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IONIC AND MOLECULAR TRANSPORT
IN BETA- AND BETA"-ALUMINA*

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IONIC AND MOLECULAR TRANSPORT
IN BETA- AND BETA"-ALUMINA*

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ABSTRACT

Investigations of rapid transport of cations and water molecules in the β - and β "-alumina family of superionic conductors are reviewed. Particular topics that are discussed include the Haven ratio and mixed-ion effects in β -alumina, and the influence of superlattice ordering on ionic transport in β "-alumina.

Introduction

Superionic conductors are solids which exhibit exceptionally high ionic conductivities compared to similar materials under the same conditions. The conductivities of some inorganic solids are nearly as high as those of molten salts or aqueous electrolytes ($\sim 1 \Omega^{-1} \text{ cm}^{-1}$), and hence the term solid electrolyte is appropriate.

Because of their technological importance and interesting properties, the family of aluminates known as the β - and β "-aluminas are among the most widely studied group of solid electrolytes. This article is a brief review of some

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of the ionic and molecular transport properties of the β - and β'' -aluminas and the models and theories proposed to account for these properties at the atomic level. The topics discussed include mixed-ion effects, the Haven ratio, superlattice ordering and its influence on conductivity, and the diffusivity of water. Regretably, for the sake of brevity, it is not possible to describe all the interesting results related to charge and mass transport in these materials. Although practical electrolytes of β - and β'' -alumina are polycrystalline ceramics, the results discussed here were obtained from measurements on single crystals.

General Properties

Beta- and beta''-alumina refer to the end members of a family of sodium aluminates whose composition ranges [1] from $\text{Na}_2\text{O}\cdot 11\text{Al}_2\text{O}_3$ to $\text{Na}_2\text{O}\cdot 5\text{Al}_2\text{O}_3$. Sodium β -alumina ($\text{Na}\beta$) has a variable composition which is represented by $(1+x)\text{Na}_2\text{O}\cdot 11\text{Al}_2\text{O}_3$, where $0.15 < x < 0.30$. A so-called nearly stoichiometric compound ($x=0$) can be prepared by a series of ion-exchange and decomposition reactions [2,3]. Sodium β'' -alumina ($\text{Na}\beta''$) is evidently not stable as a binary compound of Na_2O and Al_2O_3 , but a stable structure can be obtained by replacing a fraction of the Al^{3+} ions with an aliovalent cation (e.g. Li^+ or Mg^{2+}). For example, single crystals of Mg-stabilized $\text{Na}\beta''$ grown in this laboratory typically have the composition [4] $\text{Na}_{1.67}\text{Mg}_{0.67}\text{Al}_{10.33}\text{O}_{17}$ (i.e., $0.84\text{Na}_2\text{O}\cdot 0.68\text{MgO}\cdot 5.16\text{Al}_2\text{O}_3$). The structures of β - and β'' -alumina are similar [5,6]: dense layers of Al^{3+} and O^- ions (~ 9 Å thick) packed in a spinel-like lattice (spinel blocks) are separated by loosely packed layers (conduction layers) containing the mobile Na^+ ions and O^- ions which form a bridge between adjacent spinel blocks. The primitive cell of $\text{Na}\beta$ has hexagonal symmetry while the primitive cell of $\text{Na}\beta''$ has rhombohedral symmetry.

The details of the structures of the conduction layers are important in understanding the high ionic conductivity of β - and β'' -alumina. The conduction layers are bounded by O^- ions of the adjacent spinel blocks, and these ions together with the bridging O^- ions [denoted by $\text{O}(5)$] form special sites. As illustrated in figure 1, the plane of the $\text{O}(5)$ oxygen ions in $\text{Na}\beta$ is a mirror plane as a consequence of the same relative placement of the adjacent oxygen layers. Three special sites in this plane are labeled as the Beavers-Ross (BR), anti-Beavers-Ross (aBR), and mid-oxygen (mO) sites. An analysis of neutron diffraction data [7] shows that at room temperature the site occupancies for the Na^+ ions are 0.66, 0.36, and 0.01 for the BR, mO, and aBR sites, respectively. As suggested by Roth [8], the conduction layers are believed to contain x additional O^- ions which compensate for the $2x$ Na^+ ions. This is implied by the chemical formula above. The exact positions of the extra O^- ions are not known, but potential energy calculations suggest [9] that they are located near the mO sites as indicated in figure 1(a). In β'' -alumina, the relative displacement of the adjacent oxygen layers removes the mirror symmetry of the $\text{O}(5)$ plane, and the two special positions [figure 1(b)], which correspond to the BR and aBR sites in $\text{Na}\beta$, are now equivalent. The special positions for Na^+ ions are not fully occupied. In Mg-stabilized crystals with the composition given above, about 17% of the sites are vacant [10], while in Zn-stabilized crystals ($\text{Na}_{1.57}\text{Zn}_{0.57}\text{Al}_{10.43}\text{O}_{17}$), about 22% of the sites are vacant. Due to relaxation of the Na^+ ions toward neighboring vacant sites and to the high ionic mobility, appreciable Na^+ ion density is observed near the mO positions [10, 11b]. As a consequence of their high concentration and effective strong Coulombic interaction, the vacancies in β'' -alumina tend to order on a superlattice [11] [figure 1(b)]. This will be seen to have an important effect on the ionic conductivity.

