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β-Al_2O_3 synthesis from m-Al_2O_3

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β-Al_2O_3 formation from m-Al_2O_3 was found by a new convenient technique. By thermal decomposition of a complex compound, trioxalatoaluminate $Na_x(NH_4)_{3-x}[Al(C_2O_4)_3]yH_2O$ ($0.091 \leqslant x \leqslant 0.333$; $y = 3$), a very fine powder of m-Al_2O_3 was formed. The decomposition process was examined by thermal analysis and X-ray diffraction and the phase relation of the system Na_2O–Al_2O_3 in the mid-temperature region between 600 and 1200° C is discussed briefly. The tablet of m-Al_2O_3 was fired at 1600° C for 30 min to prepare dense β-Al_2O_3 ceramics, the apparent density of which was greater than 95% of the theoretical value. The sintered tablet was examined from the structural point of view and the electrical conductivity was measured by an a.c. method to verify that the procedure of the complex decomposition is a suitable technique for β-Al_2O_3 synthesis.

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1. Introduction

The sodium–sulphur battery is one of the most promising power sources for non-polluting electric vehicles or for load levelling and sodium beta alumina (β-Al_2O_3) is used as the electrolyte [1].

Phase equilibria of the system Na_2O–Al_2O_3 and characterization of β-Al_2O_3 have been investigated with respect to the stability of the phase [1], and recently, a new metastable phase was found to have a mullite type structure and designated m-Al_2O_3 [2] or λ-Al_2O_3 [3].

In a series of studies of the low temperature syntheses of β-Al_2O_3, the present authors have found that m-Al_2O_3 is a promising material from which to synthesize β-Al_2O_3. The m-Al_2O_3 formation was observed in the solid state reaction of $NaAlO_2$ with γ-Al_2O_3 [4] and in the decomposition reaction of a complex $Na_x(NH_4)_{3-x}[Al(C_2O_4)_3]yH_2O$ [5, 6].

For the purpose of the synthesis of β-Al_2O_3 from m-Al_2O_3, this paper describes first the decomposition process of the complex in order to make clear the phase relationship of the system Na_2O–Al_2O_3 in the mid-temperature region between 600 and 1200° C, and secondly the structural observations and the conductivity behaviour of polycrystalline β-Al_2O_3 which is related to the possibility of low temperature synthesis of β-Al_2O_3.

2. Experimental

2.1. *Preparation of the complex*

After adding an ammonium hydroxide solution to a solution of aluminium nitrate, the precipitated aluminium hydroxide was filtered, washed and added to a saturated solution of oxalic acid at 70° C. The resulting homogeneous solution was boiled with crystals of ammonium oxalate and sodium oxalate until the complex crystallized [7]. The crystalline complex was dried at 80° C and held in a desiccator. As the composition of the complex must be arranged to prepare sodium aluminate $Na_2O \cdot nAl_2O_3$ ($3 \leqslant n \leqslant 11$), the value of x in the chemical formula $Na_x(NH_4)_{3-x}[Al(C_2O_4)_3]yH_2O$ was selected to be between 0.333 and 0.091.

2.2. *Thermal analysis and X-ray diffraction*

The decomposition process of the complex was examined by thermogravimetry and differential scanning calorimetry (TG–DSC) in the range from room temperature up to 500° C in air. The heating speed was fixed to about 3° C min^{-1}.

The complex was pressed to form a tablet which was put in an alumina boat and heated in an electric furnace at various temperatures of 400–1200° C for 5–10 h in flowing oxygen. The decom-

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Table 1. Compositions of complexes without water of crystallization and decomposition products

