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Stability and Dehydration of Alumina Hydrates with the β-Alumina Structure

W. L. ROTH,* M. W. BREITER, AND G. C. FARRINGTON

General Electric Research and Development, P.O. Box 8,
Schenectady, New York 12301

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The stability of alumina hydrates with the β-alumina structure was determined over a wide range of temperature and water pressures by high temperature X-ray diffraction and thermal gravimetric analysis. There are two isomorphs, distinguished by different concentrations of intracrystalline water, which reversibly interconvert by absorption and desorption of water in the conduction planes. Quasi-equilibrium data were obtained for the composition and dehydration temperature as a function of water pressure. The hydrates are chemically stable to 700°C, then irreversibly decompose to α-Al_2O_3.

Introduction

Alumina hydrates which crystallize in the β-alumina structure have been prepared and characterized by Saalfeld *et al.* (*1a*) and Nishikawa *et al.* (*1b*). There is no completely satisfactory terminology for discussing alumina hydrates as the term alumina has been used for pure oxides, oxides which contain hydroxyl ions and water of crystallization, alkali or alkaline earth aluminates, and poorly crystallized transition phases with uncertain structures and compositions (*2*). The terminology adopted here is to consider the phases as isomorphs of Na^+ β-alumina formed by replacement of Na^+ by H_3O^+ (hydronium) ions and H^+ (protons).

Many important biological and physical processes in solids depend on diffusion of hydrogen. The β-alumina crystal structure is an exceptionally good conductor of some monovalent cations and therefore might be expected to conduct protons and hydronium ions (*3*). Hydronium β-alumina would be attractive as a solid electrolyte for fuel cells, electrolyzers, and sensors if it were a good ionic conductor and stable in water vapor at high temperature.

Saalfeld and co-workers prepared hydronium β-alumina by ion exchange of Na^+ β-alumina in concentrated sulfuric acid at about 300°C. The chemical composition of the acid treated crystals was 2.2–$2.3H_2O \cdot 11Al_2O_3$ and at 150°C additional water was absorbed from the atmosphere to reach composition $3H_2O \cdot 11Al_2O_3$. This fully hydrated form, which is stable at low temperature, will be designated H_3O^+ β-alumina.

Kato (*4*) determined the structure of H_3O^+ β-alumina by single crystal X-ray diffraction. The structure, shown in Fig. 1, is similar to Na^+ β-alumina. It is a layer structure composed of spinel-like blocks separated by "conduction planes" which contain the potentially mobile cations (*5*, *6*). There are three sets of nonequivalent cation sites in the conduction plane, Beevers–Ross (BR), anti-Beevers–Ross (aBR), and midoxygen (mO) sites. Kato found the H_3O^+ ions were in or near the BR sites. England *et al.* (*7*) investigated

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[*] Author to whom correspondence should be addressed.

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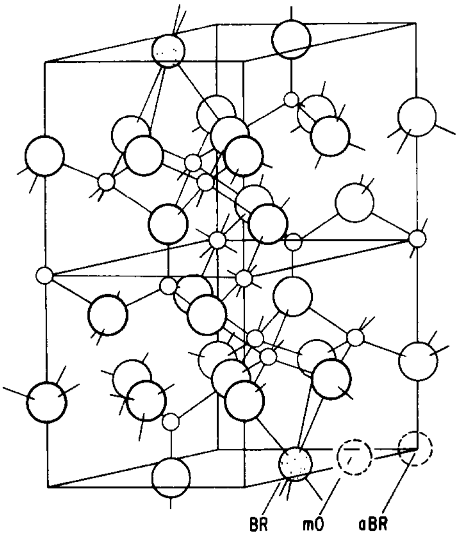

FIG. 1. Crystal structure of β-alumina. A single spinel block and conduction plane is shown. Large circles—oxygen; small circles—aluminum; shaded circle—mobile cation. The mobile cation may occupy Beevers–Ross sites (BR), anti-Beevers–Ross sites (aBR), and mid-oxygen sites (mO).

