

The location of H in the high-pressure synthetic $\text{Al}_2\text{SiO}_4(\text{OH})_2$ topaz analogue

PAUL A. NORTHRUP, KURT LEINENWEBER, JOHN B. PARISE

Center for High Pressure Research (CHiPR) and Department of Earth and Space Sciences,
State University of New York at Stony Brook, Stony Brook, New York 11794-2100, U.S.A.

ABSTRACT

The positions of H in $\text{Al}_2\text{SiO}_4(\text{OH})_2$, the fully hydrated high-pressure synthetic analogue of topaz [$\text{Al}_2\text{SiO}_4(\text{F},\text{OH})_2$], have been determined from single-crystal X-ray diffraction. Two nonequivalent H positions, approximately 2.4 Å apart, were located. The H sites are significantly displaced from the single one found in natural OH-bearing fluor-topaz and violate the mirror plane of space group $Pbnm$, at least locally. Although not resolved using X-ray data, the possibility of long-range order and the reduction of symmetry to $Pbn2_1$ is supported by a measurement of the second harmonic generation (SHG), which gave a positive value of 0.6 times that of quartz. Each H is associated with three O atoms in an irregular trifurcated H-bond arrangement. These results provide an explanation for observations of split OH-stretching bands in infrared spectra, as well as for the uniform dilatation observed for both the ^{65}Al and ^{44}Si polyhedra relative to those in fluor-topaz. The structure of a natural fluor-topaz crystal was analyzed for comparison.

INTRODUCTION

Since the determination of the crystal structure of topaz [$\text{Al}_2\text{SiO}_4(\text{F},\text{OH})_2$] 65 yr ago (Alston and West, 1928; Pauling, 1928), there has been debate concerning the nature of the F-OH solid solution and the location of H. The OH content in natural samples ranges up to 30 mol%. The crystal chemistry and physical properties of topaz are summarized in Ribbe (1980). Recently, Wunder et al. (1993) synthesized the fully hydrated composition, $\text{Al}_2\text{SiO}_4(\text{OH})_2$, and characterized its structure, optical and IR properties, phase relations, and crystal morphology. They named this synthetic compound "topaz-OH," a convention we will follow here. However, they were not able to locate H in the structure. We report here the synthesis and structure refinement of topaz-OH and the location of H as a complement to the work of Wunder et al. (1993).

The H position in a sample of natural topaz with $X_{\text{OH}} = 0.28$ was determined by Zemmann et al. (1979) using neutron diffraction. Adjacent positions of this H site are <1.5 Å apart across the mirror plane. Therefore, it has been argued (Parise et al., 1980; Barton, 1982) that only one of each pair of H sites may be occupied and that the OH content cannot exceed 50 mol%. The synthesis of topaz-OH contradicts that argument and requires explanation. The results presented here resolve this question and explain many of the observations made by Wunder et al. (1993).

EXPERIMENTAL METHODS AND RESULTS

Topaz-OH was synthesized from a dry mixture of $\text{Al}(\text{OH})_3$ and SiO_2 gel, which provided 20% excess H_2O . Starting material contained in a welded Pt capsule was placed into a solid-medium high-pressure cell equipped

with a graphite resistance furnace. The sample was held at 100 kbar and 1000 °C for 2 h in the USSA-2000 high-pressure apparatus. The recovered capsule contained a friable mixture of crystals and H_2O . The topaz-OH single crystals and twin groups were well formed, transparent, 30–300 μm in size, and of similar morphology to those synthesized by Wunder et al. (1993). Stoichiometry was confirmed by electron microprobe. Data from a single crystal (80 × 70 × 60 μm) were collected on a Picker diffractometer with a graphite monochromator using $\text{MoK}\alpha$ radiation. Unit-cell parameters were determined to be $a = 4.7203(8)$, $b = 8.9207(15)$, and $c = 8.4189(15)$ Å. Intensities (1448) were measured in two octants (+/ and -/) to 64° 2θ; systematic absences verified the space group as either $Pbnm$ or $Pbn2_1$. Data were corrected for Lorentz, polarization, and absorption ($\mu = 10.6 \text{ cm}^{-1}$) effects.

