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Single-crystal absorption and reflection infrared spectroscopy of birefringent grossular andradite garnets

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For deposit: Figures 1-5; Tables 1-5

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Appendix for "Single-Crystal Absorption and Reflection Infrared Spectroscopy of Birefringent Grossular-Andradite Garnets " by B. P. McAloon and A. M. Hofmeister.

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Figures A-E.

Photomicrographs taken under crossed polarizers of samples prepared for IR reflectance spectroscopy. Scale bar is 1.0 mm. (A) One of nine Sonoma Andradite samples prepared for this study; random crystal orientation. Spectra were obtained from areas shown by arrows. (B) Grossularite, Asbestos; random crystal orientation. Spectra were obtained from labeled areas. (C) Grossularite, Eden Mills; this piece is parallel to the (110) crystal face, showing bow-tie birefringence. Spectra were taken from labeled areas. (D) Grossularite, Eden Mills; sample was cut perpendicular to (110) face at otherwise random crystal orientation. Spectra were obtained from the labeled areas. (E) Grandite, Munam; random crystal orientation. Mid-IR data were obtained from area 1, far-IR spectra from area 2.

TABLE A. Symmetry analysis of orthorhombic* D_{2h}^{24} garnet, $X^{2+}{}_3Y^{3+}{}_2(SiO_4)_3$

Site Symmetry Analysis									
Atom	Site	Symmetry	A_g	B_{1g}	B_{2g}	B_{3g}	A_u	B_{1u}	B_{2u}	B_{3u}
X^{2+}	a+b	$2D_2(2)$	0	2	2	2	0	2	2	2
	h	$C_1(8)$	3	3	3	3	3	3	3	3
Y^{3+}	c+d	$2C_i(4)$	0	0	0	0	6	6	6	6
Si	g	$C_2{}^z(4)$	1	1	2	2	1	1	2	2
	h	$C_1(8)$	3	3	3	3	3	3	3	3
O	h	$6C_1(8)$	18	18	18	18	18	18	18	18
Total			25	27	28	28	31	33	34	34
Acoustic								1	1	1
Optical			25†	27†	28†	28†	31	32§	33§	33§
Factor Group Analysis										
Internal SiO_4			$2\nu_1$	$2\nu_1$	ν_1	ν_1	$2\nu_1$	$2\nu_1$	ν_1	ν_1
			$4\nu_2$	$4\nu_2$	$2\nu_2$	$2\nu_2$	$4\nu_2$	$4\nu_2$	$2\nu_2$	$2\nu_2$
			$4\nu_3$	$4\nu_3$	$5\nu_3$	$5\nu_3$	$4\nu_3$	$4\nu_3$	$5\nu_3$	$5\nu_3$
			$4\nu_4$	$4\nu_4$	$5\nu_4$	$5\nu_4$	$4\nu_4$	$4\nu_4$	$5\nu_4$	$5\nu_4$
Rotation SiO_4			4	4	5	5	4	4	5	5
Translation SiO_4			4	4	5	5	4	3	4	4
Translation Y			0	0	0	0	6	6	6	6
Translation X			3	5	5	5	3	5	5	5

*The *Fddd* structure has 4 primitive cells in the crystallographic unit cell and 240 total modes.

†Raman active §Infrared active

Table B. Symmetry anaylsis for *I*1bar garnet.

This structure contains 8 atoms on the octahedral site which is a center of inverstion. The remaining atoms are on sites lacking symmetry elements. From this data we construct an invariance table (W. B. White, personal communication, 1993)

Invariance Table

	E	i
8 x Ci	8	8
72 x C_1	72	0
Total	80	8

To obtain the irreducible representation, we multiply the trace of each matrix by the number of atoms possessing the symmetry.

$$E = \begin{matrix} 1 & 0 & 1 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{matrix} \qquad i = \begin{matrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{matrix}$$

So $G = 80 \times (1+1+1)\, E + 8 \times (-1 + -1 + -1)\, i$

From the character table for C_i in Cotton , F. A. "Chemical Applications of Group Theory", John Wiley, 1972.

$A_g = E + i$ and $A_u = E - i$

The only linear combination of A_g and A_u which yields G is

$G = 108\ A_g + 132\ A_u$.

Because three of the ungerade modes are translations, there are 129 IR active modes for *I*1. The gerade modes are Raman active. The total number of modes is 240 and there are no inactive modes.