Complexes		*Composition of decomposition products*
Sample	*Composition*	
complex-3	$Na_{0.333}(NH_4)_{2.667}[Al(C_2O_4)_3]$	$Na_2O \cdot 3Al_2O_3$
complex-4	$Na_{0.250}(NH_4)_{2.750}[Al(C_2O_4)_3]$	$Na_2O \cdot 4Al_2O_3$
complex-5	$Na_{0.200}(NH_4)_{2.800}[Al(C_2O_4)_3]$	$Na_2O \cdot 5Al_2O_3$
complex-6	$Na_{0.167}(NH_4)_{2.833}[Al(C_2O_4)_3]$	$Na_2O \cdot 6Al_2O_3$
complex-7	$Na_{0.143}(NH_4)_{2.857}[Al(C_2O_4)_3]$	$Na_2O \cdot 7Al_2O_3$
complex-8	$Na_{0.125}(NH_4)_{2.875}[Al(C_2O_4)_3]$	$Na_2O \cdot 8Al_2O_3$
complex-9	$Na_{0.111}(NH_4)_{2.889}[Al(C_2O_4)_3]$	$Na_2O \cdot 9Al_2O_3$
complex-11	$Na_{0.091}(NH_4)_{2.909}[Al(C_2O_4)_3]$	$Na_2O \cdot 11Al_2O_3$

position products were analyzed by X-ray diffraction using a copper target and lattice parameters were measured with the aid of a silicon internal standard.

2.3. *Conductivity measurements*

In order to measure their conductivity, the sample powders decomposed at 600, 800, 1000 and 1200° C were ground for 2 h using an alumina mortar with ethanol as the dispersing reagent and dried at 110° C. The dry powders were pressed hydrostatically at 3 x 10^5 kPa to form a tablet of about 8 mm in diameter and about 3.5 mm thick. After firing at 1600° C for 30 min in air, one of the sintered tablets was examined by X-ray diffraction and scanning electron microscope, and the flat surfaces of other tablets were coated with silver paste which served as an electrode material. The conductivities of the samples in the range of 200–450° C in a nitrogen atmosphere were measured by the use of an a.c. impedance bridge at a frequency of 100 kHz.

3. Results and discussion

3.1. *Decomposition profile of the complex*

The trioxalatoaluminates examined are listed in Table 1. As the complexes prepared in this work have the compositions to give decomposition products of $Na_2O \cdot nAl_2O_3$, the number n in the description 'complex-n' in Table 1 signifies the composition ratio $n = Al_2O_3/Na_2O$ in the decomposition product.

Comparing the TG–DSC curves of the samples $Na_x(NH_4)_{3-x}[Al(C_2O_4)_3]yH_2O$ with those of extreme composition $(NH_4)_3[Al(C_2O_4)_3] \cdot 3H_2O$ and $Na_3[Al(C_2O_4)_3]4.5H_2O$, it could be seen that any complex-n was not a simple mixture of these stoichiometric complexes but a single phase compound. This was confirmed from X-ray diffraction, that is, the diffraction pattern of the sample differed from the patterns of these complexes.

Fig. 1 shows TG–DSC curves of complex-5. The curves of the samples with other compositions had

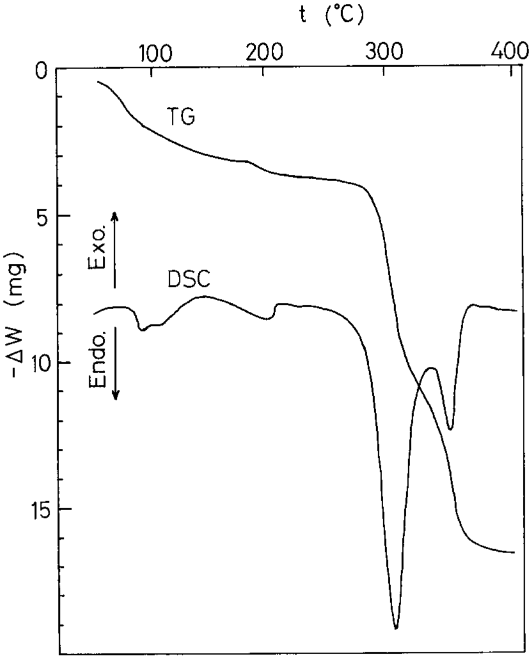

Fig. 1. TG–DSC curves of complex-5.

