

THE EFFECT OF THERMAL HISTORY ON THE IONIC CONDUCTIVITY OF Pb(II)- β "-ALUMINA

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Pb(II)- β "-alumina is one of several divalent isomorphs of the well-known fast ion conductor, Na(I)- β "-alumina. Although the ionic conductivities of Ca(II), Ba(II), and Sr(II)- β "-alumina are comparable, past measurements have indicated that Pb(II)- β "-alumina has a much higher conductivity. We have found that the ionic conductivity of Pb(II)- β "-alumina is very sensitive to the thermal history of the sample. The conductivity decreases with annealing time following rapid cooling from 400°C. Differential scanning calorimetry results indicate that a structural transformation occurs during the annealing.

1. Introduction

In 1982, Farrington and Dunn [1] reported that all of the mobile Na(I) ions in the fast ion conductor, Na(I)- β "-alumina can be replaced by a variety of divalent ions. In 1983, Seevers et al. [2] reported the ionic conductivity of four of the divalent isomorphs of Na(I)- β "-alumina (Ca(II)-, Sr(II)-, Ba(II)-, and Pb(II)- β "-alumina). Over the temperature range that was measured, the conductivities of Ca(II)-, Sr(II)-, and Ba(II)- β "-alumina are similar. However, the conductivity of Pb(II)- β "-alumina is much higher than the other three. For example, at 100°C the conductivity of Pb(II)- β "-alumina is more than 100 times greater than the conductivity of Ca(II)-, Sr(II)-, or Ba(II)- β "-alumina. In addition to the anomalously high conductivity, the slope of the Arrhenius plot changes near room temperature. Seevers et al. [2] suggest that an order-disorder interaction among the mobile cations and vacancies, which have previously been shown to influence the conductivity [3], may be responsible for this.

To find a reason for the anomalously high and non-Arrhenius conductivity, two groups of researchers investigated the structure of the mobile cation sublattice. Thomas et al. [4] found that the Pb(II) sublattice was disordered at room temperature and that the Pb(II) ions predominantly occupy BR sites. Col-

lin et al. [5] observed long range 3-D order and determined that the Pb(II) ions were distributed nearly evenly between the mO and BR sites. The later authors also observed a phase transformation at 325°C.

The unusual conductivity results and contradictory structural data have prompted this new study of the ionic conductivity of Pb(II)- β "-alumina. One possible explanation for the results described above is that the structure and, therefore, the conductivity of Pb(II)- β "-alumina is very sensitive to the thermal history of the sample. In order to test this, we have measured the conductivity of Pb(II)- β "-alumina after different thermal treatments. Also, the variation of heat capacity with temperature has been measured after different thermal treatments.

2. Experimental

Na(I)- β "-alumina crystals were grown by the flux evaporation method previously described [6]. Single crystals were cut into rectangular platelets (typically 4 mm \times 3 mm \times 0.3 mm). Next, the crystals were doped with a radioactive tracer, ^{22}Na . The Na(I)- β "-alumina was then immersed in molten PbCl_2 at 550°C in air. Completion of the ion exchange reaction was indicated by the reduction of the ^{22}Na content in the crystal to background levels.

Gold electrodes were sputtered onto opposing faces (perpendicular to the conduction planes) of each crystal. Silver paint was then applied over the gold to ensure good electrical contact with the platinum electrodes of the conductivity cell.

Conductivity measurements were made after two different thermal treatments. In the first, crystals were annealed at 400°C for 2 h. Periodic measurements indicated that the conductivity remains constant with time at this temperature. Following a rapid cooling to room temperature, which was achieved simply by removing the crystal from a furnace and placing it directly onto a cool metal surface, the crystal was annealed at an intermediate temperature. The conductivity was measured periodically from the start of annealing until a constant value was reached.

The conductivity was also measured at 20°C intervals as the temperature decreased from 400 to 100°C. The crystal was annealed at each temperature for 5 h or until an apparently constant value of the conductivity was reached.

Conductivity measurements were made with an automated frequency response analysis system (Hewlett-Packard 4192A LF impedance analyzer controlled by a Hewlett-Packard series 9000 computer) in the range 100 Hz to 13 MHz. All measurements were performed in a stream of flowing dry argon.

