Synthesis of potassium beta-alumina by thermal decomposition of a complex

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Potassium beta-alumina was synthesised from potassium m-alumina by a new technique. Thermal decomposition of a complex, trioxalatoaluminate $K_x(NH_4)_{3-x}[Al(C_2O_4)_3] \cdot 3H_2O$ $(0.091 \leqslant x \leqslant 0.333)$, resulted in the formation of a fine powder of K m-alumina with mullite-like structure. The decomposition process was studied by thermal analysis and X-ray diffraction, and the phase relation of the K_2O–Al_2O_3 system is discussed in the mid-temperature region of 600–1200° C. The a.c. conductivity, the apparent density and the lattice parameters were measured. The complex decomposition was shown to be a suitable method for K β-alumina synthesis.

1. Introduction

Compounds of the same type as β-alumina [1], i.e. ternary oxides with general formula $A_2O \cdot nB_2O_3$ $(A = Li^+, Na^+, K^+, Rb^+, Ag^+, Tl^+, H_3O^+; B = Al^{3+}, Ga^{3+}, Fe^{3+})$, form a large family of materials which are good ionic conductors. Of these compounds sodium β-alumina, $Na_2O \cdot nAl_2O_3$ $(n = 5–11)$, has been widely investigated because it serves as the solid electrolyte for the sodium–sulphur battery. In contrast, there are not so many papers on K β-alumina, $K_2O \cdot nAl_2O_3$ $(n = 5–11)$ since it shows an ionic conductivity lower than that of Na β-alumina. Nevertheless, K β-alumina is still an interesting and promising material for various applications such as galvanic cells and a K^+ ion sensor.

K β-alumina has usually been prepared by an ion exchange method [1]. Na^+ ions in Na β-alumina can be exchanged readily by K^+ ions in a K^+-ion-containing molten salt. Although K_2CO_3 and Al_2O_3 or $Al(OH)_3$ react to give $K_2O \cdot 11Al_2O_3$, the rate of reaction is not high. In a previous paper [2], the present authors showed that Na β-alumina was easily formed from Na m-alumina which is a metastable sodium aluminate with a mullite-type structure [3–5]. Na m-alumina was prepared by thermal decomposition of the complex, trioxalato-aluminate $Na_x(NH_4)_{3-x}[Al(C_2O_4)_3] \cdot 3H_2O$ [6].

In this work, K β-alumina was synthesised from K m-alumina which could be prepared by thermal decomposition of potassium trioxalatoaluminate, $K_x(NH_4)_{3-x}[Al(C_2O_4)_3] \cdot 3H_2O$. The preparation and the decomposition of the complex and the phase relation of the system K_2O–Al_2O_3 are described in this paper together with the conductivity of the polycrystalline K β-alumina.

2. Experimental

2.1. Preparation of the complex

An ammonium hydroxide solution was poured into an aluminum nitrate solution to obtain aluminum hydroxide which was washed with water before adding it to a saturated solution of oxalic acid at 70° C. Into the resulting homogeneous solution, crystals of ammonium oxalate and potassium oxalate were added. At this stage there are two methods of obtaining the crystalline complex from the aqueous solution; one is by precipitation with an organic solvent such as acetone and the other is by a concentration technique. A large amount of acetone must be used in the former method and it is troublesome to recover the solvent, so the complex was obtained by the latter technique. The crystalline complex was dried at 80° C for two days. The x value in the chemical

formula $K_x(NH_4)_{3-x}[Al(C_2O_4)_3]\cdot 3H_2O$ was chosen to be between 0.333 and 0.091, because the composition of the complex must be arranged to form potassium aluminate $K_2O\cdot nAl_2O_3$ ($3 \leqslant n \leqslant 11$).

2.2. Decomposition process and products

The decomposition process of the complex was followed by thermogravimetry and differential scanning calorimetry (TG-DSC) between room temperature and 500° C in air. The heating rate was about 3° C min^{-1}.