almost the same profiles as those shown in Fig. 1. The endothermic peaks in the DSC curve near 100 and 200° C correspond to the vaporization of adsorbed water and/or the water of crystallization. In general, after evolution of water, oxalates of the trivalent metal M^{3+} decompose in an oxidizing atmosphere as follows:

$$M_2(C_2O_4)_3 \rightarrow M_2O_3 + 3CO_2 + 3CO. \qquad (1)$$

Therefore, the decomposition gases in this work are assumed to be simple such as water, ammonia, carbon dioxide and carbon monoxide; the reaction of complex-5, for example, takes place as in the following manner

$$Na_{0.20}(NH_4)_{2.80}[Al(C_2O_4)_3]yH_2O$$
$$\rightarrow (1.40 + y)H_2O + 2.80NH_3 + 3CO_2 + 3CO$$
$$+ Na_{0.20}AlO_{1.60}. \qquad (2)$$

By the analysis of the TG curve, the endothermic peak near 300° C may correspond to the primary decomposition process accompanied by the evolution of carbon dioxide, and another endothermic peak near 350° C was assigned to the secondary decomposition reaction of the carbon monoxide evolved. Ammonia and water except yH_2O in Equation 2 would be taken out from the complex during the primary and the secondary decomposition steps. In addition, it was clarified from the TG curve that y in the formula $Na_x(NH_4)_{3-x}[Al(C_2O_4)_3]yH_2O$ was about 3.

3.2. *Formation of* m-Al_2O_3

The TG–DSC curves indicated that the thermal decomposition of all complexes was almost complete below 400° C. Fig. 2 shows the X-ray diffraction patterns of the decomposition products of complex-5. The samples heated at 400 and 500° C have the diffused patterns which suggest that the powder obtained was very fine or amorphous. The sample heated at 600° C shows clear diffraction lines corresponding to the mullite-type structure. The intensities of these lines gradually increase with increase of the decomposition temperature and have a maximum at 1000° C. The powder produced at 1050° C contains not only m-Al_2O_3, but also β''- and β-Al_2O_3, while the powder prepared at 1200° C has only β''- and β-Al_2O_3. The line intensities of the m-phase decrease with increasing intensities of the β'' or β phase. This behaviour suggests that the primary product in the decomposition process is m-Al_2O_3 and then it transforms to β''- or β-Al_2O_3 at temperatures higher than 1000° C. The transformation of β''-$Al_2O_3 \rightarrow m$-Al_2O_3, or β-$Al_2O_3 \rightarrow m$-Al_2O_3 has not been observed.

The m-phase has been found by gel crystallization technique [2], ashing filter paper [3] and solid state reaction [4]. The decomposition method of the complex compound is a new convenient technique of achieving very intimate and uniform mixing of reactants on a microscopic level. In addition, by this technique, it is possible easily to prepare m-Al_2O_3 with any desired composition.

The powder diffraction pattern of the m-phase can be indexed using an orthorhombic cell as in the case of mullite, but the lengths of two axes are nearly equal and it may be treated as a pseudotetragonal cell. On the basis of the tetragonal

