. Current lubricants are useful only to about 200 °C. For high temperature ceramic parts, a potential alternative to conventional lubrication is vapor phase lubrication which exploits the occurrence of high temperatures. It has been demonstrated [1] that certain liquids can be vaporized and caused to undergo deposition onto a substrate at high temperature. The deposited layer then forms a transient organic protective coating against wear. A project has been designed and initiated to study this novel concept. The experimental program will address the method's dependence on molecular parameters such as structure, composition, binding energies, and kinetics.

Collaborative efforts between the Tribology group and Prof. Ramalingam of the University of Minnesota have been initiated to study the wear protective properties of ceramic coatings. Samples are prepared at the University using a novel directed arc plasma coating technique and the materials are evaluated at NBS. Preliminary results on titanium nitride and zirconium nitride indicate a significant reduction in wear for the coated samples.

Lubricant-Materials Interaction Study

Effective friction and wear control under lubricated conditions have been related to the formation of thin lubricating "films" or "friction polymers" in concentrated contacts. This study is designed to: (1) develop measurement methods which will permit examination of structural details of such films, and (2) determine the effects of molecular structures on film formation.

Attempts have been made in the past to examine chemically the nature of the film, but the very small amount of the material from the film has made analysis extremely difficult. To resolve this difficulty, a high performance liquid chromatograph coupled on line to a high sensitivity atomic absorption spectrophotometer (HPLC-GFAA) analysis system has been developed. In order to generate sufficient material for analysis, a static film formation apparatus was used to study the organometallic reaction under different conditions. The organometallic compounds formed under static conditions (no rubbing) were compared to the reaction products formed under dynamic rubbing conditions (boundary lubrication) in a four-ball contact using the same starting materials. An isolated group of molecular compounds from a lubricant was selected for this purpose. The results are shown in Figs. 7 and 8. It can be seen that high molecular weight organometallic species of about the same molecular weight are formed under these two entirely different conditions. The temperature for the static case was 225 °C while the bulk temperature for the wear test was 75 °C. This suggests the temperature at the wear contact is much higher than the bulk system temperature.

In cooperation with a major engine manufacturer, the question of ceramic-lubricant interactions has been studied. It has long been thought that for all practical purposes, ceramics were chemically inert in an operating engine environment. Using the HPLC-GFAA analysis system, it was found that ceramics under engine operating conditions, in fact, do interact with lubricants. Fig. 9 shows results obtained from the interaction study of a mineral oil with a chromium oxide bonded ceramic cylinder liner surface at a temperature of 225 °C. Substantial reaction products in the form of chromium organometallics were detected. This result points to the need for a careful and thorough study of ceramic-lubricant interactions.

Molecular structural effects on the lubricating film formation have been studied using different molecules as the starting materials. Formation rates for organometallic compounds have been determined for the saturate, aromatic, and polar fractions of several lubricating base oils interacting with a steel surface. It has been found that the formation rates from the polar fractions are about an order of magnitude greater than for aromatics and saturates (see Fig. 10). Further, friction studies have shown that the subfraction with the greatest amount of organometallic compound has the lowest friction. This result suggests a more general principle, that friction characteristics might be correlated to film formation rates.

Standard Reference Materials (SRM)

The Environmental Protection Agency recently issued regulations on hazardous wastes, including a regulation of the content of polychlorinated bi-phenyl (PCB) in used oil. Consequently, calibration standards for PCB or chlorine analysis became important. Production and certification of a chlorine SRM using neutron activation analysis and x-ray fluorescence have been completed.

Production of a second SRM, sulfur in a complex hydrocarbon matrix, has also been completed. Earlier, work at NBS showed that sulfur-containing molecules have a significant effect on lubricant life. Previously there has been no standard available for measurements of low sulfur concentrations in oil matrices. Certification of the sulfur SRM was accomplished using x-ray fluorescence and microcoulometry.

SRM research is also centering on the development of separation techniques that could be used to isolate and purify reasonable quantities of specific molecular compound classes. These compound classes have unique friction and wear characteristics and could be used as standard reference materials by other researches in tribology. Functional molecules in petroleum fluids and synthetic fuels have been isolated and characterized. It has been found that some nitrogen-containing molecules and some sulfur-containing molecules exhibit strong influences on the oxidation stability and the durability of hydrocarbon mixtures.

Basestock Consistency Study

The use of rerefined oils for lubricating basestocks has increased substantially as crude sources have become less accessible. A major concern about this trend has been the ability to assess the consistency of the rerefined base oil. To address this problem, the ASTM/NBS Basestock Consistency Study (BCS) was conducted in 1980-1981 to construct a data base. The data were transferred to NBS in 1982, and the subsequent analysis of the data began with the support of the Department of Energy.

Assessment and identification of the principal variables for consistency monitoring constituted a rather remarkable achievement. By the end of the project, 191 sets of data were investigated, each test having been a possible independent variable. Numerous applications of multivariate, univariate, correlation, and multilinear regression statistical methods were utilized to reduce the data to a set of 19 primary and 11 secondary candidate variables for consistency monitoring. A general methodology was developed and applied to assess the significance of the variables for oxidation stability and wear characteristics. No previous effort in consistency monitoring of base oils has been as comprehensive or as successful as the combined ASTM/NBS/DOE projects.

[1] C.W. Lai, Masters Thesis, Penn State University, 1974.

TABLE 1

TOPOLOGICAL PREDICTORS FOR ORGANOTIN PHYSICO-CHEMICAL AND TOXICITY PROPERTIES

Property: Organotins	Measured Units	m (obsd)	constant	N	r^2
Aqueous solubility R_4M (R=alkyl; M=C,Si,Ge,Sn)	-log S molal	0.0224	0.442	9	0.992
Partition coefficient: $R_nR^1{}_{4-n}Sn$, octanol/water	log P $\Sigma\pi$	0.0263	-1.98	12	0.991
Liquid chromatographic retention: $R_nR^1{}_{4-n}Sn$, HPLC	ln k^1	0.0117	-1.94	12	0.995
Gas chromatographic retention: $R_nR^1{}_{4-n}Sn$ (R=alkyl,vinyl)	RI min	0.0525	3.64	7	0.983
Microbial uptake: R_3SnCl(R=Et,Pr,Bu)	% uptake Δg	0.459	-69.4	3	0.944
Algal reproduction (growth): $R_3SnX \cdot H_2O$ (X=Cl,Br,CO_3)	ln IC50 Sn, mg/L	-0.0365	7.69	5	0.957
Larval survival (toxicity): $R_3SnCl \cdot H_2O$ (R=alkyl,Ph,c-Hx)	ln LD50 nM	-0.0146	9.18	8	0.938

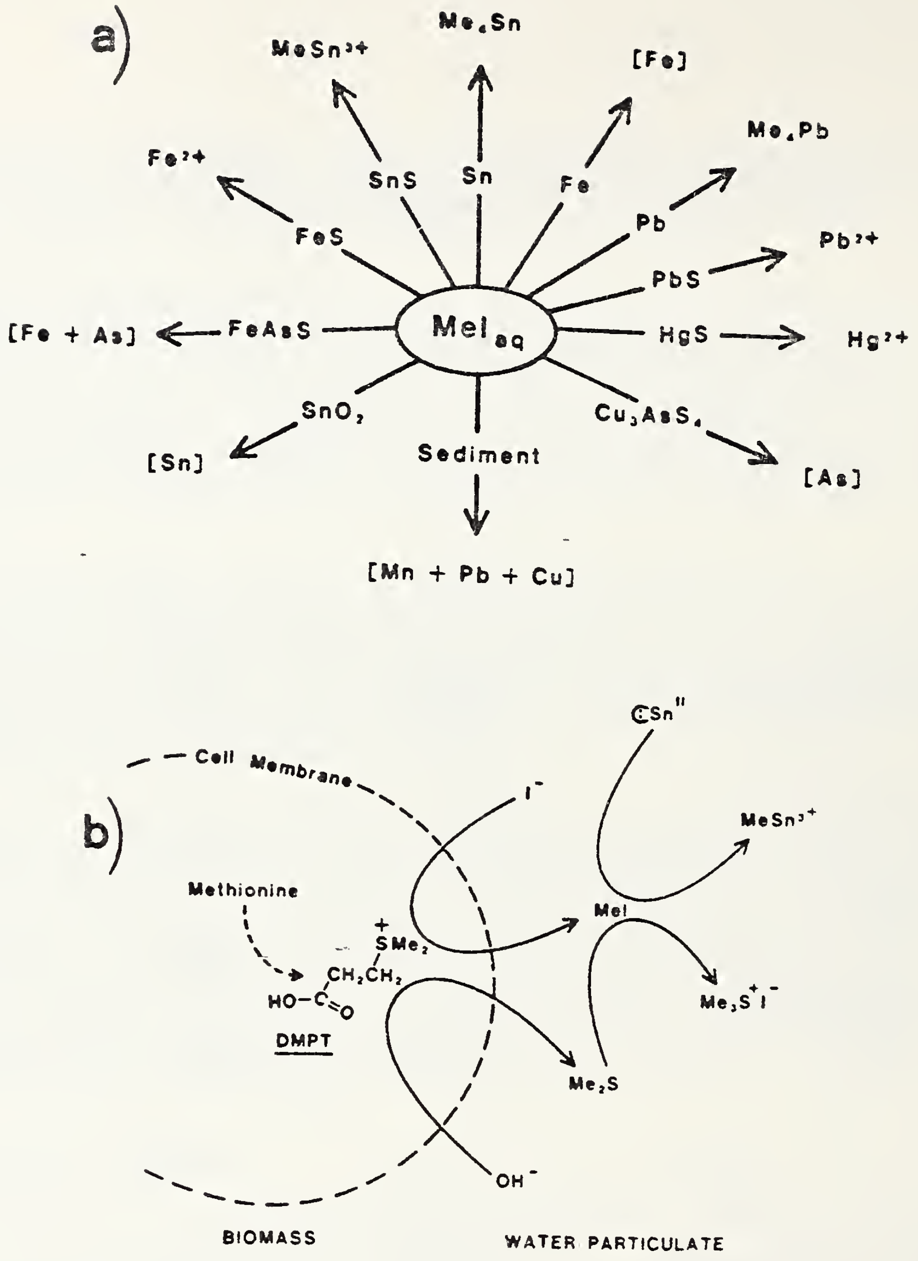


Figure 1 (a) Observed heterogeneous reactions between methyl iodide in water and bulk metals binary and ternary minerals, an oxide ore, and estuarine sediment obtained from the Chesapeake Bay are compared. Speciated methylated products and oxidation states of some metal ions are shown; the products in brackets were quantitated by GFAA. For the metal sulfides, Me_2S was the common coproduct, sometimes associated with lesser amounts of Me_2S_2. (b) Model proposed for endo- or exo-cellular methylation of metals and metalloids involves initial production of MeI via reaction between DMPT and membrane-permeable iodide followed by intra- or extra-cellular transfer of CH_3^+ to a nucleophilic center. Shown is observed exo-cellular methylation of Sn^{2+} ion following excretion of precursor MeI from a cell. Direct methylation by the DMPT metabolite of a nucleophile is not yet demonstrated. Removal of "active" methyl by environmental sulfur compounds (Me_2S) and hydroxide probably strongly competes with metal(loid) methylations.

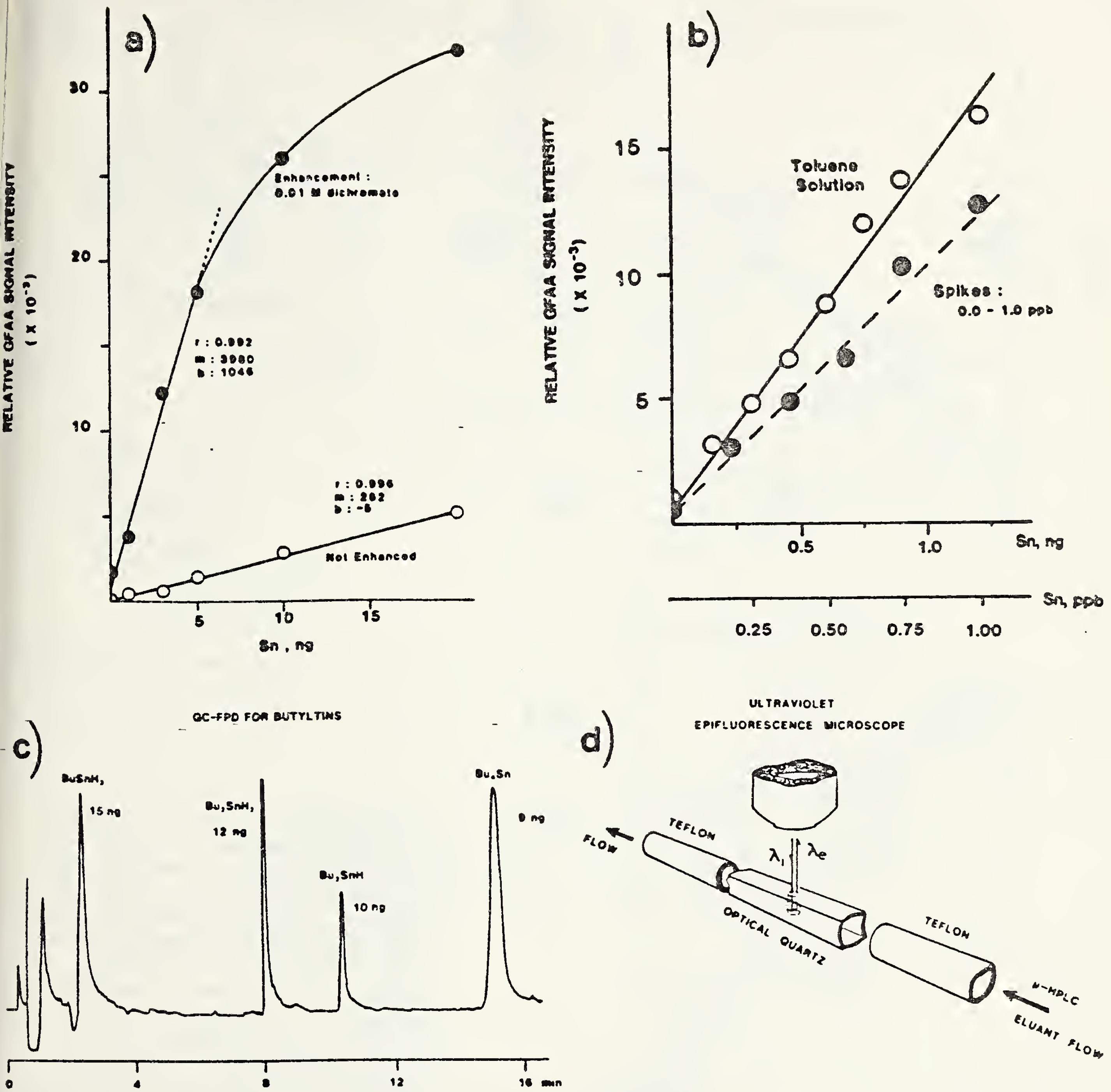
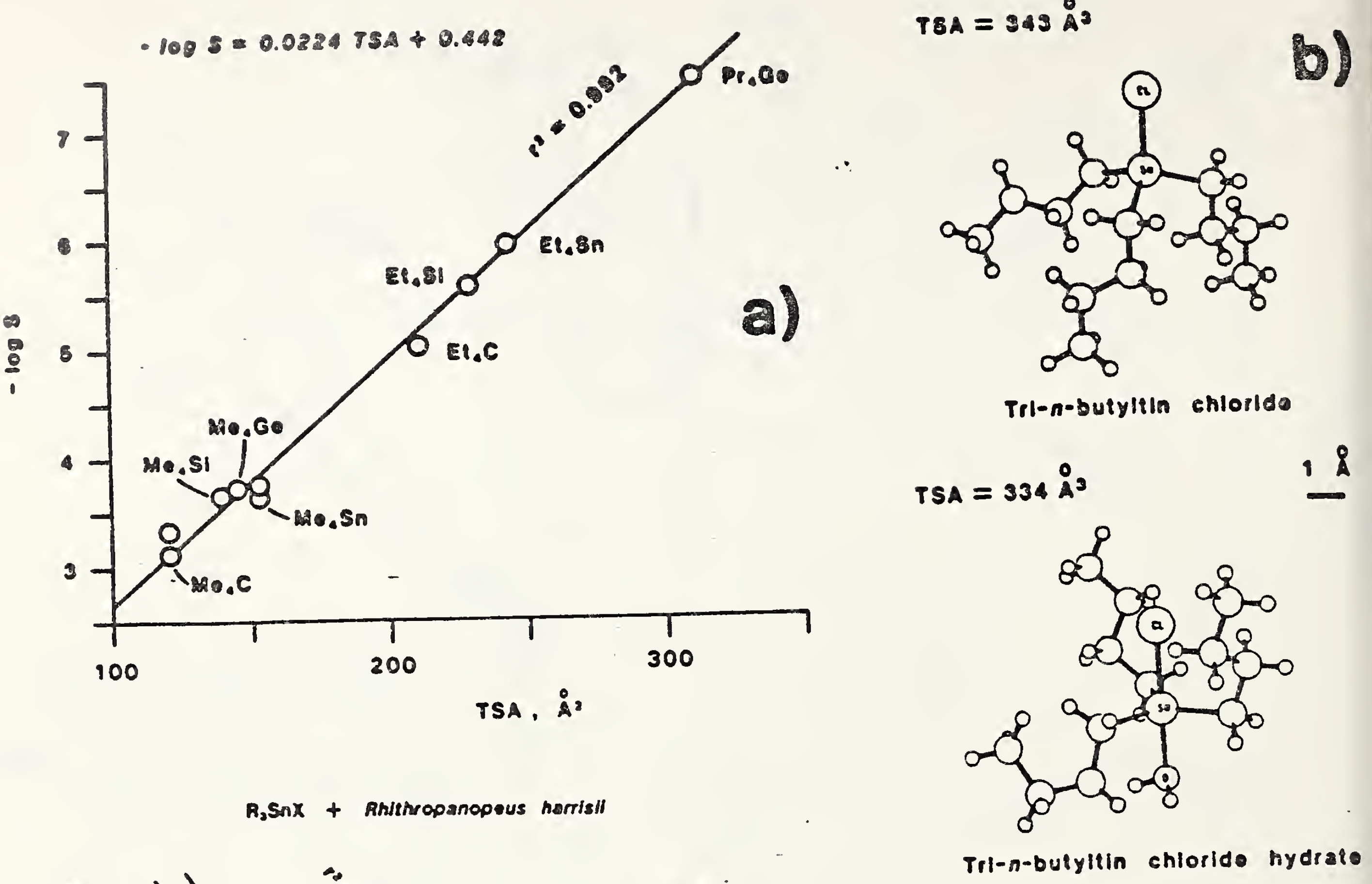


