

Electrical Conductivity in Pb(II)- and Na(I)-Pb(II)- β' -Alumina

G. S. ROHRER AND G. C. FARRINGTON

Department of Materials Science and Engineering, University of Pennsylvania, 3231 Walnut St., Philadelphia, Pennsylvania 19104

Received August 21, 1989; in revised form December 13, 1989

Pb(II)- β' -alumina, $\text{Pb}_{0.83}\text{Mg}_{0.67}\text{Al}_{10.33}\text{O}_{17}$, is a divalent isomorph of the well-known fast ion conductor, Na(I)- β' -alumina, and is distinguished by having the highest ionic conductivity of the known divalent β' -aluminas. The electrical properties of this compound are extremely sensitive to the presence of water. Pb(II)- β' -alumina reacts readily with water vapor to form a hydrated compound, $\text{Pb}_{0.83}\text{Mg}_{0.67}\text{Al}_{10.33}\text{O}_{17} \cdot (\text{H}_2\text{O})_x$, in which x varies from 0 to 0.83. Hydration greatly decreases the ionic conductivity of Pb(II)- β' -alumina, and dehydration of the electrolyte in vacuum results in the chemical reduction of Pb(II) cations in the conduction layers and an insulator to semiconductor transition. The composition dependence of the ionic conductivity of anhydrous Na(I)-Pb(II)- β' -alumina has also been studied. Enhanced charge carrier correlation produces a minimum in the ionic conductivity at the composition at which 80% of the Na(I) ions are replaced by Pb(II). This paper describes the results of a study of ionic and electronic conductivity in Pb(II)- and Na(I)-Pb(II)- β' -alumina and the influence of hydration on the properties of the material. © 1990 Academic Press, Inc.

Introduction

Na(I)- β' -alumina is a fast Na(I) conductor with the general formula, $\text{Na}_{1+x}\text{Mg}_x\text{Al}_{11-x}\text{O}_{17}$, in which x is about 0.67. The material has high ionic and low electronic conductivities, and its potential applications in batteries and other electrochemical devices have been studied extensively. Perhaps the most interesting property of Na(I)- β' -alumina is its ability to undergo rapid ion exchange reactions in which the Na(I) content is replaced by a wide variety of mono-, di-, and trivalent cations. Complete or partial exchange occurs with at least 8 monovalent, 11 divalent, and 9 trivalent cations (1, 2). This remarkable ion exchange chemistry makes it possible to synthesize a number of quite unusual β' -alumina isomorphs, many of which

are metastable at higher temperatures and only accessible by ion exchange synthesis. Some of these new materials have possible applications as solid electrolytes (3) and solid state laser hosts (4).

β' -alumina's exceptional ion transport properties originate in its unusual structure, which comprises two parts: the aluminum-oxygen framework and the conduction layers within which the mobile cations reside (see Fig. 1). The framework consists of $\sim 11\text{-\AA}$ -thick layers in which aluminum ions are octahedrally and tetrahedrally coordinated by oxygen ions. These so-called "spinel blocks" are linked by Al-O-Al bonds parallel to the c -axis. The oxygens of the Al-O-Al bonds define relatively open conduction layers in which the mobile cations are found. With the exception of small distortions, the framework of Na(I)- β' -alu-

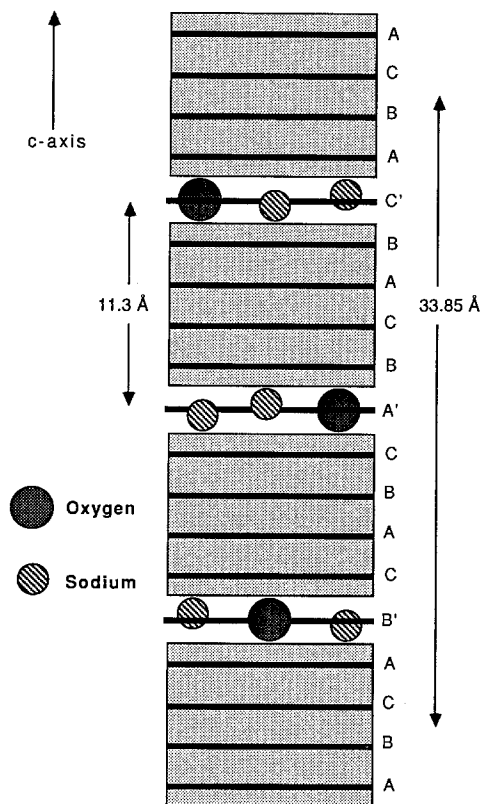


FIG. 1. Schematic illustration showing the structure of the β'' -alumina framework. Close-packed "spinel" blocks are separated by loosely packed conduction layers.

mina is unaffected as different mobile cations move into and out of the structure.

β'' -alumina isomorphs differ principally in the arrangement of mobile cations in the conduction layers. The most frequently occupied cationic sites are the tetrahedral Beavers–Ross-type (BR) site, which is coordinated by four oxygen atoms, and the roughly octahedral mid-Oxygen (mO) site, which is coordinated by six oxygen atoms. These sites are arranged on a nearly two-dimensional honeycomb lattice. The BR sites are at the three coordinate nodes of the lattice and the mO sites are at the mid-points between these nodes. The column oxygens occupy the centers of hexagons

formed by the honeycomb lattice. A schematic projection of the sites in the conduction layer is shown in Fig. 2. In general, the arrangement of the cations in the conduction layer depends on the charge, size, and polarizability of the ions.

The ionic conductivities of the Ca(II)-, Sr(II)-, Ba(II)-, Cd(II)-, Eu(II)-, and Pb(II)- β'' -alumina isomorphs have been reported previously (5–7). All of these compounds have similar conductivities, except Pb(II)- β'' -alumina, which has a room temperature conductivity approximately 10^4 times higher than that of the others. It is the highest conductivity of all of the divalent β'' -alumina isomorphs yet measured. For this reason, Pb(II)- β'' -alumina has received somewhat more attention than other compositions (8–13). We have published two preliminary reports on conductivity in Pb(II)- β'' -alumina. The present paper expands considerably upon these previous findings and describes for the first time the rather dramatic effects of hydration on the

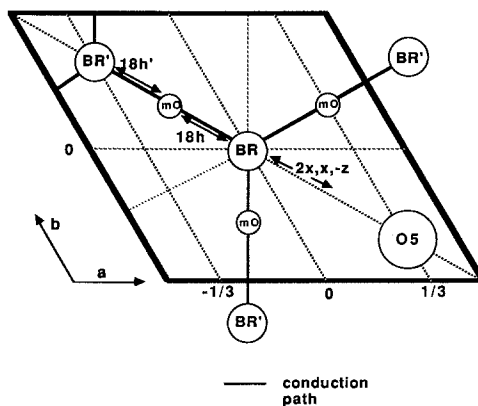


FIG. 2. Schematic diagram showing relevant sites in the β'' -alumina conduction layer. The BR and mO sites are well-defined lattice positions while the $18h$ ($2x, x, z$) is any position along the line that joins the BR and mO positions. Likewise, the $2x, x, -z$ is any position along the line that joins the BR and the O5 positions. Because the mobile ions are free to hop among these sites, the lines connecting the adjacent BR sites are known as the conduction pathways.

electrical properties of Pb(II)- β'' -alumina. In fact, many of the unexplained observations presented in other work have their origins in the curious hydration reactions of this compound.

