

# High-Temperature Behavior of Ba-Doped Boehmite Hydrothermally Prepared from $\text{Al}(\text{OH})_3$ and $\text{Ba}(\text{OH})_2$

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Minute boehmite crystals with high aspect ratios, which were hydrothermally synthesized from gibbsite in  $\text{Ba}(\text{OH})_2$  solution, occluded Ba with the Ba/Al molar ratio of about 0.03 in their interlayers. Their surface areas were about  $14 \text{ m}^2/\text{g}$ . The Ba-intercalated boehmite samples were partly used for producing  $\text{BaAl}_{12}\text{O}_{19}$  with low sinterability by externally supplementing  $\text{Ba}(\text{OH})_2$ , and for forming transient aluminas. The surface area of  $\text{BaAl}_{12}\text{O}_{19}$  obtained by firing at  $1500^\circ\text{C}$  for 3 h was  $5.3 \text{ m}^2/\text{g}$ , which was significantly lower than  $12 \text{ m}^2/\text{g}$  of the sol-gel origin. While a mixture  $\gamma$ -alumina and BaO is known to form  $\text{BaAl}_{12}\text{O}_{19}$  at  $1200^\circ\text{C}$ , solid state reaction between  $\eta$ -alumina transformed from the Ba-intercalated boehmite and BaO formed from  $\text{Ba}(\text{OH})_2$  deposited on the boehmite started above  $1300^\circ\text{C}$ . This suggests that large sized  $\text{Ba}^{2+}$  ion occluded in  $\eta$ -alumina considerably suppresses the diffusion of  $\text{Al}^{3+}$  ion. The surface area of the Ba-intercalated boehmite fired at  $1400^\circ\text{C}$  for 3h was as high as  $14 \text{ m}^2/\text{g}$  indicative of its potential applicability to combustion catalysts. But it was decreased to  $5.0 \text{ m}^2/\text{g}$  after firing at  $1500^\circ\text{C}$  for 3h, accompanied by abrupt formations of  $\alpha$ -alumina and  $\text{BaAl}_{12}\text{O}_{19}$  as main products. The suppression of  $\alpha$ -alumina formation up to  $1400^\circ\text{C}$  also suggests the significant blocking effect of  $\text{Ba}^{2+}$  ion on the diffusion of the component ions.

**Key words:** Boehmite, Hydrothermal synthesis, Ba intercalation

## I. Introduction

With recent improvements in technologies and efforts to solve problems related with the global environment and to save energy, demands for high performance ceramics are increasing.

In the field of high-temperature materials, high-temperature combustion catalysts, heat-insulative materials and heat-resistant permeative membranes are desired to be developed. As a main component of these materials, one may readily call to mind inexpensive and harmless alumina, melting point of which is as high as  $2054^\circ\text{C}$ .

Yoldas,<sup>1)</sup> and Mori et al.<sup>2,3)</sup> claimed that coating of  $\text{SiO}_2$  on  $\gamma$ -alumina was effective for preserving its comparatively high surface area due to the suppression of the  $\gamma \rightarrow \alpha$  phase transition which is responsible for the reduction of its surface area.

One method to innovate ceramics is to chemically control microstructures of their precursors, although much attention has not been paid to chemical processing at the stage of the precursor formation. Complexation of  $\gamma$ -alumina with BaO was found to be effective in preserving its surface area below  $1200^\circ\text{C}$ .<sup>4)</sup> Starting from this, Machida and Arai prepared  $\text{BaAl}_{12}\text{O}_{19}$  with comparatively high surface area by a sol-gel method.<sup>5-7)</sup> This  $\text{BaAl}_{12}\text{O}_{19}$  had a thin-plate morphology and retained the surface area higher than  $10 \text{ m}^2/\text{g}$  after firing at  $1500^\circ\text{C}$ .<sup>6)</sup> This sol-gel method is expensive and alternative methods to produce sparingly sinterable

$\text{BaAl}_{12}\text{O}_{19}$  are desirable.

The above two examples indicate that following two points are very important to produce alumina or alumina derivatives both with high surface areas; (1) reduction in directly contacting areas between grains, (2) complexation of large-sized cation (for example  $\text{Ba}^{2+}$ ) to hinder the diffusion of  $\text{Al}^{3+}$  ion.

Recently, we found that boehmite could accommodate  $\text{Ba}^{2+}$  ion in its interlayers, and concomitantly succeeded in the shape-selective preparation of boehmite crystals. This paper, after mentioning the microstructural characteristics of Ba-intercalated boehmite crystals, deals mainly with the phase transformation and accompanying surface area change of this boehmite sample during firing up to  $1500^\circ\text{C}$ . Also, a brief discussion on surface area of  $\text{BaAl}_{12}\text{O}_{19}$  obtained from a mixture of the Ba-intercalated boehmite and externally supplemented  $\text{Ba}(\text{OH})_2$  is made in connection with the practical applicability of this method.

