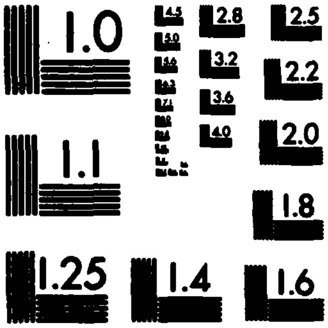
AD-A120 675 DIVALENT BETA' ALUMINAS: HIGH CONDUCTIVITY SOLID ELECTROLYTES FOR DIVALEN..(U) PENNSYLVANIA UNIV PHILADELPHIA DEPT OF MATERIALS SCIENCE AND E.. 1/1

UNCLASSIFIED G C FARRINGTON ET AL. 13 OCT 82 TR-1 F/G 7/4 NL

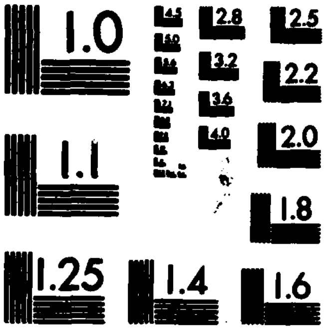
END

FILMED

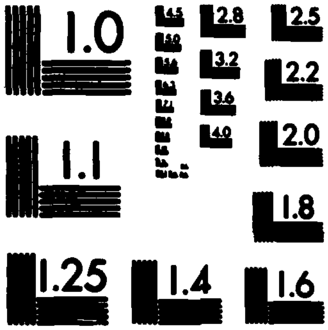
DTIC



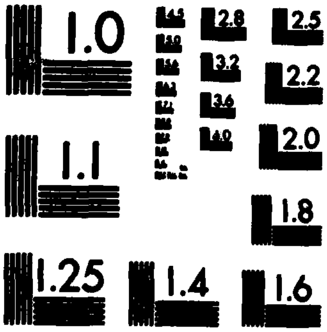
MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A



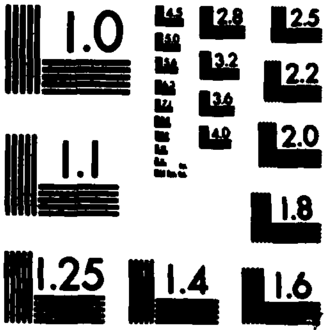
MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

①

OFFICE OF NAVAL RESEARCH

Contract N00014-81-K-0526

TECHNICAL REPORT NO. 1

DIVALENT BETA" ALUMINAS: HIGH CONDUCTIVITY SOLID ELECTROLYTES FOR DIVALENT CATIONS

by

G. C. Farrington

Prepared for Publication

in

Solid State Ionics

University of Pennsylvania
Department of Materials Science and Engineering
Philadelphia, Pennsylvania 19104

13 October 1982

[To appear in Solid State Ionics]

DIVALENT BETA" ALUMINAS: HIGH CONDUCTIVITY SOLID ELECTROLYTES FOR DIVALENT CATIONS

G. C. Farrington
Department of Materials Science and Engineering
University of Pennsylvania
3231 Walnut St.
Philadelphia, PA 19104

and

B. Dunn
Department of Materials Science and Engineering
University of California at Los Angeles
Los Angeles, CA 90024

Na(+)

Abstract

The ~~Na^+~~ content of beta" alumina can be replaced by a variety of divalent cations in simple ion exchange reactions. The resulting divalent beta" aluminas are the first family of high conductivity solid electrolytes for divalent cations. Divalent beta" aluminas which have been prepared so far include conductors of Ca(2+), Sr(2+) Ba(2+), Zn(2+), Cd(2+), Pb(2+), Hg(2+), and Mn(2+). Most have conductivities of about ~~10^{-7} (ohm-cm)$^{-1}$~~ at 40°C and ~~10^{-1} (ohm-cm)$^{-1}$~~ at 300-400°C. However, the conductivity of Pb(++) beta" alumina is ~~4.6×10^{-3} (ohm-cm)$^{-1}$~~ at 40°C, nearly equal to that of Na(+) beta" alumina. Preliminary structure studies indicate that order-disorder reactions among the divalent cations and vacancies in the conduction region of beta" alumina critically influence conductivity in the structure.

1.0 to the minus 7th power/(ohm-cm)

0.1/(ohm-cm)

0.0046/(ohm-cm)

①

Introduction

Fifteen years ago, Yao and Kummer [1] found that the Na^+ conductivity of beta alumina at room temperature is comparable to that of aqueous solutions. Their discovery excited interest throughout the world and established the field of high conductivity solid electrolytes. Since then, essentially all investigations of high cationic conductivity in solids have been of materials which conduct monovalent ions, in particular Na^+, Li^+, Ag^+, and H^+. Because high conductivity solid electrolytes for monovalent cations are rare, the possibility of finding structures which are good conductors of divalent cations has seemed remote.

Recently, however, we discovered that beta" alumina is an excellent conductor of divalent cations [2,3]. Derivatives of sodium beta" alumina in which the entire Na^+ content has been replaced by Ba^{2+}, Sr^{2+}, Ca^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, Zn^{2+} and Mn^{2+} have already been prepared. The conductivities of most are about 10^{-7} $(ohm\text{-}cm)^{-1}$ at 40°C and 10^{-1} $(ohm\text{-}cm)^{-1}$ at 300-400°C [3]. However, one composition, Pb^{2+} beta" alumina, has a conductivity at 40°C of 4.6×10^{-3} $(ohm\text{-}cm)^{-1}$, nearly equal to that of Na^+ beta" alumina, which is about 1.3×10^{-2} $(ohm\text{-}cm)^{-1}$ at the same temperature [3].

We have found only two precedents for the divalent beta" aluminas in the literature, PbI_2 and $PbCl_2$. These compounds are reported to conduct both anions and cations [4,5]. For example, the activation energy for Pb^{2+} conductivity in PbI_2 is 1.3 eV, and the conductivity attributable to Pb^{2+} motion is ca. $5x10^{-7}$ $(ohm\text{-}cm)^{-1}$ at 300°C [4,5]. We know of no other compound in which divalent cation conductivity has been reported.

The divalent beta" aluminas are a new family of materials whose properties and applications are only beginning to be explored. This paper reviews the few investigations of these compounds which have been carried out thus far. Much of the information included has not yet been published elsewhere. We are in the process of gathering most of this unpublished information into more specific, detailed papers.

Background

Divalent derivatives of the beta/beta" aluminas were first claimed in 1935 [6]. In that year Toropov [6] described his studies of the crystal phases of the binary $BaO\text{-}Al_2O_3$ system. He reported discovering an aluminate with a composition that could be expressed as $BaO.6Al_2O_3$. He recognized the structural and chemical similarities of this compound to sodium beta alumina, which then had only recently been described. He also noted that the BaO content of the barium aluminate he had discovered was higher than would be expected if the compound were a direct analog of Na^+ beta alumina, the composition of which had been defined to $Na_2O.11Al_2O_3$ by a variety of workers at the time.

Following this work, Lagerquist, Wallmark and Westgren [10] described similar phases in the systems, $CaO-Al_2O_3$ and $SrO-Al_2O_3$, for which they suggested compositions of $3CaO.16Al_2O_3$ and $3SrO.16Al_2O_3$. Adelskold [11] later assigned the formulas $BaO.6Al_2O_3$, $CaO.6Al_2O_3$, and $SrO.6Al_2O_3$ to these compounds. The formulas were the same as Toropov had assigned to the barium aluminate which he had discovered. The lattice parameters reported by Lagerquist et al. and Adelskold for these compounds correspond to those of beta alumina (see Table 1). In addition to this work, Bragg et al. [9] reported preparing a compound with the formula, $MgO.11Al_2O_3$, with lattice parameters characteristic of the beta structure. It is not clear whether these compounds have the beta alumina structure or that of the closely-related aluminates with the magneto-plumbite structure.

In a later paper, Toropov and Stukalova [10] presented the first evidence we have discovered which describes the ion exchange properties of $BaO.6Al_2O_3$. They found that crystals of this compound could interchange bases when treated with fused salts of alkali and alkaline earth elements. For example, they described one set of experiments in which finely powdered crystals of Ba^{2+} beta alumina were fused three times with potash. The precise treatment conditions were unspecified. Analysis of the product showed that the Ba^{2+} was almost completely exchanged by K^+. The compositions of the starting material and product were consistent with a formula of $1.048(Ba\ or\ K_2)O.6Al_2O_3$. They also reported that the Ba^{2+} content of their samples could be replaced with Rb^+ by fusion with Rb_2O. Toropov and Stukalova [11] also prepared Ca^{2+}, Ba^{2+}, and Sr^{2+} beta aluminas by fusing finely-crushed sodium beta alumina crystals with the appropriate chloride salts.

These early studies received little attention until Yao and Kummer discovered the high ionic conductivity of sodium beta alumina in the 1960's. In their well-known review [1] of the initial investigations of the ion exchange chemistry of beta alumina, Yao and Kummer described a series of experiments in which they attempted to replace the sodium ion content of various samples of beta alumina with divalent cations. Their results are summarized in Table 2. They noted that the partial exchange observed with many ions may result either from slow diffusion kinetics or unfavorable thermodynamic equilibria. They also mentioned that a number of divalent exchanges produced cracked crystals.

Because Yao and Kummer's results indicated that divalent ions diffuse very slowly in beta alumina, they discouraged interest in its divalent derivatives. After their work, only a few papers describing divalent cation exchange in beta alumina appeared. McWhan et al. [12] exchanged single crystals of Na^+ beta alumina of unspecified sizes in molten $EuCl_2$ at 850-900°C for 16 hours. The product appeared to be nearly pure Eu^{2+} beta alumina. Flinn and Stern [13] used polycrystalline Na^+ beta alumina to separate two $ZnCl_2$-NaCl melts at 500°C. They found that extended exposure of the Na^+ beta alumina to the melt resulted in very little ion exchange. The equilibrium apparently greatly favors Zn^{2+} in the melt. However, during electrolysis, the cell resistance increased steadily, an effect they attributed to the movement of Zn^{2+} ions into the solid electrolyte. Roumieu and Pelton [14] carried out similar experiments using polycrystalline Na^+ beta alumina to separate two $NiCl_2$-NaCl melts at 800-1000°C. After several days' exposure, they found that the beta alumina developed a thin, blue-green outer layer, which presumably resulted from partial exchange with Ni^{2+}. The center of the electrolyte remained white. Electrolysis produced a steady rise in tube resistance and caused the blue-green color to penetrate through the entire material. They estimated that 1-10% of the charge was carried by Ni^{2+}.

We have not uncovered any other work on the divalent beta aluminas and have never found a description of any investigation of the divalent beta" aluminas. Evidently, Yao and Kummer's results with beta alumina tended to confirm what seemed quite logical, that divalent cations diffuse very slowly in beta alumina, even at high temperatures. It was just as logical to infer similar behavior for beta" alumina. In light of these observations, it was especially surprising to find that divalent cations exchange very rapidly with the sodium content of single crystals of beta" alumina, although not of beta alumina.

Preparation of Divalent Beta" Aluminas

All of the divalent beta" aluminas we have studied have been prepared by the ion exchange of single crystals of Na^+ beta" alumina. In general, Na^+ beta" alumina crystals were grown by a flux evaporation method [15,16]. The crystals all had compositions of about $Na_{1.67}Mg_{0.67}Al_{10.33}O_{17}$, as determined by sodium and magnesium analysis. Another method of determining the sodium content of the crystals, that of measuring the weight change upon exchange of sodium by silver, gave results completely consistent with those of chemical analysis. Exchange experiments with beta alumina used material from a single crystal boule obtained from the Union Carbide Corporation.

The crystals were cut into convenient shapes, typically 3mm x 2mm x 0.2mm, heated to 750°C to remove any wax remaining from the sectioning, and then immersed in $NaNO_3$ at 350°C for 1-2 hours to remove any residual flux. The latter treatment produced little weight change (<1%). Yao and Kummer [1] used a similar approach to stabilize the weights of Na^+ beta alumina crystals used in their ion exchange investigations.

