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Thermal Analysis and IR Spectroscopic Studies on Na β-Alumina

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Thermograms of Na β-alumina, which were aged for 4 years at room temperature and humidity, were analyzed with the aid of infrared spectroscopic and X-ray diffraction studies. Thermogravimetric analyses (TGA) revealed that the dehydration of the aged material takes place in four different temperature regions, i.e., 70–180, 180–260, 260–420 and 420–700°C. The first three regions were also confirmed by differential scanning calorimetric analysis (DSC). The anhydrous Na β-alumina was rehydrated and analyzed using TGA and DSC. The thermograms of the rehydrated material displayed all the dehydration regions of the aged material with the exception of 350°C (260–420°C). IR spectra of Na β-alumina at 25°C and the same sample quenched at 180, 350, 520, and 820°C indicated adsorbed/absorbed water in the conduction plane existing as H_2O, H_3O^+, $H_5O_2^+$, $H_7O_3^+$, etc., and coordinated water as M–OH_2. The latter could be removed from this material only above 550°C. X-Ray diffraction of thermally treated Na β-alumina showed a single phase, with the exception of a contraction in the structure along the c axis. Complete dehydration was possible only around 700°C.

Introduction

Various researchers have studied the reactivity of water with Na β-alumina in a variety of forms including polycrystalline tubes, large single crystals, and finely-ground powders, or they mention the procedures used to obtain and keep this material in the dehydrated form. However, all investigations which have been reported agree that Na β-alumina absorb significant quantities of water into their structures. The hydration/dehydration reactions are particularly important because of the potential use of this high conductivity solid electrolyte in high energy density batteries. The presence of water within Na β-alumina greatly decreases their ionic conductivity and may conceivably influence their long-term electrochemical stability.

Kummer (*1*) and Kline *et al.* (*2*) found that the absorbed water apparently enters the conduction planes of the compound where it decreases the rate of sodium ion motion and presumably the ionic conductivity. Will (*3*) and Farrington (*4*) illustrated that the presence of adsorbed water significantly decreases the conductivity of polycrystalline Na β-alumina. Dudney *et al.* (*5*), Richter *et al.* (*6*), Flor *et al.* (*7*), and Larson *et al.* (*8*) have explored the interaction of water molecules with the structure and ion transport processes in this material. Armstrong *et al.* (*9*) reported that the absorbed water from Na β-alumina could be easily removed by evacuation whereas the strongly bonded water, as detected by IR,

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could not be easily removed even at 500°C under vacuum. However, no systematic approach has been attempted. The studies reported here were designed to characterize the hydration/dehydration reactions of Na β-alumina crystals which had been reduced to fine powders. It is believed this procedure will reveal the reactions which might proceed too slowly to be observed with large single crystals, but which might nevertheless be important if these solid electrolytes were used for a long time.

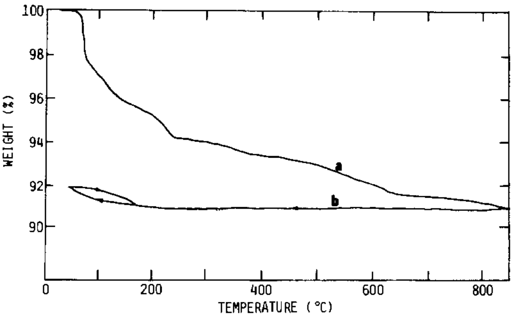


FIG. 1. (a) TGA scan of aged Na β-alumina at 1°C/minute in dry N_2. (b) Cooling cycle at 2°C/min under N_2 saturated with water vapor at 25°C.

Experimental

Single crystals of Na β-alumina were grown by slow vaporization of sodium oxide from a molten mixture of sodium oxide–aluminum oxide at 1600°C (7). The powder was prepared by grinding the single crystals and had been aged for 4 years in a sealed bottle at room temperature and humidity. Care was also taken not to expose the powder to CO_2 during removal of samples from the container. The composition of this material was $Na_{1.3}Al_{11}O_{17.15}$. All the samples used in this study were from one batch of polycrystalline powder, less than 63 μm in particle size.

