

Proton Transport in β'' -Alumina

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This paper presents the results of new investigations into the preparation, stability, conductivity, and structure of selected hydronium and ammonium/hydronium β'' -aluminas. The ammonium/hydronium and hydronium β'' -aluminas have room temperature conductivities of about 10^{-4} and 10^{-6} ($\Omega\text{-cm}$)⁻¹, respectively. They do not appear to be distinct and independent materials, but only general compositions in a continuum of protonic β'' -aluminas which contain various concentrations of water and/or ammonia. The results of thermal analyses, crystal structure studies, and ionic conductivity measurements indicate that it should be possible to convert one protonic β'' -alumina composition to another by careful thermal treatment. The β'' -alumina family of protonic compounds is thus a model system for studying the effects of solvation and hydrogen bonding on the motion of protonic species in an oxide lattice. © 1986 Academic Press, Inc.

Introduction

Sodium β'' -alumina ($\text{Na}_{1+x}\text{Mg}_x\text{Al}_{11-x}\text{O}_{17}$) is one of the most widely studied solid electrolytes. Many derivatives of β'' -alumina have been produced by ion-exchange reactions in which the mobile sodium ions are replaced by mono- (1), di- (2), or trivalent cations (3), as well as by hydrated protons (4, 5) and ammonium ions (6). The protonic derivatives are particularly interesting because they provide an opportunity to observe protonic motion in a variety of hydrated/ammoniated environments within a single stable oxide lattice.

One of the protonic β'' -aluminas is the so-called hydronium form, which can be synthesized by immersing Na^+ β'' -alumina in hot sulfuric acid. Although this material is called hydronium β'' -alumina, its exact ionic content is still not well established (5). There has been considerable disagreement in the literature over its precise characteristics, but it is generally accepted to have a moderately high protonic conductivity and good thermal stability. A second protonic β'' -alumina can be produced by the immersion of Na^+ β'' -alumina in molten ammonium nitrate. The result is a mixed ammonium/hydronium composition (6). Recent thermal stability, ionic conductivity and structural results suggest that the ammonium/hydronium and hydronium derivatives of β'' -alumina are closely related, and not distinct compounds.

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Other solid state protonic conductors studied in recent years include HUP ($\text{H}_2\text{UO}_2\text{PO}_4 \cdot 4 \text{H}_2\text{O}$) (7) and $\text{Sb}_2\text{O}_5 \cdot 4 \text{H}_2\text{O}$ (8). Both of these compounds have room temperature conductivities of about $10^{-4} (\Omega\text{-cm})^{-1}$, but each dehydrates with a substantial decrease in conductivity around 100°C . For technological applications, a conductivity of 10^{-3} to $10^{-1} (\Omega\text{-cm})^{-1}$ at $150\text{--}350^\circ\text{C}$ is needed for fuel cells and 10^{-7} to $10^{-5} (\Omega\text{-cm})^{-1}$ for sensors (8). One of the attractive characteristics of the protonic β'' -aluminas is that they are quite stable and retain their protonic conductivities to $150\text{--}250^\circ\text{C}$.

This paper summarizes the result of recent investigations of the preparation, stability, conductivity and structure of hydronium and ammonium/hydronium β'' -alumina (9).

Experimental Procedure

Single crystals of Na^+ β'' -alumina were grown from a mixture of sodium oxide, magnesium oxide, and α -alumina, either in a platinum crucible open to air at $1650\text{--}1700^\circ\text{C}$ or in an induction furnace under an overpressure of argon at 1700°C . The crystals were mechanically separated from the sodium aluminate slag and cut into rectangular pieces using a diamond wheel. The mobile Na^+ content of the crystals was labeled with $^{22}\text{Na}^+$ by ion exchange in molten NaNO_3 containing $^{22}\text{Na}^+$. The ion-exchange kinetics and extent of sodium ion replacement in subsequent exchanges were determined by measuring the residual sodium content as a function of time using a standard well-type scintillation counter. This radio-tracer technique is nondestructive and assures an accurate characterization of each individual crystal used in further experiments.