In a previous study, we reported that thermal history affects the ionic conductivity of Pb(II)- β'' -alumina crystals (12). Crystals that had been cooled very slowly had quite low ionic conductivities, while those cooled rapidly had high conductivities. In addition, slowly cooled samples of Pb(II)- β'' -alumina powder exhibited a two-step endothermic transition when heated, while rapidly cooled powders did not. These results were interpreted as showing that a phase transformation may occur in Pb(II)- β'' -alumina during slow cooling, a transformation that is inhibited during quenching. In the previous work, quite rigorous precautions were taken to maintain anhydrous conditions. However, we have now found that Pb(II)- β'' -alumina is exceptionally hygroscopic, more so than ever expected, and that what previously seemed an indication of a structural phase transition is, in fact, the result of hydration/dehydration.

We have also reported that Pb(II)- β'' -alumina undergoes a reversible coloring reaction when heated in an atmosphere with a low partial pressure of oxygen (13). Samples color upon heating either in vacuum, flowing purified argon, or hydrogen-nitrogen mixtures. An insulator-to-semiconductor transition often accompanies this coloration. This effect also occurs in Ag(I)-, Sn(II)-, and Na(I)-Bi(III)- β'' -alumina, and it now appears that water plays a critical role in bringing it about.

The suggestion that β'' -alumina is sensitive to moisture is hardly unprecedented. It has been known for some time that the properties of various β'' -alumina isomorphs are water sensitive. Thermal analysis has shown that many of the monovalent β'' -aluminas, including the Na(I), Li(I), and Ag(I) forms, react with water (14). In addition,

NMR (15) and IR (16) spectroscopy have been used to determine the arrangement of the water molecules in the conduction planes of these monovalent isomorphs. Somewhat less has been known about the hydration of the divalent isomorphs. Garbarczyk *et al.* (17) have proposed a simple dipolar interaction model to predict the tendency for various divalent β'' -aluminas to hydrate, and a previous investigation from our laboratory provided the first experimental data on the reactivity of the divalent β'' -aluminas with water (18). The present paper is the first of two which describe the hydration reactions of the divalent β'' -alumina isomorphs in detail.

The present paper also has a second focus, that of ionic conductivity in mixed-ion, Na(I)-Pb(II)- β'' -alumina compositions. Generally, the ionic conductivity of a solid electrolyte containing a mixture of two mobile ions is lower than that of the same electrolyte in which either ion is present alone. This phenomenon, known as the "mixed-ion effect," is quite common and well-known with the β - and β'' -aluminas (19, 20). Most previous studies of the mixed-ion effect have examined mixed monovalent cation systems. Mixed monovalent/divalent systems have an added degree of complexity, since the vacancy concentration changes continuously as the chemical composition is altered.

A previous study of conductivity in mixed Na(I)-Cd(II)- β -alumina clearly demonstrated that Na(I)- β -alumina conducts by an interstitialcy mechanism (21). Mixed monovalent/divalent conduction has also been studied in the β'' -aluminas, both experimentally (22) and theoretically (23). The subject of the experimental study was the Na(I)-Ca(II) system. However, the data from that study cover only a narrow range of composition. The theoretical study employed a Monte Carlo simulation technique and focused on the Na(I)-Ba(II) system. Unfortunately, little similarity was found

between the experimental and the simulated results. In this paper, we present more complete experimental results on the ionic conductivity of a mixed monovalent/divalent β'' -alumina, Na(I)-Pb(II)- β'' -alumina. The experimental results are discussed in relation to charge carrier correlation effects in the β'' -alumina system, as originally discussed by Sato and Kikuchi (24).

Experimental Procedures

Single crystals of Na(I)- β'' -alumina were grown by the flux evaporation method (25). The crystals were then doped with ^{22}Na , a radioactive tracer used to determine the extent of subsequent ion exchange. Most ion exchange reactions were carried out in molten PbCl_2 in air between 500 and 550°C. Ion exchange was considered complete when a sample showed the expected weight change and no residual ^{22}Na could be detected. Partially exchanged samples were prepared by two methods. The first, in which a crystal was briefly immersed in molten PbCl_2 , yielded crystals with moderate concentrations of Pb(II). However, exchange occurs so rapidly that an alternate method was necessary to achieve very low levels of Pb(II). In this method, crystals were buried in solid PbCl_2 and heated to 350°C, below the melting point of the salt. Because exchange occurs more slowly at low temperatures in the vapor phase, this method provided greater control over the exchange process. The compositions of partially exchanged samples were determined from the change in the ^{22}Na activity. All of the partially exchanged crystals were annealed in air at 500°C for at least 8 hr to homogenize the distribution of Pb(II) and Na(I) ions.

Some of the fully exchanged single crystal samples were crushed with an alumina mortar and pestle to prepare powders for thermal gravimetry (TG) and differential scanning calorimetry (DSC) measurements.

The powders were sieved to select particles between 40 and 150 μm in size. Samples used for the TG/evolved gas (EG) analysis measurements weighed 40 to 90 mg, and DSC samples weighed 10 to 14 mg. All TG experiments were made using a DuPont 951 TGA microbalance controlled by a Model 990 thermal analyzer. A V-G Micromass PC mass spectrometer system equipped with a silica capillary inlet attachment was used to analyze the gases evolved from samples in the TG cell. This mass spectrometer system continuously measured the partial pressures of O_2 , H_2O , CO_2 , N_2 , and Ar over a sample during thermal decomposition. Calorimetric measurements were made using a DuPont DSC controlled by a Model 990 thermal analyzer. Gases for the TG experiments were flowed at the rate of 150 cm^3/min . "Wet" gases were obtained by bubbling gas through distilled water, and "dried" gases were obtained by passing the gas over CaSO_4 . All DSC measurements were performed in nitrogen flowing at 10 cm^3/min .

