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LETTER TO THE EDITOR

Ionic conductivity of potassium β'' alumina in the very-far infrared

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Abstract. Vibrations induced by potassium ions in potassium β'' alumina give rise to absorption bands at 2 K which occur at 29 and 88 cm^{-1} and also in the region 145–175 cm^{-1} . These bands show effects of anharmonicity with increasing temperature. At 600 K the 29 cm^{-1} band has almost totally disappeared and is partly replaced by a diffusive component to the absorption. This component has been measured at energies down to 2 cm^{-1} . A simple phenomenological model reproduces temperature-induced changes in the spectrum reasonably well.

We are currently engaged in a study of absorption by crystals with the β'' alumina structure in the far infrared and we report our results here for potassium β'' alumina. This material is particularly interesting because it has an ionic conductivity at 25 °C of $\sim 0.13 (\Omega \text{ cm})^{-1}$, comparable to that of sodium β'' alumina ($\sim 0.15 \Omega \text{ cm})^{-1}$ and sodium β alumina ($0.03 (\Omega \text{ cm})^{-1}$) (see Farrington and Briant 1979).

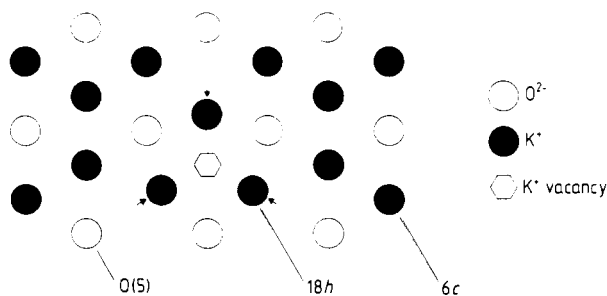


Figure 1. Schematic representation of the conduction slab of potassium β'' alumina projected on to the plane containing the O(5) bridging oxygens. 18h sites are shown, near a vacancy, as well as 6c sites.

The structure of β'' alumina materials is closely related to that of β alumina. The former has rhombohedral symmetry compared with hexagonal symmetry for the latter. This difference is associated with a triple stacking sequence of spinel-like blocks of aluminium oxide along the c axis for β'' alumina, compared with double stacking for β alumina (see e.g. Boilot *et al* 1980). In addition, the mobile ions in β'' alumina move in a conducting slab of finite thickness which in potassium β'' alumina has the value of 0.28 Å. Also, the Beevers–Ross (BR) and anti-Beevers–Ross (aBR) positions in the con-

ducting plane of β -alumina (see e.g. Hayes *et al* 1981) become equivalent in the conducting slab of β'' alumina (figure 1). The formula for the perfectly stoichiometric compound would be $K_2O \cdot MgO \cdot 5 Al_2O_3$, the structure being stabilised by Mg^{2+} ions in tetrahedrally coordinated Al^{3+} sites. The Mg^{2+} ions make it possible in principle to fill all the cation sites in the conducting slab without the necessity of introducing charge-compensating oxygen ions (see e.g. Hayes *et al* 1981 and Hayes and Holden 1982 for a discussion of effects of interstitial charge-compensating oxygen in the conducting plane of β alumina). However, as-grown sodium β'' alumina is not stoichiometric, generally containing $\geq 15\%$ of sodium vacancies (see e.g. Bates and Farrington 1981 for recent discussions) and ionic conduction occurs through vacancy migration. In the present case potassium β'' alumina crystals were prepared by heating sodium β'' alumina crystals in molten KNO_3 at $340^\circ C$ for 24 h, achieving almost complete ion exchange.

A detailed structural study of potassium β'' alumina has been carried out by Boilot *et al* (1980) using both x-ray diffuse scattering and x-ray diffraction techniques. They find evidence for two-dimensional short-range order in the conducting slab at room temperature with a coherence length ξ of 35 \AA . They conclude that the K^+ ions occupy two distinct sites in the conducting slab with about 60% on off-centred $18h$ sites and about 40% on $6c$ sites (figure 1). They also find that ξ falls between 300 and 600 K to a value of 20 \AA and that the activation energy for the ionic conductivity falls from a value of 0.21 eV for $T \leq 360 \text{ K}$ to 0.1 eV for $T \geq 360 \text{ K}$. It has been suggested by Bates *et al* (1981) that this reduction of activation energy with increasing temperature is due to break-up of ordered arrays of vacancies.