The thermal analyses were carried out with a DuPont Thermal Analysis System using both thermogravimetric analysis (TGA) and differential scanning calorimetric (DSC) modes on sample sizes ranging from 2 to 30 mg. α-aluminum oxide was used as a reference material. The dehydration and rehydration of Na β-alumina was studied in the temperature range of 20–1100°C by TGA and 20–600°C by DSC under either wet or dry nitrogen. Rehydration was observed by measuring the weight of nitrogen gas saturated with water vapor at 25°C. The rehydration was also carried out by an alternative method, i.e., the Na β-alumina which had been heated to 960°C was rehydrated at 25°C by exposure to water vapor in a closed chamber for several days. At different intervals of time, samples were withdrawn and analyzed for subsequent dehydration reactions using DSC and TGA.

All infrared analyses were carried out in the frequency range of 4000–200 cm^{-1} at room temperature. A 150-mg mixture containing 2% Na β-alumina and 98% KBr was pressed into a pellet, and this pellet was used for the IR experiment. All the experiments were carried out in a flowing N_2 atmosphere.

X-Ray diffraction patterns of the Na β-alumina were obtained using a Norelco Phillips X-ray diffractometer. The instrument was operated at 45 kV and 15 mA with a scanning rate of 1° (2θ) per minute for the analysis of phases and 0.25° (2θ) per minute for the determination of lattice parameters. The source of radiation was $CuK\alpha(\lambda = 1.548$ Å) with a diffracted-beam LiF monochromator.

Results and Discussion

Slow heating of an aged sample of Na β-alumina powder at 1°C per minute from 20 to 180°C resulted in a total weight loss of 9% (Fig. 1). The thermogram reveals several discrete loss processes. Following the evaporation of surface water a sharp weight loss (A) of 4.6% occurs in the range of 70–

TABLE I

REHYDRATION OF Na β-ALUMINA

Rehydration time (days)	Weight loss above 70°C (%)
4	1.5
10	5.4
12	5.5
355	7.8

180°C. A fairly sharp transition (B) centered around 220°C, which corresponds to a weight loss of 1.2% occurs between 180 and 260°C. Another discrete loss (C) occurs from 260 to 420°C with a weight loss of 0.75%. It is followed by a broad transition region from 420 to 700°C (D) in which a 1.95% weight loss occurs. Cooling of the anhydrous Na β-alumina obtained from the above experiment at 2°C/min in nitrogen that had been saturated with water at 25°C results in a weight gain of 1.1% which began below the 220°C transition and was completely removed upon reheating the sample from 40 to 200°C. Heating of aged material at rates up to 20°C/min revealed the same phenomena, i.e., the weight losses, A, B, C, and D, but with higher transition temperatures.

Rehydration of anhydrous material by exposure to water vapor at 25°C initially resulted in a rapid uptake of water. About 70% of the weight loss at 960°C was regained in 3 hr. This water, however, was loosely bound. The recovery of strongly bound water (i.e., water retained above 70°C) is described in Table I.

All features observed on the first dehydration scan, i.e., transition A, B, and D, could be observed after 12 days of rehydration (see Fig. 2), with the exception of a small weight loss at 350°C. Transitions up to 500°C have been confirmed by DSC analyses both on starting powders and rehydrated samples (see Fig. 3). Estimates of the heats of dehydration are: 70–100°C, $\Delta H = 11$ kcal/mole H_2O; 100–200°C, $\Delta H = 13$ kcal/mole H_2O; 200–280°C, $\Delta H_D = 17.5$ kcal/mole H_2O.