## II. Experimental Procedure

### 1. Preparation of materials

Commercially available reagents, each with the highest purity except  $\text{Al}(\text{OH})_3$ , were used as starting materials. Low-purity gibbsite ( $\text{Al}(\text{OH})_3$ ), from Wako Chem. Ind. LTD. contained 0.47 mass%  $\text{Na}_2\text{O}$  and 0.41 mass%  $\text{SiO}_2$  as impurities. These impurities were mostly separated after the  $\text{Al}(\text{OH})_3$  was hydrothermally converted into boehmite. The

**Table 1.** Typical Material Compositions for Hydrothermal Synthesis of Boehmite

Run <sup>1)</sup>	Content in reactant solution (mmol)			
	Al(OH) <sub>3</sub>	Ba(OH) <sub>2</sub> · H <sub>2</sub> O	triethanolamine	water
HT-H	40.0 <sup>2)</sup>	0	0	1111 <sup>3)</sup>
HT-B	40.0	3.333 <sup>1)</sup>	0	1111
HT-B-T	40.0	3.333	33.51 <sup>5)</sup>	830

<sup>1)</sup>Meanings of notations in this column are as follows; HT: hydrothermal H water(H<sub>2</sub>O), B: Ba(OH)<sub>2</sub>, T: triethanolamine.

<sup>2)</sup>3.12 g(1.29 cm<sup>3</sup>), <sup>3)</sup>20.00 g, <sup>4)</sup>1.05 g(0.48 cm<sup>3</sup>), <sup>5)</sup>5.00 g(4.45 cm<sup>3</sup>)

concentrations of the impurities in the resulting boehmite decreased to 0.017 and 0.10 mass% for Na<sub>2</sub>O and SiO<sub>2</sub>, respectively. It seems that complete conversion of high purity Al(OH)<sub>3</sub> into boehmite is not successful probably due to the difficulty of its dispersion in water. In addition, separation of impurities in the high purity Al(OH)<sub>3</sub> (Na<sub>2</sub>O 0.018, SiO<sub>2</sub> 0.12 mass%) was hardly achieved after the hydrothermal treatment. For these reasons, the low-purity Al(OH)<sub>3</sub> was employed in this study. The hydrothermal reactions were carried out at 105-200 °C in a teflon vessel placed in an air-tight steel reactor and the reaction conditions are shown in Table 1.

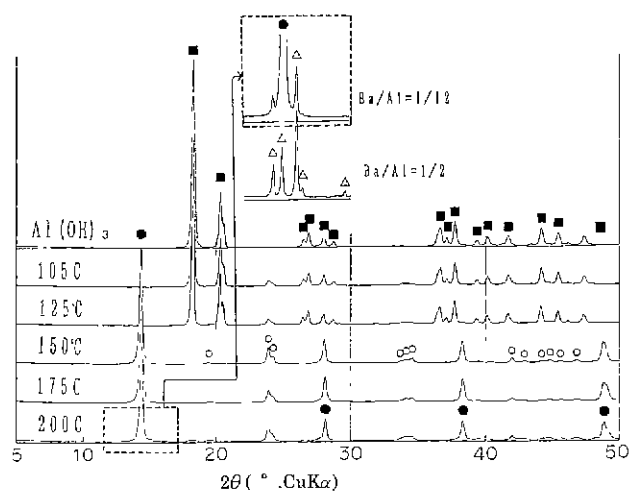
As already mentioned, boehmite formed in the presence of Ba(OH)<sub>2</sub> contained a considerable amount of Ba. The Ba-doped boehmite samples were processed further through two routes;

(1) The boehmite sample was washed at room temperature for 5 min with acetic acid solution of pH=4 to remove Ba<sup>2+</sup> ion adsorbed on its surface and then dried, this run being denoted as HT-B-A.

(2) The mixture of Ba-doped boehmite and the ambient Ba(OH)<sub>2</sub> solution in the hydrothermal reactor was heated to dryness(HT-B-D). By this procedure, Ba in the starting solution was complexed with the boehmite (Ba/Al molar ratio=1/12), although the Ba distribution was not homogeneous. These samples were heated up to a prescribed temperature with the rate of 5 °C/min and soaked, then cooled in a furnace to room temperature.