Figure 2 (a) GFAA detection of tributyltin (TBT) in deionized water with and without chemical enhancement. Abscissa values represent quantities of atomized tin, with a linear calibration calculated between 0.0 and 5.0 ng. (b) Determinations by enhanced GFAA are compared and made between TBT spikes extracted from artificial seawater and TBT added directly to toluene. (c) Speciation of solvent extracts performed using gas chromatography coupled with a tin-selective flame photometric detector per unit separation of ng amounts of Bu$_{1-4}$Sn species in methylene chloride following hydridization. (d) Schematic of the UV epifluorescence microscopy (EMI system) adapted as a detector for microbore HPLC. Extracts are analyzed in flow injection or HPLC modes using fluorescent tin ligands and the EMI system where 10^{-4} µl quantities of solution are continuously monitored at pg levels.



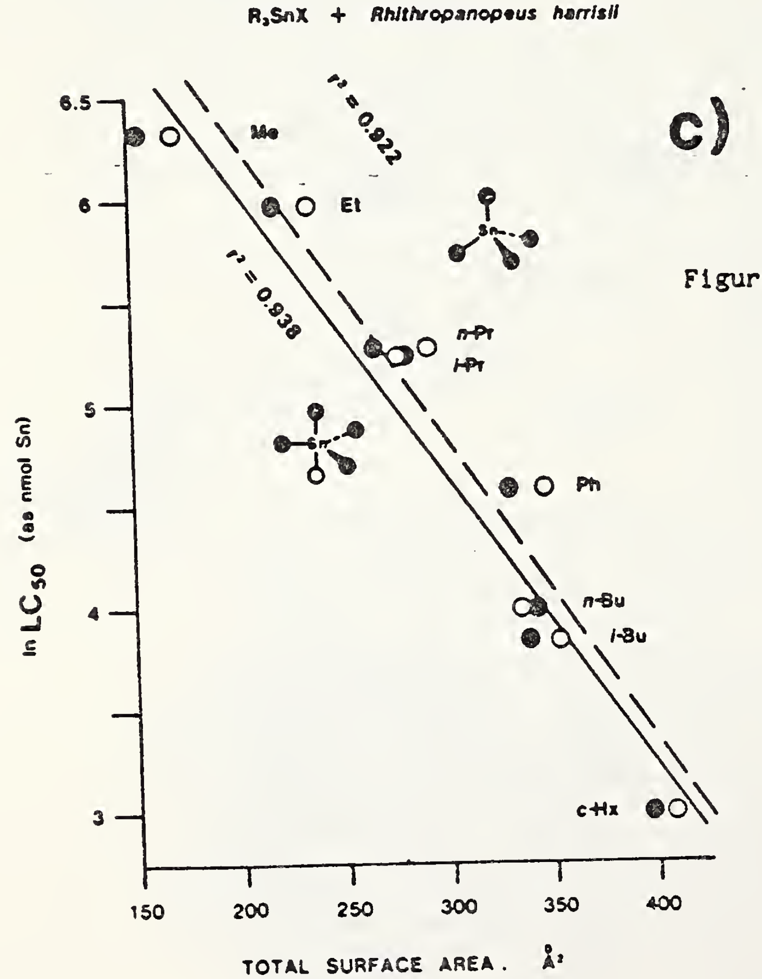


Figure 3 (a) Linear correlation between TSA calculated for a variety of tetraalkylmetals or -metalloids and their aqueous solubilities reported in literature; (b) ORTEP ball and stick representations of tetra- and penta-coordinate tributyltin species in seawater, employed in calculating TSA for most likely conformations of bioactive organotins tested for physico-chemical or toxicity properties; (c) linear correlation between observed toxicities (LD50) of various commercial triorganotins toward crab larvae, R. harrisii, in seawater and respective TSA calculated at NBS for most likely tetra- (---) or penta-coordinated (——) species.

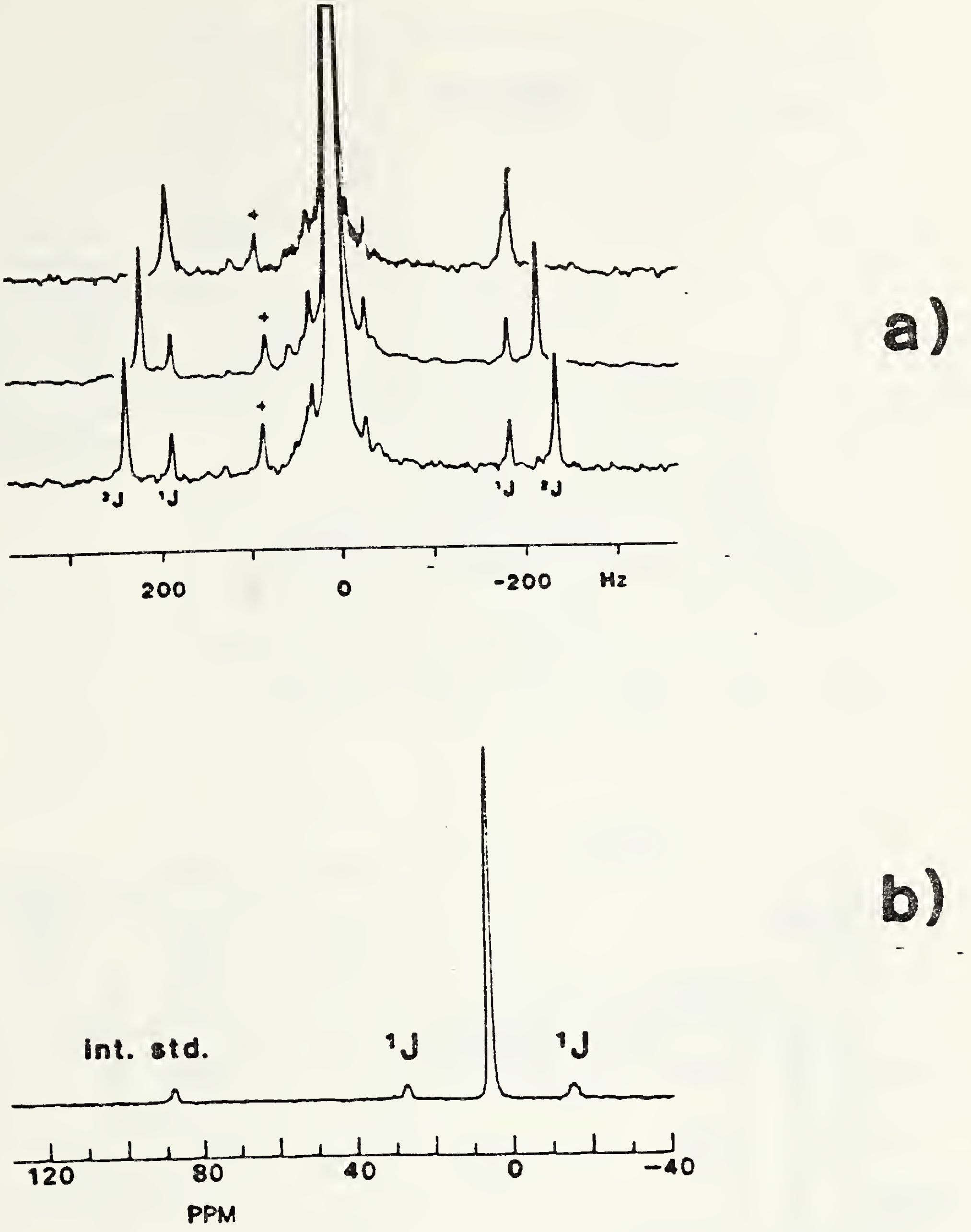


Figure 4 (a) Solvent effect on Sn-Sn spin coupling through oxygen in ^{119}Sn solution NMR of hexa-n-butyldistannoxane, (n-Bu$_3$Sn)$_2$O. Upper spectrum, CDCl$_3$; middle, pyridine; lower, n-heptane solvent. $^1J(^{119}Sn-^{13}C)$ and $^2J(^{119}Sn-^{117}Sn)$ labelled in bottom spectrum; side band marked with (+). (b) ^{13}C cross-polarized magic-angle spinning solid state NMR of amorphous dimethyltin oxide polymer (0.4 g material, 24 hour data collection time). The satellites arising from ^{13}C-^{117,119}Sn spin coupling are visible on the right hand side of the spectrum. The magnitude of J(^{13}C-^{117,119}Sn) (642 Hz) clearly indicates a pentacoordinate environment at the tin center. Delrin (ζ = 88 ppm) is present as internal standard.

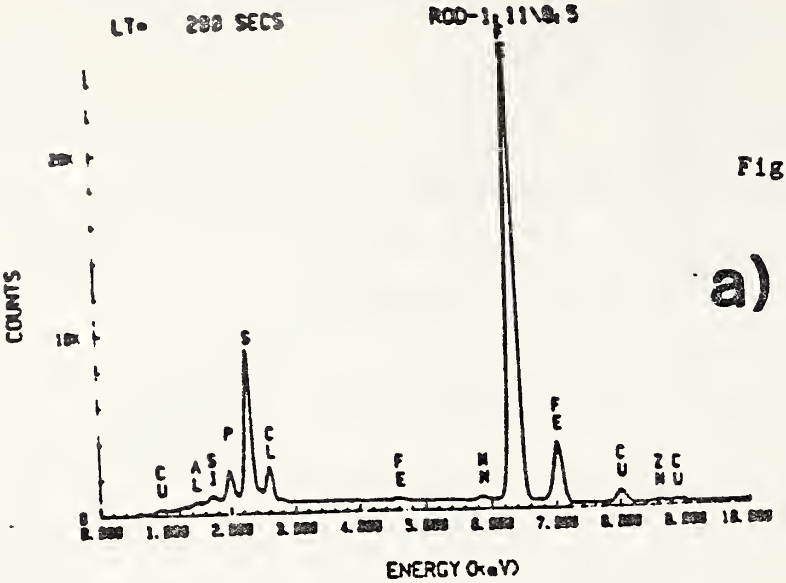
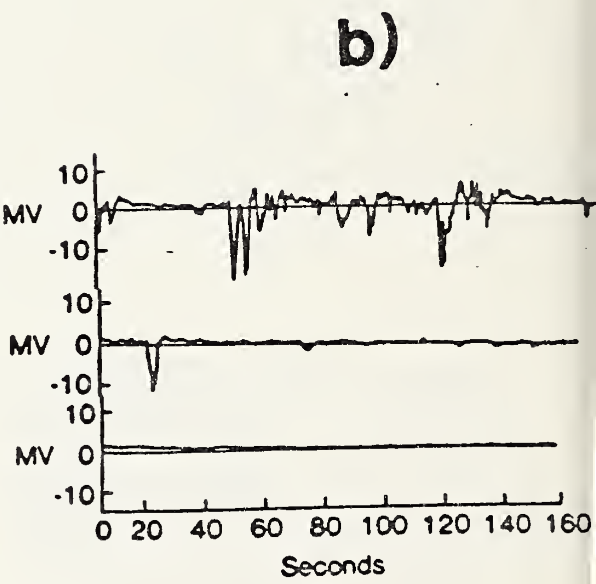
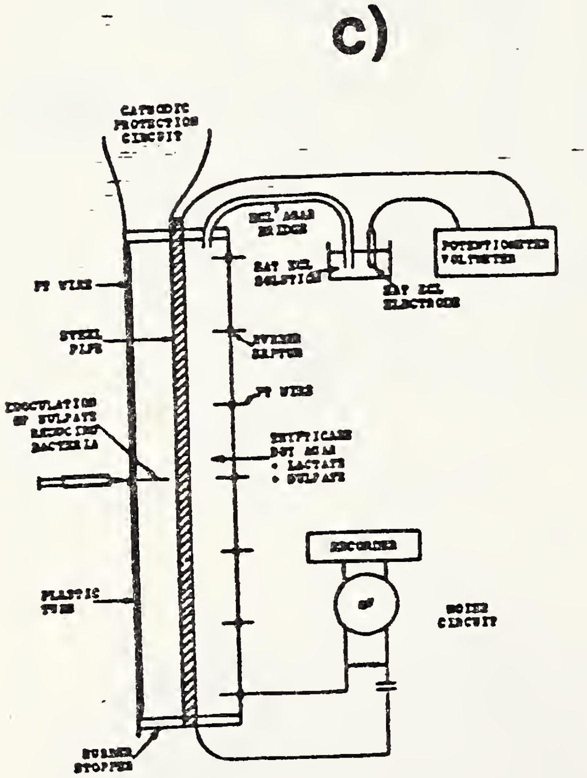


Figure 5 (a) STEM-EDAX profile of elements on corroded surface of 1020 mild steel exposed to culture-filtrate from Desulfovibrio spp. showing predominance of iron (Fe), sulfur (S), and phosphorus (P) in bacterially formed film.





(b) Field recorder tracings of electrochemical noise: (top) with platinum probe placed over underground pipe, 93 feet from pipe connection; (middle) with Pt probe located over pipe at location 25 feet west of first (top) position; (bottom) with Pt probe placed 25 feet east of first position. Pt probe was connected to a 1 Mohm resistor; electrical connection from pipe connected to a 1 mfd capacitor. Potential (mV) was measured and recorded across resistor connected in series to capacitor. (c) Laboratory set up for simulating anaerobic biocorrosion of underground pipe and related steel structures. A nutrient medium (trypticase soy agar) replaces soil. In addition to electrochemical noise monitoring, corrosion rates and potential measurements (pipe to medium and redox) are also continuously taken.