The molten salts used in the ion exchange experiments were extremely pure (99.99%) to avoid trace impurities which might influence the exchange equilibria. Most samples were exchanged in a nitrogen or argon atmosphere. After exchange, crystals were soaked in a suitable solvent (usually methanol), washed in distilled water, rinsed in 1N HNO_3 to remove any residual oxides, then rinsed in distilled water, and air dried at 300°C.

The extent of ion exchange was determined by gravimetric and radiochemical techniques. The gravimetric measurements involved measuring the change in weight resulting from the reaction:

$$Na_{1.67}Mg_{0.67}Al_{10.33}O_{17} + M^{2+} =$$
$$M_{0.84}Mg_{0.67}Al_{10.33}O_{17} + 2Na^{+}$$

Most of the ions studied yielded weight changes in the range of 200μg to 2mg. These were easily measured using an electrobalance with 0.1μg resolution. We estimate the experimental accuracy in determining the extent of exchange to be about 1%.

The radiochemical technique involved doping the starting crystals with radioactive ^{22}Na. The ^{22}Na content of a crystal could then be monitored at any point in the exchange process without destroying the sample. The activity of ^{22}Na in the crystals was chosen so that, when it was reduced to the background level, less than 0.1% of the initial sodium content remained in the samples.

<u>Ion Exchange Reactions</u>: A variety of divalent cations can replace the entire Na^{+} content of beta" alumina. The conditions for achieving complete exchange are listed in Table 3. The range of divalent cations includes representatives of Group IIa (Ca^{2+}, Sr^{2+}, and Ba^{2+}), IIb (Zn^{2+}, Cd^{2+}, Hg^{2+}), IVa (Pb^{2+}), and VIIb

(Mn^{2+}). These solid electrolytes have higher conductivities for divalent cations at moderate temperatures than any material previously reported. In contrast to the rapid diffusion of divalent cations in beta" alumina, divalent cations diffuse very slowly in beta alumina. The data in Table 4 illustrate this point [17].

Although most of the ion exchange reactions are straightforward, some are not. For example, the high vapor pressure of mercury salts makes it necessary to carry out the Hg^{2+} exchanges at relatively low temperatures, typically around 300°C. Complete exchange requires long immersion times and the use of sealed silica ampoules to prevent volatilization of the salt. We have also attempted to prepare Mg^{2+} and Cu^{2+} beta" aluminas. With Mg^{2+} ($MgCl_2$ at 750°C), the exchange process shattered the crystals [17]. Since the ionic radius of Mg^{2+} (0.66A) is substantially smaller than that of Na^+ (0.95A), tensile stresses can be expected to develop upon exchange. The mechanical failure of brittle solids due to tensile stresses is well known. Interestingly, the exchange of a similarly-sized monovalent ion, Li^+ (0.66A), also causes cracks to develop when substituted for Na^+ in beta" alumina [18]. In the case of Cu^{2+} exchange, crystals immersed in $CuCl_2$ at 600°C remain free of cracks [17,19]. However, Cu^{2+} diffusion is slow and only 37% exchange occurs after about 24 hours. If the $CuCl_2$ is impure, the exchanged crystals are highly colored. We presume that under such conditions both Cu^+ and Cu^{2+} replace Na^+ and produce the observed color centers.

Exchange Characteristics

Kinetics: The rates at which divalent cations exchange with sodium in beta" alumina are generally quite rapid. In some cases, nearly complete exchange occurs in several minutes. Most divalent cations replace a large fraction of the sodium within one hour (Table 5). As is expected, the rates of ion exchange increase with increasing temperature. For example, Hg^{2+} exchange at 300°C is much slower than Cd^{2+} exchange at 600°C. Complete plots of % replacement vs. time for Sr^{2+} [20] are shown in Fig. 1 and for Cd^{2+} and Zn^{2+} [21] are shown in Fig. 2.

Influence of Starting Composition: Recent results [22] with Zn^{2+} indicate that the nature of the ion being replaced in beta" alumina profoundly influences the rate of ion exchange. For example, we have found that Zn^{2+} exchange from $ZnCl_2$ at 500°C is essentially complete after 24 hours if the starting material is Ag^+ beta" alumina. However, if Na^+ beta" alumina crystals are used, about 19% exchange takes place in 16 hours. Insignificant exchange occurs with Li^+ beta" alumina, although this result may be spurious since Li^+ beta" alumina crystals may develop microcracks, as has been reported by Briant [18]. These results are summarized in Table 6.

This intriguing diffusion behavior may be the result of kinetics or thermodynamics. One possibility is that the interdiffusion coefficient of Zn^{2+} is very different with each of the monovalent ions. Widely different interdiffusion coefficients may result from ion-ion interactions, or from the influence that the changing c-lattice parameter has on the diffusion rate of cations leaving or entering the structure.

Another possible explanation is based on the thermodynamics of melt/solid equilibria, as discussed by Yao and Kummer [1]. They found, for example, that the direct exchange of Na^+ in beta alumina by Li^+ in $LiNO_3$ is limited by an unfavorable equilibrium. A small concentration of sodium in molten $LiNO_3$ can sustain a large fraction of sodium in beta alumina. Yao and Kummer also found that the sodium beta alumina/alkali nitrate melt equilibria are different with different alkali nitrates. Ag^+ favors beta alumina; Li^+ favors the molten salt; K^+ approaches ideal behavior.

Following this interpretation, we could suggest that the observed differences in Zn^{2+} replacement for Li^{+}, Na^{+}, and Ag^{+} in beta" alumina can be attributed to a tendency of Ag^{+} ions to favor the melt, and Li^{+} and Na^{+} ions to favor the solid. The partial exchanges observed for Zn^{2+} after 16-24 hours would then be equilibrium states which would not change when samples were reacted for longer times. In fact, the extent of Zn^{2+} exchange increases at longer reaction times. Since our observations indicate that the levels of exchange reported in Table 6 are not equilibrium compositions, we have no evidence that thermodynamics limits the ion exchange reactions. Therefore, we favor the kinetic interpretation and believe that lattice parameter changes or mixed ion effects lie behind the curious exchange behavior we have observed with Zn^{2+} ions. These phenomena deserve further study.

Re-Exchange Experiments: We also have investigated the reversibility of the ion exchange process. Divalent beta" aluminas (e.g., Ba^{2+}, Sr^{2+}, and Cd^{2+}) exchange back to the sodium form when exposed to an $NaCl$-$NaNO_3$ melt under conditions comparable to the original divalent exchanges. Multiple exchanges (e.g., $2Na^{+} \rightarrow Ba^{2+} \rightarrow Sr^{2+}$ and $2Na^{+} \rightarrow Cd^{2+} \rightarrow Ca^{2+}$) proceed without difficulty. In all cases, the crystals remain clear, crack-free, and retain the beta" alumina structure.

Ion Transport

Diffusion: Both qualitative and quantitative diffusion studies have been carried out. The qualitative investigations have been discussed in the section entitled, "Exchange Characteristics". They demonstrate that the divalent ion exchange reactions are generally rapid and that the identity of the ion being replaced in beta" alumina has a large influence on the rate of ion exchange.

Only one quantitative study of diffusion has been attempted [20]. In this work, four crystals of Na^+ beta" alumina were labeled with ^{22}Na and immersed for successive 15 second intervals in molten 1:1 $Sr(NO_3)_2$-$SrCl_2$ at 600°C. After each immersion, the samples were rapidly quenched and their remaining ^{22}Na counted.

The results are shown in Fig. 1. Considering that this experiment was preliminary, the data for the different samples agree rather well. Using Eqn. 1 (in which d is the sample thickness) to describe the diffusion reaction,

$$\text{Eqn. 1:} \quad \%\ \text{Exchange} = (200/d)\int_0^{d/2} \exp(-x^2/4Dt)\,dx$$

a best-fit value of D was found to be 3.4×10^{-5} cm^2sec^{-1} at 600°C. The solid curve in Fig. 1 is the curve calculated from this value of D and Eqn. 1.

When D is converted to conductivity by means of the Nernst-Einstein relationship (Eqn. 2) with

Eqn. 2: $$\sigma T = nq^2D/k$$

$n=5/12\ [5.8\times10^{21}]\ \mathrm{cm}^{-3}$ and $q = 2+$, a σT value of 610 $(\mathrm{ohm\text{-}cm})^{-1}\mathrm{K}$ is calculated at 600°C. The value of σT from conductivity data extrapolated to 600°C is 770 $(\mathrm{ohm\text{-}cm})^{-1}\mathrm{K}$ (see Fig. 3).

The agreement between the diffusion and conductivity data is far better than the diffusion experiment deserves. Nevertheless, it does demonstrate that divalent cations really do diffuse rapidly in beta" alumina and that there is every reason to believe that the ionic conductivities measured for these compounds result from the motion of divalent cations, not of residual sodium ions.

Conductivity: In two other publications we have reported the results of ionic conductivity measurements on single crystals of divalent beta" aluminas. The earlier paper [2] presented data for Ba^{2+}, Sr^{2+}, and Cd^{2+} beta" alumina. The later paper [3] is the product of a far more careful and thorough study of the conductivities of Ba^{2+}, Sr^{2+},

Ca^{2+}, and Pb^{2+} beta" alumina. It confirms the conductivity results previously reported for Ba^{2+} beta" alumina and revises the results for Sr^{2+} beta" alumina. No attempt to repeat the earlier Cd^{2+} beta" alumina measurements has yet been reported. In this review, we will emphasize data from the second paper [3].

All of the conductivity measurements have been made on beta" alumina crystals grown and prepared as described previously in this paper. Each sample had less than 1.0% and typically less than 0.2% residual sodium, as determined by radiochemical analysis. Conductivity measurements were made using blocking electrodes and complex admittance analysis. Complete experimental details are presented elsewhere [3]. Conductivity data for Ca^{2+}, Sr^{2+}, Ba^{2+} and Pb^{2+} beta" alumina along with data for Na^{+} beta" alumina are presented in Fig. 4. Each of these curves represents the average of data from several crystals. The reproducibility of measurements made on different crystals prepared in separate exchanges is excellent. Typical results are shown in Fig. 5 for Sr^{2+} and Pb^{2+} beta" alumina.

Conductivity values at 40°C and 300°C are listed in Table 7. The conductivities for Ca^{2+}, Sr^{2+}, Ba^{2+}, Cd^{2+} at 40°C, while many orders of magnitude higher than for any other inorganic compound, are about 10^4 times lower than that for Na^+ beta" alumina. Pb^{2+} is the surprise. Its conductivity at 40°C is only slightly less than that of Na^+ in beta" alumina. At lower temperatures (0 to -90°C), the conductivities of Pb^{2+} and Na^+ beta" alumina are nearly identical. Because the high conductivity of Pb^{2+} beta" alumina was quite unexpected, the measurements from 40°C to 400°C were repeated on eight different samples. All were consistent with the plot shown in Fig. 4, which actually is the average of the 3 samples measured over the entire temperature range.

The only other systematic study of ionic conductivity in divalent beta" aluminas has been presented by Ni, Tsai, and Whitmore [23]. They measured the ionic conductivities of single crystals of Ca^{2+} and Ca^{2+}-Na^+ beta" alumina and mixed Ca^{2+}-Na^+ compositions in polycrystalline beta" alumina. The polycrystalline measurements were directed toward characterizing the influence of small concentrations of CaO on grain and grain boundary conductivity. They found that Ca^{2+} decreases the conductivity of both the grains and grain boundaries. The polycrystalline results are primarily relevant to the development of sodium beta" alumina ceramics and will not be discussed further here.

The Ca^{2+} beta" alumina single crystals prepared by Ni et al. apparently possessed a different composition than the ones described previously in this review. Their starting composition, $Na_{1.85}Mg_{0.854}Al_{10.15}O_{17}$ contains considerably more Na^+ than the starting composition used by Seevers, Farrington, and Dunn [3]. The resulting transport properties are also different. Ni et al. report lower conductivities for Ca^{2+} beta" alumina than did Seevers et al. (Fig. 6). At 300°C, this difference is approximately one order of magnitude [3.9×10^{-3} $(\text{ohm-cm})^{-1}$ vs. 3.6×10^{-2} $(\text{ohm cm})^{-1}$]. The temperature dependence of the conductivity displays more subtle differences. Although Ni et al. [23] reported Arrhenius behavior, their smaller temperature range (250-450°C) may have indirectly concealed the curvature which was observed in the work of Seevers et al. [3]. These disparities underscore the need for a thorough study of the influence of stoichiometry on conductivity in divalent beta" aluminas.

