NSRDS-NBS 61, Part III

U.S. DEPARTMENT OF COMMERCE / National Bureau of Standards

Physical Properties Data Compilations Relevant to Energy Storage.

III. Engineering Properties of Single and Polycrystalline Sodium Beta and Beta''-Alumina

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G. R. Miller and D. G. Paquette*

Department of Materials Science and Engineering
University of Utah
Salt Lake City, Utah 84112

*Present address: Ford Aerospace and Communications Corporation, Aeroneutronic Division, Newport Beach, CA 92660.

+ National Standard Reference Data System

U.S. DEPARTMENT OF COMMERCE, Juanita M. Kreps, Secretary

Jordan J. Baruch, Assistant Secretary for Science and Technology

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Foreword

The National Standard Reference Data System provides access to the quantitative data of physical science, critically evaluated and compiled for convenience and readily accessible through a variety of distribution channels. The System was established in 1963 by action of the President's Office of Science and Technology and the Federal Council for Science and Technology, and responsibility to administer it was assigned to the National Bureau of Standards.

NSRDS receives advice and planning assistance from a Review Committee of the National Research Council of the National Academy of Sciences-National Academy of Engineering. A number of Advisory Panels, each concerned with a single technical area, meet regularly to examine major portions of the program, assign relative priorities, and identify specific key problems in need of further attention. For selected specific topics, the Advisory Panels sponsor subpanels which make detailed studies of users' needs, the present state of knowledge, and existing data resources as a basis for recommending one or more data compilation activities. This assembly of advisory services contributes greatly to the guidance of NSRDS activities.

The System now includes a complex of data centers and other activities in academic institutions and other laboratories. Components of the NSRDS produce compilations of critically evaluated data, reviews of the state of quantitative knowledge in specialized areas, and computations of useful functions derived from standard reference data. The centers and projects also establish criteria for evaluation and compilation of data and recommend improvements in experimental techniques. They are normally associated with research in the relevant field.

The technical scope of NSRDS is indicated by the categories of projects active or being planned: nuclear properties, atomic and molecular properties, solid state properties, thermodynamic and transport properties, chemical kinetics, and colloid and surface properties.

Reliable data on the properties of matter and materials are a major foundation of scientific and technical progress. Such important activities as basic scientific research, industrial quality control, development of new materials for building and other technologies, measuring and correcting environmental pollution depend on quality reference data. In NSRDS, the Bureau's responsibility to support American science, industry, and commerce is vitally fulfilled.

E. Ambler.

Ernest Ambler, *Director*

Preface

This series of publications is aimed at providing physical properties data on materials used in energy storage systems. It was inspired by a requirement in the Department of Energy's Division of Energy Storage Systems for materials property data needed by its contractors in the timely development of energy storage devices. As prime contractor for this program, the Lawrence Livermore Laboratory (LLL) has requested the Office of Standard Reference Data (OSRD) to manage the task of gathering the data, using its established network of data centers and other identified sources of expertise. The OSRD monitors the progress of work, reviews the results, and conveys the numerical data to LLL where the data are converted for entry into an automated data storage and retrieval system. Every effort is made to supply data which have been critically examined in light of the latest knowledge concerning theory and experiment. However it must be recognized that in a rapidly moving technology some of the data will be superseded rather quickly as new materials and techniques are introduced. Thus access to the data via computer terminal as well as publication in this series should help provide the practitioner with timely and useful data which he requires to solve his problems in energy storage. Funding for this series of projects from the Department of Energy, Division of Energy Storage, through the Lawrence Livermore Laboratory, is gratefully acknowledged.

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III. Engineering Properties of Single and Polycrystalline Sodium Beta and Beta″-Alumina

G. R. Miller and D. G. Paquette*

Department of Materials Science and Engineering; University of Utah; Salt Lake City, Utah 84112

A review of the properties of the two dimensional superionic conductors of the sodium beta alumina family is presented, with emphasis on the variability of properties with composition and processing. Processing methods, including methods of distributing additives, may strongly influence engineering properties of these substances through changes in microstructures. Described are common methods of measurement of properties with generally accepted ranges of property values. The need to compromise in the design of devices requiring several coincident optimal properties is, at this time, a necessary ingredient in the use of these materials as device components.

Key words: Battery application; engineering properties data; evaluated data; polycrystalline; single crystal; sodium beta alumina; sodium beta double prime alumina.

1. Introduction

1.1. General Background

The superionic conductor field has been recently pursued with vigor in an attempt to produce a detailed understanding of conduction mechanisms in the apparently large class of materials which exhibit very rapid motion of a constituent cation or anion. Of the many interesting materials having "superionic" conductivities, some are three dimensional conductors, others two and a few only one. There are two substances in the class of two dimensional conductors which are of extreme interest from a device construction point of view, the so-called sodium beta (β) and sodium beta double prime (β'')-aluminas. These materials are of interest in electrolytic device applications where a sodium ion conductor with virtually no electronic conductivity is required. Several devices with this requirement are in various stages of development in university, government and industrial laboratories. The sodium-sulfur [1][1] and sodium-antimony-alumino chloride [2] high energy and power density storage cells are in such a stage as to be considered very promising, the sodium heat engine [3] (thermoelectric device) is under strong consideration as a potentially efficient direct energy conservation device and attempts could be made to use a sodium ion superionic conductor for sodium purification via electrolytic separation. The use of β/β'' mixtures as an electrolyte in gaseous concentration cells is also of interest [4].

The sodium beta alumina family of materials seems to be the most promising solid electrolyte for these applications because it is produced from cheap, available materials and because it is relatively stable to degradation by liquid sodium.

The so-called sodium β-alumina is characterized by a hexagonal lattice structure with aluminum and oxygen ions forming spinel blocks and with sodium ions occupying positions in two dimensional channels which separate the spinel blocks [5]. In the c-direction (perpendicular to the sodium ions channels) periodicity of the crystal structure is found to occur within a distance equal to two spinel blocks and two channels, thus the term "two block" beta alumina. The β'' crystal structure is trigonal [6,7] with many of the local characteristics of the β form except that periodicity in the axial (or c-direction) requires traversing three spinel blocks and thus the term three block beta alumina is often used. Compositionally, both forms may exist over relatively wide ranges of stoichiometry, the β form having the widest range [8,9]. Nominal composition of the β form is commonly given as $Na_2O \cdot 11Al_2O_3$ although wide deviations from this formula are observed

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*Present Address: Ford Aerospace and Communications Corporation, Aeroneutronic Division, Newport Beach, CA 92660.