Samples were hydrated in the following way. First, a sample was heated in the TG cell until the weight became constant at 500 to 550°C. This was considered the "dry" weight. Next, it was cooled to room temperature at 0.5°C/min in flowing wet gas. Typical weight gains were 2% of the total dry weight. Finally, a portion of the sample was decomposed in the TG cell at 10°C/min in a flowing inert atmosphere in order to analyze the evolved gas. Other portions were decomposed in the DSC cell at 10°C/min in nitrogen to measure the enthalpy of dehydration.

AC impedance spectroscopy was used to measure the ionic conductivity of single crystals of Pb(II)- and Na(I)-Pb(II)- β'' -alumina. Single crystals were cut into rectangular slabs with dimensions approximately 0.2 \times 0.3 \times 0.025 cm. Blocking gold electrodes were sputtered onto two opposing faces of each sample, perpendicular to the

conduction layers. Silver paint was applied on top of the gold to ensure good contact with the platinum electrodes of the spring-loaded conductivity cell. Pure, dried argon was passed through the cell during the entire measurement. Impedance data were collected with an automated impedance measurement system consisting of a Hewlett-Packard 4192A LF impedance analyzer and a Micristar temperature controller, both of which were controlled by a Hewlett-Packard 9000 computer. At each temperature, the impedance was measured from 100 Hz to 13 MHz.

The conductivity experiments were carried out under a variety of conditions. Anhydrous measurements were made in a closed quartz cell through which dry argon was passed at less than 10 cm³/min. As the result of the low partial pressure of water vapor in the gas, the slow flow rate, and the small surface to bulk ratio of the monocrystals, no detectable water was absorbed by the single crystals during these measurements. Crystals treated in this way are referred to as "anhydrous" throughout this paper. Other measurements were carried out with a cell with one end open through which dry argon was passed at approximately 150 cm³/min. Samples in the open cell configuration were found to hydrate slowly and are referred to as "partially hydrated" in this paper.

Conductivity measurements were made during a variety of temperature/time profiles. The first involved partially hydrated samples with significant but undetermined concentrations of intercalated water. Samples were cooled in 20°C steps from 400° to 100°C and annealed at each temperature for 5 hr or until a constant value for the conductivity was observed.

The second treatment involved measuring the conductivity of samples at selected temperatures following quenching from a high temperature. Initially, a sample was heated at 400°C for 2 hr. Repeated measure-

ments showed the conductivity to be constant at this temperature. After this high temperature annealing step, the crystal was quenched to room temperature by removing it from the furnace and placing it directly on a cool surface. Afterwards, it was reheated to an intermediate temperature. The conductivity was measured periodically at the intermediate temperature until a constant value was observed. This entire sequence, starting with the high temperature annealing, was then repeated with a different intermediate annealing temperature for the last step.

Measurements were also made while samples were cooled in a cell under anhydrous conditions, typically from 400°C to room temperature in 25°C steps. Samples were annealed for 10 min at each temperature prior to measurement. All measurements of the mixed Na(I)-Pb(II) samples were carried out using this temperature profile and anhydrous conditions. Pure Na(I)- β'' -alumina as well as fully exchanged Pb(II)- β'' -alumina were also measured under anhydrous conditions.

All of the ionic conductivity measurements were obtained with clear, colorless, crack-free crystals. However, some crystals were deliberately colored by vacuum heating in order to study their electronic conductivity. In this process, crystals were sealed in evacuated quartz ampoules and heated above 600°C for several hours. The ampoules were then quenched to room temperature. Other samples were colored in flowing, purified argon and in forming gas (15% H₂/85% N₂). Some samples were pre-treated at high temperatures in O₂ to dry them carefully and test the importance of water to the coloring reaction. The conductivity data discussed in this paper were obtained only from vacuum-heated samples.

Electronic conductivities were determined from impedance spectra obtained using either a Solartron 1250 or 1174 frequency response analyzer controlled by a

Hewlett-Packard Series 9000 computer. Contacts to the crystals were made in the same manner as for the ionic conductivity measurements. Conductivity was measured from 1 mHz to 65 kHz. Because ionically blocking electrodes were used, no ionic conductivity should have been possible at low frequencies. Therefore, the constant, low frequency, phaseless component of the conductivity was taken to be the electronic component. Although most crystals were measured above room temperature, one was measured from 77 to 300 K. The low temperature measurement was carried out in an Oxford Instruments liquid nitrogen cryostat. Measurements above room temperature were made in dried, purified argon.

Powder diffraction patterns were obtained from finely ground samples using a sealed tube ($\text{Cu}_{K\alpha}$) Rigaku powder diffractometer operating at 50 kV and 40 mA. Hydrated powders were prepared by slow cooling in a wet gas. The anhydrous sample was quenched from 500°C before pulverizing.

Results

A thermogram for the hydration of $\text{Pb(II)-}\beta''\text{-alumina}$ is shown in Fig. 3. The sample increased in weight by 1.9% between 350 and 150°C to produce a final composition of $\text{Pb(II)}_{0.83}\text{Mg}_{0.67}\text{Al}_{10.33}\text{O}_{17} \cdot (\text{H}_2\text{O})_{0.78}$, comparable to that observed with many other samples. In each case, anhydrous $\text{Pb(II)-}\beta''\text{-alumina}$ absorbs nearly one H_2O per Pb(II) cation. Figure 4 shows the thermogram for the subsequent dehydration of the sample. A two-step weight loss occurred between 200 and 400°C. The mass spectrometer indicated two increases in the partial pressure of water vapor over the sample that were simultaneous with the two weight losses. The partial pressures of the other four gases monitored during the experiment remained constant. From this we have concluded that the increase in weight during cooling in a wet gas and the weight loss observed during heating in a dry gas are the result of the intercalation and deintercalation of water, respectively.

Figure 5 shows the DSC trace for the de-

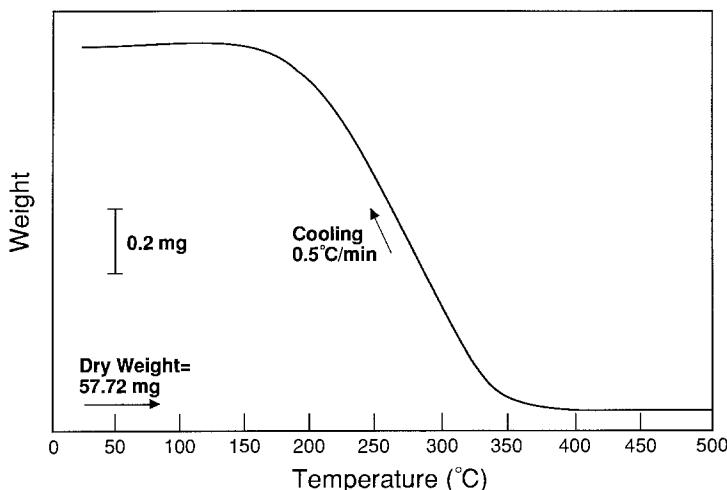


FIG. 3. Thermogram demonstrates that $\text{Pb(II)-}\beta''\text{-alumina}$ hydrates when cooled slowly in a wet gas.

