Oriented decomposition and reconstruction of hydrogarnet, 
Ca₃·Al₂·(OH)₁₂

Herrn Prof. Dr. E. Wölfel zum 70. Geburtstag gewidmet

LOTHAR SCHRÖPFER and HANS BARTL

Institut für Kristallographie und Mineralogie, Senckenberganlage 30, D-60325 Frankfurt/M., F.R.G.

Abstract: Dehydration and rehydration experiments were carried out using synthetic single crystals of tricalcium-aluminate-hexahydrate and dodecalcium-heptaaluminate; the structure and orientation of the run products were investigated by X-ray diffraction and thermoanalytical methods (TG, DTG and DSC). A new Al-rich intermediate hydrogarnetoid phase with Al in both six-fold and four-fold coordination was discovered and then prepared by topotactic hydroxylation of the Ca-aluminate

12CaO·7Al₂O₃·15H₂O, space group no. 230, Ia₃d, a₀ = 12.374(6) Å, Z = 2.

Key-words: hydrogarnet, calcium-aluminates, calcium-aluminate-hydrates, dehydration, oriented decomposition.

1 Introduction

Büssem & Eitel (1936) suggested an "interesting relationship" between the garnet phase 3CaO·Al₂O₃·6H₂O (briefly C₃A₆H₆)¹ and its dehydration product 12CaO·7Al₂O₃ (C₁₂A₇), which is independent of the contrasting stoichiometry of the two compounds. The proposed structure of C₁₂A₇ was explicitly confirmed by Bartl & Scheller (1970). Although there are no AlO₆-octahedra present in C₁₂A₇, as in garnets, Büssem & Eitel have described the aluminate structure as "garnet-like". C₃A₆H₆ has the lattice constant a₀ = 12.576 Å, with a space group of Ia₃d-O₁₀; the corresponding data for C₁₂A₇ are 11.98 Å and I₄₃d-T₃₀, respectively. Earlier investigations (Kuzel, 1969; Bartl, 1969) have merely indicated that the hydrate and its dehydration product show collinear intergrowths. In this context, it is appropriate to investigate the structural basis for the oriented decomposition C₃A₆H₆ → C₁₂A₇.

Following Kuzel's (1969) recommendation, C₃A₆H₆ single crystals were synthesized by reacting Ca(OH)₂ with excess water on Al-foil in an autoclave at 170 °C. The crystals thus obtained were clear colourless dodecahedra, with the largest ones about 0.4 mm in diameter.

In order to investigate the orientation relations of specimens before and after the reactions, samples were examined by X-ray photographic methods (mainly precession and occasionally Laue techniques). To improve intensities, the precession films were usually exposed to unfiltered Mo radiation. When high resolution was required, CuKα₁ radiation was used from a rotating anode generator, in conjunction with a focusing quartz monochromator.

The crystals were always aligned parallel to [011]; they were mounted on quartz rods by high-temperature cement and enclosed in evacuated quartz capillary tubes. This sample preparation technique made the dehydration process about four times slower than in free air. Kuzel (1969) heated the crystals only in an open atmosphere.

¹ Following the notation used in cement chemistry, C stands for CaO, A for Al₂O₃, H for H₂O.