[1] Figures in brackets indicate literature references at the end of this paper.

and all forms are rich in Na_2O as compared to the $Na_2O \cdot 11Al_2O_3$ formula.

The β'' form is given nominally as $Na_2O \cdot 5Al_2O_3$ but the structure is unstable at high temperatures (above about 1200 °C) [9], and so certain compounds are added to stabilize the structure at high temperatures and allow high temperature ceramic processing to be carried out. Common additives are Li_2O and MgO although other additives have been used for stabilization [9]. From the compensation models of Kummer [10] and Bettman and Peters [7], β''-alumina with Li_2O and MgO additives is expected to have higher conductivity than that of the nominal composition. This is due to its ability to allow more sodium ions to be inserted into the structure. The β form has been produced in relatively pure form as well as with additions of Li_2O and MgO and other additives although the positioning of the impurity ion may be different in the β form than in the β'' form [11]. In the two block form, the Li ion is normally found in the conducting channels whereas in the three block form the Li ion is probably on the Al^{+3} site near the channel.

These substances are most commonly available in polycrystalline ceramic forms and are being developed for use in devices requiring relatively high sodium ion current densities. However, electrical properties of both of these materials are usually measured with perturbative methods (low current densities). The high current density requirement of actual devices ($\gtrsim$1000 Am^{-2}) may lead to several other problems involving the otherwise insignificant electronic conductivity, local joule heating, local thermal expansion mismatch and slow crack propagation driven by electrical forces, etc. For the latter two problems, it is obvious that high mechanical strength may be a desirable characteristic and thus the production of strong polycrystalline ceramic in industrially useful shapes becomes important. Polycrystalline material also is required from the point of view of economics in that low cost forms will be required for all of the high volume applications. Much of the engineering data now available is gathered from polycrystalline samples whose microstructure (grain size, grain size distribution, grain morphology, etc.) can vary widely and which affects all of the other engineering properties—strength, ionic conductance, current carrying capability, thermal shock resistance, storability in non-vacuum conditions, etc. When one combines the desire for property optimization with the economics problems, one finds materials available with widely varying characteristics depending on the processor, the composition and the intended application.

1.2. Conductivity-Microstructure Effects

Processing of these ceramics is difficult primarily due to their inherent chemical instability at high temperatures where soda loss is rapid. Methods of manufacture must always account for rapid soda loss at temperatures which are required to attain other optimal properties and is often accomplished by encapsulating the material in platinum or packing in powders containing soda so that a high soda vapor pressure is maintained about the sample. Because of the extreme anisotropy of mechanical [11] and electrical properties, even the methods for green forming of ceramic bodies must be carefully considered. Tubular shapes may have significantly different conductance as measured radially (through tube walls) and as measured axially (parallel to the walls) due to preferred crystal orientations arising during ceramic forming operations [12,13]. Byckalo et al. [14], have produced slipcast two block sodium beta alumina samples in which the crystals exhibit a high preferred orientation whereby the poor conductivity directions of the crystals are aligned in a nearly parallel fashion. Since the single crystal resistivity anisotropy is very large [10], one must expect marked directional dependencies in the apparent resistivity in polycrystalline materials with strong preferred orientation of the crystals. Byckalo et al., for instance, report the preferred orientation anisotropy for their samples of two block beta alumina to be about 40.6. That is, the resistivity perpendicular to the preferred orientation plane is about 40.6 times greater than in any direction removed by 90° from the perpendicular. However, these effects are dependent on processing method and can be minimized.

Since these conductors are two dimensional in nature, (the sodium ions are constrained to move in a plane) there will be a different geometrical path traversed by the ions in a polycrystalline material than if a single crystal were oriented with the applied electric field parallel to a conducting plane. Attempts have been made to calculate the geometrical path effects on polycrystalline two dimensional conductors so that the tendency toward randomness can be accounted for in constructing a polycrystalline conductor from many single crystals. The fact that sodium ions must follow a tortuous path in passing through a polycrystalline sample has lead to the universally applied term "tortuosity factor," a purely geometrical factor describing the ratio of the effective path length to that which is found in an oriented single crystal. The best calculations of this geometrical term have been carried out by Mitoff [15]. He has found that for the case of random equiaxed (cubic) crystals in a 3 dimensional array, the tortuosity factor should be about 1.363 for a two dimensional conductor. This calculated result was found for uniform grain size and not for the commonly encountered duplex microstructure wherein a few very large grains (say up to 300 μm in length) are observed in a fine grain matrix where the grains are less than 3 μm mean diameter. It is expected that the tortuosity factor will increase for such microstructures. Although the tortuosity factor is relatively small, one finds that the measured dc or low frequency conductivity of the polycrystalline substance cannot be accounted for by simply multiplying the single crystal resistivity by the calculated tortuosity factor. The measured resistivity is always a factor in the range 3-5 times higher than predicted [16,17,18,19]. The reasons for this failure are presently unclear except that grain boundary effects certainly play a large part in increasing the low frequency and dc resistivity, especially at low temperatures.

The relative contributions to the total dc resistivity from the grains and the grain boundaries can be obtained by measuring the frequency dependence of the impedance of polycrystalline samples. The combination of grains in series with grain boundaries is often modeled as an electrical circuit consisting of a resistor (grain) in series with the parallel combination of a resistor (grain boundary resistance) and a capacitor (grain boundary capacitance). Analysis of the total specific resistivity or the complex impedance of a sample as a function of frequency can give approximate values for the two resistances and the capacitance provided that the frequency range of the measuring apparatus extends high enough to include the dispersive or "capacitive shorting" effects associated with the grain boundaries. Reports by Powers and Mitoff [16] and Hooper [19] have given values for the apparent relative contribution of grain boundaries to the total dc resistivity. In the case of impurity doped two block sodium beta alumina doped with Y_2O_3, CaO, and SiO_2 [20,21,22], these impurities migrate to grain boundaries and produce a high resistivity layer of such thickness and dielectric constant that shorting of the equivalent capacitive element is easily performed (at least at room temperature or below), and at frequencies often less than 100 kHz. In undoped two block beta alumina or two block beta alumina with ZnO added as a sintering aid [20], capacitive shorting is normally not observed at frequencies as high as 500 kHz to 3 MHz nor at temperatures as low as room temperature. For these relatively pure materials the grain boundary resistances have been estimated by making measurements on a series of samples with different grain sizes, and hence a variation of the relative area fraction of grain boundary material from sample to sample can be determined. This work has shown that in two block β alumina the grain boundary contribution to the dc resistivity can be minimized to a small fraction of the total resistivity even for fine grain ceramics.

