

Crystal Chemistry of Ca-Garnets from Ulchin Pb-Zn Deposits: A Study of Mineral Spectroscopy

울진 연·아연 광상에서 產出되는 Ca석류석의 결정화학: 광물분광학적 연구

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ABSTRACT: Ca-garnets (andradite and grossular) from the Ulchin Pb-Zn deposits show different physical properties (color, hardness, and specific gravity) due to the differences in their crystal chemistry. Four garnets showing different colors were systematically studied using EPMA, XRD, Mössbauer and IR spectroscopy for chemical, structural, and crystal chemical analyses. Optical and physical properties of microhardness and density were also examined.

Chemical analyses indicate that garnet colors change from pale pink through yellowish green, reddish brown, to dark green with the increase of Fe contents in the range from 0.35 to 1.92 mole %. Such substitution of Fe³⁺ for Al affects the unit cell dimension from 11.91Å to 12.06Å. Mössbauer parameters reveal that the isomer shift (δ) varying linearly from 0.372 to 0.389 mm/sec, results from the increase in Y-O distance by Fe³⁺ substitution for Al. Thus the increase in the Y-O distances should push the neighboring edge-shared X-dodecahedron and make it more distorted and lower the internal symmetry around X-cation. These produce the fingerprint IR spectra in the range of 300~360cm⁻¹, but absent in grossular. Since Z-tetrahedra are corner-shared with Y-octahedra, the effect of the substitution in Y-site on Z-site is not much noticeable. While Fe-rich andradites show no evidence of Fe²⁺, only grossular has a small amount of Fe²⁺. This apparently suggests that formation of grossular might be affected by the low oxygen fugacity in the solution.

요약: 울진 연·아연 광상의 Ca석류석은 결정화학적 성질의 차이에 따라 색, 경도, 비중과 같은 물리적 특성이 달라진다. 자기 다른 색을 보여주는 네가지의 석류석에 대하여 전자현미분석, X-선 회절분석, 뫼스bauer 및 적외선 분광분석등을 실시하여 화학적, 구조적 및 결정화학적 특징을 연구하였으며 광학적 및 물리적 특성도 연구되었다.

화학분석에 의하면 Fe함량이 0.35에서 1.92몰%로 증가함에 따라 석류석의 색이 연분홍, 황록색, 적갈색 및 암갈색의 순으로 변한다. 이러한 Al에 대한 Fe의 치환은 단위포의 크기에도 영향을 미쳐 11.91Å에서 12.06Å으로 단위포의 크기가 증가한다. 뫼스bauer 계수에 따르면 Fe치환에 따른 Y-O 거리의 증가로 δ 값이 0.372에서 0.389mm/sec로 일정하게 증가한다. 또한 능을 공유하며 이웃하는 X십이면체에 영향을 주어 내부대칭도를 떨어뜨리게 된다. 이러한 현상은 적외선 스펙트럼의 360~300cm⁻¹의 영역에서 그로술라에는 관찰되지 않는 수개의 흡수선이 안드라다이트에서는 관찰된다. 한편 소량의 Fe²⁺가 그로술라에서만 관찰됨을 미루어 석류석의 생성이 용액내의 낮은 산소분압에 영향을 받았을 것으로 추측된다.

INTRODUCTION

The garnet, one of the important rock-forming minerals, is of a diverse group of minerals in physical and chemical properties, and even in the mode of occurrence. Because of such diversity, garnet has been studied by many mineralogists and geologists in many different ways and viewpoints. In chemistry, the garnet (ideal formula, $X_3Y_2Z_3O_{12}$) has a strong ability to substitute cations with a wide range of size and valence state. Such chemical behavior leads to variation in physical properties, that is, color varies from white, through pink, dark red, brown, pale green to dark green, to black, and hardness increases from 6.5 to 7.5, and specific gravity from approximately 3.5 to 4.3 (Meagher, 1980). Most garnets are commonly found in contact and regional metamorphic environment, but they are also found in igneous rocks.

Ca-rich garnets play a very important role as one of the skarn minerals in the contact metamorphic rocks. In most skarn deposits like Zn-Pb ore deposits in Ulchin mine, garnet is closely associated with other skarn minerals such as clinopyroxenes, amphiboles, epidote, etc. Almost all of them are directly related with the ore formation in skarn deposits. Ca-rich garnet whose endmembers are andradite ($Ca_3Fe_2Si_3O_{12}$) and grossular ($Ca_3Al_2Si_3O_{12}$) ideally contains trivalent cations in the octahedral sites, while clinopyroxene as the solid solution of hedenbergite ($CaFeSi_2O_6$) and diopside ($CaMgSi_2O_6$) indicates the substitution of divalent cations in octahedral sites. Thus, the association of garnet and clinopyroxene may give a clue to the depositional environment such as oxygen fugacity.