Structure refinements were carried out using the Z software package (J. C. Calabrese, personal communication), and using statistical weights. Starting with the structure determined by Wunder et al. (1993) and H positions located in a difference-Fourier map, the fractional atomic coordinates and thermal parameters were refined in space group $Pbnm$ to $R = 0.0225$, $R_w = 0.0285$ (Table 1a and 1b¹). Two nonequivalent half-occupied H sites were found (Fig. 1). Bond distances and angles are given in Table 2a and 2b.¹ The positional parameters for Al, Si, and O were identical, within mutual errors, to those determined by

¹ A copy of Table 1b, anisotropic thermal parameters, and Table 2b, interatomic angles, may be obtained by ordering Document AM-94-556 from the Business Office, Mineralogical Society of America, 1130 Seventeenth Street NW, Suite 330, Washington, DC 20036, U.S.A. Please remit \$5.00 in advance for the microfiche.

TABLE 1a. Atomic positions and isotropic thermal parameters

	x	y	z	B_{iso}
Al	0.90303(7)	0.13090(4)	0.08283(4)	0.34(2)
	0.90499(8)	0.13210(5)	0.07984(6)	0.33(2)
Si	0.39723(9)	0.94035(5)	1/4	0.29(2)
	0.40189(10)	0.94045(7)	1/4	0.29(2)
O1	0.7036(3)	0.0321(1)	1/4	0.38(4)
	0.7104(4)	0.0262(2)	1/4	0.38(4)
O2	0.4577(3)	0.7560(1)	1/4	0.39(4)
	0.4439(3)	0.7561(2)	1/4	0.36(4)
O3	0.2102(2)	0.9892(1)	0.0924(1)	0.37(3)
	0.2141(2)	0.9929(1)	0.0943(1)	0.38(3)
F	0.5982(1)	0.2525(1)	0.0561(1)	0.52(2)
OH	0.5906(3)	0.2507(1)	0.0659(1)	0.52(3)
H1*	0.443(11)	0.199(6)	0.088(5)	2.7(12)
H2*	0.607(14)	0.281(8)	0.151(7)	7.1(23)

Note: B_{iso} is the mean of the principal axes of the thermal ellipsoid. Upper value for each entry refers to fluor-topaz; the second line refers to topaz-OH; errors apply to the last digit printed.

* H-site occupancies are fixed at 0.5; all others are 1.0.

Wunder et al. (1993), except for the OH site. This difference is most likely the result of the absence of H in their model. The existence of two half-occupied H sites suggested the possibility of ordering, resulting in loss of the mirror plane and reduction of the symmetry to $Pbn2_1$. A second harmonic generation (SHG) measurement (Kurtz and Perry, 1968) yielded a value 0.6 times that of quartz, indicating the lack of a center of symmetry. However, refinement in $Pbn2_1$ did not lead to improved discrepancy indices.

For comparison and as an experimental control, a sample of natural nearly end-member fluor-topaz from a Mexican rhyolite was also studied ($X_{OH} < 0.05$, as determined by the X-ray determinative methods of Ribbe and Rosenberg, 1971, and electron microprobe). Cell dimensions were $a = 4.652(1)$, $b = 8.801(3)$, and $c = 8.404(2)$ Å. Intensities (1392) were collected from an 80- μ m block, and the structure refined using the same procedures as for topaz-OH. Atomic positional and thermal parameters are included in Table 1; the discrepancy indices after refinement in $Pbnm$ were $R = 0.0224$, $R_w = 0.0275$. There was no evidence for reduced symmetry, and examination of difference-Fourier maps revealed no significant residual electron density near OH.