The conductivity-microstructure relations for the three block form are in much less mature condition than for the two block form. In the three block form, an impurity is always present as a stabilizing additive so that processing can take place at elevated temperatures and which will result in the existence of the three block form at the temperature of processing. Three stabilizing element systems are most common: (1) MgO in quantities up to 5 weight percent, (2) Li_2O in quantities up to about 1.1 weight percent and a mixture of the two (Li_2O-MgO) up to about 2.0 weight percent MgO plus about 1.0 weight percent Li_2O. Providing that the resulting crystalline phase is essentially all three block sodium beta alumina, (greater than 95 percent by volume) one can attain similar resistivities for temperatures from about 25 °C and higher no matter what the stabilizing element.

For an average composition, which at true equilibrium would give three block sodium beta alumina, the resistivity can be widely varied because of lack of conversion to the three block form. By this is meant the following: in the processing of polycrystalline three block beta alumina samples, chemical powders which provide the alumina, soda and stabilizing additive are mixed together and sintered. Thus a reaction between several components must take place and during this process several phases may be present depending on the state of completion of the reaction. From phase diagrams [8,9] one expects, for example, to encounter a stage whereby three block and two block sodium beta alumina coexist (not at equilibrium) with sodium aluminate ($NaAlO_2$). Since the conversion reaction to the three block form is slow and many times must be accomplished through a long, post sintering anneal treatment, it is easy to produce a system with the two block and three block form coexisting and occupying most of the volume. A third phase (such as, possibly, $NaAlO_2$) would occupy a small volume fraction. Such a mixed system, which may be promoted by poor distribution of the stabilizing additive [23], will exhibit conductivities lower than for the single phase material by amounts which depend directly upon the amount of nonequilibrium phases present. For instance, one can expect the resistivity for a sample containing ~ 70 volume percent three block (equilibrium phase) and ~ 30 percent two block phase (with a small amount of third phase) to be in the range of 0.06 to 0.12 ohm-meters at 573 K in material whose average stabilizing element composition is 0.75 percent by weight Li_2O (the exact value of the resistivity also depends on grain size) while samples with the same mean composition which are completely converted to the three block form show resistivities in the range of 0.02 to 0.06 ohm-meters at the same temperature and for the same average composition. Again the exact value will depend upon grain size.

The effect of grain boundary resistance and capacitance on the frequency dependence of sample impedances is expected to be similar to results for the two-block form. No engineering type β''-alumina has been produced for which grain boundary shorting occurs at frequencies as low as 100 kHz at room temperatures. Measurements must be carried out at higher frequencies. At 300 K grain boundary shorting begins by about 50 MHz [22]. This capacitive shorting occurs over a very wide range of frequencies and makes identification of the single crystal resistivity very difficult. However, recent measurements by Rasmussen [24] to frequencies of 300 MHz have allowed identification of the magnitude of this shortable resistive contribution. Much work remains to be done in the area of electrical conductivity-microstructure relationships in these materials.

For the β'' form doped with Li_2O as a stabilizing additive, one can develop some qualitative relations between impurity concentration and resistivity. In the case of Li_2O stabilized three block material, at constant Na_2O content, the resistivity is relatively independent of Li_2O concentration up to about 1.1 weight percent Li_2O whereupon it is claimed [25] that the Li ion enters the conducting channels rather than on an Al^{+3} site near the channel. Apparently above about 1.1 weight Li_2O, ion exchange with molten lithium salts is easily observed.

An interesting feature recently reported by Doremus [26] is the appearance that in the three block form, potassium ions which pass through the sodium ion channels in the grains (single crystals) have great difficulty in traversing the grain boundaries; in the case of the two block form, the K^+ ions appear to easily pass through grain boundaries as well as the grains. If this observation is valid, an extension of this argument would lead one to suppose that in the β'' form, the K^+ ions entering only the surface grains will cause stress buildup at the surface. This property could be useful for constructing sodium purification apparatus but may also enhance mechanical degradation.

1.3. Mixed Systems

Many experiments have been carried out to produce mixed cation conductors or new cation conductors with the two and three block beta alumina structure. These ion exchange experiments have been reported in the earlier review article by Kummer [10] and in a more recent article by Kummer and Whittingham [27]. Also, with soda concentrations in the range of about 6.8 to about 8.6 weight percent and with the addition of one of the previously mentioned additives one can produce equilibrium material in the polycrystalline form and which consists of a mixture of β and β'' phases [28,29].

1.4. Mechanical Behavior

The degradation of the ceramic via mechanical separation (cracking) can be carried out in several ways, each of which may be encountered in common device preparation and operation. The four common ways may be described as:

(1) Rapid crack propagation as experienced in most common, short time experimental tests of fracture strength.

(2) Slow crack propagation in the presence of an ambient that corrodes the material, especially at high stress regions, that is stress corrosion.

(3) Slow crack propagation under the influence of electric fields, especially at high sodium ion current densities.

(4) Cracking under the influence of rapidly changing temperatures, that is thermal shock.

Each of these modes of inducing fracture must be considered for the case of engineering design with these materials as when, for instance, rigid seals to mating components are formed, or when the material is used in a situation where high sodium ion current densities or when rapid thermal cycling is experienced in the presence of an ambient in which good thermal transfer is effected (such as liquid sodium). For each of these cases, one normally may decrease the degradation effects with a substance of high fracture toughness or high fracture strength.

In both the two and three block forms of sodium beta alumina in polycrystalline form, the microstructure attained after processing is quite variable and the fracture strength as measured in rapid four point bending tests is a strong function of both grain size and grain size distribution. For instance in β'' alumina with relatively uniform microstructure of mean size less than about 5 μm, one finds the fracture strength to be as high as 2.9 10^8 N m^{-2} (newtons per square meter) at room temperature [20,31] whereas with relatively uniform grains of mean size greater than 200 μm in a sample of the same nominal composition the fracture strength can easily be as low as about 1.0×10^8 N m^{-2} [32]. With the common duplex microstructure (containing large elongated grains whose rapid growth direction is parallel to the crystallographic basal plane), the fracture strength lies intermediate between these two values. Samples with large volume fraction of large elongated grains in the fine grain matrix tend to exhibit lower fracture strength than do samples with a large volume fraction of fine grains. Experimental data on the Li_2O stabilized three block form show a weak dependence of strength on grain size when the mean grain size is less than about 100 μm. Above this grain size, the strength drops rapidly with increasing grain size. Qualitatively the two materials (two and three block sodium β-aluminas) behave in a similar fashion for similar microstructures if treated in the same fashion. However the strength of fine grain β is generally higher than the fine grain β'' material.

