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Reaction of polycrystalline Na β''-alumina with CO_2 and H_2O and the formation of hydroxyl groups*

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The reactions of polycrystalline Na β''-alumina with CO_2 and H_2O were investigated using infrared reflectance methods. These reactions result in the replacement of Na^+ ions with H_3O^+ ions and the formation of a scale of $NaHCO_3$ or hydrated Na_2CO_3 on the surfaces of ceramic specimens. The composition of the scale formed depends on the pressures of CO_2 and H_2O: $NaHCO_3$ forms at high CO_2 pressure while $Na_2CO_3 \cdot XH_2O$ forms at low CO_2 pressures. The H_3O^+ ions dislocate by an endothermic process to produce OH^- species in the conduction layers of the grains. The removal of these species by H_2O evolution at high temperature implies that an irreversible change occurs in the composition of the surface region of the ceramic.

1. Introduction

The results of several previous studies suggest that β-alumina and β''-alumina react with water vapour and CO_2 causing the formation of a carbonate on the surface of these materials. Kummer [1] reported that Na_2CO_3 forms on the surface of fine particles of Na β-alumina when exposed to moisture and CO_2. Dunn [2] found that H_2O and CO_2 are evolved during dehydration of powdered Na β''-alumina that had been exposed to moist air. Harbach [3] reported that evidence was found in X-ray diffraction patterns for the formation of a hydrated carbonate layer ($Na_3H(CO_3)_2 \cdot H_2O$) on Na β''-alumina ceramics exposed to moisture and CO_2, while Garbarczyk *et al.* [4] claimed that their thermal analysis studies confirm the formation of hydrated Na_2CO_3 on the surface of ceramic specimens. The Na^+ ions which are removed from the conduction layers to form the carbonate are presumably replaced by H_3O^+ ions [4]. Heavens [5] observed an increase in the *c* lattice parameter of the surface region of polycrystalline Na β-alumina after exposure to air. He attributed this expansion to the replacement of Na^+ by H_3O^+ according to the reaction: $Na^+ + 2H_2O = H_3O^+ + NaOH$. DeJonghe and Feldman [6] had earlier speculated that such a reaction results in the formation of NaOH within fine cracks of ceramic samples. More recently, Keddar *et al.* [7] reported evidence from photoemission spectra for the presence of Na_2CO_3 on the surface of Na β''-alumina tubes removed from Na–S cells.

In this paper the results of infrared reflectance measurements will be presented which show that polycrystalline Na β''-alumina reacts with CO_2 and water vapour resulting in the formation of $NaHCO_3$ at high CO_2 pressures or hydrated Na_2CO_3 at low CO_2 pressures on the surfaces of the ceramic specimens. It will be shown that the Na^+ ions removed from the conduction layers are replaced by H_3O^+ ions which, on heating the ceramic specimens, dissociate to produce hydroxyl groups.

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2. Experimental procedures

Most of the samples investigated were bar-shaped specimens of lithium-stabilized Na β''-alumina (Ceramatec, Inc) with a reported composition by weight of 8.85% Na_2O, 0.75% Li_2O, and 90.4% Al_2O_3. After cutting to length, the bars measured about 4 cm × 2 cm × 0.5 cm. In photomicrographs of the small and large faces of the bars, the grains appeared as randomly oriented elongated platelets of up to 20 μm in length. Some experiments were performed on sections of electrolyte tubes produced from magnesium-stabilized Na β''-alumina, kindly supplied by F. Harbach of BBC (FDR), and on a bar-shaped specimen of polycrystalline Na β-alumina prepared at ORNL. All of the as-received specimens had impurity surface layers (described later) which were removed by grinding one or more faces on emery paper followed occasionally by heating in dry oxygen at 600° C. Specimens with freshly ground faces were treated in various atmospheres at 25° C including water-saturated carbon dioxide, air and oxygen and dry carbon dioxide.

Infrared reflectivity measurements were made on the as-received and treated specimens at 25° C and at elevated temperatures using a Fourier transform spectrometer. Samples were placed at the focus of a reflecting beam condenser in which the angle of incidence (measured from the central ray) was ~16° C. The 2.25 linear reduction of the incident light beam gave an approximate 1 cm image on the sample surface. The specular and diffuse components of the reflected light were collected at 16° with an angular spread of ~ ± 15° from the central ray. Reflectance measurements at elevated temperatures were made by attaching the specimens to a heated stainless steel block. The sample temperature was measured by a thermocouple which was pressed against the exposed surface of the specimen. The reflectance from an aluminium mirror was used as a reference for the single-beam sample reflectance spectra. The reflectance spectra shown later are presented as graphs of $\log (I_0/I)$ (i.e. $-\log$ (reflectivity)) against wave number, where I_0 is the intensity of the light reflected from the mirror, and I is the intensity of the light reflected from the sample.

Multiple internal reflection (MIR) measurements were also made on the bar-shaped specimens using KRS-5 trapezoids cut to give internal incidence angles of 60° and 45°. The large face of each bar was pressed firmly against the trapezoid during measurements of sample spectra, and the opposite side of the trapezoid was in contact with the stainless steel holder. The single beam spectrum of each trapezoid sandwiched between the steel plates was used as the background reference for the respective sets of sample spectra.

The pressure inside the evacuated sample chamber during the infrared measurements was about 10^3 Pa. Assuming that the principal contribution to this pressure is the dry air released from the air bearing, the vapour pressures of H_2O and CO_2 inside the sample chamber were estimated to be $P_{H_2O} = 7 \times 10^{-3}$ Pa and $P_{CO_2} = 0.4$ Pa, respectively.