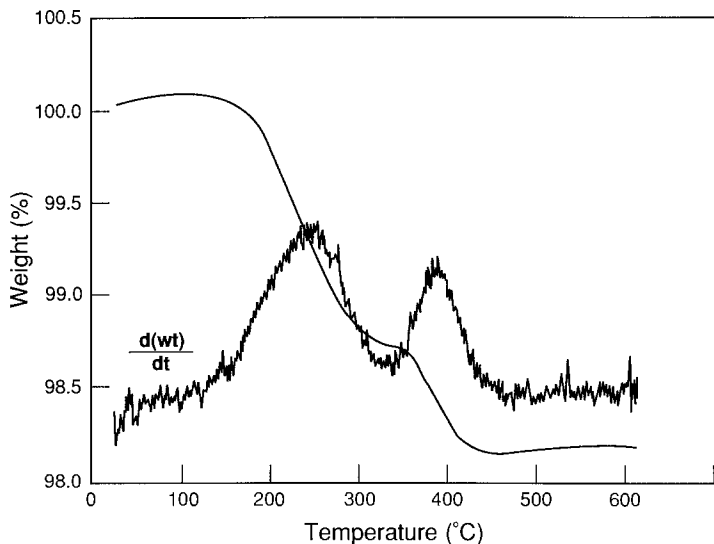


FIG. 4. This thermogram shows the thermal decomposition of hydrated Pb(II)- β'' -alumina. Two weight loss steps are revealed in the decomposition.

hydration reaction of Pb(II)- β'' -alumina heated at $10^\circ\text{C}/\text{min}$ in dry nitrogen. An endothermic transition occurs simultaneously with each weight loss and increase in water vapor pressure. The average binding energy for the water in the lattice was found to be 0.83 eV per water molecule. The binding energy for the first peak is 0.79 eV, and that of the second peak is 0.90 eV. As expected, the binding energy of the water evolved at

higher temperature is larger than that evolved at lower temperature.

An Arrhenius-type plot for the ionic conductivity of Pb(II)- β'' -alumina is shown in Fig. 6. The sample with the lowest conductivity had been slowly cooled in humid argon. It was annealed for at least 5 hr at each temperature before the conductivity was measured. A second data set was obtained from the same crystal by making measure-

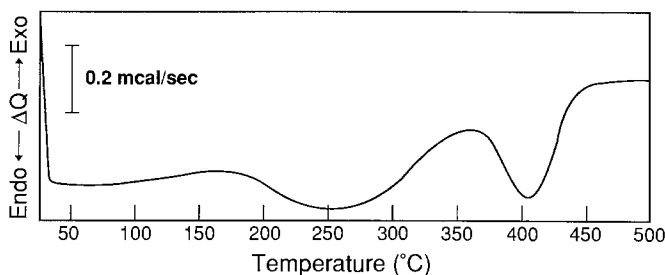


FIG. 5. DSC trace of Pb(II)- β'' -alumina shows that water is evolved in two steps during the dehydration.

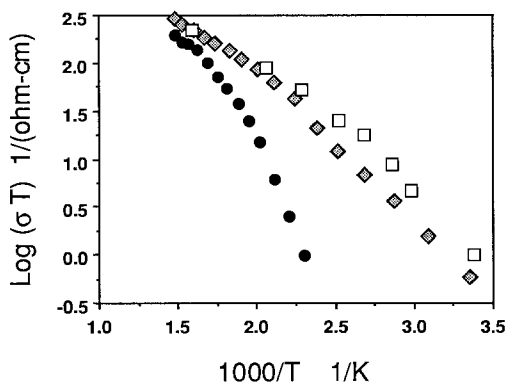


FIG. 6. Arrhenius plot for the ionic conductivity of Pb(II)- β'' -alumina. \square , Ionic conductivity of a crystal rapidly cooled from 400°C before measurement. \diamond , Ionic conductivity of a crystal cooled in the anhydrous configuration. \bullet , Ionic conductivity of the crystal used for \square , cooled very slowly in the hydrous configuration.

ments at selected temperatures immediately following quenching from 400°C. A third data set, which produced conductivity values only slightly lower than the second, was obtained from a crystal cooled under anhydrous conditions. In a separate experiment, a sample was first quenched from 400°C and then held isothermally at 160°C in a cell in wet gas. The conductivity of the sample as a function of time is shown in Fig. 7. The observed decrease in conductivity can be reversed by reheating the sample to 400°C.

Figure 8 shows the low temperature variation in the electronic conductivity of a sample that had been vacuum annealed for 8 hr at 650°C in a quartz tube with an air pressure of 8 μ m Hg. The conductivity increases with increasing temperature, but the Arrhenius-type plot is not linear. The activation energy for conduction is very small, but increases continuously with temperature. The electronic component of the conductivity of the colored samples varied greatly from sample to sample, the upper limit being approximately 5×10^{-3} (Ω -cm) $^{-1}$. However, the form of the tempera-

ture dependence was similar from sample to sample. Figure 9 is an Arrhenius-type plot showing both the electronic and ionic conductivities of Pb(II)- β'' -alumina above room temperature. The electronic component of the conductivity clearly is much lower than the ionic conductivity and has a lower activation energy.

Figure 10 shows the ionic conductivity as a function of composition for several mixed Na(I)-Pb(II)- β'' -alumina samples at three temperatures. The experimental composition versus conductivity curve is nonlinear and changes in character somewhat at different temperatures. A rapid drop in conductivity occurs when only a small amount of Pb(II) is added to the crystal, and the conductivity passes through a minimum around the composition at which 80% of the Na(I) has been replaced by Pb(II).

Discussion

This section first discusses the results of the thermal analysis experiments and then their relationship with the ionic and electronic conductivity of Pb(II)- β'' -alumina. Finally, the implications of the variation of the ionic conductivity with composition are considered.

