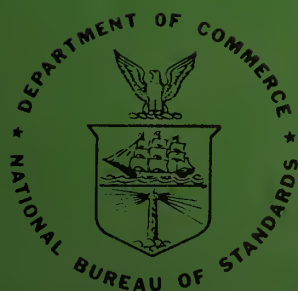




# TECHNICAL NOTE

447

## Research on High Temperature Materials at the National Bureau of Standards



U.S. DEPARTMENT OF COMMERCE  
National Bureau of Standards

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UNITED STATES DEPARTMENT OF COMMERCE  
C. R. Smith, Secretary  
NATIONAL BUREAU OF STANDARDS • A. V. Astin, Director



# TECHNICAL NOTE 447

ISSUED JULY 1968

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Edited by Elio Passaglia

Metallurgy Division  
Institute for Materials Research  
National Bureau of Standards  
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# RESEARCH ON HIGH TEMPERATURE MATERIALS

AT THE NATIONAL BUREAU OF STANDARDS

Supported by the

Advanced Research Projects Agency

of the Department of Defense

Edited by

Elio Passaglia

The National Bureau of Standards, with support from the Advanced Research Projects Agency of the Department of Defense, has begun a program on High Temperature Materials. This program includes projects on properties of high temperature materials, projects on their preparation, and others designed to explain basic phenomena limiting the use of materials at high temperatures. A summary of the progress in this program is given here.

Key words: High temperature materials, materials properties

## 1. INTRODUCTION

The National Bureau of Standards maintains a broad and active program in materials research. As part of this effort, and with support from the Advanced Research Projects Agency of the Department of Defense, the National Bureau of Standards has recently undertaken a program of research on High Temperature Materials. This report describes briefly the status of the projects being carried out under this effort. Many of these projects are relatively new and work on them has just begun. These reports should be considered as progress reports and not as finished studies. A list of the participating workers is given at the end of the report.

## 2. PROJECT SUMMARIES

### 2.1 Diffusion in Refractory Materials

J. B. Wachtman, Jr., A. L. Dragoo

Inorganic Materials Division

Institute for Materials Research

Compilations of diffusion data (frequency factors and activation energies) for the borides, carbides, and oxides of Be, Hf, Mo, Nb, Ta, Th, Ti, and Zr have been completed. These have been approved for publication by the National Bureau of Standards along with a short introduction which defines the various diffusion coefficients and discusses the reliability of the diffusion data. The compilations also provide information on the purity of the samples which have been used for diffusion studies, the preparation and properties of the samples, the methods by which the diffusion coefficients were measured, the type of diffusion coefficients measured, and the temperature ranges over which the diffusion data is valid. Many of the entries are accompanied by comments. Work on uranium compounds is in progress.

Most of the diffusion data thought to be adequate for estimates of the performance of materials in technological applications but not for calculations involved in advancing the fundamental knowledge of materials. The major sources of unreliability lie in the materials and experimental methods used. The list of difficulties include high impurity concentrations, microcleavages, grain boundaries, dislocations, pores, grain orientation, dependence of the diffusion coefficient on concentration and non-linearity in the measuring technique.

In our experimental program, analyses of oxide powders from grinding off thin sections of the rutile diffusion specimens will be carried out by converting the oxide to  $\text{CO}_2$  by means of the  $\text{AgCN}$  reduction procedure developed by Shkhashiri and Gordon<sup>1</sup>. Then the  $\text{CO}_2$  will be analyzed by an isotope ratio mass spectrometer to determine the  $^{18}\text{O}$  enrichment. Preliminary runs on simulated samples indicated that a substitute for the kerosene used in the grinding process was necessary. The kerosene yielded hydrocarbons which interfered with the mass spectrometric analysis. Perfluoroalkanes are now being tried because they will not yield decomposition products in the  $\text{CO}_2$ -mass range of the spectrometer.

The efficiency of the conversion of the oxide to  $\text{CO}_2$  is reduced by the competing reaction whereby  $\text{AgCN}$  breaks down to free  $\text{Ag}$  and cyanogen. Since the conversion reaction is most likely a solid state reaction, procedures have been developed to improve the mixing and contact between the  $\text{AgCN}$  and the oxide powder.

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1. B. Z. Shkhashiri and G. Gordon, *Talanta* 13, 142 (1966)

Vacuum lines have been set up in our laboratory for the preparation of the CO<sub>2</sub> samples. Since the isotope ratio mass spectrometer has been transferred from the University of Maryland to the University of Iowa, arrangements have been made to carry out rough analyses on a less sensitive mass spectrometer at the National Bureau of Standards and to send the samples to the University of Iowa for the more precise measurements.

In addition to the solutions to the diffusion equation for a finite slab reported previously, an exact solution has been obtained for the case of diffusion into a semi-infinite slab which is exchanging at a finite rate with a finite amount of a homogeneous gas.

## 2.2 Deformation and Fracture of Ionic Crystals

S. M. Wiederhorn, L. H. Bolz

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Institute for Materials Research

The fracture surface energies of six different commercial glasses were measured in dry nitrogen, 25°C, liquid nitrogen, -196°C, and a toluene-solid carbon dioxide mixture, -79°C, using the double-cantilever cleavage technique. Surface energy values obtained in nitrogen gas ranged from approximately 3,500 ergs/cm<sup>2</sup> for a high lead glass to 4,700 ergs/cm<sup>2</sup> for a high alumina glass. Values obtained in liquid nitrogen ranged from approximately 4,100 ergs/cm<sup>2</sup> for the lead glass to 5,300 ergs/cm<sup>2</sup> for the alumina glass. These energy values are consistent with fiber-glass strengths of  $2 \times 10^6$  psi that have been reported in the literature. The data were analyzed for the possibility of plastic deformation at the crack tips and the conclusion was reached that plastic deformation in these glasses is very unlikely at room temperature and below. The surface energy values generally increased with increasing Young's modulus and decreasing temperature; however, exceptions to this behavior were noted. The data are now being analyzed and will be written for publication in the Journal of the American Ceramic Society.