Because garnet exhibits a wide range of cation

substitution, the crystal chemistry of garnet is somewhat complex and still controversial (Amthauer, *et al.*, 1976; Huggins, *et al.*, 1976; Schwartz, *et al.*, 1980). Early crystal chemical study of garnet (Zedlitz, 1933, 1935; Kunitz, 1936; Tarte, 1960; Lehiarvi, 1966; Ito and Frondel, 1967) revealed that substitution of cation is related with a severe Si deficiency in tetrahedral sites which leads to unusual oxidation states and coordination numbers. Since Mössbauer spectroscopy was introduced to the study of crystal chemistry in the late 1960s, a number of Mössbauer spectral study of garnets were made (Dowty and Appleman, 1970; Burns and Burns, 1971; Burns, 1972; Huggins, 1975; Huggins, *et al.*, 1976, 1977a, b; Weber, *et al.*, 1975; Schwartz, *et al.*, 1980). The proportion and site populations of coexisting Fe^{2+} , Fe^{3+} , and/or Ti^{3+} , Ti^{4+} were quantitatively determined. Mössbauer spectroscopy has been used to determine the Fe^{2+}/Fe^{3+} ratios and site occupancies of Fe cation in minerals which are not possible by the conventional chemical analysis and crystal structural refinement (Burns, 1972; Bancroft, 1973; Marfunin, 1979). Thus more precise crystal chemistry requires a study of Mössbauer spectroscopy.

In this work, the authors not only compare four different garnets having different physical and chemical properties but also examine the crystal chemistry of the garnets by the aid of mineral spectroscopy, and further suggest the depositional environment of the Zn-Pb ores in the Ulchin mine area. To do so, garnets have been systematically examined by various methods: Optical properties, texture, and other paragenetic relationships were studied by the polarizing microscope and microhardness and density were also determined for each characteristic sample. Chemical analyses were done by an electron probe microanalyser. X-ray diff-

ractometer was used for structural analyses and unit cell determination. Infrared spectra were obtained for the study of mineral spectroscopy. In addition, Mössbauer spectroscopy was done especially for the investigation of the Fe-cation behavior in the garnet crystal chemistry.

EXPERIMENTAL

The garnet samples of their different colors were carefully selected. For separation, each sample was crushed and sieved into 100~150 mesh in size. The sample was cleaned and loaded on the magnetic separator and residual impurities were finally removed by hand-picking under the microscope. These separated garnets were then prepared for XRD, Mössbauer, and IR analyses. The polished thin sections were also prepared for chemical analyses and other physical tests including microscopic observation.

Chemical analyses of the garnets were made by an electron probe microanalyzer (EPMA), JEOL Superprobe 733 in the Department of Geology, Yeonse University, at 15KV with beam current $0.01\mu\text{A}$ and beam diameter of $10\mu\text{m}$. Bense and Albee's method was applied for calibration.

The X-ray powder diffraction pattern were obtained by the Fe-filtered $\text{CoK}\alpha$ radiation using the ZEOL X-ray powder diffractometer (30KV/15mA). The indexed diffraction data were refined by the least square program (Appleman and Evance, 1973; Benoit, 1987) which was implemented for the IBM PC-XT Computer (Garvey, 1986).

Mössbauer spectra were recorded on a constant acceleration ASA (Austin Science Associates) S600 Mössbauer Spectrometer, using 1024 channels of a Nuclear Data multichannel analyzer

with ^{57}Co source in a rhodium matrix (5 millicurie), available in the Department of Physics, Dongkuk University.

For the Mössbauer measurement, the separated samples were ground with acetone which helps to prevent Fe^{2+} ions from oxidizing and weighed to get total iron concentration of approximately $10\text{mg}/\text{cm}^2$. In order to obtain a relatively good absorbance in the Mössbauer spectra for the best statistics and to prevent line broadening, the total iron concentration of $5\sim 10\text{mg}/\text{cm}^2$ is the optimum range for most Fe-bearing silicates (Choi, 1983). The sample was then mounted in a holder with a round hole (2cm in diameter) and run at 300°K (room temperature). Each spectrum was accumulated for over 2 days to acquire at least 3×10^5 counts of baseline per channel for good statistics within the velocity range of $\pm 9\text{mm}/\text{sec}$ and calibrated relative to metallic Fe foil. The Mössbauer spectra were transferred to Apple II minicomputer to execute curve-fitting calculations and to plot the simulated curve. For curve-fitting, the BASIC program employed the Gauss non-linear regression method, assuming Lorentzian curve shapes with various input parameters.

Infrared absorption spectra were obtained with Perkin Elmer 283B spectrophotometer in the Department of Physics, Seoul National University. Approximately 3 mg of powdered sample was dispersed on KBr disks in the region of $4000\sim 200\text{cm}^{-1}$.