Much data on the fracture strength of these materials is obtained on sections of tubes mechanically fractured in a diametral test. This test can give inflated values for strength (as compared to three or four point bending where the maximum tensile stress is applied over a larger volume fraction of the sample than for the case of the diametral test) and, although this diametral test is useful for grading samples of tubular shape, the most common geometrical form for devices, it is not the most recommended test. Three or four point bending tests are preferred methods. For fracture tests in four point bending or a diametral tube section test, the samples are typically cut by a diamond wafering blade, and are annealed to relieve stresses and "heal" surface damage in order that the effect of damage introduced upon cutting is minimized.

An important feature of these materials with regard to their mechanical and electrical behavior is their ability to take up water in the conduction planes [33,34]. In long term storage in high humidity conditions the effects are easily measured on even large, high density samples where the surface area to volume ratio is comparatively small. Typically in the three block material, the electrical resistivity increases by up to about twenty percent and the density of the substance increases [35]. Little change in the fracture strength is noticed and the effects are easily reversed by heating in a dry atmosphere. Of greater importance is the effect of water on the Li_2O or MgO stabilized three block material which has been so processed such as to not be totally converted to the three block form even though the nominal composition would require such conversion at equilibrium. Without conversion other phases can exist, one of which is the two block form, and from the phase diagram of Weber [6], one must presume the existence of a small amount of something such as sodium aluminate which is soluble in water. Samples of Li_2O or MgO stabilized β''-alumina neither of which are totally converted to β'', exposed to water vapor over several hours up to many days, will swell and fracture. It is also suggested that MgO stabilized β''-alumina with more than about 2 weight percent MgO is especially unstable to water—probably more so than the Li_2O stabilized substances [36]. Virkar [37] has found that samples of Li_2O stabilized β''-alumina (but not totally converted to the three block form) show time dependent crack propagation; that is, the fracture strength decreases with increasing time of load application. This phenomenon could be interpreted as stress corrosion cracking from atmospheric humidity.

Virkar [38] has also investigated the mechanical behavior of completely converted Li_2O stabilized three block beta-alumina in search for evidence for stress corrosion cracking when the material is immersed in liquid sodium, the corrosive media most commonly encountered by these materials. He found that the material is not susceptible to stress corrosion failure in the presence of liquid sodium for times of a few days or less, his interpretation being based on the fact that their data did not fit any reasonably acceptable stress corrosion phenomenology (the stress intensity exponent was far too large.) Thus short term stability to stress corrosion in liquid sodium is established for at least the compositions of three block material used by Virkar and thus allows greater confidence in ceramic seal designs via conventional elastic design criteria.

Even though fracture strengths may be found to be acceptably high, and the material is found stable to degradation by stress corrosion in liquid sodium and complete conversion to the three block form helps ensure stability to water vapor attack, it is found that these materials (two and three block) degrade in another fashion. As Na ion current is passed, a mechanical failure mechanism is engendered which is correlatable with the sodium ion current density. Thus one tends to assign the terms "electromechanical degradation" or "degradation by electrolysis" to the problem.

A critical sodium ion current density appears to exist for these materials which depends upon composition and microstructure [39]. In the Li_2O stabilized three block system on which most work has been performed, the critical current density beyond which one observes short time failure (within a few hours) is a function of the Li_2O concentration. This failure is manifested by a rapid decrease in fracture strength, presumably because hypercritical cracks have been introduced into the electrolyte material.

The final comment on the mechanical behavior of these substances concerns their resistance to thermal shock. Rapid air quenching of the three block materials has shown that mechanical integrity is maintained for a ΔT (the difference between the initial specimen temperature and the ambient air) of as great as 1250 °C. With better heat transfer as in the case of a water quench, no significant change in elastic modulus or strength has been observed for a ΔT of as much as 160 °C [40]. For larger ΔT, the modulus and strength drop abruptly indicating the formation of microcracks of greater than critical length.

2. Properties: Mass Density, Lattice Parameters, and Thermal Expansion

2.1. Mass Density

In each of these substances, one expects the density to vary strongly with composition and many compositions are used. In the two block of β form, the range of Na_2O compositions is rather wide while in the three block of β'' form the Na_2O variations are smaller but the nature and concentration of stabilizing additives varies widely. Further, the three block form has been available in only polycrystalline microscopic forms and thus porosity must be accounted for in any mass density determination. X-ray lattice parameter measurements can, of course, be used along with compositional analysis to fix the density.

Peter et al. [5] have measured the mass density of two block sodium beta alumina of composition $Na_{2.58}Al_{21.81}O_{34}$ via room temperature lattice parameter measurements and have found it to be 3240±20 kg m^{-3}. The three block material at room temperature, based on x-ray lattice parameters of Bettman and Peters [7] and the nominal chemical formula $Na_2O \cdot MgO \cdot 5Al_2O_3$ has a density of 3300 ± 50 kg m^{-3}. The actual sample used by Bettman and Peters was nearer $(Na_2O)_{0.80}(MgO)_{0.64} \cdot 5Al_2O_3$ but without a detailed knowledge of the defect structure, the calculation of a mass density to greater accuracy cannot be made.

For polycrystalline Li_2O stabilized three block (β'') alumina containing 0.7 weight percent Li_2O and 8.75 weight percent Na_2O (the balance Al_2O_3), hot pressed samples showing no observable porosity give a density of 3280 ± 20 kg m^{-3} [13].

2.2. Thermal Expansion

Radzilowski [40] has measured the lattice parameters of samples of MgO stabilized sodium β'' alumina of chemical formula $(Na_2O)_{0.80}(MgO)_{0.64} \cdot 5Al_2O_3$ as a function of temperature from 25 °C to 900 °C. Table 1a gives interpolated values of and a and c lattice parameters (based on a pseudo-hexagonal lattice rather than the trigonal lattice). For sodium β-alumina the only reported data on thermal expansion exists in an NBS note of 1934 and was measured on single crystal samples of unknown composition. For completeness the data are reproduced on table 1b. Apparently the anisotropy in the thermal coefficient of expansion is much greater in the two block form than for the three block form.

3. Properties: Electrical Behavior

3.1. Electrical Contacts to Sodium Beta Aluminas

Reversible contacts for sodium ion transport measurements have been constructed from liquid sodium reservoirs, [42], from sodium tungstates [43] and from sodium amalgams [44] although only the first of these contacts has been accepted with few reservations. However, even in the case of liquid sodium contacts, one finds articles [45,46,47,48] which question the wetting

TABLE 1a. Basal and axial lattice parameters of sodium β''-alumina of chemical formula $(Na_2O)_{0.80}(MgO)_{0.64} \cdot 5Al_2O_3$. Measurements were made at atmospheric pressure. Units: Angstroms (10^{-10}m). Reference [40].