Ni et al. have also carried out the first conductivity measurements on mixed divalent-monovalent compositions of Ca^{2+}-Na^+ beta" alumina. Fig. 7 illustrates the variation in conductivity at 300°C as a function of increasing Ca^{2+} content. A small concentration of Ca^{2+} quickly dominates the conduction process, so that crystals with a fraction of Ca^{2+} as low as 0.1 have conductivities close to that of pure Ca^{2+} beta" alumina. Ni et al. report that plots of log T vs. 1/T for Ca^{2+}-Na^+ ß" alumina follow Arrhenius relationships between 250° and 450°C, the temperature range over which data were taken, except for the sample of lowest Ca^{2+} content (ca. 1.3 wt% CaO), which shows a curved Arrhenius plot. Their data also show some evidence of the mixed alkali effect, which predicts that the conductivity of the mixed compositions should pass through a minimum as the fraction of Ca^{2+} is increased. If the effect is real at 300°C, it is slight. More measurements, preferably at lower temperatures where mixed ion effects are more pronounced, are needed to understand the behavior of mixed divalent compositions.

In addition to these investigations, some preliminary results have been obtained on the conductivity of Pb^{2+} beta" alumina crystals at the microwave frequency of 9.15 GHz [24]. A cavity perturbation technique, described previously [25], was employed. Absolute conductivity values were difficult to obtain because of errors associated with the filling factor and depolarization constant. Nevertheless, the measurements do accurately determine the temperature dependence of the conductivity (see Fig. 8). In the high temperature region, above about 177K, the conductivity follows an Arrhenius relationship. The activation energy of ca. 0.10 eV which was observed is comparable to values reported for Na^+ beta" alumina (E_a = ca.0.11 eV) at this frequency and temperature region. Below ca. 200°K, a power law dependence was followed. The log σ vs. log T curves for Pb^{2+} beta" alumina indicate a T^3 dependence with a transition to T^2 at 150°K. In contrast, Na^+ beta" alumina crystals display only T^3 behavior until ca. 100°K, at which point the conductivity becomes almost independent of temperature. Strom et al. [26] interpreted a T^2 dependence for Na^+ beta alumina as arising from a quadratic density of modes for energies associated with cooperative ion motions and changes in ion configurations in the beta alumina structure. At the present time, it is not clear whether the temperature dependence of the beta" alumina crystals can be accurately described by this model. Additional work on the microwave and infrared conductivity of the divalent beta" aluminas should be pursued.

Stability of the Divalent Beta" Aluminas

No systematic study of the stabilities of the divalent beta" aluminas has been carried out. All of the compounds studied until now have been prepared by ion exchange reactions from crystals which were originally synthesized as Na^+ beta" alumina. At the temperatures used to carry out the exchanges (500-800°C), the compounds were stable for at least as long as the exchange times, typically 24 hours. The excellent reproducibility of the divalent beta" alumina conductivities measured at lower temperatures (<450°C) suggests that they are at least kinetically stable at these temperatures. The conductivity values are extremely reproducible, even for samples prepared under widely different conditions. There is no indication of hysteresis on heating or cooling. In addition, conductivity values remain constant during extended (24-48 hours) measurements at temperatures between 300 and 400°C.

Actually, there is more stability information available for divalent beta aluminas than for the beta" aluminas. As Table 1 shows, various authors have claimed to have synthesized several divalent beta aluminas directly from alkaline earth oxides and alumina in reactions which proceed above 1000°C. For example, Toropov [6] reported preparing Ba^{2+} beta alumina by fusing $BaCO_3$ with Al_2O_3 at 1830-1850°C. Other compounds which have been reported include Mg^{2+} [9], Ca^{2+} [10], Sr^{2+} [10], and Ba^{2+} [6,10] beta aluminas. Similar experiments with Cd^{2+} and Zn^{2+} are reported [27] to yield the spinel structure. As discussed earlier, the actual structures of many of these compounds, whether of the beta alumina or magneto-plumbite type, are not well established.

A thorough investigation of the solid state reactions of the divalent beta" aluminas is needed if we are to know whether or not some are metastable and transform at high temperatures into divalent beta aluminas, the magneto-plumbite structure, or simpler aluminate mixtures.

Structural Characteristics of the Divalent Beta" Aluminas

Alden et al. [28] have presented preliminary results for the structures of Ba^{2+} and Ca^{2+} beta" alumina. They find that the spatial distributions of the two cations and the locations of the O(5) column oxygens are different in the two structures. Whereas Ba^{2+} ions occupy only the 6c-(BR-type) sites, Ca^{2+} ions occupy both the 6c- and 9d-(mO) sites. O(5) in Ba^{2+} beta" alumina is located at the normal 3b-site. However, in Ca^{2+} beta" alumina, O(5) is distributed over six disordered 18h-sites. The O(5) distribution forms a star-like pattern with points of O(5) density directed toward adjacent mO sites. In addition to this work, preliminary results of an investigation of the structure of Cd^{2+} beta alumina find that Cd^{2+} ions occupy the mO sites and that O(5) is disordered around the normal 3b-site [29].

Presumably, the distributions of the divalent cations and O(5) are strongly influenced by the size of the divalent cation and the c-lattice spacing of the crystal. Table 8 lists the lattice parameters for various divalent beta" aluminas. The c-lattice parameters are plotted as a function of ionic radius in Fig. 9. It is easy to speculate about the crystal-chemical factors which determine the ionic distributions in Ca^{2+} and Ba^{2+} beta" alumina. For example, Ca^{2+} is about the same size as Na^{+} (0.99 A vs.

0.95A in radius). However, its larger charge draws the spinel blocks together and decreases the c-lattice parameter. The resulting distortion of the Al-O5-Al bridges appears to stabilize Ca^{2+} in the mO site. In contrast, Ba^{2+} (1.36A radius) expands the lattice. The Al-O5-Al bonds are stretched and cannot pucker inward to stabilize cations in the mO sites. Perhaps as a result, the Ba^{2+} ions occupy BR-type sites.

More comprehensive structure studies of single crystals of Ca^{2+}, Sr^{2+}, Ba^{2+}, and Pb^{2+} beta" aluminas are nearly complete. They clearly indicate that short range order effects among the M^{2+} ions are closely linked to the ionic conductivities of the compounds. Complete discussions of this work will appear elsewhere [30].

Hydration Reactions of the Divalent Beta" Aluminas

It is well established that many of the beta and beta" aluminas readily absorb water into the conduction planes. The details of these reactions are still unclear. However, we do know that both Na^{+} beta and beta" alumina hydrate; Li^{+} beta alumina absorbs even more water, while K^{+} beta alumina hydrates to a small extent, if at all.

Essentially no investigation of the hydration reactions of the divalent beta and beta" aluminas has been described. Preliminary results suggest that some of the compositions may absorb water into the conduction planes [31]. Additional evidence indicating that divalent beta" aluminas hydrate has been reported by Bates et al. [32]. In Raman studies of divalent beta" aluminas which had been exposed to water vapor, they detected water in the conduction planes of single crystals of Ba^{2+} beta" alumina.

Discussion

The few investigations of the divalent beta" aluminas carried out so far present at least three central concerns: (1) Are the divalent cation beta" aluminas truly ionic conductors of divalent cations? (2) If beta" alumina is such such a good divalent cation conductor, why is beta alumina so poor? (3) Finally, why does Pb^{2+} beta" alumina have such an extraordinarily high ionic conductivity at 25°C? These questions are considered in the following discussion.

With regard to the first, all of the evidence indicates that the divalent beta" aluminas truly are high conductivity solid electrolytes for divalent cations. The diffusion data clearly show that divalent cations rapidly diffuse into the beta" alumina structure. In the single attempt to correlate a calculated diffusion constant (Sr^{2+} at 600°C) with conductivity measurements, the correlation was excellent (see Fig. 3). If residual Na^+ in the divalent beta" alumina samples were the source of their ionic conductivity, then it would be very unlikely that samples prepared at different times with different salt baths would have the same Na^+ concentrations and therefore the same conductivities. Yet, in fact, our conductivities have been reproduced on many different samples. The large anisotropic thermal vibrations observed in the structural studies [28] are also consistent with the interpretation that the divalent ions are responsible for rapid ion transport in the structure. Finally, we have checked for and never found any evidence of electronic conductivity in the pure divalent beta" aluminas discussed in this review. In light of this evidence, we believe that the divalent beta" aluminas are indeed the first general family of high conductivity solid electrolytes for divalent cations.

In considering the second question, at this time we can only speculate why divalent cations diffuse rapidly in beta" alumina but slowly in beta alumina. But, the differences are real. Divalent cation exchange in beta" alumina is much faster than in beta alumina (see Table 4). Although it is possible to prepare pure divalent cation compositions in beta alumina, long reaction times at high temperatures are generally required. In addition, although the conductivities of the divalent beta" aluminas can be measured quite easily, the single attempt so far to measure the conductivity of a divalent beta alumina, the Cd^{2+} form, was unsuccessful. No conductivity greater than 10^{-7} $(\text{ohm cm})^{-1}$, the limit of detection for the technique, was observed from 40° to 400°C [19].

One aspect of these compounds which may be important in explaining their behavior involves the different mechanisms of conductivity in the two compounds. Divalent cation substitution influences the conductivity mechanism in each structure in very different ways.

To make the following discussion clearer, Fig. 10, a schematic diagram which can represent the conduction regions of either beta or beta" alumina, has been included in this paper. Readers interested in more thorough descriptions of the structures of these two compounds are referred to several other publications [1, 33, 34, 35].

Conduction in beta alumina occurs by an interstitialcy mechanism, for which a non-stoichiometric excess of Na^+ is essential. The work of Wang, Gaffari, and Choi [36] predicts that, as the value of x in the general formula for beta alumina, $Na_{1+x}Al_{11}O_{17+x/2}$, approaches zero, the ionic conductivity should decrease dramatically. When x is greater than 0, the formation of interstitial Na^+ ion pairs in adjacent mO sites decreases the activation energy for ionic diffusion. At x=0, all Na^+ are trapped in deep potential wells at BR sites. All of the BR sites are then filled, and conductivity can only occur by a high activation energy vacancy diffusion process involving the aBR and mO sites.

Thus, to preserve the interstitialcy mechanism in beta alumina, it is essential to maintain the ratio of mobile ions to BR sites at values greater than 1. This ratio equals 1 in the formula for stoichiometric beta alumina, $Na_1Al_{11}O_{17}$. The effect of divalent cation substitution for Na^+ is to reduce it below 1. For example, a typical composition of beta alumina, $Na_{1.2}Al_{11}O_{17.1}$, converts to $M_{0.6}Al_{11}O_{17.1}$ upon complete substitution of M^{2+} for Na^+.

Therefore, the most immediate effects of divalent cation substitution in beta alumina are a dramatic decrease in the mobile ion population and the substitution of a vacancy mechanism of diffusion for the interstitialcy mechanism. In the divalent beta aluminas, a fairly large population of BR sites, which are filled in stoichiometric beta alumina, are vacant. The best models advanced to explain the high conductivity of Na^+ beta alumina would predict that, in the divalent beta aluminas, cations are trapped in deep potential wells and that the activation energy for diffusion should be very high [39].

In contrast, ionic conductivity in beta" alumina occurs by a vacancy mechanism. The BR and aBR sites are equivalent in beta" alumina and often referred to as BR-type sites. In the general beta" alumina composition of $Na_{1+x}Mg_xAl_{11-x}O_{17}$, if x=1 all of these sites would be filled by Na^+. In actual compositions of beta" alumina, x is less than 1; a typical value is 0.67. The Na^+ deficit produces vacant BR-type sites, and ionic conduction occurs by vacancy migration.

Divalent cation substitution in beta" alumina increases the total vacancy population. A composition of $Na_{1.67}Mg_{0.67}Al_{10.33}O_{17}$ becomes $M_{0.84}Mg_{0.67}Al_{10.33}O_{17}$. In the former case, 16% of the BR-type sites are vacant, while in the latter, 58% are vacant. Divalent cation substitution does not change the conduction mechanism in beta" alumina, as it does in beta alumina.