$D_2O \cdot 11Al_2O_3$ by powder neutron diffraction and found at 4.5°K deuterium was bound to the spacer oxygen. At 823°K the deuterium was disordered in the BR and mO sites, which was taken as evidence for fast deuterium mobility.

Saalfeld *et al.* (*1*) found between 200 and 300°C H_3O^+ β-alumina partially and reversibly dehydrated to $1.2H_2O \cdot 11Al_2O_3$. The partially dehydrated phase will be designated H^+–H_3O^+ β-alumina. Above 700°C the residual water was lost and H^+–H_3O^+ β-alumina decomposed to α-Al_2O_3 (corundum structure). The partial dehydration between 200 and 300°C had little effect on the structure; the *a*-parameter remained constant at 5.617 Å and *c*-parameter decreased from 22.76 to 22.71 Å.

A hydrate with different structure was formed when Na^+ β-alumina was exchanged in 80% sulfuric acid (*1*). The X-ray patterns were diffuse and the structure was disordered in one dimension. The sharp reflections were indexed on a hexagonal lattice with parameters $a = 5.553$ Å and $c = 2 \times 22.59$ Å.

The transport properties of hydronium β-alumina will depend on the concentration of intracrystalline water and therefore different conductivities are expected for the isomorphs. Ion conduction could occur either by diffusion of H_3O^+ ions or by the exchange of protons between hydrogen-bonded oxygen atoms. The nature of the partially dehydrated state, H^+–H_3O^+ β-alumina, is especially interesting because of the exceptionally large Li^+ conduction in solid solutions of Li^+–Na^+ β-alumina, a phenomenon termed "co-ionic" conductivity (*8*).

As part of an evaluation of these interesting materials, the chemical stability and dehydration were investigated by thermal gravimetric analysis (TGA) and high-temperature X-ray diffraction. Companion papers on the synthesis (*9*) and conductivity (*10*) are published elsewhere.

Experimental

Preparation of H_3O^+ β-alumina. Hydronium β-alumina was prepared by ion exchange of Na^+ β-alumina powder in 97% sulfuric acid for 110 h at 300°C (*9*). Atomic absorption analysis for sodium established the Na^+ β-alumina composition was $1.3Na_2O \cdot 11Al_2O_3$. The sodium content of the exchanged product was less than 1% of that of the starting material. X-ray diffraction established the exchanged phase had the β-alumina structure and the concentration of crystalline impurities was negligible.

High-temperature X-ray diffraction. An X-ray diffraction study was made at high temperatures with a Guinier focusing camera and CrKα radiation. The patterns were recorded at constant temperatures between 25 and 600°C at 10^{-2} to 10^{-6} Torr. The camera was calibrated by an internal standard of α-Al_2O_3 mixed with the sample. The film was scanned with a densitometer and lattice parameters determined by least-squares refinement of several well-resolved diffraction peaks.

Equilibration experiments. Stability studies were made with an apparatus which consisted of a sensitive recording electric balance, high-temperature furnace, and a system for delivering controlled O_2–H_2O gas mixtures to the sample. The experimental arrangement is shown schematically in Fig. 2. The hydronium β-alumina crystals were ground to 20–100-μm particles to promote equilibration with the atmosphere. The samples typically weighed 50 mg and changes of 0.01 mg easily were observed. The specimen was contained in a small platinum crucible suspended in the furnace by a platinum wire attached to the electric balance. The furnace was resistance heated and could be lowered away from the sample by a jack. The temperature of the sample was monitored by a thermocouple inside the silica glass reaction tube.

The atmosphere was established with a flowing mixture of O_2 and H_2O at a total pressure of 760 Torr. Flow rates of 50 cm^3/min were controlled by constant head flow meters. For water containing atmospheres, oxygen was passed through a presaturator at 90°C; then the excess water was removed by passing the stream through a saturator immersed in a thermostatically controlled bath. The glass tubing and mixing bulbs were heated above the dew point with electric tape. Experiments in dry atmospheres were made by bypassing the saturator and passing the oxygen through two columns of Drierite.