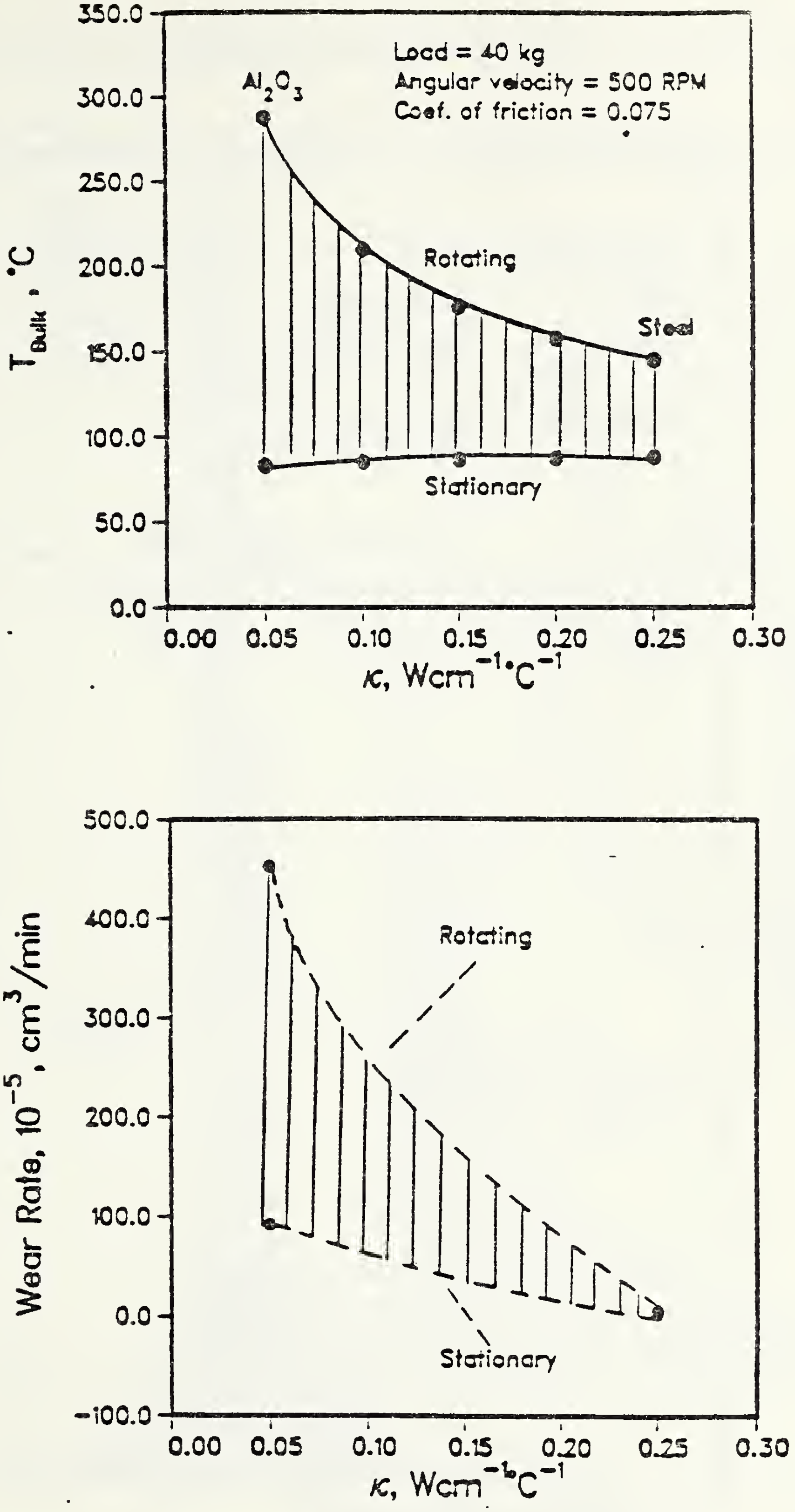


Figure 6 Theoretical predictions of temperature distributions in a 4-ball wear tester and the effects of differing temperature on observed wear rate.

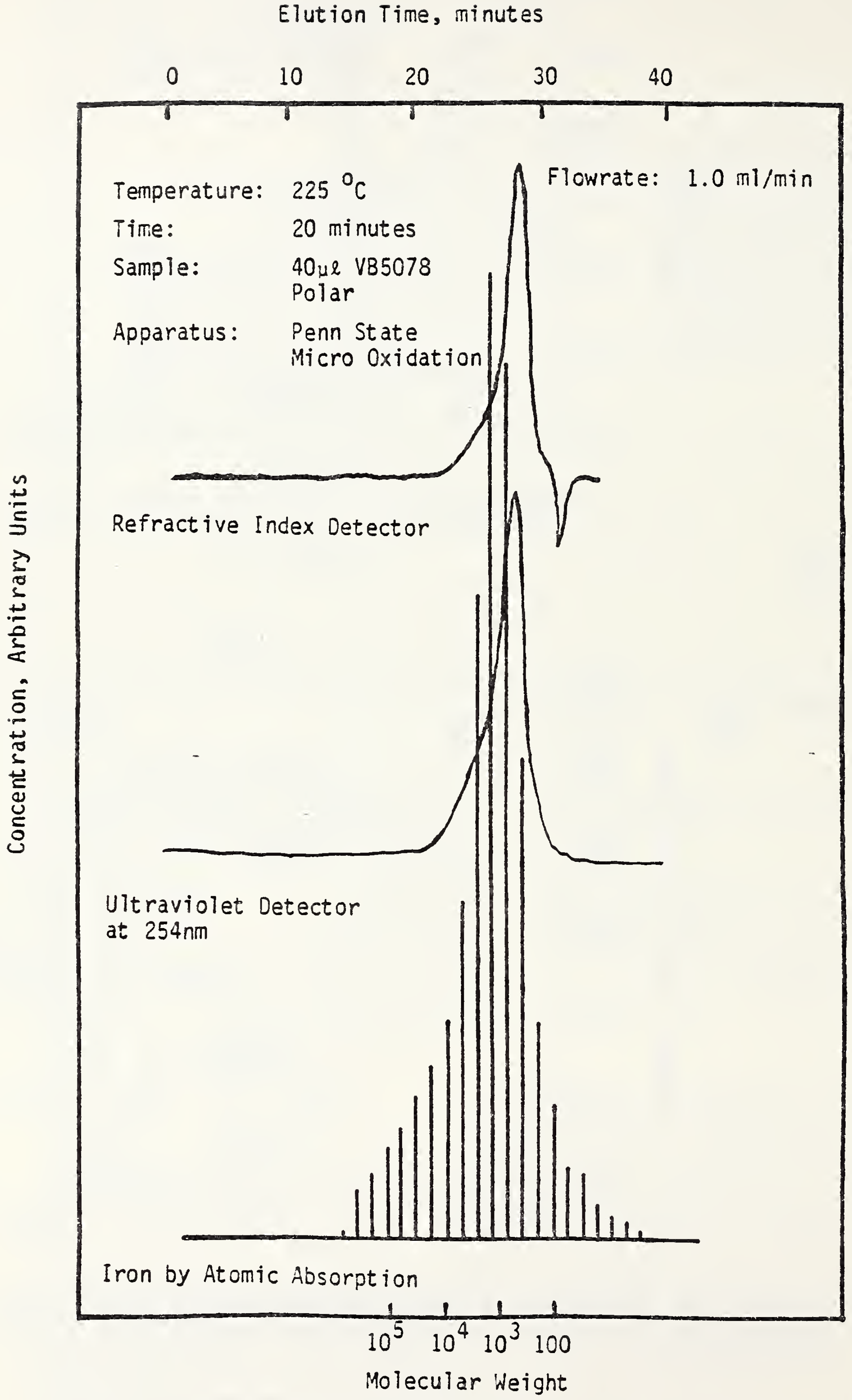


Figure 7 Analysis of the static film formation tendencies of the 600N polar fraction

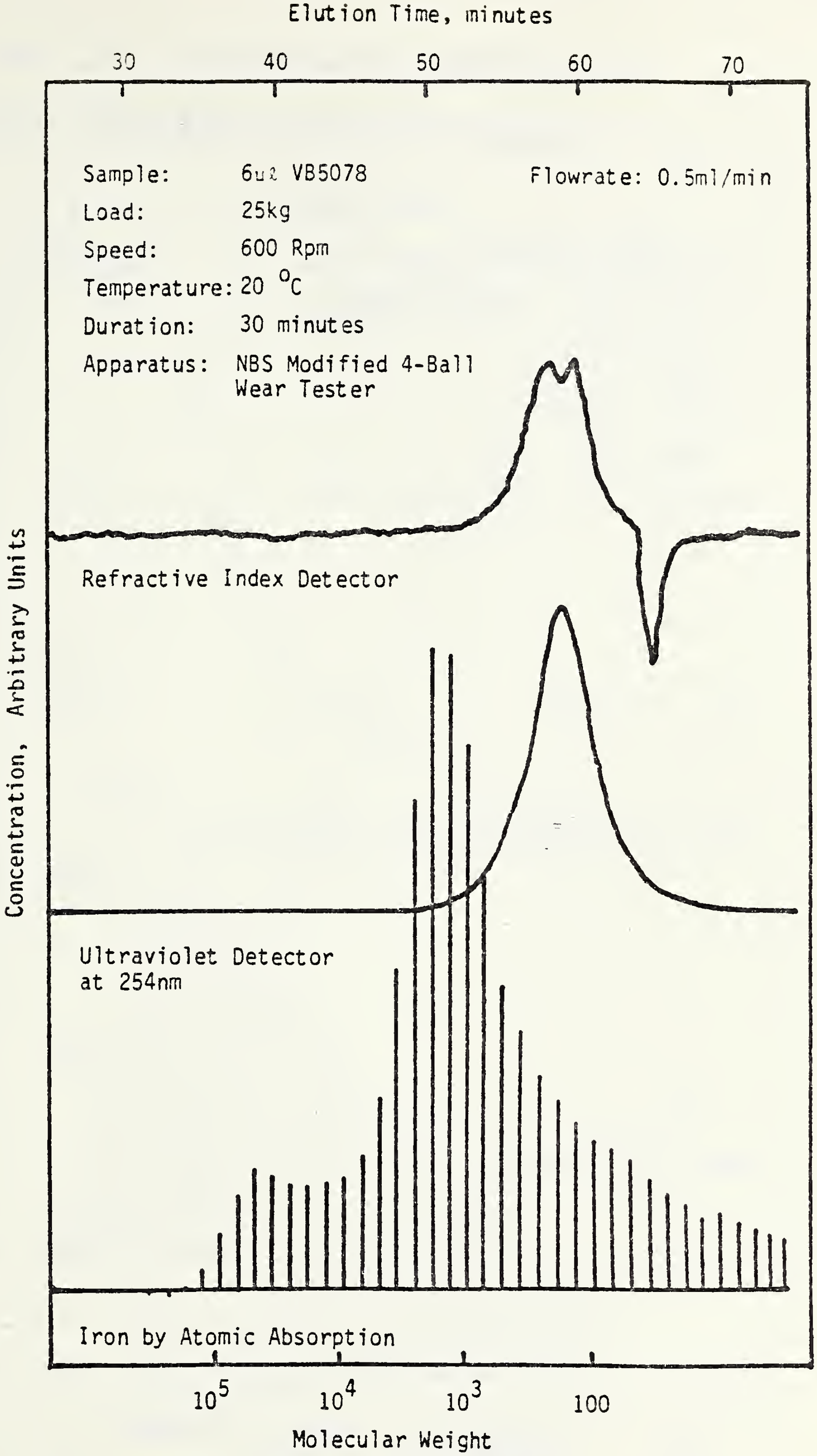


Figure 8 Analysis of the dynamic film formation tendencies of the 600N polar fraction

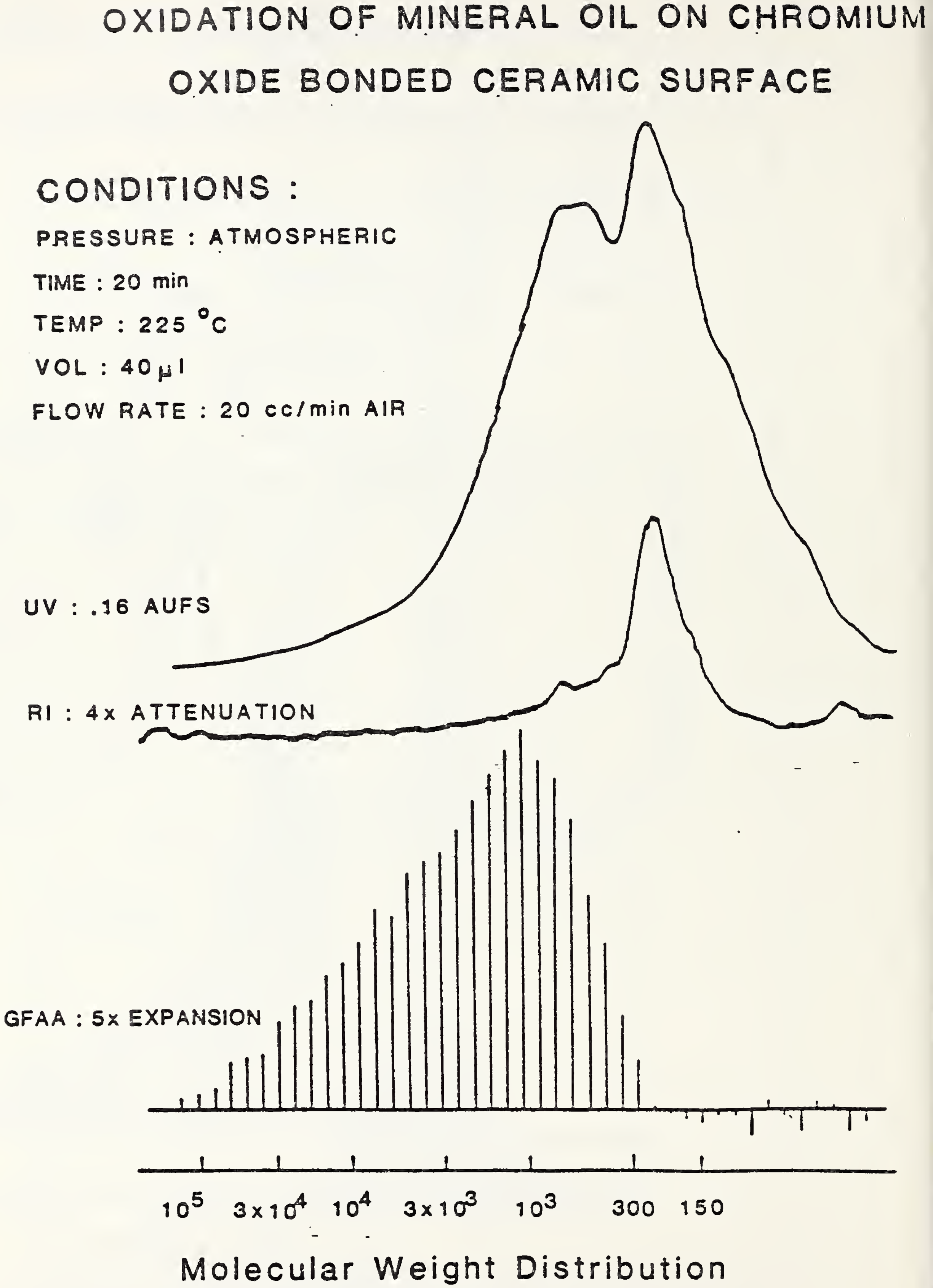


Figure 9 Evidence of a ceramic–lubricant interaction

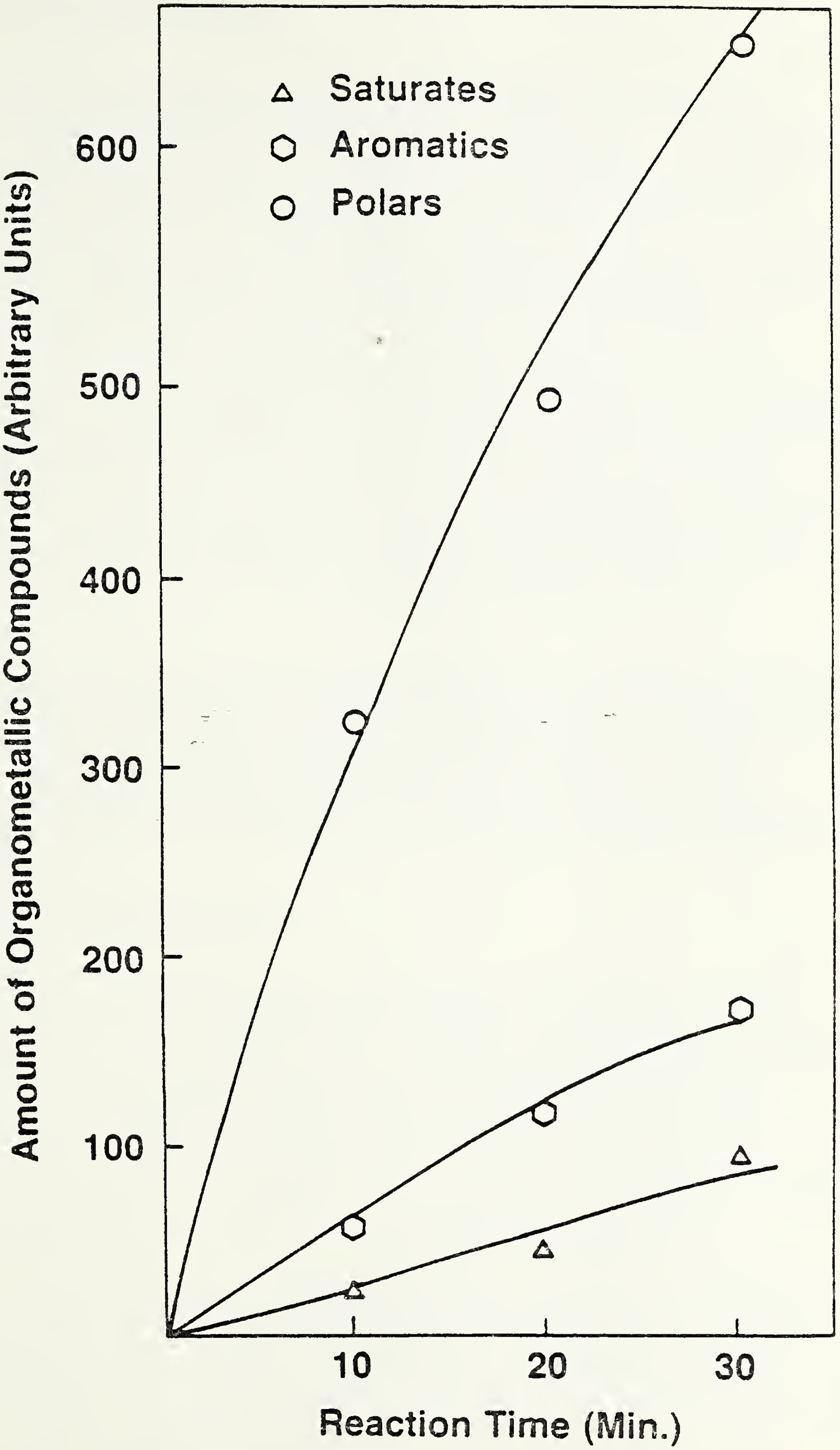


Figure 10 Effects of molecular structures on lubricating film formation rates under static conditions at 225 °C

