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A Rietveld refinement using neutron powder diffraction data of a fully deuterated topaz, $Al_2SiO_4(OD)_2$

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The structure of topaz-OD, dialuminium orthosilicate dihydroxide, $Al_2SiO_4(OD)_2$, was refined in the space group *Pbnm* by Rietveld analysis of constant wavelength neutron powder diffraction data. Two non-equivalent half-occupied deuterium positions were located. Each D atom is characterized by an irregular trifurcated hydrogen-bond geometry. The refined hydrogen-bond distances are in the ranges 2.038 (5)–2.281 (6) and 2.280 (5)–2.524 (6) Å for the two D atoms. Hydrogen-bond angles range from 83.6 (4) to 151.9 (4)°. Results indicate that it is feasible to characterize the hydrogen bonding in small-volume samples (25 mg) synthesized at high pressure and temperature.

Key indicators

Powder neutron study
T = 295 K
Mean σ(Al–O) = 0.003 Å
Disorder in main residue
R factor = 0.037
wR factor = 0.046
Data-to-parameter ratio = 106.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

This study was undertaken in order to provide more reliable information on the hydrogen-bonding geometry in a fully deuterated topaz (topaz-OD) and determine the feasibility of characterizing the hydrogen bonding in small-volume samples (Chen *et al.*, 2004). A previous X-ray single-crystal refinement showed that H atoms are located in two non-equivalent half-occupied sites, leading to the reduction of symmetry from *Pbnm* to $Pbn2_1$, at least locally (Northrup *et al.*, 1994). However, owing to the weak X-ray scattering power of hydrogen, the H-atom positions could not be determined with a high degree of accuracy. Neutron diffraction, on the other hand, is well suited to this investigation because of the large neutron scattering length of deuterium.

Topaz-OD is an orthosilicate consisting of chains of AlO_6 octahedra linked by silicate tetrahedra. D atoms reside in a cavity, lying in the (010) plane, and are disordered over four sites, which occur in pairs related by mirror symmetry (Fig. 2). The trifurcated hydrogen-bond geometry differs slightly from the previously reported arrangement (Northrup *et al.*, 1994.). D1 is hydrogen bonded to atoms O3, O2 and O4, whereas D2 is bonded to atoms O4, O1 and O2$(-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2})$ (Fig. 3), in contrast to the X-ray data with hydrogen bonds to atoms O4, O1 and O2$(-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2})$ [see Fig. 2 of the original paper by Northrup *et al.* (1994); note also that the H1$\cdots$O3 hydrogen bond is incorrectly represented in the original Fig. 2]. The weaker hydrogen bonds are associated with D2, resulting in shorter O—D2 bond length. The refined hydrogen-bond distances are in excellent agreement with the theoretical calculation and our experimental IR spectra (Churakov & Wunder, 2004; Lager *et al.*, 2005).

Experimental

A polycrystalline sample (25 mg) of topaz-OD was prepared from SiO_2, γ-Al_2O_3 and D_2O at 1023 K, 7.5 GPa, for 21 h using a rocking multi-anvil press.

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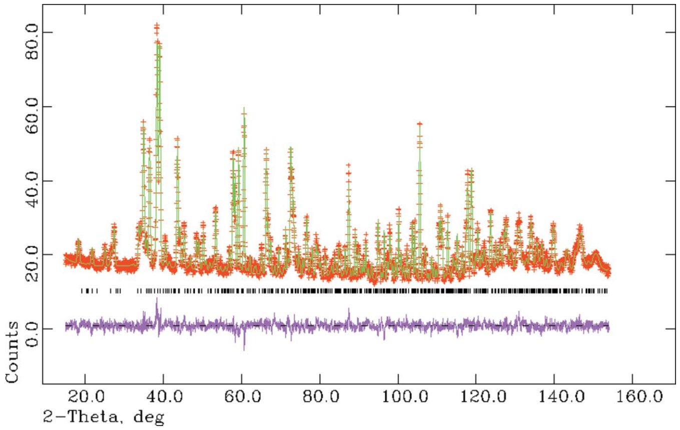

Figure 1
Observed, calculated and difference neutron powder diffraction profiles for topaz-OD. Tick marks below the profile indicate the allowed Bragg reflections.

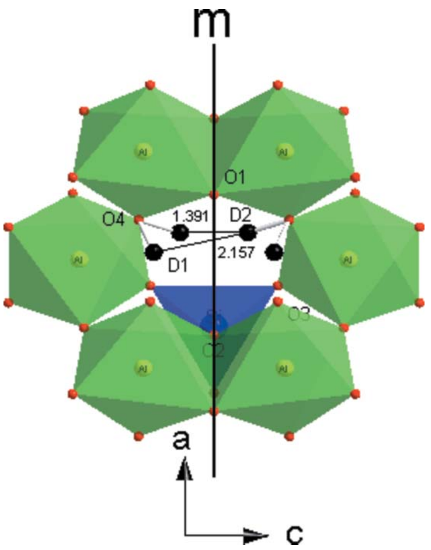

Figure 2
(010) projection of the topaz-OD structure showing the two half-occupied D-atom positions related by mirror symmetry (space group *Pbnm*). Interatomic distances for D1···D2 (1.391 Å) and D2···D2 (2.157 Å) are indicated in the diagram.