We have measured the infrared absorption spectrum of potassium β'' alumina at temperatures extending from 2 K to 600 K with the electric vector E of the incident radiation perpendicular to the c axis of the crystal. Fourier transform spectrometers were used to cover the spectral range 2 to 200 cm^{-1} . A mercury lamp was used as the source of radiation. The sensitivity required for measurement in the microwave region ($\nu \geq 2 \text{ cm}^{-1}$) was obtained by using a ^3He -cooled germanium bolometer. The absorption coefficient $\alpha(\omega)$ was determined by measuring the transmission of samples of different thickness so that surface effects could be eliminated. The conductivity $\sigma(\omega)$ was then obtained using the relationship

$$\alpha(\omega) = 4\pi\sigma(\omega)/nc \quad (1)$$

where $n \approx 4$ is the refractive index and c is the velocity of light in free space.

The spectrum at 2 K shows three main regions of absorption, at 29 and 88 cm^{-1} and in the range $145\text{--}175 \text{ cm}^{-1}$. Sodium β'' alumina from a variety of sources was used as starting material and the relative intensity of absorption in the three regions mentioned above depended on the source of material. This variation indicates that the three regions of absorption arise from different centres. Maintaining the crystal at 600 K in a vacuum for long periods of time does not change the spectrum, indicating that water in the crystal is not a determining factor. The absorption is always dominated by the peak at 88 cm^{-1} . This peak shows structure at 2 K (figure 2(a)) and can account for the bulk of K^+ ions, in both $6c$ and $18h$ sites (see Boilot *et al* 1980). However, the distribution of K^+ ions is more complex than the x-ray studies of Boilot *et al* (1980) imply. The weaker absorptions at 29 cm^{-1} and in the range $145\text{--}175 \text{ cm}^{-1}$ decay with increasing temperature. Although it is not possible to give precise models for these oscillators it seems likely that the 29 cm^{-1} peak is due to K^+ ions associated with an aggregate of three or more K^+ vacancies and the absorption in the range $145\text{--}175 \text{ cm}^{-1}$ with defect-associated interstitial K^+ .

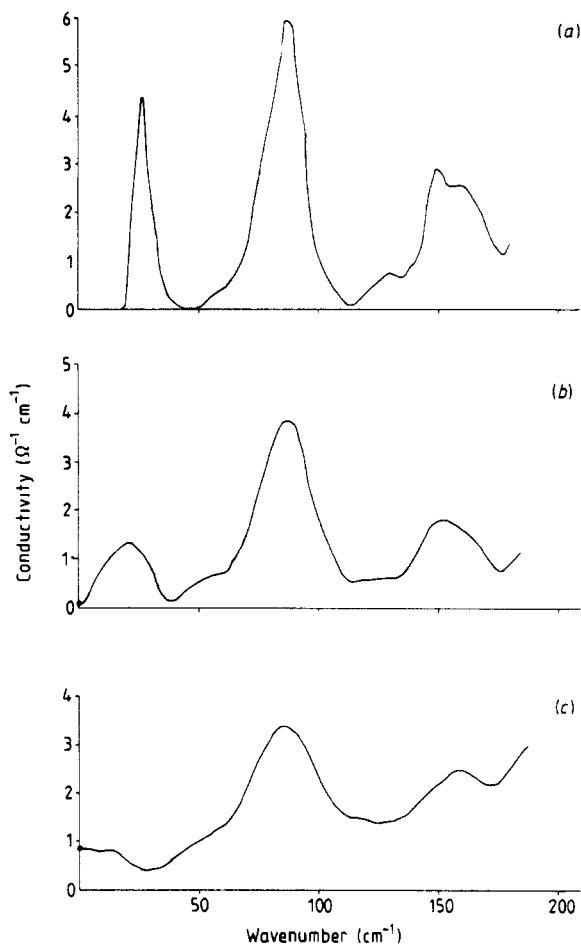


Figure 2. Infrared conductivity with $E \perp c$ of potassium β' alumina at (a) 2 K, (b) 300 K and (c) 600 K. Measured DC conductivities at 300 K and 600 K are indicated by dots (see text).