Experiments have been initiated to determine the effect of environment on crack propagation in glass. The study consists of two parts; (1) determination of the effect of water vapor on crack propagation in the six commercial glasses mentioned above, and (2) determination of the effect of various aqueous environments on crack propagation in soda-lime glass.



## 2.3 Optical Constants of Titanium

In the Visible Region of the Spectrum

Allan J. Melmed, J. J. Carroll

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Institute for Materials Research

A single crystal of 99.9% pure Ti has been obtained and prepared for determination of crystallographic orientation by back-reflection X-ray analysis. We plan to cut specimens approximately 0.020 in. thick with approximately 1/4 in. diameter circular flat surfaces for low-energy-electron diffraction characterization and optical constants measurement. These specimens will be cut in several orientations and attempts will be made to achieve atomically clean surfaces by direct heating in ultra-high vacuum. If this approach does not succeed we can resort to cleaning by argon-ion bombardment followed by ultra-high vacuum annealing, a method which has been described in the technical literature and claimed to be successful for Ti. We have some reservations about using the latter cleaning method, however, because it may introduce surface roughness which in turn may affect the optical constants measurements.

An alternative route to obtaining clean Ti surfaces will also be pursued, involving the production of Ti films by vapor deposition onto clean W surfaces in ultra-high vacuum. This kind of technique has been used successfully for several other metals deposited on field-emitter points, and will shortly be attempted in this laboratory for vapor deposits of Fe on W specimens of the same kind to be used for Ti deposits. Parallel experiments will be done using the field-electron microscope to determine the experimental conditions for producing polycrystalline and single crystal epitaxial films of Ti.

## 2.4 High Temperature Creep In Metals

A. A. O. Rukwied, W. A. Willard and D. E. Harne

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Institute for Materials Research

The objectives of this investigation are to investigate the microscopic mechanisms that control high temperature creep, i.e., creep occurring at temperature  $T > T_m/2$ , where  $T_m$  is the melting point. More specifically it is planned to study: (a) the effect of temperature on the creep rate and compare this to the temperature dependence of dislocation velocity, (b) the effect of stress and compare this to measurement of dislocation density carried out by etch pit techniques, (c) the effect of stacking fault energy through its variation in an alloy series



and (d) the effect of grain boundaries by comparison of studies in single crystals and polycrystals. For these studies copper and copper alloys have been selected to begin with, especially since etch pit techniques for these materials are already developed.

A commercial Baldwin Creep Machine has been equipped with an inert-atmosphere high-temperature furnace. The helium which is used as inert gas is being highly purified by a system containing a cryosorb trap. The machine is capable of carrying out stress and temperature cycles, however the latter ones at a relatively slow rate only. Tests have been conducted to learn more about the influence of environmental conditions on creep deformation, as well as to define the ranges of temperature and stress within which steady state creep studies could best be carried out. Furthermore, attempts have been made to determine the activation energy for high temperature creep in order to compare values obtained from our material with corresponding ones given in the literature. Indeed, the activation energies obtained by us compare very favorably with those given by Sherby and co-workers, (at Stanford University), in both the temperature ranges above and below the temperature which represents the transition above which the activation energy is the same as that for self-diffusion. Special emphasis has been put on the temperature range of the transition itself.

Testing equipment has been designed and built to conduct creep tests on single crystals at constant resolved shear stress in high vacuum ( $10^{-6}$  -  $10^{-8}$  torr (Fig. 1). The machine is capable of performing rapid temperature and stress changes, which are needed for activation analysis. The control of the resolved shear stress is accompanied by the use of an analog computer, which calculates resolved shear stress signal from the extensometer and load cell signals. This signal is compared with a set stress signal in a Position Adjusting Type control unit and the error signal is used to control the pneumatic load on the specimen.

This setup is also capable of conducting tests at constant resolved shear strain rate or any stress rate. The equipment was recently received and is presently being set up and tested. It is expected to be operative in early February 1968.