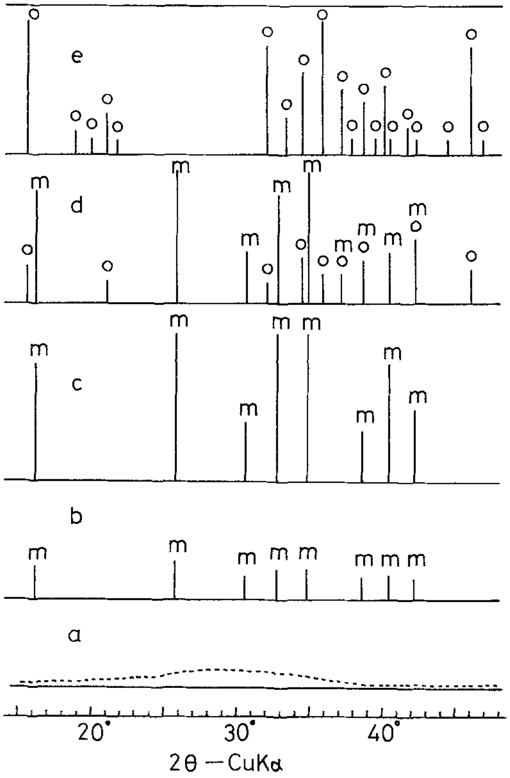

Fig. 2. X-ray diffraction patterns of complex-5 decomposed at (a) 400–500° C, (b) 600° C, (c) 1000° C, (d) 1050° C and (e) 1200° C. m, m-Al_2O_3; o, β''- and/or β-Al_2O_3.

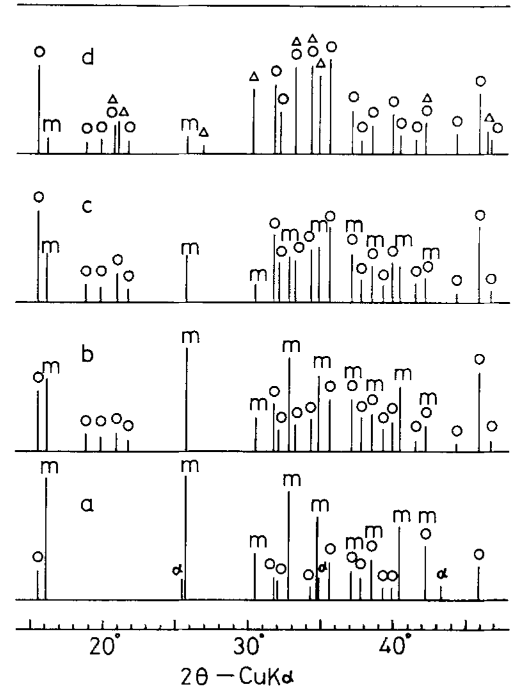

Fig. 3. X-ray diffraction patterns of samples decomposed at 1100° C from (a) complex-11, (b) complex-9, (c) complex-5 and (d) complex-3, m, m-Al_2O_3; o, β''- and/or β-Al_2O_3; α, α-Al_2O_3; Δ, $NaAlO_2$.

structure, the lattice parameters of m-Al_2O_3 formed at 1000° C were calculated to be $a = 0.770$ nm and $c = 0.290$ nm. These are independent of the compositions of the starting complexes and agree well with the values reported by Elliot and Huggins [3].

The diffraction patterns of the products with various compositions after heating at 1100° C are shown in Fig. 3. On the alumina-rich side the m-phase transforms slowly to the β''- and β-phases. Complex-11 forms a little of the α-phase as well as the m and the β'' and β-phases. On the other hand, in the alkali rich side, the transformation of the m-phase to the β'' and β-phases proceeds comparatively rapidly.

Fig. 4 summarizes the phase relationship of the decomposition products of the complexes. The m-phase is stable over the whole range of compositions at 1000° C. It transforms to the β''- and β-phases in the alkali rich region at 1050° C which is in good agreement with the temperature found in the previous paper [4]. These results also agree well with the result reported by Elliot and Huggins that the m-phase was observed over a wide range of sodium compositions below 1050° C [3]. The $m \rightarrow \beta''$ and β transition curve, however, seems to be a function of heating interval and composition at any temperature. In practice, β''- and β-Al_2O_3 could be identified in the diffraction pattern of a sample obtained by elongating the time of heating even at lower temperatures. This behaviour is similar to that observed in the solid state reaction between $NaAlO_2$ and γ-Al_2O_3 by the present authors [4]. The β-region in Fig. 4 shows the mixed phase of the β''- and β-phases. The single area of the β''- or β-phase could not be observed. This is the same result as that of Fally *et al.* [8]. They showed that the two phases always co-exist.

3.3. *Sintered tablets*

Before the conductivity measurement, the sintered tablets were examined from several view-points.