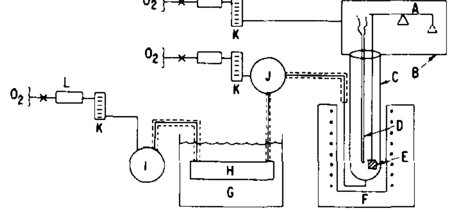

FIG. 2. Schematic diagram of apparatus for studying dehydration and hydration of hydronium β-alumina. A: electric balance. B: gas tight chamber. C: silica glass reaction tube. D: thermocouple. E: specimen in platinum cup. F: furnace. G: constant temperature bath. H: saturator. I: presaturator. J: mixing bulb. K: flowmeter. L: dessicant. M: heating tape.

The water content of the dry oxygen was determined to be about 70 ppm. A counterflow of dry oxygen was maintained through the balance case to protect the balance from water vapor.

TGA scans at constant water pressure were made by heating and cooling the powder from room temperature to 600°C. Scan rates varied from 0.5 to 10°C/min. The sample weight and temperature were recorded as a function of time and subsequently converted to weight at temperature. For isothermal measurements the partial pressure of water and the temperature were held constant while monitoring the sample weight with time.

Experimental Results

High Temperature X-Ray Diffraction

A series of X-ray diffraction photographs were taken at 20, 200, 400, and 600°C to determine whether a structure change was associated with the decomposition of H_3O^+ β-alumina to H^+–H_3O^+ β-alumina. This temperature range is sufficient to partially dehydrate H_3O^+ β-alumina without forming α-Al_2O_3. The sequence of photographs was then repeated at decreasing temperatures. The camera was evacuated to 10^{-2} Torr at room temperature and 10^{-6} Torr at elevated temperature. After completing the thermal cycle 20 $\rightarrow$ 600 $\rightarrow$ 20°C, the camera was opened and a diffraction pattern obtained after the powder had been exposed to a humid atmosphere for about 24 hr.

Figure 3 summarizes the lattice parameters measured over the temperature range 20 $\rightleftarrows$ 600°C. The powder was single phase and retained the β-alumina structure over the complete temperature range. The Bragg peaks were sharp, well resolved and characteristic of a well-crystallized solid. There was no evidence of structure disorder or formation of a superlattice. However, as the temperature was increased, and then decreased, there were unusual changes in the dimensions of the β-alumina lattice.

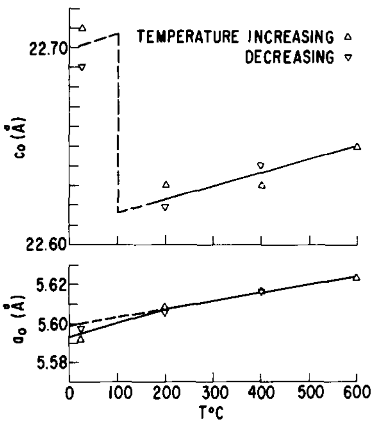

FIG. 3. Lattice parameters of hydronium β-alumina from room temperature to 600°C.

The most striking observation is as the temperature increased the c-parameter first decreased, then increased, thus reaching a minimum between room temperature and 200°C. Near 200°C there also is a slight change in the slope of a_0 vs T. The room temperature lattice constants, before temperature cycling, were $a_0 = 5.592$ Å and $c_0 = 22.71$ Å. After cooling under vacuum from 600°C, a_0 and c_0 were 5.597 and 22.69 Å, respectively. The camera then was opened and after the powder equilibrated with the atmosphere the lattice constants were found to have changed to 5.595 and 22.71 Å, more nearly equal to the original parameters.

An unusual feature of the results is the changes of unit cell dimensions are reversible, even though the powder sample is under vacuum. A possible interpretation is the lattice deformation is independent of the amount of intracrystalline water. An alternate interpretation is that H^+–H_3O^+ β-alumina is an excellent "getter" for water. Data will be presented showing the latter explanation is correct.

