Neutron-diffraction structure of a low-water grossular at 20 K

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ABSTRACT

The crystal structure of a low-water (0.16 wt% OH) grossular has been refined at 20 K by single-crystal time-of-flight neutron-diffraction methods. Comparisons with the room-temperature structure indicate that between 298 and 20 K, the silicate tetrahedron undergoes a small rigid-body rotation that results in an increase in the y parameter of oxygen. The mechanism of thermal expansion is significantly different from that at high temperature where the tetrahedra do not rotate and changes in the structure reflect only unit-cell expansion.

INTRODUCTION

Recent crystal-structure refinements of plazolite, $Ca_3Al_2(SiO_4)_{1.53}(O_4H_4)_{1.47}$ (Basso et al.,1983), and katoite, $Ca_3Al_2(SiO_4)_{0.64}(O_4H_4)_{2.36}$ (Sacerdoti and Passaglia, 1985), have shown that H can be introduced in the garnet structure via the substitution $(O_4H_4) \rightleftharpoons (SiO_4)$. In these defect grossular structures, H is bonded to oxygens surrounding tetrahedral vacancies and is distributed at random over the general position in space group $Ia3d$. Although high-water garnets like plazolite ($\sim$13 wt% H_2O) have been cited in the literature as classic hydrogarnets, recent infrared spectroscopic measurements suggest that they may be much rarer in nature than originally believed (Aines and Rossman, 1984). Most garnets contain substantially less water (<0.5 wt%).

To determine the mode of incorporation of H in these more common "low-water" garnets, the crystal structure of a grossular (0.16 wt% OH) from the McFall mine, a carbonate contact zone near Ramona, California, was refined at 20 K by single-crystal time-of-flight (TOF) neutron-diffraction methods. The infrared spectrum recorded for this grossular shows a stretching frequency in the wavenumber region 3600–3800 cm^{-1}, indicating the presence of H in an OH group (G. R. Rossman, unpub. data). Although the sensitivity of the diffraction method was not sufficient to detect such a low concentration of H (<1 atom per unit cell), the structure has been reported because of possible interest in the low-temperature neutron-diffraction data.

EXPERIMENTAL DETAILS

Single-crystal TOF neutron-diffraction data were obtained at the Intense Pulsed Neutron Source (IPNS) at Argonne National Laboratory. The experiment was carried out at low temperature (20 K) to reduce the effects of thermal vibration and to increase the probability of localizing the H atom. The TOF method is ideally suited to studies under these special environmental conditions because the crystal and detector remain in a fixed position during data collection. The instrument and data-collection procedures are discussed in detail by Schultz and Leung (1986). Experimental parameters and chemical data pertinent to this study are given in Tables 1 and 2.

Space-group symmetry at 298 K ($Ia3d$) was confirmed by single-crystal X-ray diffraction methods prior to data collection. Several (hkl) planes were also indexed at 20 K to insure that $Ia3d$ symmetry was preserved during cooling. The unit-cell parameter was determined at both 298 K [11.850(3) Å] and 20 K [11.843(4) Å] from least-squares refinement of diffraction maxima well-distributed in reciprocal space. Integrated intensities (2344) from 11 histograms ($-32 \leq h \leq 17$, $-24 \leq k \leq 24$, $-24 \leq l \leq 15$) were converted to structure-factor amplitudes using the expression $I_{hkl} = kT\phi_\lambda \epsilon_\lambda A_\lambda Y_\lambda |F_{hkl}|^2 \lambda^4/\sin^2\theta$, where k is a scale factor, T is the normalized monitor count, F_{hkl} is the structure factor, and θ is the Bragg angle (Schultz and Leung 1986). The wavelength-dependent terms are the incident flux ϕ_λ, the detector efficiency ϵ_λ, the absorption correction A_λ, and the extinction correction Y_λ. A polyhedral absorption correction was applied using absorption coefficients linearly interpolated between $\lambda = 0.7$ Å ($\mu = 0.4534$ cm^{-1}) and $\lambda = 4.2$ Å ($\mu = 0.8196$ cm^{-1}).