Some of the apparent densities estimated from

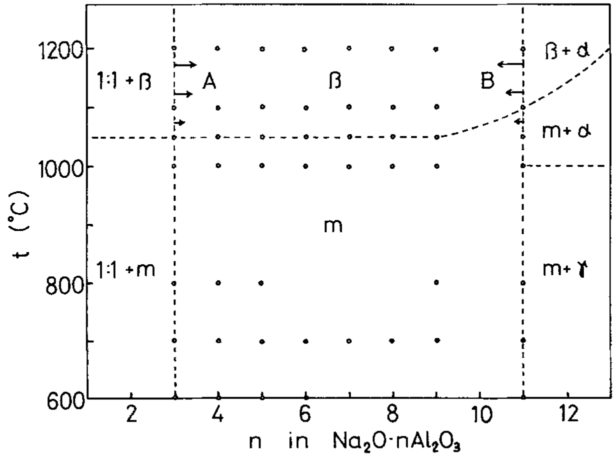

Fig. 4. Phase profile of decomposition products. m, m-Al_2O_3; β, β''- and β-Al_2O_3; α, α-Al_2O_3; 1:1, $NaAlO_2$; γ, γ-Al_2O_3. Arrows A and B show the tendencies for both 1:1 and α to expand towards β a, temperature rises.

Table 2. Apparent densities of the tablets sintered at 1600° C for 30 min

Decomposition temperature of complex (° C)	*Apparent density* (g cm^{-3})	
	from complex-5	*from complex-9*
600	3.0	2.7
800	3.1	2.7
1000	3.1	2.7
1200	3.1	2.7

the size and the weight of each tablet are indicated in Table 2. The samples prepared from complex-5 show densities higher than 95% of the theoretical value, and the samples prepared from complex-9 have somewhat lower values. It is interesting that the density is independent of the decomposition temperature of the sample.

By X-ray diffraction, the tablets prepared from both complex-5 and complex-9 were shown to contain the β''- and β-phases. The lattice parameters of the β-phase were $a = 0.560$ nm and $c = 2.260$ nm in any sample. These values are a little larger than those ($a = 0.559$ nm, $c = 2.249$ nm) reported by Thery and Briancon [9], but agree with the values ($a = 0.559$ nm, $c = 2.261$ nm) by Dyson and Johnson [10]. The lattice constants of the β''-phase were calculated to be $a = 0.560$ nm and $c = 3.394$ nm, which are independent of the composition of the sample. These are in good agreement with the values shown by other workers ($a = 0.561$ nm, $c = 3.395$ nm [9]; $a = 0.5597$ nm, $c = 3.395$ nm [10]).

Fig. 5 shows the typical microstructures of the flat surfaces of the sintered tablets. The surfaces are perpendicular to the direction of the pre-press of the samples. The tablet rich in sodium (Fig. 5a) has two kinds of grain. One is the globular grain which has a diameter between 0.5 and 2 μm, and the other is the flake-like grain which is larger than the globular one. The tablet poor in sodium (Fig. 5b) shows the single pattern of the flake-like grain. Most of the sintered β- or β''-Al$_2$O$_3$ so far reported shows large, needle-like grains which generally cause the flexural strength to decrease and the electrical resistivity to increase [11–13]. The sintered tablets prepared in the present work, however, show no such needle-like grains as seen in Fig. 5. This is one of the characteristic properties of the tablet obtained by the decomposition of the complex. Another characteristic can be seen also in Fig. 5. The flat planes of the flake-like grains, which are probably parallel to the (0 0 l) planes of β''- or β-Al$_2$O$_3$, have a tendency to orientate parallel to the direction of the pre-press of the sample. According to Elliot and Huggins, only a little structural re-arrangement is required to