## 2. Microstructural and chemical analyses of Ba-doped boehmite

XRD measurements were conducted using a Rigaku Denki RINT-1500 Diffractometer to identify minerals formed, correspondence of the XRD peaks to minerals being made using the JCPDS data. Morphological observations of minerals were carried out by using scanning electron microscope(JEOL JXA-8600S) TG-DTA measurements were conducted in the temperature range from room temperature to 1200 °C. Surface areas of the samples were measured by the BET method using N<sub>2</sub>. Chemical analysis procedures for Ba-containing samples are as follows. At first, boehmite was dissolved by concentrated HCl solution. Then Al was analyzed by the conventional EDTA titration method, and Ba by the gravimetric analysis after its precipita-



**Fig. 1.** XRD patterns of products obtained by hydrothermal reaction for 48 h under HT-B condition.

■ : gibbsite, ● : boehmite, ○ : BaCO<sub>3</sub>, △ : Ba(AlO(OH)<sub>2</sub>)<sub>2</sub>. In the figure, a narrow range of the XRD pattern for products formed in Ba(OH)<sub>2</sub>-enriched solution (200 °C, 48 h) is inserted for comparison.

tion as BaSO<sub>4</sub>. However, the samples fired at higher temperatures could not be dissolved by any acidic solution. Therefore they were melted with a mixture of Na<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub>, then the resulting melts were dissolved by HCl solution. The successive analysis process was the same as described above.

## III. Results and Discussion

### 1. Microstructure of boehmite hydrothermally prepared in the presence of Ba(OH)<sub>2</sub>

Fig. 1 demonstrates that, under the condition of the Ba/Al molar ratio=1/12, gibbsite was highly selectively converted into boehmite above 150 °C. As a minor byproduct, Ba(AlO(OH)<sub>2</sub>)<sub>2</sub> was formed. It seems worth mentioning that this by product was not formed in the presence of triethanolamine(HT-B-T run, 200 °C, 48 h). On the other hand, a major product formed at 200 °C was Ba(AlO(OH)<sub>2</sub>)<sub>2</sub>, when Ba/Al molar ratio=1/2.

Fig. 2 shows morphologies of hydrothermally prepared boehmite crystals. They were cube-like when synthesized in water, plate-like in the presence of Ba(OH)<sub>2</sub>, and columnar in the presence of triethanolamine. BET surface areas of the cube-like and the columnar boehmite samples prepared at 200 °C for 48 h, were 2 and 14 m<sup>2</sup>/g, respectively.

Boehmite has a layered structure and its sheet plane is indexed as (0 k 0).<sup>6)</sup> In the case of the plate-like crystal, this b-plane is considered to be most widely exposed plane. In the XRD measurement, the plate-like crystals were softly pressed to a glass plate to preserve the morphologies. This procedure divides the planes reflecting the incident X-ray beam poorly or well to the detector. For example, most part of the X-ray beam reflected from planes parallel to the hem faces of the plate-like crystals would not enter into the

