THE AMERICAN MINERALOGIST, VOL. 56, MAY-JUNE, 1971

ANALYSIS OF THE INFRARED ABSORPTION SPECTRUM OF ALMANDINE-PYROPE GARNET FROM NIJOSAN, OSAKA PREFECTURE, JAPAN

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ABSTRACT

The infrared absorption spectrum of almandine-pyrope garnet from Nijosan, Japan is shown in the wave number region between 1700 and 60 cm^{-1}. Factor group and site group analyses of garnet are discussed and cause of the splitting of two absorption bands for the tetrahedral SiO_4 ion is interpreted. By using Wilson's GF matrices the wave numbers of the absorption band were calculated and the force constants in the Urey-Bradley force field were determined, such as K 3.90, H 0.26 and F 0.80 md/Å for the tetrahedral SiO_4 ion and K 1.60, H 0.14 and F 0.001 md/Å for the octahedral $R^{3+}O_6$ ion. The Jacobian matrix shown was useful in the course of the calculation of the force constants and the potential energy distribution indicated was necessary for the determination of the coupling of normal modes.

INTRODUCTION

Infrared absorption spectra of garnet were studied by Launer (1952); Wickerheim, Lefever and Hanking (1960); and Tarte (1965), who indicated a variation in frequencies of the infrared absorption band of the SiO_4 ion for six end-members of garnet. Several laser-excited phonon Raman spectra of the rare earth doped garnets were studied by Koningstein and Mortensen (1968), Koningstein and Toaning-Ng (1968), and Hurrell *et al.*, (1968).

In the present paper, the infrared absorption bands of almandine-pyrope garnet obtained in the wave number region from 1700 to 60 cm^{-1} are discussed theoretically, and the frequencies of two infrared absorption bands for the tetrahedral SiO_4 ion and also those for the octahedral $R^{3+}O_6$ ion were calculated by Wilson's GF matrices method. Also the force constants in the Urey-Bradley force field were determined and the Jacobian matrix and the potential energy distribution obtained from the calculation were shown.

INFRARED ABSORPTION SPECTRUM OF ALMANDINE-PYROPE GARNET

The garnet used for the study was collected by the author from the volcano Nijosan, Osaka Prefecture, Japan, whose name in Japanese means "originated from the two isolated peaks of the volcano." Small trapezohedral grains of garnet occur abundantly in biotite andesite and are distributed as placer garnet on surrounding slopes. It is recorded even as early as AD 743 that old gem stones were polished by the placer garnets.

Garnet found in the biotite andesite is believed to be formed by crystallization in the andesite magma which was contaminated by some argillaceous sediment in its reservoir (Omori, 1942; Yamasaki, 1958; Shiroki, 1967).

The lattice constant and specific gravity of the garnet were determined as 11.542 Å and

4.104, respectively (Omori, 1942). From the chemical analysis of garnet (Kozu and Kawano, 1939) and the physical constants mentioned above, the molecular percentages of the end-members of garnet were calculated as Alm. 67.66, Py. 13.20, Sp. 4.13, Gr. 8.58 and And. 6.43. Thus, it is an almandine-pyrope garnet with a complicated molecular composition.

A specimen of garnet was powdered carefully in a diamond mortar and then in an agate mortar. A KBr disk was made by the usual method (Omori and Kerr, 1964) for infrared study in the wave number region between 4000 and 400 cm^{-1}. The infrared spectrum was recorded by using a spectrophotometer Perkin-Elmer Model 125 with gratings.

Next, the polyethylene plate method was used for the infrared study in the wave number region between 500 and 60 cm^{-1}. The plate was covered by nujol mixed with a small amount of powdered garnet. The far infrared spectrum was recorded by using a spectrophotometer Hitachi Model FIS-1 with gratings.

Although the infrared spectrum of garnet was obtained in the wave number region between 4000 and 60 cm^{-1}, only the spectrum between 1700 and 60 cm^{-1} is shown in Figure 1, and wave numbers of the absorption bands measured are given in Table 1.