Hydronium β'' -alumina samples were prepared by immersing labeled sodium β'' crystals in concentrated sulfuric acid at

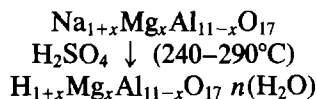
$240\text{--}290^\circ\text{C}$. Ammonium/hydronium crystals for thermal analysis and conductivity were prepared by ion exchange in molten ammonium nitrate at 190°C . All exchanges were performed in partially covered containers, open to air. The ammonium/hydronium crystal used in the structural studies was prepared by immersing a large single crystal of unlabelled Na^+ β'' -alumina in ammonium nitrate. The exchange was not monitored radiochemically, but was assumed to be complete after 45 days (10). Similar exchange reactions on comparable crystals using labeled sodium indicated that complete ion exchange would have been in fact achieved in about 6 hr (9).

Thermal analysis was carried out on powders prepared by hand grinding single crystal samples to an average particle size of $50\text{--}100 \mu\text{m}$. TGA (thermogravimetric analysis) and DSC (differential scanning calorimetry) data were collected using a DuPont 990 thermal analysis system. Ionic conductivity measurements were performed on single crystals with sputtered gold electrodes covered with silver paint to compensate for surface roughness. These crystals were analyzed at various temperatures using a Solartron 1174 frequency response analyzer.

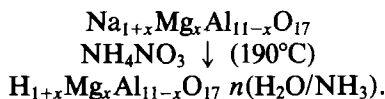
Results and Discussion

Ion-Exchange Experiments

Figure 1 shows the results of several ion-exchange reactions of the type



and



In all cases, the extent of ion exchange of sodium β'' -alumina in sulfuric acid was lin-

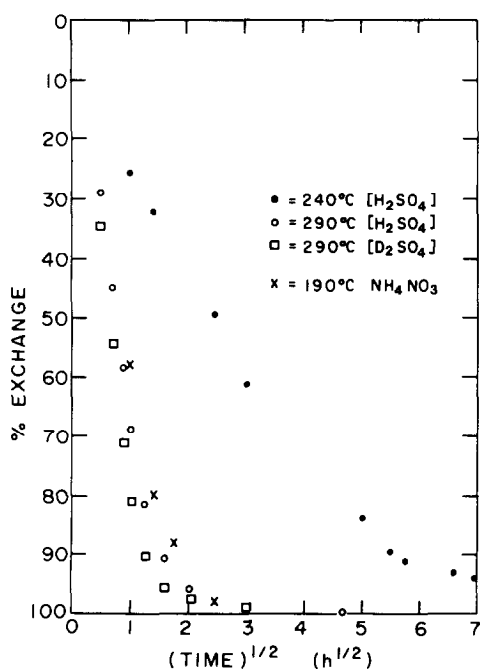


FIG. 1. Rate of Na^+ ion replacement by protonic species in β'' -alumina based on radiotracer measurements.

ear with the square root of time, as would be expected for diffusion in a quasi-one-dimensional, semi-infinite rod. The rate increased with temperature. Exchanges in deuterated and normal sulfuric acid proceeded at the same rate. For an average crystal of $3 \times 2 \times 0.2$ mm in size, the estimated chemical diffusion coefficient of hydronium species from concentrated sulfuric acid into sodium β'' -alumina at 290°C is 6×10^{-7} cm^2/sec . This value is comparable to that reported for the diffusivity of water in lithium β -alumina, 6×10^{-7} cm^2/sec at 350°C (11).

The ammonium nitrate exchange proceeded much faster than the acid exchange. While the acid severely etched the crystals and occasionally caused them to delaminate, the ammonium exchange produced clear, undamaged crystals. Different research groups (10, 12) have reported different ratios of ammonium to hydronium

species present in ammonium/hydronium β'' -alumina after ion exchange. There is no evidence that any composition is favored, rather that the specific composition of any particular sample is determined by its size and the ion-exchange conditions.

