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 Al2(SO4)3·16.61H2O 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 P21, a = 7.4125(3), b = 26.8337(16), c = 6.0775(3) Å, β = 97.312(4)°, V = 1199.01(10) Å3, 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 [SO4]-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 = 0 and y = ½, respectively. It contains the Al(H2O)6-octahedra as well as the sulfate groups centered by S1 and S2. Type B at y = ¼ and y = ¾ 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 Al(H2O)6+- and the (SO4)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

INTRODUCTION

Most of the naturally occurring hydrous aluminum sulfates are basic hydrates containing water molecules and hydroxyl groups. Examples include the minerals aluninite [Al2(SO4)(OH)3·7H2O], meta-aluninite [Al2(SO4)(OH)5·5H2O], jurbanite [Al2(SO4)(OH)5·3H2O], and rostite [Al2(SO4)(OH)3·3H2O], just to mention a few. One of the rare OH-free compounds is alunogen. Usually, alunogen is chemically described as a heptadeca-hydrate corresponding to the formula Al2(SO4)3·17H2O. Notably, the exact water content of alunogen has been a matter of debate for quite a long time and various compositions between 16 and 18 water molecules per formula unit (pfu) have been reported (Larsen and Steiger 1928; Palache et al. 1951; Bayliss 1964; Barret and Thiard 1965; Náray-Szabó 1969; Menchetti and Sabelli 1974; Fang and Robinson 1976; Chou and Soong 1984; Čiğli and Cetbişli 2009; Bai et al. 2011; Wang and Zhou 2014). This variability is a direct consequence of the fact that alunogen crystals, which are exposed to air of low relative humidity at room temperature easily start to dehydrate partially, i.e., alunogen can be considered a non-stoichiometric hydrate (Fang and Robinson 1976). In addition to uncertainties concerning the precise amount of water present in alunogen using starting materials from different sources, there are also...