The complex was pressed to form a tablet which was heated at various temperatures in the range 400–1200° C for 5 hours in an oxygen atmosphere. The decomposition products were examined by X-ray diffraction and lattice parameters were also measured.

2.3. Electrical conductivity measurement

The powders decomposed at 600, 800, 1000 and 1200° C were ground in an alumina mortar and dried at 110° C. The dry powders were pressed hydrostatically at 300 MPa to form tablets with dimensions of 8mm diameter and 3 mm thickness. The tablets were sintered at 1600° C for 30 minutes in air and then examined by X-ray diffraction and scanning electron microscopy.

Afterwards the flat surfaces of the tablets were coated with silver paste and heated at 600° C to release the organic component of the paste. The conductivities of the samples were measured in the region from 200 to 500° C in nitrogen by using an impedance bridge at 10 kHz.

3. Results and discussion

3.1. Decomposition process

The number n in the description 'complex-n' is defined as the ratio of Al_2O_3 to K_2O in the decomposition product since the complex must have the appropriate composition to give the decomposition product of $K_2O\cdot nAl_2O_3$.

Fig. 1 shows the DSC curves of one complex and three starting materials. The curve of oxalic acid is similar to that of ammonium oxalate (curves b and c). The endothermic peaks at the
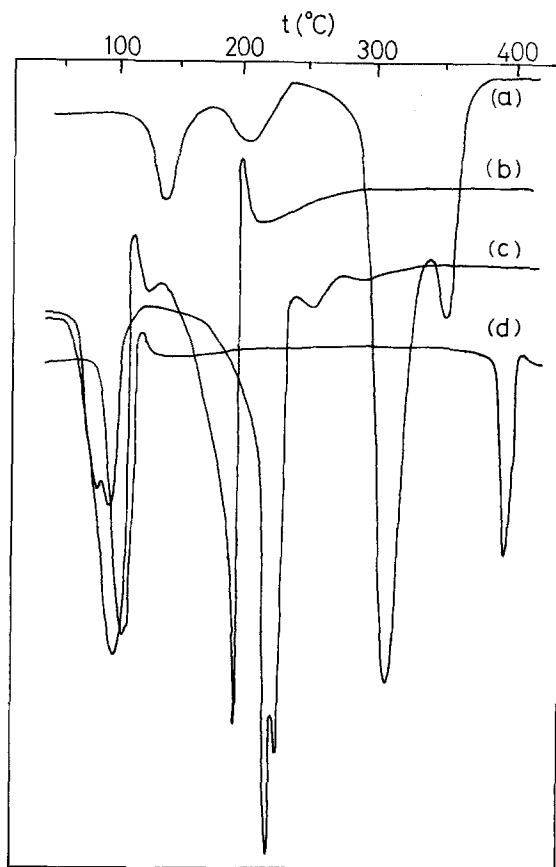

Fig. 1. DSC curves of (a) complex-7, (b) $H_2C_2O_4\cdot 2H_2O$, (c) $(NH_4)_2C_2O_4\cdot H_2O$, (d) $K_2C_2O_4\cdot H_2O$.

lower temperature indicate the evolution of the water of crystallization and the peaks in the higher region correspond to the decomposition reactions of the samples. The decomposition temperature of potassium oxalate is higher than those of the compounds mentioned above by about 200° C (curve d). On the other hand, the curve of the complex differs entirely from the curves of the other three crystals. This behaviour means that the complex is a single-phase compound; this was confirmed by X-ray diffraction.