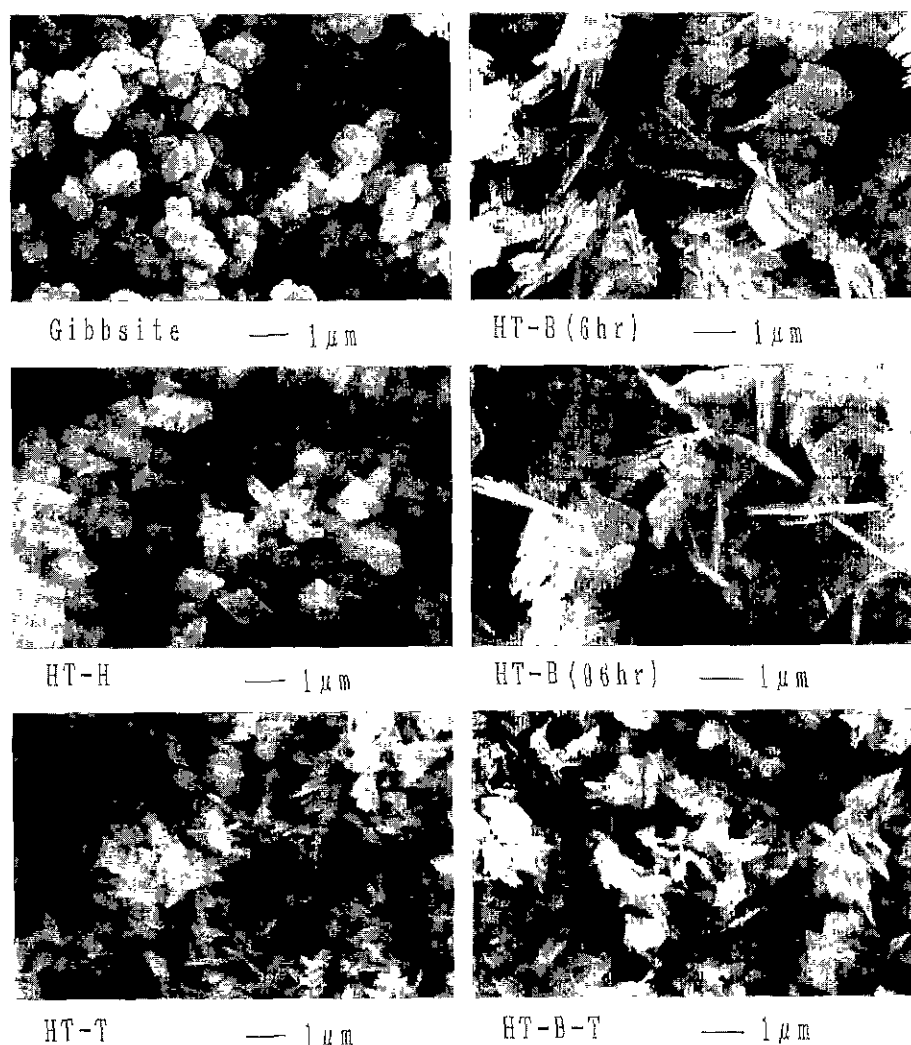


Fig. 2. SEM photographs of boehmite crystals hydrothermally synthesized at 200 °C. The reaction time was 48h unless otherwise given in parenthesis.

detector, and thus these planes would give rise to only weak diffraction peaks.

Table 2 shows relative XRD peak intensities for boehmite samples with different morphologies. In the case of the plate-like crystal (HT-B), relative intensities of (200) and (002) peaks were considerably low as compared with those of unoriented one. This indicates that the growing directions of the plate-like crystals are a and c axes. On the other hand, the growing direction of the columnar crystals

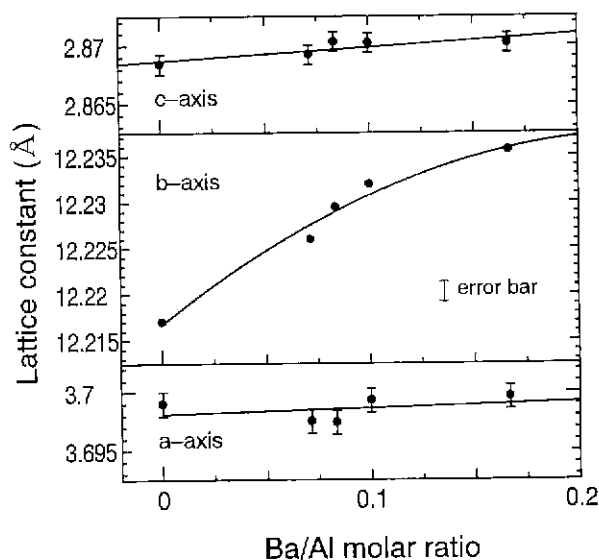
Table 2. Relative Peak Intensities for Hydrothermally Prepared Boehmite Samples

Preparation condition	Relative peak height		
	(020)	(200)	(002)
HT-B	100	10	2
HT-T	100	20	4
HT-B-T	100	23	5
JCPDS	100	25	10

$2\theta(\text{CuK}\alpha)$ ; (020): 14.5°, (200): 49.2°, (002): 65.0°.

is considered to be along c axis. This could be judged from the relatively low intensity of (002) peak as in the case of the plate-like sample, and also from the similar relative intensity of (200) peak. Table 2 suggests that triethanolamine played more decisive role than  $\text{Ba}(\text{OH})_2$  in the synthesis of shape-regulative boehmite.

A significant shift of (020) peak was observed for boehmite crystals prepared in  $\text{Ba}(\text{OH})_2$  solution. Since large-sized  $\text{Ba}^{2+}$  ion is unable to enter into the octahedral  $\text{AlO}_6$  sheet of boehmite, this shift suggests that  $\text{Ba}^{2+}$  ion was intercalated in its interlayers. Fig. 3 shows the lattice parameters of boehmite prepared in the presence of  $\text{Ba}(\text{OH})_2$  as a function of the initial  $\text{Ba}(\text{OH})_2$  concentration in the reactant solution. It is seen that the lattice constant for b axis markedly changes with the  $\text{Ba}(\text{OH})_2$  concentration. Ratios of the lattice expansion along the three crystal orientations were calculated from the differences between the respective lattice constants of Ba-incorporated boehmite (initial Ba/Al molar ratio=1/6), and those of Ba-undoped

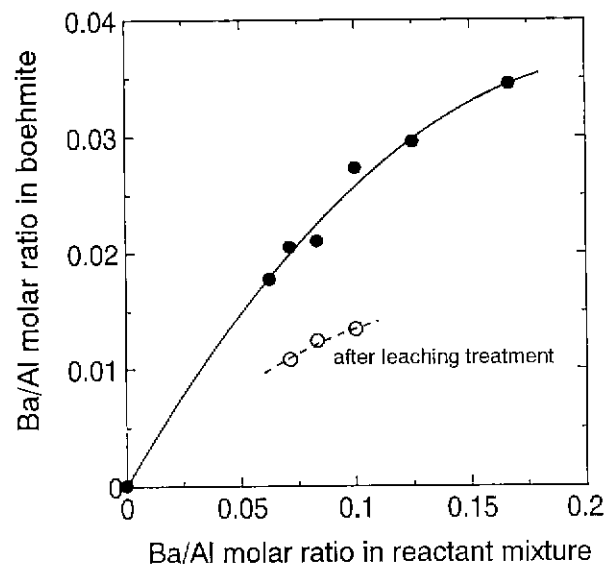


**Fig. 3.** Lattice constants of Ba-intercalated boehmite as a function of Ba/Al molar ratio in the reactant mixture. Reaction time, temperature : 48 h, 200 °C. Composition of reactants : H<sub>2</sub>O:20.0 ml, Al(OH)<sub>3</sub>:3.12g, Ba(OH)<sub>2</sub> · 8H<sub>2</sub>O:0~2.10 g.