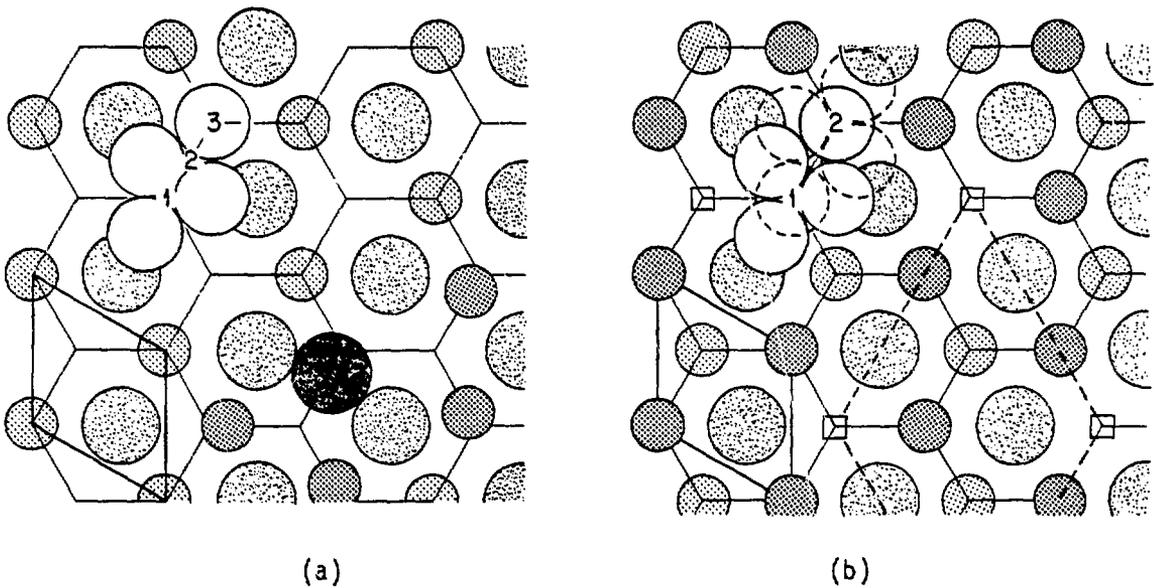


Figure 1. Schematic diagram of the conduction layers of (a) $\text{Na}\beta$ -alumina and (b) $\text{Na}\beta''$ -alumina as viewed down the c -axis. The small circles represent Na^+ ions. The large shaded circles represent bridging or $\text{O}(5)$ O^{2-} ions. The open circles (solid and dashed lines) represent O^{2-} ions in the adjacent close-packed layers above and below the plane. The heavy solid lines show the planar cell of the average structure. (a) BR, mO and aBR sites denoted by 1, 2, and 3, respectively; the large darker circle represents an excess O^{2-} ion, and the nearby small darker circles represent paired Na^+ ions. (b) Na^+ ions on sites 1 are above the plane (darker circle) and Na^+ ions on sites 2 are below the plane (lighter circle). The open boxes denote vacant Na^+ sites. The dashed line shows the superlattice cell.

Examples of conductivity data for $\text{Na}\beta$ and $\text{Na}\beta''$ are shown in figure 2. In general the graphs of $\log(\sigma T)$ vs $1/T$ are linear for the β -aluminas (Arrhenian behavior), but pronounced curvature (non-Arrhenian behavior) is typical of the conductivity graphs of the β'' -aluminas. Values of σ , activation energy, and ionic mobility for several β - and β'' -aluminas* are listed in Table I[12]. For the β'' -aluminas, the activation energies were taken from the slopes of the $\log(\sigma T)$ vs $1/T$ graphs below 100°C . A remarkable property of β - and β'' -alumina is that the conductivity is high for a variety of cations, including divalent cations in β'' -alumina[13].

Ionic Transport in β -Alumina

Conduction mechanism

Based on their measured Haven ratio of $\sim 1/3$ and on their observation that a small concentration of divalent cations reduces the sodium diffusivity, Yao

*Crystals of substituted β - and β'' -aluminas (i.e. Li^+ , Ag^+ , ...) are prepared by treatment of parent $\text{Na}\beta$ and $\text{Na}\beta''$ material in molten salts[1].

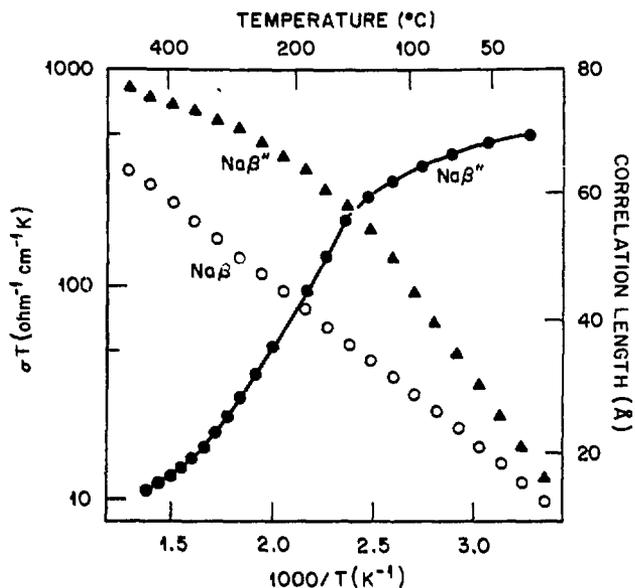


Figure 2. Conductivity data for Na β - (\circ) and Na β'' -alumina (\blacktriangle) from refs. [17] and [50]. Correlation length ξ (\bullet) for superlattice ordering from ref. [11].

Table I. Conductivity (σ)^(a), ionic mobility (μ_j)^(b) and activation energy (E_a)^(c) for several β - and β'' -aluminas at 25°C.

	Cation	$\sigma(\Omega^{-1} \text{ cm}^{-1}) \times 10^4$	$\mu_j(\text{cm}^2/\text{volt-sec}) \times 10^6$	$E_a(\text{eV})$
Beta-Alumina	Na	360	57	0.15
	Ag	130	21	0.16
	Li	30	5	0.24
Beta''-Alumina	K	1200	137	0.15
	Na	400	45	0.33
	Pb	70	8	0.27

(a) Values from refs. [17] and [50] and from unpublished measurements in this laboratory.

(b) Calculated from σT assuming 1.2 mobile ions per unit cell of volume $V = 6.1 \times 10^{-22} \text{ cm}^3$ for the β -aluminas and 1.67 mobile ions per unit cell (0.835 for Pb^{2+}) of volume $V = 3.1 \times 10^{-22} \text{ cm}^3$ for the β'' -aluminas.

