

AM-93-535

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

B. P. McAloon, A. M. Hofmeister

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

American Mineralogist, 78, 9-10, 958-968.



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

Submitted to the American Mineralogist, March 1993.

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,  $X^{2+}_3Y^{3+}_2(\text{SiO}_4)_3$

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	$C_{2z}(4)$	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 $\text{SiO}_4$			$2v_1$	$2v_1$	$v_1$	$v_1$	$2v_1$	$2v_1$	$v_1$	$v_1$
			$4v_2$	$4v_2$	$2v_2$	$2v_2$	$4v_2$	$4v_2$	$2v_2$	$2v_2$
			$4v_3$	$4v_3$	$5v_3$	$5v_3$	$4v_3$	$4v_3$	$5v_3$	$5v_3$
			$4v_4$	$4v_4$	$5v_4$	$5v_4$	$4v_4$	$4v_4$	$5v_4$	$5v_4$
Rotation $\text{SiO}_4$			4	4	5	5	4	4	5	5
Translation $\text{SiO}_4$			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 analysis for  $I\bar{1}$  garnet.

This structure contains 8 atoms on the octahedral site which is a center of inversion. 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 $C_i$	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.

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

$$\text{So } G = 80 \times (1+1+1) E + 8 \times (-1 + -1 + -1) i$$

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

$$A_g = E + i \quad \text{and} \quad A_u = E - i$$

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  $I\bar{1}$ . 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,  $X^{2+}_3Y^{3+}_2(\text{SiO}_4)_3$

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 $\text{SiO}_4$			$2v_1$			$2v_1$	$v_1$	$2v_1$			$2v_1$	$v_1$
			$4v_2$			$4v_2$	$2v_2$	$4v_2$			$4v_2$	$2v_2$
			$v_3$	$3v_3$	$3v_3$	$v_3$	$5v_3$	$v_3$	$3v_3$	$3v_3$	$v_3$	$5v_3$
			$v_4$	$3v_4$	$3v_4$	$v_4$	$5v_4$	$v_4$	$3v_4$	$3v_4$	$v_4$	$5v_4$
Rotation $\text{SiO}_4$			1	3	3	1	5	1	3	3	1	5
Translation $\text{SiO}_4$			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,  $X^{2+}_3Y^{3+}_2(\text{SiO}_4)_3$

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 $\text{SiO}_4$			$\nu_1$	$\nu_1$	$2\nu_1$	$\nu_1$	$\nu_1$	$2\nu_1$
			$2\nu_2$	$2\nu_2$	$4\nu_2$	$2\nu_2$	$2\nu_2$	$4\nu_2$
			$3\nu_3$	$3\nu_3$	$6\nu_3$	$3\nu_3$	$3\nu_3$	$6\nu_3$
			$3\nu_4$	$3\nu_4$	$6\nu_4$	$3\nu_4$	$3\nu_4$	$6\nu_4$
Rotation $\text{SiO}_4$			3	3	6	3	3	6
Translation $\text{SiO}_4$			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 <sup>2+</sup>	f	2C <sub>1</sub> (6)	6	6	6	6
Y <sup>3+</sup>	a+b	2C <sub>3i</sub> (1)	0	0	2	2
	d+e	2C <sub>i</sub> (3)	0	0	6	6
Si	f	2C <sub>1</sub> (6)	6	6	6	6
O	f	8C <sub>1</sub> (6)	24	24	24	24
Total			36	36	44	44
Acoustic					1	1
Optical			36†	36†	43§	43§
Factor Group Analysis						
Internal SiO <sub>4</sub>			2v <sub>1</sub>	2v <sub>1</sub>	2v <sub>1</sub>	2v <sub>1</sub>
			4v <sub>2</sub>	4v <sub>2</sub>	4v <sub>2</sub>	4v <sub>2</sub>
			6v <sub>3</sub>	6v <sub>3</sub>	6v <sub>3</sub>	6v <sub>3</sub>
			6v <sub>4</sub>	6v <sub>4</sub>	6v <sub>4</sub>	6v <sub>4</sub>
Rotation SiO <sub>4</sub>			6	6	6	6
Translation SiO <sub>4</sub>			6	6	5	5
Translation Y			0	0	8	8
Translation X			6	6	6	6

\*The  $R3$  structure has 240 total vibrations.

†Raman active

§Infrared active