Thermal Stability of Hydronium β'' -Alumina

The composition of hydronium β'' -alumina at various temperatures was determined by heating samples to 1000°C to drive off all protonic species and then back-calculating from the total weight loss to arrive at compositions at specific temperatures. Three assumptions are inherent to this method: (1) that all protons are driven off by 1000°C ; (2) that the value of x in the general formula $(\text{Na}_{1+x}\text{Mg}_x\text{Al}_{11-x}\text{O}_{17})$ is known; and (3) that all weight losses correspond to the evolution of water, made up of free water molecules or structural protons and oxygens.

The first assumption was tested using T_2O . Hydronium β'' -alumina samples were labeled with T_2O and then heated to 1000°C . No radioactive T remained in the samples after this treatment. The value of x was taken as 0.74(2), on the basis of recent neu-

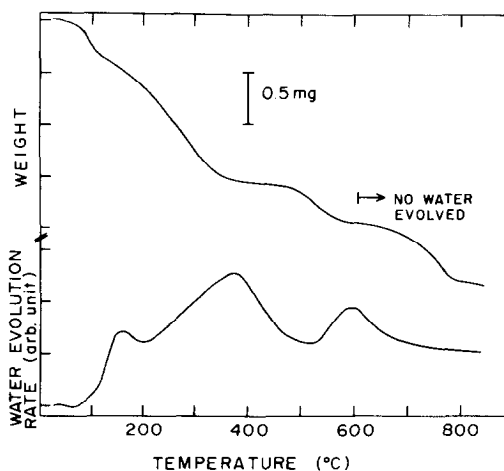


FIG. 2. Weight loss and water evolution from hydronium β'' -alumina; parent crystal grown at 1700°C in air.

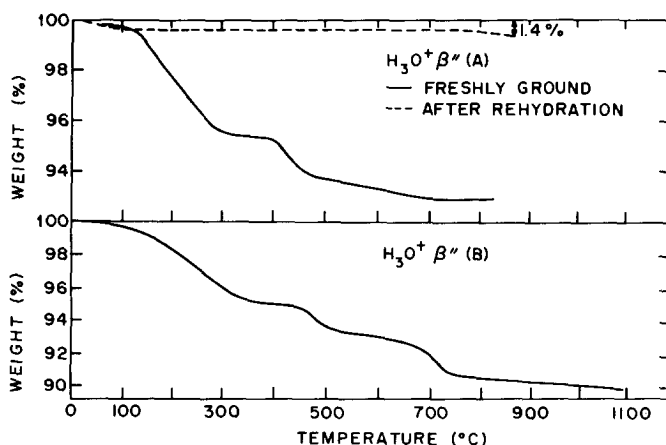


FIG. 3. TGA of hydronium β'' -alumina powders; parent crystals grown at 1700°C in argon (A) and air (B).

tron diffraction results from ammonium/hydronium β'' -alumina (10, 13, 14), sodium β'' -alumina (15), and deuterium β'' -alumina (16). A value of 0.67 derived from weight change measurements has been cited frequently in other work (17, 18).

The third assumption, that of the identity of the thermal decomposition products, was tested by attaching a P_2O_5 -type humidity sensor to the effluent gas stream of the TGA apparatus. The results, shown in Fig. 2, indicate that the weight losses below 700°C do correspond to water evolution, but that those above 700°C do not. As Fig. 3 demonstrates, it is primarily in these high-temperature weight losses that the thermal behavior of hydronium β'' -alumina samples varies among different crystal batches. In particular, crystals grown under argon (Fig. 3A) show essentially no high-temperature weight loss. Other work has indicated that the high-temperature weight losses result from the decomposition of surface carbonate species to yield CO_2 (19).