Temperature °C					
Lattice Parameter	25	100	300	600	900
Basal (a)	5.623	5.625	5.631	5.644	5.657
Axial (c)	33.510	33.528	33.569	33.645	33.717

TABLE 1b. Thermal coefficient of expansion for sodium β-alumina of unknown chemical composition. Reference [41]. Units: $10^{-6}K^{-1}$

Temperature °C Coefficient of Expansion	Room temp to 200 °C	200 °C to 300 °C	300 °C to 400 °C	400 °C to 500 °C	500 °C to 600 °C	600 °C to 700 °C
Basal (a)	5.1	6.2	6.0	5.8	5.7	6.0
Axial (c)	5.7	7.0	7.2	7.5	7.7	7.6

ability of liquid sodium on polycrystalline material. The wetting characteristics are evidently a strong function of surface roughness and the time the samples are held at high temperatures ($>\sim 620$ K). Very rough surfaces tend to be difficult for the liquid sodium to wet. Nevertheless it is also apparent that for samples with large length to cross-sectional area ratios, the partial wetting of the material is not worrisome in data gathering, especially for true, four probe dc conductivity measurements. For thin wall tubes where radial conductance is of paramount importance, where length to cross-sectional area ratios are very small and where high average current densities are encountered, this wetting problem can be more serious. This can result in low apparent conductance and/or very high local current densities. Typically one has to raise the temperature of the liquid sodium/sodium beta alumina interface to about 620 K or higher to promote the wetting of the electrolyte. Subsequently the temperature can be lowered to the temperature region where measurement is to be made (but, of course, still greater than 370 K, the melting point of sodium). One must always consider the possibility that measured resistivities may be current density dependent. All data reported here are measured with current densities of the order of only $\mathrm{mA \cdot cm^{-2}}$.

In spite of the fact that data analysis is more complex than for the dc case, low frequency ac conductivity measurement techniques have commonly been used for characterization of the beta aluminas because of the fact that experimental procedures are simpler and because more microscopic information can be obtained than from simple dc bulk conductivity data. Blocking electrodes may be used in ac measurements, and for polycrystalline materials it is possible to determine the average resistances of both the grains and the grain boundaries. Details will be discussed below.

Two classes of irreversible or "blocking" electrodes have been used: (1) those which improve contact between a metal electrode and the sample by using an ionic electrolyte containing sodium ions and (2) those which use evaporated metals, [49] metal paste electrodes or graphite. In both cases, the frequency which must be used in the measurement must be high enough so that the capacitive impedance of any blocking interface is smaller than or comparable to the sample impedance. Ionic electrolyte and evaporated metal electrodes can be used at frequencies as low as 10 kHz. For metal electrodes making less intimate contact, frequencies up to 100 MHz or even higher may be required. Graphite electrodes have been used at frequencies as low as 20 kHz [50]. Among the ionic electrodes which have been used in various temperature ranges are aqueous solutions of 2N NaOH [14], molten salts such as $NaNO_2$–$NaNO_3$ eutectic and organic solution such as 0.6M NaI and 0.6M iodine in propylene carbonate [16,52,53]. One must realize that these sodium superionic conductors have relatively low resistivities and that the molten salt or aqueous solution contacts may well have comparable resistivities. Thus, with thick electrodes, four probe measurements are advised for accuracy, using voltage probes which are intimately wetted to the sample by a molten salt or aqueous solution.

Electrodeless techniques have been used for sodium β-alumina single crystal conductivity measurements at high frequencies. Measurements in a coil at 50 MHz have been made [54] as well as microwave measurements in cavities [54,55] and into the infrared [54,56]. These measurement techniques have the advantage that conductivity artifacts arising from electrodes are nonexistent. Electrodeless techniques have not been used for conductivity measurements on industrially useful, small grain, polycrystalline beta-alumina ceramics. The reason is quite simple. No adequate theories exist which will relate cavity dielectric loss to the bulk conductivity of inhomogeneous conductors. The most relevant existing theory is one which relates dielectric loss in a capacitor geometry to the conductivity of well separated ellipsoids in an insulating dielectric matrix. The required theory would be one which would relate dielectric loss for samples which were themselves ellipsoids (or other convenient geometry) and include partially conducting grain boundaries.

3.2. Temperature Dependence of the dc Sodium Ion Conductivity in Single Crystals

3.2.1. Sodium β-alumina

Direct current and relatively low frequency ac measurements of the resistivity of sodium beta alumina single crystals grown by flux or fusion methods or obtained from cutting fusion cast bricks have shown that over a wide temperature regime the resistivity may be accurately described by the relation: [10,43,49]

$$\rho = A\ T \exp\ [E/kT] \qquad (1)$$

where, for a sample containing 16 % excess sodium ions, A is $(4.5\pm0.2)\ 10^{-6}\ \Omega\ \mathrm{m\ K}^{-1}$, the activation energy, E, is $15.44\pm0.75\ \mathrm{kJ\ mol^{-1}}$, T the absolute temperature and k is Boltzmann's constant [43]. In terms of material composition, it is generally assumed that the crystal compositions are near the low soda phase boundary, (near the nominal composition $Na_2O \cdot 11Al_2O_3$) although most crystals, when analyzed contain excess soda to place the composition in the range $Na_2O \cdot (9\text{–}10Al_2O_3)$. Table 2 shows the resistivity as a function of temperature (after Whittingham and Huggins [43]. These data

TABLE 2. Sodium ion electrical resistivity of single crystal sodium beta alumina at atmospheric pressure. Material contained 16 percent excess sodium ions from 1:11 formula. Reference [43].

Temperature °C	-150	-100	25	200	800
Resistivity (ohm-meters)	2045	3.97	0.72	0.109	0.0312

TABLE 3. Sodium ion electrical resistivity of single crystal MgO stabilized sodium β''-alumina. Reference [10].

Temperature °C	20	60	125	225	440
Resistivity (ohm-meters)	0.21	0.07	0.025	0.011	0.007

were extracted from their graph; electrodes were $Na_{0.4}WO_4$ and the field frequency was 10 kHz.