The TG-DSC curves of complex-7 are shown in Fig. 2. The complexes with other compositions showed analogous curves to those of complex-7. The curves are also similar to those of the sodium trioxalatoaluminates [2]. The endothermic peaks near 135 and 205° C in the DSC curve correspond to the vaporization of the adsorbed water and the water of crystallization. The peak near 310° C was suggested to correspond to the primary de-
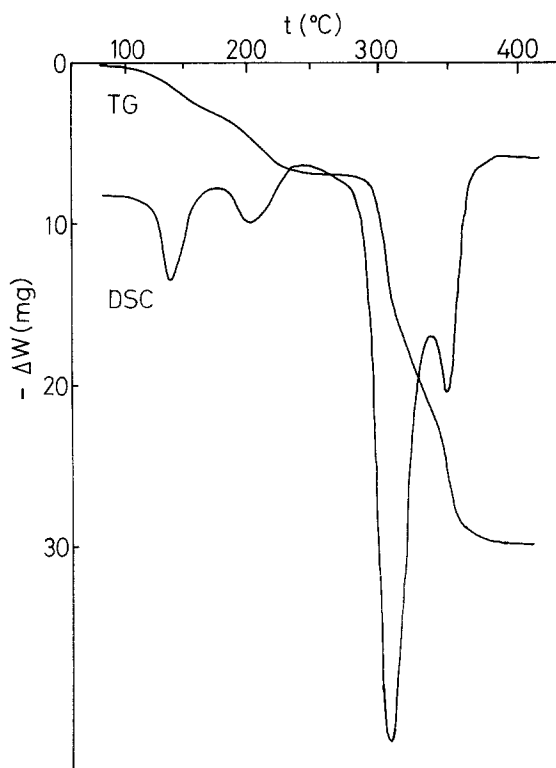
Fig. 2. TG-DSC curves of complex-7.

Fig. 3. X-ray diffraction patterns of complex-7 decomposed at (a) 600° C, (b) 700° C, (c) 1100° C, (d) 1150° C and (e) 1200° C. m, K m-alumina; o, K β- and/or β″-alumina.

composition process accompanied by the evolution of carbon dioxide, and another peak near 350° C was assigned to the secondary decomposition reaction of carbon monoxide evolution. Ammonia and water, except the water of crystallization, would be taken out from the complex during the two decomposition steps. The weight changes calculated on the assumption that the decomposition gases are water, ammonia, carbon dioxide and carbon monoxide are nearly in agreement with those obtained from the TG curve in Fig. 2.

3.2. Formation of K m-alumina and transformation to K β-alumina

The X-ray diffraction patterns of complex-7 decomposed at several temperatures are shown in Fig. 3. The specimen heated at 600° C has some detectable peaks other than the diffused patterns. The sample heated at 700° C has unambiguous diffraction lines which are identified as those of a compound with the mullite-type structure. The intensities of these lines gradually increase with
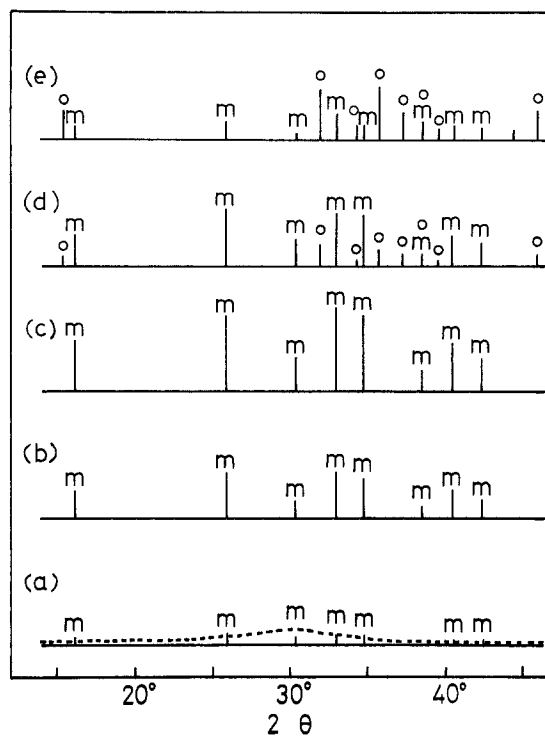
increasing decomposition temperature and have a maximum at 1100° C, which is 100° C higher than the maximum temperature of Na m-alumina [2]. The powder obtained at 1150° C shows lines of K β-alumina (containing a little K β″-alumina) as well as of K m-alumina. The line intensities of the m-phase decrease with increasing intensity of the β-phase. The samples produced at temperatures higher than 1200° C were no longer K m-alumina. These results indicate that the primary product of the decomposition process is K m-alumina which then transforms to K β-alumina at temperatures higher than 1150° C. The transition temperature of m-alumina to β-alumina seems to be a function of heating time. K β-alumina could be identified by the X-ray diffraction pattern of a sample obtained by heating for a long time at 1100° C.

