

## Investigations on alunogen under Mars-relevant temperature conditions: An example for a single-crystal-to-single-crystal phase transition

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### ABSTRACT

The low-temperature (LT) dependent behavior of a synthetic alunogen sample with composition  $\text{Al}_2(\text{SO}_4)_3 \cdot 16.61\text{H}_2\text{O}$  has been studied in the overall temperature range from  $-100$  to  $23$  °C by DSC measurements, in situ powder and single-crystal X-ray diffraction as well as Raman spectroscopy. Cooling/heating experiments using the different techniques prove that alunogen undergoes a reversible, sluggish phase transition somewhere between  $-30$  and  $-50$  °C from the triclinic room-temperature (RT) form to a previously unknown LT-polymorph. A significant hysteresis for the transition was observed with all three methods and the transition temperatures were found to depend on the employed cooling/heating rates. The crystal structure of the LT-modification has been studied at  $-100$  °C using single crystals, which have been grown from an aqueous solution. Basic crystallographic data are as follows: monoclinic symmetry, space group type  $P2_1$ ,  $a = 7.4125(3)$ ,  $b = 26.8337(16)$ ,  $c = 6.0775(3)$  Å,  $\beta = 97.312(4)^\circ$ ,  $V = 1199.01(10)$  Å<sup>3</sup>, and  $Z = 2$ . Structure analysis revealed that LT-alunogen corresponds to a non-stoichiometric hydrate with 16.61 water moieties pfu. Notably, the first-order transition results in a single-crystal-to-single-crystal transformation. In the asymmetric unit there are 2 Al-atoms, 3 [SO<sub>4</sub>]-tetrahedra, and 17 crystallographically independent sites for water molecules, whose hydrogen positions could be all located by difference-Fourier calculations. According to site-population refinements only one water position (Ow5) shows a partial occupancy. A comfortable way to rationalize the crystal structure of the LT-modification of alunogen is based on a subdivision of the whole structure into two different slabs parallel to (010). The first type of slab (type A) is about 9 Å thick and located at  $y \approx 0$  and  $y \approx \frac{1}{2}$ , respectively. It contains the  $\text{Al}(\text{H}_2\text{O})_6$ -octahedra as well as the sulfate groups centered by S1 and S2. Type B at  $y \approx \frac{1}{4}$  and  $y \approx \frac{3}{4}$  comprises the remaining tetrahedra about S3 and a total of five additional “zeolitic” water sites (Ow1–Ow5), which are not a part of a coordination polyhedron. Within slab-type A alternating chains of (unconnected) octahedra and tetrahedra can be identified, which are running parallel to [100]. In addition to electrostatic interactions between the  $\text{Al}(\text{H}_2\text{O})_6^{3+}$ - and the  $(\text{SO}_4)^{2-}$ -units, hydrogen bonds are also essential for the stability of these slabs. A detailed comparison between both modifications including a derivation from a hypothetical aristotype based on group-theoretical concepts is presented. Since alunogen has been postulated to occur in martian soils the new findings may help in the identification of the LT-form by X-ray diffraction using the Curiosity Rover’s ChemMin instrument or by Raman spectroscopy.

**Keywords:** Alunogen, low-temperature phase transition, polymorphism, crystal-structure determination, DSC-measurements, X-ray diffraction, Raman spectroscopy, multivariate data analysis, group theory