The refinement was carried out using a locally modified least-squares program for variable-wavelength data. The function

TABLE 1.   Data-collection parameters

Sample to detector distance	32.00 cm
Sample to moderator distance	662.06 cm
Detector angle, η	90.0°
ω angle	45.0°
Detector dimensions	26.30 × 27.38 cm
Neutron-source repetition rate	30 Hz
Histogram dimensions	
X, Y	85 × 85 channels
T	120 channels
Histogram-wavelength range	0.700–4.196 Å

TABLE 3.   Positional parameters, anisotropic-temperature-factor coefficients ($\times 10^5$), and neutron scattering lengths*

	O	X	Y	Z
x	0.038 17(2)**	1/8	0	3/8
y	0.045 59(2)	0	0	0
z	0.651 41(2)	1/4	0	1/4
β_{11}	27(1)	1(3)	9(4)	1(3)
β_{22}	24(2)	20(2)	9	5(2)
β_{33}	14(1)	20	9	5
β_{12}	2(1)	0	−3(2)	0
β_{23}	4(1)	1(2)	−3	0
β_{13}	−4(1)	0	−3	0
b†	0.5803	0.490	0.381(4)	0.4149

* Coefficients are of the form exp $[-(\beta_{11}h^2 + \cdots + 2\beta_{12}hk + \cdots)]$.
** Numbers in parentheses are esds and refer to the last decimal place.
† Neutron scattering lengths (cm^{-12}) are from Sears (1986).

minimized was $\sum \omega(F_{obs}^2 - F_{calc}^2)$, where $\omega = 1/\sigma(F_{obs}^2)$ and $\sigma(F_{obs}^2) = [\sigma_{counting}^2(F_{obs}^2) + (0.02F_{obs}^2)^2]^{1/2}$. Positional parameters for oxygen, anisotropic temperature factor coefficients for the non-H atoms, an anisotropic extinction (type II) correction, and scale factors for each histogram were refined with $F_{obs}^2 > 3\sigma(F_{obs}^2)$ (1613 reflections) to $R(F^2) = 0.0666$ and $R_w(F^2) = 0.0743$ (Table 3). Those reflections most severely affected by secondary extinction (>30%) were not included in the refinement (233). The largest peak of negative density (~1–2% of an oxygen atom) in the difference Fourier (ΔF) map was located 1.1 Å from oxygen at (−0.0265, 0.0496, 0.7186). Inclusion of this position in the least-squares refinement increased the isotropic temperature factor to an anomalously large value and did not significantly improve the fit. H positions reported by Basso et al. (1983) and Sacerdoti and Passaglia (1985) were not among the 80 peaks interpolated in the ΔF synthesis. In the final cycles of refinement, the occupations of the Si and H sites were varied, but no significant change in these parameters was observed.

The refined scattering length (b) for the Y site (Table 3) was consistent with the microprobe analysis (1.88Al + 0.12Fe). Observed and calculated structure-factor amplitudes are compared in Table 4.[1]

RESULTS

Table 5 compares interatomic distances and angles for the Ramona grossular at 20 K with those reported for the room-temperature grossular structure (Novak and Gibbs, 1971). These grossulars are very similar in composition and, based on the equations of Novak and Gibbs (1971),

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[1] To obtain a copy of Table 4, order Document AM-87-343 from the Business Office, Mineralogical Society of America, 1625 I Street, N.W., Suite 414, Washington, D.C. 20006, U.S.A. Please remit $5.00 in advance for the microfiche.

should show a close correspondence between structural parameters at 298 K (Table 2).