If we conclude from these observations that by 1000°C all protons have been removed from the material, that $x = 0.74$, and that weight losses above 700°C do not correspond to water evolution, then a uniform decomposition sequence can be developed

for all hydronium β'' -alumina samples, independent of crystal growth conditions (Fig. 4).

According to this scheme, the water lost below 100°C is surface water. Between 100–150°C, fully hydrated hydronium β'' -alumina exists. It contains approximately 1.14 water molecules for each proton. Colombari and Novak have studied various hydronium β'' -alumina compositions (5, 12) and have presented evidence for the existence of hydronium ions and species with higher hydration states on the basis of vibrational spectra. Unfortunately it is not clear that the material used in their study is

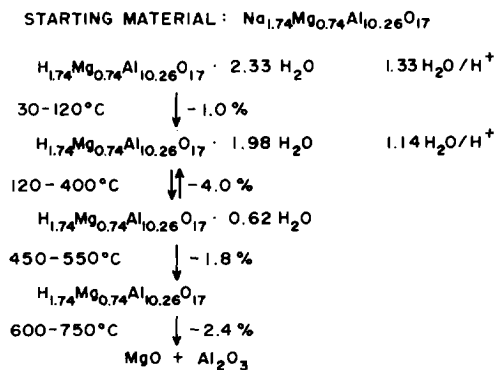


FIG. 4. Calculated thermal decomposition of hydronium β'' -alumina.

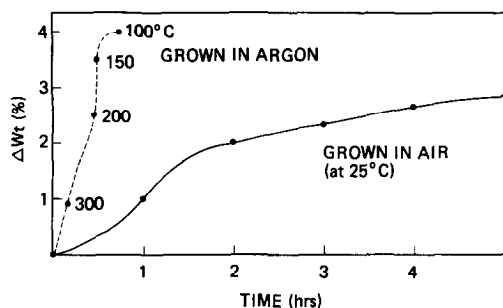


FIG. 5. Rehydration of hydronium β'' -alumina powders; parent crystals grown at 1700°C in argon and 1675°C in air.

the same as ours because of differences in the methods of preparation.

Between 150 and 400°C, hydronium β'' -alumina undergoes a partial and reversible dehydration which produces a composition in which the conduction planes contain less than one water molecule per proton. Some of the protons are probably trapped by the oxide ions of the lattice, particularly the column oxygen, O5, to form quasi-hydroxyl groups. The temperature of the midpoint of this dehydration increases slightly when the relative humidity of the sample environment is increased. The estimated binding energy of the water lost in this transition, as calculated from DSC data, is about 20 kcal/mole.

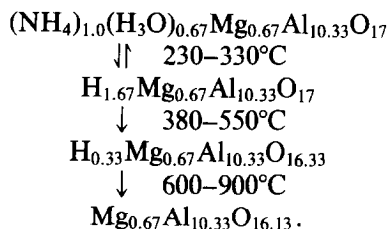
The 150–400°C dehydration is completely reversible, but the kinetics of the rehydration vary with the growth conditions of the sodium β'' -alumina parent crystal. Hydronium β'' samples derived from air-grown crystals rehydrate slowly, even at room temperature in saturated argon or nitrogen, while derivatives of the argon-grown material rehydrate rapidly even in gas streams that have less than 70 ppm water (Fig. 5). The slow rehydration of the air-grown material follows a characteristic S-shaped curve over time, which suggests that there is an initiation period, perhaps related to a critical surface layer of adsorbed water, before bulk rehydration can occur.

The next weight loss (450–550°C) is irreversible and corresponds to the removal of all of the water of hydration remaining in the conduction plane, leaving the protons "bare" and presumably bonded to spinel block oxygens. This is consistent with nmr results (20) which show isolated protons, probably as quasi-hydroxyl groups, above 400°C in hydronium β -alumina. Finally, above 550°C the conduction plane protons are lost, and the β'' -alumina structure is destroyed.