(c) Activation energies for the β'' -aluminas taken from the slope of $\log(\sigma T)$ vs $1/T$ graphs in the nearly linear region between 100°C and 25°C.

and Kummer[14] first suggested that an interstitialcy rather than a vacancy mechanism might be responsible for the high conductivity of $\text{Na}\beta$. Later, Whittingham and Huggins[15] also reported that an interstitialcy process is responsible for Na^+ transport, as a result of their estimated Haven ratio of ~ 0.6 . Following on these ideas, Wang et al.[16] used potential energy calculations to develop a detailed model of the conduction process.* The calculations show that the BR sites have the lowest energy for occupation by Na^+ ions, followed by the m0 sites and the aBR sites. The calculated energy difference for occupancy of a BR site compared to an aBR site is about 2 eV. The model predicts that, when Na^+ ions are added to the conduction layers, the BR sites are filled first. When the number of ions exceeds the number of BR sites (2 per cell), interstitial pairs of Na^+ ions are formed in which each member of the pair is located on a m0 site. Thus, if there are x extra Na^+ ions, then 2x paired ions occupy m0 sites, 2-x Na^+ ions occupy BR sites, but the aBR sites are unoccupied. The high mobility results from cooperative motion of the paired ions: one member of the pair displaces an ion on a BR site to form a new ion pair, while the other member of the initial pair falls into the vacated BR site. The aBR site is the saddle point for this interstitialcy process, and the calculated activation energy of 0.14 eV is in good agreement with the experimental value[17] of 0.15 eV. Experimental support for the interstitialcy mechanism has been obtained from conductivity measurements[2] on a nearly stoichiometric $\text{Na}\beta$ -alumina ($x \sim 0$): removing most of the excess Na^+ ions and hence the interstitial pairs caused the conductivity to decrease significantly and the activation energy to increase to about 0.6 eV. Moreover, replacing Na^+ ions with divalent cations such as Sn^{2+} or Cd^{2+} also causes a marked decrease in conductivity and an increase in activation energy, presumably because the divalent cations replace the paired Na^+ ions[14,18,19].

Recently Walker and Catlow[20] proposed an alternative model for $\text{Na}\beta$ also based on static lattice calculations (Mott-Littleton method), but in which ionic polarization was treated with the shell model, and the ions surrounding the defect were allowed to relax. According to the results of the calculations, the aBR sites are the preferred locations for paired or interstitial Na^+ ions, while the m0 position is the saddle point for the interstitialcy migration. The calculated activation energy for migration, 0.58 eV, and the high occupation of the aBR sites at low temperatures predicted by this model are in marked disagreement with experiment. A comparison of the predictions of the two models with experimental results is given in Table II.

The differences in conductivities and activation energies among the various β -aluminas can be attributed mainly to differences in the properties of the mobile ions, i.e., ionic radius, polarizability and mass[16]. But there is also an effect due to local ordering of the ions on a superlattice[21,22]. Evidence for superlattice ordering in the β -aluminas was seen in x-ray diffuse scattering measurements[22,23]. McWhan et al.[22] interpreted their diffuse scattering data in terms of short-range order and proposed several possible superlattices for the ordering of cells containing mobile ions on BR sites only, cells with paired ions, and cells with paired ions and excess O^- ions. For $\text{Na}\beta$ they found that the correlation length** ξ (SRO) was ~ 5 A and was

*The potential energy function included Coulomb, repulsive and polarization energy terms.

**The correlation lengths for a short-range order model (SRO) and the micro-domain model (MD) are related by $\xi(\text{MD}) = 2.8\xi(\text{SRO})$ [22].

Table II. Comparison of calculated and observed activation energies and site occupation factors in Na β -alumina.

	Activation Energy (eV)	Occupancy ^(a)		
		<u>BR</u>	<u>mO</u>	<u>aBR</u>
Experiment ^(b)	0.15	0.76	0.43	0.01
Wang et al. ^(c)	0.14	0.80	0.40	0
Walker and Catlow ^(d)	0.58	1.0	0	0.20

(a) Occupation per planar unit cell.

(b) Activation energy from [17]; site occupancy determined from neutron diffraction data obtained at 80 K from a crystal with composition $1.20\text{Na}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$ (Reidinger[7]).

(c) Ref. [16].

(d) Ref. [20].

essentially independent of temperature.* For several $K\beta$ crystals with different compositions ($x \approx 0.15$ to 0.42), they observed that E_a increased linearly with increasing ξ ($E_a \approx 0.2$ to 0.6 eV, $\xi \approx 6$ to 14 Å), while the conductivity decreased with increasing ξ . The extent of ordering as measured by ξ depends on the defect concentration, namely the interstitial oxygen content. Thus, reducing the excess O^- content reduces ξ and increases the conductivity. The relationship between ξ and σ is not known in this case, but it might be similar in nature to that described for β'' -alumina in a later section.

Haven Ratio

The Haven ratio is defined by $H_R = D_t/D_\sigma$, where D_t is the tracer diffusion coefficient and D_σ is the "charge diffusion coefficient" obtained from the ionic conductivity.** In solids with low concentrations of defects, the value of H_R is determined by the tracer correlation factor and so-called displacement effects[24,25] and is an indicator of the diffusion mechanism[26] (e.g, interstitial, interstitialcy, or vacancy). The situation for superionic conductors is more complicated due to the high concentration of defects, as discussed in the recent review by Murch[27]. The Haven ratio of $\sim 1/3$ reported by Yao and Kummer[14] was based on conductivity and diffusivity measurements at 25°C on the same crystal. The ratio of ≈ 0.6 reported by Whittingham and

*A small temperature dependence of ξ for $\text{Na}\beta$ was reported by Boilot et al.[23]. The strong temperature dependence of ξ observed for $\text{Ag}\beta$ was not seen in the data of McWhan et al.[22].