X-ray diffraction measurements were made on sections of scale removed from a lithium-stabilized specimen exposed to ambient air for several months and on the bar-shaped specimens used in the optical studies. Each set of data was collected over periods from 15 to 20 h in order to improve the signal-to-noise ratio of weak reflections from impurities localized near the surface.

3. Results and discussion

3.1. Reaction of Na β''-alumina with CO_2 and H_2O

Reflection spectra of the lithium-stabilized Na β''-alumina bars measured at 25° C are illustrated in Figs. 1 to 3. The curves in Fig. 1 are due to a combination of specular reflection from large grains, diffuse reflection from small grains, and absorption of the incident radiation from two or more passes through the grains. The reflectance due to the polycrystalline substrate will not be discussed here except to mention that the strong and weak features observed below 1200 cm^{-1} in curve (a) are due to phonons of Na β''-alumina. Similar features have been observed in reflectance spectra of magnesium stabilized Na β''-alumina single crystals [8] and single crystals of Na β-alumina [9, 10]. Several new features appear in the reflection spectrum after treatment in H_2O-saturated CO_2 (curve b). As will be shown below, the features at wave numbers lower than 1700 cm^{-1} are due to $NaHCO_3$. The peaks above 2000 cm^{-1} are attributed to $H(H_2O)_n^+$ and H_2O in the conduction layers of the β''-alumina grains. There is possibly some contribution to the broad bands near 3400 cm^{-1}

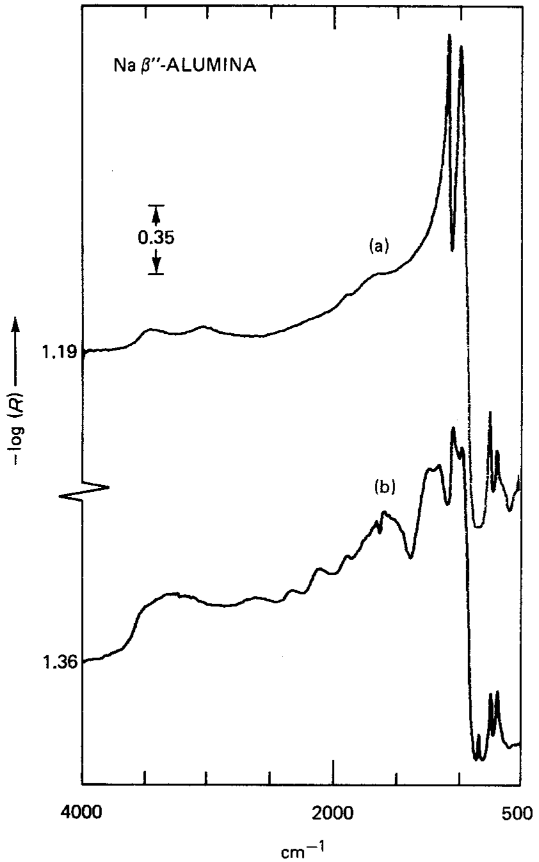

Figure 1 Reflection spectra of polycrystalline Na β''-alumina. (a) After heating of as-received specimen in dry O_2 at 600° C; (b) after treatment of specimen in H_2O-saturated CO_2 at 25° C. Measurements at 25° C.

from adsorbed H_2O. The spectral features due to $NaHCO_3$, $H(H_2O)_n^+$ and H_2O appear as absorption bands in the reflection spectra. Energy loss from absorption occurs in the incident beam and in the light reflected from the sample.

Multiple internal reflection spectra of a bar-shaped specimen and a thin film of $NaHCO_3$ are shown in Fig. 2. It can be seen that the spectra of β''-alumina obtained with the 60° and 45° trapezoids closely match the spectrum of $NaHCO_3$. There is no evidence in either spectrum for the presence of Na_2CO_3, as would be indicated by the appearance of a peak at 880 cm^{-1} [11]. Also, the strong infrared peak of β''-alumina near 850 cm^{-1} does not appear in the 60° or 45° spectra of the sample. With the 45° trapezoid, the penetration depth of the evanescent wave into the surface of the β''-alumina sample is estimated [12] to be $\approx 4\,\mu m$ at 1000 cm^{-1} ($\approx 1\,\mu m$ for the 60° trapezoid), taking 1.5 as the refractive index of the surface region, i.e. the average index of $NaHCO_3$. (The critical angle for this index is 37°). Thus, it can be concluded from the MIR experiments that, after exposure to H_2O saturated CO_2, the β''-alumina specimen was covered by a layer of $NaHCO_3$ which was at least 4 μm thick.

Reflection spectra in the region from 2000 to 4000 cm^{-1} are shown in Fig. 3. The two prominent peaks near 3450 and 3090 cm^{-1} in the spectrum of the as-received specimen, curve (a), as well as in curves (b), (c), and (d), are due to H_2O molecules located in the conduction layers of the β''-alumina grains [13]. From the analysis of infrared measurements on hydrated single crystals of Na β''-alumina [13], the peak near 3450 cm^{-1} is attributed to molecules on mid-oxygen sites, while the peak near 3090 cm^{-1} is attributed to molecules on the vacant sodium ion sites. In both cases, the peaks consist of overlapping components of the symmetric (ν_1) and antisymmetric (ν_3) stretching modes, with ν_3 contributing predominantly to the observed intensity because of the nearly random orientation of the grains and the greater transition dipole strength of this mode [13]. The net absorption strength of the two modes assuming exact coincidence and random grain orientation is given by $S = 1/3[2S(\nu_1) + S(\nu_3)]$, where $S(\nu_1)$ and $S(\nu_3)$ are the respective absorption strengths of ν_1 and ν_3. Using the values of $S(\nu_1)$ and $S(\nu_3)$ for molecules on vacant sodium sites [13], this relation gives $S(3090\,\text{cm}^{-1}) \approx 4 \times 10^5\,\text{l}\,\text{mol}^{-1}\,\text{cm}^{-2}$. If it is assumed that the grains of the specimen which yielded curve (a) in Fig. 3 contained about the same concentration of H_2O as typically observed [13] for single crystals of Na β''-alumina, then the concentration of H_2O on vacant Na sites is estimated to be about 0.2 mol l^{-1}. Taking this value, the above estimate for $S(3090\,\text{cm}^{-1})$, and the area under the 3090 cm^{-1} peak in curve (a), $\int \ln (I_0/I)\,d\nu = 1.8\,\text{cm}^{-1}$, the effective optical path for the absorbed radiation in the reflection measurements is of the order of 20 μm.§