Heat capacity measurements were performed on a powdered sample made by grinding a large (39 mg) single crystal. The sample was first annealed at 130°C for 24 h and then the heat capacity was measured from room temperature to 500°C at a heating rate of 5°C min⁻¹. After the maximum temperature was reached, the sample was cooled at a rate of 20°C min⁻¹. The measurement was then immediately repeated. After the second measurement, the sample was again annealed at 130°C for 24 h before the third measurement was made. All treatments were performed in situ under flowing dry air using a Setaram DSC 111, Calvet type differential scanning calorimeter.

3. Results and discussion

Fig. 1 shows the variation of conductivity with annealing time for a crystal rapidly cooled from 400°C

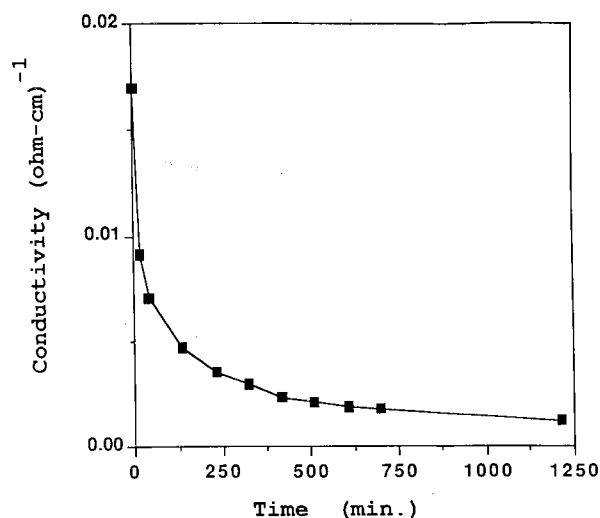


Fig. 1. The time dependence of the conductivity of Pb(II)- β'' -alumina at 160°C following rapid cool from 400°C.

to room temperature and then annealed at 160°C. Similar results were obtained when crystals were annealed at temperatures between 100 and 280°C. Samples annealed at higher temperatures reached a constant conductivity state after several hours while those annealed at the lower temperatures needed more than a day to reach equilibrium. Below this temperature range, the conductivity changed only by a small amount. Also, above this temperature range, the conductivity was constant with annealing time. Repeated thermal treatments showed that the decrease in conductivity was reversible.

Fig. 2 shows the variation of the conductivity with temperature for Pb(II)- β'' -alumina. Curve 1 shows the results of measurements made with decreasing temperature. The sample was annealed at each temperature until the conductivity remained constant. This curve, therefore, represents the conductivity at a near equilibrium condition. Curve 2 shows the initial conductivity of the same crystal heated to various temperatures immediately following a rapid cooling from 400°C to room temperature. This curve, therefore, shows the maximum conductivity at each temperature. This maximum value, is metastable and occurs only after rapidly cooling the crystal from 400°C. Although these results are from only one crystal, they are representative of results obtained from others.

Fig. 3 shows the results of the calorimetry exper-

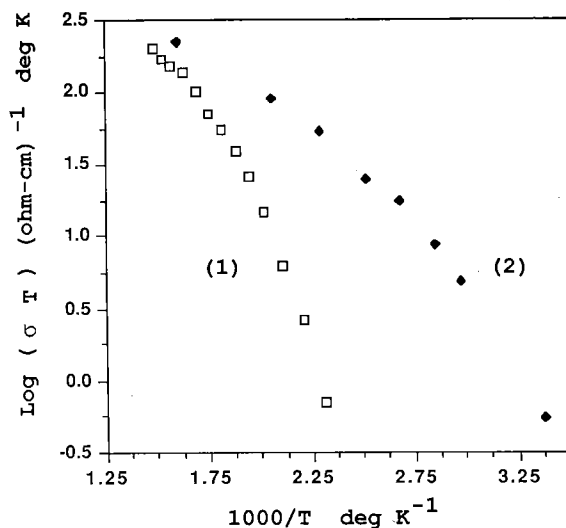


Fig. 2. The ionic conductivity of Pb(II)- β'' -alumina. Curve 1 results when the sample is cooled slowly from 400°C and curve 2 results when the sample is rapidly cooled from 400°C.

iments. Curve 1, obtained following a 24 h anneal at 130°C, shows a broad endothermic transition between 130° and 350°C that appears to have two

