

# Hydrothermal synthesis and characterization of diaspore, $\beta\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$

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An acicular single crystal of diaspore was synthesized under the conditions of 1 N NaOH, 450°C and 1200 kg cm<sup>-2</sup> and characterized by means of X-ray diffraction, scanning electron microscopy, electron diffraction and infrared spectroscopy. The reactivity of three kinds of natural ores containing diaspore which were used as a seed crystal for synthesis of diaspore was also compared.

## 1. Introduction

Alumina in various forms is one of the most important inorganic materials. In particular,  $\alpha\text{-Al}_2\text{O}_3$  has been produced by the calcination of aluminium hydroxides such as gibbsite ( $\alpha\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ) and bayerite ( $\beta\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ) at higher temperatures  $\sim 1300^\circ\text{C}$ , and used in large quantities as ceramics, refractories and abrasive. The subject of reactive  $\alpha\text{-Al}_2\text{O}_3$  production and its advanced ceramic use is now of considerable technological importance. The properties and reactivity of alumina are closely related to the structure of the hydroxides and their behaviour during thermal decomposition. Diaspore ( $\beta\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ) decomposes directly to  $\alpha\text{-Al}_2\text{O}_3$  at the lower temperature  $\sim 500^\circ\text{C}$ , and the resulting  $\alpha\text{-Al}_2\text{O}_3$  is expected to be more reactive. However, because of the high temperature and pressure conditions required for its preparation, diaspore has not been commercially utilized for the production of  $\alpha\text{-Al}_2\text{O}_3$ .

The purpose of the present study is to prepare and characterize diaspore prior to obtaining some information about the reactivity of  $\alpha\text{-Al}_2\text{O}_3$  which is obtained by the thermal decomposition of diaspore.

## 2. Experimental procedure

Bayerite or pseudoboehmite was used for the hydrothermal synthesis of diaspore. The preparation procedures of bayerite and pseudoboehmite were described previously [1]. These starting powders were mixed in an agate mortar with 10 to 35 wt % pulverized diaspore ore, which is a seed crystal. The mixture ( $\sim 500$  to 650 mg) was packed into a silver tube (diameter = 4 mm, length = 100 mm) together with 0.5 or 1 N NaOH solution and then sealed. The tube was placed in a 5 ml incoloy 800H microbomb and heated under various temperatures and pressures. As a seed crystal, three kinds of natural ores containing diaspore were used to compare the reactivity: Japanese diaspore ore from Syokozan mine, Chinese bauxite ore supplied from Nippon Light Metal Co., and Chinese diaspore ore.

Powder X-ray diffraction (XRD) was carried out

with a Geigerflex 2141 (Rigaku Denki Co.) using nickel-filtered  $\text{CuK}\alpha$  radiation (25 kV, 10 mA).

Scanning electron microscopy (SEM) was carried out with a JSM-35CF apparatus (Jeol) at an accelerating voltage of 25 kV. Samples were dispersed in ethanol by ultrasonication and placed on brass stubs and then coated with a sputter-deposited gold film about 20 nm thick using a JFC-1100 ion-sputtering apparatus.

The electron diffraction pattern was recorded with a H-700H TEM (Hitachi) operating at an accelerating voltage of 200 kV.

Infrared spectra were measured by the diffuse reflectance method with a Model 5M Fourier transform infrared (FTIR) spectrometer (Japan Spectroscopic Co.). Samples were prepared by mixing with potassium bromide (3 wt % sample, 97 wt % KBr) in an agate mortar and scanned 1000 times in the range 400 to 4300 cm<sup>-1</sup>.

## 3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns for the pulverized natural ores containing diaspore and a synthetic diaspore crystal. Japanese diaspore ore (Fig. 1a) contains diaspore  $\geq \alpha\text{-Al}_2\text{O}_3 \gg$  pyrophyllite  $>$  dickite  $\gg \alpha\text{-SiO}_2$ . The observation for as-received ore with the naked eye showed that diaspore (grey) was deposited on the surface of  $\alpha\text{-Al}_2\text{O}_3$  crystal (blue) which was dispersed in the matrix of pyrophyllite and dickite (white). Chinese bauxite ore (Fig. 1b) is light brownish as a whole and contains diaspore  $\gg$  kaolinite  $\gg$  anatase. The latter two impurity crystals were observed to be segregated in the diaspore matrix with an optical microscope. Chinese diaspore ore (Fig. 1c) is greyish oolitic ore and contains diaspore  $\gg$  sericite, pyrophyllite, anatase and rutile. The part of oolite was pure diaspore. These three diaspore-containing ores were pulverized prior to use as a seed crystal.