** $D_\sigma = kT\sigma(o)/nq^2 = kT\mu_i/q$ where $\sigma(o)$ is the dc conductivity, n is the number density of mobile ions with charge q , T is the absolute temperature, k is Boltzman's constant, and μ_i is the ionic mobility.

Huggins[15] was obtained using their conductivity data and the diffusivity data of Yao and Kummer measured as a function of temperature. Haven[28] corrected this value to account for the extra Na^+ ions and obtained $H_R \approx 0.70$. A definitive determination of H_R for Na β -alumina was reported by Kim et al.[29]. In these experiments, D_t and D_σ were obtained from tracer diffusion and conductivity measurements on single crystals cut from the same boule and, in some instances, from the same crystals. Representative values of H_R determined from these measurements are shown in figure 3. A marked temperature dependence of H_R is obvious: H_R increases from ~ 0.29 at 0°C to ~ 0.42 near 480°C . The jog in H_R near 200°C is caused by a jog which appears in the D_t data but not in the D_σ results (cf. figure 4 of [29]). This discontinuity was considered possibly to have a spurious origin and to be too small to warrant interpretation. Chandrashekhar and Kim[30] extended the measurements of H_R to nearly -80°C (figure 3). Their results show that H_R continues to decrease to ~ 0.18 at -78.5°C .

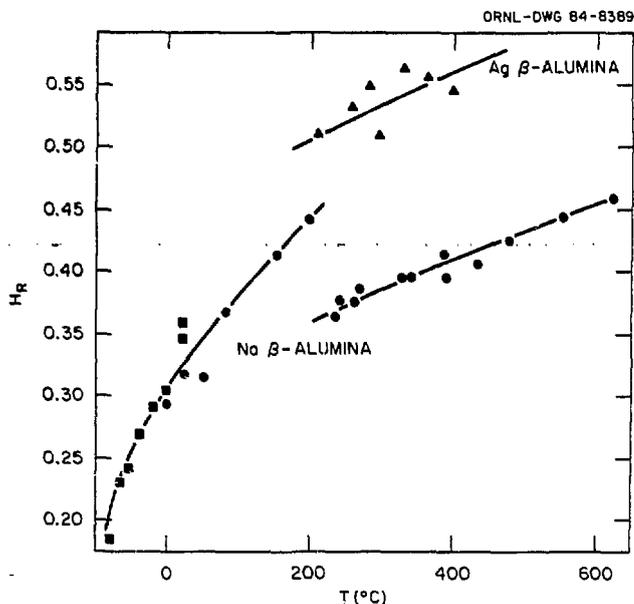


Figure 3. Haven ratios for Na and Ag β -alumina. \bullet — data from [29]; \blacksquare — data from [30]; \blacktriangle — data from [37]. The lines through the data points are visual guidelines.

Several theories have been advanced to account for the magnitude and temperature dependence of H_R [31-34]. Wolf[31] proposed the existence of associated or bound regions of Na^+ ions surrounding the excess O^- ions and found that correlation effects, and consequently H_R , were sensitive to the size and shape of the associated region. The increase in H_R with increasing temperature was attributed to a corresponding decrease in the size of the associated regions. Wolf's calculations agree well with the experimental results above 100°C , but they predict a limiting value of ~ 0.28 at low temperatures (-200°C), in disagreement with the observed trend. Sato and co-workers[32-34] used the path probability method (PPM) developed earlier for β -alumina[35] to explain the temperature dependence of H_R and the jog in H_R near 200°C . In this theory $H_R = f/f_I$, where f is the geometric correlation factor for tracer diffusion, and f_I is defined as a physical correlation factor for ionic conduction.* The temperature dependence of H_R is attributed[32] to (i) a change

*See Murch[27] for a careful analysis of this factor.

of population of the conducting ions among the BR and aBR sites and (ii) the temperature dependence of f and f_I . While the theoretical curve shows a decrease in H_R with T at low temperatures, the zero T limit of ~ 0.33 is far from the observed value of 0.18 at -78.5°C [30]. The jog in H_R was attributed to a percolation difficulty for the tracer atoms which is revealed when the time average of f is used rather than the ensemble average in calculating H_R . Wang[36], however, has shown that when the adjustable parameters of the PPM are fit to the experimental D_t and D_σ data, no jog appears in the D_t curve calculated by the PPM, and the agreement between the observed and theoretical values of H_R is poor. The situation at present is that there is no theoretical model which can account satisfactorily for the observed Haven ratio in Na β -alumina. A suitable model must be able to explain not only the strong temperature dependence of H_R but also the difference in Haven ratios for Na and Ag β -alumina[37] (figure 2).

Mixed Ion Effects

A phenomenon termed the mixed-alkali effect is well known in glasses and refers to the nonadditive behavior of certain properties when one alkali ion replaces a fraction of another[38]. It is observed, for example, that the ionic conductivity goes through a minimum while the pre-exponential factor and activation energy pass through a maximum at some intermediate composition. Radzilowski et al.[39] first reported a similar effect for β -alumina in which the activation energy of a polycrystalline Na-K β -alumina was observed to reach a maximum value when the fraction of K^+ ions was about 0.3 of the mobile cations ($[\text{K}]=0.3$). The first extensive measurements of mixed-ion effects in β -alumina were reported by Chandrashekar and Foster[40] from a study of Na-K β -alumina and the isomorphous Na-K β gallate. They found that the conductivity of Na_3 at 150°C decreased by more than three orders of magnitude near $[\text{K}]=0.25$, while the activation energy increased by more than a factor of two. Marked decreases in conductivity and increases in activation energy were also observed for mixed Na-Li[18,41] and K-Li[18] β -aluminas. Recently, similar mixed ion behavior was reported for Na-Ag β -alumina[42].