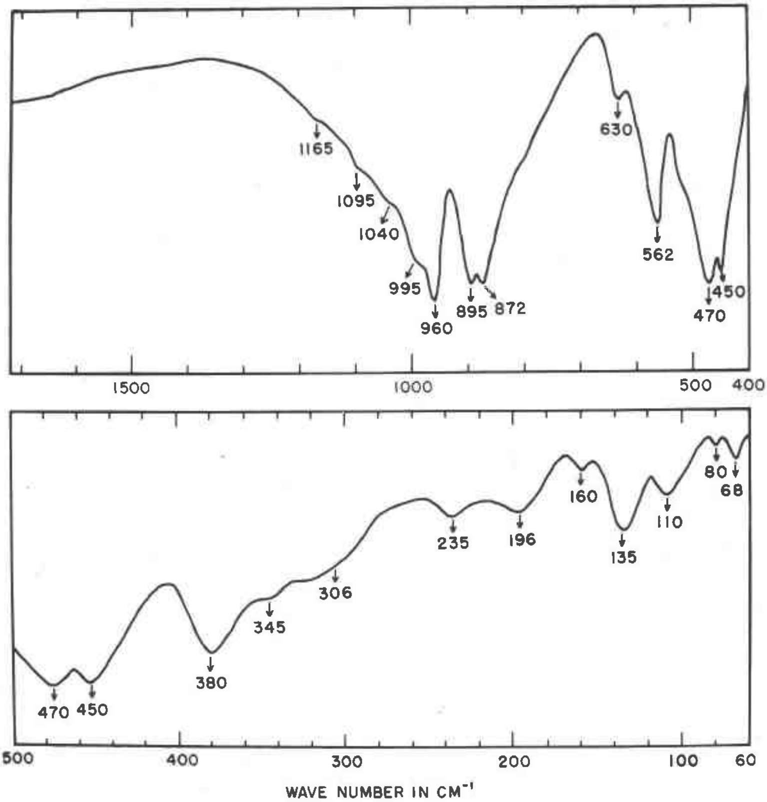

FIG. 1. Infrared absorption spectrum of almandine-pyrope garnet from Nijosan, Osaka Prefecture, Japan.

TABLE 1. WAVE NUMBERS MEASURED AND CALCULATED OF THE INFRARED ABSORPTION BANDS FOR ALMANDINE-PYROPE GARNET FROM NIJOSAN, JAPAN

Wave number (cm^{-1}) measured				Wave number (cm^{-1}) calculated		
1165	vw(sh)					
1095	vw(sh)					
1040	vw(sh)					
995	vw(sh)					
960	vs	ν_3	F_{1u}			
895	vs	ν_3	F_{1u}	920	ν_3	$F_2(SiO_4)$
872	vs	ν_3	F_{1u}			
630	m	ν_5	F_{1u}	632	ν_5	$F_{1u}(RO_6)$
562	s	ν_4	F_{1u}			
470	vs	ν_4	F_{1u}	510	ν_4	$F_2(SiO_4)$
450	vs	ν_4	F_{1u}			
380	s		F_{1u}			
345	vw(sh)					
306	vw(sh)					
235	m	ν_6	F_{1u}	234	ν_6	$F_{1u}(RO_6)$
196	m		F_{1u}			
160	w		F_{1u}			
135	s		F_{1u}			
110	m		F_{1u}			
80	w		F_{1u}			
68	m		F_{1u}			

Remarks: vs, s, m, w and vw indicate very strong, strong, medium, weak and very weak absorption bands and sh in parentheses shows a shoulder of the band.

