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NOTES

COMPARISON OF EXPERIMENTAL AND CALCULATED X-RAY POWDER DIFFRACTION DATA FOR BOEHMITE

Key Words—Boehmite, Crystallite size, Debye scattering equation, Stacking faults, X-ray powder diffraction.

Boehmite (AlOOH) has a layer structure in the xz plane (Reichertz and Yost, 1946; Christoph *et al.*, 1979) and exhibits an unusually large variation in crystallite[1] size from sample to sample (Papée *et al.*, 1958; Tettenhorst and Hofmann, 1980). Most boehmites are fine grained, generally less than a few micrometers in size, however, crystals large enough to study by single-crystal X-ray diffraction (XRD) have been described (Sahama *et al.*, 1973; Hill, 1981). Broad X-ray powder diffraction maxima and excess (non-stoichiometric) water are two consequences of the small crystal size of boehmite.

On the basis of their study of 31 synthetic boehmites, Tettenhorst and Hofmann (1980) found that excess water and breadth of diffraction maxima were inversely proportional to synthesis temperature. Excess water was commonly intercalated between the layers, usually randomly, but sometimes regularly. Baker and Pearson (1974) showed that some excess water likely was bonded to the crystallite's surfaces. They noted that for very small crystals the amount of such water can be significant (see also Papée *et al.*, 1958).

The first XRD maximum of boehmite is the 020 reflection with d ~6.12 Å, corresponding to about 14.4°2θ for CuKα radiation. Many investigators have observed that this reflection is shifted to small 2θ angles for fine-grained boehmite compared with the position of the same reflection from large crystals. Tettenhorst and Hofmann (1980) showed that the magnitude of this shift was directly proportional to the peak breadth and, thereby, inversely proportional to crystallite size.

Subsequently, Grebille and coworkers (Grebille *et al.*, 1983; Grebille and Bérar, 1985, 1986) studied the synthesis and properties of boehmite and corroborated the conclusion of Tettenhorst and Hofmann (1980) that crystallite size has a major effect on the XRD pattern. Grebille and Bérar (1985, 1986) developed a method to calculate XRD peak shapes and obtained good agreement with peak shapes of synthetic boehmites. They concluded that stacking faults must be considered along with crystallite size to reconcile calculated and observed data. Grebille and Bérar (1986) stated that "it was necessary to introduce in our calculations the probability of a stacking fault between the layers of the structure, in order to explain the shift of the 020 line and of this line only." Stacking faults are possible in boemite; however, the objective of the present study is to show that peaks other than 020 can also be shifted (and broadened) and that shifts of peaks other than 020 can be predicted from crystallite size alone.

METHOD OF INVESTIGATION

Experimental

Details of the synthesis procedure are given in Tettenhorst and Hofmann (1980). From the XRD patterns reported by these authors breadth (β) and position (2θ) were measured for the 021 and 130 peaks and the 150/002 doublet at about 28.2°, 38.4°, and 49.2°2θ, respectively (CuKα radiation). All *hkl* values reported herein refer to space group *Cmcm* (Corbató *et al.*, 1985). Experimental breadths (B) were measured at half-maximum intensity and corrected for instrumental broadening by subtracting the breadth of a nearby peak of a fine-grained quartz sample (b). Thus, the pure diffraction breadth $\beta = B - b$. Peak positions were measured at the midpoint of a chord drawn at half-maximum intensity. Peak positions (2θ) are used here rather than their associated d-values because 2θ is the measured quantity. Conservative estimates of breadths and peak positions for small breadths are ±0.02°2θ; breadths and peak positions for large breadths (≥3°2θ) are probably accurate to ±0.1°2θ. All XRD patterns were taken with Ni-filtered CuKα radiation.

Theoretical

The Debye scattering equation (Warren, 1969), also termed the Debye interference function (Tiensuu *et al.*, 1964), was used to calculate XRD profiles of boehmite in three dimensions. Tiensuu *et al.* (1964) used this equation to model diffraction profiles of diamond crys-

[1] The term crystallite is herein used to mean the coherent X-ray scattering volume which is normally less than or equal to the volume of the "crystal" (if it is an individual) or a "grain" if it is composed of one or more crystals.