Further evidence supporting this decomposition scheme comes from experiments with D_2O . Powdered hydronium β'' -alumina samples were exposed to D_2O vapor at 50°C in the TGA apparatus. A rapid weight gain of 0.75% was observed, followed by a slower gain to a total of 1.1%. According to the decomposition sequence in Fig. 4, replacement of all of the "free" waters, those written to the right of the formula, by D_2O would produce a weight gain of 0.78%, while replacement of all of the protons by deuterons corresponds to a weight gain of 1.07%. The agreement between these observed and calculated weight changes is remarkable, and suggests that in the first hour H/D scrambling of the free waters occurs, followed in the next several hours by the scrambling of the charge-compensation protons as well.

Thermal Stability of Ammonium/Hydronium β'' -Alumina

In 1979 Farrington and Briant (6) reported the following decomposition scheme for one sample of ammonium/hydronium material, based on thermal and chemical analysis:



However, there is no reason to expect that the same initial composition is formed in every exchange reaction in molten ammonium nitrate. In fact, room-temperature structural analysis by neutron diffraction of a large single crystal of this material found a starting composition of $(\text{NH}_4)_{1.56}(\text{H}_3\text{O})_{0.19}\text{Mg}_{0.75}\text{Al}_{10.25}\text{O}_{17}-0.25(\text{H}_2\text{O})$.

Thermal analysis of ammonium-hydroxonium β'' -alumina prepared for this study has shown a first large weight loss at temperatures (100–230°C) slightly lower than previously reported by Farrington and Briant (6), followed by two weight losses that occur at comparable temperatures to those previously described. Mass spectrometric analysis of the gas evolved in the low-temperature weight loss shows a complicated pattern of species, dominated by water and ammonia. These results suggest that the evolution of ammonia and water from powders at low temperatures may produce a series of quasi-equilibrium compositions. It therefore may not be possible to attain identical compositions in large single crystals because of the slow kinetics of the decomposition reactions.

Ionic Conductivity

Protonic motion in the solid state can occur by several mechanisms: quasi-liquid diffusion, in which the proton moves through a region of high water concentration which approximates a liquid; ionic migration, in which protons are transported by larger protonic species, such as H_3O^+ or NH_4^+ ; and the Grotthuss mechanism, in which the proton is transferred between donor and acceptor molecules, followed by reorientation of the larger molecules to reset the mechanism (7, 21). All of these mechanisms are sensitive to the nature of the protonic environment, so it is reasonable to expect the conductivity of the protonic β'' -aluminas to be dependent upon the extent of hydration and the defect structure

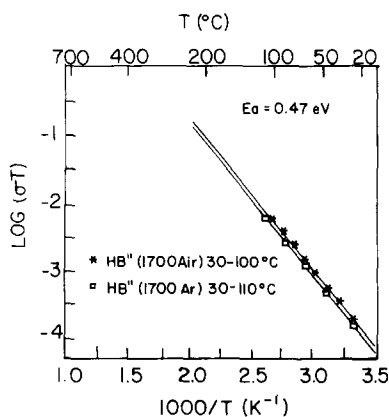


FIG. 6. Arrhenius plot of hydronium (1700°C air and 1700°C argon) β'' -alumina single crystals.

of particular samples and the conductivity of the hydronium or ammonium-hydroxonium β'' -alumina crystals should change when heated above the temperatures at which they lose water and ammonia.

For powders, the weight-loss kinetics are fairly rapid, and new quasi-equilibrium compositions are quickly established. The situation is not so simple with the much larger samples used for conductivity measurements. With these, equilibrium is approached much more slowly. In fact, for conductivity-size crystals it appears that the equivalent weight losses seen for powders are not achieved during the heating cycle of the conductivity experiment. The conductivity experiments do not, therefore, measure the true conductivities of completely equilibrated crystals.