Table I shows the representative experimental conditions and results on hydrothermal synthesis of diaspore. These experimental conditions were

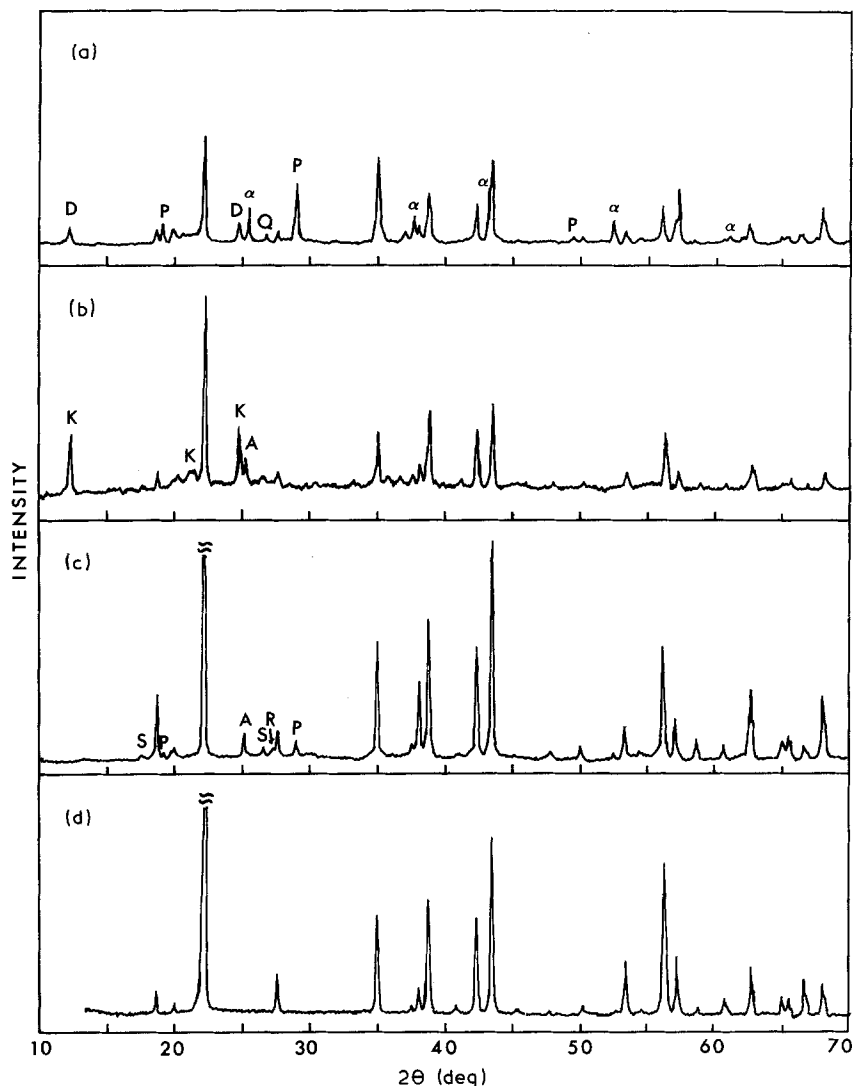


Figure 1 X-ray diffraction patterns for natural ores containing diaspore, (a) Japanese diaspore ore, (b) Chinese bauxite ore, (c) Chinese diaspore ore, and (d) a synthetic diaspore (run S). D, dickite; P, pyrophyllite;  $\alpha$ ,  $\alpha$ - $\text{Al}_2\text{O}_3$ ; Q,  $\alpha$ - $\text{SiO}_2$ ; K, kaolinite; A, anatase; R, rutile; S, sericite. Unmarked peaks are assigned to diaspore.

determined on the basis of the phase diagram of the system  $\text{Al}_2\text{O}_3$ - $\text{H}_2\text{O}$  by Yanagida and Yamaguchi [2]. In the absence of a seed crystal (run Z), boehmite instead of diaspore was formed. In contrast, the crystal growth of diaspore was observed in the presence of Chinese bauxite ore (run M) and Chinese diaspore ore (run O). Japanese diaspore ore was not preferred as a seed crystal to prepare pure diaspore, because of the coexistence of  $\alpha$ - $\text{Al}_2\text{O}_3$  (run D). The yield of diaspore increased using a pulverized seed crystal rather than a coarse grain (compare run O with run P) and the higher NaOH concentration (compare run E with run F). By using the products in run O and run Q as a seed crystal for the subsequent experiments, run Q and run

S, purer diaspore crystal was synthesized. The X-ray diffraction patterns for the diaspore synthesized in run S is shown in Fig. 1d. It is found that a synthetic diaspore is a single phase without impurity crystals.