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tallites that were as much as 35 Å on an edge (10 × 10 × 10 unit cells) and that contained 8 × 10^3 atoms. Minami and Ino (1979) used a modified version of the Debye equation to calculate XRD profiles for cristobalite crystallites that were as much as 37 Å on an edge (5 × 5 × 5 unit cells) and that contained 3 × 10^3 atoms.

Most of the calculations in the present investigation were made on approximately equant crystals whose dimensions were n*a*·m*b*·n*c* (hereafter designated n·m·n), where n = 4m and *a*, *b*, and *c* are the unit-cell dimensions given by Christoph *et al.* (1979). The most reasonable match of calculated patterns with the experimental patterns of Tettenhorst and Hofmann (1980) were obtained using approximately equant crystals. Calculated patterns for elongate and planar crystals yielded a mixture of broad and sharp peaks and bore little resemblance to those of experimental patterns. All calculated patterns were made using the atom positions and thermal parameters given by Christoph *et al.* (1979). XRD profiles were calculated for crystal sizes as large as 150 Å on an edge (48·12·48 unit cells) that contained about 3.3 × 10^5 atoms. The computation for crystals having 48·12·48 unit cells required 2064K bytes of computer memory and took nearly 13 min to execute on an IBM 3081 computer. Some computations were made for a distribution of crystal sizes and, because the boehmite unit cell contains two octahedrally coordinated AlOOH layers perpendicular to the *y* direction, some calculations were made at half-cell increments (*b*/2). The Debye equation allows peak positions and breadths to be simulated as a function of crystal size. Further, the effect on various XRD peaks of dissimilar crystal dimensions was assessed. Peak shapes calculated using only the Debye equation did not match well with experimental peak shapes.

RESULTS AND DISCUSSION

A plot of peak position vs. peak breadth for the 021 reflection is shown in Figure 1 for the 31 synthetic boehmite samples of Tettenhorst and Hofmann (1980). The largest peak shift is about 0.5°2θ toward small angles (large apparent d-values) for the finest grained boehmite compared with the peak position shown by large grains. These data are similar to those reported by Tettenhorst and Hofmann (1980) for 020, but the shifts here are not as large. These data do not support the contention of Grebille and Bérar (1986) that only the 020 peak shifts. Violante and Huang (1984, Table 1) also presented some evidence which indicates that the 021 peak shifts to small angles with a decrease in crystallite size.

XRD profiles for several crystallite sizes calculated with the Debye equation are shown in Figure 2. Diffraction ripples are evident at small values of 2θ, but these can be attenuated by combining several crystallite sizes. A comparison of the calculated XRD profiles in

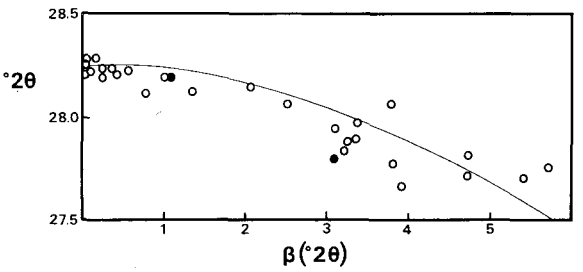


Figure 1. Peak position (°2θ) vs. diffraction breadth (β) of the 021 X-ray diffraction peaks of 31 synthetic boehmites (CuKα radiation). Open circles represent experimental data; solid circles represent superimposed data points. The solid line represents a smooth curve passing through the calculated values for nearly equant crystallites.

Figure 2 with experimental patterns of boehmites in Figure 3 of Tettenhorst and Hofmann (1980) is useful. Profile 8·2·8 matches their profile 7 (43°C synthesis temperature), and profile 48·12·48 matches their profile 23 (200°C synthesis temperature). An exact match was not expected because the real boehmite samples (1) contained a distribution of crystallite sizes, (2) had some water between the layers, and (3) may have been elongated along particular crystallographic directions. Also, all calculated data assumed atom positions and thermal parameters which were obtained from a well-crystallized powder (Christoph *et al.*, 1979). In reality, the atom positions and water content of the boehmites synthesized at low temperatures may not be identical with the parameters of boehmites synthesized at elevated temperatures. Any of these factors can alter the intensities, positions, and peak breadths.

Papée *et al.* (1958) and Violante and Huang (1984) reported XRD patterns which lacked 020 reflections. Tettenhorst and Hofmann (1980) stated that these unusual XRD patterns of boehmite likely were due to the presence of single boehmite layers, perhaps mixed with crystallites containing a few layers at most. Pattern 4·1/2·4 in Figure 2 illustrates this feature.