TABLE 2a. Al-O and Si-O distances (Å)

		Fluor-topaz	Topaz-OH	Δ
Al	O1	1.892(1)	1.946(1)	0.054
	O2	1.896(1)	1.945(1)	0.049
	O3	1.885(1)	1.922(1)	0.037
	O3a	1.896(1)	1.926(1)	0.030
	F-OH	1.798(1)	1.834(1)	0.036
	Fa-OHa	1.788(1)	1.826(1)	0.038
Mean	(Al-O)	1.892	1.935	0.043
	(Al-(F-OH))	1.793	1.830	0.037
Si	O1	1.636(1)	1.645(2)	0.009
	O2	1.645(1)	1.657(2)	0.012
	O3 \times 2	1.6395(8)	1.651(1)	0.0115
Mean	(Si-O)	1.640	1.651	0.011

TABLE 3. H distances and angles in topaz-OH

	Distance (Å)		Angle (°)	
H1	OHa	0.86(5)		
	OHb	2.156(51)	OHa-H1-OHb	112(4)
	O2	2.330(53)	OHa-H1-O2	129(4)
	O3	2.129(57)	OHa-H1-O3	152(5)
	Al	2.07(5)	Al-OHa-H1	109(4)
	H2a	2.43(7)	Ala-OHa-H1	94(3)
H2	OHb	0.78(6)		
	O1	2.459(67)	OHb-H2-O1	130(6)
	O2	2.290(66)	OHb-H2-O2	114(6)
	OHa	2.377(58)	OHb-H2-OHa	153(7)
	Al	2.02(7)	Al-OHb-H2	92(4)
	H1a	2.43(7)	Ala-OHb-H2	118(5)

DISCUSSION

Because of the close (1.5 Å) H-H distance that would be required, the H position previously found in natural topaz cannot apply to topaz-OH. The present work revealed that this H position is split into two nonequivalent sites with an H-H distance of 2.4 Å (Fig. 1). That each H site is one-half occupied and that a diagonal configuration of H atoms provides a geometrically reasonable model suggest the possibility of long-range order and symmetry reduction to $Pbn2_1$. The use of X-rays, however, is insufficient to resolve this detail. The SHG measurement indicated a noncentrosymmetric structure; however, the small value obtained may indicate only domains of order rather than complete long-range order. A neutron diffraction study may be able to prove whether topaz-OH crystallizes in space group $Pbn2_1$.

Rather than a single H bond, we found the nearly symmetrical trifurcated H-bond arrangements shown in Figure 2. H1 is H-bonded to O3, OH, and, somewhat less strongly, to O2 (Table 3). Calculated bond strengths (Brown, 1992) are 0.13, 0.12, and 0.10 vu, respectively. H2 is H-bonded to O2, OH, and O1, with bonds of 0.10, 0.09, and 0.08 vu, respectively. The H1 site has stronger H bonding than the H2 site, resulting in more condensed thermal vibration (Table 1). Wunder et al. (1993), on the basis of bond valence sums, noted the lack of an obvious single H-bond acceptor. Their findings agree with the H-bonding arrangement presented here, in which the H bonding is distributed among several O atoms. The O-H...O angles range from 112 to 152° (Table 3). H1 is oriented above the OH-O3-OHb face of the $^{[6]}Al$ octahedron, attached by an OH bond to one apex and by O...H bonds to the other two (Fig. 2). The third O...H bond is to the nearby O2 atom. H2 is similarly oriented above the OH-O1-O2 $^{[6]}Al$ octahedral face, but its third O...H bond is to the opposite OH (Fig. 2). In this arrangement, there are very close H-Al distances (2.1 and 2.0 Å). The close packing of the three O atoms of the face of the octahedron probably shields the H. The presence of these H bonds may stabilize the topaz-OH structure at high pressure and can explain several of the observations of Wunder et al. (1993).

There is a uniform expansion of cation polyhedra in topaz-OH relative to fluor-topaz (Wunder et al., 1993).

