MICROSTRUCTURAL CHARACTERIZATION OF WATER-RICH BOEHMITE (AlO(OH)): TEM CORRELATION OF APPARENTLY DIVERGENT XRD AND TGA RESULTS


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An understanding of the solid-phase thermodynamics and aqueous speciation of aluminum is critical to our ability to understand and predict processes in a wide variety of geologic and industrial settings. Boehmite (AlO(OH)) is an important phase in the system Al₂O₃·H₂O that has been the subject of a number of structural and thermodynamic studies since its initial synthesis [1] and discovery in nature [2]. Unfortunately, it has long been recognized that thermogravimetric analysis (TGA) of both synthetic and natural boehmite samples (that appear well crystallized by powder XRD methods) yields significant excess water - typically losing 16-16.5 wt. % on heating as compared with a nominal expected weight loss of 15.0 wt. % [3,4].

The boehmite used in our experiments was synthesized hydrothermally from acid-washed gibbsite (Al(OH)$_3$) at 200°C. Powder XRD and SEM examination showed no evidence of the presence of a contaminant phase. The TGA patterns do not suggest that this is due to adsorbed water, so a structural source is likely. We therefore undertook to examine this material by TEM to clarify this phenomenon.

Boehmite is orthorhombic (a = 0.0285nm, b = 0.1224nm and c = 0.0365nm, Amam). The crystals were tabular with major surfaces normal to <010>. Simple powder dispersals onto holey carbon films typically resulted in b-axis orientations parallel to the electron beam. To view other orientations, specimens were milled in M-Bond epoxy, pressed between plates of single-crystal Si (aligning the boehmite tablets parallel to the Si plates) while the epoxy cured. Electron transparent thin foils normal to the silicon plates were produced by argon ion milling techniques. Sample stability in the electron beam was dramatically improved by cooling to -140°C using LN$_2$ cold stage.

Figures 1 and 2 are low and high magnification images of a typical area of the synthetic boehmite, clearly showing the presence of a second phase. This phase is plate-like, and essentially layer-parallel with the boehmite. The electron diffraction pattern from Fig. 2 is shown in Fig. 3. The dominant pattern is that of the boehmite. The presence of a second set of weak, diffuse reflections in the diffraction pattern and the observed presence of lattice fringes in some plates indicates that the inclusions are crystalline. The absence of extra peaks in XRD patterns from this specimen is likely explained by the narrow width of the plates, which are individually too small to give rise to significant diffracted intensity in a standard powder pattern. The parallel nature of the inclusions suggests that these may be remnants of original gibbsite crystallites. Accurate measurements from electron diffraction patterns and lattice images were obtained by calibration of the experimental diffraction patterns and lattice images using thin edges of the included silicon crystals. These yielded d-values for the boehmite pattern of 0.6110 and 0.3698nm, equivalent to the (020) and (100) reported interplanar spacings [5] which imply that for this image the beam is parallel to the <002> zone axis.

The weak secondary diffraction pattern in Fig. 3 is clearly aligned with the principal boehmite directions. The diffuse reflections circled give d-values of 0.197 and 0.141nm. These do not fit closely the reported or calculated d-values for gibbsite or other known aluminum hydroxides or oxyhydroxides. However, the alignment suggests that the boundary between the two materials may be coherent or semi-coherent. As the lattice parameters for boehmite do not correspond closely to those of gibbsite (a = 0.8624nm, b = 0.5060nm, c = 1.350nm, b = 45.94°, P21/c), this may indicate that the small gibbsite inclusions experience considerable strain, deforming the lattice. If so, the pattern indicates that the 0.197nm value may be smaller than the unstrained lattice parameter, and the 0.141nm value may be larger.[6]
References

5. N.B.S. (U.S.), Circ 539, 338, 1954; PDF #21-1307

FIG. 1- Thin edge of boehmite crystal showing plate-like inclusions.
FIG. 2- Higher magnification of FIG. 1, showing boehmite lattice and fringes within inclusions.
FIG. 3- $<002>$ boehmite zone axis diffraction pattern from area of inclusions; showing orientation of gibbsite plates.