The rapid water uptake by powders of Na β-alumina has been previously reported. However, this water is easily removed. Bulk diffusion is necessary to recover the strongly-bound water. Over 1 year is needed at room temperature for complete rehydration to occur. The total water uptake on the basis of formula $Na_{1.3}Al_{11}O_{17.15}$ is approximately equivalent to 3 mole water per formula weight. As can be easily seen from more complete discussions of the structure of Na β-alumina (*9*, *10*), this quantity of water corresponds to complete saturation of the conduction planes of the

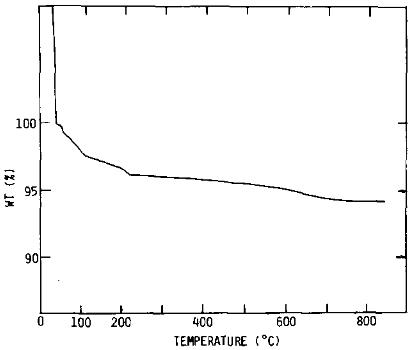


FIG. 2. TGA scan of Na β-alumina which had been heated to 960°C then rehydrated at room temperature for 12 days. Heating rate 1°C/minute.

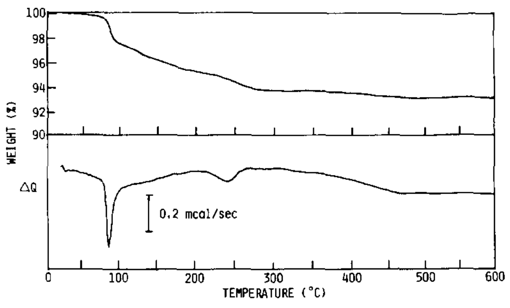


FIG. 3. TGA and DSC scans of Na β-alumina showing transitions corresponding to observed weight loss. Heating rate 5°C/minute.

compound. This hydration cannot occur without producing a very large decrease in the ionic conductivity of Na β-alumina. Most surprising is the observation that about 3% water remains in the samples to temperatures above 400°C. Its existence may influence the conductivity and high temperature stability of this material.

To identify the nature and inquire about the possible entities such as OH, H_2O, H_3O, etc., infrared spectra were taken for Na β-alumina calcined in the TGA pan and quenched at temperatures corresponding to the four regions observed in the TGA curve (Fig. 1). The IR spectra for this material at 25°C and the same quenched at 180, 350, 520, and 820°C are shown in Fig. 4. The infrared absorption frequencies and their assignment with different functional groups or molecules are given in Table II.

The spectra of this material at 25°C show the following characteristic peaks, i.e., a pair of small sharp peaks at 3585 cm^{-1} with a shoulder at 3520 cm^{-1}, a broad intense peak comprised of two absorption peaks at 3380 and 3235 cm^{-1}, two weak broad bands at 2900 and 2550 cm^{-1}, a small peak at 1660 cm^{-1}, two intense sharp peaks at 1460 and 1320 cm^{-1}, and an intense strong peak at 1025 cm^{-1}.

Inspection of the spectra shows that the general absorption pattern below 900 cm^{-1} is similar for all samples, except for an unclear band broadening in the aged specimen. The Al–O bands characteristic of spinel blocks are also identical. The 4000–900 cm^{-1} region, on the other hand, varies considerably with different thermal treatment of Na β-alumina samples. Hence, the discussion is focused only on this region.

The peaks at 3585 and 3545 cm^{-1} are assigned to the hydrogen bonds formed by water molecules attached to the H_3O^+ ion because they are very similar to those observed at 3580 and 3500 cm^{-1} in the $H_7O_3^+$–ClO_4^- spectrum (*12*). The absorptions at 3520 and 3508 are assigned to the H_3O^+ ion.