The peaks at 2128 and 2336 cm^{-1} which were observed in the spectra of as-received specimens (curve a of Fig. 3) disappeared after rubbing a

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§The effective optical path length was taken as $[\int \ln (I_0/I)d\nu]/SC$ where C is the concentration of H_2O in mol l^{-1}. This assumes a uniform distribution of H_2O in the region of the specimen sampled by the infrared beam.

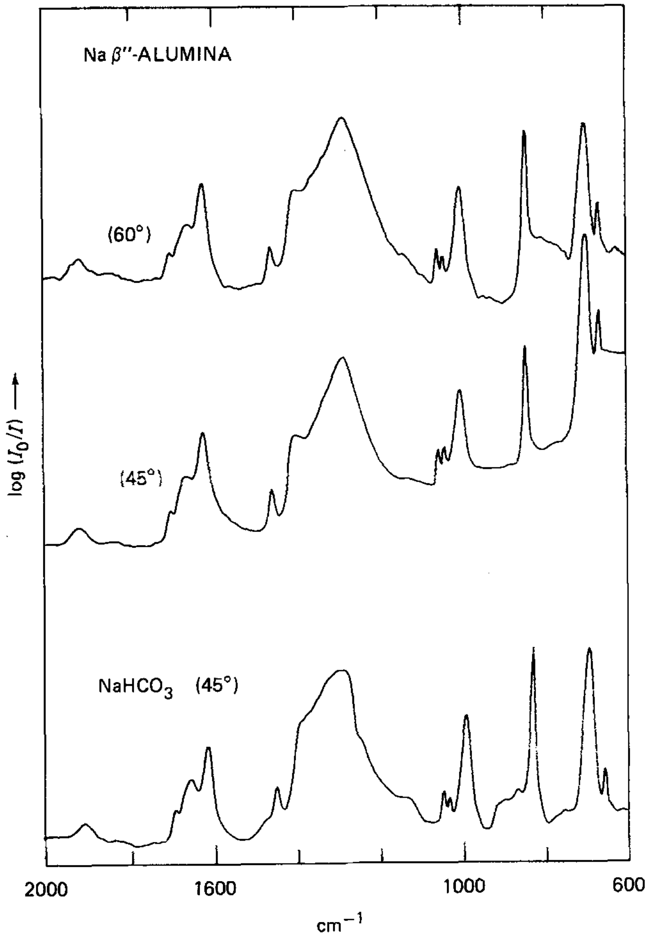

Figure 2 Multiple internal reflection spectra of polycrystalline Na β''-alumina after treatment in H_2O-saturated CO_2 obtained using KRS-5 trapezoids with internal incidence angles of 60° (top curve) and 45° (middle curve). Lower curve is the MIR spectrum of an evaporated film of $NaHCO_3$ on KRS-5. Measurements at 25° C.

specimen on emery paper or after heating it in oxygen at 600° C (Fig. 3b). These peaks reappeared after treatment in H_2O-saturated CO_2 at 25° C (Fig. 3e). In addition, new broad features were observed at 2685 and 3550 cm^{-1}, the latter of which consists of two or more overlapping components. The features of 2128, 2336, 2685 and 3350 cm^{-1} are attributed to the stretching modes of $H(H_2O)_n^+$ species in the conduction layers of the β''-alumina grains. Specific assignments of these bands to H_3O^+ or $H_3O^+ \cdot H_2O$ [14] and perhaps $H_5O_2^+$ [15–17] are uncertain,¶ but it is reasonable to conclude that a fraction of the Na^+ ions in the conduction layers have been replaced by hydrated protons. Since the peaks due to these species were not seen in spectra after treatment of samples in moist oxygen or in dry carbon dioxide (Figs. 3c and d), we conclude that H_3O^+ replaces Na^+ as a consequence of the reaction of Na β''-alumina with CO_2 and H_2O. Since $NaHCO_3$ has also been identified as a product of this reaction, the following process is plausible:

$$Na\beta'' + CO_{2(g)} + 2H_2O_{(g)} = NaHCO_{3(s)} + H_3O\beta''. \qquad (1a)$$

The thermochemical properties of Na β''-alumina and H_3O β''-alumina are not known, but using literature values of ΔG° for $NaHCO_3$ [18], H_2O [19] and CO_2 [19], the free energy change ΔG (kJ mol^{-1}) for the reaction in Equation 1 at 298 K can be expressed as

$$\Delta G_1 = 0.38 + 2.48 \ln \left(\frac{1}{P_{CO_2} P_{H_2O}^2} \right) + \Delta G^\circ(H_3O\beta'') - \Delta G^\circ(Na\beta''). \qquad (1b)$$

Under the conditions of the experiment, $P_{CO_2} = 100$ kPa and $P_{H_2O} = 3$ kPa, $\Delta G_1 = 17.9 + \Delta G^\circ(H_3O\beta'') - \Delta G^\circ(Na\beta'')$. Since $\Delta G_1 < 0$,

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¶Hereafter reference will be made only to H_3O^+ with the understanding that the infrared bands(s) in question might be due to hydrated H_3O^+, $H_3O^+ \cdot H_2O$ and/or to $H_5O_2^+$ species.

