

LETTER

**Hydrothermal synthesis and crystal structure of  $\text{AlSO}_4(\text{OH})$ : A titanite-group member**

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**ABSTRACT**

Aluminum hydroxysulfate,  $\text{AlSO}_4(\text{OH})$ , 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  $\text{AlSO}_4(\text{OH})$  crystal at 700 °C and ~1.0 GPa in a hydrothermal diamond-anvil cell from a mixture of 95%  $\text{H}_2\text{SO}_4$  and  $\text{Al}_2\text{O}_3$  powder and its structure determination from single-crystal X-ray diffraction data.  $\text{AlSO}_4(\text{OH})$  is monoclinic with space group  $C2/c$  and unit-cell parameters  $a = 7.1110(4)$ ,  $b = 7.0311(5)$ ,  $c = 7.0088(4)$  Å,  $\beta = 119.281(2)^\circ$ , and  $V = 305.65(3)$  Å<sup>3</sup>. Its crystal structure is characterized by kinked chains of corner-sharing  $\text{AlO}_6$  octahedra that run parallel to the  $c$ -axis. These chains are linked together by  $\text{SO}_4$  tetrahedra and hydrogen bonds, forming an octahedral-tetrahedral framework. Except for the numbers and positions of H atoms,  $\text{AlSO}_4(\text{OH})$  is isostructural with the kieselite-type minerals, a subgroup of the titanite group of minerals. A comparison of powder X-ray diffraction patterns indicates that our  $\text{AlSO}_4(\text{OH})$  is the same as that obtained by Shanks et al. (1981) through hydrolysis of  $\text{Al}_2(\text{SO}_4)_3$  solutions at temperatures above 310 °C. To date,  $\text{AlSO}_4(\text{OH})$  has been synthesized only at temperatures above 290 °C, implying that it may not be stable in low-temperature environments, such as acidic soils and mine waters. The possible environments to find  $\text{Al}(\text{OH})\text{SO}_4$  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:**  $\text{AlSO}_4(\text{OH})$ , aluminum hydroxysulfate, X-ray diffraction, crystal structure, Raman spectroscopy, high temperature