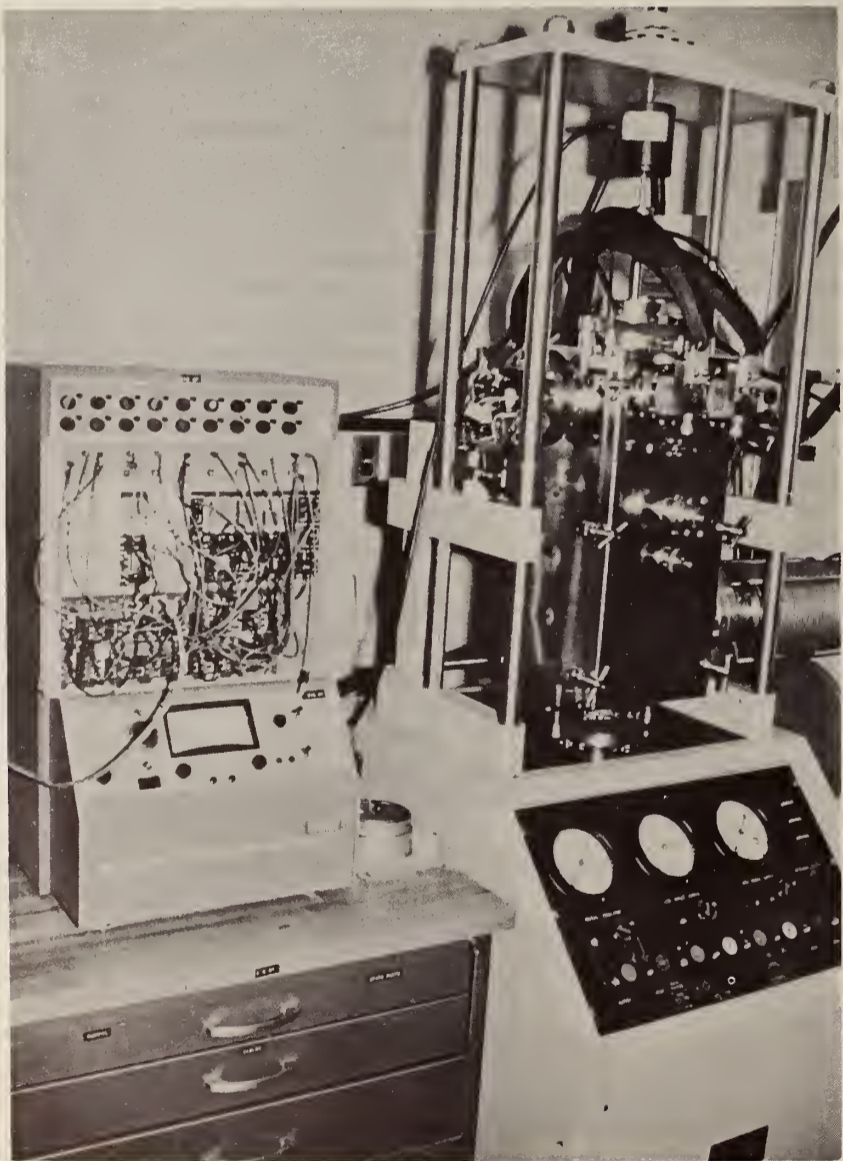


Fig. 1. Single Crystal Creep Testing Unit;  
Furnace Chest and Analog Computer.

## 2.5 Electronic Structure of Refractory Hard Metals

J. R. Cuthill, A. J. McAlister

Metallurgy Division

Institute for Materials Research

This is a new project begun in December, 1967. Its objective is to study relationships in the changing density of states upon compound formation in representative refractory hard intermetallic binary compounds. Such information is expected to contribute to the understanding of basic relationships necessary for the intelligent design of high temperature alloys with prescribed properties.

Measurements will be made which give information on aspects of the electronic structure, such as density of states and internal magnetic and electric fields as a function of temperature, which are important to an understanding of bonding and the physical properties of refractory hard binary intermetallic compounds. The representative class of compounds upon which measurements will be made are those which are characterized by one constituent element having an incomplete d-or-f-shell and the other constituent element having no d- or f-electrons. They will also exhibit aspects of metallic character at elevated temperature. One or more series of compounds of this type will be studied experimentally. The various series of borides, aluminides, beryllides and silicides of the metals of the first and second transition series are compounds of the above type. Compounds to be included in the experimental program will be selected from those meeting the above criteria, on the basis of the possibility of obtaining well characterized samples. Soft X-ray (valence band) emission spectra will be obtained from the compounds as a function of temperature and compared with the corresponding spectra from the pure components. The emission spectrum is related to the density of occupied states in the valence band. A 2-meter grazing incidence spectrometer with electronic detection and digital recording will be used. In each case, many scans will be summed to obtain a high order of statistical significance to the detail in the spectra. Corroborative information on internal magnetic and electric fields and the shape of the density of states at the Fermi energy will be obtained from NMR, Mossbauer, magnetic susceptibility, and electronic specific heat measurements.

## 2.6 Crystal Growth from Vapor

H. S. Parker, C. A. Harding

Inorganic Materials Division

Institute for Materials Research

This project was initiated in July 1967 in response to both technological and research needs for single crystals of greater crystalline perfection, chemical purity and high temperature capability.



Vapor growth techniques offer remarkable promise for producing such crystals. Because the growth temperature is below the melting point of the crystal, the technique can be applied to materials which may be difficult or impossible to grow by other techniques due to the high melting point, high vapor pressure, or destructive phase changes. The objectives of this program are to obtain an understanding of the parameters controlling perfection, purity, and distribution of dopants in crystals grown by this technique and to extend the technique to the growth of a wider range of oxide materials.

During this reporting period, a vapor growth system for the growth of aluminum oxide, similar to that described by Schaffer<sup>2</sup> and constructed by Lexington Laboratories, was installed at NBS. This system is of the continuous flow type in which the reactants, generally a halide or other volatile compound of the desired cation and a suitable source of controlled partial pressure of oxygen are separately introduced into the growth chamber and as a result of vapor phase reaction at or near the surface of the seed, single crystal overgrowth occurs on the seed.

So far, efforts have been devoted to preliminary growth runs to familiarize operating personnel with the system characteristics which present difficulties, for instance to ensure safety for personnel. Runs have been made at growth temperatures in the 1735 - 1760°C temperature range at total system pressures of 5 to 15 torr. At the lower pressures, satisfactory growth was obtained. Higher total pressures resulted in very poor quality growth with the formation of large amounts of powder.

