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LETTER

Hydrothermal synthesis and crystal structure of $AlSO_4(OH)$: A titanite-group member

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ABSTRACT

Aluminum hydroxysulfate, $AlSO_4(OH)$, is postulated to play a vital role in controlling the solubility of aluminum in sulfate-rich acidic soils and ground waters, but it has not yet been confirmed in nature. This study reports the synthesis of an $AlSO_4(OH)$ crystal at 700 °C and ~1.0 GPa in a hydrothermal diamond-anvil cell from a mixture of 95% H_2SO_4 and Al_2O_3 powder and its structure determination from single-crystal X-ray diffraction data. $AlSO_4(OH)$ is monoclinic with space group $C2/c$ and unit-cell parameters a = 7.1110(4), b = 7.0311(5), c = 7.0088(4) Å, β = 119.281(2)°, and V = 305.65(3) Å^3. Its crystal structure is characterized by kinked chains of corner-sharing AlO_6 octahedra that run parallel to the c-axis. These chains are linked together by SO_4 tetrahedra and hydrogen bonds, forming an octahedral-tetrahedral framework. Except for the numbers and positions of H atoms, $AlSO_4(OH)$ is isostructural with the kieserite-type minerals, a subgroup of the titanite group of minerals. A comparison of powder X-ray diffraction patterns indicates that our $AlSO_4(OH)$ is the same as that obtained by Shanks et al. (1981) through hydrolysis of $Al_2(SO_4)_3$ solutions at temperatures above 310 °C. To date, $AlSO_4(OH)$ has been synthesized only at temperatures above 290 °C, implying that it may not stable in low-temperature environments, such as acidic soils and mine waters. The possible environments to find $Al(OH)SO_4$ may include places where sulfur-rich magma-derived fluids react with aluminous rocks under elevated temperature and pressure, and on Venus where a sulfur-rich atmosphere interacts with surface rocks at temperatures above 400 °C.

Keywords: $AlSO_4(OH)$, aluminum hydroxysulfate, X-ray diffraction, crystal structure, Raman spectroscopy, high temperature