MECHANICAL PROPERTIES OF CERAMICS
Task 15419

Ceramic materials are used where special properties, such as extreme hardness, chemical resistance to corrosive environments, mechanical resistance to erosion and wear, and mechanical and chemical resistance to temperature extremes, are required. In practical applications they are used as optical fiber wave guides, substrates for electronic packaging, linings for geothermal wells, components for high-temperature gas turbines and heat exchangers, cutting tools for the shaping and finishing operations used in the manufacture of various machines and tools, and insulating linings for reactors and furnaces in the coal-conversion and petrochemical industries. In defense applications, they are used in radomes, missile nose cones, turbine components in portable electric-generating facilities, electronic guidance systems and bearing surfaces in gyroscopes. Because they are brittle, ceramics are usually over-designed mechanically to avoid fracture during use. Investigations of fracture and deformation properties are needed to overcome technical difficulties associated with this brittle behavior, so that ceramics might be used in a wider range of applications. From a purely scientific standpoint, brittle fracture systems provide fundamental information on the cohesive properties of solids, surface physics and chemistry, and material microstructure.

Our program on ceramics has as its broad objectives: (1) the generation of new theories and data to elucidate fracture and deformation mechanisms in brittle materials; (2) the development of new techniques for studying the fracture of and identifying defects in these materials; (3) the collection of engineering data for structural applications; (4) the investigation of processes that result in strength degradation and wear; (5) the investigation of ceramic microstructure and its relationship to mechanical behavior.

FY 84 Significant Accomplishments

- Experiments in which hardness is measured as a function of loading rate and time at load show that the incidence of cracking in the vicinity of the indenter depends on the load, loading rate, time and content of water in the environment. Cracking can occur well after completion of the contact cycle due to the presence of residual driving forces about hardness impressions. These results have important implications with regard to extrapolation of strength data into the ultra-small flaw region and on the use of conventional tests for assuring component reliability. A theoretical model explaining the rate dependence of crack initiation has been developed.

- Deviations of indentation fracture data from previously developed models have quantitatively demonstrated the influence on failure of grain-localized stresses in alumina, barium titanate and a lithia-alumina-silica glass ceramic. The existence of these stresses, which can arise due to thermal expansion anisotropy or phase transformations, can lead to strengths which are significantly lower than those that would be predicted from classical fracture mechanics tests. This difference in behavior between "large" and "small" flaws is shown to be significant for design with ceramics.

- A study has been made of the way indentation cracks "age" on post-formation exposure to moist environments. Such aging progressively reduces the severity of the indentation flaws, even though the cracks are observed to expand during this period. The explanation of this anomalous response has led to a new description of strength in terms of flaw characteristics, with particular implications concerning the fundamental structure of crack tips in brittle solids.

- Direct correlations have been obtained between environmentally enhanced crack growth and changes in the infrared spectra of binary alkali silicate glasses. Only those environments i.e. water, hydrazine, formamide, which enhanced crack growth rates in Li_2O-SiO_2 and Na_2O-SiO_2 glasses produced any significant changes in the infrared spectra of these materials after immersion in the liquid. Further, these results were confirmed through atomic absorption spectroscopy performed on the liquid itself after reaction with the glasses. These results have been interpreted in terms of the influence of the modifier ions on the reactivity of the Si-O bond.

- Microstructural analysis with the scanning transmission analytical electron microscope is being carried out concurrently with the high temperature creep and stress rupture tests on alumina, silicon nitride and silicon carbide. Careful examination and analysis of the tensile and compressive regions of four point bend specimens has shown that stress induced transformations occur during the creep tests. The identification of the microstructural changes was crucial to the formulation of creep mechanisms. In the case of alumina, crystallization occurs in the glass bonding phase and changes the composition of the glass. This process produced toughening of the alumina and improved the creep resistance at 1000 °C. In yttria doped silicon nitride, the nucleation and growth of cavities was observed and could be related to changes in the creep rate as a function of stress and temperature.

- A new theoretical creep analysis has been developed for ceramics which allows one to compare creep rates obtained in tension, compression and in combined four point bend tests. The analysis uses compression and four-point bend data obtained on alumina and silicon nitride. A recently devised tensile jig is being used to obtain tensile stress data at temperatures up to 1400 °C for use in the analysis.

- A multiple scattering theory for SANS to extend the range of this technique to flaw sizes of the order of one μm has been developed and experimentally confirmed. Data from well characterized powders with different particle sizes consistently fell upon the theoretical curve. SANS has also successfully been used to monitor changes in the degree of sintering of an $YCrO_3$ ceramic.

- A photoacoustic system using laser generated thermal waves has been constructed. Indentation flaws in alumina have been detected with this system, illustrating thermal wave potential as a flaw characterization technique. Signal amplitude measurements as a function of modulation frequency have also been measured and compared with theoretical predictions.

Contact Damage and Flaw Studies
Subtask 1 of Task 15419

B.R. Lawn, E.R. Fuller, Jr., S.M. Wiederhorn, D.E. Roberts, A.C. Gonzalez, and R..F. Cook[1]

[1] Guest Worker, University of New South Wales

Contact damage studies using indentation methods provide valuable insight into the fundamental deformation and fracture properties of materials. They are now used widely in the ceramics testing community (perhaps more than any other technique) as a means for evaluating critical material fracture properties. They are used for determining surface stresses in high-strength ceramics, as a basis for modelling wear, erosion and machining properties of brittle materials, in the design of ceramic components for potential strength-degrading applications and as model flaw systems in order to study the underlying physical and chemical processes which are responsible for the initiation of small cracks. As such, contact damage techniques afford a powerful route to the systematic study of the micromechanics of small flaws which control the strength of ceramics.

During the past year, our effort has been directed toward a number of basic and practical applications of contact damage. These applications are being supported by contracts from the Office of Naval Research and Sandia Laboratories. They include: (i) rate effects in crack initiation, (ii) aging effects in crack propagation, (iii) surface stress analysis, (iv) effect of sliding contact on strength.

Rate effects in crack initiation are of critical importance in our understanding of flaw generation processes. The strength of a ceramic is determined by the characteristics of "the worst flaw", so we need to know something about how severe flaws are produced in the first place. In optical fibers, for instance, the initiation of one single crack from an embryo flaw center can degrade the strength by over an order of magnitude, thereby rendering the fiber system inoperative. We now have an indentation system mounted onto the stage of an inverted microscope to allow for direct observation of such initiation events. The indenter is used to create a hardness impression, or simulated "flaw center", from which the cracks are generated. The critical conditions for initiation can thus be investigated in terms of such variables as contact force, contact duration, and chemical environment.

The findings from these observations are leading to revolutionary concepts in the small-scale mechanical behavior of ceramics. Electron microscopic examination of the indentation sites in glasses reveals that the material deforms by a catastrophic "shear fault" mode. This mode is totally different from the classical dislocation mode traditionally used to describe slip processes in softer materials (e.g. metals). Moreover, the shear faulting is dramatically enhanced by water, and is thereby highly rate-sensitive. We have now established that these faults are the necessary precursors to crack initiation. A considerable amount of data on the initiation kinetics in various glasses has now been accumulated, and a theoretical model for incorporating these kinetics is being developed.

Once initiated, the cracks are fully propagating, and accordingly become subject to post-formation aging effects. Particular attention is being devoted to this aspect of indentation fracture because it shows a behavior totally inconsistent with the conventional description of flaws. It is observed that the newly generated cracks continue to grow from the impression corners well after removal of the contact load. However, the strength of specimens containing such flaws actually increases with post-contact time; according to the "accepted" theory of strength, materials should get weaker as the flaws become larger. Systematic investigation of the crack growth patterns in both the post-contact and subsequent stressing-to-failure stages reveals the reason for the apparently anomalous behavior. The local stresses initially responsible for creating the cracks remain after contact as a persistent fracture driving force, but are relaxed as the crack pattern develops. This relaxation is manifested in a failure test as an increased stress to produce failure instability. A newly constituted theory of strength has been developed to account for these residual stress effects. It is expected that such aging phenomena are quite general, and not restricted to indentation flaws.

The above aging study has also led to a rethinking of the question as to the fundamental structure of crack tips in brittle solids. After one day the aging "saturates"; the cracks (on exposure to moisture) expand under the action of the residual stress until, at some critical relaxation point, the growth ceases. This cessation of crack growth has hitherto been attributed to a "blunting" of the crack tip. However, it is found that the post-contact strength increase also saturates at this point, contrary to expectation from the blunting hypothesis. (Blunting is expected to reduce the stress-concentrating power of a crack.) The new picture that is emerging is that the crack tip remains atomically sharp, and that the saturation is caused by crack closure forces at the crack interface behind the tip. The concepts of surface chemistry are being applied to investigate this alternative hypothesis more fully.

A third area of study is in surface stress analysis. The pre-existence of tensile or compressive stresses in the surface of a brittle solid can enhance or inhibit the growth of flaws in subsequently applied external loads. The evaluation of these stresses can be extremely difficult in practice. We have developed a technique for measuring surface stresses, based on the amount of expansion or contraction of a controlled indentation-induced surface crack. A theoretical fracture mechanics analysis has been developed for quantitative evaluation. The method should be useful for determining surface stress levels associated with radiation treatment (including ion implantation), coating procedures, machining and abrasion, transformation toughening, etc.

The effect of sliding contact on strength has been studied, with the specific aim of producing design criteria for maintaining the structural integrity of heat engine components. In heat engines, moving ceramic parts can be in contact, and the frictional contact forces thus developed can produce strength-degrading cracks. We have studied this kind of contact damage in a number of structural ceramics, both at room and elevated temperatures. It has been found, somewhat surprisingly, that the strength degradation is not sensitive to the coefficient of contact friction, contrary to previous (intuitive) belief. A theoretical analysis of the crack formation mechanics under sliding contact condition is consistent with these experimental findings, and yields a simple mathematical formula for the design engineer.

There are several other areas of contact damage which are being explored. Some of these relate to materials evaluation (e.g. determination of toughness and crack velocity parameters). Others relate to specific problems in different programs within the Mechanical Properties Group, and will be discussed under appropriate headings below.

Chemically Enhanced Crack Growth
Subtask 2 of Task 15419

S.W. Freiman, G.S. White, L. Chuck, E.R. Fuller, Jr., T.L. Baker, and J.B. Wachtman, Jr.[1]

[1]Rutgers University, Piscataway, NJ

The objective of this portion of our work is to understand the mechanisms by which a chemical environment can enhance crack growth rates in glasses and ceramics. Our present state of understanding of chemically enhanced fracture is primitive in the sense what while we can measure crack growth or strength degradation rates, our lack of knowledge of specific mechanisms prevents us from selecting materials that have a maximum resistance to crack growth. This same lack of knowledge prevents us from applying fracture mechanics theory to predict component lifetimes which extend much beyond the time range of the experimental data. Our research program is a means of obtaining this knowledge.

In an attempt to clarify the process of chemically enhanced fracture, we have undertaken experiments relating the effects of different environments on glasses which have been modified by the addition of alkali ions to vitreous silica. Research during this past year has concentrated on binary Na_2O-SiO_2 and Li_2O-SiO_2 glasses. The study has shown that only those environments which enhance crack growth in vitreous silica do so in alkali containing glasses. However, the data suggest that the presence of glass modifiers changes the reactivity of the adjacent Si-O bridging bond as well as affects the elastic properties of the silica network. This could be seen because both the positions and the slopes of the crack growth curves in the modified glasses differed from those in pure vitreous silica and, in fact, differed from each other. The curves in the modified glasses were also more complicated than those in silica, with some of the environments which enhance crack growth also exhibiting velocity regions where water impurities, rather than the bulk environment, cause the crack growth. We attribute this behavior to ion exchange/dissolution mechanisms which appear to come into play at velocities $<10^{-8}$ m/sec. Direct correlations between crack growth behavior and changes in surface chemistry, as measured by infrared spectroscopy (IR) and atomic absorption spectroscopy (AA) have been obtained. In fact, only those environments which cause changes in the IR spectra and dissolution, as seen in the AA, cause enhanced crack growth. The reasons for this are not known, but work has been progressing on developing a theoretical understanding of the system.

A fracture mechanics model is being developed to incorporate effects of the molecular structure, modifying ions, and environments on the changes in slope and position of the crack velocity versus stress intensity factor curves for different glasses. The model assumes that the forces acting on the Si-O bond at a crack tip can be expressed as a function of the compliance of the system and the Si-O bond force, including possible modifications due to the presence of other ions in the glass or to the adsorption of external chemical environments. In its current state, the model appears to explain, in a consistent manner, data obtained from all of the silica glasses we have studied. We are also working with Professor G. Gibbs of VPI on molecular orbital (MO) calculations to determine the electronic structure and reactivity of the Si-O bond at large strains. These calculations take into account effects of modifying ions as well as effects of differing environments. Results from the MO calculations should provide information on the Si-O bond/environment interactions which will permit the model discussed above to be expanded and used to make predictions of crack growth behavior.

In addition to advances in theory, progress has been made in improving experimental techniques. For example, because of its stability, the drilled compression, double cleavage (DCDC) specimen is particularly useful for the determination of environmental effects on crack growth. During this past year stress intensity calibrations of this specimen were carried out both using a photoelastic technique and an experimental crack growth procedure. The calibrations allow the stress intensity factor to be evaluated for any crack length and applied load, making possible much more reproducible and accurate crack growth data.

Finally, a computerized data input and retrieval system was developed for oxide glasses. Fracture mechanics parameters such as toughness and crack growth exponents have been compiled from published literature and from private sources. The system has been designed to allow these parameters to be plotted as a function of glass composition or elastic modulus. A paper describing the system is being prepared for publication in the J. of Phys. and Chem. Ref. Data.

Flaw Propagation and Microstructural Effects
Subtask 3 of Task 15419

S.W. Freiman, B.R. Lawn, A.C. Gonzalez, E.R. Fuller, Jr., T.L. Baker, and R.F. Cook[1]

[1] Guest Worker, University of New South Wales

Because the crack propagation resistance of ceramics is relatively low, critical flaw sizes are reduced to a level at which they can become comparable to the size of microstructural features (typically 5-50 µm). This comparability of flaw and grain sizes can lead to additional driving forces on small-scale cracks, e.g. due to thermal expansion anisotropy. It can also lead to an increase in the intrinsic toughness, as a result of crack deflection processes, as fracture proceeds. An understanding of the mechanisms of crack-microstructure interactions, and the implications of these phenomena in relation to design with ceramics, are the objectives of our work in this area.

Indentation fracture measurements have been conducted on two groups of alumina specimens of the same nominal chemical composition but different grain size, 3µm and 20 µm. For large indentations the strength rises systematically with diminishing contact load, as predicted from continuum fracture mechanics theory. However, there is a distinctive leveling off of strength at smaller indentation loads, with the plateau level an inverse function of grain size. This behavior suggests that there are grain-localized forces which dominate the fracture process for flaws comparable in size to the grains. A modified indentation fracture model has been derived which accounts for the observed behavior. From a practical point of view, this behavior implies that the use of classic fracture mechanics tests will yield non-conservative estimates for the strength of a material containing natural flaws. Similar strength -indentation load behavior has been observed for $BaTiO_3$, PZT and a $Li_2O-Al_2O_3-SiO_2$ glass-ceramic.