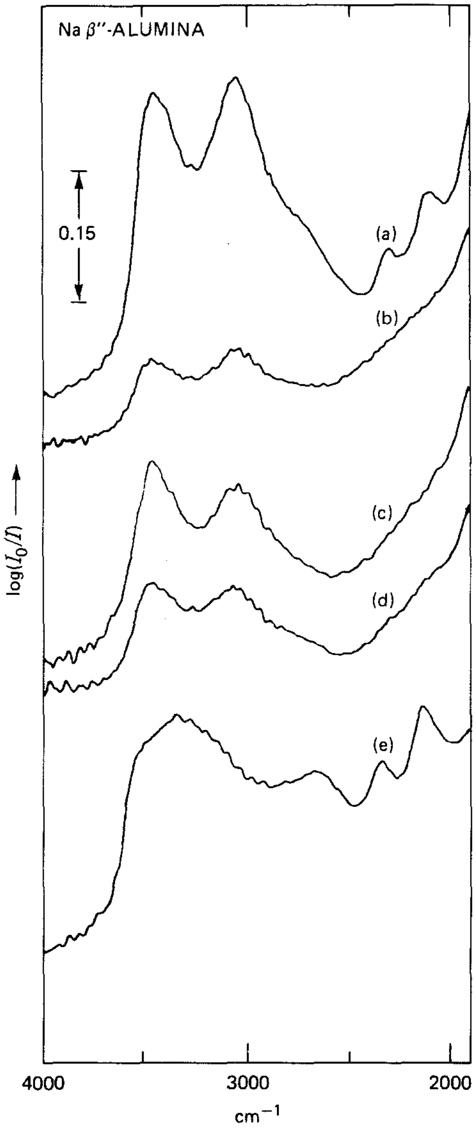

Figure 3 Reflection spectra of Na β''-alumina: (a) as-received; (b) after heating in dry O_2 at 600° C; (c) after treatment in H_2O-saturated O_2 following (b); (d) after treatment in dry CO_2 following (b); (e) after treatment in H_2O-saturated CO_2 following (b). Measurements at 25° C.

then $\Delta G°(H_3O\beta'') < \Delta G°(Na\beta'') - 17.9$. Thus, the formation of $NaHCO_3$ according to Equation 1 requires $\Delta G°$ for hydronium β''- alumina to be lower than $\Delta G°$ for sodium β''- alumina by about 18 kJ mol^{-1} (~0.2 eV).

After exposure of Na β''-alumina specimens to H_2O-saturated laboratory air at 25° C, the peaks at 2128 and 2336 cm^{-1} were clearly defined in the external reflection spectra. The appearance of these peaks assigned to H_3O^+ shows that a reaction occurred in air, although the reflection spectra above ~2500 cm^{-1} differ somewhat from those observed from samples treated in H_2O-saturated CO_2. The MIR spectra below 2000 cm^{-1} of H_2O-air-treated samples also differed markedly from those of H_2O–CO_2-treated specimens. Whereas, the latter contained much structure characteristic of $NaHCO_3$ (Fig. 2), only two peaks at 1440 and 1380 cm^{-1} could be identified in the spectra of the former. The relative intensities and wave numbers of these peaks are consistent with their assignment to split components of the ν_3 mode of CO_3^{2-} in $Na_2CO_3 \cdot 7H_2O$ or $Na_2CO_3 \cdot 10H_2O$ [20, 21]. After remaining in the spectrometer vacuum chamber, a single peak was observed at ~1435 cm^{-1}. The position of this peak is close to that observed for the overlapping components of ν_3 in the MIR spectrum of anhydrous Na_2CO_3 [11]. While these results are not conclusive, they indicate that a hydrated sodium carbonate is formed when Na β''-alumina is treated in H_2O-saturated air. The hydrated compound is not stable in the low humidity environment of the spectrometer (see below), and so the conversion to Na_2CO_3 occurs.

The formation of $Na_2CO_3 \cdot 10H_2O$ in H_2O-saturated air can be written as

$$2Na\beta'' + CO_2 + 13H_2O = Na_2CO_3 \cdot 10H_2O + 2H_3O\beta'', \qquad (2a)$$

with

$$\Delta G_2 = -6.23 + 2.48 \ln\left(\frac{1}{P_{CO_2} P_{H_2O}^{13}}\right) + 2[\Delta G°(H_3O\beta'') - \Delta G°(Na\beta'')]. \qquad (2b)$$

Under the treatment conditions, $P_{CO_2} = 33$ Pa and $P_{H_2O} = 3$ kPa, $\Delta G_2 = 70.5 + 2[\Delta G°(H_3O\beta'') - \Delta G°(Na\beta'')]$ kJ mol^{-1} of the decahydrate formed. This reaction has the lowest ΔG compared to the free energies for the formation of $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$, $Na_2CO_3 \cdot 3NaHCO_3$, or lower hydrates of Na_2CO_3 [18] under the treatment conditions. Formation of Na_2CO_3 is favoured when P_{H_2O} is lower than about 7×10^2 Pa. In the vacuum chamber of the spectrometer, $P_{H_2O} \approx 7 \times 10^{-3}$ Pa so that complete dehydration of the $Na_2CO_3 \cdot 10H_2O$ initially present on the Na β''-alumina specimen is expected.

