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THE REACTIVITY OF SELECTED DIVALENT β"-ALUMINAS WITH WATER

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ABSTRACT Na-ß"-alumina is a well-known fast ion conductor of sodium ions. We have synthesized four divalent isomorphs of this material by ion exchange. All react readily with water to form hydrated compounds with the general formula $M_{0.83}Mg_{0.67}Al_{10.33}O_{17}\cdot(H_2O)_x$ where M is Ca(II), Ba(II), Pb(II) or Sn(II). Thermogravimetric analysis has been used to determine the extent of the reaction (value of x) for each compound. Evolved gas analysis has shown definitively that water is the reactive species. In addition, differential scanning calorimetry has been used to determine the enthalpy of the water evolution reaction for each cation. Both the extent of the reaction as well as the enthalpy of dehydration are affected to some degree by the mobile cation. However, the reactivity of the divalent ß"-aluminas with water seems to be a property common to the entire class of materials. Hydration affects the physical properties of the divalent ß"-aluminas in several significant ways. Both the ionic conductivity and fluorescent intensity of several isomorphs are dramatically reduced as a result of hydration. For this reason, any measurements of the structural or physical properties of these materials must be carried out under strictly anhydrous conditions.

MATERIALS INDEX: ß"-alumina, solid electrolytes

Introduction

Na(I)-ß"-alumina is a well-known fast ionic conductor of Na(I) ions and has the general formula, $Na_{1+x}Mg_xAl_{11-x}O_{17}$, where x is about 0.67. This material is best known for its high ionic conductivity and low electronic conductivity, which qualifies it as a promising solid electrolyte for use in batteries and electrochemical devices. As a result, a great deal of research has been devoted to the development of high conductivity polycrystalline ceramics for these applications.

Among other effects, it results in a reduction of the ionic conductivity and a reduction in fluorescent efficiency.

Experimental

Single crystals of Na-β"-alumina were grown by the flux evaporation method described previously (16). The crystals were then doped with ^{22}Na, which functions as a radioactive tracer and is used to determine the extent of the subsequent ion exchange. All ion exchange reactions were carried out in molten salts as described elsewhere (2). The completion of the ion exchange reactions was indicated both by the correct theoretical weight change and by the absence of the ^{22}Na tracer. Following ion exchange, single crystal samples were crushed with an alumina mortar and pestle to prepare powders for the TGA and DSC measurements. The crystals were sieved so that the size of the particles ranged between 40 μ and 150 μ. Samples used for the TGA/EGA measurements weighed 40 mg to 90 mg, and DSC samples weighed 10 mg to 14 mg.

All thermal gravimetry experiments used a DuPont 951 TGA microbalance controlled by a model 990 thermal analyzer. A V-G Micromass PC mass spectrometer system equipped with a stainless steel capillary inlet attachment was used to analyze the gases evolved from the sample in the TGA cell (Evolved Gas Analysis). This mass spectrometer system continuously measured the partial pressures of O_2, H_2O, CO_2, N_2 and Ar over the sample during the dehydration reaction. Calorimetric measurements were made using a DuPont DSC controlled by a model 990 thermal analyzer. Gases for the TGA experiments were flowed at the rate of 150 cc/min. 'Wet' gases were obtained by bubbling the 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 cc/min.

The crushed samples were hydrated in the following way. First, they were heated in the TGA cell until the weight became constant at high temperature, typically 550°C. When a constant weight was obtained at high temperature, it was considered the 'dry' weight. Next, the sample was cooled to room temperature at 0.5°C/min in a flowing wet gas. Typical weight gains were 2%. Afterwards, portions of the samples were decomposed in the TGA 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.

Results

We have chosen to present in this paper detailed results for only Sn(II)-β"-alumina. Corresponding results from the other compounds studied are summarized in Table 1. The thermal analysis and structural data for each compound will be compared and contrasted in detail in a later paper (17).

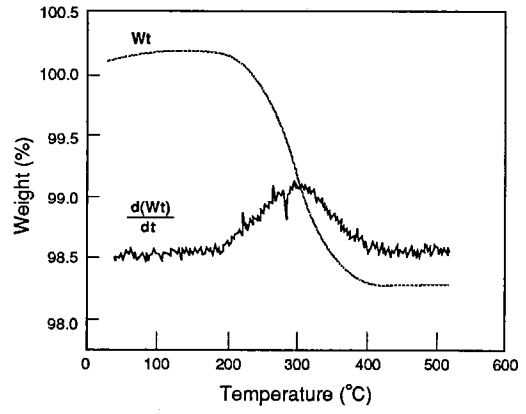

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Figure 2. Thermogram shows the dehydration of Sn(II)-ß"-alumina. The sample was heated at 10°C per min. in flowing dry N_2.