We have also used indentation fracture procedures to develop a link between electrical failure in multilayer ceramic capacitors and the presence of cracks. Leakage currents were measured for multilayer capacitors with and without the presence of indentation-induced cracks. Both sets were submitted to a short soak in a NaCl solution, cleaned, and dried. Uncracked capacitors or those with small cracks showed no change in current, while those containing cracks large enough to cut through two electrode layers showed at least an order of magnitude increase in current. In addition, by monitoring the current in indented capacitors during loading in a test machine, it was shown that times to electrical failure could be predicted from the fracture mechanics parameters obtained on the ceramic.

From the above, somewhat idealized, ceramic materials, work on microstructural effects have been carried over to much more complex materials, concrete and mortar. Cracking mechanisms in concrete and mortar have been the subject of research interest for many years now. Relatively few studies have been attempted to elucidate microstructural details of fracture zones that develop around propagating cracks in these materials. This lack of information has hindered the development of more realistic fracture mechanics theories based on micromechanisms of cracking. Collaborative research (with researchers from the Center for Building Technology, the University of Virginia and the Inorganic Materials Division) explores the use of a fluorescent thin section technique for observing microstructural details of fracture zones around propagating cracks. Concrete mortar was used to illustrate the technique. Cracks were propagated in wedge-loaded double-cantilever beam specimens that were loaded both monotonically and cyclically; the specimens were then impregnated with an epoxy containing fluorescent dye and sectioned. Crack widths of two to three micrometers were easily discerned. Preliminary observations indicate tortuous crack paths with some branching, but very little microcracking not directly connected with a main crack branch.

High-Temperature Deformation and Fracture
Subtask 4 of Task 15419

S.M. Wiederhorn, E.R. Fuller, Jr., T.-J. Chuang, N.J. Tighe, R.F. Krause, Jr., B.J. Hockey, C.L. McDaniel, L. Chuck, G.A. Danko, K. Jakus[1]

[1]University of Massachusetts, Amherst, MA

The development of new ceramics provides hope for high efficiency, enhanced performance of structural systems in high temperature, stress-bearing environments. However, before ceramics can be used in industrial applications, issues concerning reliability and service life remain to be resolved. With this in mind, our program on high-temperature properties of ceramics entails five objectives: (i) the development of new theories that are capable of predicting time-dependent fracture and deformation behavior at specified loads and temperature; (ii) the development of new experimental techniques that can produce reliable creep data; (iii) the generation of a data base on commercially available ceramics and refractories; (iv) the investigation of kinetic processes that result in strength degradation and delayed failure; (v) the examination of microstructures that promote understanding of mechanisms loading to creep and creep rupture.

To meet these goals, our group has invented a special tensile loading technique which eliminates problems normally associated with simple tension tests. Quantitative measurements on time-dependent deformation behavior using this new technique have been carried out for several structural ceramics and refractories. A simple, unique data reducing scheme which revises conventional procedures has been developed, resulting in improved data quality. Existing theories on creep damage and delayed failure have been reviewed along the line of cavity growth by mass transport processes in the interface region. Several crack-like creep cavities, characteristic of diffusive growth, were discovered by STEM micrographs at grain boundary locations, confirming a theory developed earlier in our group. Reliability maps of up to three distinctive stages were produced as a means of displaying data on long-term time-dependent strength.

A major part of our program is directed toward elucidation of creep deformation processes. Time-dependent deformation is being studied on four-point bend specimens of silicon nitride doped with magnesia (commercial NC132) and with yttria (NCX34) for temperatures up to 1400 °C and stresses between 200 and 400 MPa. With the magnesia doped material, apparent steady states were observed within the first 200 hr of the test period. For NC132, the apparent steady-state creep rates can be described by a power law in stress with a stress exponent of 2.5 for all temperatures tested. Scanning transmission electron microscope micrographs showed that cavities appeared only in the tensile side, suggesting cavity growth plays an important role in creep deformation. A theory based on crack growth also predicts the same stress dependence on creep, in agreement with microstructural evidence. In the case of NCX34, the stress exponents were in the neighborhood of 4 for temperature up to 1250 °C, above which the slope changed to unity indicating there is a shift in deformation mechanism (possibly from crack growth to viscous flow at the grain boundary phases) as test temperature increases.

In view of the substantial amount of literature data generated from bending tests which indicate that tension differs from compression behavior, an analysis capable of accounting for tension as well as compression power-law creep solely from bend test data was developed. It was concluded that it is necessary to revise the data reduction scheme commonly used in the ceramic community and on occasion to implement a supplemental program, either in simple tension or compression, so as to avoid erroneous results.

A simple tension test device was invented by our group in recognition of a need to implement a uniaxial test program. The loading fixtures contain two thick smooth-notched plates sandwiched with a roller so that a push on a load train results in action in simple tension at the site where the specimen is located. This innovative design eliminates problems of gripping and alignment usually connected with simple tension tests. To demonstrate the usage, several creep curves in strain vs time were successfully produced for tension specimens.

A second major directive in our research program is creep fracture. It is now well established that the lifetime and strength of a ceramic component under service are strongly affected by how fast and where cavities nucleate along the grain boundary sites. Existing theories of creep rupture based on diffusive mechanisms have been reviewed in seeking to understand how applied stresses exert an influence on the rate of crack propagation. Classical models of cavities including Hull-Rimmer and Chuang-Rice treatments have been considered, with the former characteristic of rounded slopes and the latter of long, constant-thickness, crack-like shapes.

Microstructural analyses were performed on fractured beam specimens of yttria-doped silicon nitride and alumina. Several crack-like cavities at a size scale of nanometers were discovered along grain boundaries. These cavities possess a common feature, viz. they are long, thin and of uniform thickness, in conformity with the Chuang-Rice model. These findings strongly suggest that the cavity tip movements are driven by mass transport mechanisms.

Time-dependent strength degradation of structural ceramics is presented in terms of reliability maps for the purpose of evaluating material performance under service conditions. On a plot of stress versus time the maps contain up to three distinctive stages as a demonstration of causes for strength degradation. In general, with a duration of a few hours to several days, the strength increased under load, owing to the healing of surface cracks produced by machining damage and closure of internal pores and flaws left as sintering residues. As the creep test continues, the strength begins to fall, due to cavitation. Hence, the long-term strength degradation and the ultimate failure can be attributed to creep damage caused by cavitation. Reliability maps including the main features described above have been constructed for yttria doped silicon nitride, magnesia doped silicon nitride and α-silicon carbide.

Non Destructive Evaluation of Ceramics
Subtask 5 of Task 15419

K.A. Rhyne, G.S. White, E.R. Fuller, Jr., N.J. Tighe

Group emphasis in nondestructive evaluation (NDE) this past year has centered on the development and application to ceramics of two NDE techniques: (i) small angle neutron scattering (SANS) and (ii) thermal wave scattering. Both techniques are relatively new and, consequently, advances in theoretical understanding, standardization of experimental techniques and interpretations and evaluation of range of applicability are needed.

Work on small angle neutron scattering falls into three categories. First, advances in the incoherent multiple scattering theory are being made, with N.F. Berk of the Reactor Radiation Division. The theory has been applied to data obtained from well characterized alumina powders. The data were taken at several wavelengths on specimens of varying densities and thicknesses. Predictions of powder size from the new theory were in agreement with evaluations made from other methods. Finally, when the data were plotted as sample thickness/mean free path against neutron scattering radius of curvature, they fell on a single curve predicted by the theory.

The second application of SANS involved defining signal interpretations and expanding the range of applicability to silicon carbide specimens which had received different thermal treatments. All specimens contained graphite in fibrous forms. As received specimens exhibited microcracks to a small degree at the intersection of stacking faults at grain boundaries and within the fibrous graphite packets. Specimens which had been held at 1200 °C for 3500 hours exhibited fewer microcracks. SANS was able to detect this difference in microcrack density. Because SANS is incapable of distinguishing between scattering caused by cracks, voids, and inclusions, electron microscopy was used to complement the SANS analysis by identifying the scattering defects.

The third aspect of SANS work consisted of extending SANS applications to the study of green ceramics. Specimens of $YCrO_3$ were isobarically pressed at 35 MPa and 200 MPa; those pressed at 35 MPa exhibited more porosity. Pore size was monitored at different firing states, and SANS detected a change from 0.8 μm voids in the green state to 0.4 μm voids in the fired state. Spinel samples containing 0, 2, and 20% of fired spinel agglomerates were also prepared. Because they were also spinel, SANS could not directly distinguish between the agglomerates and the bulk specimen. Instead, effects of the agglomerates, such as pore and void sizes, were measured. For example, porosity, in all of the green spinel compacts was ~41%. However, the void size in the specimens with 20% agglomerates was 0.41 μm whereas, in the specimen with no agglomerates, it was 0.35 μm. It is also important to note that, on sintering the specimens, the amount of scattering decreased dramatically. These SANS results were correlated with strength measurements which showed that the specimens containing the 20% agglomerates had ~72% of the strength of those with no agglomerates.

The second major NDE thrust of the group involved developing a working thermal wave apparatus with which ceramic specimens could be investigated. Thermal waves are generated by periodic heating of a specimen, causing thermal pulses to diffuse through the materials in a manner exactly equivalent to highly damped travelling waves. The waves interact with changes in the thermal properties of the material in the same ways that ultrasonic or optical waves interact with changes in the elastic or optical properties. Because thermal waves are highly damped, however, their useful range is only of the order of the thermal skin depth, μ, where $\mu = (2K/\rho C\omega)^{1/2}$; K is the thermal conductivity, ρ is the density, C is the heat capacity and ω is (2π) x (modulation frequency). Therefore, the resolution and penetration depth are about the same and are proportional to $1/\sqrt{\omega}$.

The first stage of the program has been to construct a photoacoustic cell in which thermal waves can be measured. The experimental arrangement consists of a 10.6 μm light beam, emitted from a 3 watt CO_2 laser, which is modulated by a mechanical chopper before passing through a window in the photoacoustic cell and striking the specimen. The resulting thermal pulses in the specimen heat the air just above the site where the laser beam has struck the specimen and the periodic pressure variations are detected by a microphone.

An alumina specimen was indented by pressing a Vickers diamond indenter into the specimen surface at loads which create defect sizes, d, such that $d_1 < \mu$, $d_2 \approx \mu$, and $d_3 > \mu$. The sizes of the indentations and radial crack systems were measured using dye penetrant and an optical microscope. Although the photoacoustic effect (PAE) is not sensitive to closed vertical cracks, it should detect both the indentations and the lateral crack networks. Signals were obtained in a scan across the center of each indentation and all three defects were observed although d_1 was approaching the resolution limit of the apparatus.

Finally, the observation was made that most of the apparent noise determined by scanning an alumina specimen past the focussed laser beam was in fact a reproducible function of specimen position. Whether the system is detecting variations in grain orientation, thickness, or some other property is not known, but some types of thermal changes are being detected in an optically uniform specimen.

OUTPUTS/INTERACTIONS

INVITED TALKS

Theoretical Analysis of the Systems $CaCO_3$-$MgCO_3$ and Fe_2O_3-$FeTiO_3$
University of Maryland, College Park, MD
B. P. Burton
September 1983

Bacterial Corrosion
Conference on the Durability of Steel Pilings in Soil and Coastal Marine Environments
NBS, Washington, DC
W. P. Iverson
October 1983

Calculation of Phase Diagrams by the Cluster Variation Method
Geophysical Laboratory, Washington, DC
B. P. Burton
October 1983

CVM Analysis of the Systems $CaCO_3$-$MgCO_3$, Fe_2O_3-$FeTiO_3$, and $CaMgSi_2O_6$-$NaAlSi_2O_6$
U. S. Geological Survey, Reston, VA
B. P. Burton
October 1983

Elementary Fracture Processes in Brittle Materials
Case Western Reserve University, Cleveland, OH
E. R. Fuller, Jr.
October 1983

Interactions of Additives and Lubricating Base Oils
1983 SAE International Fuels and Lubricants Meeting and Exposition, San Francisco, CA
S. M. Hsu
October 1983

Molecular Properties of Tin- and Lead-bearing Macromolecules: Poly(triorganotin)methacrylates and Copolymer of 4-vinyl, Triphenyllead and Octadecyl Methacrylate
XI International Conference on Organometallic Chemistry, Atlanta, GA
E. J. Parks
October 1983

Small Angle Neutron Scattering Measurements on Green Compacts of $YCrO_3$
TMS-AIME, Philadelphia, PA
K. A. Hardman-Rhyne
October 1983

Solubilization of Sedimentary Metals by Aqueous Methyl Iodide
6th International Symposium on Environmental Biogeochemistry, Santa Fe, NM
G.J. Olson and F. E. Brinckman
October 1983

Studies of Ceramic Materials at NBS using Small Angle Neutron Scattering Techniques
Massachusetts Institute of Technology, Cambridge, MA
K. A. Hardman-Rhyne
October 1983

Studies of Ceramic Materials at NBS using Small Angle Neutron Scattering Techniques
Bell Telephone Labs, Murray Hill, NJ
K. A. Hardman-Rhyne
October 1983

Thermogravimetric Analysis of Lubricants
1983 SAE International Fuels and Lubricants Meeting & Exposition, San Francsico, CA
S. M. Hsu
October 1983

Ceramic Powder Characterization Laboratory--A Brief Overview and A New Dimension in Submicron Particle Size Analysis
NBS, Washington, DC
C. R. Robbins and K. Sinclair
November 1983

A Laboratory Oxidation Test for Consistency Monitoring
5th International Conference on Used Oil Recovery and Reuse, Las Vegas, NV
S. M. Hsu
November 1983

NBS Advanced Ceramic Processing Program
University of Missouri-Rolla, Rolla, MO
S. J. Schneider
November 1983

Proposed Consistency Tests for Re-refined Engine Oil Basestocks
5th International Conference on Used Oil Recovery and Reuse, Las Vegas NV
S. M. Hsu
November 1983

Structure-Activity Relationships for Organotin Compounds
4th Annual Meeting, Society of Environmental Toxicology and Chemistry, Arlington, VA
R. B. Laughlin, Jr. and F. E. Brinckman
November 1983

U. S. Army/NBS Engine Testing Program for Consistency Monitoring
5th International Conference on Used Oil Recovery and Reuse, Las Vegas, NV
S. M. Hsu
November 1983

Oxidation Mechanism of Lubricants
ASTM Symposium on Oxidation, Miami, FL
S. M. Hsu
December 1983

Microbiological Cleaning and Processing of Coal
Electric Power Research Institute, Palo Alto, CA
G. J. Olson
January 1984

Applications of the Theory of Brittle Fracture
Massachusetts Institute of Technology, Cambridge, MA
B. R. Lawn
March 1984

Atomistics of Crack Growth
Massachusetts Institute of Technology, Cambridge, MA
E. R. Fuller, Jr.
March 1984

Color Graphics on Dot Matrix Printers
Hewlett Packard, Rockville, MD
P. K. Schenck
March 1984

Densification of Si Quartz Using H.I.P.
Metallurgy Division Powder Processing Seminar, NBS, Gaithersburg, MD
J. E. Blendell
March 1984

Fracture of Brittle Materials
The American Physical Society Meeting, Detroit, MI
B. R. Lawn
March 1984

Lubricants
1984 SAE International Congress and Exposition, Detroit, MI
S. M. Hsu
March 1984

New Techniques and Opportunities in High Temperature Mass Spectrometry
Inorganic Materials Division, NBS, Gaithersburg, MD
J. W. Hastie
March 1984

A Review of Anaerobic Corrosion by Sulfate-reducing Bacteria Including Mechanism of Action
84th Annual Meeting American Society for Microbiology, St. Louis, MO
W. P. Iverson
March 1984

Synthesis and Characterization of Protonic β"-aluminas
University of Pennsylvania, Philadelphia, PA
K. G. Frase
March 1984

Applications of Indentation Fracture
IBM East Fishkill Facility, Hopewell Junction, NY
B. R. Lawn
April 1984

Computerized Data Base for Ceramic Phase Diagrams
Fourth International Symposium on High Temperature and Energy-Related Materials, Santa Fe, NM
J. W. Hastie and L. P. Cook
April 1984

Effect of Particle Size on Sintering and Densification Kinetics of Anorthite Powders
American Ceramic Society, Pittsburgh, PA
L. P. Cook
April 1984

Evaluation of Ceramic Materials for High Temperature Tribological Applications
Deere and Company Technical Center, Moline, IL
S. M. Hsu
April 1984

Mechanical Properties of Ceramics
Rensselaer Polytechnic Institute, Troy, NY
B. R. Lawn
April 1984