A second vapor growth technique that of vapor phase transport as described by Schafer<sup>3</sup> has been applied to the growth of Ta<sub>2</sub>O<sub>5</sub>. Schafer reported that the transport of Ta<sub>2</sub>O<sub>5</sub> could be obtained using either chlorine, chromium tetrachloride or tantalum pentachloride at temperatures in the 650° - 900°C range.

Using a two-zone furnace, a series of transport experiments using TaCl<sub>5</sub> as the transporting agent have been conducted. The transport occurs as a result of the reaction: Ta<sub>2</sub>O<sub>5</sub> (s) + 3TaCl<sub>5</sub> (g) = 5TaOCl<sub>3</sub> (g) at the hotter end and the reverse reaction at the colder end of the transport tube. The transport tube consisted of a silica glass tube 1.9 cm i.d. X 22 cm long, with tapered ends. After introduction of the desired amounts of reactants, the tubes were evacuated and sealed. The overall temperature gradient in the furnace was maintained at 100°C with the growth end at a temperature of 650°C. Results to date indicate that at calculated total pressures of 1.0 to 1.2 atmospheres, 5 grams of Ta<sub>2</sub>O<sub>5</sub> can be transported in periods of 120 hours or less. These pressures correspond to an excess of TaOCl<sub>3</sub> pressure of about 0.28 to 0.31 atmospheres at the growth end of the tube.

2. Schaffer, P. S., 'Vapor-Phase Growth of Alpha Alumina Single Crystals, J. Am. Ceram. Soc. 48, 508 (1965).

3. Schafer, H., Chemical Transport Reactions, Academic Press, New York 1964.



Tube fills corresponding to 0.8 atmosphere total pressure and 0.26 atmosphere excess  $TaOCl_3$  pressure resulted in little or no transport in 100 hour heatings.

The transported material was deposited primarily in the form of spherulites and blocky overgrowths. Some small clear crystal in the form of hexagonal plates and prisms of the order of 0.5 to 0.75 mm in diameter and 0.25 to 0.5 mm thickness were identified by x-ray diffraction as  $Ta_2O_5$ . Attempts to obtain growth on seeds have so far failed.

During the next reporting period, it is planned to investigate the effect of seed orientation on crystal perfection of vapor-grown  $Al_2O_3$  and to attempt the growth of bicrystals of controlled orientation. In addition, a separate injector is being constructed to attempt the growth of magnesium oxide by vapor phase reaction. In this case, because of the low volatility of the magnesium halides, the injector will be placed within the growth chamber and be heated by a separate furnace. Temperatures in excess of  $1000^\circ C$  will be required for the use of magnesium chloride as a source of magnesium. If possible, elemental magnesium will be used as a source which would permit lower operating temperatures. Oxidation at the source must be avoided. This condition presents a somewhat novel experimental problem.

Attempts to reduce spontaneous nucleation in the growth of  $Ta_2O_5$  while maintaining reasonable transport rates will be continued.

## 2.7 High Temperature Crystal Growth from Solvents

J. Ito and Harold Johnson

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Institute for Materials Research

### Apatite

The development of the technique for crystal growth of rare-earth fluoro-silicate apatites and oxyapatites of wide variations in chemical composition is of interest for detailed structure analysis of apatite, a stable phase with an exceptional tendency to accommodate cations and anions of diverse shapes and sizes. Specific practical applications are not kept in mind, but apatites are potentially useful laser hosts and apatites could be used for high temperature application.

An extended search showed that sodium fluoride is the most effective flux for the fluoro-silicate apatites, and that sodium tungstate is useful for silicate oxyapatites.

Growth by isothermal evaporation at high temperature relying on spontaneous nucleation in 25 ml platinum crucibles, produced transparent crystals of  $Na_2Ln_8Si_6O_{24}F_2$  (apatite, Ln = La, Pr, Nd, Sm and Gd) up to 8.0 mm in size with well developed faces (Fig. 2).

Short prismatic crystals with [10,0] [10,1] and [00,1] are common. Also thick tabular crystals with [11,1] [10,1] and [10,0] with relatively large [00,1] were formed. Optimum temperatures for evaporation and charge composition were determined (see Table 1). The colors of the crystals were characteristic of each type of trivalent rare earth ion. Unit cell dimensions of all analogues were determined (see Table 1). Experiments on europium and terbium doping of the gadolinium compound in order to produce intense luminescent crystals are under way.

A specially designed furnace using MgO crucibles was used, because sodium fluoride corrodes alumina and mullite-type ceramic parts. An outer crucible (2 1/2 X 9 1/4") of 250 ml capacity was used as a core for 20 gauge, 80% Pt./20% Rh winding (9-1/4" turns on side and one spiral at the bottom containing a total of 40 feet of wire.) An inner MgO crucible of 200 ml capacity was used for double protections. The top cover of the furnace was made of two platinum plates 1 inch apart and the lower cover was kept two inches from the top of the crucibles. Most of the evaporated NaF flux and other volatile compounds were trapped between the two platinum shields.

Low solubility of the oxyapatite composition in sodium tungstate flux limited the crystal size of the oxyapatite  $\text{NaLa}_9\text{Si}_6\text{O}_{26}$ . Only very small crystals (0.05 mm) were obtained by slow cooling of the melt from 1,150 to 750°C at the rate of 1°C per hour. A charge: flux ratio of 1:20 was used.

