

## Synthesis and Infrared Spectra of $\text{Ca}_3\text{Mn}_2\text{Si}_3\text{O}_{12}$ and $\text{Cd}_3\text{B}_2\text{Si}_3\text{O}_{12}$ (B: Al, Ga, Cr, V, Fe, Mn) Garnets

HITOSHI NISHIZAWA, AND MITSUE KOIZUMI

*The Institute of Scientific and Industrial Research,  
Osaka University,  
Yamadakami, Suita, Osaka 565, Japan*

### Abstract

The garnets  $\text{Ca}_3\text{Mn}_2\text{Si}_3\text{O}_{12}$  and  $\text{Cd}_3\text{Mn}_2\text{Si}_3\text{O}_{12}$  were synthesized at high pressures and temperatures. They have a cubic structure with  $a_0 = 12.060 \text{ \AA}$  and  $a_0 = 11.987 \text{ \AA}$ , respectively. Infrared spectra suggest that the  $\text{SiO}_4$  tetrahedra in these silicate garnets are strongly affected by the Jahn-Teller distortion of the  $\text{MnO}_6$  octahedra and so are highly distorted.

### Introduction

The garnet mineral family is based on a structure containing independent  $\text{SiO}_4$  tetrahedra. The garnets, general formula  $A_3B_2C_3O_{12}$ , contain metal ions in eight, six, and four coordinated sites and thus provide a fruitful field for investigation of the influence of ionic substitution on properties and an excellent model for crystal chemical studies.

Recently Novak and Gibbs (1971) determined the effects of substituent cations on polyhedral interactions, bond lengths, and angles by comparing refined structures of eight natural garnets with that of synthetic pyrope. They showed that the regularity of the independent  $\text{SiO}_4$  tetrahedra in the garnet structure was strongly influenced by the ionic radius of *A* cation in the eight-coordinated site, but not by that of *B* cation in the six-coordinated site. Gaudefroy *et al* (1969) reported that the new mineral henritermierite  $\text{Ca}_3(\text{Mn}_{1.5}\text{Al}_{0.5})[(\text{SiO}_4)_2/(\text{OH})_4]$  containing  $\text{Mn}^{3+}$  ions as *B* cations had a tetragonally distorted garnet structure. In order to know the role of  $\text{Mn}^{3+}$  ions in this garnet, it is necessary to investigate the end-member composition  $\text{Ca}_3\text{Mn}_2\text{Si}_3\text{O}_{12}$ . In the type formula  $\text{Ca}_3\text{B}_2\text{Si}_3\text{O}_{12}$ , the following cations have been successfully introduced for *B* cations: Al, Cr, Ga, V, Fe, Sc, and In (Geller, 1967).  $\text{Ca}_3\text{Mn}_2\text{Si}_3\text{O}_{12}$  with the garnet structure has not been synthesized under any experimental conditions. It is possible that distortion produced by  $\text{Mn}^{3+}$  ions destabilizes the garnet structure (Strens, 1965).

In this paper, we report the synthesis of  $\text{Ca}_3\text{Mn}_2\text{Si}_3\text{O}_{12}$  under high temperature and high

pressure and from infrared data estimate the effect of  $\text{Mn}^{3+}$  ions with the  $3d^4$  electron configuration on polyhedral interaction. Then we describe the synthesis of the series  $\text{Cd}_3\text{B}_2\text{Si}_3\text{O}_{12}$  (B: Al, Cr, Fe, Ga, V, Mn) and compare their X-ray and infrared spectra data with those of the series  $\text{Ca}_3\text{B}_2\text{Si}_3\text{O}_{12}$ .

### Experimental Methods

In the syntheses of  $\text{Ca}_3\text{Mn}_2\text{Si}_3\text{O}_{12}$  and of the series  $\text{Cd}_3\text{B}_2\text{Si}_3\text{O}_{12}$  (B: Al, Cr, Ga, Fe, V, Mn), starting materials were prepared by mixing oxides, nitrates, or carbonates of the cations with colloidal silica in stoichiometric proportions. The starting materials were then dried and heated at  $750^\circ\text{C}$  in most cases for at least four hours. This temperature was varied somewhat with the materials used since it had to be high enough to decompose the starting materials without causing any volatilization. After this heating, the starting materials were reground and remixed. For hydrothermal runs, the starting materials were enclosed in sealed gold tubes which were placed in a "test-tube" type pressure vessel and heated in a Kanthal-wound furnace. Piston-cylinder type and cubic-type apparatus were used for high temperature and pressure experiments at 10 to 60 kbar (Shimada, Kume, and Koizumi, 1968). The starting materials were packed into a platinum capsule and compressed. The pressures generated in a cell were calibrated by the change of volume of  $\text{AgNO}_3$  (9.8 kbar), of  $\text{KBr}$  (17.9 kbar), and of electric resistance of Bi-II (25.4 kbar) and BaI-II (55 kbar). After treatment at 10 to 60 kbar and  $1100^\circ\text{C}$  for one hour, the samples

were rapidly cooled to room temperature, and the pressure was released. The product was identified by X-ray powder diffraction and optical microscopy. Infrared spectra were obtained using a Hitachi Model 225 spectrophotometer and the Nujol mull technique.