Another difference between beta and beta" alumina which may influence their divalent cation diffusion rates involves the interstitial oxygen ions which occur in the conduction region of beta alumina but not of beta" alumina. It is generally accepted that the charge of the excess Na^+ in beta alumina is compensated by these extra oxygens, which occupy mO sites. In contrast, the excess Na^+ in beta" alumina is compensated by substituting a lower valence ion, such as Mg^{2+} or Li^+, for Al^{3+} in the spinel block. The interstitial oxygens in beta alumina may act as coulombic traps for divalent cations. They may be the centers of relatively immobile ion pairs or clusters which block the conduction pathways in beta alumina.

At this time, all we can do is speculate as to why these structures, which are otherwise so similar, are such different hosts for divalent cation diffusion. Much more theoretical and experimental investigation is needed before some understanding will emerge. However, the beta and beta" aluminas are obvious models for attempting to identify the characteristics necessary for fast divalent cation diffusion in a crystalline solid.

The third major question we have raised in this section is that of why the ionic conductivity of Pb^{2+} beta" alumina is so high. Pb^{2+} ions are nearly as conductive in beta" alumina as in aqueous solutions. We first prepared Pb^{2+} beta" alumina primarily because Pb^{2+} ions are the only divalent cations which exhibit significant conductivity in a classical solid, PbI_2. The present results show that the introduction of these ions into the beta" alumina structure does indeed produce exceptional behavior. Pb^{2+} beta" alumina demonstrates that the divalent beta" aluminas are not only reasonable ionic conductors, but that at least one is truly a high conductivity solid electrolyte at moderate temperatures.

The extraordinary conductivity of Pb^{2+} beta" alumina most likely arises from ion-vacancy interactions which critically influence ion transport in the divalent beta" aluminas and in the monovalents as well. The large vacancy concentration and enhanced coulombic repulsion among the mobile ions in the divalent beta" aluminas makes it almost certain that, below some temperature, a highly ordered distribution of ions and vacancies will be established in the conduction regions. For example, the simultaneous occupation of two adjacent BR-type sites by divalent cations should be energetically far less favorable that a distribution in which each divalent cation is surrounded by three vacant BR-type sites. So, it is reasonable to expect that order-disorder reactions, which may occur over a broad temperature range and can be viewed as processes involving the gradual dissociation of bound vacancies to free vacancies, will be very important in understanding conduction in the divalent beta" aluminas.

Analogous order-disorder reactions have already been reported for monovalent beta" aluminas. Recent structural studies with Na^+ and K^+ beta" alumina have shown that the mobile ions tend to become ordered on a 2-dimensional superlattice at temperatures less than 200°C [40]. The degree of order, as indicated by the correlation lengths measured from diffuse x-ray scattering, is related to the activation energy for conduction. An increase in ordering produces a larger activation energy because of long range coulombic interactions among vacancies [41]. There is a transition to a lower activation energy state as the temperature is raised (see Fig. 4) as a result of a decrease in vacancy ordering, as indicated by shorter correlation lengths. The sensitivity of the activation energy to the degree of ordering has been discussed by Wang et al. [39].

Pb^{2+} beta" alumina exhibits non-Arrhenius behavior in much the same fashion as Na^+ beta" alumina (Fig. 4). Furthermore, we suggest [3] that the plot for Ca^{2+} beta" alumina may be just beginning to make the transition to a low activation energy region around 300°C. It is not clear whether Sr^{2+} and Ba^{2+} beta" aluminas will also exhibit transitions at temperatures greater than 400°C. Although diffuse x-ray scattering studies have yet to be reported for Pb^{2+} and Ca^{2+} beta" aluminas, their conductivity behavior suggests that we may expect similar order/disorder models for these materials. The high activation energy regions can be associated with ordered distributions of ions and vacancies in the conduction regions. In the low activation energy regions, these ordered distributions dissociate into highly disordered states. Specific ions will surely differ in the energy difference between the two states, and, therefore, the temperature region over which the transformation occurs.

From this reasoning, we propose that the activation energy for conduction contains two separate components; one related to the dissociation of vacancies from their ordered super-lattice positions and another related to ion migration. At lower temperatures the ordered state prevails, and both components are significant. At higher temperatures, the vacancies are no longer ordered, and the migration energy dominates. The strength of the ion-vacancy interactions determines both the magnitude of the dissociation energy term as well as the temperature region in which the vacancy disorder increases (i.e., the transition between the high and low activation energy regions). According to this model, Pb^{2+} beta" alumina is characterized by weak ion-vacancy interactions. It transforms to the disordered, high conductivity state at relatively low temperatures.

Although this model is qualitative, it does provide some basis for understanding the variations in conductivity observed among the divalent beta" aluminas. It makes specific predictions about order and disorder in the conduction regions which can be tested by structure and diffuse scattering investigations. A number of experiments of this type are currently underway.

Applications and Future Research

The principal applications of the divalent beta" aluminas will probably be in electrochemical devices. These new materials make it possible to prepare an entirely new group of Nernstian-type sensors for various heavy metals. Divalent cation conductors may also be useful in the electrorefining of metals, particularly for preparing very pure metals, and possibly in direct electrorefining from molten salts. This application has already been demonstrated with the monovalent beta aluminas [37]. It is not clear whether divalent ion conductors will be useful for high energy density batteries. Although the alkaline earth metals, for example, are significantly less hazardous to use than the alkali metals, most of the divalent beta" aluminas are significantly lower in conductivity than the monovalent conductors, and the energy densities which can be projected for most divalent systems are not substantially greater than those achieved with the lighter alkali metals. It simply is too early in the investigation of these materials to know whether they will have a major impact on technology. Regardless of their future applications, the divalent beta" aluminas raise an enormous number of fascinating scientific questions. We still know very little about why divalent cation diffusion is so rapid in beta" alumina and so slow in beta alumina. Very few structure investigations have been completed. No NMR investigations have been carried out. Only a few initial experiments using Raman spectroscopy, ESR, EPR, and diffuse scattering measurements are underway.

We do not even know the full range of divalent beta" alumina compositions which can be prepared. Many more forms than those already prepared, including transition metal derivatives as well as lanthanide forms, may be possible. After the pure divalents come the mixed valence compounds, such as Cu^{+}-Cu^{2+}, which may be electronic conductors as well as ionic conductors. Trivalent beta" aluminas may also be possible, although initial attempts to synthesize La^{3+} beta" alumina were not completely successful [19].

We also do not know whether beta" alumina is unique in its support of rapid divalent cation diffusion. Other structures which are good divalent cation conductors may exist. The existence of the divalent beta" aluminas shows that the search for similar materials has at least some chance of success.

The divalent beta" aluminas are exciting materials. They demonstrate that the phenomenon of rapid ionic diffusion in crystalline solids is not limited to Na^+, Li^+, K^+, Ag^+, and a few other monovalent cations and anions. In fact, when conditions are appropriate, a large number of ions from across the periodic chart can diffuse rapidly in a crystalline solid. They also show once again that the beta aluminas, whose properties were first pointed out in the now-classic work of Yao and Kummer, are extraordinary materials. Sufficient information is known about some, such as Na^+ beta alumina, that we may begin to understand the ion-ion and ion-lattice interactions responsible for fast ionic diffusion in the solid state. Other compositions are exciting new materials which offer fresh challenges and continue to expand the field of high conductivity solid electrolytes.

Acknowledgements

The authors are grateful to the Office of Naval Research, Contract No. N00014-81-K-0526, and the National Science Foundation, MRL Program, Grant No. DMR-7923647 for supporting this work. We also appreciate the experimental assistance of R.M. Ostrom, V. Tellkamp, D.L. Yang, R. Seevers, J. DeNuzzio, K. Frase, B. Mani, B. Ghosal, and B. Karcher.

References

1. Y-F.Y. Yao and J.T. Kummer, *J. Inorg. Nucl. Chem.*, *29*, 2453 (1967)
2. B. Dunn and G.C. Farrington, *Mat. Res. Bull.*, *15*, 1773 (1980)
3. R. Seevers, G.C. Farrington, and B. Dunn, submitted to *Journal of the Electrochemical Society*
4. W. Seith, *Z. Phys.*, *57*, 869 (1929)
5. G. Schwab and G. Eulitz, *Z. physik. Chem.*, *55*, 179 (1967)
6. N. Toropov, *C.R. Acad. Sci. URSS*, *I*, 147 (1935)
7. K. Lagerqvist, S. Wallmark, and A. Westgren, *Z. anorg. Chem.*, *234*, 1 (1937)
8. V. Adelskold, *Arkiv Kemi, Mineral. Geol.*, *12A*, No. 29, 9 (1938)
9. W.L. Bragg, G. Gottfried, and J. West, *Z.Kristallogr.*, *77*, 255 (1931)
10. N.A. Toropov and M.M. Stukalova, *C.R. (Dok.) Acad. Sci. URSS*, *24*, 459 (1939)
11. N.A. Toropov and M.M. Stukalova, *C.R. (Dok.) Acad. Sci. URSS*, *27*, 974 (1940)
12. D.B. McWhan, P.D. Dernier. C. Vettier, A.S. Cooper, and J.P. Remeika, *Phys. Rev. B*, *17*, 4043 (1978)
13. D.R. Flinn and K.H. Stern, *J. Electrochem. Soc.*, *123*, 978 (1976)
14. R. Roumieu and A.D. Pelton, *J. Electrochem. Soc.*, *128*, 50 (1981)
15. J.T. Kummer, *Prog. Solid State Chem.*, *7*, 141 (1972)
16. G.C. Farrington and J.L. Briant, *Mat. Res. Bull.*, *13*, 763 (1978)
17. B. Dunn. R. Ostrum, R. Seevers, and G.C. Farrington, *Solid State Ionics*, *5*, 203 (1981)
18. J.L. Briant, private communication
19. B. Karcher, G.C. Farrington, and B. Dunn, to be published
20. J. DeNuzzio, R. Seevers, G.C. Farrington, and B. Dunn, to be published
21. B. Dunn, B. Karcher, and G.C. Farrington, to be published
22. D.L. Yang, unpublished results
23. J. Ni, Y.T. Tsai, and D.H. Whitmore, *Solid State Ionics*, *5*, 199 (1981)
24. R.M. Ostrum, C. Jackson, G. Gruner, and B. Dunn, to be published
25. S.K. Khanna, G. Gruner, R. Orbach, and H.U. Beyeler, *Phys. Rev. Letts.*, *47*, 255 (1981)
26. U. Strom, P.C. Taylor, S.G. Bishopo, T.L. Reinecke, and K.L. Ngai, *Phys. Rev. B*, *13*, 3329 (1976
27. D.J. Dyson and W. Johnson, *Trans. J. Brit. Ceram. Soc.*, *72*, 49 (1973)
28. M. Alden, J.O. Thomas, and G.C. Farrington, *Solid State Ionics*, *5*, 205 (1981)
29. B. Karcher, P. Carroll, and G.C. Farrington, to be published

30. M. Alden, J.O. Thomas, and G.C. Farrington, unpublished results
31. A. McGhie and G.C. Farrington, to be published
32. N. Dudney and J. Bates, private communication
33. C.R. Peters, M. Bettman, J.W. Moore, and M.D. Glick, Acta Crystallogr. Sect. B, 27, 1826 (1971)
34. G.C. Farrington and J.L. Briant, Science, 204, 1371 (1979)
35. M. Bettman and C.R. Peters, J. Phys. Chem., 73, 1774 (1969)
36. J.C. Wang, M. Gaffari, and S. Choi, J. Chem. Phys., 631, 772 (1975)
37. R. Gee and D.J. Fray, Electrochim. Acta, 24, 765 (1979)
38. J.L. Briant and G.C. Farrington, J. Solid State Chem., 33, 385 (1980)
39. J.C. Wang, J.B. Bates, N.J. Dudney, and H.Engstrom, Solid State Ionics, 5, 35 (1981)
40. J.P. Boilot, G. Collin, Ph. Colomban, and R. Comes, Phys. Rev. B., 22, 5912 (1980)
41. J.B. Bates, H. Engstrom, J.C. Wang, B.C. Larson, N.J. Dudney, and W.E. Brundage, Solid State Ionics, 5, 159 (1981)

TABLE 1

Structural Properties of the Divalent Beta Aluminas and Related Compounds

Phase	Formula	Unit Cell Dimensions, A		Ref.
		a	c	
Na Beta	$Na_2O\cdot 11Al_2O_3$	5.58	22.45	1
Mg Beta*	$MgO\cdot 11Al_2O_3$	5.56	22.55	11
Ca Beta*	$CaO\cdot 6Al_2O_3$	5.54	21.83	9
Sr Beta*	$SrO\cdot 6Al_2O_3$	5.56	21.95	9
Ba Beta*	$BaO\cdot 6Al_2O_3$	5.58	22.67	10

* as claimed by original authors.