GENERAL MINERALOGY

Occurrences

In the Ulchin mine area near the eastern margin of the Taebaegsan metallogenic belt in the middle eastern part of southern Korea, garnet is a very common skarn mineral throughout the deposits. The garnet is usually asso-

Crystal Chemistry of Ca-Garnets

ciated with clinopyroxenes in the exoskarn near rhyodacite. Most of garnets are crystallized in the early stage of skarnization, but sometimes form in the late stage as veinlets along with quartz. The garnets are usually found as coarse-grained euhedral aggregates commonly with clinopyroxenes of diopsidic to ferrosalite composition and calcite, and less commonly with pyrrhotite, epidote, actinolite, and quartz.

Skarns are developed mainly in limestone of the Myobong Slate and the Pungchon Limestone in contact with biotite granite (297 ± 2.0 Ma) or rhyodacite (49.3 ± 2.0 Ma) (Kim and Yoon, 1972; Yun and Park, 1979). Chimney-like Zn-Pb ore body ranging from 100 to 150m in height is developed crossing the skarnized roofpendant of Cambrian formations within the granites. Detailed occurrence of ores and skarns are given by Yun and Einaudi (1982).

Physical Properties

Garnet is usually found as dodecahedral to trapezohedral coarse-grained aggregates in the range of 1~2cm in size. Garnets exhibit various characteristic colors: pale pink, yellowish green, reddish brown, and dark green. Their physical and optical properties are summarized in Table 1.

Garnet Structure

Because of the characteristic crystal morpho-

logy, the structure of garnet has been well established with the powder diffraction study of grossular (Menzer, 1926). Later, Menzer (1928) suggested that remaining common natural garnets were structurally analogous to the grossular which considered to be isometric with body-centered unit cell of space group symmetry Ia3d and their general formula is $X_3Y_2Z_3O_{12}$ with eight formulae units per cell. The X-, Y-, and Z-cations respectively occupy their own special sites in the structure which are determined by the space group symmetry.

Recently, more detailed X-ray study and crystal chemistry of natural garnets were established by Novak and Gibbs (1971). They illustrated polyhedral configuration of the ideal garnet structure (Fig. 1). According to Novak and Gibbs (1971), X-cations are coordinated by eight oxygens making a distorted cube which is described as a triangular dodecahedron (See Fig. 1). X-cation sites have the permissible range of radii (r_x) of 0.8 to 1.1 Å (Zemann, 1962) and are usually occupied by Mg, Fe²⁺, Mn, and Ca. Y-cations are coordinated by six oxygens at the vertices of a slightly distorted octahedron. Octahedral Y-cations are typically Al, Fe³⁺, Cr with minor occupancies for V³⁺, Ti and Fe²⁺ and occupy a position of point symmetry $\bar{3}$ (Meagher, 1975). Z-cations

Table 1. Physical and optical properties of the garnet from the Ulchin mine.

Sample	Color	Specific gravity	Vickers hardness	Birefringent	Twining	Zonning
Grossular	pale pink (colorless in thin section)	3.76	1184~1268	birefringent	second twinning	common
Andradite	yellowish green (pale brown in thin section)	3.85	1145~1192	weakly birefringent at the margin	thin lamella twin	less common
Andradite	reddish brown (pale brown in thin section)	3.82	1160~1181	birefringent at the margin	thin lamella twin	n.d.
Andradite	dark green (pale brown with greenish tint in thin section)	3.92	1232~1286	nearly isotropic	n.d.	n.d.

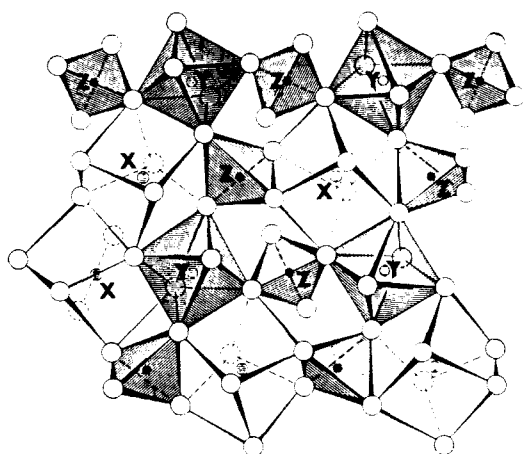


Fig. 1. The garnet structure projected down the c axis (after Novak and Gibbs, 1971).

a distorted tetrahedron which are mainly occupied by Si^{4+} cations and minor amounts of Fe^{2+} , Fe^{3+} , Ti^{4+} , and Al have been reported in these sites.