## Results

### $Ca_3Mn_2Si_3O_{12}$

X-ray diffraction patterns of the products synthesized at 1000°C in air and at 600°C hydrothermally under the pressures from 1000 to 2000 bars were completely indexed as a mixture of wollastonite ( $CaSiO_3$ ) and  $\alpha$ - $Mn_2O_3$ . The products synthesized under the pressures from 30 to 60 kbar at 1100°C were reddish brown and quite different in color from the mixture of wollastonite and  $\alpha$ - $Mn_2O_3$ . Their X-ray diffraction patterns, which resembled andradite's ( $Ca_3Fe_2Si_3O_{12}$ ), were completely indexed on the basis of the cubic unit cell with  $a_0 = 12.060$  Å. X-ray diffraction data are listed in Table 1.

### $Cd_3B_2Si_3O_{12}$ (B: Al, Cr, Ga, V, Fe, Mn)

The single phase garnets  $Cd_3Al_2Si_3O_{12}$  and  $Cd_3V_2Si_3O_{12}$  have been already synthesized by Gentile and Roy (1960) and Mill (1964) under atmospheric and hydrothermal conditions respectively. We also obtained them under similar conditions. The other garnets in this series with trivalent Fe, Cr, and Ga ions were synthesized at 1000°C but only above 15 kbar. Higher pressure was needed to synthesize the garnet phase of  $Cd_3Mn_2Si_3O_{12}$ , and the products synthesized below

TABLE 1. X-ray Powder Data of  $Ca_3Mn_2Si_3O_{12}$ \*

hkl	$d_{obs}$	$I_{obs}$
400	3.015	55
420	2.696	100
332	2.571	15
422	2.462	45
510	2.365	20
521	2.202	20
611	1.956	25
620	1.907	10
444	1.740	10
640	1.673	25
721	1.641	5
642	1.611	60
800	1.507	15

\* Indexed on the basis of  $a_0 = 12.060$  Å.

TABLE 2. Lattice Constants and Colors of Synthetic Garnets

	Lattice Constant (Å)	Color
$Ca_3Mn_2Si_3O_{12}$	12.060	reddish brown
$Cd_3Al_2Si_3O_{12}$	11.824	white
$Cd_3Cr_2Si_3O_{12}$	11.943	green
$Cd_3Ga_2Si_3O_{12}$	11.932	white
$Cd_3V_2Si_3O_{12}$	12.023	black
$Cd_3Fe_2Si_3O_{12}$	12.010	tan gray
$Cd_3Mn_2Si_3O_{12}$	11.987	reddish brown

30 kbar at 1000°C were a mixture of cadmium metasilicate ( $CdSiO_3$ ) and  $\alpha$ - $Mn_2O_3$ .

The calculated lattice constants and colors of the garnets synthesized are given in Table 2. The relation between lattice constants and the ionic radii of six-fold coordinated cations in the cadmium garnet series are shown in Figure 1 on the basis of Shannon and Prewitt's effective radii (1969). The same relationship for the calcium garnet series  $Ca_3B_2Si_3O_{12}$  was also drawn. These relationships are very similar with some slight irregularities. The effective radii are not considered to be adapted to ions in every crystal structure. More evidence will be necessary to confirm these results.

### Infrared Spectra

The infrared spectra of the synthesized garnets (Fig. 2) are qualitatively similar in the region from

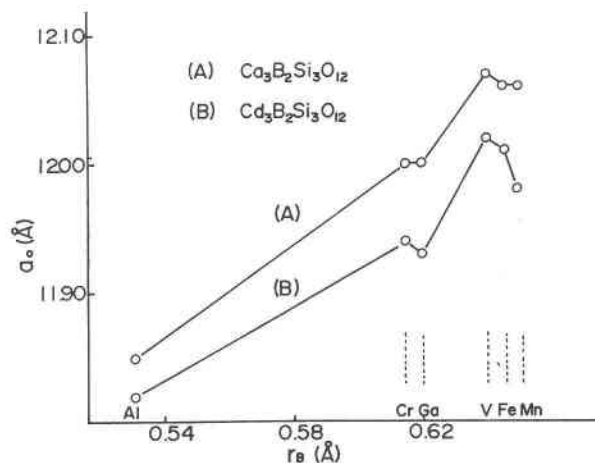


FIG. 1. Lattice constants  $a_0$  vs ionic radii of trivalent octahedrally coordinated cations in the calcium and cadmium garnet series. Data are derived from Table 1 and from Geller (1967).