The occurrence of Reaction 2a requires the standard free energy of H_3O β''-alumina to be lower than that of Na β''-alumina by at least

35.2 kJ mol^{-1} ($\sim$ 0.4 eV). Most of this energy difference is likely due to hydrogen bonding. If there are three hydrogen bonds formed per H_3O^+ ion, then, with 1.67 H_3O^+ ions per formula unit, this contribution could amount to 140 kJ mol^{-1} ($\sim$ 1.5 eV), taking 28 kJ mol^{-1} as the energy gained per bond.[*] However, part of the energy gained from hydrogen bond formation and from an increase in polarization energy will be offset by the energy required to expand the lattice along the *c*-direction, which evidently occurs on replacement of Na^+ by H_3O^+[†].

The presence of the reaction products obtained after treatment in H_2O-saturated CO_2 and H_2O-saturated air, $NaHCO_3$ and hydrated $NaCO_3$, respectively, were confirmed in the X-ray diffraction measurements. Of particular interest was the identification of $NaHCO_3$ and hydrated Na_2CO_3 in a sample which had first been treated in H_2O-saturated CO_2 and then exposed to laboratory air for about a month. The incomplete conversion of $NaHCO_3$ to the carbonate is probably due to the formation of an outer layer or crust of hydrated Na_2CO_3 on the surface of the specimen which retards the diffusion of H_2O and CO_2 and slows the decomposition of $NaHCO_3$.

It is interesting to compare the depth to which Na^+ ions are removed with the thickness of the bicarbonate scale formed using a simple model which assumes planar layers and ideal densities. As noted above, the MIR spectra of an H_2O–CO_2 treated specimen indicate that a layer of $NaHCO_3$ with a minimum thickness of $\sim 4\,\mu$m forms on the specimen's surfaces. For a uniformly thick $4\,\mu$m layer of $NaHCO_3$ with a density of 2.0 g cm^{-3}, all of the Na^+ ions to a depth of $\sim 11\,\mu$m must be removed and replaced with H_3O^+ ions, assuming 1.67 Na^+ ion per formula unit of β''-alumina and a density of 3.28 g cm^{-3}. The total calculated thickness of $15\,\mu$m for the degraded surface layer is on the order of the estimated thickness of 20 to $50\,\mu$m based on the necessary amount of material removed by polishing to eliminate all traces of the H_3O^+ bands from the reflection spectra.

In addition to the reaction of CO_2 and H_2O with Na β''-alumina, similar reactions are expected with impurity phases in the ceramic specimens such as $NaAlO_2$ and Na β-alumina [23]. In the case of $NaAlO_2$, $2NaAlO_2 + 2CO_2 + H_2O = 2NaHCO_3 + Al_2O_3$ is a possible reaction, with $\Delta G = -61.8$ kJ mol^{-1} in H_2O-saturated CO_2.

3.2. Formation of hydroxyl groups

The spectra observed in the 2000 to 4000 cm^{-1} region of H_2O–CO_2 treated specimens at elevated temperatures are illustrated in Fig. 4. With increasing temperature, the intensities of the broad H_3O^+ bands decreased, while the intensities of sharper peaks near 3640 and 3525 cm^{-1} increased. The peak near 3640 cm^{-1} consists of overlapping components which, at 330° C, for example, were resolved at 3652 and 3633 cm^{-1}. In the spectrum of a specimen treated in D_2O–CO_2 and measured at 330° C (Fig. 4), two bands were observed near 2685 and 2600 cm^{-1}, in addition to the two peaks at 3640 and 3525 cm^{-1}. The peak at 2685 was resolved into two components at 2694 and 2681 cm^{-1}. Because of their wave numbers, relatively narrow widths and ν_H/ν_D ratios (1.36), the 3640 and 3525 cm^{-1} bands are attributed to the O–H$^-$ species. The fact that these bands appeared at the same positions in spectra of the D_2O–CO_2 treated specimen lends strong support to this assignment [16]. The presence of several components in the spectra indicates that there are several types of OH^- groups having different orientations within the conduction layers, as found in the case of OH^- in Li β-alumina [16].

The OH^- peaks appear at elevated temperatures only when the bands assigned to H_3O^+ appear in the room temperature spectrum. When samples were treated in H_2O-saturated O_2 or dry CO_2, for example, the OH^- peaks did not appear in the high-temperature reflection spectra. Thus, since the increase in the intensities of the OH^- peaks with increasing temperature was accompanied by a decrease in the intensities of the H_3O^+ bands as noted above, it is reasonable to conclude that OH^- is formed from the dissociation of H_3O^+. A possible reaction is

$$O^{2-}_{(s)} + H_3O^+_{(s)} = OH^-_{(s)} + H_2O_{(g)}, \qquad (3)$$

where $O^{2-}_{(s)}$ represents an oxygen ion of the host lattice. (Here we do not distinguish among the different types of OH^- species produced.) If ΔG_3

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[*] Based on the energy per hydrogen bond in Ice-I. See [22].

[†] Colomban and Novak [15] quote *c*-parameters for dehydrated and fully hydrated $H(H_2O)_n^+$ β''-alumina of 34.35 and 34.51 Å for Na β''-alumina.