New Techniques and Opportunities in High Temperature Mass Spectrometry
Fourth International Symposium on High Temperature and Energy-Related Materials, Santa Fe, NM
J. W. Hastie
April 1984

A Predictive Phase Equilibrium Model for Multicomponent Oxide Mixtures
Fourth International Symposium on High Temperature and Energy-Related Materials, Santa Fe, NM
J. W. Hastie
April 1984

Submicron Creep Crack Growth in Structural Ceramics
Dept. of Mechanical Engineering, SUNY at Stony Brook
T.-J. Chuang
April 1984

Syntheses of Phases in the System BaO-TiO_2 from Amorphous Precipitated Powders
A. T. and T. Bell Telelphone Laboratories, Murray Hill, NJ
R. S. Roth
April 1984

The Use of Computer Graphics at the NBS Phase Diagrams for Ceramists Data Center and in the Evaluation of Data in Laser Experiments
The American University, Washington, DC
P. K. Schenck
April 1984

Atomic Absorption Spectroscopy for Trace Metal Analysis and Speciation
Association of Official Analytical Chemists, Philadelphia, PA
F. E. Brinckman
May 1984

Chemical and Biological Extraction for Chromatographic Speciation of Tributyltin for Assessment of Environmental Fate and Impact
VIII International Symposium on Column Liquid Chromatography, New York, NY
W. R. Blair
May 1984

Corrosion Failures--Chemistry of Crack Growth
Massachusetts Institute of Technology, Cambridge, MA
S. W. Freiman
May 1984

Direct Determination of Relative Ionization Cross Sections by Transpiration Mass Spectrometry
32nd Annual Conference on Mass Spectrometry and Allied Topics, San Antonio, TX
D. W. Bonnell
May 1984

Electrochemical Noise as an Indicator of Anaerobic Biological Corrosion
ASTM Committees: E-7 and G-1 Meetings, Montreal, Canada
W. P. Iverson
May 1984

High Temperature Electrial Properties of Boron Nitride
American Ceramic Annual Society, Pittsburgh, PA
H.P.R. Frederikse, A. H. Kahn, and A. L. Dragoo
May 1984

Implications of Molecular Speciation of Environmental Organometals and Organometalloids
The Johns Hopkins University, Baltimore, MD
F. E. Brinckman
May 1984

Molecular Nature of Tin in Cellular Media
University of Scranton, Scranton, PA
F. E. Brinckman
May 1984

NBS Standards Glass SRM's for Science and Industry
David L. Lawrence Convention Center, Pittsburgh, PA
M. J. Cellarosi and W. K. Haller
May 1984

Phase Relations and Vapor Pressures in the System $Li_2O-Al_2O_3$
American Ceramic Society Annual Meeting, Pittsburgh, PA
L. P. Cook
May 1984

The Role of Iron and Copper in the Oxidative Degradation of Lubricating Oils
American Society of Lubrication Engineers (ASLE), Chicago, IL
S. M. Hsu
May 1984

A Study on the Nature of Boundary Lubrication Films, Part 1: SEC-GFAA Method Development
ASLE 1984 Annual Meeting, Chicago, IL
S. M. Hsu
May 1984

A Study on the Nature of Boundary Lubrication Films, Part II: Static and Dynamic Wear Tests
ASLE 1984 Annual Meeting, Chicago, IL
S. M. Hsu
May 1984

Surface Roughness Effects and Temperature Modeling of Ceramic Wear Systems
Cummins Engine Co., Columbus, IN
S. M. Hsu
May 1984

Chemistry of Slow Crack Propagation in Glasses
American Ceramic Society and The Metallurgical Society, Williamsburg, VA
S. M. Wiederhorn
June 1984

Protonic β"-alumina: Transport and Structure
Ceramatec Inc., Salt Lake City, UT
K. G. Frase
June 1984

Structure-Property Relationships in Single Crystal β"-alumina
Massachusetts Institute of Technology, Cambridge, MA
K. G. Frase
June 1984

Time Resolved Laser Ablation Mass Spectrometry Studies
Rice University, Houston, TX
D. W. Bonnell
June 1984

Tribology: A Link Between Physics and Chemistry at Concentrated Contacts
Gordon Research Conference on Tribology, New London, NH
S. M. Hsu
June 1984

XRD Standard Reference Materials
X-ray Clinic, New York State University, Albany, NY
C. R. Hubbard
June 1984

Case Histories in Ceramic Processing
Martin Marietta Laboratories, Baltimore, MD
W. Coblenz
July 1984

Environmentally Enhanced Crack Growth in Ceramics
Oak Ridge National Laboratories
S. W. Freiman
July 1984

Laser Vaporization Mass Spectroscopy of Graphite and BN
Gordon Research Conference, Wolfeboro, NH
D. W. Bonnell, P. K. Schenck, and J. W. Hastie
July 1984

Mechanisms of Deformation and Fracture in Ceramics and Glasses
ASTM, 17th Annual Meeting of the International Metallographic Soc., Philadelphia, PA
B. R. Lawn
July 1984

Microstructure Analysis of Creep Cavitation and Crack Growth in Si_3N_4 and SiC
Microbeam Analysis Soc., Lehigh University, Bethlehem, PA
N. J. Tighe
July 1984

Optogalvanic Spectroscopy of High Temperature Species in Flames
Gordon Research Conference, Wolfeboro, NH
P. K. Schenck
July 1984

Transpiration Mass Spectrometric Analysis of the As_xO_y System
High Temperature Chemistry Gordon Research Conference, Wolfeboro, NH
J. W. Hastie
July 1984

A Critical Assessment of Lubricating Basestock Parameters for Quality and Consistency
1984 ACS Annual Meeting, Philadelphia, PA
R. G. Munro
August 1984

Epifluorescence Microscope Detector Coupled with Microbore HPLC for Speciation of Bioactive Organotins at Sub-Picomolar Levels
Symposium on Optical Detectors in Liquid Chromatography, 188th ACS National Meeting, Philadelphia, PA
F. E. Brinckman
August 1984

Neutron Scattering Techniques
NDE Gordon Research Conference, Meriden, NH
K. A. Rhyne
August 1984

The Piezo-optic Effect in Crystalline Materials
Seminar, Lawrence Livermore National Lab.
A. Feldman
August 1984

SANS in Ceramic Material Characterization
31st Sagamore Army Materials Research Conference, Lake Luzerne, NY
K. A. Rhyne
August 1984

Solid-Liquid-Vapor Interaction in Alkali Rich Coal Slag
Annual Meeting of Chemical Society, Philadelphia, PA
L. P. Cook and J. W. Hastie
August 1984

Thin-Film Oxidation Test: Relationship Between Composition and Additive Response for Re-refined Oils
1984 ACS Annual Meeting, Philadelphia, PA
S. M. Hsu
August 1984

Ultra Sensitive Optogalvanic Spectroscopy
The American Chemical Society, Philadelphia, PA
J. C. Travis, G. C. Turk, and P. K. Schenck
August 1984

Bacterial Corrosion
West Virginia Corrosion Control Coordinating Committee, Clarksburg, W. VA
W. P. Iverson
September 1984

Environmental Significance of Organometallic and Organometalloidal Compounds
Medical Chemistry Institut, Karl-Franzens University, Graz, Austria
F. E. Brinckman
September 1984

Fracture Behavior of Piezoelectric Ceramics
Pennsylvania State University, State College, PA
S. W. Freiman
September 1984

Implications of Molecular Speciation and Topology for Uptake and Toxicity of Organotins
International Tin Research Institute, London, England
G. J. Olson
September 1984

Microbial Solubilization and Transformations of Metals
University of Mainz, Mainz, West Germany
G. J. Olson
September 1984

Nondestructive Characterization of Distributed Defects in Ceramics
The Second Annual Workshop on Advanced Materials, Traverse City, MI
E. R. Fuller, Jr.
September 1984

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SRM 674 - X-ray Powder Diffraction Intensity Set
C. R. Hubbard, 1983

EXTERNAL RECOGNITION

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January 1984

SEMINARS ORGANIZED

The Division maintains an active Seminar Program in which lectures by distinguished visitors on scientific topics of interest to the Division are supplemented by presentations of current work by Division scientists. In FY 84, the Division sponsored three to four seminars per month, of which 94 percent were presented by scientists from outside NBS.

Scale Effects in Deformation and Fracture
I. Gruntfest
Environmental Protection Agency, Washington, DC
October 1983

Ceramic Powder Characterization Laboratory--A Brief Overview
C. R. Robbins
Nat. Bur. Stand., Gaithersburg, MD
A New Dimension in Submicron Particle Size Analysis
K. Sinclair
Coultier Electronics
November 1983

Transformation Toughening in Ceramics
A. H. Heuer
Case Western Reserve University, Cleveland, OH
November 1983

High Pressure Liquid Chromatography Coupled with Fourier Transform Infrared Spectrometry
L. T. Taylor
Virginia Polytechnic Institute and State University, Blacksburg, VA
November 1983

Optical Evaluation Techniques for Thin Films
J. M. Bennett
Naval Weapons Center, China Lake, CA
November 1983

Small Angle Neutron Scattering of Creep Cavity Nucleation and Growth in Sintered Alumina
R. Page
Southwest Research Institute, San Antonio, TX
December 1983

Sol-Gel Processing of Glassy Membranes and Shapes
L. C. Klein
Rutgers University, Piscataway, NJ
December 1983

Subcritical Fracture in Geological Materials
P. L. Swanson
University of Colorado, Boulder, CO
December 1983

On Rayleigh Waves and Rayleigh Wave Extension of Surface Micro-Cracks
J. F. Cardenas-Garcia
University of Maryland, College Park, MD
December 1983

Gas-Crystal Molecular Structure Differences
I. Hargittai
University of Connecticut, Storrs, CT
January 1984

Powder Dispersions for Tape Casting with Non-Aqueous Solvents
W. R. Cannon
Rutgers University, Piscataway, NJ
January 1984

Synthesis and Processing of Ideal Ceramic Powders
S. C. Danforth
Rutgers University, Piscataway, NJ
January 1984

A Study of the SiO Bonding in the Silica Polymorphs
G. V. Gibbs
Virginia Polytechnic Institute and State University, Blacksburg, VA
February 1984

Ceramic R & D at AMMRC
R. N. Katz
U.S. Army, Materials and Mechanics Research Center, Watertown, MA
February 1984

Grain Boundaries in Alumina and Spinel
C. B. Carter
Cornell University, Ithaca, NY
February 1984

Position Sensitive Detectors in X-Ray Powder Diffraction
R. L. Snyder
New York State College of Ceramics, Alfred University, NY
February 1984

The Response of Multiphase Materials to Different Forms of Wear:
Preliminary Findings
N. H. Macmillan
The Pennsylvania State University, University Park, PA
March 1984

Glass and Glass Ceramic Research at Sandia National Laboratories
R. J. Eagan
Sandia National Laboratories, Albuquerque, NM
March 1984

Fully Reversible Oxide/Water Interfaces and Aging Phenomena
G. Onoda, Jr.
IBM Thomas J. Watson Research Center, Yorktown Heights, NY
March 1984

New Techniques and Opportunities in High Temperature Mass Spectrometry
J. W. Hastie
National Bureau of Standards, Gaithersburg, MD
March 1984

Microstructure of Titanium Carbonitride-Based Cutting Tools
A. H. Heuer
Case Western Reserve University, Cleveland, OH
March 1984

Float Polishing and Some Applications
Y. Namba
Osaka University, JAPAN
April 1984

Geomycology and Bio-Corrosion: Aspects of Accumulation and Transformation of Metals and Minerals by Fungi
S. M. Siegel
Pacific Biomedical Research Center, University of Hawaii at Manoa
April 1984

Structure and Properties of Coatings
B. E. Jacobson
Linkoping University, Linkoping, Sweden
April 1984

Metastable Phases in Partially Stabilized Zirconia
D. G. Brandon
Technion, Haifa, Israel
April 1984

^{119}Sn NMR Study of Carboxylate Exchange in Tributyltin Carboxylates
W. F. Manders
National Bureau of Standards, Gaithersburg, MD
April 1984

Japanese Strategy for R&D in Ceramics
H. Yanagida
University of Tokyo, Tokyo, Japan
April 1984

Thermodynamic Activity Measurements and Modeling in Multicomponent Mixtures
M. Allibert
Institut, National Polytechnique, France
April 1984

Ceramics Research at the Technology University of Eindhoven
R. Metselaar
Technological University, Eindhoven, The Netherlands
May 1984

Diffusion Mechanisms in Transition Metal Oxides
N. L. Peterson
Argonne National Laboratory, Argonne, IL
June 1984

NMR Methods for Rapid Multicomponent Analysis of Bioactive Materials
P. J. Sadler
University of London, London, UK
July 1984

Potential of High Temperature Mass Spectromety for the Study of Condensed Phases and Gaseous Molecules
K. Hilpert
Institute of Applied Physical Chemistry, FRG
July 1984

Temperature and Surface Effects in Hardness
T. F. Page
University of Cambridge, Cambridge, England
July 1984

Laser Enhanced Ionization At Chalmers University
L. O. Axner
Chalmers University of Technology, Gothenburg, Sweden
August 1984

Fracture Measurements in Cement-Based Composites
Y-W. Mai
University of Sydney, Sydney, Australia
September 1984

Heavy Metal Fluoride Glass Fibers and Their Applications in Telecommunications
D. C. Tran
U.S. Naval Research Laboratory, Washington, DC
September 1984

TECHNICAL/PROFESSIONAL COMMITTEE ACTIVITIES

- American Ceramic Society
  - Basic Science Division
    - N. J. Tighe, Secretary
  - Committee on Government Liaison
    - M. J. Cellarosi, Member
  - Committee on Publications
    - Subcommittee on "Phase Diagrams for Ceramists"
    - R. S. Roth, Chairman
  - Committee on Reference Materials
    - W. K. Haller, Member
  - Glass Division
    - S. W. Freiman, Chairman
    - Committee on Glass Standards Classification and Nonmenclature
      - M. J. Cellarosi, Chairman
    - Editorial Committee
      - B. R. Lawn, Chairman
      - S. M. Wiederhorn, Subchairman
    - Membership Committee
      - G. S. White, Member
  - Phase Equilibria Data Center Advisory Committee
    - L. P. Cook, Chairman
    - J. W. Hastie, Member
  - Phase Equilibria Program Coordinating Committee
    - S. J. Schneider, Member
  - Standardization of Test Methods Committee
    - S. J. Schneider, Member
  - Working Group on Tribology
    - S. M. Hsu, Member

- American Chemical Society
  - Inorganic Materials Division--Nomenclature Committee
    - T. D. Coyle, Chairman
  - Nomenclature Committee
    - T. D. Coyle, Member

- American Crystallographic Association
  - Apparatus and Standards Committee
    - C. R. Hubbard, Member

- American National Standards Institute (ANSI)
  - Committee N43--Equipment for Ionizing Radiation
    - S. Block, Member
  - Committee 43.1--Safety Standards for X-ray Diffraction and Fluorescence Analysis Equipment
    - S. Block, Chairman
    - F. A. Mauer, Secretary

- American Petroleum Institute
  - Task Group on Cements for Geothermal Wells
    - E. R. Fuller, Jr., Member
    - R. F. Krause, Jr., Member

- American Physical Society Editorial Board
  - Review of Scientific Instruments
    - P. K. Schenck, Member

- American Society for Metals
  - Executive Committee--Washington Chapter
    - N. J. Tighe

- American Society for Testing and Materials
  - C8: Refractories
    - Awards Committee
      - S. J. Schneider, Chairman
    - Conditions of Tests
      - S. J. Schneider, Member
    - Specifications
      - S. J. Schneider, Member
  - C9: Concrete and Concrete Aggregates
    - C. R. Robbins, Member
  - C14: Glass and Glass Products
    - M. J. Cellarosi, Chairman
    - C14.01: Nomenclature of Glass and Glass Products
      - M. J. Cellarosi, Chairman
    - C14.03: Chemical Properties of Glass
      - W. K. Haller, Member
    - C14.04: Physical and Mechanical Properties of Glass
      - M. J. Cellarosi, Member
    - C14.08: Flat Glass
      - M. J. Cellarosi, Member
  - C18: Natural Building Stones
    - C. R. Robbins, Member
    - C18:034: Sandstone
      - C. R. Robbins, Member
    - C18.07: Environmental Properties, Behavior and Cleaning
      - C. R. Robbins, Member
  - D2: Petroleum Products and Lubricants
    - S. M. Hsu, Member
    - D2.0B: Automotive Lubricants
      - S. M. Hsu, Member
      - B-1: Passenger Car Oils
      - B-2: Diesel and Truck Oils
    - D2.0P: Recycled Petroleum Products
      - S. M. Hsu, Chairman
      - P-0: Advisory
      - P-1: Automotive Lubricants
      - P-2: Used Oils and Basestocks
      - P-3: Fuel Oils
      - P-4: Industrial and Hydraulic Oils
      - P-6: Miscellaneous Products
      - P-7: Editorial
    - D2.04: Hydrocarbon Analysis
      - P. T. Pei, Member
      - 4A: Preparation of Standard Hydrocarbon Blends
      - 4B: Methods by Chemical Means
      - 4C: Liquid Phase Chromatography

