

## BRIEF COMMUNICATIONS

### Ion-Exchange Reaction of Barium $\beta$ -Alumina

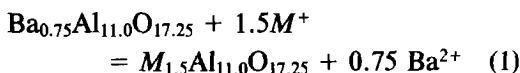
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#### Introduction

Systematic ion-exchange experiments on  $\beta$ -alumina ( $\beta$ - $\text{Al}_2\text{O}_3$ ) compounds were first reported by Yao and Kummer (1). Since then, the exchange reactions of  $\text{Na}^+$  in  $\beta$ - $\text{Al}_2\text{O}_3$  with other monovalent cations have been widely applied to prepare some  $\beta$ - $\text{Al}_2\text{O}_3$  which cannot be obtained directly. These facts show that ion-exchange reaction is very common to  $\beta$ - $\text{Al}_2\text{O}_3$  compounds. In the previous paper (2), we revealed barium hexaaluminate phase I to be of  $\beta$ -alumina structure and attributed the nonstoichiometry to the same "interstitial oxygen mechanism" as was found in  $M^{1+}\beta$ - $\text{Al}_2\text{O}_3$ . If monovalent ion exchange  $\text{Ba}^{2+}$  in barium hexaaluminate phase I ( $\text{Ba } \beta$ - $\text{Al}_2\text{O}_3$ ), then twice as many cations as  $\text{Ba}^{2+}$  would enter according to the reaction



(where  $M^+$  stands for monovalent cation).

The ion-exchange reaction of " $\text{BaO} \cdot 6\text{Al}_2\text{O}_3$ " was previously reported by Toropov and Stukalova (3) in 1939, however, the reaction equation as well as the formula and structure of the starting material " $\text{BaO}$

$\cdot 6\text{Al}_2\text{O}_3$ " was not made clear at that time.

We have made ion-exchange experiments on  $\text{Ba } \beta$ - $\text{Al}_2\text{O}_3$  and  $\text{BaMgAl}_{10}\text{O}_{17}(\text{Ba} \cdot \text{Mg } \beta$ - $\text{Al}_2\text{O}_3)$  in order to obtain completely exchanged specimens for examination.

#### Experimental

Single crystals of  $\text{Ba } \beta$ - $\text{Al}_2\text{O}_3$  and  $\text{Ba} \cdot \text{Mg } \beta$ - $\text{Al}_2\text{O}_3$  grown by the floating zone method were used as the starting materials (4). Unless otherwise described, they were cut into about  $0.4 \times 0.4 \times 0.4$ -mm<sup>3</sup> cubes, which were treated with a large excess of molten salt (more than 300 times in weight) in a Pt crucible under air. The resultant crystals were examined by means of electron probe microanalyzer (EPMA) to check the extent of replacement. The powder X-ray diffraction data were obtained by a Philips diffractometer and the lattice parameters were calculated by the least-square method. To ascertain the retention of  $P6_3/mmc$  space group symmetry during the ion exchange, the obtained specimens were examined by the precession photographs taken by using  $\text{MoK}\alpha$  radiation. Density was measured according to the method of Archimedes.

In the previous paper, " $\text{Ba}_{0.79}\text{Al}_{10.9}\text{O}_{17.14}$ "

was chosen as the formula of Ba  $\beta$ -Al<sub>2</sub>O<sub>3</sub>, but the result of wet chemical analysis (5) indicates that the formula "Ba<sub>0.75</sub>Al<sub>11.0</sub>O<sub>17.25</sub>," which was derived from the structure analysis of Ba  $\beta$ -Al<sub>2</sub>O<sub>3</sub> (2, 6), would be preferable. Hereafter we use "Ba<sub>0.75</sub>Al<sub>11.0</sub>O<sub>17.25</sub>" as the formula of Ba  $\beta$ -Al<sub>2</sub>O<sub>3</sub>.