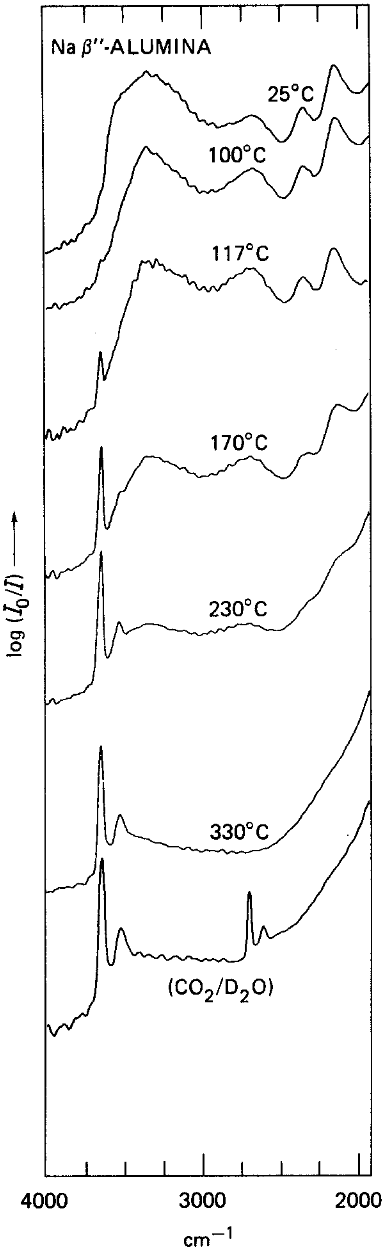

Figure 4 Reflection spectra of Na β''-alumina after treatment in H_2O-saturated CO_2. The bottom curve was obtained after treatment in D_2O-saturated CO_2. The sample temperature during each measurement is indicated above each spectrum.

is the free energy change accompanying this reaction, then

$$\frac{[OH^-]}{[H_3O^+]} = \frac{[O^{2-}]}{P_{H_2O}} e^{-\Delta G_3/kT}.$$

Assuming $[O^{2-}]$ remains essentially unchanged for low concentrations of OH^-, then with a constant P_{H_2O}, $[OH^-]/[H_3O^+] = Ke^{-\Delta H_3/kT}$, where $K = ([O^{2-}]/P_{H_2O})\, e^{\Delta S_3/k}$. Since $[OH^-] + [H_2O^+] = C$ (a constant), then

$$[H_3O^+] = \frac{C}{1 + Ke^{-\Delta H_3/kT}}, \qquad (4a)$$

and

$$[OH^-] = \frac{CKe^{-\Delta H_3/kT}}{1 + Ke^{-\Delta H_3/kT}}. \qquad (4b)$$

Values of the integrated intensities of the H_3O^+ band at 2685 cm^{-1} and the OH^- component at 3634 cm^{-1} plotted as a function of $1/T$ are shown in Fig. 5. The intensities were obtained from least-squares fits of the reflectance spectra to a function consisting of a sum of Lorentzians plus linear background terms [16]. The error bars are the uncertainties from the least-squares analysis of two spectra at each end of the temperature range. The data points shown in Fig. 5 were taken from the analysis of spectra from several temperature scans of two different specimens which accounts for the spread of intensity values at a given temperature.

The solid lines in Figs. 5a and b are the graphs of the right-hand side of Equations 4a and b, respectively, using the values of C, K and ΔH_3 obtained from a least-squares fit of these equations to the observed intensities. From the fit to the 2685 cm^{-1} peak intensity, $\Delta H_3 =$ 35 kJ mol^{-1} and $K = 3.3 \times 10^4$, while from the fit to the 3634 cm^{-1} peak intensity, $\Delta H_3 =$ 33 kJ mol^{-1} and $K = 3.6 \times 10^4$. The good agreement between respective pairs of fitted parameters lends support to the mechanism proposed for the formation of OH^- by the reaction in Equation 3. It is assumed in this analysis that the samples were in equilibrium with the atmosphere inside the evacuated spectrometer chamber at each temperature. Spectra were recorded just after a stable thermocouple reading was attained and after holding at temperature for 30 to 40 min. In some instances, samples were held at temperature for up to 24 h. At the lowest temperature at which the strongest OH^- peak is well-resolved, ~115° C, only a small increase in peak intensity was observed after holding at temperature for 30 min, and essentially no change was observed after holding at temperature for longer times. However, on cooling from 330° C, the intensities of the H_3O^+ peaks recover faster than the intensities of the

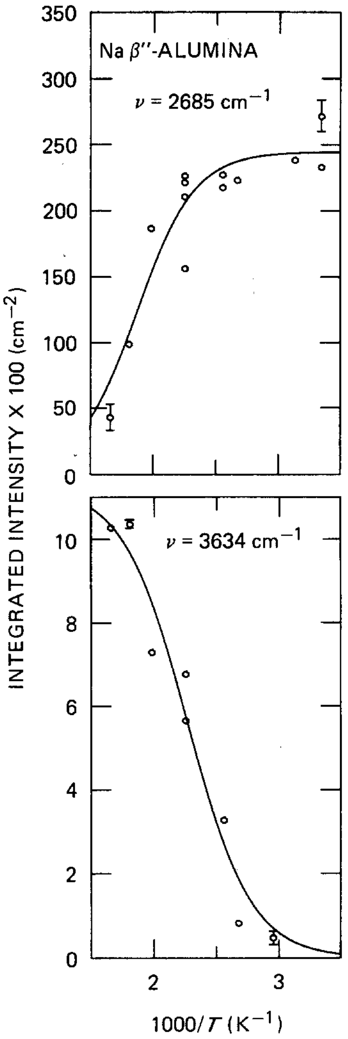

Figure 5 Integrated intensities (data points) of the 2685 cm^{-1} H_3O^+ band and the 3634 cm^{-1} OH^- band from curve fitting spectra of several Na β''-alumina specimens measured at fixed temperatures during heating and cooling cycles. The error bars indicate the uncertainty of the intensities from least-squares analysis of a single spectrum. The solid lines are graphs of the functions in Equations 4a and b using the parameters obtained from least-squares fits to the respective sets of data points.

OH^- peaks decrease. Even after remaining in the spectrometer at 25° C for 24 h, the strong OH^- peak is clearly evident in the reflection spectra together with the H_3O^+ bands observed before the heating cycle.