3.2.2. Sodium β''-Alumina

Since large single crystals of the three block form have not been routinely available, only limited data on single crystal conductivity is available. The data of Weber [10] on very small, flux-grown single crystals of the β'' form stabilized by the addition of magnesia (MgO) of unknown concentration provide the only low frequency direct measurements known. Data were taken in the temperature range of 350 K to 870 K. The general behavior of the temperature dependence of conductivity is roughly corroborated by indirect measurements on polycrystalline samples where the polycrystalline effects (grain boundaries) have been subtracted out [57]. The two main features of the data on the β'' single crystals in comparison with that on single crystals of the two block (β) form are (1) the resistivity is generally lower and (2) the diffusional form of equation (1) is not obeyed. The material apparently exhibits a conductivity which increases with increasing temperature but at a decreasing rate. As temperature is increased one finds, for instance, resistivity activation energies ranging from 30 ± 5 kJ mol near room temperature to 11 ± 2 kJ mol^{-1}near 300 K. The resistivity, taken from graphical data by Weber is found in table 3. Electrodes were platinum and the field frequency was 1 MHz.

One should note that there is some indirect evidence [57] which supports Weber's data on the "curvature" of the Arrhenius plot for sodium β''-alumina resistivity which has been gathered from polycrystalline lithia (Li_2O) stabilized material instead of MgO stabilized material. These data, corrected by a reasonable tortuosity factor of 1-2, would tend to point to the suggestion that this particular lithia stabilized material may have intrinsic sodium ion conductivity as little as one third that of the conductivity of the MgO stabilized material used by Weber. Since the stoichiometry range for the sodium β'' alumina is apparently very narrow, the sodium ion concentrations for both the lithia and magnesia stabilized material are likely similar, the possible difference in sodium ion concentrations is not able to account for the difference in conductivities.

3.3. Frequency Dependence of the Impedance of Single Crystal Sodium β and β''-Alumina

Since single crystal samples of only the two block form have been available, all data on the frequency dependence of the real and imaginary parts of the crystal impedance have been carried out on the two block material. Frequency ranges covered, usually in steps of only a few decades by a single measuring technique, include dc and extend into the infrared. At relatively high frequencies near 1800 GHz at 4.2 K to 350 K a large dielectric resonance is observed in the conductance or imaginary portions of the dielectric constant [54,55]. The magnitude and position of this conductance peak is relatively independent of temperature. However, at 300 K a second conductance peak has been observed at ~ 500 GHz [54] which is not present at low temperatures and has not yet been explained. It is logical to interpret the results of these high frequency measurements of conductivity in terms of a collective response of the mobile sodium ions rather than in terms of a single particle model.

Below about 10 GHz the conductivity of single crystal sodium beta alumina is found to be almost frequency independent from temperatures as low as 4.2 K up to 300 K.

3.4. Sodium Ion Resistivity as a Function of Temperature in Polycrystalline Sodium Beta and Beta''-Alumina

3.4.1. Two Block Sodium Beta Alumina

Since the two block form may be prepared as a stable substance without additives, dc and low frequency (<10 MHz) sodium ion resistivities characteristic of the nearly pure (undoped) substances are available. However, since processing variables can strongly influence the conductivity results, one must take great care in specifying: (1) the average soda concentration, (2) the concentration profile of soda, especially near surfaces where soda loss may have occurred during preparation, and (3) the microstructure of polycrystalline bodies both in the bulk and near surfaces. Resistivities of the two block substances at 573 K may vary from 0.025 to 0.11 Ω m, depending on the methods of sample preparation. Table 4 gives low frequency values for the resistivity of polycrystalline sodium beta aluminas over the narrow temperature range of 526 K to 667 K [58].

Almost universally one finds that the resistivities for polycrystalline beta aluminas do not obey the relation given in equation (1) over wide temperature ranges. The apparent conductivity activation energies decrease with increasing temperature in a manner similar to the single crystal three block material and range from about 30 kJ mol^{-1} at 25 °C to about 14.6 kJ mol^{-1} at 300 °C (±4 kJ mol^{-1}). The apparent temperature dependent activation energy can be attributed to the effect of grain boundary regions which are electrically in series with the grains. The activation energy associated with the grain boundaries is usually significantly higher than that associated with the grains and single crystals. Thus, the higher the temperature the less the grain boundaries affect the total conductivity, while at low enough temperatures the grain boundaries can dominate the conductivity.

3.4.2. Three Block Sodium Beta Alumina

Assuming that the ceramic processing steps used in making polycrystalline three block sodium beta alumina cause essentially complete conversion to three block form ($>95\% \beta''$), the resulting resistivities may be made reasonably reproducible and almost independent of the concentration of stablilizing additive (Li_2O or MgO or combinations of the two). The assumption is made that reasonably high purity material has been used to prepare samples so that stray impurity effects, which often show up as enchanced grain boundary resistance, are not present.

Unfortunately, because the present primary use of these materials is in high temperature energy storage and conversion devices, reported resistivity data are most prevalent for temperatures of about 250 °C to 400 °C where the resistivity is low enough to allow the design of practical devices. Within this range of temperatures, the resistivity, excluding any preferred orientation effects can be approximated by an Arrhenius relation. Resistivity activation energies lie in a range of 13 to 30 kJ mol^{-1}. Resistivities at 573 K, the most common reporting temperature, lie in a range of 0.02 to 0.06 ohm-meters with most materials (production types) showing resistivities in the range of 0.03 to 0.05 ohm-meters at 573 K. (Table 5 gives resistivity data measured on polycrystalline Li_2O stabilized sodium β'' aluminas, the electrodes being $NaNO_2$-$NaNO_3$ electrodes for measurements near 300 °C and NaI or I^- in propylene carbonate for low temperature measurements.) The low resistivity of 0.02 ohm-meters is many times associated with a coarse grained microstructure or at least a large volume fraction of very large elongated grains within a fine grain matrix (duplex microstructure). For the sake of optimum mechanical integrity, this microstructure condition is generally to be avoided although avoidance is often difficult to achieve. Ormrod and Kirk [59] have measured the conductivity of sodium β'' alumina stabilized with either Li_2O alone or with mixtures of Li_2O and MgO at temperatures between about 226 °C and 400 °C and have developed relations for the resistivity.

Mixed dopants (Li_2O-MgO):

$$\rho=3.9\cdot 10^{-4} \exp\ [(23.84\pm 0.19)\ \mathrm{kJ}/kT]\ \text{ohm-meters}$$

Li_2O dopants:

$$\rho=5.8\cdot 10^{-4} \exp\ [(21.81\pm 0.19)\ \mathrm{kJ}/kT]\ \text{ohm-meters}$$

Data for development of these equations was taken at 15 kHz with molten sodium salts.

Silver blocking electrodes were also used by Ormrod and Kirk to determine the resistivity as a function of temperature between 25 °C and 800 °C at a field frequency of 500 kHz. The relation developed was highly consistent with that obtained at 15 kHz with sodium salt electrodes.