As shown in Fig. 1, the garnet structure exhibits the alternative linkage of ZO_4 tetrahedra and YO_6 octahedra where tetrahedra share each corner with adjacent octahedra and vice versa to constitute a continuous three dimensional arrangement. It is noted that two tetrahedra never share a common corner with each other, so classified as an orthosilicate. YO_6 octahedra share half of their own edges with adjacent dodecahedron indicating neither share of corners nor edges with one another. Only XO_8 dodecahedra show a edge-shared arrangement in the

are tetrahedrally coordinated by oxygens in

Table 2. Chemical analyses of Ca-garnets by EPMA.

	pale pink grossular		yellowish brown andradite		reddish brown andradite		dark green andradite	
	1-1	1-2	2-1	2-2	3-1	3-1	4-1	4-2
SiO_2	37.33	37.60	36.04	35.97	35.41	34.26	34.54	35.06
TiO_2	—	—	—	0.06	0.04	0.02	0.84	0.40
Al_2O_3	19.08	18.12	5.27	8.39	2.95	2.86	0.34	0.87
Fe_2O_3	5.69	6.50	24.16	20.62	27.58	28.15	30.69	30.15
FeO^*	0.20	0.23	—	—	—	—	—	—
MnO	1.16	1.18	1.84	2.53	1.38	1.12	—	—
MgO	0.02	—	0.11	0.10	0.07	0.04	0.19	0.11
CaO	35.55	35.68	32.28	32.67	33.49	32.75	33.36	33.35
Total	99.04	99.31	99.70	100.34	100.02	99.20	99.96	99.93

Numbers of ions on the basis of 24 oxygens

Si	5.813	6.00	5.859	6.00	5.965	6.00	5.858	6.00	5.835	6.00	5.814	6.00	5.850	5.91	5.916	6.00
Al	0.187	—	0.141	—	0.035	—	0.142	—	0.165	—	0.186	—	0.061	—	0.084	—
Al	3.314	—	3.182	—	0.989	—	1.472	—	0.425	—	0.385	—	—	—	0.099	—
Ti	—	4.00	—	3.98	—	4.00	0.010	4.01	0.010	3.93	—	3.98	0.112	4.02	0.051	4.00
Fe^{3+}	0.690	—	0.793	—	3.102	—	2.523	—	3.497	—	3.590	—	3.910	—	3.836	—
Mg	—	—	—	—	0.034	—	0.020	—	0.020	—	0.010	—	0.051	—	0.030	—
Fe^{2+}	0.003	6.09	0.003	6.11	—	6.02	—	6.07	—	6.28	—	6.13	—	6.11	—	6.07
Mn	0.150	—	0.159	—	0.258	—	0.352	—	0.193	—	0.163	—	—	—	—	—
Ca	5.934	—	5.953	—	5.727	—	5.702	—	6.069	—	5.957	—	6.059	—	6.038	—
Andradite	0.17	0.20	0.75	0.63	0.89	0.90	1.00	0.97	—	—	—	—	—	—	—	—
Grossular	0.83	0.80	0.25	0.37	0.11	0.10	—	—	—	—	—	—	—	—	—	—

*: determined by a Mössbauer spectroscopic method.

garnet structure.

RESULTS AND DISCUSSION

Chemical Analyses

Chemical analyses of garnets are given in Table 2, indicating that the garnets belong to andradite-grossular series in composition. Pale pink garnet is grossular-rich (Gr: 80~83mole%), whereas other types of garnets are strikingly andraditic (An: 63~100mole%) in composition. Some titaniferous (TiO_2 : 0.04~0.84 wt%) members are found in the andradite-rich garnets. All the garnets except for the dark green member contain considerable amounts (1.12~2.53wt%) of Mn. Mössbauer spectroscopic examination of the garnets shows that only pale pink grossular contains trace amounts (0.20~2.53wt%) of ferrous iron.

X-ray Powder Diffraction Analysis

The X-ray diffraction patterns for four different garnets are illustrated in Fig. 2. Refined diffraction data and calculate unit-cell data (a) are given in Tables 3 and 4, respectively.

As shown in Table 3, characteristic reflection of the garnets are 4.251~4.265Å (220), 2.974~3.016Å (400), and 2.660~2.698Å (420). The other major peaks of the garnets show a distinct shift toward the lower two theta angle with increasing Fe contents due to the substitution of bigger Fe for Al. It is noted that the reflection of (220) is missing in the pale pink grossular, while the reflection of (230) is only found in this one. In general, cation substitutions in crystallographic sites result in the change of space group symmetry. As far as the Ca-garnet structure is concerned, indexing can be made on the basis of the body-centered cell of space group symmetry $Ia\bar{3}d$ and the (230) reflection is forbidden by the extinction rule. One