The problem of equilibration should be insignificant at temperatures less than 150°C at which the as-exchanged compositions are stable. Figure 6 shows an Arrhenius plot at low temperature for two crystals of hydronium β'' -alumina, one derived from sodium β'' -alumina grown under argon at 1700°C and one from Na^+ β'' -alumina grown at 1700°C in air. The conductivities are essentially identical and can be considered those of the composition of hydronium β'' -alumina stable in this temperature range.

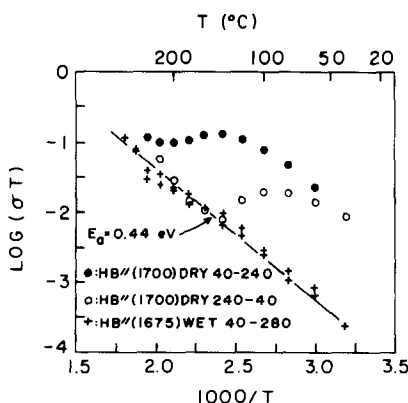


FIG. 7. Arrhenius plot from temperature cycles on hydronium β'' -alumina single crystals; parent crystals grown in air at 1675°C and 1700°C.

All samples of hydronium β'' -alumina powders decrease in water content upon heating above about 150°C. An Arrhenius plot for hydronium β'' -alumina derived from sodium β'' -alumina grown in air at 1700°C (Fig. 7) shows a corresponding decrease in conductivity above 150°C which correlates well with the dehydration observed in thermal analysis. This original conductivity is restored when the sample is cooled, presumably as the result of sample rehydration. There is no indication that the conductivity observed above 150°C is the intrinsic conductivity of the composition stable in that temperature range. Rather, the reversibility of the effect suggests that crystals initially lose water around the edges, and then regain it upon cooling. It is interesting that the samples rehydrate even in a nominally dry gas stream. This illustrates the extreme hygroscopic nature of partially dehydrated hydronium β'' -alumina.

There is some indication that the temperature of crystal growth influences the rate at which a large crystal loses water above 150°C. Figure 7 shows the conductivity of a single crystal of hydronium β'' -alumina grown at 1675°C in air. No drop in conductivity is observed above 150°C, although the thermal analysis of this material shows a

weight loss of 4% between 150 and 400°C. It is not clear whether the slower rate of dehydration is truly the result of sample differences produced by the conditions of crystal growth. The difference, if real, does not persist to higher temperatures. Above 240°C, the conductivities of samples initially grown at 1675°C in air and at 1700°C in air are essentially identical.

Similar behavior is observed for ammonium/hydronium β'' -alumina. The initial conductivity of the material is much higher than that of hydronium β'' -alumina. The conductivity of a sample decreases when it is heated to 240°C. After cooling in a gas stream saturated with water vapor, the conductivity of the ammonium/hydronium β'' -alumina sample was essentially the same as that of a fresh hydronium β'' -alumina crystal (1675° air). It appears that ammonium/hydronium β'' -alumina may be transformed by this process to hydronium β'' -alumina. Such a transformation has been postulated in the protonic β -alumina family, where the ammonium and hydronium compounds appear to convert to a common hydrogen (protonic) compound at 500°C (22).

Crystal Structure

In 1979, Thomas and Farrington (10) studied the structure of a single crystal of ammonium/hydronium β'' -alumina at room temperature using neutron diffraction. After storage for 2 years in ambient conditions, the same crystal was reanalyzed, again by neutron diffraction, at the Institut Laue-Langevin in Grenoble, at 25 (start), 180, 350, 450, and again at 25°C (end) to observe the effect of temperature on the atomic parameters (9, 13, 14). Test reflections were monitored throughout the data collections; no significant variations were observed in them across a given data set.

The 25 (start) and 180°C structures confirmed the results of Thomas and Farrington, in which the ammonium ions were found to occupy 75% of the BR-type sites,

with hydronium ions or water molecules located near the BR sites that did not have ammonium ions present. The ammonium molecule has one hydrogen along the (3) axis and three in 6*h* sites. There is significant hydrogen bonding between all of these protons and those of the water and hydronium molecules to spinel block oxygens. In fact the N–H–O bond up the (3) axis is the shortest yet reported (2.58 Å). The same refined composition was found at 25°C (start) as in (10).