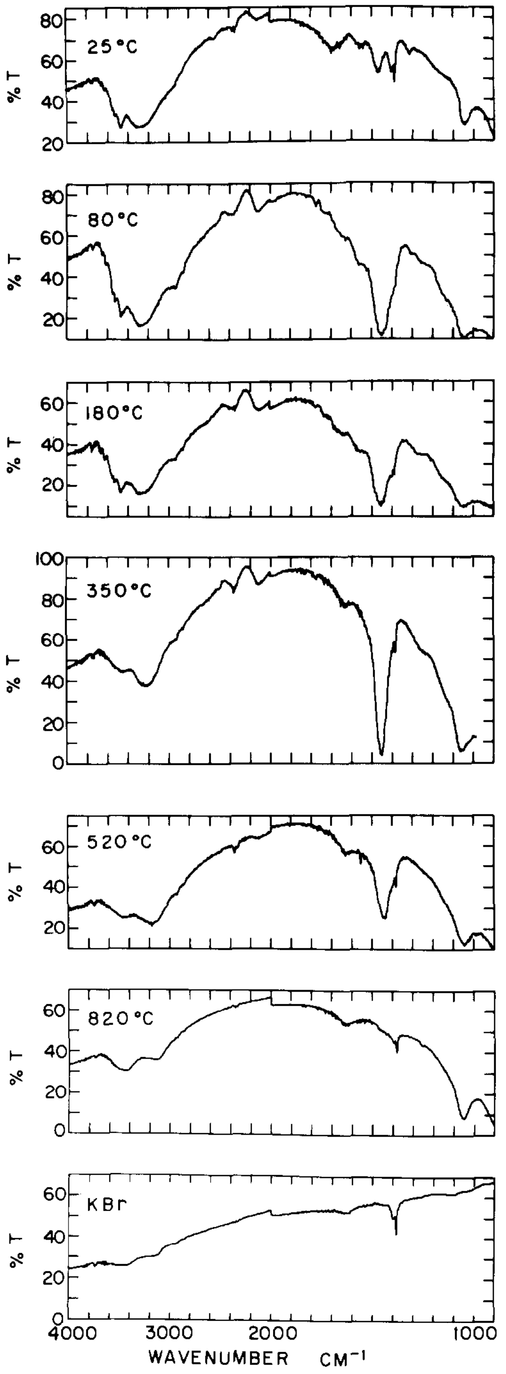
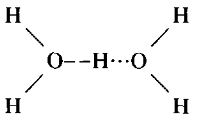


FIG. 4. IR spectra of aged Na β-alumina heated to different temperatures.

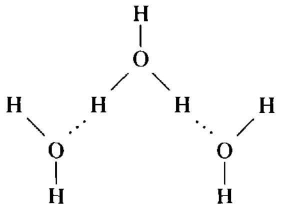
TABLE II

INFRARED ABSORPTION FREQUENCIES OF Na β-ALUMINA

Wavenumbers (cm^{-1}) Maximum[a]	Range	Description	Assignment (*12*)	
3585_{sm}	3600–3580	OH Stretching	Terminal water	(II)
3545_{sh}	3560–3540	OH Stretching		
3520_{sm}	3540–3520	OH Stretching	H_3O^+ ion	(I)
3508_{vs}	3520–3420	OH Stretching		
$3380_{s,b}$	3400–3150	OH Stretching	Terminal water	(I)
$3235_{s,b}$		OH Stretching	Terminal H_3O^+	(II)
2900_{sm}	2910–2890	OH Stretching	Terminal H_3O^+	(I)
2550_{sm}	2520–2580	OH Stretching	Central O–H . . . O	(I)
1660_{sm}	1670–1650	H–O–H Bending	Terminal water	(I)
1470_{vs}	1490–1430	M–OH_2 Asymmetric	Coordinated water	
1320_{s}	1330–1300	M–OH_2 Symmetric		
1025_{s}	1070–1000	OH Stretching or Al–O	Terminal H_3O^+ or Al–O	(I)



(I)



(II)

[a] vs: very strong; s: strong; sm: small; sh: shoulder; b: broad.

The relatively strong intensity of these two bands in this material compared with the peaks for H_3O^+ β-alumina was reported earlier (*13*). The peak at 3380 cm^{-1} is assigned to the H_2O molecule, which is bonded with neighboring oxygen atoms of spinel blocks.