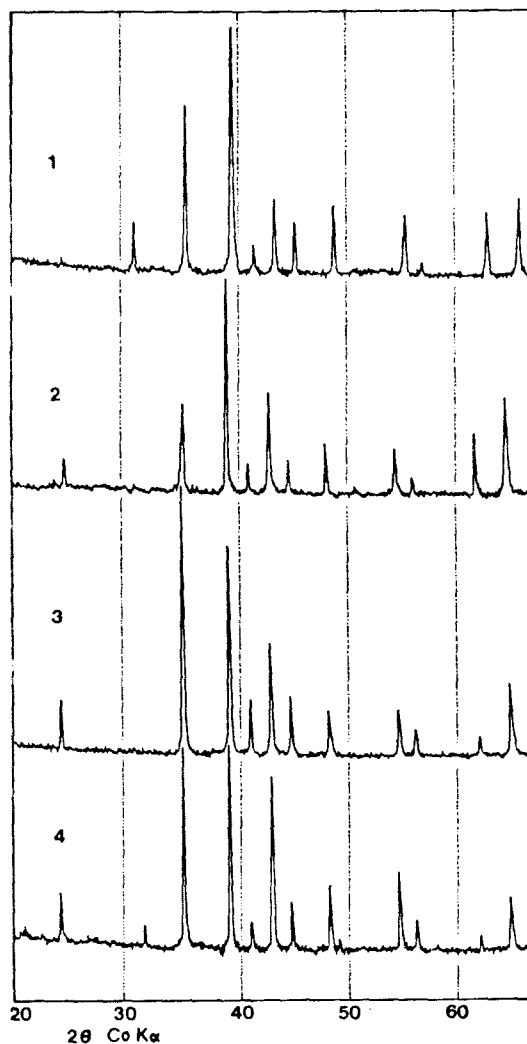


Fig. 2. X-ray diffraction patterns of the Ca-garnets. (1) pale pink grossular, (2) yellowish green andradite, (3) reddish brown andradite, (4) dark green andradite.

possible explanation is that the substitution of Fe^{3+} by smaller Al causes the size of octahedral sites decrease and forms more distorted shape. It may lower the symmetry and decrease in local symmetry makes it possible to generate the (230) found in pale pink grossular.

Unit-cell parameters are closely related with the garnet chemistry (Table 4), that is, substitution of Al for Fe in the YO_6 site results in the decrease of unit-cell dimension from

Table 3. Observed and refined X-ray powder diffraction data for Ca-garnets.

hkl	Pale pink grossular			Yellowish green andradite			Reddish brown andradite			Dark green andradite		
	<i>d</i> (cal)	<i>d</i> (obs)	<i>I</i> / <i>I</i> ₀	<i>d</i> (cal)	<i>d</i> (obs)	<i>I</i> / <i>I</i> ₀	<i>d</i> (cal)	<i>d</i> (obs)	<i>I</i> / <i>I</i> ₀	<i>d</i> (cal)	<i>d</i> (obs)	<i>I</i> / <i>I</i> ₀
220	—	—	—	4.26	4.25	10	4.26	4.25	15	4.26	4.25	20
230	3.30	3.34	20	—	—	—	—	—	—	—	—	—
321	—	—	—	—	—	—	—	—	—	3.22	3.25	7
400	2.98	2.98	80	3.01	3.01	30	3.01	3.01	100	3.01	3.01	100
420	2.66	2.66	100	2.69	2.69	100	2.70	2.69	70	2.70	2.70	100
332	2.53	2.54	10	2.57	2.57	10	2.57	2.57	15	2.57	2.57	10
422	2.43	2.43	30	2.46	2.46	40	2.46	2.46	30	2.46	2.50	80
510, 431	2.34	2.33	20	2.36	2.36	15	2.36	2.36	15	2.36	2.36	20
521	2.17	2.17	25	2.19	2.20	20	2.20	2.20	10	2.20	2.20	30
440	—	—	—	—	—	—	—	—	—	2.13	2.17	3
611, 532	1.932	1.933	20	1.953	1.953	20	1.956	1.959	10	1.955	1.956	40
620	1.883	1.885	3	1.904	1.904	5	1.906	1.905	7	1.906	1.907	20
444	1.719	1.717	25	1.738	1.741	20	1.740	1.741	3	1.740	1.741	5
640	1.651	1.650	30	1.670	1.671	30	1.672	1.672	25	1.672	1.673	20

Table 4. Unit cell parameters of Ca-garnets.

Sample	Composition of X and Y	<i>a</i>	<i>a</i> *
Pale pink grossular	(Fe _{0.35} ³⁺ Al _{1.166}) (Si _{2.91} Al _{0.09})	11.908	11.895
Yellowish green andradite	(Fe _{1.55} ³⁺ Al _{0.49}) (Si _{2.98} Al _{0.02})	12.041	12.038
Reddish brown andradite	(Fe _{1.50} ³⁺ Al _{0.19}) (Si _{2.91} Al _{0.09})	12.051	12.050
Dark green andradite	(Fe _{1.62} ³⁺ Al _{0.05}) (Si _{2.98} Al _{0.04})	12.056	12.054
Grossular**	Al ₂ Si ₃	11.851	
Andradite**	Fe ₂ Si ₃	12.048	

* Data obtained from the empirical equation (Novak and Gibbs, 1971).