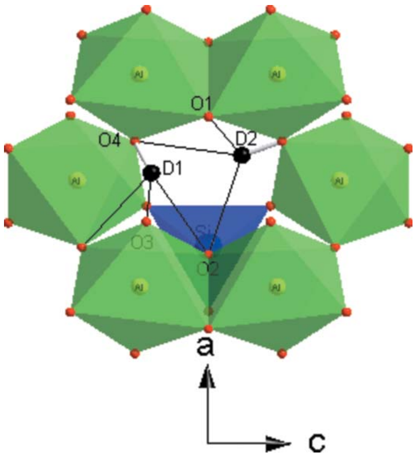

Figure 3
(010) projection of the topaz-OD structure, showing the trifurcated hydrogen-bond arrangement.

Crystal data

$Al_2SiO_4(OD)_2$
M_r = 182.07
Orthorhombic, *Pbnm*
a = 4.7282 (1) Å
b = 8.9320 (2) Å
c = 8.4309 (2) Å
V = 356.06 (1) Å^3
Z = 4
D_x = 3.396 Mg m^{-3}
Neutron radiation
Wavelength of incident radiation: 1.37404 Å
T = 295 K
White
Specimen shape: cylinder
4 × 4 × 4 mm
Particle morphology: equi-dimensional 10 µm crystals

Data collection

PSD powder diffractometer D20, at ILL
Specimen mounting: loose powder in can
Specimen mounted in reflection mode
$2\theta_{min}$ = 5.0231, $2\theta_{max}$ = 154.0119°
Increment in 2θ = 0.025°

Refinement

R_p = 0.0368
R_{wp} = 0.0464
R_{exp} = 0.0353
S = 1.32
$2\theta_{min}$ = 15.0175, $2\theta_{max}$ = 154.0119°
Excluded region(s): <15.0°/2θ
CW profile function number 2 with 18 terms; profile coefficients for Simpson's rule integration of pseudo-Voigt function (Howard, 1982; Thompson *et al.*, 1987).
5560 reflections
52 parameters
$(\Delta/\sigma)_{max}$ = 0.01
Preferred orientation correction: none

Table 1
Selected geometric parameters (Å, °).

Al—O1	1.974 (3)	Si—O1^{v}	1.631 (4)
Al—O2^{i}	1.951 (3)	Si—O2	1.666 (4)
Al—O3^{ii}	1.918 (3)	Si—O3	1.656 (3)
Al—O3^{iii}	1.917 (3)	Si—O3^{vi}	1.656 (3)
Al—O4	1.829 (3)	D1—O4	0.971 (5)
Al—O4^{iv}	1.825 (3)	D2—O4	0.941 (5)
Al—O4—D1	104.0 (3)	Al^{vii}—O4—D1	101.7 (4)
Al—O4—D2	111.3 (4)	Al^{vii}—O4—D2	107.1 (4)

Symmetry codes: (i) $\frac{3}{2}-x, y-\frac{1}{2}, z$; (ii) $1+x, y-1, z$; (iii) $1-x, 1-y, -z$; (iv) $\frac{1}{2}+x, \frac{1}{2}-y, -z$; (v) $x, 1+y, z$; (vi) $x, y, \frac{1}{2}-z$; (vii) $x-\frac{1}{2}, \frac{1}{2}-y, -z$.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—D1···O4^{vii}	0.971 (5)	2.253 (6)	2.614 (2)	100.7 (4)
O4—D1···O2^{viii}	0.971 (5)	2.281 (6)	2.966 (2)	126.8 (4)
O4—D1···O3^{ix}	0.971 (5)	2.038 (5)	2.930 (2)	151.9 (4)
O4—D2···O1	0.941 (5)	2.524 (6)	2.593 (2)	83.6 (4)
O4—D2···O2^{viii}	0.941 (5)	2.363 (6)	2.966 (2)	121.6 (4)
O4—D2···O4^{vi}	0.941 (5)	2.280 (5)	3.101 (2)	145.3 (4)

Symmetry codes: (vi) $x, y, \frac{1}{2}-z$; (vii) $x-\frac{1}{2}, \frac{1}{2}-y, -z$; (viii) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$; (ix) $x, y-1, z$.

Constant wavelength (CW) neutron diffraction data were collected for about 2 h on the D20 powder diffractometer at Institut Laue—Langevin, Grenoble, France. The 25 mg sample was contained in a vanadium can. Data were analysed by the Rietveld method using the program *GSAS* (Larson & Von Dreele, 2000). Neutron scattering lengths of 0.3349, 0.4149, 0.5803 and 0.6671 × 10^{-12} cm for Al, Si, O and D, respectively, were used (Rauch & Waschowski, 2003). The structure of topaz–OH (Northrup *et al.*, 1994) was used as a trial model. Refinements were carried out in space groups *Pbnm* and *Pbn*2$_1$. However, the refinement in *Pbn*2$_1$ did not converge, suggesting that the powder data cannot be used to resolve the possible symmetry reduction. Refined occupancies of D1 and D2 were within one s.u. of 0.5 and were fixed to this value in subsequent refinements. The 52 parameters in the refinement comprised a scale factor, six profile coefficients (Thompson–Cox–Hastings pseudo-Voigt function), 12 background coefficients (shifted Chebyshev function), the zero error, the unit-cell parameters, the atomic positional parameters and isotropic displacement parameters.

Data collection: *MAD* (local program in D20 diffractometer); cell refinement: *GSAS* (Larson & Von Dreele, 2000); data reduction: *LAMP* (Richard *et al.*, 2004); program(s) used to refine structure: *GSAS*; molecular graphics: *DIAMOND* (Brandenburg, 2005); software used to prepare material for publication: *GSAS*; program(s) used to solve structure: used coordinates from X-ray work.

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