Experimental report

20/05/2016

Proposal: 5-11-407 **Council:** 10/2014

Title: H-bonding network in allactite, Mn7(AsO4)2(OH)8

Research area: Other...

This proposal is a new proposal

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Samples: Mn7(AsO4)2(OH)8

Instrument	Requested days	Allocated days	From	To
D19	5	0		
D9	15	14	18/06/2015	02/07/2015

Abstract:

The aim of the present study is a reinvestigation of the crystal structure of allactite, Mn7(AsO4)2(OH)8, at 20 K by single-crystal neutron diffraction, in order to provide: a) an unambiguous location of all the proton sites and the description of the complex H-bonding network expected in allactite structure; b) the anisotropic displacement parameters of all the atomic sites, including the H-sites. The vibrational regime of protons is significant at room-T in this class of materials, and so low-T data are needed for a better localization of protons. As X-ray diffraction data have proven to be inadequate to locate directly the H atoms in allactite structure, single-crystal neutron diffraction represents the best experimental technique to answer the open questions about the crystal structure/crystal chemistry of this hydrous Mn-arsenate.

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H-bonding network in allactite, $Mn_7(AsO_4)_2(OH)_8$

by G. Diego Gatta

The crystal chemistry of allactite from Långban, Värmland (Sweden) was investigated by single-crystal X-ray and neutron diffraction, optical absorption spectroscopy, Fourier-transform infra-red spectroscopy (FTIR) and electron microprobe analysis by wavelength dispersive spectroscopy (EPMA-WDS). The optical spectra show indications for the presence of Mn in the valence state 2+ only. Assuming 16 O atoms per formula unit, arsenic as As^{5+} and the (OH) content calculated by charge balance, the resulting unit formula based on the EPMA-WDS data is $(Mn^{2+}_{6.73}Ca_{0.13}Mg_{0.12}Zn_{0.02})_{\Sigma 7.00}(As^{5+})_{2.00}O_{16}H_8$, very close to the ideal composition $Mn_7(AsO_4)_2(OH)_8$. In the unpolarised FTIR-spectrum of allactite, fundamental (OH)-stretching bands are observed at 3236, 3288, 3387, 3446, 3484, 3562 and 3570 cm^{-1}, suggesting that a number of (OH) environments, with different hydrogen bond strengths, occur in the structure.

A millimetric prismatic crystal of allactite (3.8 x 3.2 x 2.8 mm), free of defects under the polarised optical microscope, was selected for the neutron diffraction experiments. Neutron-diffraction data were measured at 293 K and at 100 K on the four-circle diffractometer D9, with a neutron beam of wavelength 0.8370(2) Å, obtained by reflection from a Cu(220) monochromator. Diffraction data were collected up θ_{max} of 34.6° and 32.6° at 293 K and 100 K, respectively. For all data, background corrections following Wilkinson et al. (1988) and Lorentz corrections were applied. Absorption corrections were made by Gaussian integration (Coppens et al., 1965), using the calculated attenuation coefficient with account taken of the wavelength dependence of the absorption for the hydrogen content (Howard et al., 1987). Initial structural refinements showed that extinction affected only a few reflections, and could be well accounted for by the simple isotropic extinction model in SHELX-97 (Sheldrick, 2008). The low degree of extinction meant that the data for could be averaged over symmetry-equivalent reflections. Averaging in the 2/m Laue class of the 2222 (at 293 K) and 2063 (at 100 K) reflections scanned gave 1561 (at 293 K) and 1278 (at 100 K) unique reflections with an internal discrepancy index of 0.0403 (at 293 K) and 0.0255 (at 100 K). Since the three-dimensional count distribution around each reflection was observed, the centroids of all scanned reflections could be found. Least-squares matching of the observed and calculated centroids of a few hundreds of strongest reflections for the collections at 293 K and at 100 K gave the following lattice constants: a = 5.482(1) Å, b = 12.153(2) Å, c = 10.014(2) Å and β = 95.55(1)° at 293 K, a = 5.4786(8) Å, b = 12.156(2) Å, c = 10.008(1) Å and β = 95.574(8)° at 100 K. The reflection conditions suggested the space group $P2_1/n$.

The neutron structure refinement shows that four independent H sites occur in allactite with full site occupancy, all as members of hydroxyl groups. The complex hydrogen bonding scheme in the allactite structure is now well defined, with at least nine hydrogen bonds energetically favorable with mono-, bi- and tri-furcated configurations (Fig. 1).

A manuscript, with the experimental findings of this study, is in press:

Gatta G.D., Bosi F. Fernandez Diaz M.T. Halenius U. (2016) H-bonding scheme in allactite: A combined single-crystal neutron/X-ray diffraction, EPMA-WDS, FTIR and OAS study. *Mineralogical Magazine.*

Figure 1: The complex H-bonding network in allactite, based on the neutron structure refinement of this study.