Wang et al.[43] proposed a model for mixed-ion β -aluminas based on potential energy calculations and the methods described in earlier work[16]. According to this model, when a cation with a larger ionic radius (e.g. K^+) replaces a fraction of the ions with a smaller radius (e.g. Na^+), the larger ion tends to occupy BR sites. On the other hand, when smaller ions replace a fraction of larger ions, the energy is minimized when the smaller ion occupies a m0 site and forms a mixed-ion pair (e.g. Na^+-K^+). For example, the calculated energy difference for two possible configurations in the Na-K system is $E(\text{Na}--\text{K},\text{Na}) - E(\text{Na}--\text{Na},\text{K}) = 0.11$ eV, where $x--y$ denotes the ions in pairs on m0 sites and z denotes the ions on BR sites. The model also predicts that the energy required for the smaller ion to escape from a mixed-ion pair is lower than the energy for escape of the larger ion. For example, $E_a(\text{Na}^*--\text{K},\text{K}) = 0.16$ eV and $E_a(\text{Na}--\text{K}^*,\text{K}) = 0.37$ eV, where K^* signifies the escaping ion. Since $E_a(\text{K}--\text{K}^*,\text{K}) = 0.27$ eV, one expects on the basis of this model that in the Na-K system, the maximum in activation energy will occur at the potassium-rich composition in which all the BR sites and one-half of the m0 sites are occupied by K^* ions. In a crystal with $x=0.23$, the predicted maximum is at $[\text{K}]=0.81$, which is close to the experimental value* (between 0.75 and 0.8) reported by

*The maximum in E_a reported by Chandrashekar and Foster[40] is close to $[\text{K}]=0.25$. The cause of the large discrepancy between the two experimental results is not known.

Bruce and Ingram[42]. However, the experimental activation energy at this composition, $E_a=0.6$ eV, is larger than expected from the model calculations. In the isomorphous Na-K β -gallate system with $x=0.36$, the maximum in E_a (minimum in σ) was observed[44] near $[K]=0.8$ compared to the predicted value of 0.73. From an x-ray structure determination[45] of a Na-K β -gallate crystal with $[K]=0.8$, the K^+ ions were found only on the m0 sites, as predicted. Thus, it seems that the simple model based on the idea of interstitial or paired ions can account for at least some of the mixed ion effects observed in β -alumina and the isomorphous β -gallate. Other observations remain unexplained, however, such as the maximum in E_a observed[41] in Na-Li β -alumina near $[Na]=0.2$ ($[Na]=0.81$ predicted) and the sharp rise in the pre-exponential factor in Na-K β -gallate near the conductivity minimum[44].

Ionic Transport in β'' -Alumina

Superlattice Ordering

The ordering of the mobile ions on a two-dimensional superlattice in Na β'' -alumina was observed by Collin et al.[11] from x-ray diffuse scattering measurements. The $\sqrt{3}a_0 \times \sqrt{3}a_0$ unit cell of the superlattice, where a_0 is the cell parameter of the average structure (i.e., the host structure), is illustrated in figure 1(b). This lattice is easily visualized as an ordered arrangement of the Na^+ ion vacancies. The construction of figure 1(b) is a special case in which 1/6 of the Na^+ sites are vacant.* Since there are 2 Na^+ sites per average cell, this corresponds to a structure with 1.67 Na^+ ions per formula unit. It is interesting that crystals of Mg-stabilized Na β'' -alumina grown by flux evaporation at high temperature typically have the composition $Na_{1.67}Mg_{0.67}Al_{10.33}O_{17}$ [10,46]. In contrast to $Na\beta$, the correlation length of the ordered region in $Na\beta''$ (micro-domain model) is strongly temperature dependent: ξ decreases from ~ 70 Å at 25°C to ~ 10 Å above 400°C[11] as illustrated in figure 2. Similar behavior was observed for $K\beta''$, but at 25°C, $\xi \sim 35$ Å or about one-half the value for that of $Na\beta''$. McWhan et al.[22] report a correlation between K^+ ions and Co^{2+} ions in the spinel block in cobalt-stabilized crystals. This interplanar correlation, in contrast to the strong intraplanar correlation, was not seen by Boilot et al.[11b] in their Mg-stabilized crystals, possibly due to the much smaller scattering power of Mg^{2+} ions. Quite different superlattice ordering was observed for $Ag\beta''$ [47]. Only a weak intraplanar ion-ion correlation was found, $\xi \sim 10$ Å (25°C), but rods of diffuse scattering were observed along the c^* -axis of the reciprocal lattice with a modulation pattern suggesting interplanar correlation. A 3-d hexagonal supercell was proposed with alternating occupied and vacant sites along the c direction.

The tendency of the mobile ions in Na and $K\beta''$ -aluminas to order on a superlattice can be understood, at least qualitatively, as due to the high concentration of vacancies and the strong effective Coulomb interaction among them[48]. When the sample temperature is lowered, the vacancies adopt the configuration which minimizes the free energy. As the sample temperature is

*Because of the tetrahedral arrangement of $O^=$ ions of the adjacent close-packed layers above and below the Na^+ sites, the Na^+ ions are displaced from the O(5) plane toward the three $O^=$ ions as illustrated in figure 1(b). The special superlattice shown has the vacancies replacing one type of Na^+ ion, i.e., those below the O(5) plane.

increased, there is a gradual disordering of the superlattice as evidenced by a decrease in the correlation length (figure 2). This behavior has an important effect on the ionic conductivity.