## Result and Discussion

### K<sup>+</sup> Ion

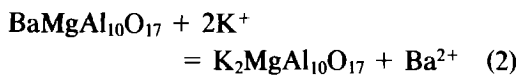
**Ba  $\beta$ -Al<sub>2</sub>O<sub>3</sub>.** Ba  $\beta$ -Al<sub>2</sub>O<sub>3</sub> exchanged successfully with molten K<sub>2</sub>CO<sub>3</sub> at 980°C for 20 hr, giving transparent potassium  $\beta$ -Al<sub>2</sub>O<sub>3</sub> crystals with the formula K<sub>1.5</sub>Al<sub>11.0</sub>O<sub>17.25</sub> (K<sub>1.5</sub>  $\beta$ -Al<sub>2</sub>O<sub>3</sub>) as can be expected from the reaction equation (1). They were free from cracks but very brittle. The remaining BaO was revealed to be only of the order of 0.1 mole% by EPMA. The crystal has hexagonal symmetry with the lattice parameters  $a = 5.599 \text{ \AA}$ ,  $c = 22.73 \text{ \AA}$ , and X-ray powder diffraction data are shown in Table I. The density of 3.39 g/cm<sup>3</sup> is well in accordance with the formula. The precession photographs showed the systematic absence of  $l = 2n + 1$  for  $hhl$  reflections, where  $n$  is an integer. There were also observed diffuse superstructure reflections, but the average structure agreed with the  $P6_3/mmc$  space group which  $\beta$ -alumina compounds usually take. When a specimen 1.5 mm in length perpendicular to the  $c$ -axis was used, the BaO content was unchanged near the center of the crystal under the same exchange condition. Treatment at the lower temperature of 600°C with molten KOH for 20 hr lead to only partial replacement in the periphery.

**Ba · Mg  $\beta$ -Al<sub>2</sub>O<sub>3</sub>.** K<sup>+</sup> ion successfully replaced Ba<sup>2+</sup> ion in Ba · Mg  $\beta$ -Al<sub>2</sub>O<sub>3</sub> when K<sub>2</sub>CO<sub>3</sub> flux was applied for 20 hr at 980°C. The crystals lost transparency owing to tiny cracks. The compositions of the starting and resultant crystals, which were deter-

TABLE I  
X-RAY POWDER DATA FOR K<sup>+</sup>-EXCHANGED  
Ba  $\beta$ -Al<sub>2</sub>O<sub>3</sub>

$h$	$k$	$l$	$d_{\text{obs}}$	$d_{\text{calc}}$	$l/l_0$
0	0	2	11.382	11.369	85
0	0	4	5.689	5.685	43
0	1	2	4.462	4.461	16
0	1	3	4.083	4.085	4
0	1	6	2.987	2.986	5
0	0	8	2.843	2.842	18
1	1	0	2.800	2.800	26
0	1	7	2.700	2.699	100
1	1	4	2.511	2.512	42
0	1	8	2.453	2.452	6
0	2	1	2.411	2.411	23
0	2	2	2.371	2.371	17
0	0	10	2.275	2.274	14
1	1	6	2.252	2.252	16
0	2	4	2.231	2.230	12
0	2	5	2.140	2.140	20
0	1	10	2.060	2.059	3
0	2	6	2.043	2.042	31
0	2	7	1.943	1.943	16
0	2	8	1.846	1.845	8
1	2	2	1.812	1.810	3
1	1	10	1.768	1.765	3
0	2	9	1.749	1.749	3
0	2	10	1.658	1.659	3
0	1	13	1.645	1.645	2
0	0	14	1.624	1.624	3
1	2	7	1.596	1.596	17
0	2	11	1.573	1.573	16
1	1	12	1.569	1.569	16
0	3	4	1.554	1.555	5
0	1	14	1.540	1.540	3

mined by EPMA, are given in Table II. The starting material has a little Ba-deficiency. These data clearly show the equimolar interchange between BaO and K<sub>2</sub>O, so the reaction equation could be written ideally as



The starting material Ba · Mg  $\beta$ -Al<sub>2</sub>O<sub>3</sub> have a typical  $\beta$ -alumina structure with a symmetry of  $P6_3/mmc$  (7). The ion-exchanged product was also proved to have the same space group symmetry by the precession

TABLE II  
COMPOSITION OF Ba · Mg  $\beta$ -Al<sub>2</sub>O<sub>3</sub> BEFORE AND  
AFTER K<sup>+</sup> EXCHANGE

Material	Composition (mole%) <sup>a</sup>			
	BaO	K <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>
Ba · Mg $\beta$ -Al <sub>2</sub> O <sub>3</sub>	13.75	—	13.85	72.40
After K <sup>+</sup> exchange	0.32	13.53	13.31	72.84

<sup>a</sup> By EPMA.

camera. There appeared no reflections due to superstructure. The lattice parameters  $a = 5.641 \text{ \AA}$  and  $c = 22.64 \text{ \AA}$  were obtained by using  $2\theta$ -data of 20 reflections collected on the four-circle diffractometer.