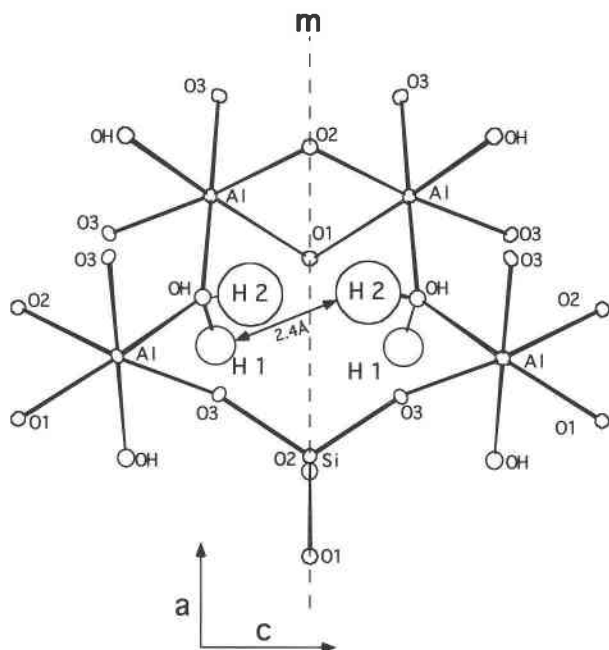


Fig. 1. ORTEP (Johnson, 1965) diagram of part of the structure of topaz-OH, viewed down **b**, showing half-occupied H positions refined in space group *Pbnm*. Note the (dashed) mirror plane. Thermal ellipsoids (50% probability) and bond orientations are shown. Two possible OH-HO orientations may exist, each violating the mirror locally. If long-range ordering exists, the space group is reduced to *Pbn2₁*.

The Al-OH and Al-O distances are all approximately 2% greater than the corresponding Al-F and Al-O distances, and the mean Si-O distance is 0.5% greater (Table 2). Moreover, there is little distortion of the $\text{AlO}_4(\text{OH})_2$ octahedron relative to its AlO_4F_2 counterpart. This may be explained by the described H-bonding configuration. Because each H bond diverts some of the bond strength of an O atom away from its Al-O and Si-O bonds, those bonds are weaker and longer. Since every O atom is involved, there is a uniform expansion of the ^{61}Al and ^{41}Si polyhedra.

A position ($x = 0.424$, $y = 0.184$, $z = 0.081$) only 0.16 Å from our H1 was predicted by Abbott (1990) for the topaz-OH composition on the basis of theoretical energy calculations. However, his model did not anticipate the nonequivalent H2 site. The identification of two distinct H sites in topaz-OH is in agreement with its IR spectra, which show two bands at 3600 and 3520 cm^{-1} (Wunder et al., 1993). The two sites found are significantly different in environment and bonding. Moreover, the decrease in wavelength of the O-H stretching bands in topaz-OH relative to natural topaz may result from the H-bonding restraints. Also, both $2V$ and the a and b cell parameters deviate from the correlations with X_{OH} determined by Ribbe and Rosenberg (1971) for F-rich compositions (Wunder et al., 1993). The structural differences observed in topaz-OH apparently have an effect beyond that of simple linear dependence on X_{OH} .