Conduction Mechanism and Ion-Ion Correlations

Comparing the graphs of ξ vs T and $\log(\sigma T)$ vs $1/T$ in figure 2 suggests that there is a connection between the extent of superlattice ordering and ionic conductivity in β "-alumina[10,11,48]. In their first report of x-ray diffuse scattering from $\text{Na}\beta$ ", Collin et al.[11a] remark that the temperature variation of the correlation length is probably the cause of the non-Arrhenian behavior of the conductivity data. Wang[49] has recently proposed a theory to account for the effect of superlattice ordering on conductivity. From the experimental conductivity data, the activation enthalpy* for conduction decreases from ~ 0.33 eV near 25°C to ~ 0.03 eV near 480°C . The calculated activation enthalpy for diffusion of a single vacancy in an ideal $\text{Na}\beta$ " lattice** was ~ 0.02 eV, which is close to experimental value at high temperature. Thus, at high temperature where the ion-ion correlation length is vanishingly small, conduction is due to the hopping motion of nearly "free" vacancies. To understand conduction at low temperatures, Wang assumed that at $T=0$ K the vacancies order on a perfect superlattice as shown in figure 1(b). Because of the superlattice ordering, the vacancies are trapped in deep potential wells. At finite temperatures, some of the vacancies are excited out of their special superlattice positions and form Frenkel-like defects (vacancy excess regions). Wang postulates that conduction at low temperatures is mainly due to motion of these Frenkel defects. The activation enthalpy is then the sum of one-half the energy required to form a Frenkel defect (ΔH_F) and the energy of migration (ΔH_M): $\Delta H(T) = \Delta H_F(T)/2 + \Delta H_M$. It is supposed that ΔH_M is the migration energy for free vacancies (~ 0.02 eV). A relation between ΔH_F and ξ is obtained by assuming that the vacancies are ordered within a circular region of radius ξ but are randomly placed outside of this region. By considering the Coulomb energy required to create a vacancy depleted region and form a Frenkel defect within the ordered region, the expression $\Delta H_F = a - b/\xi$ is obtained, where a and b are constants. The results of fitting a and b to the experimental values of activation enthalpy[50] and correlation lengths[11] are shown in figure 4.

The theory described above accounts for the effect of superlattice ordering on the conductivity of β "-alumina, and in particular it explains the characteristic non-Arrhenian behavior exhibited by Na and $\text{K}\beta$ ". Several observations summarized in Table III provide added support for this theory[4]: crystals of $\text{Na}\beta$ " grown at 1650 and 1700°C have identical compositions (within experimental error) but different values of E_a and ξ , and it is seen that the crystals which have the larger correlation length have higher activation energy.*** Also, when Na^+ is replaced with K^+ , the correlation length decreases, and so does the activation energy. The data for Zn-stabilized

*The temperature-dependent Gibbs free energy of activation is given by $\Delta G(T) = \Delta H(T) - T\Delta S(T)$. It is shown by Wang[49] that experimental values of $\Delta H(T)$ can be obtained from the experimental data by calculating the slope at a given T: $\Delta H(T) = -d\ln(\sigma T)/d(1/kT)$.

**One vacant site and all other 6c sites ($R\bar{3}m$) occupied by Na^+ ions.

***The cause of the difference in the correlation lengths of the two kinds of crystals is not known, but it might be due to a difference in the ordering of Mg^{2+} ions in the spinel layers.

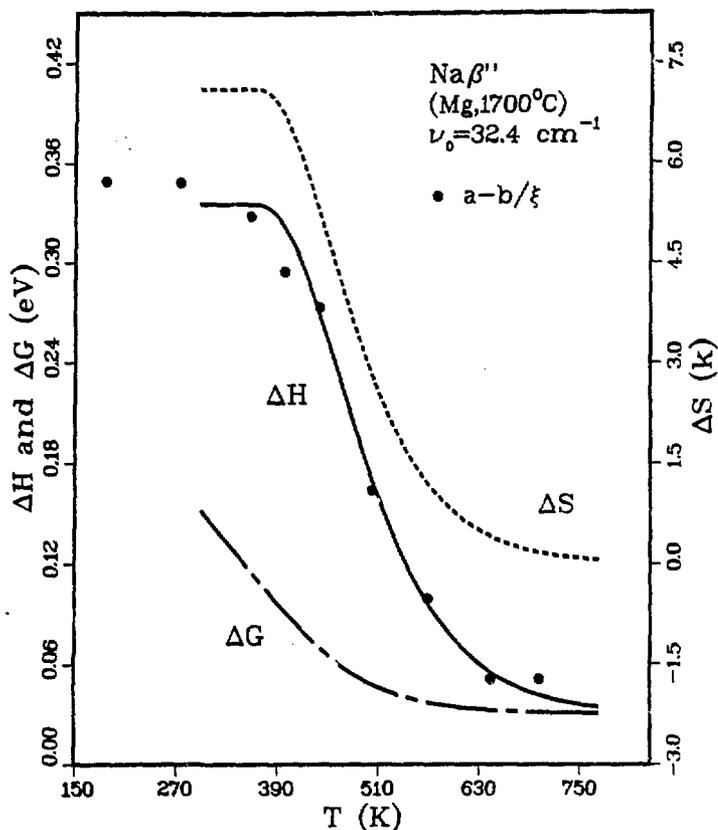


Figure 4. Activation entropy (ΔS), enthalpy (ΔH), and Gibbs free energy (ΔG) for Na β'' alumina calculated from the conductivity data. Solid points are values of $\Delta H = a - b/\xi(T)$. From ref. [49].

Table III. Correlation lengths ξ , activation energies E_a , and conductivities σ of Mg- and Zn-stabilized crystals of β'' -alumina at 25°C. (a)

Material (b)	ξ (Å)	E_a (eV)	σ ($\Omega^{-1}\text{cm}^{-1}$)
Na β'' Mg (1700°C)	67	0.33	0.01
Na β'' Mg (1650°C)	57	0.26	0.04
K β'' Mg (1700°C)	30	0.15	0.12
Na β'' Zn (1700°C)	55	0.14	0.10

(a) Data from Ref. [4].

(b) Na β'' Mg (1700°C) denotes Mg-stabilized Na β'' grown at 1700°C.