Above 200°C the unit cell dimensions increase smoothly with temperature. Coefficients of thermal expansion parallel to the principal axes were calculated from the temperature dependence of a_0 and c_0 between 200 and 600°C. The results show, unexpectedly, the expansion is highly anisotropic with $\alpha_{(a)} = 7.2 \times 10^{-6}$ and $\alpha_{(c)} = 2.9 \times 10^{-6}$ deg^{-1}. Below 200°C there is a small increase in $\alpha_{(a)}$. The dotted line in Fig. 3 is consistent with $\alpha_{(c)} > 0$ below the transition and a discontinuous change in c_0 near 100°C.

Isobaric Measurements

In agreement with Saalfeld *et al.*, H_3O^+ β-alumina was found to partially dehydrate at elevated temperatures. The reverse reaction, hydration of H^+–H_3O^+ β-alumina, also is rapid, at least in fine powder at temperatures above 200°C.

The water desorbed when H_3O^+ β-alumina dehydrates is regained at slightly lower temperature when the sample cools in wet oxygen. The rate of water absorption is slow, particularly below 200°C, resulting in hysteresis. Experiments at several heating and cooling rates, and in atmospheres with high and low pressures of water vapor, confirmed the reversibility of the reaction and indicated hysteresis was due to slow transport of water into the β-alumina crystals.

Typical TGA scans at increasing and decreasing temperatures are shown in Fig. 4. The scans were reproducible and powders were dehydrated and rehydrated several times with no apparent effect on their properties. The characteristic features of the isobars are approximately constant weight between room temperature and 200°C, a large weight loss over a small range of temperature near 250°C, and an extended plateau between 300 and

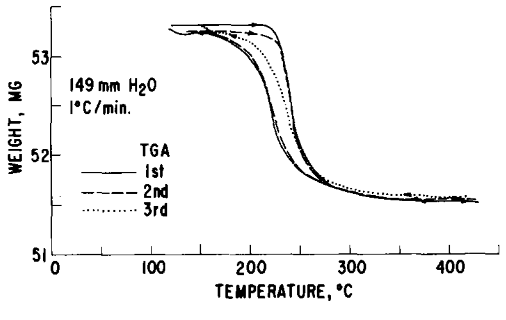

FIG. 4. Absorption and desorption of water in hydronium β-alumina at constant water pressure.

700°C. The weight decreased slightly with increasing temperature in both plateau regions. Both H_3O^+ β-alumina and H^+–H_3O^+ β-alumina are stable over an extended composition range and desorb a portion of their bound water without converting to the next higher-temperature phase. The water loss is reversible and the decrease in weight on heating is regained on cooling. A small weight loss near 100°C is observed on the first heating, probably due to absorbed surface water.

TGA experiments were made at increasing and decreasing temperatures and 5×10^{-2} to 234 Torr water pressure. Average dehydration and hydration temperatures, taken as the temperature at which 50% of the water either was gained or lost, were used to characterize the transformation.

The temperature at which hydration occurred was always less than the dehydration temperature. A series of experiments was made at 10, 5, 1 and 0.5°/min to determine if the transition was sharp, and therefore possibly first order, or gradual, and possibly second order. The results suggest the transformation may be second order. Although hysteresis was reduced, it persisted at the slowest practical scanning rate and the weight changes continued to occur over a range of temperature.

Table I summarizes the effect of water pressure on the dehydration temperature and hysteresis. Increasing the pressure from 32 to 234 Torr increased the dehydration temperature from about 200 to 240°C and decreased the hysteresis from 50 to 30°C.

H^+–H_3O^+ β-alumina is an excellent dessicant as shown by the following experiment. A 54.66-mg sample was cooled from 480°C at 1°C/min in oxygen that had passed through two columns of Drierite. The water partial pressure was 70 ppm. Between 150 and 40°C the powder weight increased 1.4%, and after an additional 40 hr at room temperature the phase was 99% converted to H_3O^+ β-alumina. Most of the water was absorbed between 20 and 150°C, in reasonable agreement with the change in c_0 at 10^{-2} Torr observed by high-temperature X-ray diffraction.