Mixed Dopants (Li_2O-MgO):

$$\rho= 5.0 \cdot 10^{-4} \exp\ [23.64\pm 0.19)\ \mathrm{kJ}/kT)\ \text{ohm-meters}$$

TABLE 4. Sodium ion electrical resistivity of polycrystalline tubular forms of sodium β-alumina containing 8.11 weight percent Na_2O. Reference [58].

Temperature °C	253	300	350	394
Resistivity (ohm-meters)	0.220	0.166	0.137	0.116

TABLE 5. Sodium ion electrical resistivity of completely converted Li_2O stabilized sodium β''-alumina. Electrodes were NaI or I in propylene carbonate for low temperature measurements and $NaNO_3$-$NaNO_2$ eutectic electrodes for the 300 °C measurements. The field frequency was about 30 kHz and the composition was 0.75 wt. % Li_2O, 8.75 wt. % Na_2O, 90.5 wt. % Al_2O_3. Reference [38].

Temperature °C	22	79	138	202	300
Resistivity (ohm-meters)	6.7	1.0	0.3	0.10	0.045

One should note that these authors experienced some serious polarization losses in using the sodium tungsten bronzes as suggested by Whittingham and Huggins, [43] giving much higher resistivities (an order of magnitude) than when the silver electrodes were used.

3.4.3. Equilibrium Mixed and Three Block Sodium Beta Alumina

With soda concentrations in the range of about 6.8 to about 8.6 weight percent and usually with the addition of one of the previously mentioned additives one can produce material in the polycrystalline form which consists of a mixture of β and β'' phases. Generally one can consider the electrical conductivity characteristics in the dc or low frequency regions to be intermediate between the cases, of the pure β or pure β'' phases [28].

3.5. Electronic Conduction in the Sodium β and β''-Aluminas

The contributions to conductivity by electronic transference are not well known for these materials. Generally, one can deduce that the electronic transference number is less than about 10^{-2} at 573 K to 673 K because the Faradaic efficiency for sodium ion transfer in sodium cells is nearly 100 percent. The only reasonably accurate values thus far reported are those by Weber [3] and relate to the three block material in polycrystalline form with duplex microstructure and containing Li_2O as a stabilizing element. Weber has calculated the electronic resistivity from sodium/sodium thermoelectric generator cells in which total electrical currents were measured and ionic evaporation currents were subtracted. His values for electronic resistivity vary from about 1000 ohm-meters at 752 K to about 10 ohm-meters at 979 K (table 6). The electrodes placed upon the electrolyte tubes were composed of porous molybdenum.

One expects that the magnitude of electronic conductivity will be dependent on impurity additions and temperatures as well as such other variables such as oxygen pressure, etc., but little data are reported. The lack of data in this area and especially the lack of data as a function of common impurity contents and microstructural change makes research on electronic conduction in these normally ionic conductors imperative. Conduction by electrons or holes will be of extreme interest in the use of these materials for two primary reasons. The first, of course, involves electronic shorting of the ion conductor. Reasonable design limits on the allowable electronic conductance can be calculated for any given device. Second, for polycrystalline forms formed by sintering processes, one always encounters the existence of defects, especially pores. Small but non-zero electronic conductance can, over a long period of time, allow the formation of a metal (sodium in this instance) at free surfaces such as the surface of pores or pre-existing cracks. Electrically this can result in effectively shorting the ion current in local regions if the porosity is connected or in pressure buildup in the pores over a period of time.

TABLE 6. Electronic resistivity of Li_2O stabilized sodium β''-alumina as calculated from thermoelectric generator cell data. Reference [3].

Temperature °C	479	578	706
Resistivity (ohm-meters)	1000	100	10

4. Properties: Mechanical Behavior

4.1. Young's Modulus

The elastic moduli of these materials have as yet not been carefully measured on single crystals and only limited data are available on polycrystalline samples. Since the modulus is expected to decrease rapidly with porosity, care must be taken to use dense material for characterization. A lone value for Young's modulus of sodium beta alumina was used in the work of Stevens [60] and given as $1.6 \cdot 10^{11}$ N m^{-2}. The source of this value is, however, unknown. Measurements of Young's modulus on samples of Li_2O stabilized sodium β''-alumina of density greater than 3200 kg m^{-3} using longitudinal wave resonance and electromagnetic excitation [61] show a value of $1.96 \cdot 10 \pm 0.14 \cdot 10^{11}$ N m^{-2}. These values for both the two and three block forms were measured at 25 °C.

4.2. Fracture Strength

The fracture strength of both forms is a strong function of grain size, grain size distribution and the method of measurement. Since ceramics fail at lowest stress under tension and pre-existing flaws in the ceramic often determine the stress for fracture, one must take care to sample a volume under tension which contains the average flaw density. As a result, diametral testing ususally gives average fracture stresses (over many samples) which are higher than in, say, three or four point bending where the volume of material under tension is large. For either two or three block material in four point bending, composed of uniform, fine grained material with mean grain size less than 2-3 μm, the fracture strength at room temperature is often as high as $2.9 \cdot 10^8$ N m^{-2}; for large grain material (mean grain size

200 μm) the fracture strength is as low as $1.0 \cdot 10^8$ Nm^{-2} (60,62,63).

4.3. Fracture Strength-Electromechanical Degradation

The effect ot electric current flow on the fracture strength of Li_2O stabilized sodium β''-alumina has been studied via the following test [39]: Samples of material were contacted with $NaNO_2$-$NaNO_3$ eutectic salt electrodes at 300 °C and a predetermined current density was passed for a period of 10 minutes, after which the fracture strength was determined. As shown in table 7, the average fracture strength decreases with sodium ion current density, dropping to less than half its pre-electrolysis strength when a current of $1.75 \cdot 10^4$ A m^{-2} has been passed. One should note that this effect is a function of microstructure and the composition of the material. Demott and Redfern [64] have found that the three block form stabilized with Li_2O appears to be far more stable than that made with the mixed additives (Li_2O-MgO) of similar microstructures. As much as $3 \cdot 10^4$ Am^{-2} can be passed through tubes of their material over long periods of time (corresponding to charge transfer of 10^7 ampere hours per m^2) without degradation. The critical current density, above which degradation occurs, decreases drastically as temperature is lowered. Very high Li_2O concentrations cause degradation at lower current densities. This behavior is not unique to the three block from but also occurs in the two block material [65]. It is also evident that the phenomenon of cracking proceeds from the electrolyte-electrode interface. deJonghe [66] has prepared samples of "dog bone" shape which allowed as much as 10^{-5}A m^{-2} to be passed through the small area neck of the sample and no mechanical degradation has been observed. To date several models have arisen to explain this electromechanical degradation [64,67,68,69].