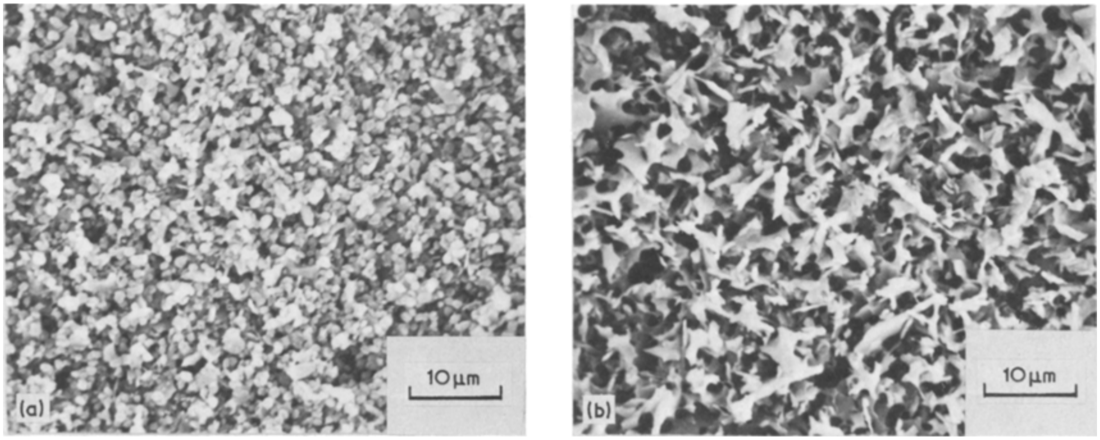

Fig. 5. Scanning electron micrographs of sintered tablets prepared from (a) complex-5 and (b) complex-9. Both samples were etched by boiling conc. phosphoric acid for 3 min.

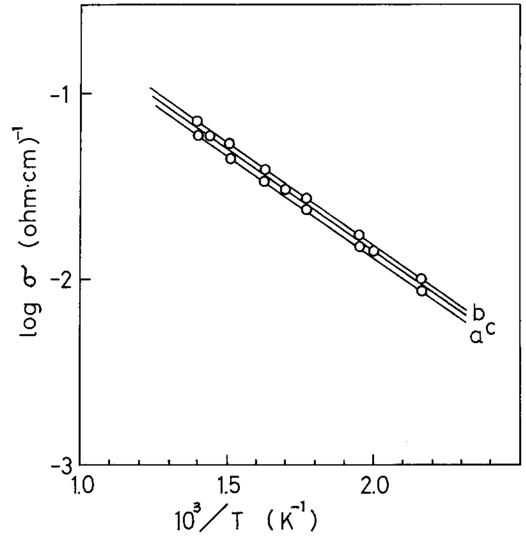

Fig. 6. Electrical conductivities of β-Al_2O_3 prepared from (a) complex-5 decomposed at 600–1000° C and sintered at 1600° C; (b) complex-5 decomposed at 1200° C and sintered at 1600° C, and (c) solid state reaction between $NaAlO_2$–γ-Al_2O_3 fired at 1600° C.

transform m-Al_2O_3 to β-Al_2O_3, where the c-axis for β-Al_2O_3 will run approximately in the [1 1 0] direction of m-Al_2O_3 [3]. Thus, if the tube or cylinder oriented predominantly in the (0 0 1) plane of the m-Al_2O_3 powder compact could be prepared, the β-Al_2O_3 ceramics having a plane parallel to the c-axis would be manufactured after sintering. The result obtained in this experiment supports the prediction by Elliot and Huggins.

3.4. *Electrical conductivity*

Fig. 6 shows the Arrhenius plot of the conductivities of the tablets obtained by firing at 1600° C after the decomposition of complex-5 at several temperatures. The samples obtained from m-Al_2O_3 which was prepared at 600–1000° C have conductivities nearly equal to those of the sample fabricated from β-Al_2O_3 which was formed at 1200° C. The conductivity of the sample made by the solid state reaction of $NaAlO_2$–γ-Al_2O_3 [14, 15] is also plotted in this figure. There is little difference between these values and these curves indicate the linearity. The apparent activation energy for conduction calculated from the slopes of the curves is about 21 kJ mol^{-1} which is comparable to the values for the polycrystalline specimens [16].