TABLE 2

Divalent Cation Exchange with Beta Alumina

Starting material	Melt composition	Temp (°C)	Time	%Na Replaced
Na^+beta ~ 1 mm	$PbCl_2$	550	70 hr	86
Na^+beta ~ 1 mm	SrI_2	620	3 days	92
Li^+beta ~ 80 mesh	$LiNO_3/Ca(NO_3)_2$ 1:1	400	4 days	88
Na^+beta ~ 80 mesh	$ZnCl_2$	300	6 days	0
Ag^+beta ~ 1 mm	Zn	720	1 day	100
Na^+beta ~ 1 mm	$FeCl_2$	700	3 days	28
Na^+beta ~ 100 mesh	$MnCl_2$	550	1 day	31
Na^+beta ~ 80 mesh	$CuCl_2$	550	6 days	10
Na^+beta ~ 1 mm	$HgCl_2$	350	14 days	0
Na^+beta ~ 300 mesh	$SnCl_2$	300	6 days	37
Na^+beta ~ 300 mesh	CdI_2	450	3 days	0
Li^+beta ~ 80 mesh	$LiNO_3/Ba(NO_3)_2$ 1:1	495	4 days	21
Ag^+beta ~ 1 mm	Hg	300	3 days	0

(All data from Ref. 1)

TABLE 3

Conditions for Complete Ion Exchange

	Ion	Melt Composition (mole%)	Temperature (°C)	Time (hrs)
*	Ca^{2+}	$CaCl_2$	770	23
	Sr^{2+}	$47\ Sr(NO_3)_2 \cdot 53\ SrCl_2$	550	20
	Ba^{2+}	$62\ Ba(NO_3)_2 \cdot 38\ BaCl_2$	550	20
*	Zn^{2+}	$ZnCl_2$	500	24
	Cd^{2+}	$CdCl_2$	600	20
	Hg^{2+}	$HgCl_2$	300	14 days
	Pb^{2+}	$PbCl_2$	525	20
	Mn^{2+}	$MnCl_2$	650	15

* Using Ag^+ beta" alumina as starting material

(Actual exchanges may take less time than noted.)

TABLE 4

Divalent β/β" Alumina Preparation

Ion	Conditions	% Exchange	
		β	β"
Ba^{++}	$Ba(NO_3)_2/BaCl_2$ 550° 20 hrs	5	100
Sr^{++}	$Sr(NO_3)_2/SrCl_2$ 550° 20 hrs	18	100
Cd^{++}	$CdCl_2$ 600° 20 hrs	100	100

Crystal size: 3 x 2 x 0.2 mm

TABLE 5

Preparation of Divalent Beta" Aluminas

Extent of Exchange after 1 Hour

	Ion	Salt	Temperature (°C)	% Exchange
	Cd^{2+}	$CdCl_2$	600	87
	Pb^{2+}	$PbCl_2$	525	>95
*	Zn^{2+}	$ZnCl_2$	500	40
	Sr^{2+}	$SrCl_2/Sr(NO_3)_2$	550	100
	Ba^{2+}	$BaCl_2/Ba(NO_3)_2$	550	100
*	Hg^{2+}	$HgCl_2$	275	35 (4 hour exchange)

* Using Ag^+ beta" alumina as starting material

TABLE 6

Influence of Starting Material on Zn^{2+} Exchange

Starting Material	Exchange Time (hrs.)	Result
Li^+ beta" alumina	16	<2%
Na^+ beta" alumina	16	10-19% exchange
Ag^+ beta" alumina	24	100% exchange

[$ZnCl_2$ at 500°C; crystal size 2mm x 2mm x 0.5mm]

TABLE 7

Conductivities of Various Crystals at 40°C and 300°C

Crystal	σ at 40°C ($\Omega^{-1}cm^{-1}$)	σ at 300°C ($\Omega^{-1}cm^{-1}$)	E_A (eV)	Ref.
$Na^{+}-\beta''$	1.3×10^{-2}	9.1×10^{-1}	*	38
$Pb^{2+}-\beta''$	4.6×10^{-3}	1.5×10^{-1}	*	3
$Ca^{2+}-\beta''$	3.9×10^{-6}	3.9×10^{-2}	*	3
		3.9×10^{-3}	0.57	23
$Sr^{2+}-\beta''$	2.4×10^{-6}	2.4×10^{-2}	0.57	3
$Ba^{2+}-\beta''$	2.8×10^{-6}	1.9×10^{-2}	0.58	3

* Curved Arrhenius Plot

TABLE 8

Unit Cell Dimensions of the Divalent Beta" Aluminas

Ion	Unit Cell Dimensions(Å)			Ionic Radius(Å)	Ref.
	a	b	c		
Zn^{++}	-----		33.46	0.74	22
Na^{+}	5.61		33.54	0.95	40
Cd^{++}	5.620		33.146	0.97	30
Ca^{++}	5.613		33.270	0.99	30
Hg^{++}	-----		33.77	1.10	22
Sr^{++}	5.610		33.720	1.13	30
Pb^{++}	5.610		33.967	1.20	30
Ba^{++}	5.619		34.084	1.35	30

Figure Captions

1. **Ion Exchange of Na^+ Beta" Alumina with Sr^{++}.**
[Data for four samples shown. Typical crystal size was 1mm x 2mm x 0.2mm. Solid curve is theoretical rate of exchange assuming $D = 3.4 \times 10^{-5}$ at 600°C.]

2. **Ion Exchange of Na^+ Beta" Alumina with Cd^{++} and Zn^{++}.**
[Typical crystal size was 3mm x 2mm x 0.2mm; Zn^{++} exchange in $ZnCl_2$ at 500°C; Cd^{++} exchange in $CdCl_2$ at 600°C.]

3. **Ionic Conductivity of Sr^{++} Beta" Alumina.**
[Solid points are data from conductivity measurements. Cross at 600°C is conductivity calculated with Nernst-Einstein equation from diffusion data.]

4. **Ionic Conductivities of Na^+, Pb^{++}, Ca^{++}, Sr^{++}, and Ba^{++} Beta" Alumina.**
[Na^+ beta" alumina data from ref. 38]

5. **Ionic Conductivities of Sr^{++} and Pb^{++} Beta" Alumina.**
[Length of bar at each temperature indicates spread of data for multiple crystals. Solid lines are least squares fits to average of data. Four crystals measured for Sr^{++}; three for Pb^{++}.]

6. **Ionic Conductivity of Ca^{++} Beta" Alumina.**
[Upper curve from ref. 3; lower curve from ref. 23. Data are taken on samples with different compositions.]

7. **Ionic Conductivity of Mixed Ca^{++}-Na^+ Beta" Alumina at 300°C.** [From ref. 23]

8. **Conductivity vs. Temperature at 9.15 GHz for Single Crystal Pb^{++} Beta" Alumina**

9. **Variation of c Lattice Parameter with Ionic Radius.**
[Na from ref. 40; Hg and Zn from ref. 22; others from ref. 30]

10. **Conduction Region of Beta and Beta" Alumina.**
[Large normal circles are lower close-packed layer of oxygens; large bold circles are column oxygens; Na^+ sites shown as d (Beevers-Ross, BR), mid-oxygen (mO), and b (anti-Beevers-Ross, aBR); Upper layer of close-packed oxygens is not shown, but its orientation determines the crystallographic symmetries of the sites. In beta alumina, the BR and aBR sites are inequivalent. In beta" alumina, they are equivalent.]

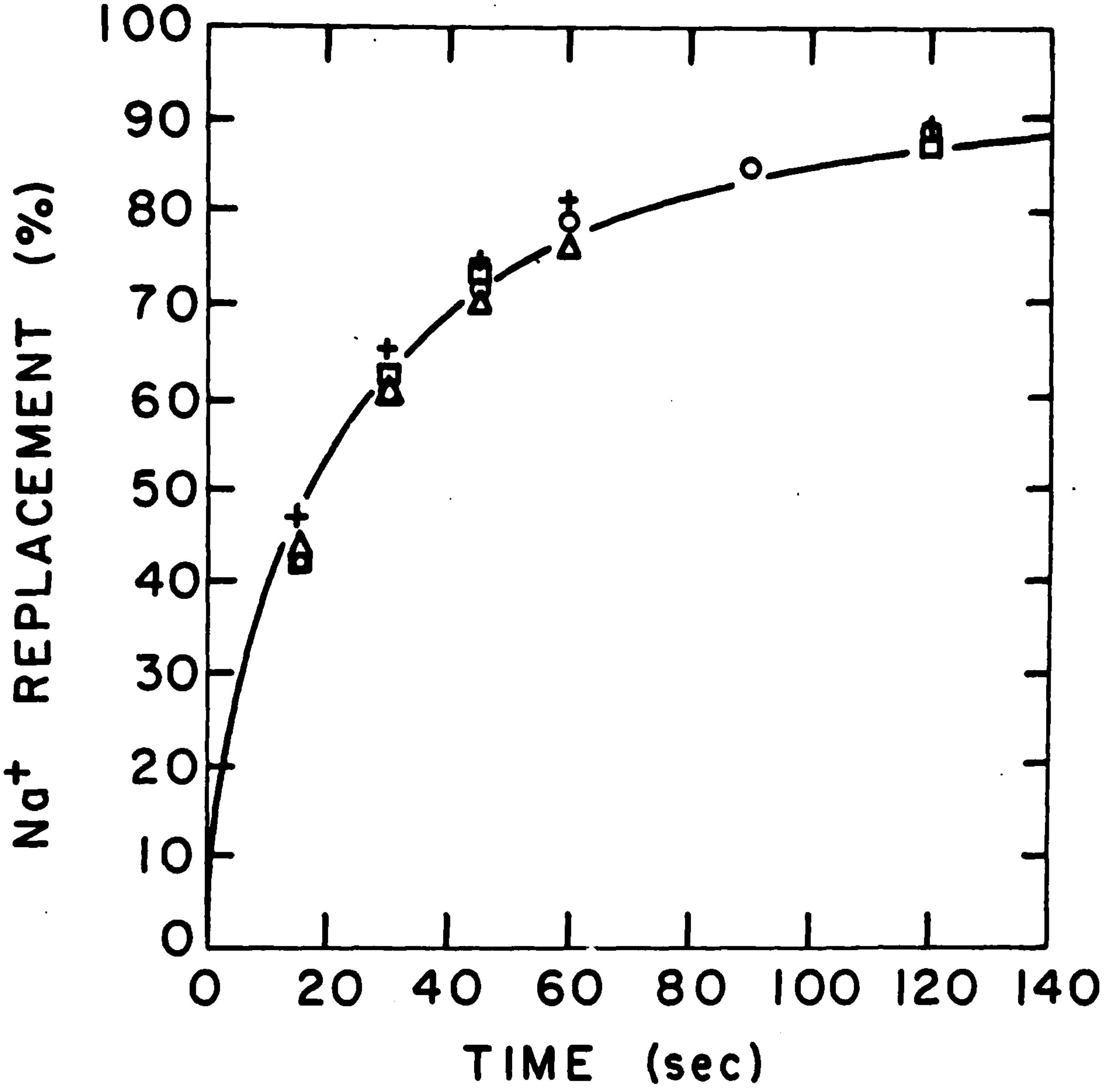

Na+ REPLACEMENT (%)
0
10
20
30
40
50
60
70
80
90
100
TIME (sec)
0
20
40
60
80
100
120
140