The formation of K m-alumina and its transformation to K β-alumina can be interpreted as follows. K⁺ ions will be adsorbed on the surface of γ-alumina which is formed immediately after the thermal decomposition of the complex. They probably enter by diffusion into those octahedral
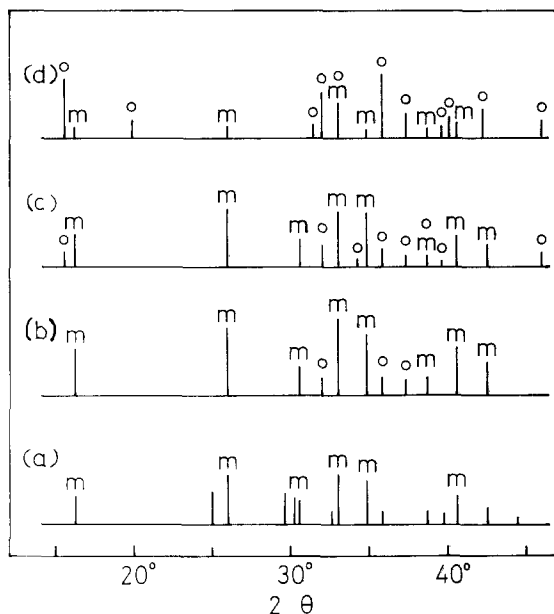
Fig. 4. X-ray diffraction patterns of samples decomposed at 1150° C from (a) complex-3, (b) complex-5, (c) complex-7 and (d) complex-11. m, K m-alumina; o, K β- and/or β''-alumina.

Fig. 5. Lattice parameters of K m-alumina prepared at 1000° C. The broken lines show the lattice constants of Na m-alumina.

sites of the γ-alumina which are unoccupied by Al³⁺ ions. In this case, the spinel-type structure cannot be maintained as the K⁺ ion is larger than the Al³⁺ ion and a stable phase with a mullite-type structure will predominantly be formed. On the other hand, the layer structure of K β-alumina consists of alternate blocks of [KO] ⁻ and [Al₁₁O₁₆] ⁺ which contain the same defect spinel structure as γ-alumina. By raising the temperature, K⁺ ions in K m-alumina migrate in the direction of the c axis to form with O²⁻ ions the [KO] ⁻ layer of the closest packed arrangement, where-as the parts impoverished in K⁺ ions revert again to the [Al₁₁O₁₆] ⁺ layer with the defect spinel structure.