Isothermal Measurements

The preceding experiments indicated it should be possible to determine the composition of hydronium β-alumina in equilibrium with water vapor. Figure 5 summarizes results of a series of measurements at constant temperature. In most cases the final state was approached from compositions with higher and lower water contents by decreasing and increasing the partial pressure of water over the powder. Constant weight was established in 2–5 hr above 300°C but water absorption and desorption was slow at lower temperatures. In such cases the equilibrium composition was estimated from the weights measured as the final state was approached from opposite directions. The isotherms in Fig. 5 are averages of several measurements and the errors are estimates of reproducibility and the rate the weight of the powder was changing as equilibrium was approached.

Both dehydration and hydration is slow at

TABLE I

DEHYDRATION TEMPERATURES AND HYSTERESIS OF HYDRONIUM β-ALUMINA

	Temperature (°C)			
Water pressure (Torr)	Dehydration	Hydration	Average	Hysteresis
32	223	173	201	50
55	235	198	216	37
92	236	207	219	29
149	252	226	239	26
234	255	223	239	32

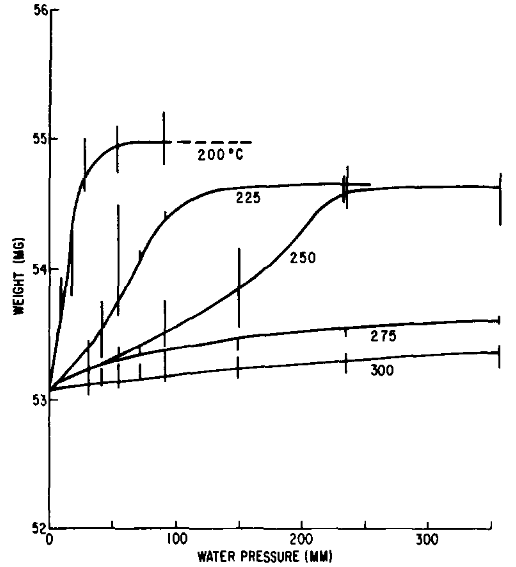

FIG. 5. Hydronium β-alumina isotherms.

low temperature, as indicated by the following experiment. The water pressure over a 54-mg sample of H^+–H_3O^+ β-alumina at 200°C was decreased from 17.5 to 9.2 Torr. After 166 hr the powder weight had decreased 0.64 mg, and was still decreasing at the rate of 0.04 mg/day.

Despite the approximate nature of the equilibrium results, the isotherms in Fig. 5 confirm that the transformation temperature between H_3O^+ β-alumina and H^+–H_3O^+ β-alumina decreases with decreasing water pressure. This agrees with the results of thermal gravimetric analysis at constant pressure and high-temperature X-ray diffraction.

Discussion

Structure

The two β-alumina hydrates are crystalline isomorphs with nearly identical lattice dimensions and widely different concentrations of intracrystalline water. The phases interconvert by absorption and desorption of water. The transformation is accomplished with ease because the water molecule is small and can diffuse in the channels of the conduction plane without altering the framework of the β-alumina structure.

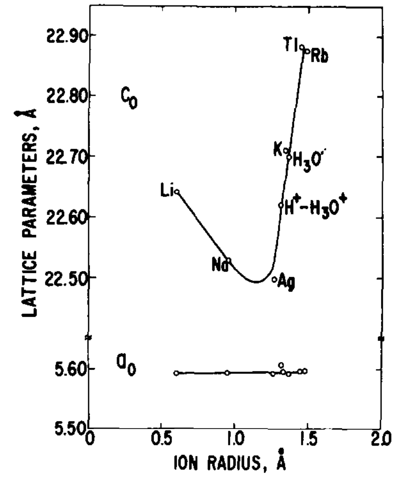

FIG. 6. Lattice parameters of β-alumina isomorphs.