The 29 cm^{-1} peak is very anharmonic, shifting to 20 cm^{-1} at 300 K (figure 2(b)). At 600 K the peak has been largely replaced by a diffusive component, although there is a residual peak visible at 14 cm^{-1} (figure 2(c)). There is also a weak band at $\sim 60 \text{ cm}^{-1}$ which grows in intensity with increasing temperature (figure 2). Again, it is likely that this is due to a K^+ ion associated with a vacancy aggregate smaller than that giving rise to the 29 cm^{-1} peak, and that its growth in intensity is to some extent at the expense of the 29 cm^{-1} peak. It is clear that the changes occurring in the conducting slab with increasing temperature are complex and that the K^+ ions giving rise to the 29 cm^{-1} peak are important in determining the conductivity at small ω . Our spectra do not show any effects of a superlattice arising from ordering of vacancies (see Boilot *et al* 1980 and Bates *et al* 1981).

For $T < 300 \text{ K}$ the sensitivity of our spectrometer is not sufficiently great to detect diffusive motion (see Strom and Ngai 1981 for a discussion of the dynamics of sodium β alumina in the frequency range 10^2 – 10^{11} Hz at low temperatures). However, the

diffusive motion is sufficiently prevalent at $T \geq 300$ K to be detected for $\nu \geq 2 \text{ cm}^{-1}$ (figures 2(b, c)). Measured DC conductivities (Farrington and Briant 1979) are indicated in figures 2(b, c). We have assumed in these figures that $\sigma(\nu = 0) = \sigma(\nu = 2 \text{ cm}^{-1})$. The background rising with increasing energy at higher temperatures is due largely to disorder-induced phonon absorption in the spinel blocks.

We have also carried out a study of the far infrared absorption of potassium β alumina with $E \perp c$, finding a spectrum at 2 K dominated by three bands, at 69, 84 and 107 cm^{-1} (Hayes *et al* 1980). The peak at 89 cm^{-1} was the most intense and was assigned to vibration of K^+ ions in BR sites, analogous to 6c sites in the β'' compound. The peaks at 69 and 107 cm^{-1} were not present in nearly-stoichiometric crystals and it was assumed that they were due to association of K^+ ions with charge-compensating interstitial oxygens.

The Raman spectrum of potassium β'' alumina has been measured by Bates *et al* (1979), who find an intense band of E_{2g} symmetry at 116 cm^{-1} , due to vibrations of the spinel blocks. There is a corresponding band in potassium β alumina at 123 cm^{-1} (Hao *et al* 1976). In addition, Bates *et al* (1979) find weaker Raman excitations of singlet character at 73, 78 and 90 cm^{-1} and also at 170 cm^{-1} , extending to lower energy. The 73, 78 and 90 cm^{-1} bands fall within the envelope of the infrared band at 88 cm^{-1} and, presumably, have a similar origin. The Raman scattering for $\nu < 170 \text{ cm}^{-1}$ may also be related to the infrared absorption in the range $145\text{--}175 \text{ cm}^{-1}$. There is no evidence for the presence of a Raman peak associated with the infrared peak at 29 cm^{-1} (figure 2(a)).

The description of the diffusion of ions in a solid is a complex theoretical problem (see Dieterich *et al* 1980 for a review relevant to superionics). Various approximations have been employed but all approaches predict two peaks in the frequency dependence of the conductivity. One peak, centred on $\omega = 0$, is associated with long-range diffusion of the ions and the other, at a finite frequency, is associated with vibrations of ions temporarily immobilised in a potential well (see figure 9 of Kleppmann and Zeyher 1980).

We outline here a simple phenomenological approach to the far infrared conductivity of potassium β'' alumina based on a description of disorder in liquids given by Rahman *et al* (1962). This description was subsequently elaborated for solids by Huberman and Sen (1974) and Sen and Huberman (1975). We assume that the K^+ ions have two types of motion, (i) an oscillatory motion in a lattice site and (ii) a diffusive motion, with no correlation between the two. We shall also assume as we vary the infrared frequency $\nu = 1/\tau$ that the ionic response is oscillatory for $\tau_0 > \tau$, where $\tau_0 = 2\pi/\omega_0$ is the time between K^+ jumps, and diffusive for $\tau_0 < \tau$. We shall concern ourselves only with the spectrum of energies less than 120 cm^{-1} (figure 2) and assume for simplicity that at 2 K we are dealing with only two damped harmonic oscillators with peak frequencies $\omega_1 = 29$ and $\omega_2 = 88 \text{ cm}^{-1}$. As we heat the crystals, diffusive motion gradually occurs and we take the ionic conductivity to be given by

$$\sigma(\omega) = (Ne^2/M)[f_0\gamma/(\gamma^2 + \omega^2) + f_1\rho(\omega)L(\omega, \omega_1, \Gamma_1) + f_2\rho(\omega)L(\omega, \omega_2, \Gamma_2)] \quad (2)$$