4D: Properties by Physical Means
4F: Absorption Spectroscopy Method
4G: Manual on Hydrocarbon Type Analysis
4K Correlative Methods
4.01: Gas Chromatography
4M: Mass Spectroscopy Methods
D2.06: Analysis of Lubricants
S. M. Hsu, Member
P. T. Pei, Member
D2.07: Flow Properties
S. M. Hsu, Member
D2.09: Oxidation
C. S. Ku, Member
S. M. Hsu, Member
9D: Lubricants and Hydraulic Fluids
9F: Used Oil Oxidation/Nitration
9G: Additive Response of Base Oils
S. M. Hsu, Chairman
C. S. Ku, Member
E19: Chromatography
E. J. Parks, Member
E20: Temperature
S. J. Schneider, Member
E24: Fracture
Subcommittee E24.07 on Fracture of Non-Metals
S. W. Freiman, Member
E. R. Fuller, Jr., Member
Task Group E24.07.01 Fracture Toughness Testing of Concretes and Rocks
E. R. Fuller, Jr., Member
Task Group E24.07.02 Double-Torsion Technique
E. R. Fuller, Jr., Member
E34: Occuptional Health and Safety Aspects of Materials,
Physical and Biological Agents
F. E. Brinckman, Member
E38: Resource Recovery
M. J. Cellarosi, Member
E44: Solar Energy Conversion
F1.02: Laser
A. Feldman, Subcommittee Editor
E47: Biological Effects and Environmental Fate
F. E. Brinckman. Member
G. J. Olson, Member
G01: Corrosion in Soils
W. P. Iverson, Member
TG: Electrochemical Polarization Techniques for Measurement of Corrosion Rates in Soils
W. P. Iverson, Member

American Society of Automotive Engineers
Fuels and Lubricant Committee
S. M. Hsu, Member

American Society of Lubrication Engineers
    Annual Meeting Program Committee
        S. M. Hsu
    Committee on Wear
        S. M. Hsu, Chairman
        R. S. Gates, Member
    Lubrication Fundamentals Committee
        S. M. Hsu, Member
        R. S. Gates, Member
        C. S. Ku, Member
    Technical Coordinator for Wear Committee
        S. M. Hsu
    Technical Coordinator for Metal-working Committee
        S. M. Hsu
    Technical Coordinator for Mining Committee
        S. M. Hsu
    Technical Coordinator for Seals Committee
        S. M. Hsu

American Society of Mechanical Engineers Under ASME
    Ceramics Committee
        N. J. Tighe, Member
    Gas Turbine Division
        N. J. Tighe, Member
    Research Committee on Tribology
        S. M. Hsu, Member

Gordon Research Conference on Tribology
    S. M. Hsu, Vice Chairman

High Temperature Materials Laboratory Advisory Committee
    Oak Ridge National Laboratory
        S. M. Wiederhorn

High Temperature Science Editorial Advisory Board
    J. W. Hastie, Member

IEEE
    International Symposium on Application of Ferroelectrics
        H. P. R. Frederikse, Local Chairman

InterAmerican Conferences on Materials Technology
    Executive Committee
        S. J. Schneider, Member

International Commission on Glass
- Subcommittee A.II: Durability and Analysis
  - W. K. Haller, Member
- Subcommittee VIII: Standard Reference Glasses
  - W. K. Haller, Vice President
- U.S. Representative
  - W. K. Haller

International Union of Crystallography
- Commission on Crystallography at Controlled Pressures and Temperatures
  - G. J. Piermarini, Member

International Union of Pure and Applied Chemistry
- Commission II-2: Nomenclature of Inorganic Materials
  - T. D. Coyle, Titular, Secretary
- Commission II-3: High Temperature and Solid State Chemistry
  - J. W. Hastie, Associate Member
- Interdivisional Committee on Nomenclature and Symbols
  - T. D. Coyle, Titular Member
- Conferences on Refractories for Energy Applications Planning and Program Committees
  - S. J. Schneider, Member

JCPDS-International Centre for Diffraction Data
- S. Block, Member
- C. R. Hubbard, Member and Vice-Chairman
  - Board of Directors
  - Technical Committee
  - Long-range Planning Committee
  - Data Collection and Analysis Subcommittee
  - Data Base Subcommittee
  - Search/Match Methods Subcommittee

Joint ASTM-ASLE Committee on Industrial Lubricants
- S. M. Hsu, Member
- Subsection 1: Falex Wear Test Development
- Subsection 2: Four-ball Wear Test Development
- Subsection 8: Friction Test Development

Joint Electron Devices Engineering Councils
- X-ray and Implosion TV Standards Committee
  - M. J. Cellarosi, Member

Journal of Physical and Chemical Reference Data
- Editorial Board
  - H. M. Ondik, Member

The Metals Properties Council, Inc.
- Subcommittee 9--Coal Conversion
  - S. J. Schneider, Member

National Association of Corrosion Engineers
    T3: Corrosion Science and Technology
    T3L: Electrochemical and Electrical Techniques for Corrosion Measurement and Control
        W. P. Iverson, Member

National Materials Advisory Board
    Committee on Application of Nonmetallic Materials to Guns and Gun Tubes
        S. W. Freiman, Member
    Committee on Mineral Resources Technology
        S. J. Schneider, Liaison Representative

National Materials Review Board (MRB) for Nuclear Waste Management (DoE)
    Data and Testing Procedures Committee
        H. P. R. Frederikse, Member

National Research Council
    Committee on High Temperature Science and Technology
        J. W. Hastie, Chairman
    Committee on Recommendations for U.S. Army Basic Scientific Research
        S. M. Wiederhorn, Member

Optical Society of America
    Committee on Standards
        A. Feldman, Member

Permanent International Committee for Research on Preservation of Materials in the Marine Environment
    National Bureau of Standards Delegates
        F. E. Brinckman, Member
        W. R. Blair, Member

Safety Glazing Council
    Board of Director
        M. J. Cellarosi, Member

INDUSTRIAL AND ACADEMIC INTERACTIONS

The research programs of the Inorganic Materials Division are designed and carried out in support of industrial and scientific needs. Interactions with industry, universities, and professional organizations are viewed as an important element of our work with collaborative programs, consulting and general involvement with outside groups being a long standing practice.

In 1984, the Division performed collaborative research with over 50 private organizations through its Industrial Research and Guest Worker programs and other joint arrangements. Representative examples of such interactions include:

INDUSTRIAL

1. American Ceramic Society
(Ceramics Industry)

    The High Temperature Processes Group interacts with the Ceramics Industry, through the Joint NBS/ACerS Phase Diagrams for Ceramists Program. The ceramics industry provides information to NBS on phase diagram needs and priorities through their participation in ACerS-NBS Committees and through direct interactions (visits) between industrial and NBS management and technical personnel. The industry is also funding a Ceramic Society program for Research Associateships to expand the NBS Data Center on ceramic phase diagrams. The Ceramic Society publishes and disseminates the Data Center outputs which have included five hard cover volumes containing 6500 evaluated phase diagrams, and which in the future will also include on-line computer services to industry.

2. Joint Committee for X-ray Powder Diffraction Standards
(JCPDS)--International Centre for Diffraction Data

    For nearly 30 years this cooperative program with industry (JCPDS) has served as the focal point for the provision of high quality reference powder patterns for inclusion in the JCPDS's Powder Diffraction File. Under an expanded relationship with JCPDS, the program at NBS now includes critical evaluation of published data, development of a numerical data base, and research on producing accurate data and on the use of these data in phase identification.

    The JCPDS publishes the well known Powder Diffraction File, the oldest numerical data compilation for analytical purposes in the world (over 20 different publications covering powder and single crystal diffraction data are offered). C. Hubbard (Ceramic Processing Group) provides overall technical guidance to ten research associates sponsored by JCPDS in the provision of reference patterns, coordinates the activity with other data centers and develops standard reference materials for calibration of x-ray diffraction equipment. The JCPDS disseminates the data through numerous mechanisms.

3. Westinghouse Research Laboratory

In collaborative work, C. Robbins (Ceramic Processing Group) and Dr. B. Yoldas (Westinghouse) are defining important physical and chemical properties of sol gel derived ceramic powders (e.g., alumina and zirconia sythesized by hyrolysis of alkoxide solutions). Westinghouse develops various preparative procedures and furnishes powders for characterization (phase analysis, size, size distribution, surface area, etc.,) at NBS.

4. A. T. and T. Bell Laboratories

Research on the crystallographic characterization of ionic ceramic conductors is being carried out in a collaborative program between R. J. Cava and D. W. Murphy of Bell Laboratories and R. S. Roth (Ceramic Processing Group) and A. Santoro (Reactor Division) of NBS. Lithium inserted oxides are prepared at Bell Labs and characterized at NBS using the neutron diffraction total profile (Rietveld) analysis. The neutron diffraction data and analysis techniques uniquely locates the position of the Lithium ion in the structure. Current emphasis of the joint work is on alkali niobium-tungsten-vanandium oxide phases having the pyrochlore type structure.

5. A. T. and T. Bell Laboratories

The High Temperature Processes Group (E. Plante) provides basic solution/vaporization thermodynamics experimental data on fiber optic glass materials for process models developed by Bell Laboratories. Bell Laboratories (R. Laudise) provide samples and results from pilot plant experience and their process models.

6. DuPont Savannah River Laboratory

DuPont (Dr. John Plodinec) prepares samples and provides applied data from pilot plant experience, and NBS provides high precision basic data on vaporization rates of simulated nuclear waste glass materials needed for optimizing plant conditions for minimization of vaporization losses. DuPont is currently incorporating recent NBS results into an engineering model of the off-gas behavior in their nuclear waste glass process.

7. Hewlett Packard

The High Temperature Processes Group (P. Schenck and D. Bonnell) provides HP with software developments in computer graphics and modeling programs for multicomponent equilibria. The HP (Dr. Martin Wang) Ceramics Theory and Research Group (Palo Alto, CA) is sharing its complementary modeling programs with NBS for use on HP computer systems.

8. AFG Industries

Research on spontaneous fracture of tempered safety glass as caused by microscopic inclusions is being carried out in collaboration between W. C. Cooke (AFG) and W. Haller (Glass Group). NBS investigates production samples and conducts on-site investigation of installed glazing. The goal of the studies is prevention and/or early detection of fracture initiating inclusions.

9. Martin Marietta Aerospace

W. Haller (NBS Glass Group) and B. C. Clark (Martin Marietta) have been collaborating on the simulation of meteor dust. Such simulated meteor dust particles are used in testing the efficiency of high velocity collectors under development for the planned encounter between Halley's comet and a research satellite.

10. Cummins Engine Company

Cooperative research between the Tribology Group and Mr. Gordon Starr (Cummins) involves ceramic tribology related to heat engine development. Research centers on the mechanism of failure, surface topography effects, and microstructural influence on wear of ceramic coatings and parts.

11. General Motors

Cooperative research between Dr. S. Hsu (Tribology Group) and Dr. N. Hakim (GM) is being carried out on the lubrication mechanism of ceramic parts in engine contacts.

12. Martin Marietta

A joint experimental and theoretical research project between Dr. S. Hsu (Tribology Group) and Dr. F. Lockwood (Marietta) investigates the heat of absorption model on friction and wear under lubricated sliding conditions. A predictive model on wear, based on the adsorption theory, is being developed.

13. ASTM
(Oil/Lubricant Industry)

Collaborative interaction is being carried out between Dr. C. Ku (Tribology Group) and 12 major oil companies on a NBS developed thin film oxygen uptake test, which simulates an expensive engine test. Round robin testing is being conducted between NBS and Exxon, Chevron, Shell, Mobil, Ciba Geigy, Amoco, Gulf, Arco, Caltex, Gulf Canada, Lubrizol, and National Research Council of Canada.

14. Office of Naval Research (ONR)

In cooperation with ONR, an aqueous tributytin research material for use in an international comparison of organotin measurement methods has been prepared chromatographically by the Chemical and Biodegradation Processes Group and distributed to 45 laborabories world-wide. Recipients include industrial, academic, and government research laboratories. Analytical results for total tin and/or tin species determined in the research material are returned to NBS for statistical analysis and evaluation of the analytical methods employed. With increasing industrial usage of organotins over the past 20-30 years, concern for the environmental fate and effect of these compounds has also increased, resulting in development of numerous methods for organotin determination and speciation. Our methods comparison is important as the first attempt to evaluate the various analytical methods being employed on an international level. The results of this methods study will help establish a basis for production of an organotin SRM and for recommending specific organotin measurement methods with the accuracy required for international comparisons of organotin measurement data.

15. Electric Power Research Institute

EPRI's Advanced Power Systems division and the Chemical and Biodegradation Processes Group are collaborating in a critical literature review and basic research on microbiological processing for upgrading domestic coal reserves. G. J. Olson and F. E. Brinckman are directing the project which has as its goals the determination of chemical and biological factors affecting quality and quantity of product fuel, monitoring measurements needs, and the potential usefulness of microorganisms which degrade materials containing molecular structural components similar to coal (i.e., lignin). Members of the Chemical Stability and Tribology Group are also collaborating on product fuels characterization. Our data will help guide EPRI and the electric power industry in basic future decisions on pursuing biotechnological raw materials processing.

16. Gas Transmission Industry

Through leadership of DOT, Public Service Commission of West Virginia (Gas Pipeline Safety Section of the Engineering Division) and various gas pipeline companies, a basic bio-corrosion monitoring project has evolved. A serious rupture of a pipeline in West Virginia occurred on August 8, 1982, followed by an explosion and fire resulting in 9 injuries. This failure was definitely identified as being due to bacterial corrosion. As a result of this accident, the gas pipeline safety section of the Public Service Commission of West Virginia became concerned and contacted the Chemical and Biodegradation Processes Group at NBS for assistance in locating areas of biological corrosion which could result in similar disasters in the future. A number of gas pipeline transmission companies also indicated their interest and assistance in this area. These companies included: Columbia Gas Transmission Company, Consolidated Gas Supply Corporation, Tennessee Gas Transmission Company and the Cabot Corporation. The Office of Operations and Enforcement, Department of Transportation (DOT) also expressed serious concern and a Guest Worker from DOT was provided to NBS during FY83-84 to assist Dr. Warren P. Iverson, Chemical and Biodegradation Processes Group, in the project. Preliminary efforts to detect areas of biological corrosion on pipelines in the field, using electrochemical noise measurements, appear promising and continuation of the project in FY85 has been proposed by DOT.

17. General Electric Corporation

A collaboration is underway between the Chemical and Biodegradation Processes Group and Dr. M. F. Garbauskas at General Electric Corporation, Schenectady, NY, to carry out complete structural analysis of organotin compounds (by x-ray crystallography). Data will be used in developing an empirical relationship between organotin topology and the magnitude of ^{119}Sn-^{117}Sn spin coupling through oxygen in distannoxanes.

INDUSTRIAL/UNIVERSITIES

1. A. T. and T. Bell Laboratories, Trans Tech Division of Alpha Industries, University of Pennsylvania and Arizona State University

A joint program on dielectric ceramics having important microwave applications is being carried out by R. S. Roth, J. J. Ritter, W. Coblenz, and J. Blendell (Ceramic Processing Group) in association with R. J. Cava, H. O'Bryan (Bell Labs), T. Negas (Alpha Industries), P. Davies (U. of Pennsylvania) and A. Olsen (Arizona State U.). Powders of barium poly-titanates (pure and doped) are synthesized from alkoxide precursors, conditioned, compacted and densified at NBS with phase equilibria and crystal chemistry determined at each processing step. Characterization of microwave properties (dielectric constant, Q, TCK, etc.,) is performed on NBS prepared powders and compacts by the Industrial organizations. The University groups investigate the materials using high resolution electron microscopy lattice imaging techniques, correlating observed and calculated lattice image defects with the dielectric and thermodynamic properties.

2. Martin Marietta Laboratories and Johns Hopkins University

A cooperative program on Advanced Ceramics was recently established between the Inorganic Materials Division, Martin Marietta Laboratories, and Johns Hopkins University to investigate the critical features of ceramic processing which introduce property limiting defects and degrade reliability. The program will focus on structural ceramics, particularly non-oxide (e.g., SiC) monolithic and composite structures. NBS will concentrate on microstructural development, phase equilibria and mechanical properties; Martin Marietta Labs on the application of surface science techniques to the properties of powders and interfaces, and Johns Hopkins on NDE characterization (e.g., acoustic) and process (parametric) modeling. The initial effort involves correlation of NDE (acoustic) data with SANS and powder characterization data obtained at NBS. The overall program when fully underway will entail the exchange of samples and data as well as joint analysis and scientific publications.