The unit cell dimensions are consistent with either H_3O^+ or H_2O in the conduction plane. Figure 6 compares the lattice parameters of β-alumina isomorphs in which the radius of the monovalent cation varies over the range 0.6 (Li^+) to 1.48 Å (Rb^+). The *a*-parameter is determined by the interatomic distances in the aluminum–oxygen network and is the same for all isomorphs. The *c*-parameter is sensitive to the composition in the conduction plane, probably because the dielectric properties determine the coulombic forces between the spinel blocks. The effects of the hydrogen-containing cations are similar to spherical monovalent alkali ions with radii 1.25 and 1.40 Å, respectively. This is compatible with H_2O, H_3O^+, or $H_5O_2{}^+$ since for most hydrogen bonds between oxygen atoms the O———O distance lies between 2.50 and 2.80 Å, equal to the closest approach of spheres with radii of 1.25 and 1.40 Å. The absorption of between one and two molecules of water in the hexagonal cell expands c_0 by 0.08 Å, consistent with the rapid increase of c_0 for ions larger than Ag^+.

Figure 1 shows there are three sites in the conduction plane for the cations: BR (Beevers–Ross), aBR (anti-Beevers–Ross), and mO (midoxygen). Kato (*4*) showed H_3O^+ is probably in the BR site. The H_3O^+ ion is pyramidal and probably is hydrogen bonded to oxygen atoms in the spinel block. Residual H_2O may occupy aBR or mO sites. For purposes of simplification, the interstitial oxygen atoms in mO sites (*6*) have been neglected.

An interesting question arises whether H_3O^+ and H_2O are distinguishable species in the conduction plane. If the composition is $4H_2O \cdot 11Al_2O_3$, which is expected if each Na^+ in our Na^+ β-alumina is replaced by H_3O^+, there is about $\frac{4}{3}$ H_3O available for the large number of available sites in the conduction plane. If the protons are labile they will interchange between H_3O^+ and H_2O, if present, and might form hydrated hydronium ions.

$$H_3O^+ + H_2O \rightleftharpoons H_2O + H_3O^+ \rightleftharpoons H_5O_2^+. \quad (1)$$

As shown by Farrington *et al.* (*10*), the conductivity of H_3O^+ β-alumina is very small, about 10^{-11} (ohm-cm)$^{-1}$ at 20°C, which indicates the equilibria described in Eq. (1) do not represent a major pathway for proton diffusion.

The anisotropic thermal expansion of H^+–H_3O^+ β-alumina probably results from the dissociation of H_3O^+ into protons and water.

$$H_3O^+ \rightleftharpoons H^+ + H_2O. \quad (2)$$

The small expansion parallel to the *c*-axis can be understood as the result of two effects in opposition–thermal motion, which increases the interatomic distances between all of the atoms and expands the structure, and loss of water from the conduction plane, which contracts the structure along the *c*-axis. This interpretation is supported by the desorption of up to $\frac{1}{2}$ molecule H_2O from H^+–H_3O^+ β-alumina as the temperature is increased from 300 to 600°C.

The partial dehydration of H_3O^+ β-alumina is accompanied by a decrease in conductivity of several orders of magnitude (*10*). The conductivity decrease is due principally to an increase in the activation energy from 18 to 29 kcal/mole. Since the change in the structure is insignificant, the difference is probably due to immobilization of protons by strong hydrogen bonds. Assuming the structures of partially dehydrated H_3O^+ β-alumina and deuterium β-alumina are similar, the O–H bond distances may be approximately 2.5 Å (*7*). There also may be a small decrease in the preexponential term, which would be consistent with a decreased concentration of H_3O^+ carriers.

Stability and Vapor Pressure

The pressure–temperature stability fields of H_3O^+ β-alumina and H^+–H_3O^+ β-alumina are summarized in Fig. 7. The phases coexist along II and H^+–H_3O^+ β-alumina decomposes to α–Al_2O_3 along III. If the transformation is second order, as is likely, boundary II will extend over a finite area in P–T space.