FACTOR GROUP AND SITE GROUP ANALYSES OF GARNET AND ASSIGNMENT OF THE ABSORPTION BANDS

The 240 degrees of freedom for 80 atoms contained in the Bravais unit cell of garnet were classified under the irreducible representation of the factor group O_h shown in Table 2, which predicts 18 vibrations in the only infrared active species F_{1u} (Hurrell *et al.*, 1968; Koningstein and Toaning-Ng, 1968; Koningstein and Mortensen, 1968). One of these is the acoustic mode leaving an expected 17 infrared active modes. Thus, in Table 1 the distinct 15 normal mode frequencies measured are assigned as species F_{1u}.

Since the site groups are subgroups of the factor group, the factor group can be decomposed into the site groups. The representations of both S_4 and S_6 site groups for the SiO_4 and the $R^{3+}O_6$ ions, respectively, are composed of the characters of O_h, which are shown in column of the site group in Table 2, where the infrared active species are B, E, Au, and Eu.

TABLE 2. REDUCTION OF THE FREE SiO_4 AND AlO_6 IONS INTO THE FACTOR GROUP REPRESENTATIONS OF GARNET AND THE SELECTION RULE OF THE INFRARED ACTIVE SPECIES

Factor group							Site group							Free ion						
O_h	Si	Al	Ca	O	Total	Translation	$S_4(SiO_4)$			$S_6(AlO_6)$				$T_d(SiO_4)$			$O_h(AlO_6)$			
							A	B	E	A_g	A_u	E_g	E_u	A_1	E	F_2	A_{1g}	E_g	F_{1u}	F_{2g}
A_{1g}	0	0	0	3	3	0	1	0	0	1	0	0	0	1	1	0	1	0	0	1
A_{1u}	1	1	0	3	5	0	0	1	0	0	1	0	0	0	1	1	0	0	1	0
A_{2g}	1	0	1	3	5	0	0	1	0	1	0	0	0	0	1	1	1	0	0	1
A_{2u}	0	1	1	3	5	0	1	0	0	0	1	0	0	1	1	0	0	0	1	0
E_g	1	0	1	6	8	0	1	1	0	0	0	2	0	1	2	1	0	2	0	2
E_u	1	2	1	6	10	0	1	1	0	0	0	0	2	1	2	1	0	0	2	0
F_{1g}	2	0	3	9	14	0	1	0	2	1	0	2	0	1	1	2	1	2	0	3
F_{1u}	3	3	3	9	18	1	0	1	2	0	1	0	2	0	1	3	0	0	3	0
F_{2g}	3	0	2	9	14	0	0	1	2	1	0	2	0	0	1	3	1	2	0	3
F_{2u}	2	3	2	9	16	0	1	0	2	0	1	0	2	1	1	2	0	0	3	0
Infrared active species								I	I		I		I			I			I	

Likewise, the representations of both T_d and O_h groups for the free SiO_4 and the $R^{3+}O_6$ ions, respectively, are shown in the free ion column in Table 2, where the infrared active species are F_2 (ν_3 and ν_4) and F_{1u} (ν_5 and ν_6).

In the Bravais unit cell of garnet there are 12 SiO_4 tetrahedra and there are 12 of each of these kinds of vibrations. In the free SiO_4 ion these modes would all have the same frequency but in the crystal they are coupled and the simple molecular-like frequencies are distributed among the various irreducible representations of the factor group. Only a few appear in the infrared active F_{1u} representation and these are responsible, along with the site group splitting caused by the S_4 symmetry of the tetrahedral site, for the multiplicity of bands which appear in the SiO_4 stretching region of the spectrum. There are, in fact, many fundamentals which are observed on the other hand in the Raman spectrum and these in turn have frequencies somewhat different from the equivalent infrared frequencies because of the factor group splitting.

ANALYSIS OF THE NORMAL MODES OF VIBRATION OF THE TETRAHEDRAL SiO_4 ION IN GARNET

There should be strong coupling between the various polyhedral ions in the unit cell and this coupling is not taken into account in the normal coordinate analysis. The coupling that leads to the factor group splitting is of this type.