Fig. 2 shows the scanning electron micrographs of a synthetic diaspore crystal (run S). As shown in Figs 2a and b, the crystals are stumpy rods (width  $\approx 20$  to  $30 \mu\text{m}$ , length  $\approx 50 \mu\text{m}$ ). On crushing slightly, they cleaved along the longest crystal axis and changed to acicular microcrystals (width  $< 1 \mu\text{m}$ , length  $< 10 \mu\text{m}$ ) shown in Fig. 2c. The shape of this acicular crystal was very similar to that observed by Torkar and Krischner [3]. A synthetic diaspore showed a DTA endothermic peak due to the dehydration at

TABLE I The experimental conditions and results of hydrothermal synthesis of diaspore

Run	Starting materials	Hydrothermal conditions				Products <sup>†</sup>
		NaOH(N)	°C	kg cm <sup>-2</sup>	h or d	
D	Pseudoboehmite + 9.5% Japanese diaspore ore	0.5,	450,	1200,	161 h	Bo $\gg$ D > $\alpha$
E	Bayerite + 15.1% Chinese bauxite ore	0.5,	480,	1200,	171 h	Bo > D*
F	Bayerite + 15.1% Chinese bauxite ore	1.0,	480,	1200,	151 h	Bo > D**
M	Bayerite + 13.4% Chinese bauxite ore	1.0,	400,	1200,	21 d	Bo $\approx$ D
O	Bayerite + 13.6% Chinese diaspore ore	1.0,	400,	1200,	28 d	D > Bo
P	Bayerite + 13.9% Chinese diaspore ore (coarse grain)	1.0,	400,	1200,	28 d	Bo $\gg$ D
Q	Bayerite + 35.2% products in run O	1.0,	450,	1200,	35 d	D
S	Bayerite + 30.3% products in run Q	1.0,	450,	1200,	33 d	D
Z	Bayerite	1.0,	400,	1200,	33 d	Bo

<sup>†</sup> Bo, boehmite; D, diaspore;  $\alpha$ ,  $\alpha$ - $\text{Al}_2\text{O}_3$ ; D\*\* > D\*.

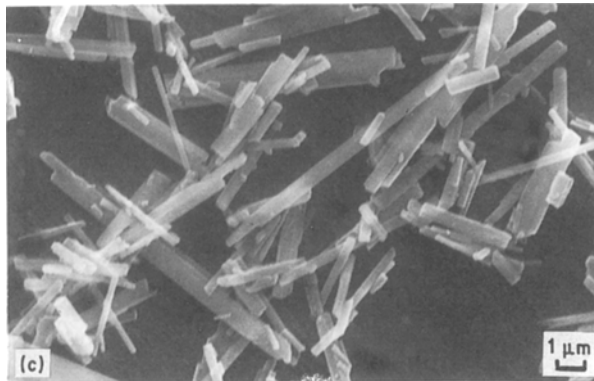
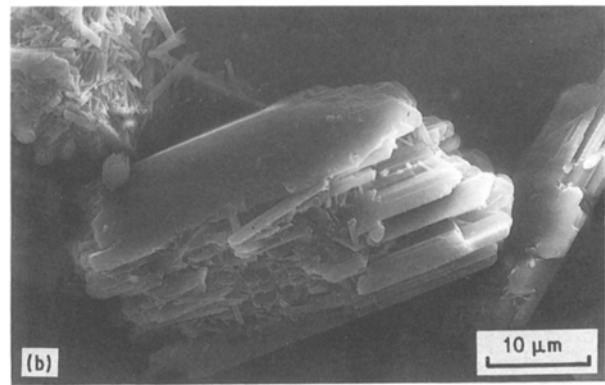
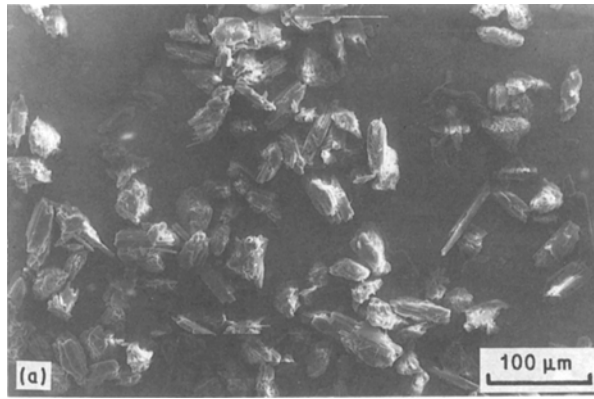


Figure 2 Scanning electron micrographs of a synthetic diaspore (run S). On crushing slightly, the crystal shown in (a) and (b) (higher magnification of (a)) fractured to acicular microcrystals shown in (c).