H_3O^+ β-alumina will dehydrate only if its vapor pressure exceeds the partial pressure of water over the solid. The vapor pressure of H_3O^+ β-alumina estimated from dehydration temperatures is shown in Fig. 8. The heat of vaporization is $\Delta H = 29$ kcal/mole. This equals the activation energy of conduction of H^+–H_3O^+ β-alumina (10), but the agreement may be coincidental. The vapor pressure is derived from relatively few measurements over a small temperature range and is proposed

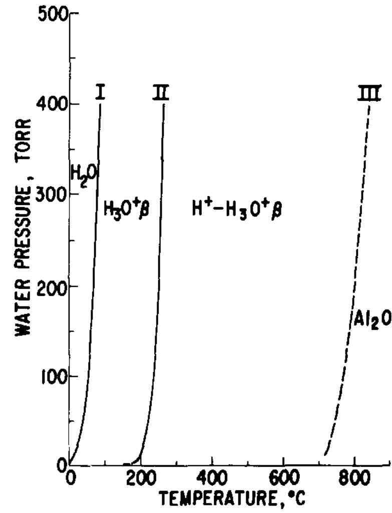

FIG. 7. Proposed phase diagram for β-alumina hydrates.

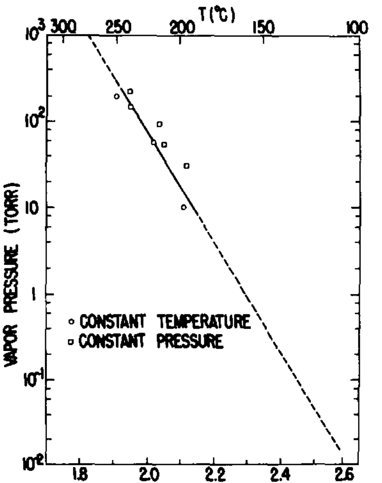

FIG. 8. Vapor pressure of H_3O^+ β-alumina.

only as a rough guide to the material properties. The approximate correctness of Fig. 8 is indicated by extrapolating the dehydration temperature to low pressure for comparison with the phase transformation obtained by X-ray diffraction. The predicted dehydration temperature at 10^{-2} Torr is 110°C, which agrees with the discontinuity in c_0 shown in Fig. 3.

Composition and Molecular Formula of Hydronium β-Alumina

Writing the molecular formula of H_3O^+ β-alumina as $n_AH_2O \cdot 11Al_2O_3$ and H^+–H_3O^+ β-alumina as $n_BH_2O \cdot 11Al_2O_3$, dehydration proceeds by the following sequence of reactions:

$$n_AH_2O \cdot 11Al_2O_3 \rightleftharpoons n_BH_2O \cdot 11Al_2O_3 + (n_A - n_B)H_2O, \qquad (3)$$

$$n_BH_2O \cdot 11Al_2O_3 \xrightarrow[>700°C]{} 11Al_2O_3 + n_BH_2O. \qquad (4)$$

Table II summarizes values for n calculated from the water content measured at various stages of hydration. The identification of n with n_A and n_B is possible if the weight changes are due exclusively to differences in the amount of bound, intracrystalline water.

The composition of H^+–H_3O^+ β-alumina extends from $n_B = 2.6$ at 330°C to $n_B = 2.2$ at 700°C at a water partial pressure of about 22 Torr. The composition in the middle of the phase field agrees with that obtained by thermal gravimetric analysis (Breiter *et al.* (*9*)) and the weight of millimeter-sized, partially dehydrated crystals (Farrington *et al.* (*10*)). The variable stoichiometry probably is due to the partial dissociation of H_3O^+ into $H^+ + H_2O$, in accordance with Eq. (2). At 500°C the conduction plane contains about equal numbers of H_3O^+ and H^+ ions, and the concentration of H^+ increases with increasing temperature. The desorption of this intracrystalline water from H^+–H_3O^+ β-alumina accounts for the small coefficient of thermal expansion along c_0.