$\text{Na}\beta''$, however, indicate that other factors must be considered. Although the correlation length $\xi = 55 \text{ \AA}$ is comparable to that of the Mg-stabilized crystals grown at 1650°C , the activation energy is considerably smaller. One can speculate that since the vacancy concentration is appreciably higher in $\text{Na}\beta''(\text{Zn})$ but the size of the ordered regions is comparable to that of $\text{Na}\beta''(\text{Mg})$, the lower activation energy and higher conductivity is due to a larger number of vacancies that are not on ordered superlattice positions. These "free" vacancies are expected to have a much higher mobility than the ordered ones and are therefore responsible for the high conductivity at low temperatures. The reduced curvature in the $\log(\sigma T)$ vs $1/T$ graphs of $\text{Na}\beta''(\text{Zn})$ [4,50] compared to those of $\text{Na}\beta''(\text{Mg})$ is consistent with this reasoning.

Diffusion of Water and Protons in β - and β'' -Alumina

Kummer reported in his early review[1] that crystals of Na and Li β -alumina absorb water into their conduction layers when exposed to room temperature air. The results of more recent studies[51-53] indicate that exposure of polycrystalline specimens of β - and β'' -alumina to water vapor causes a decrease in conductivity and mechanical strength. The reaction of water with β - and β'' -alumina is therefore a subject of technological importance. In the following sections, the results of studies related to the diffusion of water in β - and β'' -alumina single crystals are reviewed. Proton transport in β'' -alumina will also be discussed briefly.

β -Alumina

Dudney et al.[54] have shown that the water content of Na and Li β -alumina can be varied continuously and reversibly up to the saturation limit. In $\text{Li}\beta$, this limit is about 2 H_2O molecules per unit cell*[55]. For a crystal containing about 1.6 H_2O /unit cell, it was determined by neutron diffraction[55] that the oxygen atoms of water molecules occupy sites in the conduction plane between the $m0$ and aBR positions ($\sim 0.7 \text{ \AA}$ from the $m0$ site); while the protons are located above and below the plane.** Polarized infrared absorption measurements[55] indicate that water molecules in hydrated $\text{Na}\beta$ are located on the same kinds of sites and have the same orientation as in $\text{Li}\beta$. The hydration enthalpies[54], -102 kJ/mol for $\text{Li}\beta$ and about -84 kJ/mol for $\text{Na}\beta$, are largely determined by the strong ion-dipole attraction between the alkali ions and the water molecules.

In general, the rates of hydration are controlled by the diffusivity of water in the conduction layers of the material. Infrared absorption measurements of

*The saturation limit is believed[55] to be equal to the number of aBR sites (2 per cell) minus the number of excess O^- ions (~ 0.15 to 0.3 per cell). The same limit is expected for $\text{Na}\beta$, but the maximum concentration that has been observed is $\sim 0.3 \text{ H}_2\text{O}/\text{unit cell}$ [54].

**A line drawn between the protons of H_2O is parallel to the c -axis and intersects the conduction plane at a point $\sim 0.4 \text{ \AA}$ from the aBR site. The protons form hydrogen bonds with the O^- ions (in the spinel blocks) that are directly above and below the aBR site[55] (figure 1(a)).

the kind illustrated in figure 5 show that the diffusivity of H_2O in $Li\beta$ is considerably larger than in $Na\beta$. From the analysis of similar absorbance profiles, the chemical diffusion coefficient of H_2O in $Li\beta$ at 350° was determined to be $5.8 \times 10^{-7} \text{ cm}^2/\text{s}$ [56]. For comparison, Kummer[1] found that the self diffusion coefficient of Li^+ ions at the same temperature is $1.3 \times 10^{-6} \text{ cm}^2/\text{s}$.

A mechanism which accounts for the fast diffusion of water in $Li\beta$ was proposed by Dudney et al.[57]. The first step in this mechanism (illustrated in figure 6) is the dissociation of H_2O molecules. Next, the original water oxygen atom, now an interstitial $O^=$ ion in the transition state, displaces an $O(5)$ oxygen ion which then recombines with the protons to form H_2O at a new location. Evidence that a fraction of the H_2O molecules in $Li\beta$ dissociate to form OH^- and $H(H_2O)^+n$ ($n=1,2$) can be seen in the infrared absorption spectra (figure 5): the sharp peaks above 3400 cm^{-1} are due to OH^- species[55], while the broader features below 2900 cm^{-1} have been assigned to H_3O^+ and $H_5O_2^+$ [54,55]. Following the treatment of anhydrous crystals in $H_2^{18}O$, it was found[57] that the ^{18}O (as measured by the OH^- peak) was concentrated near the edge of the samples, although the distribution of OH^- and H_2O was homogeneous from the center to the edge of the samples. Thus, the mechanism is supported by experiment, and it explains how water can move through the conduction layers by a process which does not require major displacements of the lithium ions.

There is no evidence that water molecules dissociate in the conduction layers of $Na\beta$ -alumina. In figure 5, for example, the peaks assigned to OH^- species in the absorption spectra of $Li\beta$ do not appear in the spectra of $Na\beta$. Therefore, diffusion of water in $Na\beta$ probably occurs by a different mechanism than in $Li\beta$; possibly water molecules move by a process that requires considerable displacement of Na^+ and excess $O^=$ ions and therefore has a higher activation energy. This might explain the much slower diffusion of water in $Na\beta$ compared to $Li\beta$.

β "-Alumina

Water diffuses much more rapidly in $Na\beta$ " than in $Na\beta$. Infrared absorption spectra and packing considerations indicate[58] that H_2O molecules occupy vacant Na^+ sites and mO sites in the conduction layers. The saturation limit appears to be governed by the vacancy concentration[59], which is $\sim 0.33/\text{unit}$ cell for Mg -stabilized crystals and $\sim 0.43/\text{unit}$ cell for Zn -stabilized crystals.