Figure 1

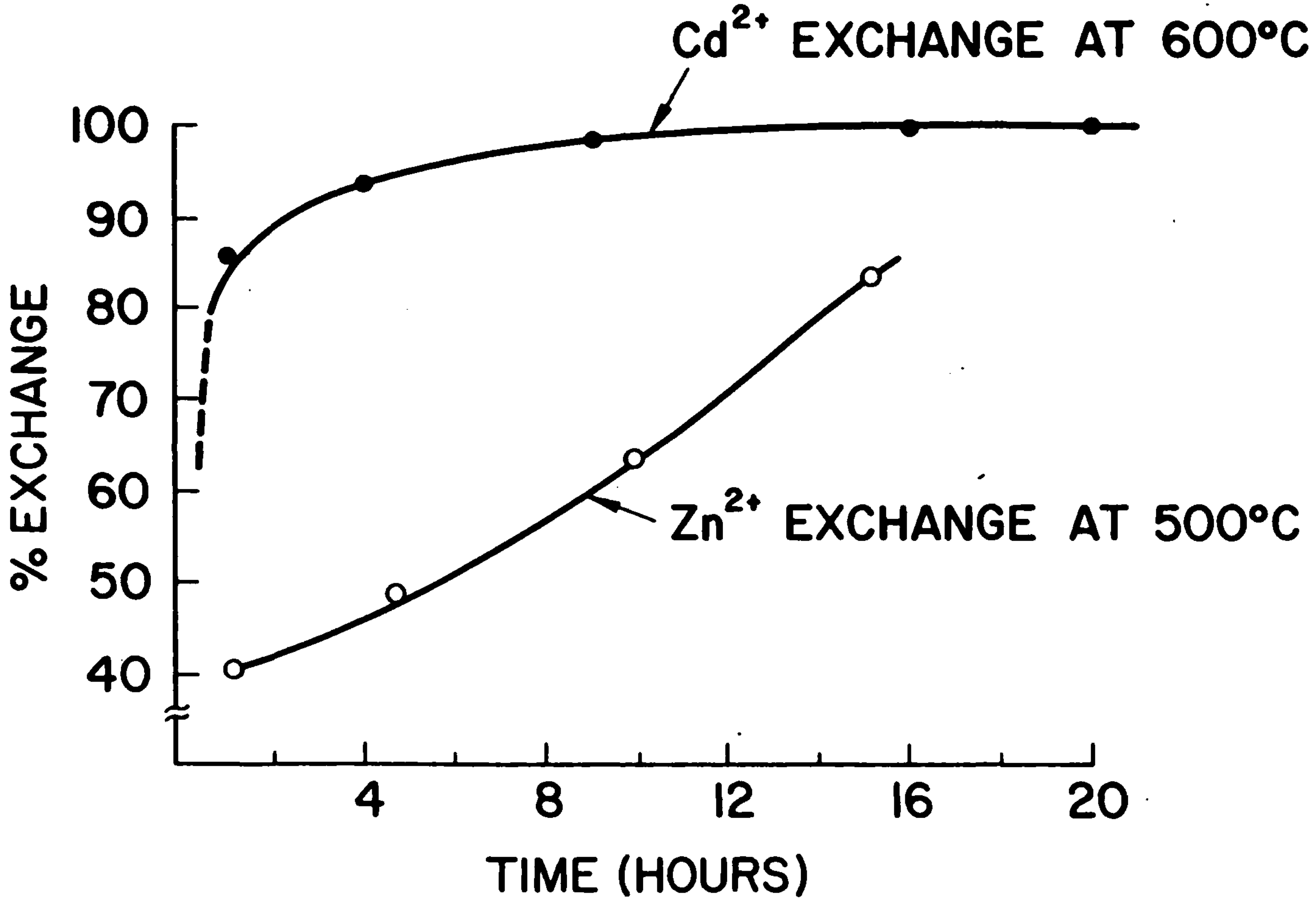

Cd^{2+} EXCHANGE AT 600°C
Zn^{2+} EXCHANGE AT 500°C
% EXCHANGE
100
90
80
70
60
50
40
4
8
12
16
20
TIME (HOURS)

Figure 2

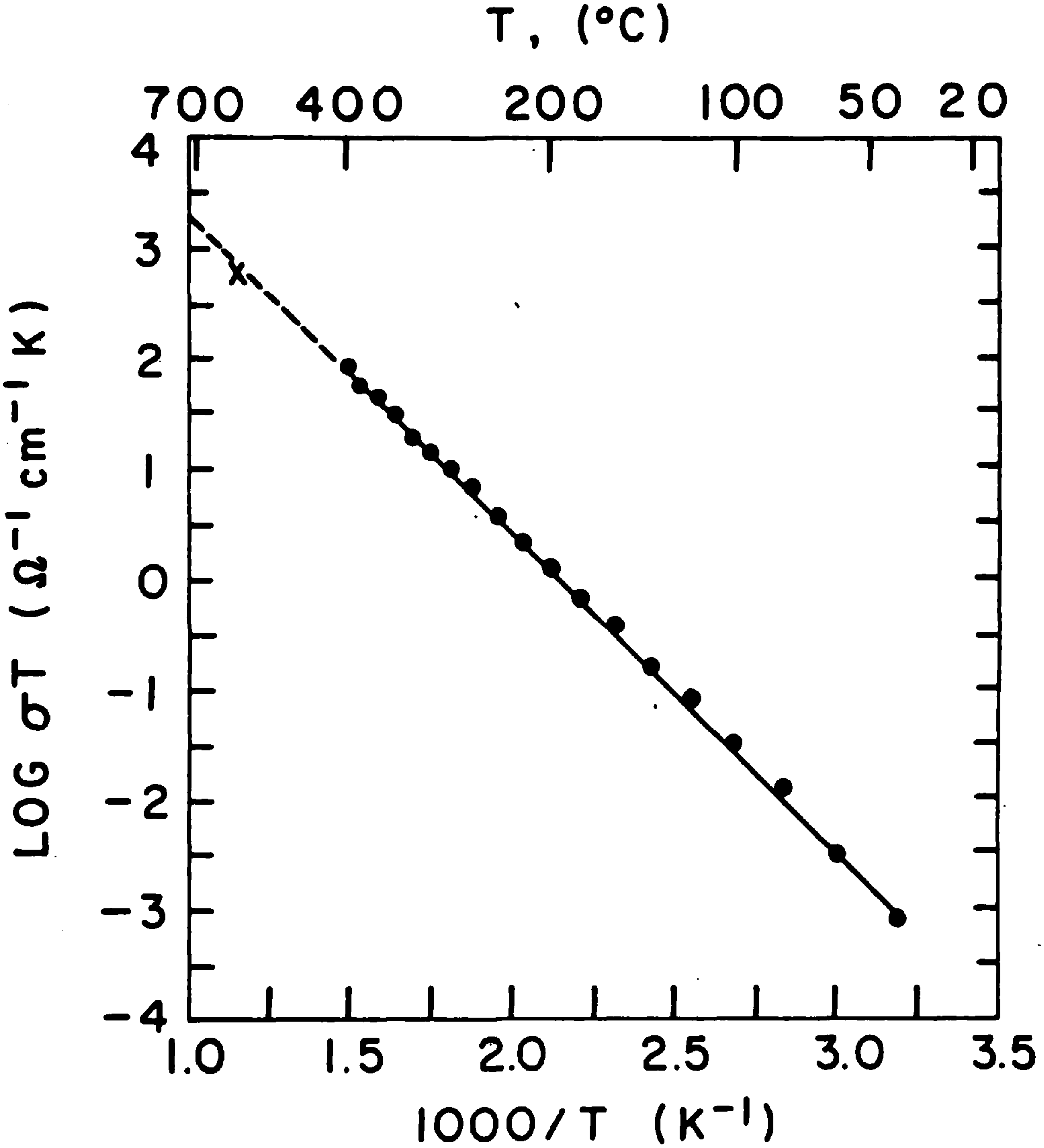

T, (°C)
700
400
200
100
50
20
LOG σT (Ω⁻¹ cm⁻¹ K)
4
3
2
1
0
−1
−2
−3
−4
X
1.0
1.5
2.0
2.5
3.0
3.5
1000/T (K⁻¹)

Figure 3

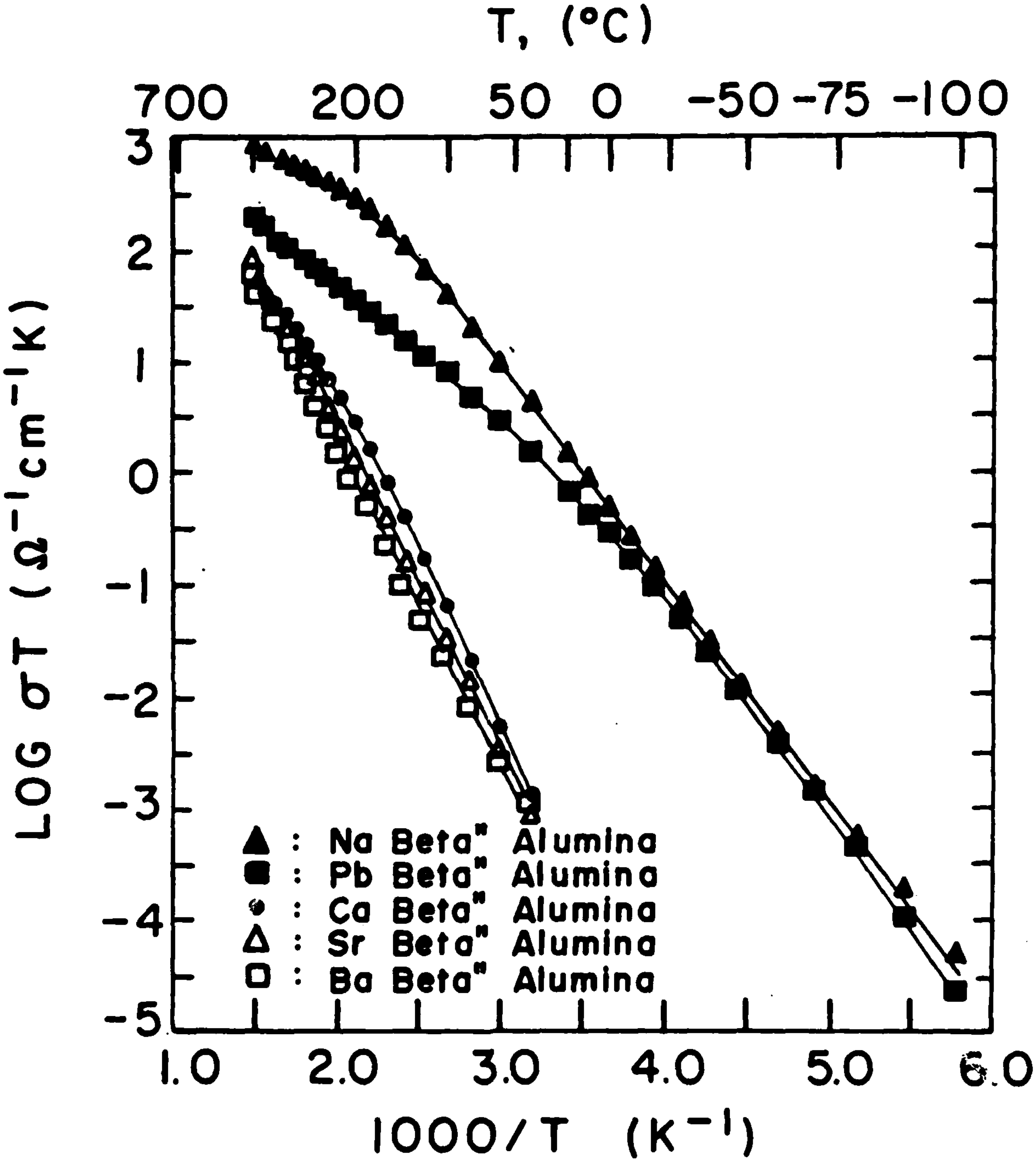
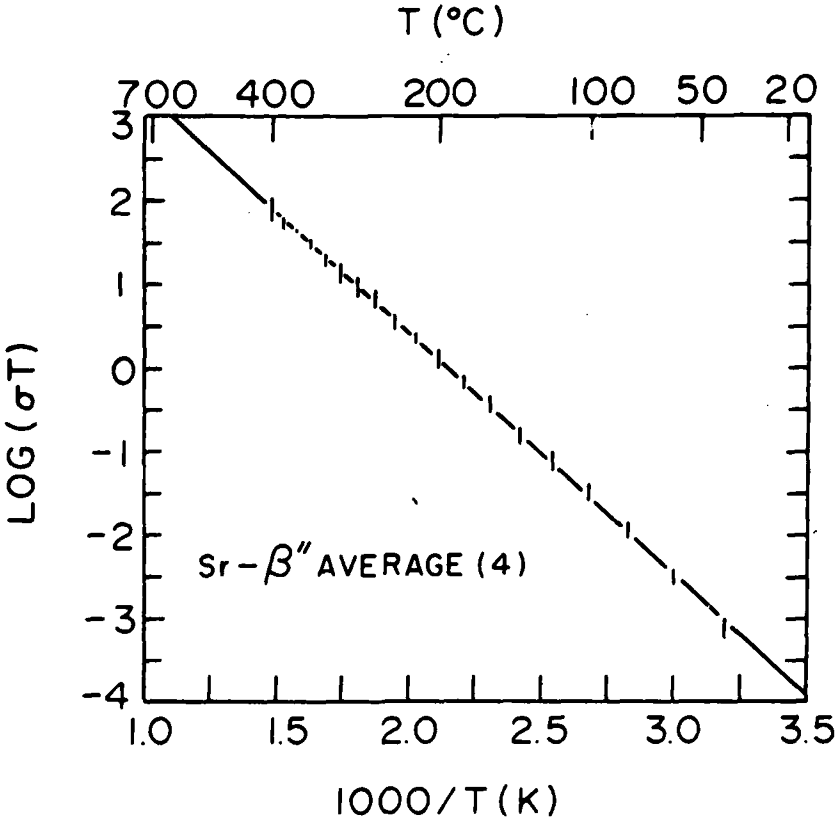