As the crystal was heated for 16 hr at 350°C, the test reflections indicated changes in the crystal parameters. When no further changes were observed, the data collection was begun. The structure at 350°C corresponds to a quasi-equilibrium composition in which some ammonia has been lost: $(\text{NH}_4)_{1.32}(\text{H}_3\text{O})_{0.19}\text{H}_{0.19}\text{Mg}_{0.75}\text{Al}_{10.25}\text{O}_{17} \cdot 0.25 \text{H}_2\text{O}$. The lost ammonia molecule preferentially takes with it the three 6*h* protons, leaving behind the proton on the (3) axis. This is consistent with the strength of the hydrogen bond between the axial proton and the spinel block oxygen above it. The protons left behind by this evolution of ammonia form hydroxyl groups with spinel block oxygens directly above the BR sites on the (3) axis. There is also a reordering of the water and hydroxyl species in the conduction plane, and a new hydrogen bond network is established.

At 450°C this ammonia evolution continues, and the new hydrogen bond network is retained upon cooling to 25°C (end). Considerable disorder is apparent in the 450 and 25°C (end) data sets. There may be some indication of breakdown in the spinel block, and there appears to be a definite change in the average mosaic block size of the crystal as a result of thermal decomposition. The hydrogen bond networks observed before and after heating have three common features: a "ring" of 12 proton positions around the column oxygen, O5; wa-

ter/hydronium species located along the conduction path; and hydrogen bonding of the protonic species to the spinel block oxygens as well as to O5.

The new proton positions observed after ammonia is lost from the crystal are consistent with other structural work on the protonic β/β'' -aluminas (23). For example, previous studies of hydrogen β -alumina have concluded that the protons prefer a ring of sites around O5 (24). Two studies of hydronium β'' -alumina have found proton positions which match the (3) axis hydroxyl group and the O5 proton positions observed here (16, 25).

It appears that the loss of ammonia from ammonium/hydronium β'' -alumina leaves a material which closely resembles the acid-derived hydronium β'' -alumina, in terms of structure as well as conductivity. It is reasonable to suggest that there is in fact a single protonic β'' -alumina, which can be solvated to various degrees by ammonia, water, or a combination of the two.

Conclusions

Despite the large body of experimental data which has accumulated over the past five years on the protonic β'' -aluminas, it is clear that our understanding of them is far from complete. Such diverse influences as the growth conditions of the parent crystal, the past thermal history of the parent and exchanged materials, the crystal environment and grain size of the sample under study all appear to affect the observed properties. Many variables must be controlled, and it is understandable that seemingly contradictory results are obtained by different research groups using different techniques, when studying such a complex system.

Both ammonium–hydronium and hydronium β'' -alumina are good protonic solid electrolytes at temperatures below about 400°C under conditions of moderate rela-

tive humidity, and their conductivity behavior can be directly correlated to their thermal decomposition reactions.

The thermal decomposition of ammonium/hydronium β'' -alumina crystals is accompanied by a rearrangement of the hydrogen bonding network near the conduction slab. The properties and structure of the deammoniated material closely resemble those of hydronium β'' -alumina. The results presented here suggest that ammonium/hydronium and hydronium compounds are not distinct and independent materials but only two specific examples of a continuum of protonic β'' -alumina compositions, in which the sodium ions of β'' -alumina are replaced by protons and varying concentrations of water and/or ammonia. In particular, the results from thermal analysis, crystal structure determinations and ionic conductivity measurements all suggest that it may be possible to convert one protonic β'' -alumina composition to another by careful thermal treatment. The β'' -alumina family of protonic compounds is thus a model system for studying the effects of solvation and hydrogen bonding on the motion of protonic species in an oxide lattice.