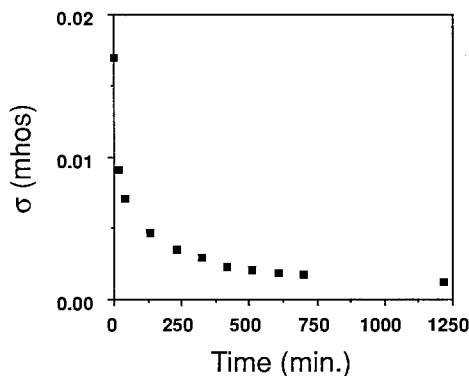


FIG. 7. Ionic conductivity as a function of time for a crystal of Pb(II)- β'' -alumina rapidly cooled and then annealed at 160°C in the hydrous configuration.

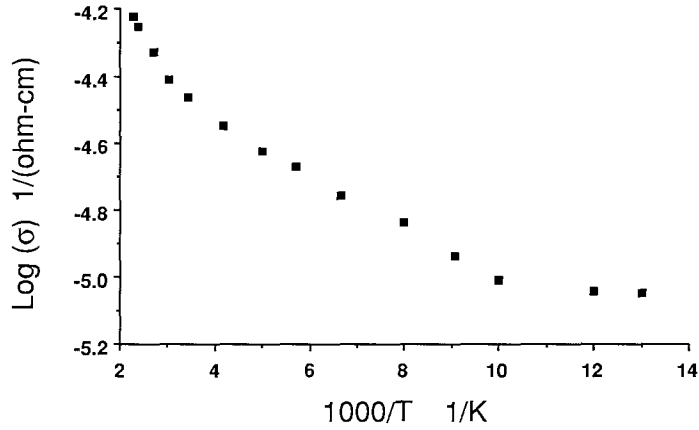


FIG. 8. Low temperature electronic conductivity of vacuum-dehydrated Pb(II)- β'' -alumina.

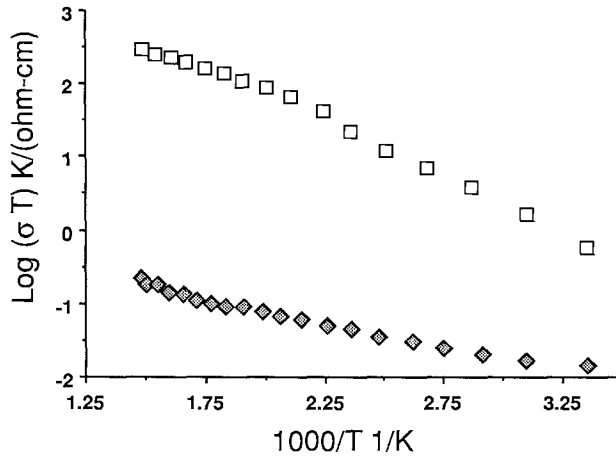


FIG. 9. Comparison of the electronic and ionic conductivity of Pb(II)- β'' -alumina.

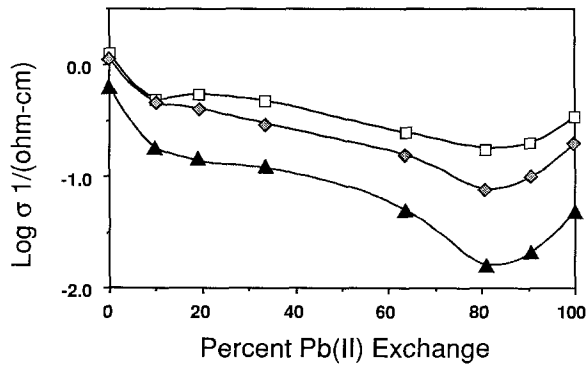


FIG. 10. Ionic conductivity as a function of composition for Na(I)-Pb(II)- β'' -alumina at three different temperatures. \square , 350°C; \diamond , 250°C; \blacktriangle , 150°C.

Thermal Analysis

The thermal analysis experiments clearly demonstrate that water reacts with Pb(II)- β'' -alumina to form a hydrated compound with a well-defined composition. Hydration occurs by the intercalation of water into the conduction planes. The result is an expansion of the β'' -alumina unit cell in the c -direction, as shown by a refinement of peak positions in the X-ray powder patterns of hydrated and anhydrous Pb(II)- β'' -alumina which indicate c -axis dimensions of 34.05(0) Å (hydrated) and 33.82(6) Å (anhydrous). Because the addition of water increases the scattering power of the conduction planes, the intensities of the (0 0 1) peaks increase uniformly as the compound hydrates. Similar water intercalation reactions have been observed with other monovalent and divalent β'' -alumina isomorphs (26).

The process of dehydration is quite interesting because it occurs in two distinct steps, which are apparent in both thermogravimetric and calorimetric analyses. Evolved gas analysis has verified that these steps result from the loss of water. It should be pointed out that, while the amount of water evolved in the first step was always greater than the second, the ratio between the two was not the same in every TG experiment. The calculated binding energy for the water evolved in the low temperature step is 0.79 eV, while that evolved from the high temperature step is 0.90 eV. One possible explanation for this behavior is that there are two separate conduction layer sites or two separate binding mechanisms with different stabilities with respect to dehydration. For example, it is possible that the water evolved in the first step is due to molecular water while that evolved in the second step is due to water bound as (OH)⁻ groups.

The results of additional thermal analysis experiments also show that Pb(II)- β'' -alu-

mina is remarkably hygroscopic. A powder of Pb(II)- β'' -alumina heated at 150°C in air, dried over CaSO₄ and P₂O₅ and flowing at 150 cm³/min hydrates to the composition Pb_{0.83}Mg_{0.67}Al_{10.33}O₁₇(H₂O)_{0.20} within 16 hr. As a result, our preliminary suggestion (12) that the conductivity of Pb(II)- β'' -alumina is strongly influenced by thermal history of the material appears to be wrong. The conductivity measurements in the previous work were made under precisely the conditions just described, and the samples were mistakenly considered to be anhydrous. It now is obvious that Pb(II)- β'' -alumina hydrates under these conditions, and also hydrates in air at room temperature. This was shown by exposing an anhydrous powder of Pb(II)- β'' -alumina (40 to 150 μm particle size) to laboratory air at room temperature for 7 days. At the end of this period, thermogravimetric analysis found the composition to be Pb_{0.83}Mg_{0.67}Al_{10.33}O₁₇(H₂O)_{0.27}.

Larger single crystals also hydrate, though more slowly. A 74-mg single crystal of Pb(II)- β'' -alumina hydrated to a composition of Pb_{0.83}Mg_{0.67}Al_{10.33}O₁₇(H₂O)_{0.27} upon heating for 14 days at 150°C in wet oxygen. In addition, thermogravimetric analysis on this sample showed that it took 90 min to dehydrate at 550°C. Because the surface to bulk ratio is small in large single crystals, the dehydration kinetics are rather slow. The important conclusion from these experiments is that crystals of Pb(II)- β'' -alumina exposed to gases containing even very small concentrations of water vapor hydrate readily and that water may remain in the bulk of the crystal for over an hour even in a sample heated to well above the dehydration temperature.