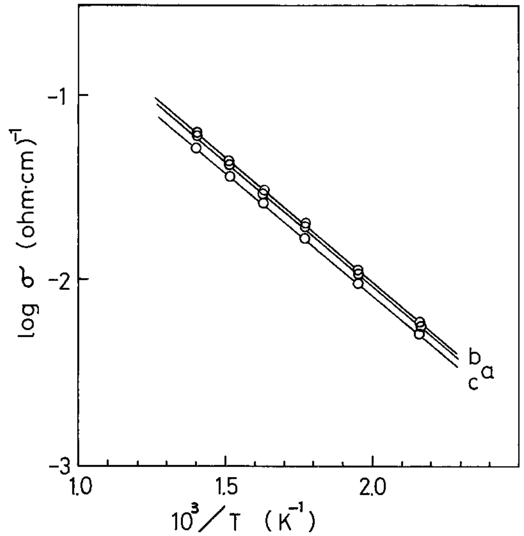

Fig. 7. Electrical conductivities of β-Al_2O_3 prepared from complex-9 decomposed at (a) 600° C, (b) 800–1000° C and (c) 1200° C.

The conductivities of the tablets produced by sintering after decomposition of complex-9 at four temperatures are plotted in Fig. 7. The linearity of the curves is clear and the conductivities are also nearly equal to each other, although the sample prepared from decomposition at 1200° C shows a somewhat lower value than the samples obtained from decomposition at 600–1000° C. The apparent activation energy is estimated to be about 26 kJ mol^{-1}.

Hence the complex decomposition technique is a new and promising procedure for manufacturing the dense β-Al_2O_3 ceramics without calcination.

References

[1] J. T. Kummer, 'Progress in Solid State Chemistry' (Edited by H. Reiss and J. O. McCaldin) Vol. 7, Pergamon, Oxford (1972) p. 141.

[2] A. J. Perrotta and J. E. Young, Jr., *J. Amer. Ceram. Soc.* 57 (1974) 405.

[3] A. G. Elliot and R. A. Huggins, *ibid* 58 (1975) 497.

[4] T. Takahashi and K. Kuwabara, *J. Solid State Chem.*, to be published.

[5] J. Paris and R. Paris, *Bull. Soc. Chim. France* 4 (1965) 1138.

[6] L. N. Glyzina, V. I. Fadeeva and Yu. D. Tret'yakob, *Izv. Akad. Nauk SSSR. Neorg. Mater.* **11** (1975) 1088.

[7] J. C. Bailar, Jr. and E. M. Jones, 'Inorganic Syntheses' (Edited by H. S. Booth) Vol. I, McGraw-Hill, New York (1939) p. 35.

[8] J. Fally, C. Lasne, Y. Lazennec, Y. LeCars and P. Margotin, *J. Electrochem. Soc.* **120** (1973) 1296.

[9] J. Thery and D. Briancon, *Rev. Hautes Temp. Refract.* **1** (1964) 221.
[10] D. J. Dyson and W. Johnson, *Trans. J. Brit. Ceram. Soc.* **72** (1973) 49.
[11] T. L. Francis, F. E. Phelps and G. MacZura, *Ceram. Bull.* **50** (1971) 615.
[12] T. J. Whalen, G. J. Tennenhouse and C. Meyer, *J. Amer. Ceram. Soc.* **57** (1974) 497.
[13] G. E. Youngblood, A. V. Virkar, W. G. Cannon and R. S. Gordon, *Ceram Bull.* **56** (1977) 206.
[14] T. Takahashi, K. Kuwabara and H. Iwahara, Extended Abstract of *27th JCS Fall Meeting*, Nagoya, Vol. I (1972) p. 624.
[15] I. Uei, K. Hayashi and T. Nishida, *Annual Report of The Asahi Glass Foundation for the Contribution to Industrial Technology* **15** (1971) 69.
[16] A. Imai and M. Harata, *Japan J. Appl. Phys.* **11** (1972) 180.