TABLE C. Symmetry analysis of tetragonal* D_{4h}^{20} garnet, $X^{2+}{}_3Y^{3+}{}_2(SiO_4)_3$

Site Symmetry Analysis											
Atom	Site	Symmetry	A_{1g}	A_{2g}	B_{1g}	B_{2g}	E_g	A_{1u}	A_{2u}	B_{1u}	B_{2u}	E_u
X^{2+}	a	$S_4(4)$	0	0	1	1	2	1	1	0	0	2
	e	$C_2(8)$	1	2	1	2	3	1	2	1	2	3
Y^{3+}	c	$C_i(8)$	0	0	0	0	0	3	3	3	3	6
Si	b	$D_2''(4)$	0	1	1	0	2	0	1	1	0	2
	e	$C_2'(8)$	1	2	2	1	3	1	2	2	1	3
O	g	$3C_1(16)$	9	9	9	9	18	9	9	9	9	18
Total			11	14	14	13	28	15	18	16	15	34
Acoustic									1			1
Optical			11†	14	14†	13	28†	15	17§	16	15	33§
Factor Group Analysis												
Internal SiO_4			$2\nu_1$			$2\nu_1$	ν_1	$2\nu_1$			$2\nu_1$	ν_1
			$4\nu_2$			$4\nu_2$	$2\nu_2$	$4\nu_2$			$4\nu_2$	$2\nu_2$
			ν_3	$3\nu_3$	$3\nu_3$	ν_3	$5\nu_3$	ν_3	$3\nu_3$	$3\nu_3$	ν_3	$5\nu_3$
			ν_4	$3\nu_4$	$3\nu_4$	ν_4	$5\nu_4$	ν_4	$3\nu_4$	$3\nu_4$	ν_4	$5\nu_4$
Rotation SiO_4			1	3	3	1	5	1	3	3	1	5
Translation SiO_4			1	3	3	1	5	1	2	3	1	4
Translation Y			0	0	0	0	0	3	3	3	3	6
Translation X			1	2	2	3	5	2	3	1	2	5

*The $I4_1/acd$ structure has 2 primitive cells in the crystallographic unit cell with 240 total vibrations.

†Raman active

§Infrared active

TABLE D. Symmetry analysis of rhombohedral* D_{3d}^6 garnet, $X^{2+}_3Y^{3+}_2(SiO_4)_3$

Site Symmetry Analysis								
Atom	Site	Symmetry	A_{1g}	A_{2g}	E_g	A_{1u}	A_{2u}	E_u
X^{2+}	f	$C_1(12)$	3	3	6	3	3	6
Y^{3+}	b	$C_{3i}(2)$	0	0	0	1	1	2
	d	$C_i(6)$	0	0	0	3	3	6
Si	f	$C_1(12)$	3	3	6	3	3	6
O	f	$4C_1(12)$	12	12	24	12	12	24
Total			18	18	36	22	22	44
Acoustic							1	1
Optical			18†	18	36†	22	21§	43§
Factor Group Analysis								
Internal SiO_4			ν_1	ν_1	$2\nu_1$	ν_1	ν_1	$2\nu_1$
			$2\nu_2$	$2\nu_2$	$4\nu_2$	$2\nu_2$	$2\nu_2$	$4\nu_2$
			$3\nu_3$	$3\nu_3$	$6\nu_3$	$3\nu_3$	$3\nu_3$	$6\nu_3$
			$3\nu_4$	$3\nu_4$	$6\nu_4$	$3\nu_4$	$3\nu_4$	$6\nu_4$
Rotation SiO_4			3	3	6	3	3	6
Translation SiO_4			3	3	6	3	2	5
Translation Y			0	0	0	4	4	8
Translation X			3	3	6	3	3	6

* The $R3c$ structure has 240 total vibrations

†Raman active §Infrared active

TABLE E. Symmetry analysis of rhombohedral* C_{3i}^2 garnet, $X^{2+}_3Y^{3+}_2(SiO_4)_3$

Site Symmetry Analysis						
Atom	Site	Symmetry	A_g	E_g	A_u	E_u
X^{2+}	f	$2C_1(6)$	6	6	6	6
Y^{3+}	a+b	$2C_{3i}(1)$	0	0	2	2
	d+e	$2C_i(3)$	0	0	6	6
Si	f	$2C_1(6)$	6	6	6	6
O	f	$8C_1(6)$	24	24	24	24
Total			36	36	44	44
Acoustic					1	1
Optical			36†	36†	43§	43§
Factor Group Analysis						
Internal SiO_4			$2\nu_1$	$2\nu_1$	$2\nu_1$	$2\nu_1$
			$4\nu_2$	$4\nu_2$	$4\nu_2$	$4\nu_2$
			$6\nu_3$	$6\nu_3$	$6\nu_3$	$6\nu_3$
			$6\nu_4$	$6\nu_4$	$6\nu_4$	$6\nu_4$
Rotation SiO_4			6	6	6	6
Translation SiO_4			6	6	5	5
Translation Y			0	0	8	8
Translation X			6	6	6	6

*The *R*3 structure has 240 total vibrations.

†Raman active

§Infrared active