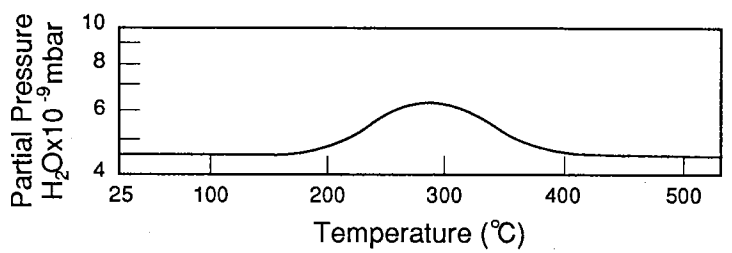

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Figure 3. Thermogram shows the partial pressure of H_2O over Sn(II)-ß"-alumina during the dehydration reaction. This thermogram was recorded simultaneously with that shown in Figure 2.

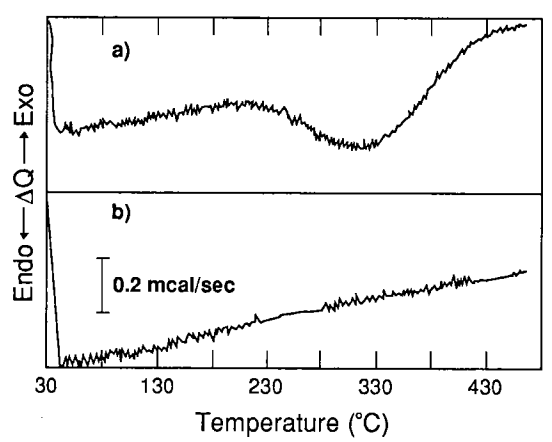

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Figure 4. Differential scanning calorimetry trace for Sn(II)-ß"-alumina heated at 10°C per min. in dry N_2. Figure 4a shows the trace from the initial heating following the synthesis. (See Figure 1.) Figure 4b shows the repeat run following a quench from 500°C.

Hydration has important consequences for the properties of these materials. For example, we have observed that the ionic conductivity of a single crystal of Pb(II)-ß"-alumina decreases significantly after exposure to water vapor. As water is incorporated into the conduction layers, it presumably blocks the conduction pathways and lowers the conductivity. In addition, we have found that the luminescent intensity of Sn(II)-ß"-alumina is greatly decreased after exposure to water vapor. This same luminescent quenching has been noted for the Eu(II) (19) and Nd(III) (20) isomorphs. Also, single crystal X-ray refinements performed on hydrated crystals indicate that the mobile ion distribution in the conduction layer is greatly altered by hydration. These consequences of hydration will be discussed in a later paper (17).

Perhaps the most important result of our study is simply the demonstration that divalent ß"-aluminas hydrate readily, even under nominally 'dry' conditions such as at 130° to 250°C in flowing gas dried over P_2O_5. The implication is that samples that have been heated at moderate temperatures for long times for whatever reason are at least partially hydrated. This has particular consequences for the so-called order/disorder transformations which have been claimed on the basis of calorimetric measurements. In fact, they are most likely the result of the evolution of small amounts of water from the samples studied. Also, anomalies observed in the variation of the ionic conductivity of divalent ß"-aluminas with temperature may be due to absorption of water at lower temperatures. Hydration may also affect the luminescent spectrum of Eu(II)-ß"-alumina observed following very long heating at 130°C.

It is also important to note that some divalent ß"-isomorphs hydrate at room temperature in normal air. This has important consequences for diffraction studies carried out in air. Excess charge has sometimes been detected in the conduction layers and taken as an indication of an abnormally large cation concentration ($x>0.83$) (21,22). It is likely that these results are due to the presence of water. Also, because hydration can alter the mobile cation arrangement, the various inconsistent results that have been reported for cation site occupations may be explained by the presence of undetected water in the conduction layers of samples analyzed in different laboratories (e.g., compare results in refs. 15 and 23).

We do not mean to suggest that every unusual aspect of the structure and properties of the divalent ß"-aluminas is the result of hydration. However, our results do clearly show that: (1) hydration of divalent beta"-aluminas is extremely difficult to avoid; and (2) hydration affects the structure and properties of these materials. Since the effects of hydration on the divalent ß"-aluminas have been almost completely ignored in the literature, it is important to reconsider some conclusions on the basis of our findings.

Conclusion

The four divalent isomorphs of ß"-alumina considered in this paper all react with water to form hydrated compounds. The reactions are quite similar, and to a first approximation, are cation-independent. It is reasonable to expect that other divalent isomorphs of ß"-alumina hydrate in a similar way. Hydration has a strong influence on conductivity, structure, and spectroscopy in these compounds. Therefore, it is critically important, albeit not always simple, to exclude water during any investigation of the structural or physical properties of these materials.

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