Provided that the temperature did not exceed the arbitrarily chosen limit of 350° C, the samples behaved reversibly in that the same spectral features were observed at corresponding temperatures on heating or cooling. When the sample temperature was increased to 600° C, however, the OH^- peaks vanished rapidly, and they did not reappear when the sample was cooled to 25° C in the spectrometer. This suggests that OH^- is removed from the conduction layers by a process in which H_2O is formed and released to the vapour phase: $2OH^-_{(s)} = H_2O_{(g)} + O^{2-}_{(s)}$. Such a process could account for the "burst" of H_2O released from Na β''-alumina at 500° C reported by Hunt *et al.* [24]. The combined process of reaction of Na β''-alumina with CO_2 and H_2O, the dissociation of H_3O^+ to form OH^-, and the removal of OH^- by release of H_2O amounts to a net irreversible loss of sodium and oxygen from the conduction layers of the grains near the surface of ceramic samples.

The concentration of OH^- species in the conduction layers of Na β''-alumina grains can only be roughly estimated due to the uncertainties in optical path length and line strengths. The latter were estimated using the procedure described elsewhere [16]. Assuming a random orientation of the grains, $S = 1/3(S_\parallel + 2S_\perp)$, where $S_\parallel$ and $S_\perp$ are the estimated line strengths for light polarized parallel and perpendicular, respectively, to the *c*-axis. Since $S_\parallel$ and $S_\perp$ scale with the band width [16], two values of S were used, one for the sharper pair of OH bands near 3634 cm^{-1} and the other for the broader band near 3525 cm^{-1}: $S = 1.3 \times 10^4\,l\,mol^{-1}\,cm^{-2}$ and $S = 4.16 \times 10^4\,l\,mol^{-1}\,cm^{-2}$, respectively. Using the fitted peak areas at 330° C and the estimated effective path length of 20 μm, [OH] $\approx$ 2 mol l^{-1} or 0.37/unit cell. This value is about five times smaller than expected if all of the Na^+ ions are replaced by H_3O^+ to a depth of $\sim 20\,\mu$m and if all of the H_3O^+ is converted to OH^-. However, the combined error of S and the effective path length could easily be as large as a factor of 5.

Based on the spectrum in Fig. 4, the relative OH^- and OD^- concentrations in the D_2O–CO_2 treated specimen indicates that the initial concentration of hydronium ions is less than the initial concentration of H_2O. The ratio, $\nu_{OD}S_{OH}/\nu_{OH}S_{OD}$ = [OH]/[OD] = 2.5 obtained from the fitted peak areas of the two high frequency bands implies that $[H_2O]/[D_3O^+] > 1$, assuming no hydrogen contamination of the D_2O (< 1% by analysis). This result, however, could be misleading because it assumes that isotope exchange occurs only with the water molecules initially present in the conduction layers which contain D_3O^+. It is more likely that isotope exchange of deuterium in D_3O^+ and OD^- occurred with H_2O molecules which diffused out of the bulk of the ceramic specimen and through the grains in the surface region at elevated temperatures. This possibility relieves the inconsistency between the high [OH]/[OD] ratio and the assumed high initial concentration of D_3O^+.

3.3. Magnesium-stabilized β''-alumina and Na β-alumina

No major differences were observed between the spectra of magnesium-stabilized and lithium-stabilized Na β''-alumina after treatment in CO_2–H_2O. The broad bands attributed to H_3O^+ as well as the sharper peaks assigned to OH^- occurred at slightly higher wave numbers in spectra of the magnesium-stabilized samples. The largest shift was $\sim 100\,\mathrm{cm}^{-1}$ for the band near $2685\,\mathrm{cm}^{-1}$. For the magnesium-stabilized samples, the intensities of the OH^- peaks decreased when the sample temperature was increased from 280 to 330° C, whereas, for the lithium-stabilized material, the intensities remained essentially constant over this temperature range. Although the respective values of $\Delta G°(\mathrm{Na}\beta'')$ and $\Delta G°(\mathrm{H_3O}\beta'')$ of the two materials will likely differ, it is reasonable to assume that magnesium- and lithium-stabilized Na β''-alumina will display essentially the same chemical behaviour when exposed to CO_2 and H_2O.

The report that Na_2CO_3 was detected on fine particles of Na β-alumina after exposure to moisture and CO_2 [1] and the results presented in this work suggest that Na β-alumina and Na β''-alumina undergo similar reactions with CO_2 and H_2O. The reflection spectra of a hot-pressed disc of Na β-alumina measured after exposure to H_2O saturated CO_2 displayed several features below $2000\,\mathrm{cm}^{-1}$ characteristic of $NaHCO_3$ with intensities comparable to those observed with Na β''-alumina. However, in contrast to the case for Na β''-alumina, the bands at 2128 and $2336\,\mathrm{cm}^{-1}$ were barely discernible in the spectra of Na β-alumina. The difference in the intensities of these bands in the two materials could be due to a difference in concentration and/or orientation of H_3O^+ in the conduction layers. The reflection spectra above $2000\,\mathrm{cm}^{-1}$ change much more slowly with increasing temperature for Na β-alumina than observed for Na β''-alumina. After about 1 h at 450° C, a small reduction in the intensity of a broad band near $3200\,\mathrm{cm}^{-1}$ (due either to H_2O or H_3O^+) was observed while a sharp peak near $3640\,\mathrm{cm}^{-1}$ was detected just above the noise level. This peak, evidently due to OH^-, was also identified after heating a specimen at 170° C for about 15 h. The much faster rate of OH^- formation in Na β''-alumina compared to Na β-alumina is probably due to the considerably higher diffusivity of H_2O in Na β''-alumina [13].