Effect of Hydration on the Ionic Conductivity

The conductivity of a single crystal of Pb(II)- β'' -alumina cooled slowly in an atmosphere containing water vapor is much

lower than one cooled rapidly or one cooled in an anhydrous atmosphere. Furthermore, the ionic conductivity of the *a* crystal that has been rapidly quenched from 400°C to room temperature in a humid atmosphere is comparable to that observed for same crystal cooled slowly in an anhydrous atmosphere. The thermal analysis data clearly show that Pb(II)- β'' -alumina dehydrates at 400°C and that crystals rapidly cooled from this temperature are at least temporarily anhydrous. The close agreement between the data from quenched samples and from crystals cooled under anhydrous conditions demonstrates that it is possible to keep a single crystal dry even during a slow cooling cycle so long as the atmosphere is sufficiently water-free. This provides confidence that it is possible to determine the true ionic conductivities of β'' -alumina crystals containing Pb(II) without the interference of intercalated water.

Previous reports attributed the decrease in ionic conductivity observed for Pb(II)- β'' -alumina after long annealing or during very slow cooling to a slow process of ion/vacancy ordering. It now appears they were incorrect. The effect can be rather simply explained by a hydration reaction, albeit a particularly enthusiastic reaction that occurs under even nominally anhydrous conditions. The occurrence of a slow ordering process seemed quite reasonable previously, more so because investigations of other β'' -compositions had claimed to see evidence of similar ordering processes (27–29). Now it seems likely that those results were also produced by hydration.

However, it is gratifying to note that the original measurements of the conductivity of Pb(II)- β'' -alumina (6), published 6 years ago, have again been confirmed by the experiments described in this paper. They fortuitously were made under conditions as close to anhydrous as achieved in this work.

Electronic Conductivity in Colored Pb(II)- β'' -Alumina

It has previously been reported that single crystals of Pb(II)- β'' -alumina, when heated in argon or vacuum at 650°C, become colored and undergo an insulator to semiconductor transition. Since Pb(II)- β'' -alumina is extremely hygroscopic, even at room temperature, it was suggested that water might play a role in this reaction. To test this possibility, a single crystal of Pb(II)- β'' -alumina was heated in flowing dried oxygen at 650°C for 3.5 hr. Since thermal analysis data indicate that the hydrated form of the crystal is not stable under these conditions, the sample was most certainly anhydrous. Then the gas supply was switched to argon that had been passed over copper turnings at 485°C to remove any residual oxygen. The crystal remained colorless. It was then partially hydrated by cooling slowly in humid oxygen from 300 to 100°C, and then reheated to 650°C in purified argon. This time the crystal colored. This reaction could be easily repeated and demonstrates that well-dried crystals do not color in purified argon, though partially hydrated crystals do. It was also observed that all crystals, regardless of their pretreatment, color at 650°C in a mixture of 15% H₂/85% N₂ (forming gas).

On the basis of these observations, we propose that during dehydration, water diffusing out of the bulk of a crystal of partially hydrated Pb(II)- β'' -alumina reduces Pb(II) ions at the crystal–vacuum interface. The protons produced presumably bond to structural oxygens forming hydroxyl-like groups to maintain charge neutrality. The reduced conduction layer cations absorb light in the visible range and color the sample. Spectroscopic data are consistent with the presence of Pb₂ centers (30). Similarly, when samples are heated in forming gas, gaseous hydrogen can reduce conduction layer cations directly, so water is not essen-

tial for the reaction to proceed. Coloration during dehydration takes approximately the same time as dehydration. It is important to note that coloration reactions of this type are quite common among transition metal zeolites and occur by a mechanism similar to that proposed here (31, 32).

An alternate explanation for the coloration reaction is that it results from oxygen loss from the β'' -alumina structure, presumably oxygen ions in or nearby the conduction layers. If this were the case, the coloration should occur when the partial pressure of oxygen in the surrounding atmosphere is sufficiently low, regardless of whether or not water is present. The partial pressure of oxygen in the experiment above was fixed and the crystal colored only when partially hydrated, which indicates that water-splitting is the key to the reaction, not structural oxygen loss.

It is clear that Pb(II)- β'' -alumina can develop considerable electronic conductivity under the right (arguably the wrong) conditions and easily become, in ionic terms, a "leaky" electrolyte. It is also clear that seemingly well-intentioned methods of producing Pb(II)- β'' -alumina in a standard state, such as heating at high temperature to remove water, are almost as likely to introduce an entirely new population of electronic and ionic defects as to yield well-standardized samples.

Ionic Conductivity in Na(I)-Pb(II)- β'' -Alumina

The effects of order/disorder transformations and ion-vacancy correlations on the conductivity of various β'' -alumina isomorphs have been discussed by a number of authors (24, 33, 34). As the degree of ion-vacancy order increases, the movement of the diffusing cations is more and more correlated. Simply stated, increased order in the conduction plane of β'' -alumina increases the probability that a vacancy will be surrounded by ions rather than other va-

cancies. If one of the ions jumps into the vacancy, its more probable next jump will be right back where it came from, the vacancy it left behind. Thus, two jumps will have taken place without any net ion transport having occurred. The so-called "correlation factor" is a measure of the relative efficiency with which jumps produce net ion diffusion. As the degree of order on the mobile ion sublattice increases, the tendency to form ordered configurations and the correlation factor increase, and the ionic conductivity can be expected to decrease.

A Monte Carlo computer simulation technique has already been used to study the effect of vacancy concentration on the charge carrier correlation factor and the ionic conductivity in the β'' -alumina system (35). What is particularly intriguing is that the mixed Na(I)-Pb(II)- β'' -alumina system can be used to study the effect experimentally. To make this comparison of model and experiment, we have had to make certain assumptions about the structure of mixed Na(I)-Pb(II)- β'' -alumina, specifically that only the BR and the nearby $2x$, x , $\pm z$ sites are available for occupation by Na(I) and Pb(II) cations. Some structural studies support the assumption (36, 8), while others have found that there is also partial mO occupation (37). Because of the proximity of the BR sites and the $2x$, x , $\pm z$ sites which surround them, simultaneous occupation of adjacent sites is not possible. Together, these sites form a group. Since only one site of each group can be occupied at one time, they are simply referred to here as a BR site. In Na(I)- β'' -alumina, the concentration of vacant BR sites is 17%, while in pure Pb(II)- β'' -alumina, the vacancy concentration is 58%. The vacancy concentration can be experimentally adjusted to any intermediate value by preparing a sample with the appropriate Na(I)/Pb(II) ratio.