** Data taken from Skinner (1956).

12.06 Å in dark green andradite to 11.91 Å in pale pink grossular. The relationship between the chemistry and the crystal structure of garnets has been studied for past two decades (Zemann, 1962; Geller, 1967; Novak and Gibbs, 1971). Using the 'hard-sphere ionic model', Novak and Gibbs (1971) established the empirical equation to relate the unit-cell with garnet chemistry. If one knows the mean radii of X- and Y-cations (r_X and r_Y , respectively), he can

estimate the unit-cell parameter (*a*) using the following empirical equation:

$$a(\text{Å}) = 9.04 + 1.61(r_X) + 1.89(r_Y)$$

According to equation using effective ionic radii (Shannon and Prewitt, 1969), cell parameters (*a*) for dark green andradite and pale pink grossular are calculated as 12.054 Å and 11.895 Å, respectively. These values match well with the X-ray diffraction data shown in Table 4.

Mössbauer Spectroscopy

Final fitted spectra are shown in Fig. 3 and calculated Mössbauer parameters are summarized in Table 5. The Mössbauer absorbance increa-

ses with Fe content from 7 to 15%. All spectra except pale pink grossular (Fig. 3-1) show two distinguished peaks which allow the resolution of one doublet being assigned to Fe³⁺ cations in octahedral Y-site on the basis of

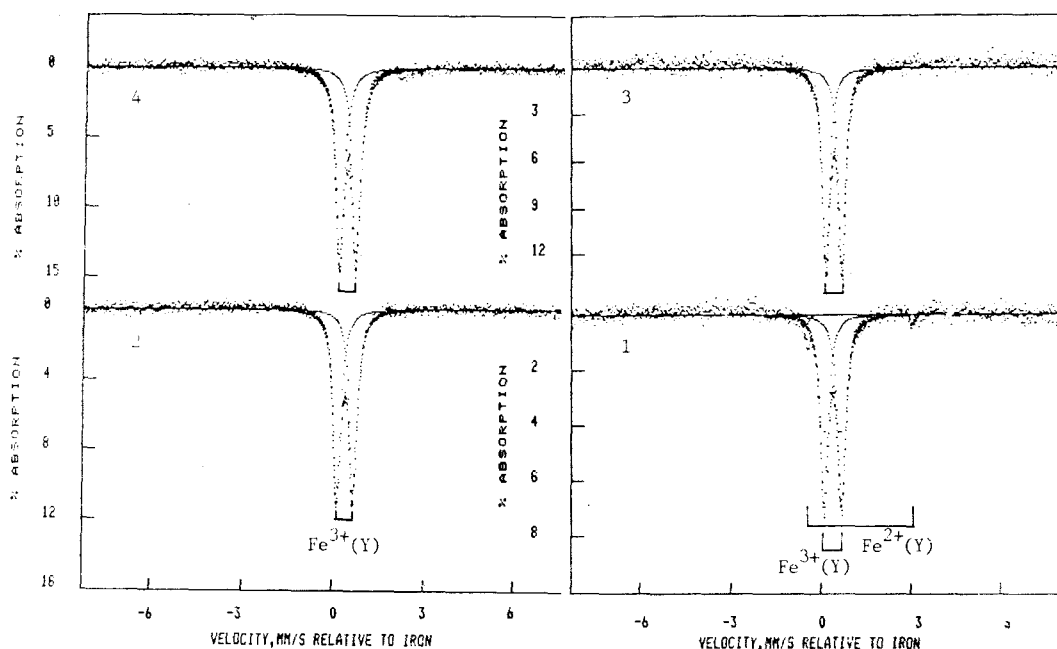


Fig. 3. The fitted Mossbauer spectra of the Ca-garnets. (1) pale pink grossular, (2) yellowish green andradite, (3) reddish brown andradite, (4) dark green andradite.

Table 5. Mössbauer parameters for the Ca-garnets.