boehmite. The ratios were  $6.5 \times 10^{-5}$  along a axis,  $1.5 \times 10^{-3}$  along b axis, and  $6.2 \times 10^{-3}$  along c axis. These results clearly demonstrate that Ba<sup>2+</sup> ion was not included in the AlO<sub>6</sub> sheets but intercalated in the interlayers.

To further investigate the intercalation mechanism, pH measurements were carried out for the solution parts of the reactants. Before the hydrothermal reaction, pH of the solution part of the HT-H reactant at room temperature was 9.0, and after the reaction at 200 °C for 48h, it changed to 11.9. As described in the experimental section, these alkaline natures of the solution parts seems to be caused by the impurity NaOH. Addition of 1.00 g of BaCl<sub>2</sub> to the HT-H reactant hardly changed the pH of its solution part. After the hydrothermal reaction at 200 °C for 48h, pH of the solution part of the HT-H-BaCl<sub>2</sub> reactant changed to 6.1. This alkaline to acidic change during the hydrothermal reaction indicates that the intercalated Ba<sup>2+</sup> ion substituted for two H<sup>+</sup> ions present in the interlayers of boehmite.

TG-DTA analysis of the Ba-intercalated boehmite revealed



**Fig. 4.** Ba/Al molar ratio in Ba-intercalated boehmite as a function of Ba/Al molar ratio in the reactant mixture. Reaction conditions and reactant compositions are the same as described in Fig. 3. Leaching treatment : Ba(OH)<sub>2</sub> on the surface and in the surface layer of boehmite crystals was leached by immersing them in acetic acid solution of pH=4 at room temperature for about 5 min followed by rapid filtration of the solution.

that it liberated water vapor at 510 °C, which is significantly lower than 530 °C reported for pure boehmite,<sup>10)</sup> and 540 °C measured for the Ba-undoped boehmite prepared under the HT-H condition in this study. The difference in the decomposition temperature seems to be related with the presence of the large-sized Ba<sup>2+</sup> ion in the interlayer through which water vapor diffuses.

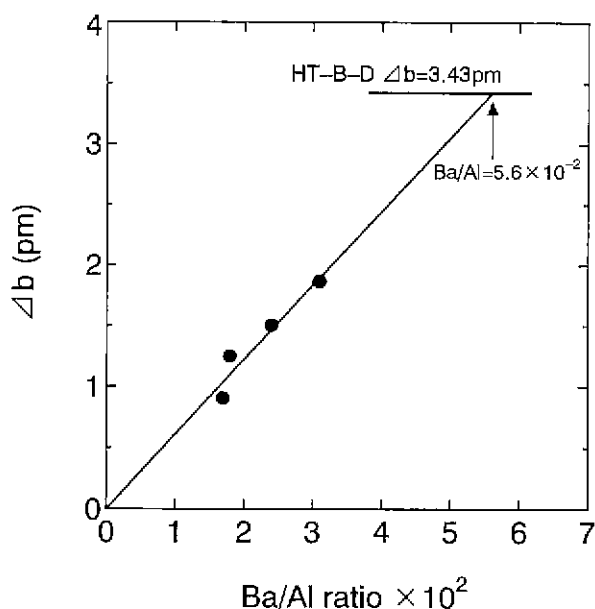
## 2. Relation between the Ba concentration in boehmite and starting Ba(OH)<sub>2</sub> solution.

Fig. 4 shows that the amount of the intercalated BaO increased with the initial Ba(OH)<sub>2</sub> concentration in the reactant solution. The increase of Ba(OH)<sub>2</sub>/Al(OH)<sub>3</sub> ratio to 1/2 resulted in the selective formation of Ba(AlO(OH)<sub>2</sub>)<sub>2</sub>. This means that the concentration of BaO intercalated in boehmite could not be increased so much.