The molecular formula of H_3O^+ β-alumina is less certain than H^+–H_3O^+ β-alumina. It has

TABLE II

WATER CONTENT AND CHEMICAL FORMULA OF HYDRONIUM β-ALUMINA

Temperature (°C)	Phase	Water (wt%)	n in $nH_2O \cdot 11Al_2O_3$[a] I	n in $nH_2O \cdot 11Al_2O_3$[a] II
20	H_3O^+ β-alumina	6.89	4.61	3.90
100	H_3O^+ β-alumina	7.12	4.78	4.06
210	H_3O^+ β-alumina	6.89	4.61	3.90
330	H^+–H_3O^+ β-alumina	4.02	2.61	2.61
700	H^+–H_3O^+ β-alumina	3.36	2.17	2.17
900	H^+–H_3O^+ β-alumina	0.09	0.06	0.06
1000	α-Al_2O_3	0	0	0

[a] I is calculated assuming excess H_2O is intercalated in the conduction planes, II excess H_2O is adsorbed on the crystal surfaces.

proven difficult to determine unique values of n_A for the completely hydrated phase because water slowly is absorbed from the atmosphere (Breiter *et al.* (*9*)). An intriguing question is whether the water absorbed at low temperature is intracrystalline or surface water. The question is closely related to the general problem of nonstoichiometry in β-alumina type phases.

It is useful to write the formulas of Na^+ β-alumina and H_3O^+ β-alumina in a form which distinguishes the composition in the conduction plane from that in the spinel block. Taking $1.33Na_2O \cdot 11Al_2O_3$ for the composition of Na^+ β-alumina, as found by chemical analysis, and assuming each Na^+ is replaced by H_3O^+, the chemical formulas of the spinel block and adjoining conduction plane are:

	Na^+ β-Alumina	H_3O^+ β-Alumina
Composition (X2)	$1.33Na_2O \cdot 11Al_2O_3$	$4H_2O \cdot 11Al_2O_3$
Spinel Block	$Al_{11}O_{16}{}^+$	$Al_{11}O_{16}{}^+$
Conduction Plane	$Na^+ + \frac{1}{6}Na_2O + O^{2-}_{(5)}$	$H_3O^+ + \frac{1}{2}H_2O + O^{2-}_{(5)}$

$O_{(5)}$ is the column oxygen which is shared between aluminum atoms in adjacent spinal blocks. The formulas assume excess Na^+ is charge compensated by oxygen in the conduction plane, in agreement with silver exchange experiments and neutron diffraction (*6*). The predicted composition is disordered because only $1H_3O^+ + \frac{1}{6}(H_3O)_2O$ ($\frac{1}{2}H_2O$) are available to occupy BR, aBR, and mO sites in the conduction plane.

The composition determined for H_3O^+ β-alumina powder which was in quasi-equilibrium with water vapor from 32 to 324 Torr pressure was $4.6H_2O \cdot 11Al_2O_3$ over the temperature range 150 to 210°C. This amount of H_2O is greater than $n_A = 3.7$ to 3.9 determined for similar material by thermal gravimetric analysis (*9*) and by partial dehydration of millimeter-sized crystals (*10*). Alternate explanations that can be proposed for $n > 4$ are (a) absorption of water on the crystallite surfaces, or (b) intercalation of intracrystalline water in the conduction planes. The first interpretation requires equal binding energies for the surface and intracrystalline water since the dehydration–rehydration experiments show they are desorbed and reabsorbed at the same temperature. Since the heat of vaporization of water from H_3O^+ β-alumina is about 29 kcal/mole, the surface water would be chemisorbed on the crystallite surfaces. The alternate explanation is that the "excess" water is intercalated as neutral molecules in unoccupied sites of the conduction plane. There is ample room for additional H_2O; for example, if the BR and aBR sites are filled, and the mO sites are vacant, the predicted composition is $4.5H_2O \cdot 11Al_2O_3$.

The isotherms in this paper do not discriminate between these alternate absorption mechanisms. Previous studies by X-ray diffraction (*11*), infra-red (*3*), and nuclear magnetic resonance (*12*) have shown that water will intercalate in Li^+ β-alumina (3) and Na^+ β-alumina (*3*, *11*, *12*). The size of the alkali ion may be critical since no indication was found that water molecules enter the planes of K^+, Rb^+ and Tl^+ β-alumina even after exposure to 25 Torr water at 300°C (*3*). The intercalation of H_2O in the alkali plane of Li^+ and Na^+ β-alumina is analogous to Eq. (1) for H_3O^+ ions:

$$M^+ + H_2O \rightleftharpoons MH_2O^+. \qquad (4)$$

Acknowledgments

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