Papée *et al.* (1958) and other investigators noted that the 020 reflection of boehmite may be broader than other reflections. This differential broadening suggests that the crystallites were relatively elongated in the *x* and *z* directions as can be seen by comparing patterns 12·3·12 and 24·3·24 in Figure 2. This effect is also evident on some of the XRD patterns of Tettenhorst and Hofmann (1980).

The 2θ and β values for the 021 reflection were measured on the calculated patterns (Figure 2) for n = 1 to 12 (and m = 4n). A smooth curve approximating these values is shown on Figure 1. This curve is not inconsistent with the experimental data and thus indicates also that the 021 peak should shift to small angles as peak breadth increases, i.e., as crystal size decreases.

The 130 peak (at about 38.4°2θ) and the 150/002

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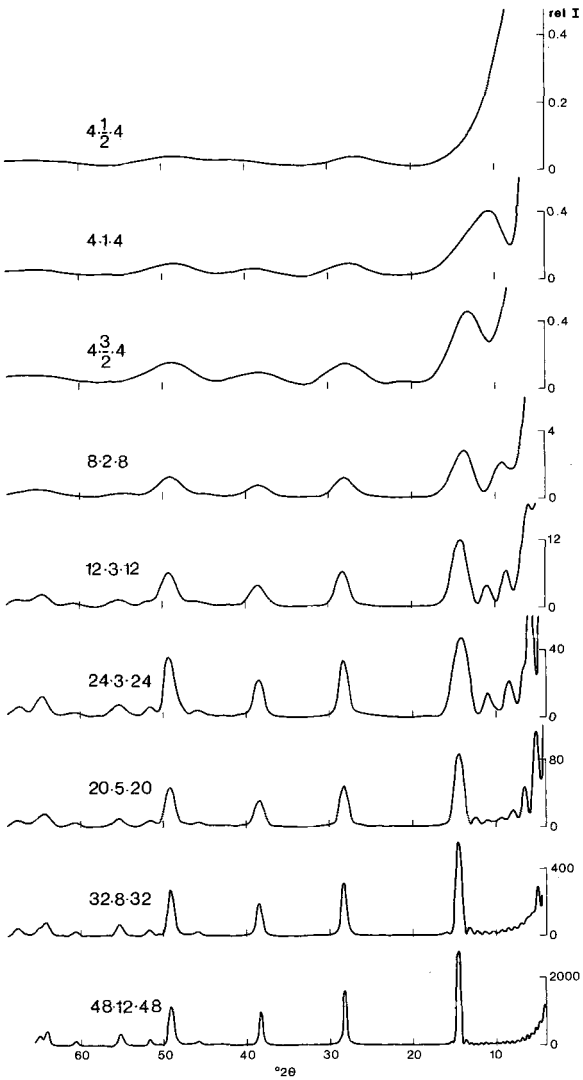


Figure 2. X-ray powder diffraction profiles for boehmite crystallites calculated with the Debye scattering equation (CuKα radiation). Numbers n·m·n represent the number of unit cells per crystallite in the *x*, *y*, and *z* directions, respectively. Natural boehmites show major peaks at about 14.4° (020 reflection), 28.2° (021), 38.4° (130), and 49.2°2θ (150/002 doublet).

doublet (at about 49°2θ) also shifted with a decrease in crystallite size. These shifts were seen on both the experimental and calculated profiles. The 130 peak appeared to shift by as much as 0.5°2θ to *large* angles (i.e., small apparent d-values), whereas the largest shift of the 150/002 doublet was only 0.2°2θ to small angles. These shift directions were observed for the calculated patterns if nearly equant crystal shapes are considered. These results show, however, that the shifts may be in the opposite direction if highly anisotropic crystallite shapes are considered.

In summary, both experimental and calculated XRD profiles show that peak shifts and increased peak breadths are characteristic of fine-grained boehmite. Large peak breadths $\geq 5°2\theta$ and patterns showing no 020 reflection suggest that small boehmite crystals may be composed of only one or a few layers. Non-stoichiometric water (Baker and Pearson, 1974) is also a consequence of small crystallite size. Stacking faults may help explain the XRD peak shapes; however, peak positions and broad peaks are consistent with small crystal size alone.

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