As Pb(II) is added to Na(I)- β'' -alumina, at least four characteristics of the material are

affected. First, the dimension of the unit cell increases in the c -direction as the concentration of Pb(II) increases. The precise variation of the size of the c -axis with composition has not been determined. Even if it were known, its effect on the local structure of the conduction layer and the activation energies for hopping of the individual ions is not known. The second factor is an increase in the vacancy concentration. One new vacancy is created for each Pb(II) cation added to crystal. An increase in the vacancy concentration, in the absence of other factors, should increase the ionic conductivity. Third, the average mobility of the charge carriers decreases, since Pb(II) cations of lower mobility are replacing Na(I) cations with higher mobility. This effect should decrease the ionic conductivity. The assumption of the lower mobility of the divalent cation is justified by the lower conductivity of the fully exchanged material. Lastly, the charge carrier correlation factor changes. Increased charge carrier correlation decreases ionic conductivity. This effect is not expected to be a linear function of composition.

The experimental results demonstrate that the gradual substitution of Pb(II) for Na(I) lowers the conductivity of Na(I)- β'' -alumina. The overall decrease in conductiv-

ity across the composition range is most reasonably the result of the increased population of lower mobility Pb(II) ions. If all the ions acted independently and formed an ideal solid solution in the conduction layer, a linear decrease across the composition range would be expected. However, the overall decrease in conductivity observed experimentally is not linear. The most likely explanation for the nonlinear behavior is the variation of the charge carrier correlation factor with composition. Monte Carlo studies by Pechenik *et al.* (35) of the charge carrier correlation factor for equivalent ions on a planar honeycomb lattice support this suggestion. The results they calculated for the composition range explored in our study are shown in Fig. 11. The simulated values were calculated at a relative temperature defined in the original reference. It is therefore somewhat complicated to compare their results to measurements made at an absolute temperature. However, our experimental data follow the predicted characteristic shape over the temperature range investigated, and the qualitative comparison between the two curves is quite good.

The most striking similarity between the calculated charge correlation factor and the observed conductivity data is the minimum

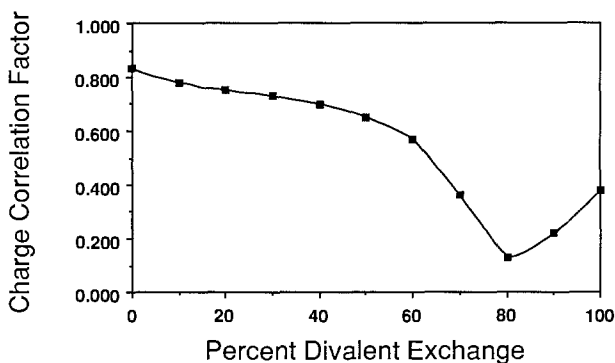


FIG. 11. The charge carrier correlation factor for identical ions on a honeycomb lattice calculated from a Monte Carlo simulation. These data are from Ref. (35).

that occurs at approximately 80% Pb(II) exchange. This composition is the point at which 50% of the BR sites are occupied. Coulombic repulsions would favor the formation of ion-vacancy pairs at this composition. This would naturally lead to increased correlation and decreased conductivity. Another similarity is the gentle downward slope in the region between 10 and 45% Pb(II) exchange. In this region, the conductivity is only weakly affected by composition. One difference between the simulation and experiment is the rapid initial decrease in the actual conductivity at very low Pb(II) concentrations. This drop is not observed in the calculated charge correlation factor. One may speculate that Pb(II) ions surround themselves with vacancies in this compositional region and effectively lower the number of vacancies available to the more mobile Na(I) ions. This may cause a decrease in the conductivity. It is also possible that the mobility of the Pb(II) cations at low Pb(II) concentrations is limited by the dimensions of the lattice, which in this compositional region are presumably closer to those of the pure Na(I) material than the fully exchanged Pb(II) material.

Our results support the conclusion that the two most important factors which determine the compositional dependence of the ionic conductivity in mixed Na(I)-Pb(II)- β'' -alumina are the lower mobility of the divalent ions and the correlated charge carrier motion that results from short range order between the cations and vacancies. Although without a doubt other factors play a role, it appears that the two mentioned here are of principal importance. It should also be pointed out that the results of a recent and more detailed experimental study of ionic conductivity in the Na(I)-Ba(II)- β'' -alumina system by C. A. Lane *et al.* agree qualitatively with our results (38).

We should also mention that our data bear no similarity to the results of a theoretical study of the Na(I)-Ba(II)- β'' alumina

system or an experimental study of the Na(I)-Ca(II)- β'' -alumina system reported in two other papers (22, 23). In one, the conductivities of Na(I)-Ba(II) compositions at 200°C were modeled using Monte Carlo techniques. This model predicted that the conductivities of Na(I)-rich compositions (<20% Ba(II) exchanged) would be higher than the conductivity of pure Na(I)- β'' -alumina. After reaching a conductivity maximum at 20% Ba(II) exchange, the conductivities of the mixed compositions were predicted to decrease as more Na(I) is exchanged for Ba(II), until a conductivity minimum is reached at 100% Ba(II) exchange (23). These predictions bear no resemblance to our observations. The second paper reported results of an experimental study of the Na(I)-Ca(II)- β'' -alumina system showing that the conductivity at 300°C drops by two orders of magnitude between 0 and 10% replacement of Na(I) by Ca(II) (22). However, no data were reported past 30% sodium replacement. Although we observed an initial drop in the ionic conductivity of the Na(I)-Pb(II) system, it was by only a factor of about two at the same temperature. However, the composition of the Na(I)- β'' -alumina crystals used as the starting material in the previous study was different from ours, and the Na(I) ions were exchanged with Ca(II), which is known to be much less mobile in β'' -alumina than Pb(II). In addition, the Ca(II) ions in the Na(I)-Ca(II) material were not uniformly distributed throughout the crystal (23).

Conclusions

The electrical properties of Pb(II)- β'' -alumina are dramatically affected by the intercalation of water. Thermal analysis data indicate that there are two different sites or binding mechanisms for water in the conduction layer. Because the material is extremely hygroscopic, it is difficult to keep it from at least partially hydrating, particu-

larly at temperatures between 100 and 250°C.

Hydration decreases the normally high ionic conductivity of Pb(II)- β'' -alumina. It appears that previous reports attributing the decrease in ionic conductivity observed for Pb(II)- β'' -alumina after long annealing or during very slow cooling to a slow process of ion/vacancy ordering were incorrect. The effect can be rather simply explained by hydration as can reports that other β'' -compositions exhibit ion/vacancy ordering upon slow cooling (27–29).