Assuming that the crystal can be separated into various molecular units, one fundamental frequency was calculated for a particular molecular motion when there should be many if the full unit cell is included. In the calculation of the normal coordinate analysis for the crystal usually such assumptions and limitations are inherent.

Normal modes of vibration can be analyzed theoretically by Wilson's method using the GF matrices (Wilson, Decius, and Cross, 1955; Colthup, Daly, and Wiberley, 1964). The G matrix is given by the relation of matrix multiplication form, $G=UgU'$, where U is the matrix formed by the coefficients of the symmetry coordinates, U' is the transpose of U, and g is the kinetic energy matrix given from the internal coordinates of the ion examined. The F matrix is given by the relation showing the same form, $F=UfU'$, where f is the potential energy matrix formed by the force constants.

From the G and F matrices the secular determinant is obtained as $|GF-E\lambda|=0$, where E is the unity matrix and λ is the eigenvalue of the frequency for the normal mode of vibration. Then, the frequency ν in cm^{-1} can be calculated from the relation $\nu=\sqrt{\lambda}/2\pi c$, where c is the velocity of light.

Then, the elements of the G and F matrices of the F_2 mode of vibration for the tetrahedral SiO_4 ion were calculated by using the following relations.

$$G_{11}=\mu_{(O)}+\frac{4}{3}\mu_{(Si)} \qquad F_{11}=K+1.2F$$

$$G_{12}=-\frac{8}{3\gamma}\mu_{(Si)} \qquad F_{12}=0.6rF$$

$$G_{22}=\frac{1}{\gamma^2}\left(\frac{16}{3}\mu_{(Si)}+2\mu_{(O)}\right) \qquad F_{22}=r^2(H+0.5F),$$

where $\mu_{(O)}$ and $\mu_{(Si)}$ were the reciprocal mass of the oxygen and silicon atoms, respectively; r was the bond length between the oxygen and silicon atoms; and the constants K, H, and F are the force constants in the Urey-Bradley force field (Urey and Bradley, 1931). For the SiO_4 ion K is the stretching force constant between Si-O; H is the bending force constant between O-Si-O; and F is the repulsive force constant between two oxygens O · · · O.

The force constants K 3.90, H 0.26 and F 0.80 md/Å were determined from several calculations using a computer, upon which the Jacobian matrix obtained was reflected.

The frequencies calculated, $\nu_3=920$ and $\nu_4=510$ cm^{-1}, are nearly similar to the following average values of the corresponding wave numbers measured $\nu_3=922$ and $\nu_4=511$ cm^{-1}, respectively.

The Jacobian matrix J was useful for the determination of the force constants.

$$J = \begin{bmatrix} \delta\lambda_3/\delta K & \delta\lambda_4/\delta K \\ \delta\lambda_3/\delta H & \delta\lambda_4/\delta H \\ \delta\lambda_3/\delta F & \delta\lambda_4/\delta F \end{bmatrix} = \begin{bmatrix} 0.1098875 & 0.0001887 \\ 0.0935618 & 0.2213096 \\ 0.0569697 & 0.1186374 \end{bmatrix}.$$

And the potential energy distribution (Morino and Kuchitsu, 1952) was calculated as

$$\begin{bmatrix} 0.5340518 & 0.0009174 \\ 0.0617507 & 0.1460642 \end{bmatrix},$$

from which it is known that there are couplings between the stretching vibration and the bending vibration, which are the cause of the high hardness of garnet.

The force constant K 3.90 md/Å for the SiO_4 ion in garnet is smaller than the constant K 6.00 md/Å for the SO_4 ion in alunite (Omori, 1970a) and 6.45 md/Å for sulfohalite (Omori, 1970b). The increase of the force constant K varies linearly with the decrease of specific gravity of garnet 4.104, alunite 2.82, and sulfohalite 2.48. Thus, it is found that the large frequencies of the stretching vibration occur in the lighter mineral and the small frequencies of the stretching vibration occur in the heavier mineral.