Diffusion coefficients of water in $Na\beta$ " have been reported for temperatures of 25, 45, and 70°C [58]. Infrared absorbance profiles were obtained from measurements through a small circular aperture following treatment of initially anhydrous samples in water vapor. The diffusion coefficients obtained by least-squares fits* of the measured absorbances are $5.2(\pm 1.3) \times 10^{-10}$, $5.3(\pm 1.3) \times 10^{-9}$, and $1.4(\pm 0.4) \times 10^{-8} \text{ cm}^2/\text{s}$ at 25, 45, and 70°C , respectively.**

*The fitting function involved an integration over the circular aperture at each position x , and the concentration was assumed to have the form $C(x) = C_0 \text{erfc}(x/2\sqrt{Dt})$, where C_0 is the surface concentration, D is the diffusion coefficient, and t is the diffusion time.

**The uncertainties were estimated from errors in the absorbance values and from the diffusion coefficients determined for different samples. Systematic errors in the measuring technique[58] are unknown and might be larger than the quoted uncertainties.

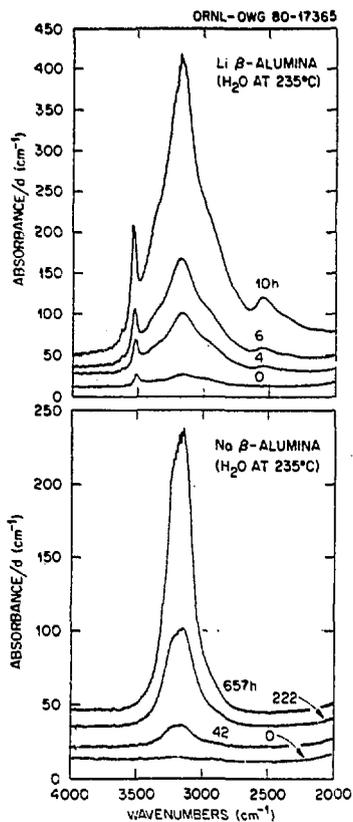


Figure 5. Infrared absorption spectra of Li and Na β -alumina measured at 25°C before and after treatment in water vapor at 235°C for the specified time in hours. The strong, broad peak near 3150 cm⁻¹ is due to the symmetric stretching mode of H₂O molecules in the conduction layers. From [55].

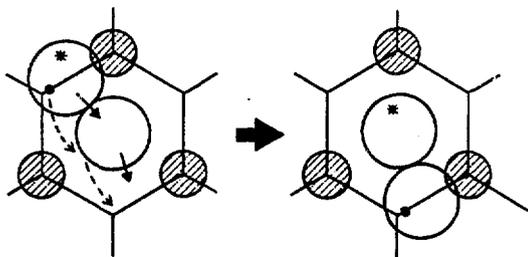


Figure 6. Mechanism for diffusion of H₂O in Li β -alumina. The small solid circle represents a proton (located above the conduction plane), and * denotes a tagged oxygen atom. The shaded circles represent Na⁺ ions. From [57].

The diffusivity of water in $\text{Na}\beta$ is high even when compared with that of Na^+ ions ($D_{\sigma} \approx 3 \times 10^{-6} \text{ cm}^2/\text{s}$ at 25°C), and it is orders of magnitude larger than the estimated diffusivities for H_2O in $\text{Na}\beta$. There is no evidence that OH^- is formed in $\text{Na}\beta$ at temperatures from 25 to 400°C [60], so it does not appear that dissociation is involved in the diffusion mechanism. The high diffusivity of water is likely associated with the high mobility of the cation vacancies.

Farrington and Briant[61] have observed high proton conductivity in ammonium-hydronium β -alumina with the composition $(\text{NH}_4)_{1.00}(\text{H}_3\text{O})_{0.67}\text{Al}_{10.33}\text{O}_{17}$. At 25°C , $\sigma \approx 1 \times 10^{-4} \Omega^{-1} \text{ cm}^{-1}$, and at 190°C , $\sigma \approx 6 \times 10^{-3} \Omega^{-1} \text{ cm}^{-1}$. The corresponding values of D_{σ} are $\sim 8 \times 10^{-10} \text{ cm}^2/\text{s}$ and $\sim 8 \times 10^{-8} \text{ cm}^2/\text{s}$, respectively, using the total proton concentration. A Grothuss-type proton transfer* involving the NH_4^+ , H_3O^+ , and $\text{O}(5) \text{O}^=$ was suggested as a possible mechanism for the high conductivity.

Rapid proton diffusion has been recently observed in $\text{Pb}\beta$ [59;64]. Hydrogen in the form of H^+ and/or OH^- , diffuses into the conduction layers during ion exchange of $\text{Na}\beta$ in PbCl_2 [59]. The hydrogen is bound as OH^- , and several types of hydroxyl species distinguished by different stretching frequencies and orientations of the O-H bond were identified. Tracer diffusion coefficients were measured using the optical technique mentioned above[59]. At 455°C , for example, $D_t \approx 5 \times 10^{-7} \text{ cm}^2/\text{s}$, with an estimated activation energy of 0.5 eV. By comparison, for Pb^{2+} ions at the same temperature, $D_{\sigma} = 8 \times 10^{-5} \text{ cm}^2/\text{s}$; with an activation energy of about 0.3 eV.** At present, the mechanism for the high proton diffusivity in $\text{Pb}\beta$ is not known.

Summary

The β - and β'' -aluminas are a remarkable family of superionic conductors in that they display high conductivities for many cations, including protons and doubly charged ions, and high diffusivities for H_2O molecules. Studies of these materials have provided important insights into the nature of ionic transport in highly defective solids and, in some respects, they can be classified as model compounds. Yet, some important observations, such as the Haven ratio and mixed-ion effects in β -alumina, are not completely understood.

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The author thanks N. J. Dudney and J. C. Wang for their helpful comments on this manuscript.

*The Grothuss mechanism [62] is represented by $\text{H}_2\text{O} + \text{H}_3\text{O}^+ = \text{H}_3\text{O}^+ + \text{H}_2\text{O}$, i.e. it is a proton jump from one molecule to another and possibly involves molecular reorientation.

**Activation energy calculated from the slope of $\ln \sigma T$ vs $1/T$ for several points in the temperature range near 455°C .

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