where N is the density of K^+ vacancies in the conductivity slab, e is the charge and M is the mass of the K^+ ions. The first term in equation (2) represents a Drude-type conductivity and the second and third terms represent a damped harmonic oscillator response. In the first term $\gamma = A 2\pi/\tau_i$, where τ_i is a transit time given by $\tau_i \sim r_0(M/k_B T)^{1/2}$ and r_0 is a jump distance taken to be the distance between neighbouring K^+ sites (3.3 \AA). The value of A is determined at any temperature by comparison with the measured DC conductivity. The function $\rho(\omega)$ describes the degree to which hopping reduces the

oscillatory response and is taken to be

$$\begin{aligned} \rho(\omega) &= 1 - \omega_0/\omega & \omega_0 < \omega \\ &= 0 & \omega_0 > \omega \end{aligned} \tag{3}$$

for an oscillator of frequency ω .

Assuming that the area under the $\sigma(\omega)$ - ω curve does not change with temperature, we write

$$f_0 = f_1[1 - \rho(\omega_1)] + f_2[1 - \rho(\omega_2)] \tag{4}$$

$$= f_1\omega_0/\omega_1 + f_2\omega_0/\omega_2 \tag{5}$$

where f_0 is the fraction of K^+ ions giving a Drude-type response and $f_1 + f_2 = 1$. The value of ω_0 is temperature dependent and we assume it has the form $\omega_0 = \omega_\infty e^{-U/k_B T}$ where U is the activation energy for motion of K^+ ions which we take to be 0.1 eV (see above). The damped harmonic oscillator response has the form

$$L(\omega, \omega_1, \Gamma_1) = \frac{2\Gamma_1\omega_1\omega^2}{(\omega^2 - \omega_1^2)^2 + 4\Gamma_1^2\omega_1^2\omega^2} \tag{6}$$

where $2\Gamma_1\omega_1$ is the full width at half height. $L(\omega, \omega_2, \Gamma_2)$ has a similar form to equation (6).

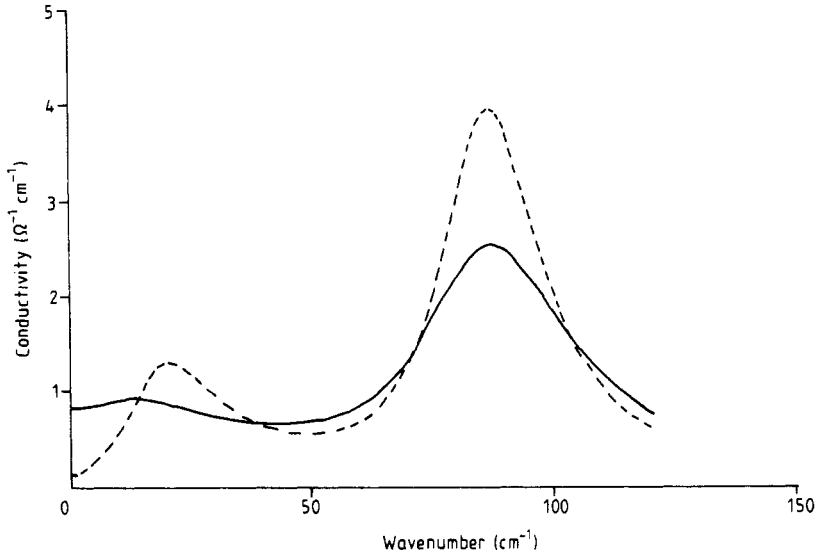


Figure 3. Computed infrared conductivity of potassium β'' alumina at 300 K (broken curve) and 600 K (full curve).

We show in figure 3 values of $\sigma(\omega)$ calculated from equation (2) using the following values of the parameters:

	cm ⁻¹					A	Γ_1	Γ_2	f ₁	f ₂
	ω_1	ω_2	ω_0	ω_∞	γ					
300 K	20	86	1.9	90	35	0.22	0.6	0.14	0.25	0.75
600 K	14	86	13	90	60	0.22	0.6	0.2	0.25	0.75

Comparison with figures 2(b), (c) show that the changes produced in $\sigma(\omega)$ by heating the crystal are reproduced reasonably well. The change in the low-energy conductivity caused by the switch from oscillatory to diffusive motion is apparent. This effect is accounted for in our model by the closeness of ω_0 at 600 K (13 cm^{-1}) to ω_1 (14 cm^{-1}) (see above).

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