### Beryl

As an extension of the scandium beryl study, done at Harvard University under ARPA-SD-88, an indium analogue of beryl,  $\text{Be}_3\text{In}_2\text{Si}_6\text{O}_{18}$ , was synthesized hydrothermally (420-450°C, 2 kilobars). Fast growth of this indium compound is expected at low temperature under ultra high pressure, but no such experiment is planned here.

### Yttrium Pyrosilicate

$\text{Y}_2\text{Si}_2\text{O}_7$  was studied as a possible fluorescent light emitter. It gives intense luminescence under mercury excitation, when activated by europium (red) and terbium (yellow). A phase study was carried out with special emphasis on the use of reactive, precipitated amorphous gels of stoichiometric composition prepared using cation exchange resin. In the range of 1,000 to 1,400°C, hexagonal  $\alpha\text{-Y}_2\text{Si}_2\text{O}_7$  (low) and  $\beta\text{-Y}_2\text{Si}_2\text{O}_7$  (high) were obtained. The transition temperature was determined as  $1,160 \pm 10^\circ\text{C}$ .  $\alpha\text{-Y}_2\text{Si}_2\text{O}_7$  is found as yttrialite in nature and  $\beta\text{-Y}_2\text{Si}_2\text{O}_7$  was found to be isostructural with  $\text{Sc}_2\text{Si}_2\text{O}_7$  (thortveitite). We found In, Ho, Yb, Er, Ho, and  $\beta\text{-Y}$  compounds that were all isomorphous with  $\text{Sc}_2\text{Si}_2\text{O}_7$ . Er and Ho analogues showed  $\alpha$  phase (low) together with  $\beta$  phase and one other phase ( $\text{Ln}_2\text{Si}_3\text{O}_9$ ) with transitions, at 980°C and 1,020°C respectively. No  $\alpha\text{-}\beta$  transformation was observed with Sc, In, Lu, and Yb analogues but at the lower temperatures at which it might be expected to occur, the transformation may be too sluggish. Continuous changes of unit cell dimensions of above series (monoclinic C 2/m) are given in Figure 3.

$\text{Li}_2\text{W}_2\text{O}_7$  was a useful flux for the growth of  $\text{Y}_2\text{Si}_2\text{O}_7$ . Small crystals of 1 X 1 X 0.5 mm were obtained by slow cooling of saturated melts from 1,200 to 950°C. A charge: flux ratio of 1:5 was used.

Formula	Temp °C	Max. Size mm	Color	SiO <sub>2</sub>	Charges, g Ln <sub>2</sub> O <sub>3</sub>	Charges, g NaF	Unit Cell Dimensions a b c
Na <sub>2</sub> La <sub>8</sub> Si <sub>6</sub> O <sub>24</sub> F <sub>2</sub>	1,300	6.0	Colorless	3.0	10.0	50	9.68 7.19
Na <sub>2</sub> Pr <sub>8</sub> Si <sub>6</sub> O <sub>24</sub> F <sub>2</sub>	1,260	2.0	Blue-green	1.4	4.0	30	9.60 7.09
Na <sub>2</sub> Nd <sub>8</sub> Si <sub>6</sub> O <sub>24</sub> F <sub>2</sub>	1,250	8.0	Purple (Reflected) Grey (Transmitted)	1.4	4.0	28	9.55 7.03
Na <sub>2</sub> Sm <sub>8</sub> Si <sub>6</sub> O <sub>24</sub> F <sub>2</sub>	1,250	5.0	Yellow	1.6	5.0	30	9.49 6.96
Na <sub>2</sub> Gd <sub>8</sub> Si <sub>6</sub> O <sub>24</sub> F <sub>2</sub>	1,230	2.0	Colorless	1.5	4.0	30	9.42 6.89
(Na <sub>2</sub> WO <sub>4</sub> 2H <sub>2</sub> O)							
NaLa <sub>9</sub> Si <sub>6</sub> O <sub>13</sub>	1,150 to 750 1/°C	0.1	Colorless	0.6	2.0	40	9.69 7.18

Table 1. Data on the growth for rare-earth fluoro silicate apatites and oxyapatites.



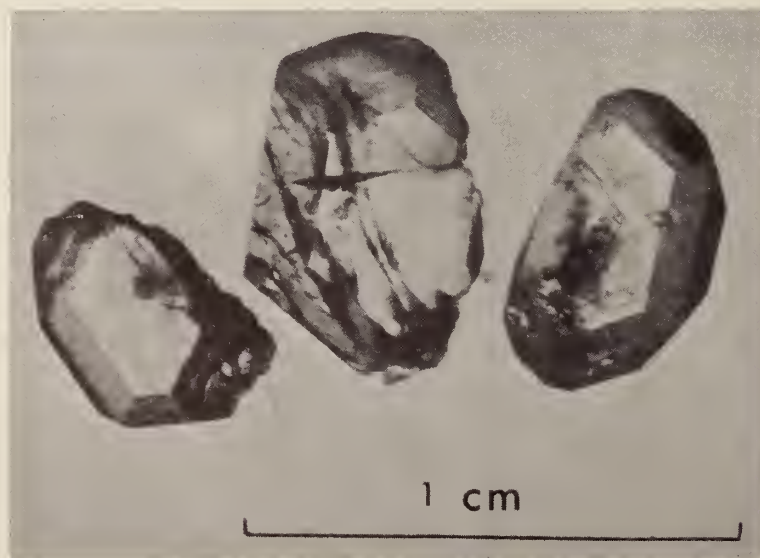


Fig. 2 Photographs of the crystals of  $\text{Na}_2\text{La}_8\text{Si}_6\text{O}_{24}\text{F}_2$ .