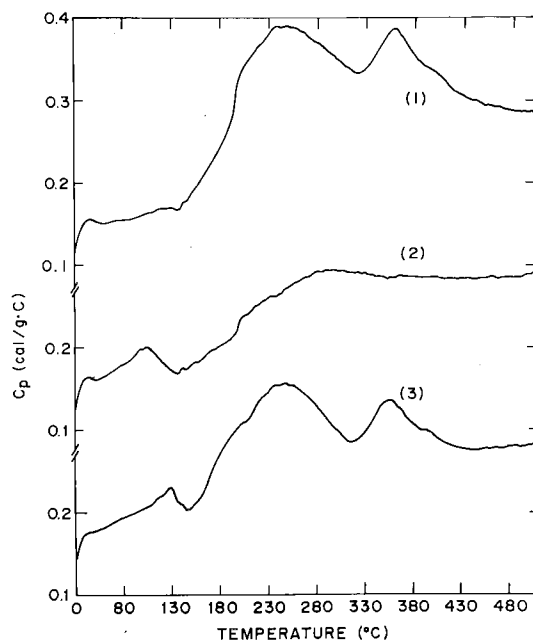


Fig. 3. DSC trace for Pb(II)- β'' -alumina. Curve 1 resulted following a 130°C anneal. Curve 2 resulted following a rapid cool from 550°C and curve 3 resulted after a second 130°C anneal.

peaks. This endotherm is absent after rapid cooling, (curve 2) but appears again following another annealing at 130°C (curve 3).

These results indicate that the change in conductivity may be linked to a structural transformation. It is likely that the rapid cooling "freezes" in a high temperature (high conductivity) structure and annealing converts it to a low temperature (low conductivity) structure. After annealing, the conversion of the low temperature structure to the high temperature structure upon heating is detected as an endothermic transition. During equilibrium cooling, the change from the high temperature structure to the low temperature structure causes a change in slope in the Arrhenius plot (an increase in the activation energy for conduction) at approximately 280°C. The more subtle change in slope exhibited by the rapidly cooled sample is probably due to imperfect quenching and partial conversion to the low conductivity state. The decrease in conductivity with time that occurs for rapidly cooled samples is due to the conversion of the high temperature structure, which is metastable below 280°C, to the low temperature structure. This transformation, which cannot occur at room temperature, occurs more and more quickly as 280°C is approached.

It should be pointed out that the increase in the activation energy for conduction from 0.28 to 0.88 eV for a sample cooled under near-equilibrium conditions (curve 1 of fig. 1) occurs at approximately the same temperature as the peak of the endotherm (280°C). These conductivity data resemble those found for the other divalent β'' -alumina isomorphs [2], while curve 2 of fig. 1 resembles the data obtained by Seevers et al. [2] for Pb(II)- β'' -alumina in which measurements were made after only a 10 minute annealing at each temperature.

The structural differences observed by Collin et al. [5] and Thomas et al. [4] (i.e. the presence and absence of long range cation-vacancy order, respectively) may have been due to differences in the thermal history of the samples. However, the presence or absence of cation-vacancy ordering alone is not sufficient to account for the magnitude of the thermal transition.

One characteristic that distinguishes the Pb(II) ion from Ca(II), Sr(II), and Ba(II) is the "lone pair" of electrons in its outermost shell. This may explain

why Pb(II)- β'' -alumina is so different from Ca(II), Sr(II), and Ba(II)- β'' -alumina. In other oxides of Pb(II), repulsions between the lone pair and the oxygen ions result in an asymmetric coordination shell [7]. The distortions in the coordination shell occur to reduce the Coulombic energy between the lone pair and the ligands. In rapidly cooled Pb(II)- β'' -alumina, repulsion between the lone pair and oxygen ions may cause the Pb(II) ion to be less tightly bound to a particular site and therefore have a high mobility. However, a reduction of this repulsive energy as the result of a framework distortion would cause the Pb(II) ion to be more tightly bound to a particular site and therefore decrease the conductivity. The observation that Pb(II)- β'' -alumina does not go to the low conductivity state at room temperature, despite the high Pb(II) ion mobility indicates that the kinetics of the transformation depend on the mobility of the framework ions.

4. Conclusions

It is clear that thermal history has a great effect on the ion transport properties in Pb(II)- β'' -alumina. New structural studies carried out under controlled conditions will be necessary to determine the exact nature of the structural change which occurs when Pb(II)- β'' -alumina is transformed from the high conductivity state to the low conductivity state. Also, some insight may be gained by a detailed study of

Sn(II)- β'' -alumina. The Sn(II) ion is known to have a greater lone pair effect than the Pb(II) ion.

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Note added in proof

Subsequent studies by the authors have shown that the apparent phase transitions discussed in the paper are the result of subtle hydration reactions.

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