As the distances between two oxygens in the SiO_4 ion of garnet are given as 2.56 Å(2) and 2.72 Å(4), where the numbers in parentheses show the numbers of occurrence (Abrahams and Geller, 1958; Euler and Bruce, 1965), it is known that the form of the SiO_4 ion is distorted from the form of T_d. Three splitting bands of the triple degenerate species are caused by the slight distortion of the SiO_4 ion (Wickerheim, Lefever, and Hanking, 1960).

ANALYSIS OF THE MODES OF VIBRATION OF THE OCTAHEDRAL $R^{3+}O_6$ ION IN GARNET

Since the octahedral $R^{3+}O_6$ ion is larger than the tetrahedral SiO_4 ion and it is believed that the bonding of R to oxygen is of the same order of strength as the bonding of oxygen to other parts of the structure, the octahedral ion vibrates much more weakly than the tetrahedral ion, thus the absorption bands of the octahedral ion appear weakly in the smaller wave number region than the tetrahedral ion. But, it seems that the determination of the force constants of the octahedral ion are not useless, because these can be compared with the constants of the tetrahedral ion.

The wave numbers of the octahedral RO_6 ion were calculated by using the following elements in the G and F matrices.

$$G_{11} = \mu_{(O)} + 2\mu_{(R)} \qquad F_{11} = K + 1.8F$$

$$G_{12} = -\frac{4}{\gamma}\mu_{(R)} \qquad F_{12} = 0.9rF$$

$$G_{22} = \frac{2}{\gamma^2}(\mu_{(O)} + 4\mu_{(R)}) \qquad F_{22} = r^2(H + 0.55F),$$

where $\mu_{(O)}$ and $\mu_{(R)}$ are the reciprocal masses of the oxygen atom and the R atom respectively, and r is a bond length between oxygen and the R atom. The force constants in the Urey-Bradley force field were K 1.60, H 0.14, and F 0.001 md/Å, obtained from the similar calculations mentioned above. The calculated wave numbers, $\nu_5=632$ cm^{-1} and $\nu_6=234$ cm^{-1}, are similar to the measured wave numbers, $\nu_5=630$ cm^{-1} and $\nu_6=235$ cm^{-1}, respectively, where the Jacobian matrix obtained was

$$J = \begin{bmatrix} 0.1294661 & 0.0023918 \\ 0.1995772 & 0.2028793 \\ 0.0534694 & 0.1555413 \end{bmatrix}$$

and the potential energy distribution calculated was

$$\begin{bmatrix} 0.2071457 & 0.0038268 \\ 0.0000000 & 0.0285146 \end{bmatrix},$$

from which it is known that the ν_5 band is the pure stretching vibration (R—O), but the ν_6 band is the bending vibration (O-R-O) coupled with the stretching vibration.

CONCLUSIONS

The infrared absorption spectrum of almandine-pyrope garnet from Nijosan, Osaka Prefecture, Japan was obtained in the wave number region between 1700 and 60 cm^{-1} and the wave numbers of the absorption bands were measured. The cause of the splits of the absorption bands of ν_3 and ν_4 are interpreted.

It is important in the infrared study of minerals that the absorption bands should be theoretically analyzed. The factor group and the site group analyses for the Bravais unit cell of garnet were discussed and the numbers of the infrared active mode of vibration obtained from the selection rule were similar to the numbers of the absorption band obtained.

It is believed that there are strong couplings between the various SiO_4 ions in the structure of garnet, and the vibration of the RO_6 ion is weaker than the SiO_4 ion. But, it is useful to determine the force constants of these ions.

By using Wilson's *GF* matrices the wave numbers of the absorption bands were calculated and were compared with the wave numbers measured as shown in Table 1. The Jacobian matrix was useful in the course of the calculation of the force constant, and the potential energy distribution obtained was also necessary to know the existence of the coupling between the vibrations.