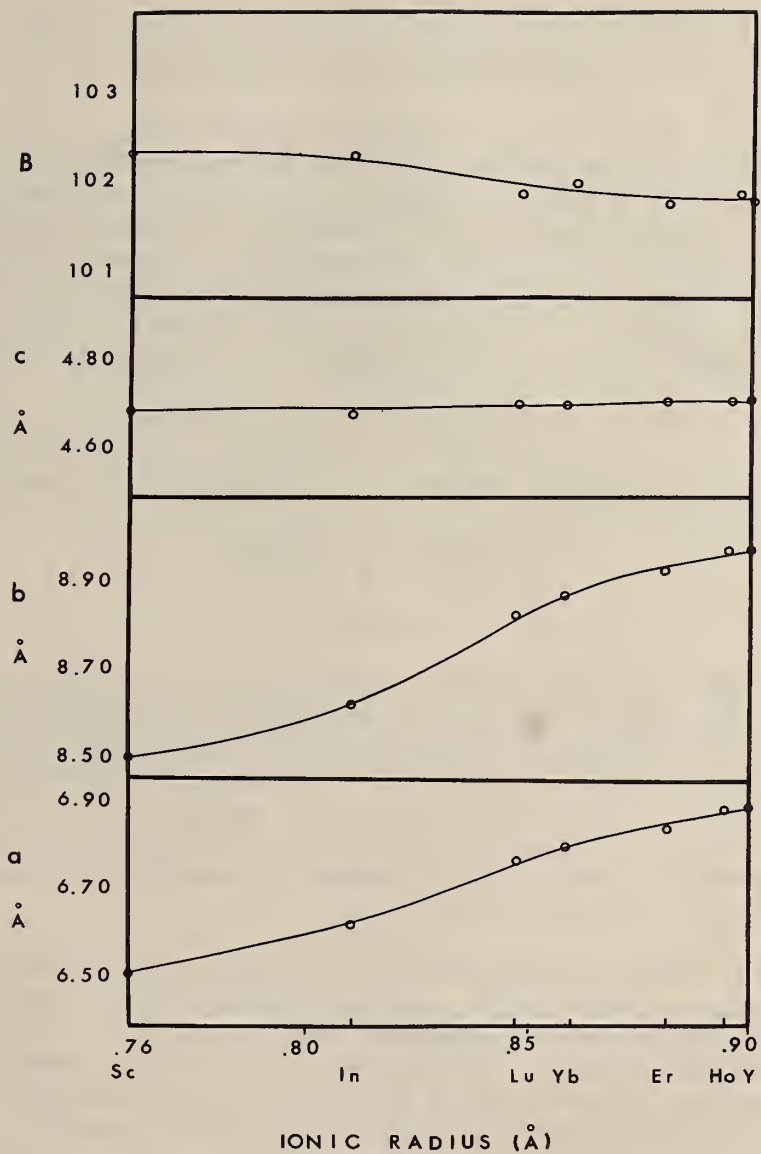


Fig. 3 Unit cell dimensions of  $\beta Y_2Si_2O_7$  and its analogues extended to  $Sc_2Si_2O_7$

## 2.8 High Temperature Thermodynamics

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Heat Division

Institute for Basic Standards

One of the important high temperature materials is pyrolytic graphite, but as yet no reliable data on its thermodynamic properties at high temperature have been published. What data there are indicate that its properties are quite different from those of other graphites. It is therefore planned to measure the enthalpy of pyrolytic graphite from 1000°K to 2500°K and from this calculate  $C_p$ ,  $S$  and the Gibbs free energy. These will be compared to the properties of a spectroscopic grade of graphite. Samples have been obtained and are now being machined.

## 2.9 The Volatilization and Decomposition of Materials

J. H. Flynn, S. Strauss, L. A. Dunlap, L. A. Wall

Polymers Division

Institute for Materials Research

When we measure the thermal decomposition of polymeric materials we normally assume that the rate of vaporization is determined by the bond rupture process not by the simple molecular vaporization process. However when the volatiles are relatively large, some questions arise. Since there was little information on the question of the molecular vaporization of large organic molecules, we are investigating this area for the purpose of enabling us to interpret data on the degradative volatilization of polymeric materials.

Rates of volatilization of three straight-chain hydrocarbons,  $n\text{-C}_{19}\text{H}_{40}$ ,  $n\text{-C}_{24}\text{H}_{50}$  and  $n\text{-C}_{36}\text{H}_{74}$  and twenty-one representative commercial plasticisers for polymeric materials were obtained by both isothermal and nonisothermal methods. Effects due to shape and composition of sample buckets were investigated in an apparatus featuring a sensitive vacuum electrobalance and a quickly equilibrating internal furnace.

Heats of vaporization,  $\Delta H_v$ , which are equivalent to activation energies for the volatilization process,  $E$ , were calculated by a method developed to obtain values of  $E$  over a broad mosaic of conversions and temperatures. This method is illustrated in Fig. 4. The logarithms of isothermal reaction times are plotted against the reciprocal absolute temperature,  $1/T$ , from a nonisothermal (TGA) experiment for a series of temperatures and degrees of conversion,  $C$ . As the slope of the isothermals is  $-0.457 E/R$  and the distance between isothermals along the isoconversionals is  $\frac{.4343}{R} \left( \frac{1}{T_i} - \frac{1}{T_j} \right) E$ , the applicability of a single

Arrhenius-type temperature dependence to the system may be critically tested over the whole mosaic of C and T values. This method has been further developed to analyze complex volatilization processes.