The structural variations that occur in the Ramona grossular at low temperature reflect both a contraction of the unit cell and an increase in the y parameter of oxygen. The displacement of the oxygen position results from a small rigid-body rotation of the silicate tetrahedron. Meagher (1975) defined this rotation in terms of the γ angle, which is "the smaller of two angles between the tetrahedral O–O edge normal to the $\bar{4}$ axis and the two crystallographic axes normal to the $\bar{4}$ axis." The γ angle in grossular, which remains constant (24.5°) in the temperature range 298–948 K, increases at lower temperature (24.8°). The magnitude of this change is similar to that observed in pyrope (Meagher, 1975) over the temperature interval 298–1023 K. Tetrahedral rotation to smaller γ angles is an effective way of increasing the size of the dodecahedron at high temperature. It also permits the shared octahedral edge to expand at a greater rate than the unshared edge, which decreases the bond-angle strain. The octahedral bond-angle strain also decreases in grossular at low temperature, but, in this case, the unshared edge increases slightly whereas the shared edge remains constant. It is interesting to note that a value of 2.68 Å (length of unshared octahedral edge in grossular) may represent the lower limit for an unshared octahedral edge in silicate garnets (Novak and Gibbs, 1971; Meagher, 1975). The structural instability associated with a shortening of this edge may serve to constrain the thermal expansion of grossular at lower temperatures.

TABLE 2.   Chemical and crystallographic data for Ramona and Asbestos grossulars

Ramona grossular
$(Ca_{2.99}Mn_{0.01})(Al_{1.90}Fe_{0.10})(SiO_4)_{2.99}(O_4H_4)_{0.01}$*
$a = 11.850(3)$ Å; O(x, y, z)** = 0.038 02, 0.044 56, 0.651 25
Asbestos grossular (Novak and Gibbs, 1971)
$(Ca_{2.96}Mn_{0.04})(Al_{1.95}Fe_{0.05})(SiO_4)_3$
$a = 11.845(1)$ Å; O(x, y, z) = 0.038 08(11), 0.044 93(11), 0.651 40(9)

* H content determined by infrared spectroscopic techniques (Aines and Rossman, 1984); non-H content by electron-microprobe analysis.
** Calculated from Equations 3–5 of Novak and Gibbs (1971).

TABLE 5.   Comparison of interatomic distances (Å) and angles (°) for Ramona (20 K) and Asbestos grossulars

Si–O	1.647(1)	[1.645(1)]			
2 O(1)–O(2)	2.572(1)	[2.567(2)]	O(1)–Si–O(2)	102.70(2)	[102.53(8)]
4 O(1)–O(3)	2.746(1)	[2.745(1)]	O(1)–Si–O(3)	112.96(2)	[113.05(4)]
Al–O	1.926(1)	[1.924(1)]			
6 O(1)–O(4)	2.756(2)	[2.756(2)]	O(1)–Al–O(4)	91.33(2)	[91.46(5)]
6 O(1)–O(5)	2.693(1)	[2.686(2)]	O(1)–Al–O(5)	88.67(2)	[88.54(5)]
4 Ca(1)–O(4)	2.321(1)	[2.319(1)]			
4 Ca(2)–O(4)	2.483(1)	[2.490(1)]			
2 O(1)–O(2)	2.572(1)	[2.567(2)]	O(1)–Ca(2)–O(2)	67.30(2)	[67.20(6)]
4 O(1)–O(4)	2.756(1)	[2.756(2)]	O(1)–Ca(2)–O(4)	69.92(2)	[69.84(4)]
4 O(4)–O(6)	2.964(1)	[2.973(2)]	O(4)–Ca(2)–O(6)	76.11(1)	[76.28(6)]
2 O(4)–O(7)	2.854(1)	[2.866(2)]	O(4)–Ca(2)–O(7)	70.18(2)	[70.27(6)]
4 O(1)–O(7)	3.450(1)	[3.450(1)]	O(1)–Ca(2)–O(7)	91.74(2)	[91.61(4)]
2 O(8)–O(7)	4.111(1)	[4.121(2)]	O(8)–Ca(2)–O(7)	111.77(2)	[111.66(6)]

Note: Numbers in brackets refer to 298-K grossular structure refined by Novak and Gibbs (1971).

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