T, (°C)
700
200
50
0
-50
-75
-100
3
2
1
0
-1
-2
-3
-4
-5
LOG σT (Ω⁻¹cm⁻¹K)
1.0
2.0
3.0
4.0
5.0
6.0
1000/T (K⁻¹)
▲ : Na Beta" Alumina
■ : Pb Beta" Alumina
● : Ca Beta" Alumina
△ : Sr Beta" Alumina
□ : Ba Beta" Alumina

Figure 4


T (°C)
700
400
200
100
50
20
3
2
1
0
-1
-2
-3
-4
LOG (σT)
Sr-β″ AVERAGE (4)
1.0
1.5
2.0
2.5
3.0
3.5
1000/T (K)

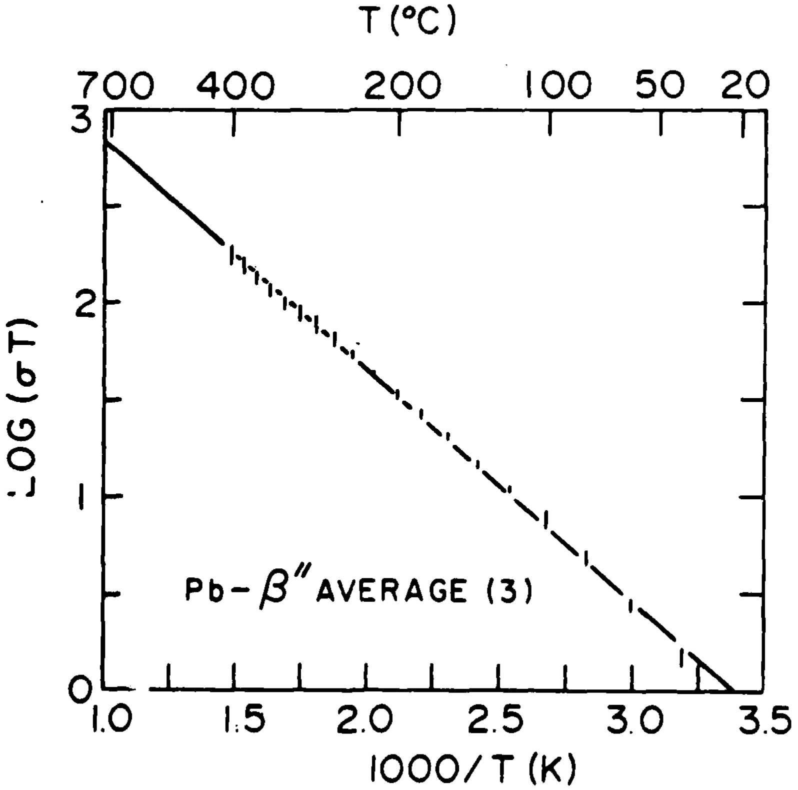

T (°C)
700
400
200
100
50
20
3
2
1
0
LOG (σT)
Pb-β″ AVERAGE (3)
1.0
1.5
2.0
2.5
3.0
3.5
1000/T (K)

Figure 5

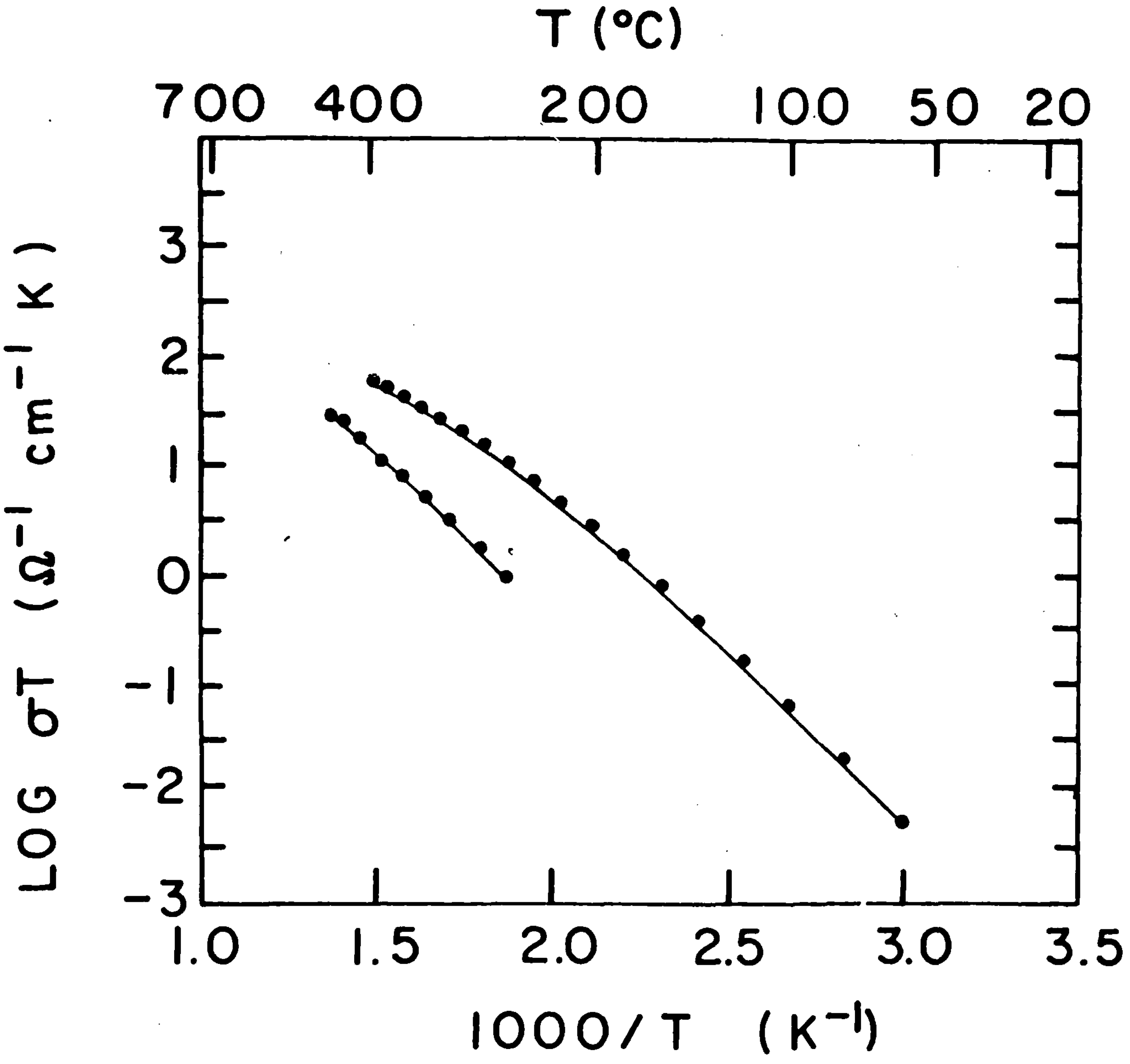

T (°C)
700
400
200
100
50
20
LOG σT (Ω⁻¹ cm⁻¹ K)
3
2
1
0
-1
-2
-3
1.0
1.5
2.0
2.5
3.0
3.5
1000/T (K⁻¹)