Values of  $\Delta H_V$  for the hydrocarbons from nonequilibrium volatilizations at low temperatures and pressures compared well with values in literature determined calorimetrically or from equilibrium vapor pressure data.

Much of the effort in dealing with these latter data has been in the direction of forcing conformity to empirical or semi-empirical equations so a careful direct redetermination of heats of vaporization from original P-T data was undertaken. This investigation exposed a hitherto undetected irregularity in the heats of vaporization.

Heats of vaporization are plotted against number of carbon atoms, n, at temperatures of 0, 50, 100, 150 and 200°C in Fig. 5. An indication of breaks in the curves at 9 and 17 carbon atoms suggests that at these chain lengths sufficient points of van der Waal's attraction are available to establish a preference for conformations of one or two kinks or folds, respectively. This is in line with a prediction by Huggins<sup>4</sup> in 1939 that straight chain molecules would be coiled in the vapor phase and, therefore, heats of vaporization should be proportional to  $n^{2/3}$  rather than to n.

A lack of accurate data at low pressures and temperatures for these substances points up the urgent need that exists for high vacuum volatilization kinetic studies both of materials of basic interest such as hydrocarbons, and of those of applied utility such as polymer plasticisers.

4. M. L. Huggins, J. Phys. Chem. 43, 1037 (1939).

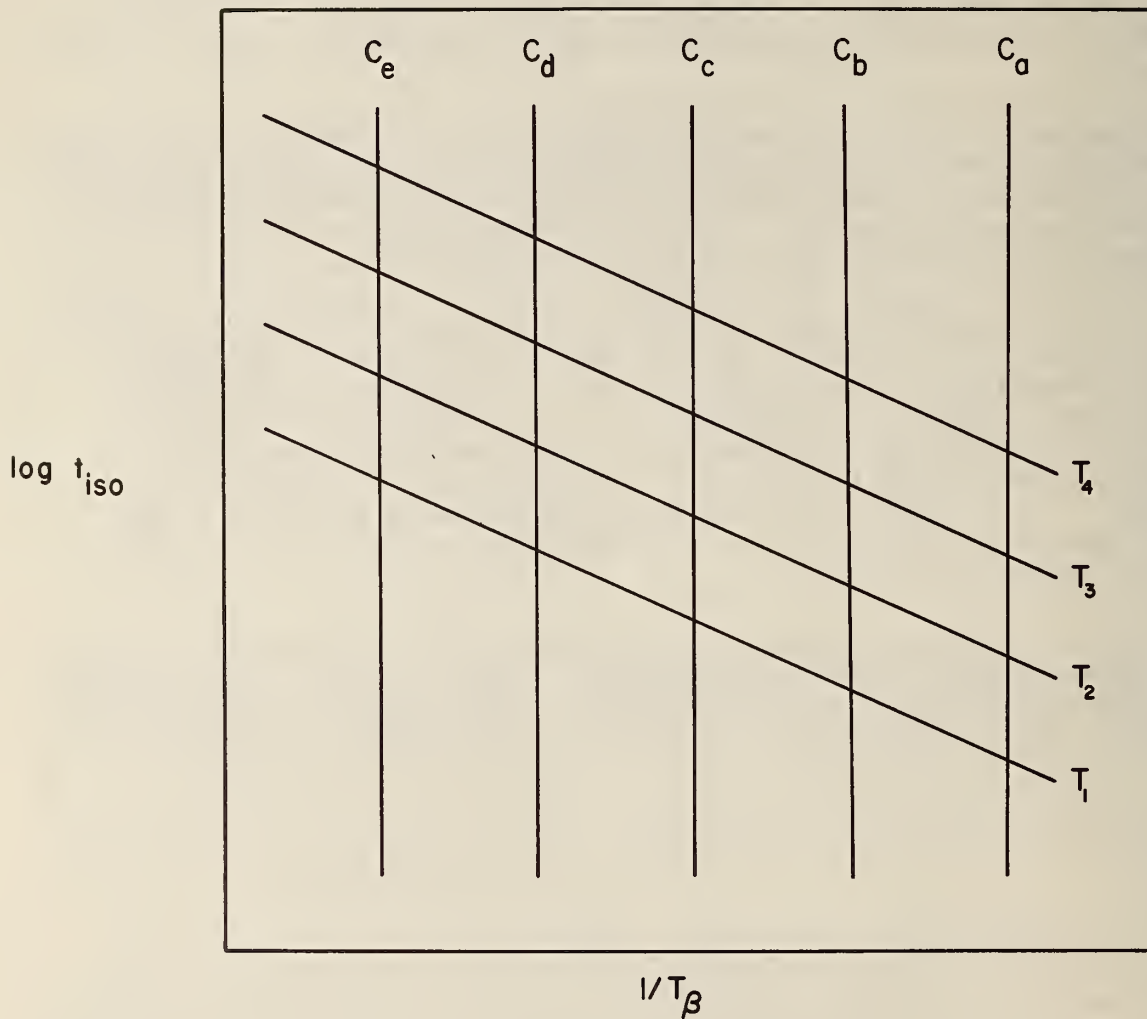


Fig. 4 Isothermal reaction time vs. reciprocal temperature at which conversion took place on the TGA.