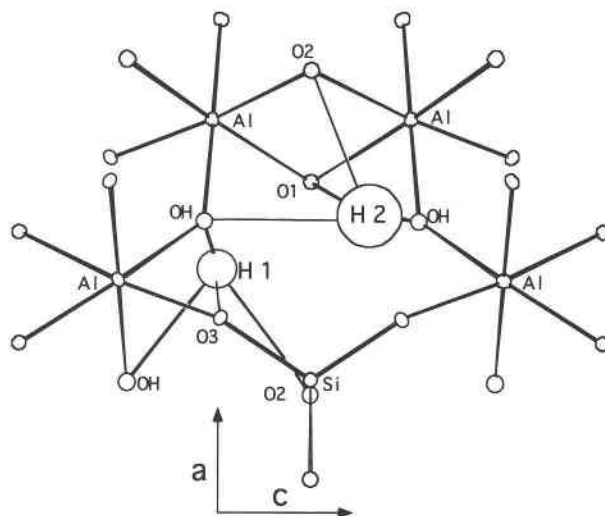


Fig. 2. H-bonding configurations in $\text{Al}_2\text{SiO}_4(\text{OH})_2$ showing only one of the two possible pairs of H sites in Fig. 1. H...O distances and angles are given in Table 3.

This work has important implications for topaz solid solutions. There is now recognized the possibility of this configuration of OH-HO pairs in natural examples. Such orientational ordering would be in addition to the OH-F chemical ordering common in natural topaz (Akizuki et al., 1979; Parise et al., 1980) and should be considered in future thermodynamic and crystallographic investigations. A reevaluation of the end-members and phase relationships for the topaz solid solution is in order. In addition, other minerals with OH-F substitutions, and high-pressure hydrous phases may contain H in similar arrangements.

ACKNOWLEDGMENTS

The authors are grateful to Charlie Torardi and William Greene of the DuPont company for the SHG measurement. We also recognize and appreciate the work done by Wunder et al. in so fully characterizing this phase that our work was greatly simplified. This research was supported by NSF grants DMR-9024249 to J.B.P. and EAR-8920329 to CHiPR (MPI contribution no. 114).

REFERENCES CITED

- Abbott, R.N., Jr. (1990) Topaz: Energy calculations bearing on the location of hydrogen. *Canadian Mineralogist*, 28, 827-833.
- Akizuki, M., Hampar, M.S., and Zussman, H. (1979) An explanation of anomalous optical properties of topaz. *Mineralogical Magazine*, 43, 237-241.
- Alston, N.A., and West, J. (1928) The structure of topaz. *Proceedings of the Royal Society A*, 121, 358-367.
- Barton, M.D. (1982) The thermodynamic properties of topaz solid solutions and some petrologic applications. *American Mineralogist*, 67, 956-974.
- Brown, I.D. (1992) Chemical and steric constraints in inorganic solids. *Acta Crystallographica*, B48, 553-572.
- Johnson, C.K. (1965) ORTEP: A Fortran thermal-ellipsoid plot program for crystal structure illustrations. Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- Kurtz, S.K., and Perry, T.T. (1968) A powder technique for the evaluation of nonlinear optical materials. *Journal of Applied Physics*, 39, 3798.

- Parise, J.B., Cuff, C., and Moore, F.H. (1980) A neutron diffraction study of topaz: Evidence for lower symmetry. *Mineralogical Magazine*, 43, 943–944.
- Pauling, L. (1928) The crystal structure of topaz. *Proceedings of the National Academy of Science, USA*, 14, 603–606.
- Ribbe, P.H. (1980) Topaz. In *Mineralogical Society of America Reviews in Mineralogy*, 5, 215–230.
- Ribbe, P.H., and Rosenberg, P.E. (1971) Optical and X-ray determinative methods for fluorine in topaz. *American Mineralogist*, 56, 1812–1821.
- Wunder, B., Rubie, D.C., Ross, C.R., II, Medenbach, O., Seifert, F., and Schreyer, W. (1993) Synthesis, stability, and properties of $\text{Al}_2\text{SiO}_5(\text{OH})_2$: A fully hydrated analogue of topaz. *American Mineralogist*, 78, 285–297.
- Zemann, J., Zobetz, E., Heger, G., and Vollenkle, H. (1979) Strukturbestimmung eines OH-reichen Topases. *Österreichische Akademie der Wissenschaften, mathematisch-naturwissenschaftliche Klasse*, 116, 145–147.

MANUSCRIPT RECEIVED JANUARY 7, 1994

MANUSCRIPT ACCEPTED FEBRUARY 9, 1994