

LETTER

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

ALAN J. ANDERSON,¹ HEXIONG YANG^{2,*} AND ROBERT T. DOWNS²

¹Department of Earth Sciences, St. Francis Xavier University, Antigonish, Nova Scotia B2G 2W5, Canada

²Department of Geosciences, University of Arizona, Tucson, Arizona 85721-0077, U.S.A.

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% H_2SO_4 and Al_2O_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, $\beta = 119.281(2)$ °, and $V = 305.65(3)$ Å³. 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, $\text{AlSO}_4(\text{OH})$ 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 $\text{AlSO}_4(\text{OH})$ 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 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