ACKNOWLEDGMENTS

The author is grateful to Newberry Professor Em. Paul F. Kerr of Columbia University for encouragement in the study and critical reviews of the manuscript, and to Professor Taro Isobe and Mr. Shinji Onodera of the Chemical Research Institute of Non-Aqueous Solutions, Tohoku University and Dr. Junnosuke Fujita of the Department of Chemistry, Tohoku University for help in conducting the infrared study.

REFERENCES

ABRAHAMS, S. C., AND S. GELLER (1958) Refinement of the structure of a grossularite. *Acta Crystallogr.* **11,** 437–441.

COLTHUP, N. B., L. H. DALY, AND S. E. WIBERLEY (1964) *Introduction to Infrared and Raman Spectroscopy.* Academic Press, New York.

EULER, F., AND J. A. BRUCE (1965) Oxygen coordinates of compounds with garnet structure. *Acta Crystallogr.* **19,** 971–978.

HURRELL, J. P., AND S. P. S. PORTO (1968) Optical phonons of yttrium aluminum garnet. *Phys. Rev.* **173,** 851–856.

KONINGSTEIN, J. A., AND O. SONNICH MORTENSEN (1968) Laser-excited phonon Raman spectrum of garnets. *J. Mol. Spectrosc.* **27,** 343–350.

——— AND TOANING-NG (1968) Laser-induced phonon spectrum of an oriented crystal of thulium gallium garnet. *J. Opt. Soc. Amer.* **58,** 1462–1465.

KOZU, S., AND Y. KAWANO (1939) Chemical composition of garnet from Anamushi. *J. Jap. Ass. Mineral. Petrology Econ. Geol.* **21,** 80–85 [in Japanese].

LAUNER, P. J. (1952) Regularities in the infrared absorption spectra of silicate minerals. *Amer. Mineral.* **37,** 764–784.

MORINO, Y., AND K. KUCHITSU (1952) A note on the classification of normal vibrations of molecules. *J. Chem. Phys.* **20,** 1809–1810.

OMORI, K. (1942) Studies of garnets in the andesites forming the volcano Nijosan. *J. Jap. Ass. Mineral. Petrology Econ. Geol.* **27,** 27–58, 69–87 [in Japanese].

——— (1970a) Normal modes of vibration of alunite. *J. Mineral. Soc. Jap.* **10,** 1–9 [in Japanese].

——— (1970b) Infrared study of sulfohalite. *Amer. Mineral.* **55,** 1897–1910.

——— AND P. F. KERR (1964) Infrared studies of sulfates from 11 to 25 microns. *Sci. Rep. Tohoku Univ.*, Ser. 3, **9,** 1–55.

SHIROKI, K. (1967) Chromium contents of the garnets and biotites in Nijosan volcanic rocks. *J. Jap. Ass. Mineral. Petrology Econ. Geol.* **57,** 25–30 [in Japanese].

TARTE, P. (1965) Étude experimentale et interprétation du spectre infra-rouge des silicates et des germanates. *Mém. Acad. Roy. Belg.* **35,** no. 4a, 1–260, no. 4b, 1–134.

UREY, H. C., AND C. A. BRADLEY (1931) The vibrations of pentatonic tetrahedral molecules. *Phys. Rev.* **38,** 1969–1978.

WICKERHEIM, K. A., R. A. LEFEVER, AND B. M. HANKING (1960) Infrared absorption spectrum of silicate ion in the garnet structure. *J. Chem. Phys.* **32,** 271–276.

WILSON, E. B., J. C. DECIUS, AND P. C. CROSS (1955) *Molecular Vibrations.* McGraw-Hill, New York.

YAMASAKI, M. (1958) Notes on rock-forming minerals (2), Garnet from volcanic rocks. *J. Geol. Soc. Jap.* **64,** 601–604 [in Japanese].

Manuscript received, July 21, 1970; accepted for publication, January 18, 1971.