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In situ dehydration behavior of veszelyite $(Cu,Zn)_2Zn(PO_4)(OH)_3{\cdot}2H_2O$: A single-crystal X-ray study

ROSA MICAELA DANISI,[1,*] THOMAS ARMBRUSTER,[1] BILJANA LAZIC,[1] PREDRAG VULIĆ,[2]
REINHARD KAINDL,[3,4] RADOVAN DIMITRIJEVIĆ,[2] AND VOLKER KAHLENBERG[4]

[1]Mineralogical Crystallography, Institute of Geological Sciences, University of Bern, Freiestrasse 3, 3012 Bern, Switzerland
[2]Laboratory of Crystallography, Faculty of Mining and Geology, University of Belgrade, Djusina 7, 11000 Belgrade, Serbia
[3]MATERIALS—Institute for Surface Technologies and Photonics, Joanneum Research, Leobner Strasse 94, 8712 Niklasdorf, Austria
[4]Institute of Mineralogy and Petrography, University of Innsbruck, Innrain 52f, 6020 Innsbruck, Austria

ABSTRACT

The rare mixed copper-zinc phosphate mineral veszelyite $(Cu,Zn)_2Zn(PO_4)(OH)_3{\cdot}2H_2O$ [space group $P2_1/c$, a = 7.5096(2), b = 10.2281(2), c = 9.8258(2) Å, β = 103.3040(10)°, V = 734.45(3) Å^3] was investigated by in situ temperature-dependent single-crystal X-ray structure refinements. The atomic arrangement of veszelyite consists of an alternation of octahedral and tetrahedral sheets. The Jahn-Teller distorted CuO_6 octahedra form sheets with eight-membered rings. The tetrahedral sheet composed of PO_4 and $ZnO_3(OH)$ tetrahedra shows strong topological similarities to that of cavansite, gismondine, and kipushite.

Diffraction data of a sample from Zdravo Vrelo, near Kreševo (Bosnia and Herzegovina) have been measured in steps of 25 up to 225 °C. Hydrogen positions and the hydrogen-bond system were determined experimentally from the structure refinements of data collected up to 125 °C. At 200 °C, the hydrogen-bonding scheme was inferred from bond-valence calculations and donor-acceptor distances. The hydrogen-bond system connects the tetrahedral sheet to the octahedral sheet and also braces the Cu sheet.

At 150 °C, the H_2O molecule at H_2O2 was released and the Cu coordination (Cu1 and Cu2) decreased from originally six- to fivefold. Cu1 has a square planar coordination by four OH groups and an elongate distance to O3, whereas Cu2 has the Jahn-Teller characteristic elongate bond to H_2O1. The unit-cell volume decreased 7% from originally 734.45(3) to 686.4(4) Å^3 leading to a formula with 1 H_2O pfu. The new phase observed above 150 °C is characterized by an increase of the **c** axis and a shortening of the **b** axis. The bending of T-O-T angles causes an increasing elliptical shape of the eight-membered rings in the tetrahedral and octahedral sheets. Moreover a rearrangement of the hydrogen-bond system was observed.

At 225 °C, the structure degrades to an X-ray amorphous residual due to release of the last H_2O molecule at H_2O1. The stronger Jahn-Teller distortion of Cu1 relative to Cu2 suggests that Cu1 is fully occupied by Cu, whereas Cu2 bears significant Zn. H_2O1 is the fifth ligand of Cu2. Zn at Cu2 is not favorable to adopt planar fourfold coordination. Thus, if the last water molecule is expelled the structure is destabilized.

This study contributes to understanding the dehydration mechanism and thermal stability of supergene minerals characterized by Jahn-Teller distorted octahedra with mixed Cu, Zn occupancy.

Keywords: Veszelyite, Jahn-Teller effect, dehydration, crystal structure, hydrogen bonding