3.4. Na–Zn β''-alumina

The results of infrared measurements on a single crystal of magnesium-stabilized Na β''-alumina treated in molten $ZnCl_2$ are presented here because they confirm that the spectral features attributed to H_3O^+ and OH^- are due to species located in the conduction layers of single crystal grains. The extent of ion exchange of this crystal was not known. Farrington and Dunn [25] reported $\sim 19\%$ exchange of small crystals ($\sim 0.4\,\mathrm{mm}^3$) after 16 h treatment in $ZnCl_2$ at 500° C, and we expect a comparable per cent exchange in our sample. Examples of absorption spectra of the Na–Zn β''-alumina crystal in the region from 2000 to $4000\,\mathrm{cm}^{-1}$ measured with the electric field of the incident unpolarized light perpendicular to the c-axis are shown in Fig. 6. These spectra are quite distinct from that of the hydrated parent crystal measured before treatment in $ZnCl_2$ (compare with spectra in [13]). The two peaks below $2500\,\mathrm{cm}^{-1}$ occur at the same positions observed with the polycrystalline samples, while sharp peaks above $3500\,\mathrm{cm}^{-1}$, which appear more distinctly at elevated temperatures, are close to the positions of the OH^- peaks observed in spectra of the polycrstalline samples. Also, the strong, broad band near $3300\,\mathrm{cm}^{-1}$ and the shoulder at $\sim 2900\,\mathrm{cm}^{-1}$ occur in the same region as the broad features observed in the spectra of polycrystalline Na β''-alumina. These broad bands as well as the pair below $2500\,\mathrm{cm}^{-1}$ are also attributed to H_3O^+ as discussed above, but for Na–Zn β''-alumina, H_3O^+ and OH^- are probably formed by dissociation of H_2O as in the case of Li β-alumina [16, 17]. The small, doubly charged Zn^{2+} ion is responsible for the dissociation of H_2O in the mixed ion crystal, since no evidence for OH^- formation was observed in the absorption spectra of Na β''-alumina measured at high temperatures. The increase in the intensity of the OH^- peaks near $3530\,\mathrm{cm}^{-1}$ with increasing temperature could

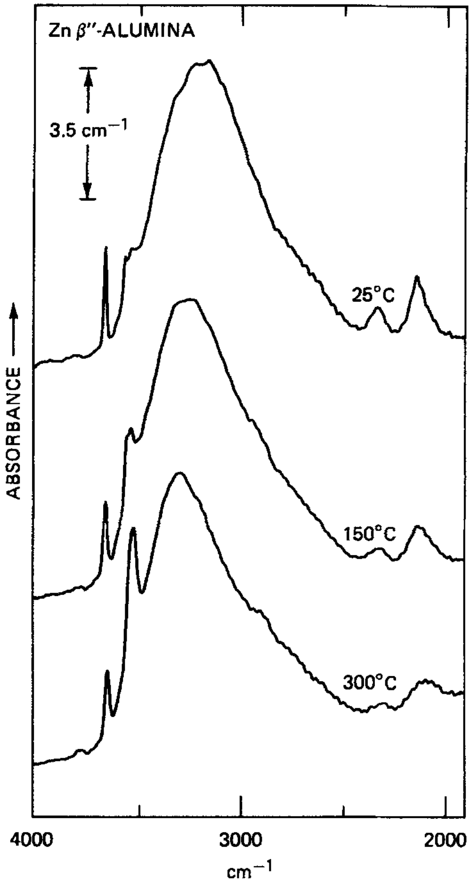

Figure 6 Absorption spectra of a single crystal of Na-Zn β''-alumina with the electric field vector of the incident unpolarized light perpendicular to the crystallographic *c*-axis.

thus be due to dissociation of residual H_2O as well as H_3O^+.

The absorption spectrum of Na–Zn β''-alumina measured with $E \parallel c$ shows more structure in the OH^- region than observed for $E \perp c$, and it was observed that the pair of bands below 2500 cm^{-1} are considerably more intense in the $E \parallel c$ spectrum. The 2128 and 2336 cm^{-1} bands have also been observed in $E \parallel c$ spectra of Na β''-alumina crystals that were stored in air for many months, but they are typically too weak to be observed in spectra recorded with $E \perp c$. The strong dichroic ratios observed with these and the OH^- bands pose additional difficulties in obtaining reliable estimates of the concentration of OH^- and H_3O^+ species from reflection measurements on polycrystalline samples. It is evident from these measurements on the single crystal that the features observed above ~2500 cm^{-1} in the reflection spectra of polycrystalline Na β''-alumina which were attributed to OH^- or H_3O^+ are indeed due to proton-containing species located in the conduction layers of single crystal grains.

4. Conclusions

Sodium β''-alumina reacts with CO_2 and H_2O to form $NaHCO_3$ at high P_{CO_2} pressures or $Na_2CO_3 \cdot xH_2O$ at low P_{CO_2} pressures. The bicarbonate or carbonate is formed on the surface of polycrystalline specimens by a process involving the replacement of Na^+ by H_3O^+ ($H(H_2O)_n^+$) in the conduction layers of the β''-alumina grains. The net negative free energy change in these reactions requires that $\Delta G°(H_3O\beta'') < \Delta G°(Na\beta'')$, with a difference as large as 35 kJ mol^{-1} based on the formation of hydrated Na_2CO_3. The bicarbonate or carbonate produced in the reaction forms a crust or scale on the β''-alumina which eventually retards further corrosion of the surface. The thickness of the bicarbonate scale appears to be of the order of 20 μm.

The H_3O^+ ions in the β''-alumina grains dissociate by an endothermic process to produce OH^- species. The concentration of OH^- reaches a maximum at a temperature between 230 and 280° C and remains constant at 330° C even at low H_2O pressures. At high temperatures, ~600° C, the OH^- is rapidly removed from β''-alumina, probably by the formation and evolution of H_2O. The net result of reaction with CO_2 and H_2O, dissociation of H_3O^+, and removal of OH^- according to the processes discussed above is to change irreversibly the composition of the grains in the degraded region near the surface.

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