Acknowledgments

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References

1. Y. F-Y. YAO AND J. T. KUMMER, *J. Inorg. Nucl. Chem.* **29**, 2453 (1967).
2. G. C. FARRINGTON AND B. DUNN, *Solid State Ionics* **7**, 267 (1982).
3. B. DUNN AND G. C. FARRINGTON, *Solid State Ionics* **9/10**, 223 (1983).
4. G. C. FARRINGTON AND J. L. BRIANT, *Mater. Res. Bull.* **13**, 763 (1978).
5. PH. COLOMBAN AND A. NOVAK, *Solid State Commun.* **32**, 467 (1979).
6. G. C. FARRINGTON AND J. L. BRIANT, "Fast Ionic Transport in Solids" (P. Vashishta, J. N. Mundy and G. K. Shenoy, Eds.), p. 395, North-Holland, Amsterdam, 1979.
7. F. W. POULSEN, "Solid State Protonic Conductors" (J. Jensen and M. Kleitz, Eds.), p. 21, Odense Univ. Press, Odense, 1982.
8. J. JENSEN, "Solid State Protonic Conductors" (J. Jensen and M. Kleitz, Eds.), p. 3, Odense Univ. Press, Odense, 1982.
9. K. G. FRASE, Ph.D. thesis, University of Pennsylvania, 1983.
10. J. O. THOMAS AND G. C. FARRINGTON, *Acta Crystallogr. Sect. B* **39**, 227 (1983).
11. N. J. DUDNEY, J. B. BATES, J. C. WANG, G. M. BROWN, B. C. LARSON, AND H. ENGSTROM, *Solid State Ionics* **5**, 225 (1981).
12. PH. COLOMBAN AND A. NOVAK, "Solid State Protonic Conductors" (J. Jensen and M. Kleitz, Eds.), p. 153, Odense Univ. Press, Odense, 1982.
13. J. O. THOMAS, K. G. FRASE, G. J. MCINTYRE, AND G. C. FARRINGTON, *Solid State Ionics* **9/10**, 1029 (1983).
14. J. O. THOMAS, K. G. FRASE, G. J. MCINTYRE, AND G. C. FARRINGTON, to be published.
15. K. G. FRASE, J. O. THOMAS, AND G. C. FARRINGTON, *Solid State Ionics* **9/10**, 307 (1983).
16. J. O. THOMAS, unpublished results.
17. N. WEBER AND A. F. VENERO, Publication preprint SR 69-102, Ford Motor Co., 1969.
18. W. L. ROTH, F. REIDINGER, AND S. LAPLACA, "Superionic Conductors" (G. D. Mahan and W. L. Roth, Eds.), p. 223, Plenum, New York, 1977.
19. G. FLOR, A. MARINI, V. MAZZAROTTI, AND M. VILLA, *Solid State Ionics* **3**, 195 (1981).
20. G. C. FARRINGTON, J. L. BRIANT, H. S. STORY, AND W. C. BAILEY, *Electrochim. Acta* **24**, 769 (1979).
21. L. GLASSER, *Chem. Rev.* **75**, 21 (1975).
22. B. C. TOFIELD, "Intercalation Chemistry" (M. S. Whittingham and A. J. Jacobsen, Eds.), Chap. 6, Academic Press, New York, 1982.
23. K. G. FRASE, G. C. FARRINGTON, AND J. O. THOMAS, *Annu. Rev. Mater. Sci.* **14**, 279 (1984).
24. J. M. NEWSAM, B. C. TOFIELD, W. A. ENGLAND, AND A. J. JACOBSEN, "Fast Ionic Transport in Solids" (P. Vashishta, J. N. Mundy, and G. K. Shenoy, Eds.), p. 405, North-Holland, Amsterdam, 1979.
25. M. ANNE, D. TRANQUI, AND W. L. ROTH, "Solid State Protonic Conductors" (J. Jensen and M. Kleitz, Eds.), p. 202, Odense Univ. Press, Odense, 1982.