Crystal structures of the minerals stichtite and woodallite using Rietveld refinement

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Stichtite [$Mg_6Cr_2(OH)_{16}CO_3.4H_2O$] and woodallite [$Mg_6Cr_2(OH)_{16}Cl_2.4H_2O$] are both chromium-containing minerals with R-3m layered hydrotalcite-type structures. Single-crystal diffraction studies have not been possible to date as no sufficiently large crystals have been found. Powder diffraction patterns for both of these minerals have been described in the literature but no attempt has been made to study the details of the crystal structures using Rietveld refinement techniques.

The samples were small quantities of natural minerals. The small quantity and tendency to orient indicated capillary geometry as the most suitable. A pseudo-variable count method for data collection was used where the counting time was increased at higher angles. Weighting was also used during the refinement to further access the structural detail present in the higher order reflections. Analysis of the data was done using TOPAS version 4.1.

Pawley unit cell refinement showed that both materials exhibit anisotropic peak broadening, especially noticeable in the woodallite. The *hkl*-dependent behaviour allowed this broadening to be assigned to {0001} twinning rather than stacking faults. A reciprocal-space relationship developed for work on lithium battery materials was successfully used to empirically model the broadening during the structure refinement.

The structure of woodallite was expected to be the same as its iron-containing analogue iowaite, but problematic refined compositions and the lack of a suitable carbonate site lead to the examination of other possibilities. The anion site for woodallite was moved from the 18h to the 18g site, which affects the diffraction pattern very little but surrounds a 3-fold site suitable for the carbonate. Hydrotalcites have mixed and partially occupied sites, so some form of constraint must be used to produce meaningful results. Stichtite has a well-defined composition, so a charge-balancing constraint could be used successfully. The composition of woodallite is less reliable, but fixing the carbonate content to that described in the type-paper with the alternative anion site yielded a refinement with a good fit and refined composition consistent with that expected.