#### Na<sup>+</sup> Ion

*Ba  $\beta$ -Al<sub>2</sub>O<sub>3</sub>.* Complete exchange of Ba<sup>2+</sup> in Ba  $\beta$ -Al<sub>2</sub>O<sub>3</sub> for Na<sup>+</sup> was attained in the molten Na<sub>2</sub>CO<sub>3</sub> at 980°C for 20 hr, yielding crystals with some tiny cracks. No remaining Ba<sup>2+</sup> was detected by EPMA but Na content tended to vary because of the migration of Na<sup>+</sup> ion during the analysis and/or the inhomogeneity of the Na content in a specimen itself. On the average, the content of NaO was shown about 10–20% larger than that expected from the formula Na<sub>1.5</sub>Al<sub>11.0</sub>O<sub>17.25</sub>. To determine the exact Na content, wet chemical analysis is now on progress, so in this paper it is tentatively denoted as “Na<sub>1.5</sub>Al<sub>11.0</sub>O<sub>17.25</sub>(Na<sub>1.5</sub>  $\beta$ -Al<sub>2</sub>O<sub>3</sub>).” It possesses hexagonal symmetry with lattice parameters  $a = 5.591 \text{ \AA}$  and  $c = 22.62 \text{ \AA}$ . X-Ray powder diffraction data are given in Table III. The retention of the space group symmetry  $P6_3/mmc$  was confirmed by the precession photographs; density was 3.29 g/cm<sup>3</sup>. Exchange reactions were also undertaken on the specimen of 1.2 mm in length perpendicular to the  $c$ -axis, yielding a completely exchanged crystal. This fact suggests the faster exchange rate as compared with the case of K<sub>1.5</sub>  $\beta$ -Al<sub>2</sub>O<sub>3</sub>.

Treatment of Ba  $\beta$ -Al<sub>2</sub>O<sub>3</sub> with excess

molten NaCl–NaNO<sub>3</sub> (3:7 mole ratio) for 72 hr at 650°C resulted in only partially exchanged crystals in the periphery. When K<sub>1.5</sub>  $\beta$ -Al<sub>2</sub>O<sub>3</sub> was used instead of Ba  $\beta$ -Al<sub>2</sub>O<sub>3</sub>, Na<sup>+</sup> ion replaced completely K<sup>+</sup> in K<sub>1.5</sub>  $\beta$ -Al<sub>2</sub>O<sub>3</sub> after 22 hr at 600°C. The resultant crystal remained transparent and free from cracks.

In conclusion, complete replacement of Ba<sup>2+</sup> by monovalent cations was shown to take place according to the reaction equations (1) and (2) at least in the K<sup>+</sup>-exchange case. Furthermore, the retention of space group symmetry was proved for all ion-exchanged products. This means no alteration of the host lattice of  $\beta$ -alumina. Other  $\beta$ -Al<sub>2</sub>O<sub>3</sub> compounds could be obtained by further ion exchange of K<sub>1.5</sub>  $\beta$ -Al<sub>2</sub>O<sub>3</sub> or “Na<sub>1.5</sub>  $\beta$ -Al<sub>2</sub>O<sub>3</sub>,” so this method would present a new route to prepare highly cation-excess M<sup>1+</sup>  $\beta$ -Al<sub>2</sub>O<sub>3</sub>.

TABLE III  
X-RAY POWDER DATA FOR Na<sup>+</sup>-EXCHANGED  
Ba  $\beta$ -Al<sub>2</sub>O<sub>3</sub>

$h$	$k$	$l$	$d_{\text{obs}}$	$d_{\text{calc}}$	$l/l_0$
0	0	2	11.255	11.312	100
0	0	4	5.632	5.656	51
0	1	1	4.751	4.735	1
0	1	2	4.464	4.451	4
0	1	3	4.081	4.075	4
0	0	6	3.755	3.771	1
0	1	6	2.970	2.975	1
0	0	8	2.814	2.828	4
1	1	0	2.802	2.796	7
0	1	7	2.682	2.688	18
1	1	4	2.509	2.506	11
0	1	8	2.435	2.442	3
0	2	1	2.413	2.407	9
0	2	2	2.373	2.367	3
0	0	10	2.250	2.262	6
1	1	6	2.246	2.246	7
0	2	4	2.227	2.226	3
0	2	5	2.136	2.135	6
0	2	6	2.038	2.037	9
0	2	7	1.937	1.938	5
0	2	8	1.838	1.839	2
1	2	7	1.592	1.593	5
1	1	12	1.563	1.563	3
0	3	4	1.553	1.552	1

The X-ray single-crystal structure analysis is now on progress to reveal the sites of monovalent cations.

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### References

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