3. General Electric and Rice University

NBS participates in a joint program with NASA for materials processing in space. Dr. D. W. Bonnell (High Temperature Processes Group) plans, supervises, and participates in experiments jointly with personnel from GE and Rice University at the King of Prussia laboratory (PA). These experiments involve use of a state-of-the-art facility designed by Dr. Bonnell for levitation melting of tungsten and other refractory metals coupled with drop calorimetry, needed for the determination of basic thermodynamic information.

4. University of Tennessee Space Research Institute (UTSI)

UTSI functions are primarily of an industrial R & D nature. Their interaction with NBS has been long standing and revolves around their development of coal fired MHD systems and their need for NBS basic data and models and the MHD slag behavior. UTSI provides NBS (Dr. E. Plante) with slag samples from their pilot plant tests, and the NBS carries out basic vaporization and phase equilibria measurements on these samples. The results are used by UTSI and also by NBS (Dr. D. Bonnell) to develop predictive models of slag thermochemistry under actual MHD use conditions. NBS recently completed development of a highly successful model, which is now in use by Dr. Lloyd Crawford of UTSI. This model can predict the vaporization, seed retention, and phase equilibria behavior of complex MHD slags containing oxides of Na, K, Ca, Mg, Al, Si, and Fe.

UNIVERSITIES

1. Massachusetts Institute of Technology (MIT)

Joint work with R. Coble (MIT), J. Blendell and K. Rhyne (Ceramic Processing Group) and C. Handwerker (Metallurgy Division) involves the characterization of flaws (pores) in alumina ceramics, by SANS and conventional microstructural techniques. Samples having different porosities are prepared at MIT and analyzed at NBS with the goal of correlating pore size distributions with SANS data; an important result will be the effect on pore size distribution caused by polishing and etching.

2. University of Maryland

The University of Maryland (J. Iriarte) and J. Ritter (Ceramic Processing Group) have been collaborating on problems related to the synthesis of barium titanates precursors from mixed alkoxides. The work is important to the industrial development of ceramics having tailored properties for microwave applications. Specifically, the joint investigation is designed to isolate and characterize the intermediate reaction products which occur during synthesis. The information gained from these studies will improve the understanding of the chemistry and structure that persist when alkoxides are mixed and how these factors influence the development of the precursors upon hyrolysis.

3. Ohio State University

Joint work with C. Semler (Ohio State University) and S. Schneider (Ceramic Processing Group) is under way to investigative alternates to zirconia based materials for transformation toughened ceramics, needed for heat engine applications. The research focuses on the processing of silicate-based materials (e.g., calcium silicate) which have martensitic transformation and includes complete phase equilibria determination as well as powder/compact characterization.

4. Alfred University

R. Snyder (Alfred U.) and C. Hubbard (Ceramic Processing Group) are collaborating on the development of computer techniques for automated quantitative phase analysis by the x-ray diffraction method.

5. Pennsylvania State University

The Phase Diagrams for Ceramists Data Center has an ongoing contractual/collaborative interaction with Dr. K. Spear of the Materials Science Department. He is developing the mathematical basis and computer software for including NBS developed solution models into phase diagram optimization/prediction codes. At the present time, existing computer codes for phase diagram modeling, developed for relatively simple alloy and molten salt systems, are not applicable to the more complex ceramic systems, e.g., oxides. This technical advance is necessary to the successful implementation of the NBS/ACerS five year development program for a computerized ceramic phase diagram data base.

6. Rice University

The High Temperature Processes Group (D. W. Bonnell) interacts with Dr. J. L. Margrave of the Chemistry Department at Rice University for the purpose of developing (and applying) state-of-the-art levitation calorimetric techniques. These techniques are needed for the determination of basic thermodynamic quantities of refractory materials (e.g., W, Ta, carbides) in their solid and liquid states. The collaborative effort is sponsored by the NASA Materials Processing in Space Program, and General Electric is a third member of this Government-University-Industry team.

7. University of California, Lawrence Livermore National Laboratory

Joint work with M. Weber (LLNL) and D. Blackburn and W. Haller (glass Group) involves the luminescent behavior of various elements in glass matrices. Matrix composition and processing conditions affect such parameters as emission wavelength, band width, life time and quantum yield which are of importance to glass lasers and optical frequency convertors. Oxide and non-iron-oxide glasses with emitting elements are developed at NBS and characterized for glass forming and element loading capability. LLNL measures optical parameters, and the results are correlated to glass composition. The goal of this work is to improve the understanding of luminescence and may lead to novel types of lasers.

In another joint work between NBS and LLNL, W. Haller (Glass Group) collaborated with T. Bernat, D. Miller and other members of LLNL in the development of high pore volume aerogels. Aerogels of this type are used to study equation of state behavior under extreme conditions.

8. Pennsylvania State University

Several joint research projects involving Prof. E. E. Klaus, Prof. L. Duda, and Prof. N. Macmillan and their graduate students (Mr. Douglas Deckman, Mr. Jeffrey Yellets, Miss Tracy Gary, and Mr. Richard Gates) of Penn State and Dr. S. Hsu (Tribology Group) include:

a. Vapor phase deposition of lubricants

The project is between Dr. S. Hsu (Tribology Group) and Prof. Duda, Prof. Klaus, and Mr. Douglas Deckman. Various organic molecules are being studied for ceramic lubrication at 800 °F.

b. Microstructural effects on ceramic wear

Collaborative project between Dr. S. Hsu (Tribology Group) and Prof. N. Macmillan on microstructural effects on wear of ceramics. Alumina oxide and partially stabilized zirconia are characterized before and after the laboratory wear test and engine test.

c. Ceramic wear tester design

Joint effort between Dr. S. Hsu (NBS) and Prof. Klaus, Prof. Duda, and Mr. Jeffrey Yellets (Penn State) on a state-of-the-art high temperature friction and wear Tribometer design.

d. Ceramic wear modeling

Joint research project between Dr. S. Hsu, Dr. R. Munro (Tribology Group) and Prof. Duda, Prof. Macmillan, Miss T. Gary, and Mr. R. Gates (Penn State) on the theoretical understanding of ceramic wear processes.

9. Northwestern University

Joint research involves lubrication modeling between Dr. S. Hsu (Tribology Group) and Prof. Herbert Cheng. The research focuses on the microelastohydrodynamic theories under wearing conditions. This is the first attempt at combining surface chemistry with surface mechanics to create a predictive wear model.

10. University of Minnesota

Cooperative research is underway between Dr. S. Hsu (Tribology Group) and Prof. Ramalingam on ceramic coating and coating evaluation for advanced technological concepts.

11. Virginia Polytechnic Institute and State University

Cooperative research between Dr. P. Pei, Dr. K. Jewett (Tribology Group) and Prof. Larry Taylor (VPI) investigates surface reaction product analysis under wearing conditions.

12. University of Cincinnati

Scientific collaboration with Prof. John S. Thayer on molecular mechanisms of metal solubilization and transformation by biogenic metabolites is being pursued. G. J. Olson and F. E. Brinckman of the Chemical and Biodegradation Processes Group are co-authoring patent with Thayer on using biogenic methyl iodide as a novel metal ore extraction process.

13. University of Maryland

Several members of the Chemical and Biodegradation Processes Group are collaborating with Professors Jay Means and Michael Bellama on biological and chemical transformations of organometallic materials in environmental situations.

14. University of New Hampshire

The Chemical and Biodegradation Processes Group is collaborating with Prof. Richard H. Blakemore on characterization of metal particle formation rates and sites in magnetite-depositing bacteria, using SANS characterization. G. J. Olson, F. E. Brinckman, and K. Rhyne are participating in the research.

15. Rensselaer Polytechnic Institute

G. J. Olson and F. E. Brinckman of the Chemical and Biodegradation Processes Group are collaborating with Professor Henry L. Ehrlich on mechanisms of silver ore solubilization and resistance in metal ore processing bacteria.

16. Washington University

Chemical and Biodegradation Processes Group members, G. J. Olson and F. E. Brinckman, are collaborating with Prof. Simon Silver on the molecular biology of metal resistance and transformations in commercially applied metal ore processing bacteria.

APPENDIX

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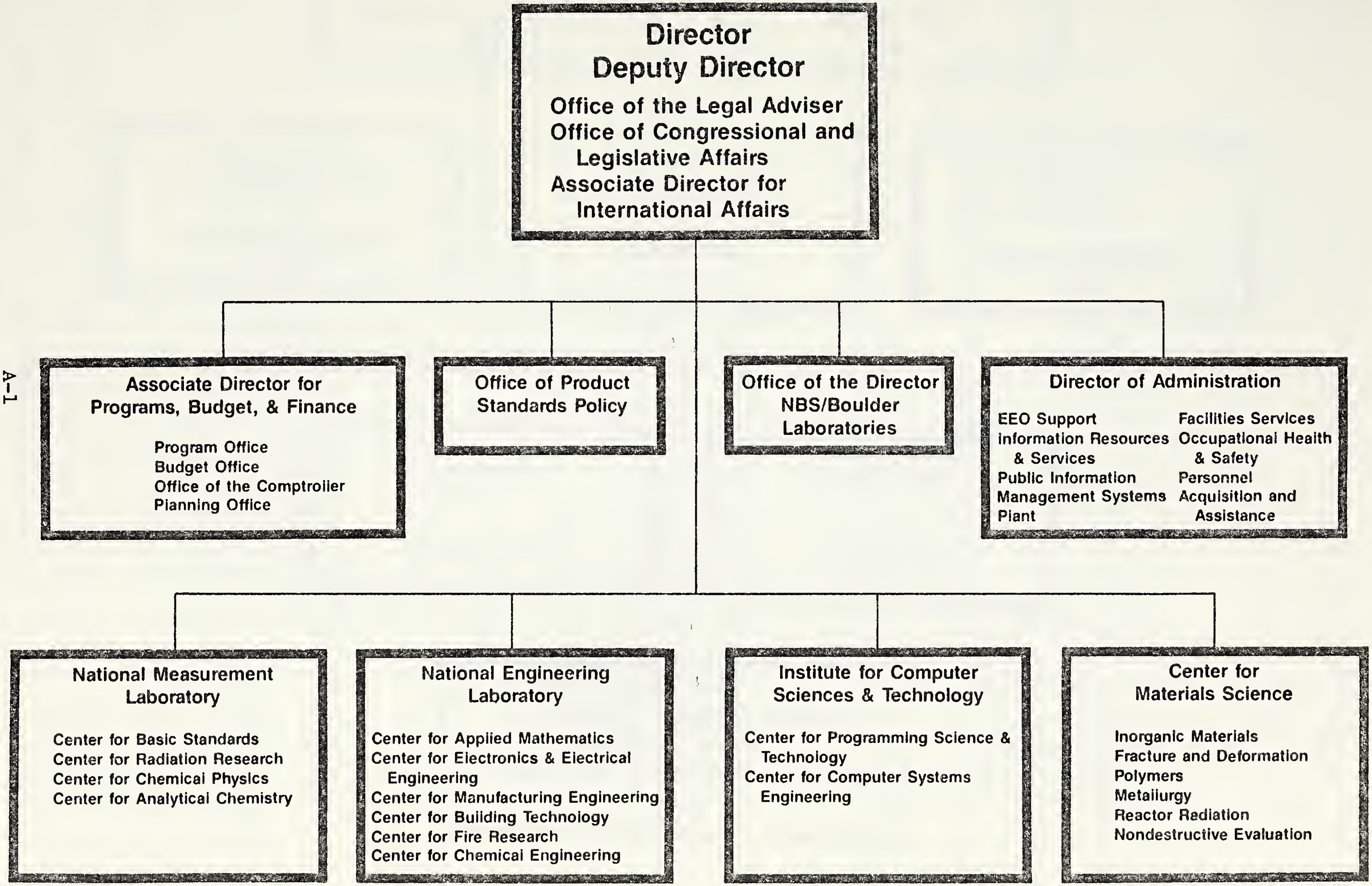

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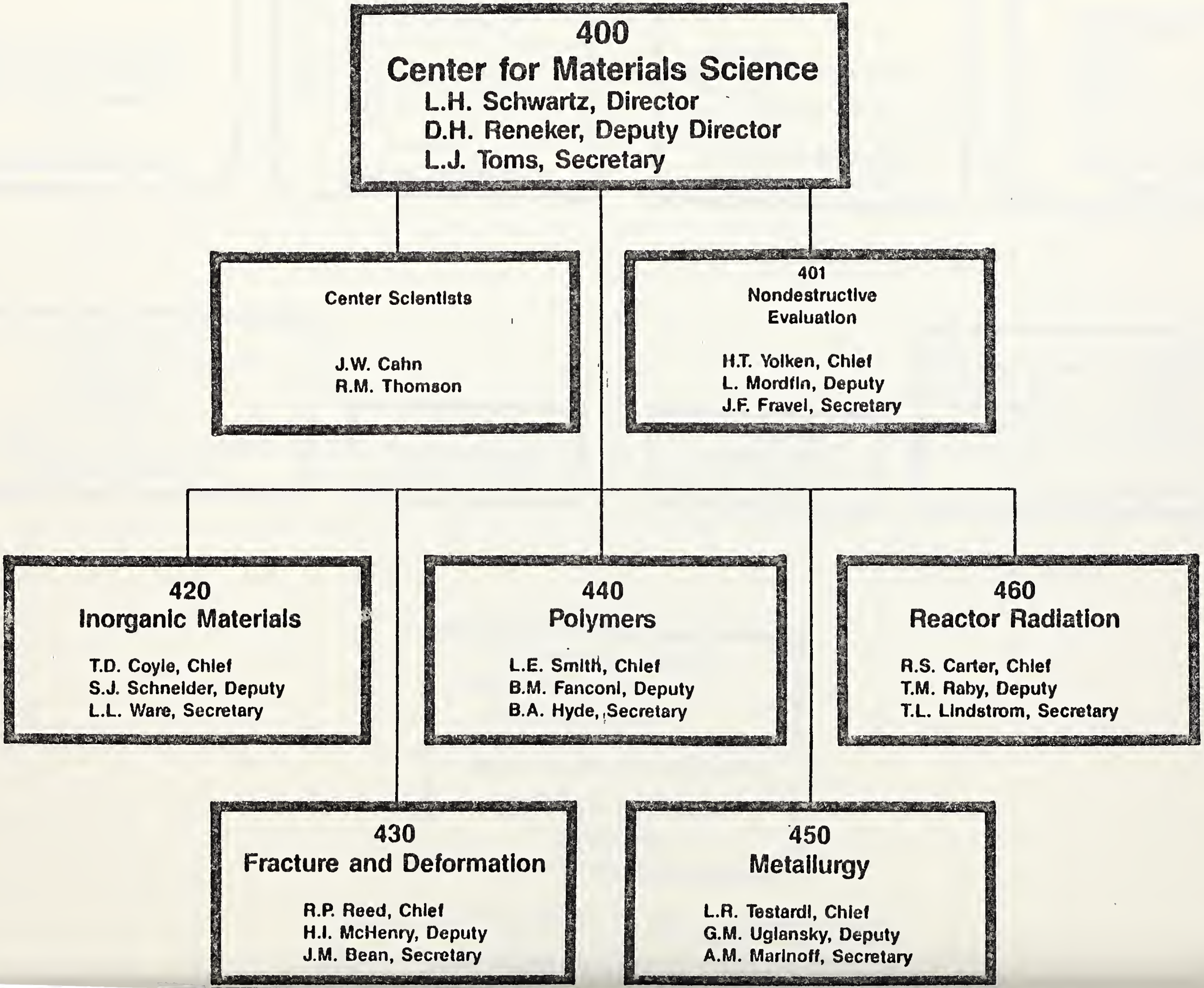

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10. SUPPLEMENTARY NOTES

☐ Document describes a computer program; SF-185, FIPS Software Summary, is attached.

11. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here)*

This report is a summary of the 1984 research activities of the Inorganic Materials Division, Center for Materials Science, National Bureau of Standards. It includes descriptive information on the work (in progress) carried out through the five technical tasks of the Division:

High Temperature Materials Chemistry for Processing and Durability

Ceramic Processing and Characterization

Glass and Optical Materials

Materials Processing and Durability Chemistry

Mechanical Properties of Ceramics

It also provides auxiliary information important to Division research such as recent publications and invited talks, professional/standard committee activities, and industrial/academic interactions.

12. KEY WORDS *(Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)*

biodegradation; ceramic processing; ceramics; glass; inorganic materials; mechanical properties

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