**Table 3.** Concentration of BaO Included in Boehmite Obtained by Hydrothermal Reaction of Gibbsite in Bariumacetate

Run	Reactant composition (mmol)			pH of reactant solution		BaO/AlOOH molar ratio × 10 <sup>3</sup>
	Al(OH) <sub>3</sub>	BaAc <sub>2</sub>	water	before react.	after react.	
1	40.26 <sup>2)</sup>	1.00 <sup>1)</sup>	1110 <sup>3)</sup>	7.23	6.67	4.5
2		3.32		7.40	6.51	6.0
3		3.99		7.42	6.51	5.6
4		5.00		7.44	6.51	6.5
5		6.66		7.46	6.54	6.3
6		7.51		7.49	6.48	6.6
7		10.00		7.56	6.53	7.2
8		15.00		7.63	6.52	7.8
9		20.00 <sup>1)</sup>		7.85	6.62	8.7
10		29.36		7.85	6.76	9.8

<sup>1)</sup>0.25 g, <sup>2)</sup>3.12 g, <sup>3)</sup>20.0 g, <sup>4)</sup>5.11 g. reaction condition: 200 °C, 48 h; pH was measured at room temperature.



**Fig. 5.** Relationship between Ba/Al molar ratio in Ba-intercalated boehmite and increase of its b-axis lattice constant from that of pure boehmite. Sample preparation conditions: the same as described in Fig. 3.

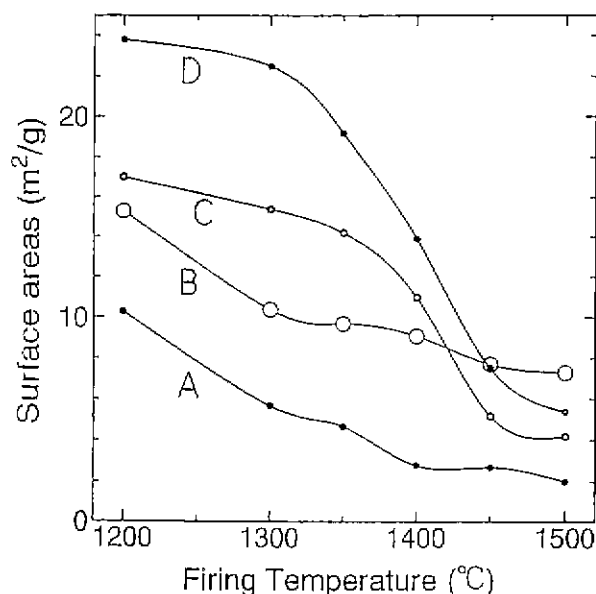
In the hydrothermal reaction, a substitution of Ba ( $\text{CH}_3\text{COO}$ )<sub>2</sub> (hereafter abbreviated as  $\text{BaAc}_2$ ) for  $\text{Ba}(\text{OH})_2$  was attempted to examine whether this substitution is effective to increase the amount of the intercalated  $\text{Ba}^{2+}$  ion. The results shown in Table 3 indicate that  $\text{Ba}^{2+}$  from  $\text{Ba}(\text{OH})_2$  is more readily intercalated than that from  $\text{BaAc}_2$ . This may tentatively be explained as follows. Alkaline solution of  $\text{Ba}(\text{OH})_2$  is liable to pull out  $\text{H}^+$  ion from boehmite. This would accelerate the intrusion of  $\text{Ba}^{2+}$  ion in the solution into the interlayers.

As shown in Fig. 5, a linear relationship was found between an increment of the c axis lattice constant and the Ba/Al molar ratio in the Ba intercalated boehmite. Here, a level line which is inserted in the figure with the name of dryness indicates the lattice constant of the HT-B-D sample described in the experimental section. The molar ratio of the intercalated Ba to Al in this HT-B-D sample is estimated to be 0.056 from the point of intersection of the extrapolated linear line and the level line.

These results lead to the assumption that the molar ratio of the intercalated Ba to Al would not go up 0.083, this value corresponding to the stoichiometry of  $\text{BaAl}_{12}\text{O}_{19}$ .

### 3. High temperature reaction between Ba-intercalated boehmite and $\text{Ba}(\text{OH})_2$ deposited on it

The surface area of an assembly of the columnar boehmite crystals with  $\text{Ba}(\text{OH})_2$  deposited on them increased from 14 to 33  $\text{m}^2/\text{g}$  after its heating above 600 °C. This results probably from vigorous release of water vapor. It is expected that the comparatively high surface area of this decomposed product would be retained at higher tempera-



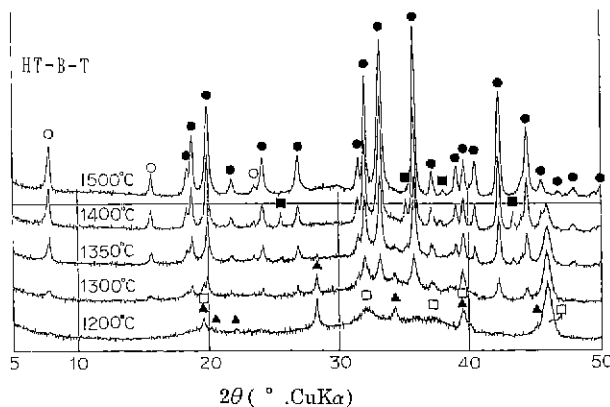
**Fig. 6.** Relation between firing temperature and surface area of fired sample. Firing time: 3 h; samples and their preparation procedures, A:  $\text{Al}(\text{OH})_3$ , gibbsite, B: mixture of  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  and  $\text{Al}(\text{OH})_3$  (molar ratio 1:12), C: Ba-intercalated boehmite after acid-leaching treatment (HT-B-A), D: boehmite with deposited  $\text{Ba}(\text{OH})_2$  prepared under HT-B-T-D condition (200 °C, 48 h, drying treatment).