$C_i$  isoconversional

$T_i$  isothermals

$$\text{slope of isothermals} = \frac{-0.457 E}{R}$$

$$\text{distance between isothermals} = \frac{.4343}{R} \left( \frac{1}{T} - \frac{1}{T_j} \right) E$$



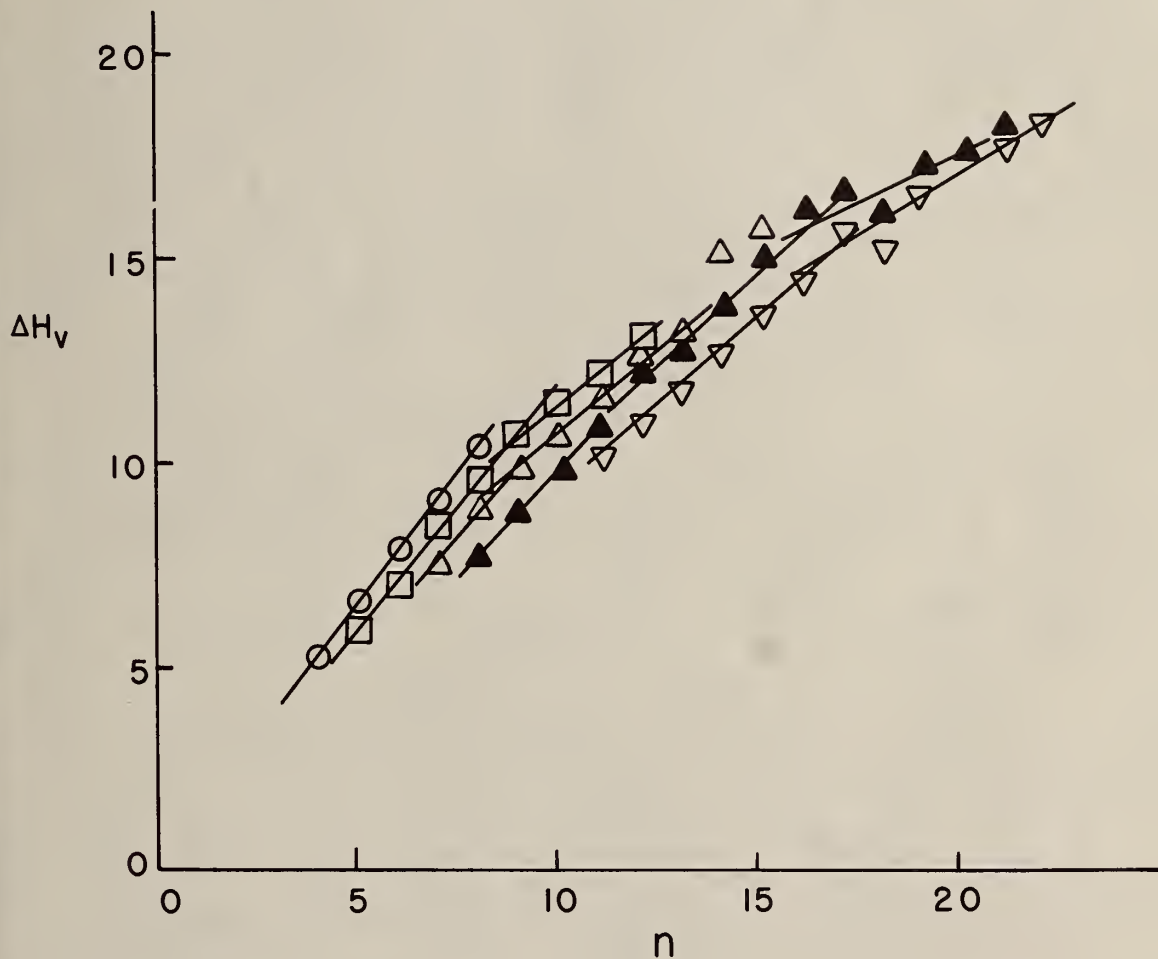


Fig. 5 Heats of vaporization for normal alkanes ( $C_n H_{2n+2}$ ) vs. number of carbon atoms, n.

○	0°C	▲	150°C
□	50°C	▽	200°C
△	100°C		

## 2.10 Relaxations Near the Melting Point in Crystalline Polymers

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If the dynamic mechanical properties of mats of single crystals of polyethylene are measured with a torsion pendulum, the apparent temperature of the  $\alpha$  (higher temperature) relaxation depends upon the time-temperature history of the sample. For example, samples which have been annealed for four weeks at  $80^{\circ}\text{C}$  exhibit a relaxation temperature which is  $15^{\circ}\text{C}$  higher than that for a sample which has been annealed for about thirty minutes at  $80^{\circ}\text{C}$ . As both samples are annealed for thirty minute periods at higher temperatures, the difference between the relaxation temperature decreases as the annealing temperature is increased. In the same samples, there is no significant difference between the  $\gamma$  relaxation temperatures. Also, other parameters which are a measure of the  $\alpha$  and  $\gamma$  relaxations exhibit little, if any, difference in the two samples. We are attempting to determine the cause of these effects which would result from a number of possible mechanisms, including structural and morphological differences. The samples have been shown to have the same lamella thickness, and initial measurements show that they have the same unit cell dimensions. We shall also examine the stagger of the molecules within the lamellar crystals. This angle of stagger changes upon annealing.

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