		1	2	3	4	5	6
Fe ³⁺ /Oct	I.S.	0.372	0.382	0.385	0.389	0.420	0.431
	Q.S.	0.581	0.537	0.538	0.558	0.560	0.589
	Width	0.297	0.290	0.278	0.318	0.260	0.285
	%Area	96.2	100.0	100.0	100.0	100.0	94.8
Fe ²⁺ /Oct	I.S.	1.252	—	—	—	—	1.162
	Q.D.	3.534	—	—	—	—	2.587
	Width	0.384	—	—	—	—	0.327
	%Area	3.8	—	—	—	—	5.2
	χ ²	17.1	53.0	24.3	46.8	—	—

All values of I.S., Q.S., and width in mm/sec relative to metallic foil.
 1. pale pink grossular; 2. yellowish green andradite; 3. reddish brown andradite; 4. dark green andradite;
 5. andradite, alkali syenite, from Semarule, Botswana (Schwartz, *et al.*, 1980); 6. melanite, serpentine from San Benito, California (Schwartz, *et al.*, 1980)

Mössbauer parameters. Pale pink grossular exhibits one distinct doublet due to absorption by Fe^{3+} in Y-site, too. In addition, it has a couple of small peaks of which one is found near the limb of the Fe^{3+} peak in the lower velocity region and the other is located at the velocity of approximately 3mm/sec. This small doublet is attributed to the absorption of Fe^{2+} in Y-site.

The isomer shift (δ) and quadrupole splitting (Δ) obtained for Fe^{3+} in Ca-garnets are in the range of 0.372~0.389mm/sec and 0.537~0.581 mm/sec, respectively and show consistency with one another. The δ values obtained in this study are slightly lower than that of the Sema-rule andradite (Table 5-5, 0.420mm/sec). It seems that the difference is attributed to the different occurrences. However, these values agree well with the isomer shift for Fe^{3+} in octahedral sites found in other silicates. The isomer shift and quadrupole splitting for Fe^{2+} from pale pink grossular are 1.252 and 3.534 mm/sec, respectively. The isomer shift here is somewhat large for Fe^{2+} in octahedral site (in most cases, the range of δ for $\text{Fe}^{2+}/\text{oct}$ is between 1.10 and 1.20mm/sec). This apparently indicates an error in the computer fitting. Such an experimental error may easily be

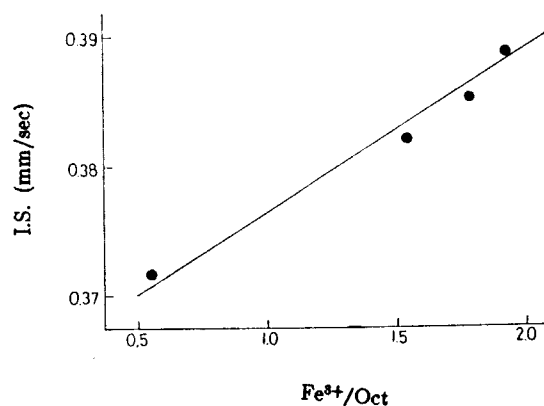


Fig. 4. The variation of isomer shift with respect to ferric cation in the YO_6 site.

generated by fitting of low intensity peaks.

Two interesting results are derived from the Mössbauer spectral study. First, the isomer shifts for Fe^{3+} have a linear relationship with varying Fe contents. Fig. 4 illustrates the linear trend of isomer shift with respect to Fe contents in Ca-garnets. The isomer shift increases with increasing Fe content. Increase of Fe^{3+} occupancies within YO_6 site implies the increase in average metal-oxygen distance. Decrease in s -electron density around Fe nucleus results in increase of isomer shift. This satisfies the well-known nature of isomer shift.

Second, only the pale pink garnet with the least Fe content has small amount of Fe^{2+} cation while the other garnets have no evidence of Fe^{2+} presence (Table 5). This may suggest that the pale pink garnet formed under low oxygen fugacity.

Infrared Absorption Spectroscopy

The infrared absorption spectra of four different garnets are shown in Fig. 5. The infrared absorption bands for Ca-garnets are characterized by the range of 1,000~800 cm^{-1} due to Si-O stretching vibration (ν_3) in the symmetry of tetrahedral sites (S_4), 620~500 cm^{-1} to O-Si-O bending (ν_2 & ν_4) in the same symmetry (S_4), 490~460 cm^{-1} to Fe (or Al)-O stretching in the octahedral symmetry (S_6), and by the region below 450 cm^{-1} ascribed to Ca-O stretching in the symmetry of 8-fold coordination (D_2) (Moore and White, 1971). As shown in Fig. 5, pale pink grossular garnet (Fig. 5-1) is readily distinguishable from other andraditic garnets by their finger-print spectra in the range of 360~300 cm^{-1} . It is also noted that the absorption bands of ν_2 , ν_3 , and ν_4 in the grossular are shifted to the direction of increasing wavenumber by approximately 20 cm^{-1} relative to those of andradites.