492° C and transformed directly to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. Even on further heating to 1300° C, the original external shape of the diaspore crystal was not destroyed, which indicates that diaspore transformed topotactically to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. Diaspore is orthorhombic, space group Pbnm, and the cell dimensions are  $a = 0.4401$ ,  $b = 0.9421$  and  $c = 0.2845$  nm [4]. According to the orientation relationship of the diaspore–corundum ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>) transformation [5, 6],  $3a_d$  of diaspore (1.3203 nm) corresponds to  $c$  of corundum (1.297 nm),  $b_d$  (0.9421 nm) corresponds to  $2a_c$  (0.950 nm), and  $3c_d$  (0.8535 nm) corresponds to  $2a_c \times 3^{1/2}/2 = 3^{1/2}a_c$  (0.8227 nm). This means that there is a small contraction of 1.76% along the  $a$  axis of diaspore, a very slight expansion of 0.84% along the  $b$  direction, and a small contraction of 3.61% along the  $c$  direction of diaspore.

Fig. 3 shows an electron micrograph and electron diffraction patterns of a synthetic diaspore crystal (run S). The diffraction pattern is indexed as in Fig. 3, and then it is found that the longest crystal axis corresponds to the  $c$  direction of diaspore. The plane parallel to this  $a$ - $c$  plane, that is, the (0 1 0) plane, is a cleavage plane [7].

Fig. 4 shows infrared spectra of a synthetic diaspore (run S) and Chinese natural diaspore ore. The four absorption bands at 1990, 2120, 2330 (overlapped with C–O stretching vibration due to atmospheric carbon dioxide at 2350 cm<sup>-1</sup>) and 3000 cm<sup>-1</sup> are assigned to O–H stretching vibrations and two bands at 960 and 1080 cm<sup>-1</sup> to O–H bending vibrations [7]. It is found that all bands of a synthetic diaspore are considerably sharper than those of natural diaspore ore. This may be attributable to a well-developed single crystal of a synthetic diaspore.

A study of the dehydration kinetics of diaspore and the reactivity of the resulting  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> will be presented in a forthcoming paper.

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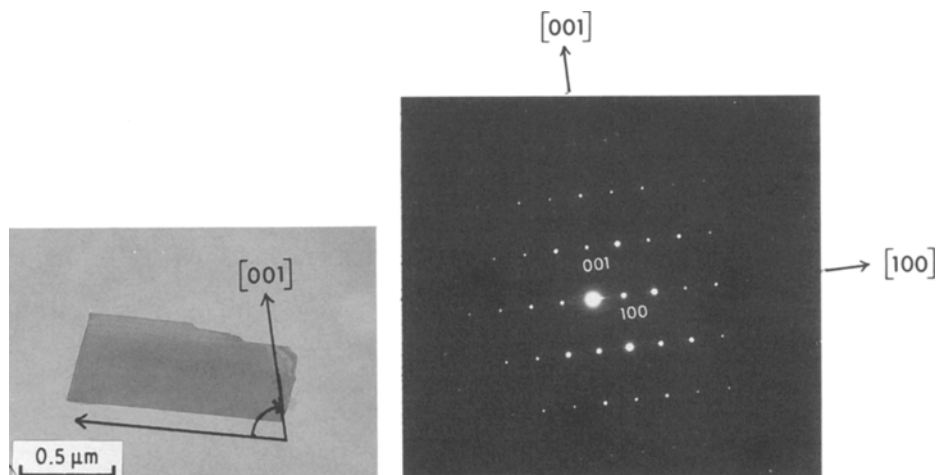


Figure 3 Transmission electron micrograph and [0 1 0] diffraction pattern of a synthetic diaspore (run S).

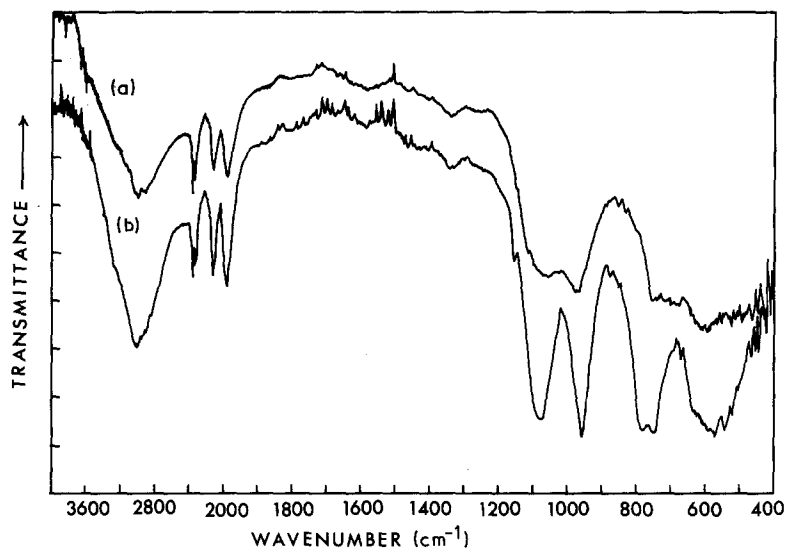


Figure 4 FT-IR spectra of (a) Chinese natural diasporo ore and (b) a synthetic diasporo (run S).

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