Figure 6

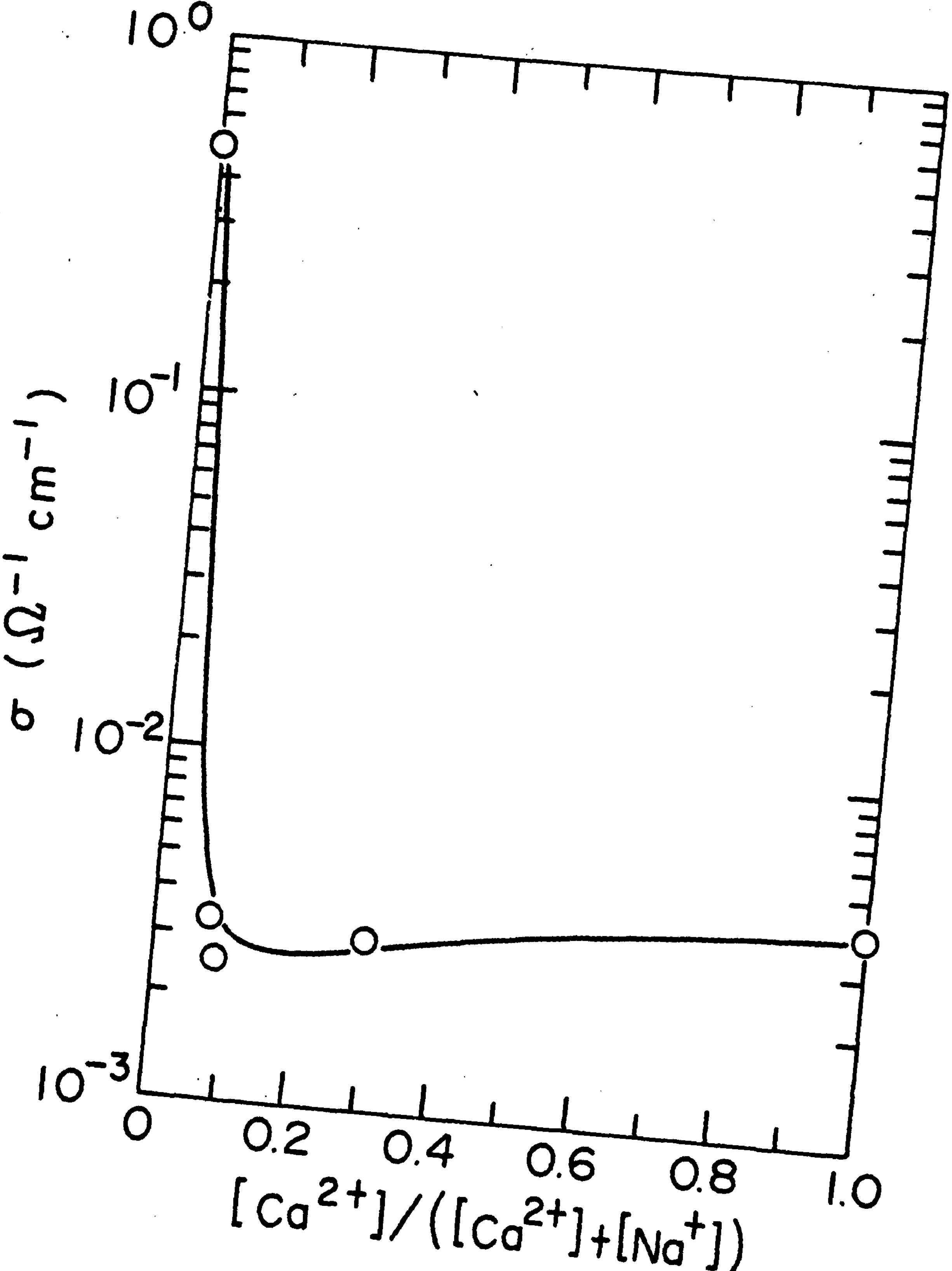


Figure 7

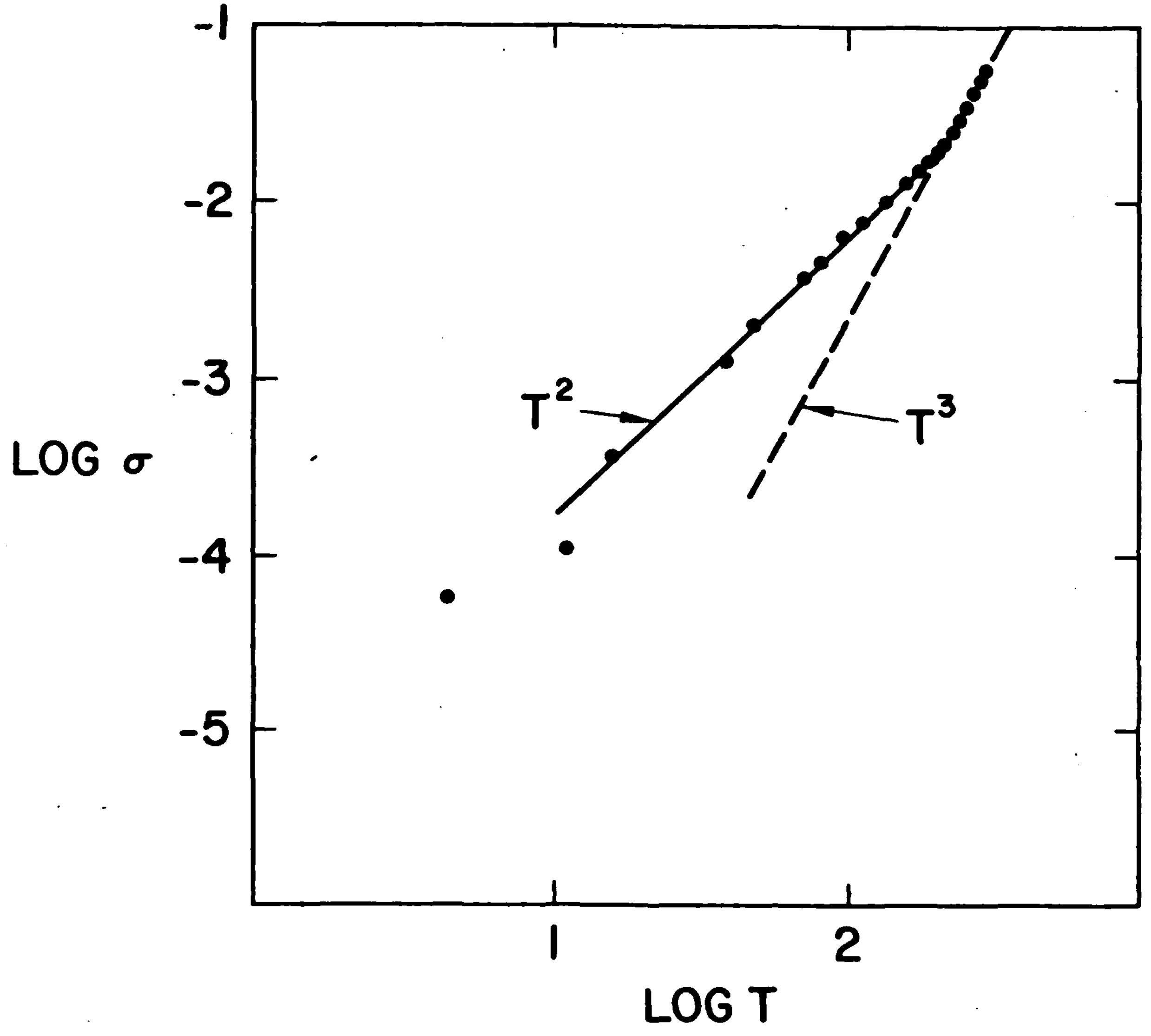


Figure 8

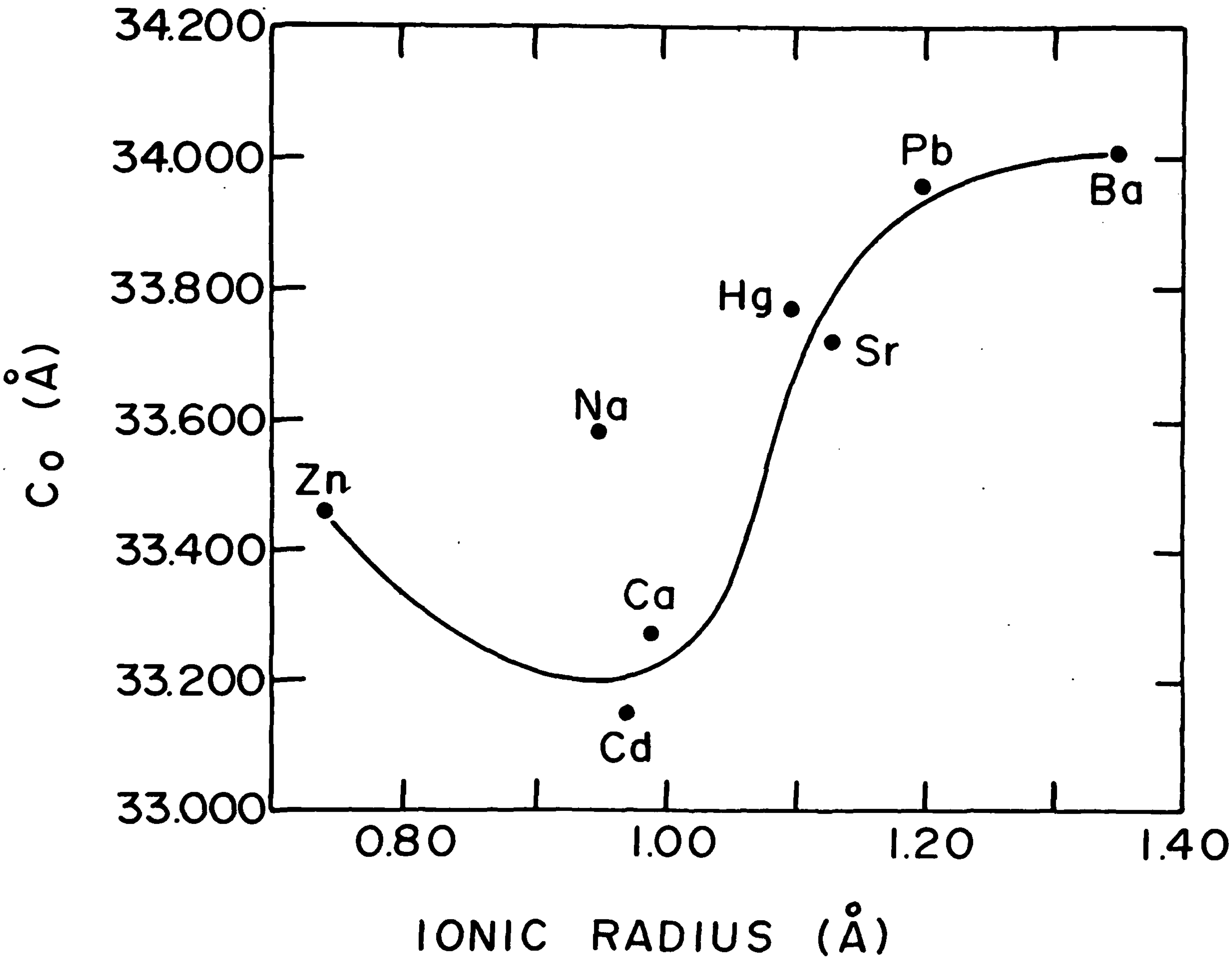

34.200
34.000
33.800
33.600
33.400
33.200
33.000
Co (Å)
0.80
1.00
1.20
1.40
IONIC RADIUS (Å)
Zn
Na
Ca
Cd
Hg
Sr
Pb
Ba

Figure 9

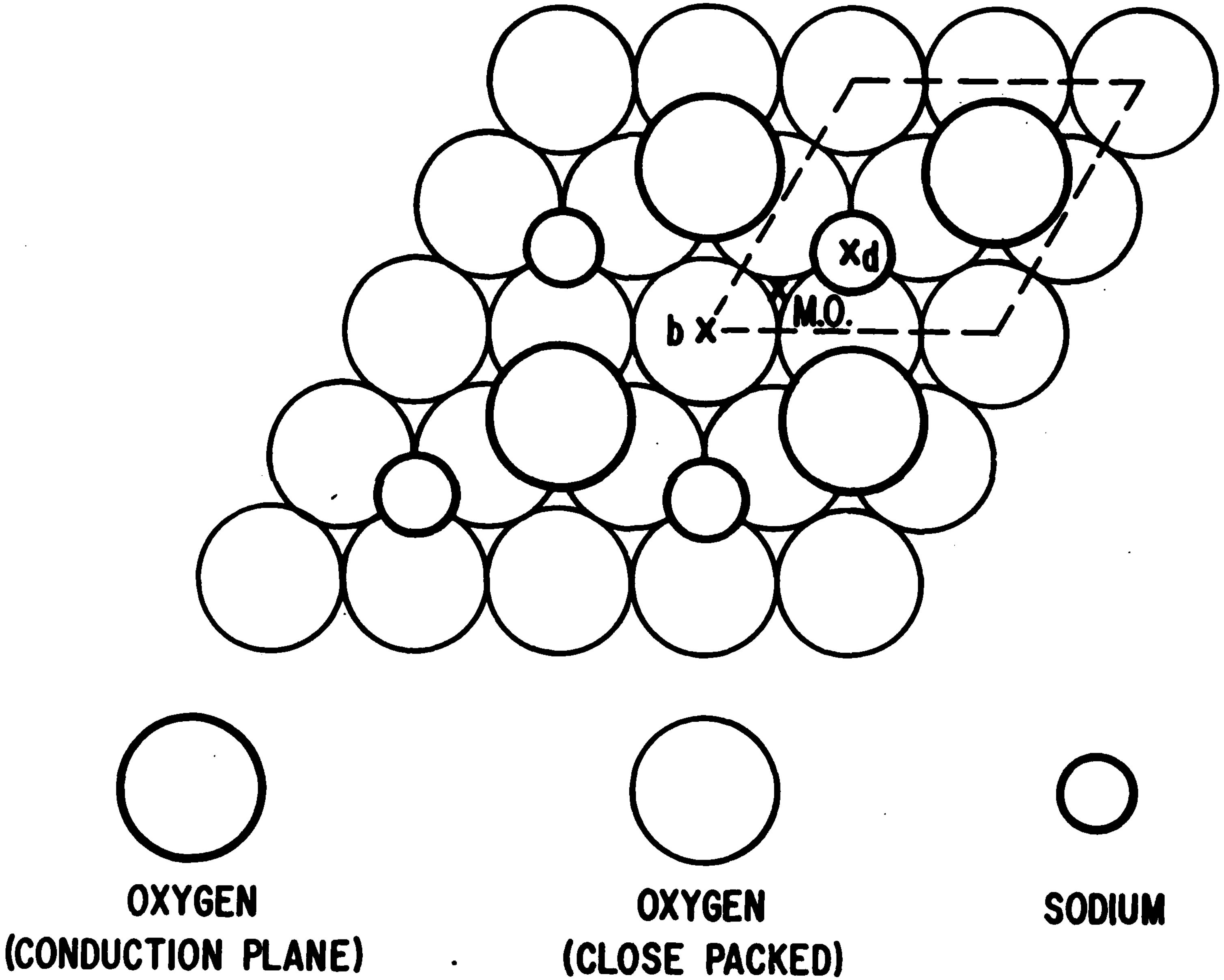

x_d
b x
M.O.
OXYGEN
(CONDUCTION PLANE)
OXYGEN
(CLOSE PACKED)
SODIUM

Figure 10

END