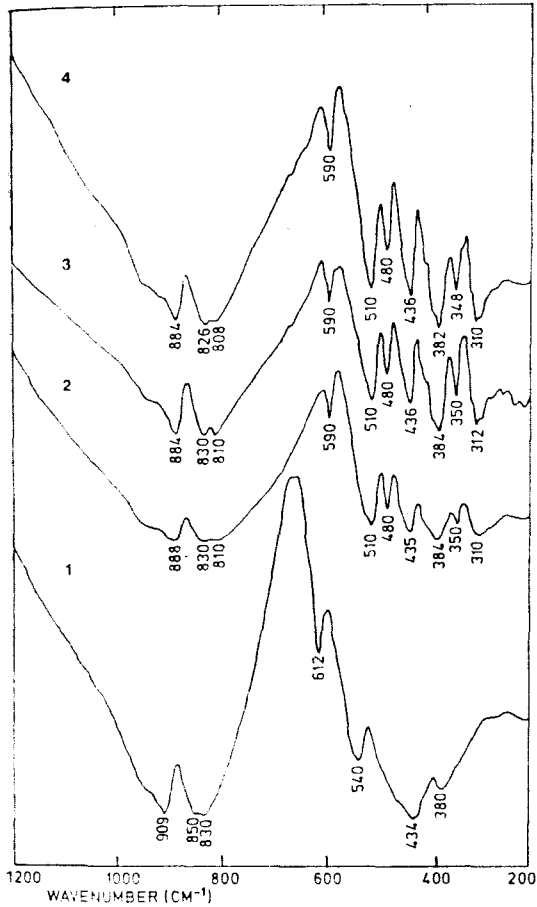


Fig. 5. IR spectral patterns of the Ca-garnets. (1) pale pink grossular, (2) yellowish green andradite, (3) reddish brown andradite, (4) dark green andradite.

Comparing infrared absorption spectra of Ca-garnets with one another, substitution of Fe by Al in octahedral sites decreases the metal-oxygen distances and thus sharing oxygen of neighboring tetrahedron become stretching out, leading to increase of vibration energy which results in a shift of absorption bands. The absorption of Ca-O vibration expect to be affected by the cation occupancy in the YO_6 site, because both sites are edge-shared. Actually, in the Ca-garnets as mean radius of Y-site increases from 0.53Å in grossular to 0.64Å in andradite, Ca-O distance increases by 0.03Å (Novak and Gibbs,

1971). This makes XO_6 site more or less distorted, resulting in more stretching and bending vibration in andradite than in grossular.

From the infrared spectral analyses, it is recognized that the site occupancy in octahedral Y-site plays an important role to affect the neighboring both XO_6 and ZO_4 sites. Although no clear correlation between Si-O distance and the Y-cation substitution is found, infrared spectra indicate that Y-cation substitution may affect the neighboring cation-oxygen and oxygen-oxygen interactions. As mentioned already, the value of X-O distances are significantly affected by the Y-O and octahedral O-O distances in the neighboring octahedra.

CONCLUSION

The study on four different Ca-garnets from the Ulchin mine leads to the following conclusions:

(1) The increase of Fe contents in Ca-garnets in the range of 0.35 and 1.92 mole% parallels with the change in color from pale pink, through yellowish green, reddish brown, to dark green. This parallels also with the changes in other physical properties, that is, specific gravity changes from 3.76 to 3.92 and hardness from 1184~1268 to 1230~1280 in Viker hardness scale, respectively.

(2) Unit cell dimensions change from 11.91Å in pale pink grossular to 12.06Å in dark green andradite. These values are well-agreed with those calculated from the empirical equation derived by Novak and Gibbs (1971). It is noted from the XRD patterns that the reflection of (220) is missing in pale pink grossular, while the reflection of (230) is only found in this one. This may ascribe to the lowering of internal symmetry around the octahedral Y-site due to substitution of Fe^{3+} cation by the smaller Al.

(3) Mössbauer parameters show that isomer shift for Fe³⁺ increases linearly from 0.372 to 0.389mm/sec with increase of Fe³⁺ occupancies in the octahedral site. This indicates the increase in average metal-oxygen distances in Y-sites, leading to decrease in *s*-electrons around Fe nuclei, which results in the increase in the isomer shift. Mössbauer spectra reveal that only pale pink grossular contains a small amount of Fe²⁺, while Fe-rich andradites show no evidence of Fe²⁺ presence. This may suggest that the pale pink grossular formed under low oxygen fugacity.

(4) IR spectra show that pale pink grossular is readily distinguishable from other andradite by their finger-print spectra due to Ca-O stretching vibration in the range of 360~300cm⁻¹. This phenomena indicate that the site occupancies in octahedral Y-site severely affect the neighboring dodecahedral X-site as well as tetrahedral Z-site. Since X-site is edge-shared with Y-site, an increase in the Y-octahedral site push the neighboring polyhedra around X-cation to make it more distorted one lowering the internal symmetry around X-site. Other absorption bands in the grossular are shifted to the higher energy region by approximately 20cm⁻¹ relative to those of andradites. Although the change in Y-site does not affect Z-site significantly, small decrease in Z-site may reduce the stretching and bending vibrations in the Si-O bonding resulting in the shift of IR spectra of andradites.

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Crystal Chemistry of Ca-Garnets

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