TABLE 7. Fracture strength of polycrystal Li_2O stabilized sodium β''-alumina after electrolysis for 10 minutes at given current density in $NaNO_2$-$NaNO_3$ salt electrodes at 300 °C. Reference [39].

Current Density A m^{-2}	0	$1 \cdot 10^4$	$1.25 \cdot 10^4$	$1.\ 5 \cdot 10^4$	$1.75 \cdot 10^4$
Fracture Strength N m^{-2}	$1.71 \cdot 10^8$	$1.3 \cdot 10^8$	$1.\ 1 \cdot 10^8$	$0.80 \cdot 10^8$	$0.72 \cdot 10^8$

4. Summary

It is quite clear that these materials show great promise as economical fast sodium ion conductors but the potential user must be wary of the pitfalls that are encountered in incomplete specification of material characteristics. Application of these materials to devices requires several properties that are simultaneously optimized, the two that are most important being electrical conductance for sodium ions and good mechanical properties. It is somewhat unfortunate that insofar as presently available data is concerned, the mechanical characteristics of the polycrystalline three block material are far better understood than those of the two block form whereas the relative knowledge of the electrical characteristics is in an inverted state. Presumably this state of affairs is traceable to the recent commercial exploitation of the three block form and the availability of single crystals of the two block form which do not require the addition of a "complicating" additive. Fortunately significant progress has been made at several laboratories to make available polycrystalline forms of both high strength and low electrical resistivity.

Six major areas in which data are lacking for both substances are: (1) the electronic transference number and its dependence on temperature and oxygen partial pressure, (2) the microstructure-conductivity relations, (3) the mechanism for electromechanical degradation under high current densities (4) electrical and mechanical data on single crystal β''-alumina, (5) thermal coefficient of expansion of single crystal β-alumina and (6) thermal conductivity and thermal diffusivity on both types of material. Although data are beginning to appear regarding electromechanical failure, precise modeling of the phennomena is required before lifetime extrapolations will be possible and even then the ability to model and make lifetime extrapolations may depend strongly on the nature of the electrodes with which these materials are in contact.

A need still exists for careful, systematic studies of the properties of these materials. Characterization of samples, careful calibration of equipment, running of standards, etc., are too often neglected. As a result, the data reported here must be considered approximate and tentative, to be replaced by data taken in future studies.

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

A review of the properties of the two dimensional superionic conductors of the sodium beta alumina family is presented, with emphasis on the variability of properties with composition and processing. Processing methods, including methods of distributing additives, may strongly influence engineering properties of these substances through changes in microstructures. Described are common methods of measurement of properties with generally accepted ranges of property values. The need to compromise in the design of devices requiring several coincident optimal properties is, at this time, a necessary ingredient in the use of these materials as device components.

17. KEY WORDS *(six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons)*

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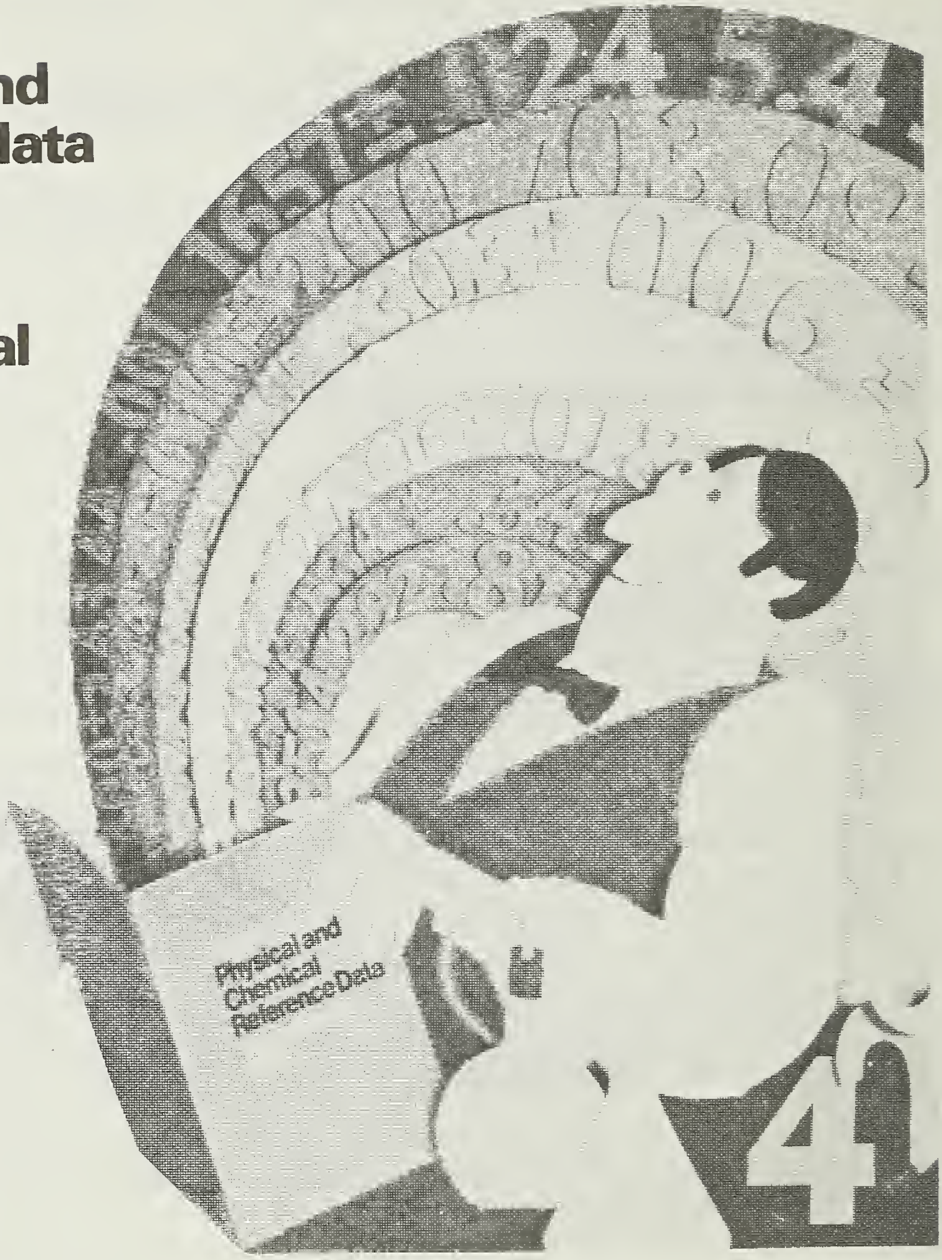

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