The additional broad band at 3235 cm^{-1} is due to the hydrogen bond of the H_3O^+ ion and can be compared with the broad band near 3180 cm^{-1} of the $H_7O_3^+$ spectrum (*12*). The small band noticed at 2900 and 2550 cm^{-1} can be assigned to the simplest species next to the H_3O^+ ion, i.e., to the diaquohydrogen ion which may be asymmetric H_3O^+ H_2O. In this case the 2550 cm^{-1} band corresponds to the shortest hydrogen bond linking OH groups of H_3O^+ ion to the oxygen atom of a water molecule. The 2900-cm^{-1} band is due to the terminal OH groups of the H_3O^+ ion. Another reasonable explanation for these absorptions is that they possibly arose from carbonation reactions which these powders underwent during handling, in air, for the different experiments. The formation of carbonates and bicarbonates was previously reported by Bates (*14*) and Garbarcz (*15*) *et al.* However, the reported (*14*) sharp water absorption peaks at 3264, 2684, and 2128 cm^{-1} are not observed for this material. The intensity of all these peaks decreases and shifts with the thermal treatment of the Na β-alumina.

An intense peak at 1470 cm^{-1} and a shoulder at 1320 cm^{-1} are observed for the Na β-alumina and its intensity is maximum for the sample heated at 350°C. Similar

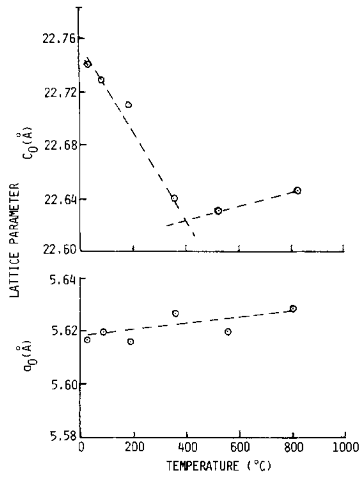


FIG. 5. Lattice parameter of Na β-alumina at different temperatures.

peaks in the IR spectrum of Na β-alumina were not reported in the literature. The absorption in this region is considered to be due to coordinated water, i.e., M–OH_2 because they are very similar to those observed at 1470 cm^{-1} and in the region 1340–1320 cm^{-1} in the spectrum of M–NO_2 (*16*). The former is due to asymmetric (γ_a) and the latter is due to symmetric (γ_s) modes. The absorption band corresponding to this stretching mode should appear near 1025 cm^{-1} by analogy with the stetching mode of Cr–H_2O in chromium aquo complexes (*17*). As evidence, a peak at this frequency is noticed in this study. Alternatively, this intense peak could be due to OH stretching in H_3O^+ ion or very strong Al–O absorption (*18*). The coordinated water is removed only above 550°C as evidenced by the disappearance of this peak in the spectrum.

A series of X-ray diffraction patterns were taken for Na β-alumina at 25°C and the same quenched at 180, 350, 520, and 820°C to determine whether a structure change was associated with the thermal treatment of this material. Figure 5 summarizes the lattice parameters measured over the temperature range 25 to 820°C.

The material was single phase and retained the Na β-alumina structure over the complete temperature range. However, there were shifts in peak position and changes in the dimensions of the Na β-alumina lattice. The most striking observation is that as the quenching temperature increased, the "c_0" parameter first decreased, then increased, thus reaching a minimum between room temperature and 350°C. Note, no appreciable change in the "a_0" parameter is noticed. These results are similar to those observed by Farrington *et al.* (*19–21*). The anhydrous phase and hydrated phase interconvert by absorption and desorption of water. The transformation is accomplished with ease because the water molecule is small and can diffuse in the channels of the conduction plane without altering the framework of the β-alumina structure. The "c_0" parameter is sensitive to the conduction plane, probably because the dielectric properties determine coulombic forces between spinel blocks. The effects of the hydrogen-containing cations are similar to spherical monovalent alkali ions with radii 1.25 and 1.40 Å. This is compatible with H_2O, H_3O^+, or $H_5O_2^+$ since, for most hydrogen bonds between oxygen atoms, the O–O distance lies between 2.50 and 2.80 Å equal to the closest approach of spheres with radii 1.25 and 1.40 Å. That absorption between one and two molecules of water in the hexagonal cell expands "c_0" by 0.08 Å is consistent with the rapid increase of "c_0".

Acknowledgments

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