

SINGLE CRYSTAL RAMAN STUDIES OF SIX-FOLD GIBBSITE TWINS

F. Lee¹, G. Parkinson², M. Reyhani², W. van Bronswijk^{1*} and C. Vernon³

A J Parker Cooperative Research Centre for Hydrometallurgy

¹ Department of Applied Chemistry, Curtin University of Technology, Australia; E-Mail: Felicia.Lee@csiro.au, w.vanbronswijk@curtin.edu.au

² Nanochemistry Research Institute, Curtin University of Technology, Australia; E-Mail: G.Parkinson@curtin.edu.au, M.Reyhani@curtin.edu.au

³ Commonwealth Scientific and Industrial Research Organisation (CSIRO), Australia; E-Mail: Chris.Vernon@csiro.au

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Abstract: This contribution reports on the Raman spectra and polarised light images obtained for hexagonal six-fold twinned and diamond shaped single crystals of synthetic and industrial gibbsite. The results are interpreted in terms of a possible growth mechanism for gibbsite.

The successful precipitation of gibbsite, $\gamma\text{Al}(\text{OH})_3$, is the crucial step in alumina production via the Bayer process. Gaining an understanding of the gibbsite growth mechanism will facilitate the optimisation of the precipitation process, which should lead to increased efficiency and improvements in product quality. Individual crystals of gibbsite generally exhibit a hexagonal plate-like morphology; sometimes a diamond-like morphology is also seen, particularly as secondary nuclei generated at the basal surface [1]. Recently, Sweegers et al. [2] demonstrated that the hexagonal particles that had been assumed to be single crystals could also be multiply twinned. In our work, the use of polarized light microscopy identified six-fold twinning for synthetic and industrial gibbsite in the hexagonal morphology as well as identifying un-twinned crystals in the hexagonal and diamond morphologies (shown in Figure 1).

Single crystal Raman spectroscopy was used to characterise the different gibbsite crystal morphologies and determine the orientation of the crystallographic axes. Un-twinned hexagonal and diamond crystals polarised along the a axis show distinct bands at 3621 and 3526 cm^{-1} . These bands are indicative of intralayer hydroxyl groups that are orientated in the same direction as the a axis in the gibbsite structure [3]. When the polarisation direction is projected along the b axis the band at 3522 cm^{-1} becomes apparent. This band is associated with an intralayer hydroxyl group that is orientated almost parallel to the b axis [3]. By observing the relative intensities of these bands, the crystallographic axes of the two crystal types were determined (Figure 3). Spectra in the 200-1800 cm^{-1} region showed similar effects. Diamond and un-twinned hexagons depicted similar crystal structures suggesting that the two may be linked to a common growth mechanism. Figure 2a shows the possible transformation from diamond to hexagonal morphology via the decreased growth rate of the $\{100\}$ face relative to the $\{110\}$ faces.

Gibbsite hexagons may also form as the result of six-fold twinning. This behaviour is observed in industrial and synthetically produced gibbsite. On analysis of each twin domain using Raman spectroscopy, it was concluded that each twin domain was its own crystal having its own distinct a and b axis but a common c (shown in Figure 2b). Each twin was separated by a twin boundary 5-10 μm thick. Raman spectroscopy showed that this boundary is crystalline having the same crystallographic axes as the centre of the twinned crystal and the first twin domain. This suggests that twinning may have occurred after nucleation, the result of growth from an un-twinned hexagonal nucleus. Six-fold twinned hexagons are more common than un-twinned hexagons suggesting it is more energetically favourable to form a six-fold twin than for the hexagon to continue growth as a single crystal.

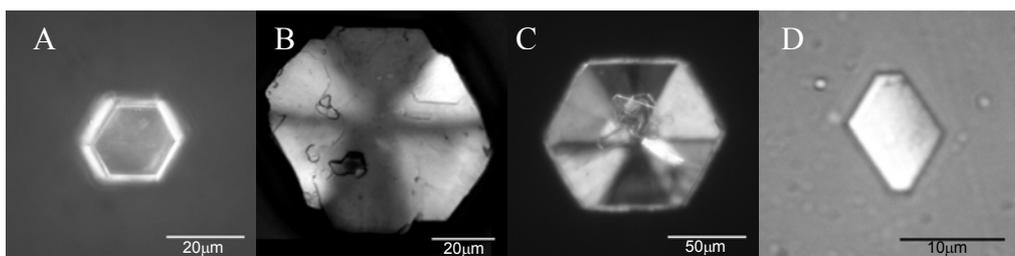


Fig. 1. Polarized light micrographs of gibbsite.
 A: Synthetic singularly twinned hexagon
 B: Industrial six-fold twinned hexagon
 C: Synthetic six-fold twinned hexagon
 D: Synthetic diamond

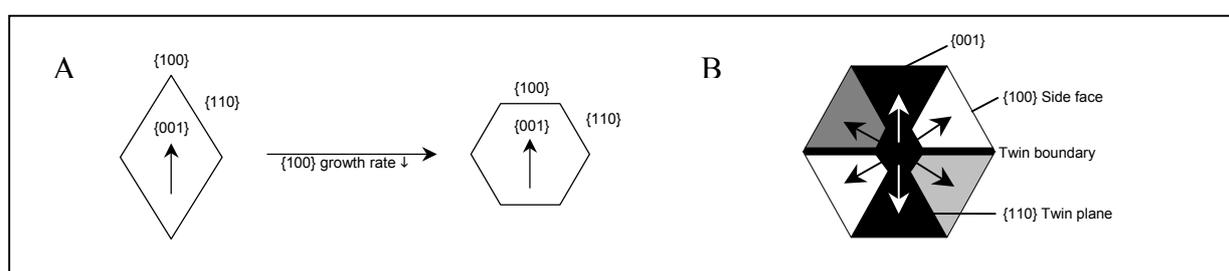


Fig. 2. Schematic showing the two hexagonal morphologies of gibbsite.
 A: Diamond to hexagonal transformation.
 B: Twinned hexagonal morphology showing the six twin domains and boundaries
 Arrows indicate the direction of the a-axis. Crystal faces have been indexed.

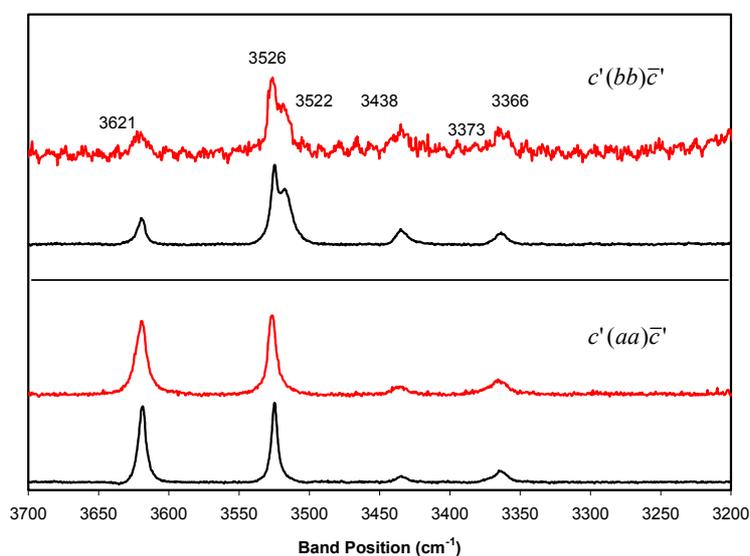


Fig. 3. Single-crystal Raman spectra comparing hexagonal (black) and diamond (red) gibbsite morphologies at different polarization directions.

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