Vacuum dehydration of Pb(II)- β'' -alumina results in a coloration reaction and an insulator to semiconductor transition. The electronic conductivity produced is at least one order of magnitude lower than the ionic conductivity at room temperature.

The work discussed in this paper has also shown that the composition dependence of the conductivity of mixed Na(I)-Pb(II)- β'' -alumina is governed by the lower mobility of the Pb(II) ions and by the charge carrier correlations of the mobile cations. These results support the findings of previous Monte Carlo simulations of the variation of the correlation factor in β'' -alumina with ion/vacancy population in the conduction planes.

Acknowledgments

This research was supported by the National Science Foundation, Materials Research Laboratory Program, under grant DMR-8519059. Additional support from the Office of Naval Research is gratefully acknowledged. We also appreciated several helpful discussions with Professor Kenneth Poeplemeier of Northwestern University.

References

1. G. C. FARRINGTON AND J. BRIANT, in "Fast Ion Transport in Solids" (Vashista, Mundy, and Shenoy, Eds.), North Holland, Inc. (1977), p. 395.
2. S. SATTAR, B. GHOSAL, M. L. UNDERWOOD, H. MERTWOY, M. A. SALTZBERG, W. S. FRYDRYCH,

- G. S. ROHRER, AND G. C. FARRINGTON, *J. Solid State Chem.* **65**, 231 (1986).
3. T. COLE, *Science* **221**, 915 (1983).
4. G. C. FARRINGTON, B. DUNN, AND J. O. THOMAS, *Cryst. Lattice Defects Amorph. Mater.* **12**, 497 (1985).
5. B. DUNN, R. M. OSTROM, R. SEEVERS, AND G. C. FARRINGTON, *Solid State Ionics* **5**, 203 (1981).
6. R. SEEVERS, J. DENUZZIO, G. C. FARRINGTON, AND B. DUNN, *J. Solid State Chem.* **50**, 146 (1983).
7. B. GHOSAL, E. A. MANGLE, M. R. TOPP, B. DUNN, AND G. C. FARRINGTON, *Solid State Ionics* **9/10**, 273 (1983).
8. J. O. THOMAS, M. ALDEN, AND G. C. FARRINGTON, *Solid State Ionics* **9/10**, 301 (1983).
9. J. TEGENFELDT, M. UNDERWOOD, AND G. C. FARRINGTON, *Solid State Ionics* **18/19**, 668 (1983).
10. W. HAYES, K. KJAER, F. L. PRATT, AND B. SCHONFELD, *J. Phys. C: Solid State Phys.* **18**, L567 (1985).
11. W. HAYES AND F. L. PRATT, *J. Phys. C: Solid State Phys.* **19**, 929 (1986).
12. G. S. ROHRER, P. K. DAVIES, AND G. C. FARRINGTON, *Solid State Ionics* **28–30**, 354 (1988).
13. G. S. ROHRER AND G. C. FARRINGTON, *Solid State Ionics* **28–30**, 1142 (1988).
14. J. GARBARCZYK, W. JAKUBOWSKI, AND M. WASIUCONEK, *Solid State Ionics* **9/10**, 249 (1983).
15. P. L. KUHNS, L. J. RICHTER, AND M. S. CONRADI, *J. Chem. Phys.* **76**, 6 (1982).
16. J. B. BATES, J. C. WANG, N. J. DUDNEY, AND W. E. BRUNDAGE, *Solid State Ionics* **9/10**, 237 (1983), and N. J. DUDNEY AND J. B. BATES, *J. Amer. Ceram. Soc.* **70**, 816 (1987).
17. J. GARBARCZYK, W. JAKUBOWSKI, AND M. WASIUCONEK, *Solid State Ionics* **18/19**, 653 (1986).
18. G. S. ROHRER AND G. C. FARRINGTON, *Mater. Res. Bull.* **23**, 1747 (1988).
19. P. K. DAVIES AND S. CANFIELD, *Commun. Amer. Ceram. Soc.* **69**, C-62 (1986).
20. T. TSURUMI, G. SINGH, AND P. S. NICHOLSON, *Solid State Ionics* **22**, 225 (1987).
21. P. H. SUTTER, L. CRATTY, M. SALTZBERG, AND G. C. FARRINGTON, *Solid State Ionics* **9/10**, 295 (1983).
22. J. NI, Y. T. TSAI, AND D. H. WHITMORE, *Solid State Ionics* **5**, 199 (1981).
23. A. PECHENIK, D. H. WHITMORE, AND MARK RATNER, *J. Solid State Chem.* **58**, 103 (1985).
24. H. SATO AND R. KIKUCHI, *J. Chem. Phys.* **55**, 677 (1971).
25. J. DE NUZZIO, Ph.D. thesis, University of Pennsylvania, 1986.

26. G. S. ROHRER, J. O. THOMAS, AND G. C. FARRINGTON, to be published.
27. G. COLLIN, J. P. BOILOT, PH. COLOMBAN, AND R. COMES, *Solid State Ionics* **18/19**, 663 (1986).
28. M. A. SALZBERG, P. K. DAVIES, AND G. C. FARRINGTON, *Mater. Res. Bull.* **21**, 1533 (1986).
29. F. H. GARZON AND P. K. DAVIES, *Solid State Ionics* **28-30**, 377 (1988).
30. G. S. ROHRER AND G. C. FARRINGTON, *Chem. Mater.* **1**, 438 (1989).
31. L. R. GELLENS, W. J. MORTIER, R. A. SCHOONHEYDT, AND J. B. UYTTERHOEVEN, *J. Phys. Chem.* **85**, 2783 (1981).
32. H. BEYER, P. A. JACOBS, AND J. B. UYTTERHOEVEN, *J. Chem. Soc. Faraday Trans. 1* **72**, 674 (1976).
33. G. E. MURCH AND R. J. THORN, *Philos. Mag.* **35**, 493 (1977).
34. A. PECHENIK, D. H. WHITMORE, AND M. A. RATNER, *Solid State Ionics* **9/10**, 287 (1983).
35. A. PECHENIK, D. H. WHITMORE, AND M. A. RATNER, *J. Chem. Phys.* **84**, 2827 (1986).
36. W. FRYDRYCH, Ph.D. thesis, University of Pennsylvania, 1986.
37. G. COLLIN, J. P. BOILOT, PH. COLOMBAN, AND R. COMES, *Solid State Ionics* **18/19**, 663 (1986).
38. C. A. LANE AND G. C. FARRINGTON, *Solid State Ionics*, in press.