tures ( $\geq 1400$  °C), if  $\text{BaAl}_{12}\text{O}_{19}$  was directly formed from the decomposed product the Ba sources of which was partly from the intercalated Ba and partly from the deposited  $\text{Ba}(\text{OH})_2$ . Its successive heating gradually decreased the surface area. The variation of its surface area in the range 1200-1500 °C is shown in Fig. 6 with those of Al-based materials. Although the surface area of this HT-B-T-D sample fired at 1500 °C was much lower than 11  $\text{m}^2/\text{g}$  which the sol-gel derived  $\text{BaAl}_{12}\text{O}_{19}$  heated at 1600 °C exhibited,<sup>6)</sup> that fired at 1400 °C was as high as 14  $\text{m}^2/\text{g}$ . To explain the surface area profile, microstructural investigation was carried out for the HT-B-T-D sample.

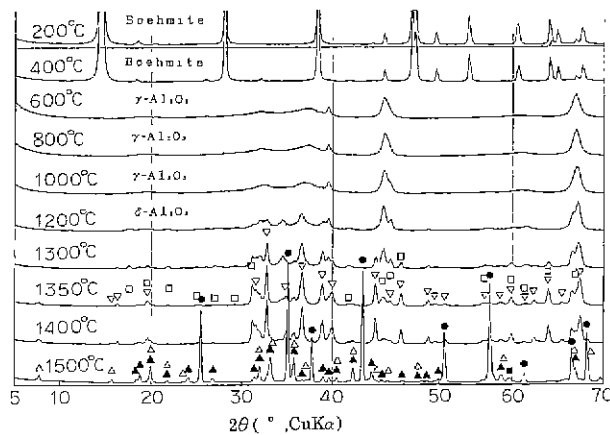
Fig. 7 shows XRD patterns of the HT-B-T-D sample heated at 1200-1500 °C. In the case of a solid-solid reaction between  $\text{BaCO}_3$  and  $\gamma$ -alumina, main products at 1200 °C were reported to be  $\text{BaAl}_2\text{O}_4$  and  $\text{BaAl}_{12}\text{O}_{19}$ .<sup>6)</sup> In contrast, this figure clearly demonstrates that  $\text{BaAl}_{12}\text{O}_{19}$  was not formed by heating at 1200 °C. Its formation started at 1300 °C. In addition,  $\eta$ -alumina which has been stated to convert into  $\alpha$ -alumina above 1100 °C via  $\theta$ -alumina<sup>11,12)</sup> existed at 1400 °C. These results indicate that the doped Ba stabilized the transient alumina and eventually decreased its reactivity. The comparatively high surface area of the HT-B-T-D sample heated at 1400 °C may be correlated with the presence of the residual  $\eta$ -alumina, which completely disappeared at 1500 °C.

### 4. High temperature behavior of Ba-intercalated boehmite

Ba-intercalated boehmite obtained by the hydrothermal



**Fig. 7.** XRD patterns of a mixture of Ba-intercalated boehmite and  $\text{Ba}(\text{OH})_2$  fired at various temperatures for 3 h. ○:  $\beta$ -alumina, □:  $\gamma$ -alumina, ●:  $\text{BaO} \cdot 6\text{Al}_2\text{O}_3$ , ▲:  $\text{BaO} \cdot \text{Al}_2\text{O}_3$ , ■:  $\alpha$ -alumina. Ba-intercalated boehmite: formed by the reaction at 200 °C for 48 h under the HT-B-T condition; mixture: the resulting Ba-intercalated boehmite together with the ambient solution containing  $\text{Ba}(\text{OH})_2$  and triethanolamine was heated to dryness. Then, the molar ratio of Ba/Al in the mixture became 1/12. As for the content of Ba occluded in the boehmite, see Fig. 5. dryness and related description in the text.



