Experimental report

16/04/2019

Proposal: **5-11-430** **Council:** 4/2018

Title: On the crystal chemistry of the wardite, $NaAl_3(PO_4)_2(OH)_4 \times 2H_2O$

Research area: Other...

This proposal is a new proposal

Main proposer: **Giacomo Diego GATTA**

Experimental team:

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Samples: $NaAl_3(PO_4)_2(OH)_4 \times 2H_2O$

Instrument	Requested days	Allocated days	From	To
D19	4	2	24/05/2018	28/05/2018
D9	8	0		

Abstract:

Wardite, ideally $NaAl_3(PO_4)_2(OH)_4 \times 2H_2O$, is a hydrothermal mineral, which occurs in phosphate-rich zones of granite pegmatites. Its crystal structure was solved and refined by Fanfani et al. (1970). To the best of our knowledge, no more recent data are available in the open literature. The structure contain a total amount of 18 wt% of H_2O. The quality of the data at that time (by Wissenberg method with multiple-film integrated photographs) did not allow to locate unambiguously the H sites, leaving open questions about the configuration of the H_2O molecules and OH-groups and, as a consequence, about the H-bonding scheme in wardite structure, which is completely unknown. The aim of this study is to provide a single-crystal neutron structure refinement of wardite based on modern standards and with a general improvement of the whole structure model. More specifically, we expect to provide: a) the reliable location of the proton sites and the real topological configuration of the OH-groups and H_2O molecules, for a full description of the atomic relationship via the H-bonds; b) the anisotropic displacement parameters of all the atomic sites, H-sites included.

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Chemical composition of the wardite used in this study was obtained using a CAMECA SX-50 electron microprobe equipped with four wavelength-dispersive spectrometers and one energy-dispersive spectrometer. The operating conditions were 20 kV accelerating voltage, 5 nA beam current and 10 µm beam diameter. Counting times were 10 s at the peak and 5 s at the background for major elements, and 20 to 100 s at peak and background for minor elements. X-ray counts were converted into oxide weight percentages using the PAP correction program (Pouchou and Pichoir 1991). Calibration was performed using natural and synthetic international standards, in part supplied by Cameca and in part kindly provided by the Smithsonian National Museum of Natural History (Smithsonian Microbeam Standards). The following reference materials, lines, and analysing crystals were used: wollastonite (Si*K*α-TAP); diopside (Ca*K*α-PET); albite (Na*K*α-TAP); fluorapatite (P*K*α-TAP); corundum (Al*K*α-TAP); $MnTiO_3$ (Ti*K*α-PET); FeO (Fe*K*α-LIF); $MnTiO_3$ (Mn*K*α-LIF); orthoclase (K*K*α-PET); AsGa (As*L*α, TAP). The elements K and As (and even F) were sought but resulted below the experimental detection limits (*i.e.*, less than 0.03 wt%). Minor evidence of sample dehydration, under the electron beam, were observed. The empirical formula of the sample used in this study is: $(Na_{0.91}Ca_{0.01})_{\Sigma=0.92}(Al_{2.97}Fe^{3+}_{0.05}Ti_{0.01})_{\Sigma=3.03}(P_{2.10}O_8)(OH)_4\cdot 1.74H_2O$.

Neutron diffraction data were collected on the four-circle diffractometer D19 with Cu(331)-monochromated radiation (take-off angle $2\vartheta_M = 70°$), providing neutrons with a wavelength of 0.9460 Å. The sample was glued on a ϕ = 0.5 mm vanadium pin and placed on a close-circuit displex device operated at 20.0(5) K (Archer and Lehmann 1986). The measurement strategy consists of omega (ω) scans of 64 or 79° with steps of 0.07° at different χ and φ positions. A total of 25 ω-scans were collected to complete almost half-Ewald sphere. The Multi-Detector Acquisition Data Software (MAD) from ILL was used for data collection. The unit-cell determination was done by using PFIND and DIRAX programs (Duisenberg 1992). The integration of the raw data and refinement of the UB-matrix, including the off-sets, were done using RETREAT and RAFD19 programs, respectively (Wilkinson et al. 1988). The lattice was found to be metrically tetragonal, and the reflections conditions agreed with the space group $P4_12_12$, as previously reported by Fanfani et al. (1970). A total of 20478 reflections were integrated, out of which 3109 were unique reflections (Laue group 4/*mmm*, R_{int} = 0.0411). The absorption correction, mainly due to the hydrogen content of the sample (*ca*. 0.132 mm^{-1}), was carried out using D19abs program (Matthewman et al. 1982). Further details pertaining to the data collection strategy are listed in Table 2 and in Gatta et al. (2018a).

Anisotropic crystal-structure refinement based on the neutron intensity data was done in the space group $P4_12_12$ using the SHELXL-2014 software (Sheldrick 2008, 2014), starting from the structure model of Fanfani et al. (1970), without any H atom. The neutron scattering lengths of Na, Al, Fe, P, O and H were taken from Sears (1986). Secondary isotropic extinction effect was corrected according to the formalism of Larson (1967), as implemented in the SHELXL package. Convergence was rapidly reached after the first cycles of refinement with a series of intense negative residual peaks in the final difference-Fourier map of the nuclear density. Minima in the difference-Fourier maps of the nuclear density showed no evidence of positional or dynamic disorder. Further cycles of refinement were done with H sites assigned to these peaks (as H has a negative neutron scattering length). At the end of the refinement (with $R_1(F)$ = 0.0219 for 3106 reflections with $F_O > 4\sigma(F_O)$ and 129 refined parameters), all variable parameters converged with all the principal mean-square atomic displacement parameters positive, including those for the H sites. The variance-covariance matrix showed no significant correlation among the refined variables.

The neutron diffraction data confirm that the crystal structure wardite can be described with a tetragonal symmetry and consists of sheets made by edge-sharing Na-polyhedra and Al-octahedra along with vertex-sharing Al-octahedra, parallel to (001), connected by P-tetrahedra and H-bonds to form a (001) layer-type structure, which well explains the pronounced {001} cleavage of the wardite crystals. The present data show that four crystallographically independent H sites occur into the structure of wardite, two belonging to a H_2O molecule (*i.e.*, H1-O6-H2) and two forming hydroxyl groups (*i.e.*, O5-H3 and O7-H4). The location of the hydrogen atoms allows us to define the extensive network of H-bonds: the H-atoms belonging to the H_2O molecule form strong H-bonds, whereas both the H-atoms belonging to the two independent hydroxyl groups form weak interactions with bifurcated bonding schemes. As shown by the root-mean-square components of the displacement ellipsoids, oxygen and hydrogen atoms have slightly larger anisotropic displacement parameters if compared to the other sites (populated by P, Al and Na). The maximum ratio of the *max* and *min* root-mean-square components of the displacement ellipsoids is observed for the protons of the hydroxyl groups, which experience bifurcated H-bonding schemes.

References:

Gatta GD, Fabelo Rosa OR, Fernandez-Diaz MT (2018) On the crystal chemistry of the wardite, $NaAl_3(PO_4)_2(OH)_4 \times 2H_2O$. Institut Laue-Langevin (ILL, Grenoble). https ://doi.org/10.5291/ ILL-DATA.5-11-430.

Gatta G.D., Guastoni A., Fabelo O., Fernandez-Diaz M.T. (2019) A single-crystal neutron diffraction study of wardite, $NaAl_3(PO_4)_2(OH)_4{\cdot}2H_2O$. *Phys. Chem. Minerals*, 46, 427-435.