Fig. 4. shows the diffraction patterns of the products for various compositions heated at 1150° C. The sample rich in alkali content not only has the lines of K m-alumina but probably also the lines of potassium aluminate. The product from complex-5 indicates the mixed lines of K m- and K β-alumina. The intensities of the lines of the β-phase increase with increase of alumina content. This means that the m-phase in the alumina-rich side transforms to the β-phase more rapidly than in the alkali-rich side.
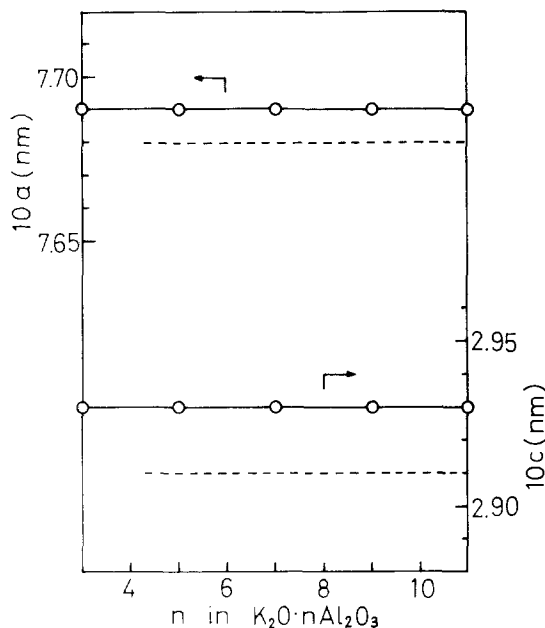
The powder diffraction pattern of the m-phase

was indexed by using the same pseudotetragonal cell as that of Na m-alumina [2]. The lattice parameters of K m-alumina formed at 1000° C are plotted in Fig. 5, together with the values of Na m-alumina. As can be seen, the lengths of both the a and c axes are independent of the compositions of the starting complexes. Fig. 6 summarizes the phase relation of the decomposition products of the complexes. The m-phase is stable over the whole composition range at 1050° C, but transforms to the β-phase (including the β''-phase as a minor component) at 1100° C, which is higher by 50° C than the transformation temperature of Na m-alumina [2]. In other words, K m-alumina is more stable than Na m-alumina. This seems to be due to the difference of the degree of fit of the alkali ions to the sites in the mullite-type structure. There are double tunnels formed by two adjacent cells in the structure. The alkali ions can be accommodated quite easily in the empty oxygen sites in the double tunnels. The ionic radius of the K⁺ ion (0.133 nm) is nearly equal to that of the O²⁻ ion (0.140 nm), while that of the Na⁺ ion (0.097 nm) is somewhat less than that of oxygen. Thus, the K⁺ ion gives a better fit than the Na⁺ ion. Since the maximum concentration of the potassium oxide in the aluminate can be estimated
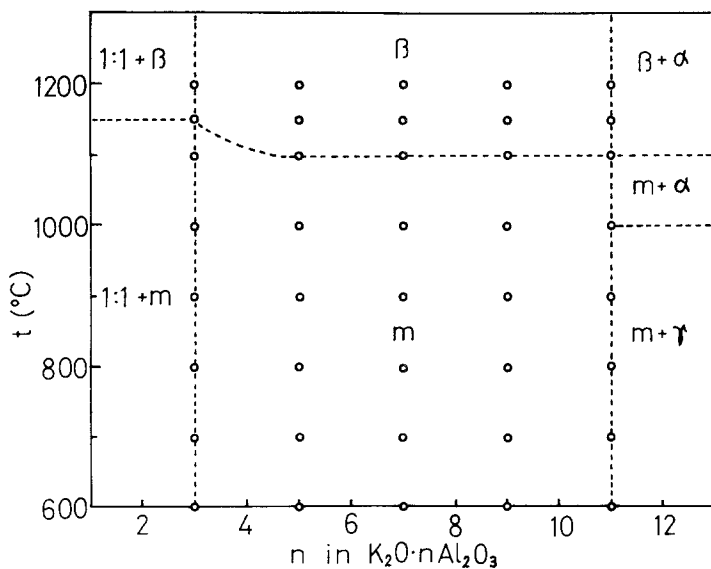
Fig. 6. Phase profile of decomposition products. m, K *m*-alumina; β, K β- and β''-alumina; α, α-alumina, 1:1, KAlO$_2$; γ, γ-alumina.

to be 25 mol% [4], the limiting composition rich in alkali is given to be K$_2$O·3Al$_2$O$_3$, which may be the most stable from the structural point of view. Consequently, K *m*-alumina in the alkali-poor region transforms to K β-alumina a little more rapidly than that in the alkali-rich region, as seen in Fig. 6.