**Fig. 8.** XRD patterns of boehmite prepared through the HT-B-A process and that fired at various temperatures for 1 h. □:  $\delta$ -alumina, ▽:  $\theta$ -alumina, △:  $\beta$ -alumina, ●:  $\alpha$ -alumina, ▲:  $\text{BaO} \cdot 6\text{Al}_2\text{O}_3$ .

reaction at 200 °C for 48h under the HT-B condition followed by washing with  $\text{CH}_3\text{COOH}$  solution contained Ba as 4.6 mass% BaO, and it was used to examine its high temperature behavior. Fig. 8 shows XRD patterns of this HT-B-A sample heated at various temperatures. It is seen that the Ba-intercalated boehmite transformed to  $\gamma$ -alumina (600-1000 °C),  $\delta$ -alumina (1200-1300 °C),  $\theta$ -alumina (1350-1400 °C) and finally to  $\alpha$ -alumina (>1400 °C). At 1500 °C,  $\alpha$ -alumina was formed as a main product accompanied by  $\beta$ -alumina and  $\text{BaAl}_{12}\text{O}_{19}$  as byproducts. The surface area of this boehmite after firing for 3h at 1000 °C was 20  $\text{m}^2/\text{g}$ , and 15  $\text{m}^2/\text{g}$  after firing at 1400 °C. Firing at 1500 °C markedly decreased its surface area to 4  $\text{m}^2/\text{g}$ . These results clearly demonstrate that Ba present in the interior of alumina enhances the stabilities of transient aluminas.

Amato<sup>41</sup> claimed that Ba occupying the Al vacancy in  $\gamma$ -alumina significantly depressed the bulk diffusion of Al and thus suppressed its transformation to  $\alpha$ -alumina and the accompanying sintering. He also pointed out that the Ba could exert this effect only below 1200 °C. In this study, however, the doped Ba was effective in the suppression of the transformation of transient aluminas to  $\alpha$ -alumina even at a temperature as high as 1400 °C. In the Amato's case, the diffusion-blocking efficiency of Ba would markedly be reduced by the heterogeneous distribution of Ba, but in the present case, Ba initially present homogeneously in the interlayers of boehmite is considered to be distributed in the transient aluminas also homogeneously even after the firing above 1200 °C. This assumption may be supported by the fact that firing of the Ba-intercalated boehmite yielded neither  $\text{BaAl}_2\text{O}_4$  nor  $\text{BaAl}_{12}\text{O}_{19}$  below 1400 °C. The homogeneously distributed Ba seems to contribute to the stabilization of transient aluminas.

Horiuchi and co-workers<sup>31</sup> reported that the surface area of silica-coated porous alumina heated at 1400 °C was as high as 17  $\text{m}^2/\text{g}$ . As mentioned above, the present Ba-doped alumina had the surface area of 15  $\text{m}^2/\text{g}$  which is comparable with that of the silica-coated alumina. This value satisfies the general requirement for high temperature combustion catalysts that the supports must maintain a surface area of at least 10  $\text{m}^2/\text{g}$  above 1400 °C.<sup>61</sup>

As this study started only recently, scrutinies of the starting materials, the additives and the preparation processes were not fully done to improve the characteristics of the precursors and the fired products. The present authors expect that some improvements will be achieved in the shape regulation of the boehmite crystals (aspect ratio, size), and also that the intercalation ability of boehmite will be applicable to produce many useful materials.

## IV. Conclusion

1. Hydrothermal treatments of gibbsite in  $\text{Ba}(\text{OH})_2$  solution mixed with and without triethanolamine yielded, respectively, columnar and plate-like crystals of boehmite intercalated with about 3 mol% of Ba.

2. The assembly of the columnar boehmite crystals was complexed with  $\text{Ba}(\text{OH})_2$  and then fired to form  $\text{BaAl}_{12}\text{O}_{19}$  plate-like crystals. The surface area of  $\text{BaAl}_{12}\text{O}_{19}$  obtained by firing at 1500 °C was 5.3  $\text{m}^2/\text{g}$ , significantly lower than 10  $\text{m}^2/\text{g}$  which is the generally accepted value for a high temperature combustion catalyst to exceed. This result indicates that the processing method using the Ba-intercalated boehmite is practically inapplicable.

3. Ba in the interior of alumina was found to enhance the stability of transient aluminas. Transient aluminas generally transform to  $\alpha$ -alumina on heating about 1200 °C, but formation of  $\alpha$ -alumina from the Ba-containing transient alumina did not occur below 1400 °C. The surface area of the sample obtained by firing the Ba-intercalated boehmite at 1400 °C for 3h was as high as 14  $\text{m}^2/\text{g}$ . This suggests that

it is practically applicable to combustion catalysts operated below 1400 °C.

4. It is reasonable to consider that large-sized Ba<sup>2+</sup> ion comparatively homogeneously distributed in transient aluminas suppressed the diffusion of Al<sup>3+</sup> and O<sup>2-</sup> ions, and eventually hindered their transformation to α-alumina. Heating of the Ba-intercalated boehmite sample at 1500 °C for 3h decreased the surface area of the sample to 5.0 m<sup>2</sup>/g accompanying the formation of α-alumina and BaAl<sub>12</sub>O<sub>19</sub>.

5. It was pointed out that this intercalation phenomenon seems to be extensively applicable to produce not only sparingly sinterable materials herein described but also many other useful functional materials.

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