3.3. Sintered samples and their conductivities

The tablets sintered at 1600° C were shown by X-ray diffraction to contain the β-phase as the major component and the β''-phase as a minor component. The lattice parameters of the β-phase, $a = 0.561$ nm, $c = 2.275$ nm, were obtained using the (110) and (017) lines. These are somewhat greater than the values reported ($a = 0.5595$ nm, $c = 2.271$ nm) [7]. The lattice constants of the β''-phase were calculated by the use of the (110) and (003) lines. They were $a = 0.563$ nm and $c = 3.407$ nm, which are nearly equal to the values, $a = 0.5603$ nm, $c = 3.404$ nm, for the compound K$_2$O·6Al$_2$O$_3$ [8].

The sintered samples prepared by the present method were observed by SEM photographs to show a single pattern of a flake-like grain. The diameter of the grain was smaller than 2 μm. The needle-like grains could not be observed, as in the previous paper [2].

Fig. 7 shows the conductivities of the two kinds of tablets sintered at 1600° C. One is the sample fabricated from K *m*-alumina prepared by decomposition of complex-5 at 800° C, and the other is the sample obtained from K β-alumina formed by the decomposition at 1200° C. Although the absolute value of the conductivity can not be discussed precisely (because the apparent
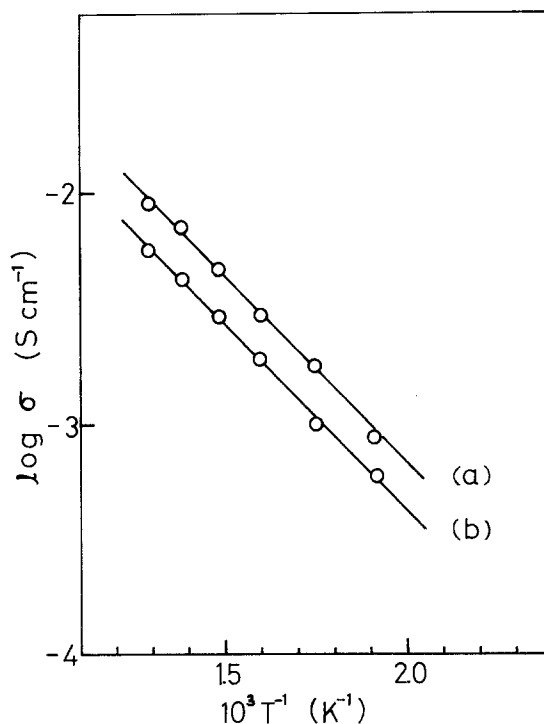

Fig. 7. Electrical conductivities of K β-alumina prepared from (a) K *m*-alumina and (b) K β-alumina.

densities of the tablets are low, 60% of theoretical) it seems that K m-alumina is superior to K β-alumina as the starting material for the sinters of K β-alumina. K$^+$ ion conductivity of K β-alumina has scarcely been reported. One datum for a single crystal shows the value of 2.8×10^{-2} S cm^{-1} at 200° C [9], which was calculated from the diffusion coefficient using the Nernst–Einstein equation with the correlation factor of three. The conductivity of the present sample at 200° C is lower by two orders of magnitude than the value of the single crystal, and the apparent activation energy for conduction is 34.8 kJ mol^{-1}. This is probably due to the low density of the tablet and the relatively low frequency used. A higher conductivity would be obtained if a denser tablet could be prepared and a higher frequency used. A detailed study of the conductivity of the doped K β-alumina will be reported in the near future.

4. Summary

It has been shown that a new technique for K β-alumina synthesis from K m-alumina is practical. The sintered tablet of K β-alumina had a small and uniform grain size. The flat surface of the tablet showed a preferred orientation of the crystallographic plane suitable for potassium ion conduction.

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