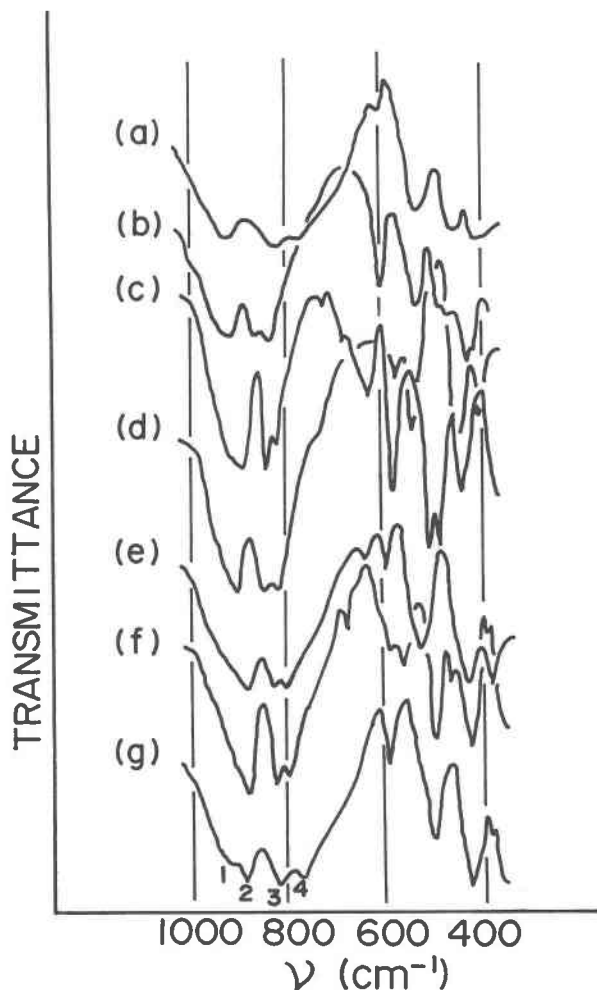


FIG. 2. Infrared spectra of synthetic garnets. **a**:  $\text{Ca}_3\text{Mn}_2\text{Si}_3\text{O}_{12}$ ; **b-g**:  $\text{Cd}_3\text{B}_2\text{Si}_3\text{O}_{12}$  ( $B$ : Al, Cr, Ga, V, Fe, Mn).

800 to 1100  $\text{cm}^{-1}$ . There are three strong and sharp bands (2, 3, 4, in curve **g**) with almost equal intensity, which arise from the site-group splitting of  $\nu_3$  due to the distortion of the tetrahedron in the garnet structure (Wickersheim, Lefever, and Hanking, 1960). A weak and diffused band 1 also appears as a shoulder just above the three strong bands in frequency, but its origin is not clear at the present time (Moore, White, and Long, 1971).

According to crystallographic data, the  $\text{SiO}_4$  ions in the silicate garnets are not completely independent and do not form perfect tetrahedra. The  $\text{SiO}_4$  tetrahedra are distorted along the  $S_4$  axes so that two oxygen-to-oxygen distances are considerably shorter than the remaining four (Novak and Gibbs, 1971). Such an axial distortion will remove

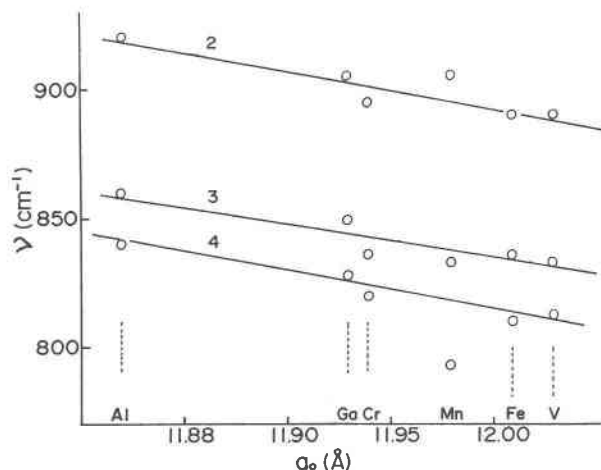


FIG. 3. Lattice constants vs wavenumber for absorption bands 2, 3, and 4 in  $\text{Cd}_3\text{B}_2\text{Si}_3\text{O}_{12}$  ( $B$ : Al, Cr, Ga, V, Fe, Mn).

some of the degeneracy. Moore *et al* (1971) considered that the band splitting of  $\nu_3$  apparently correlated with the distortion of the  $\text{SiO}_4$  tetrahedron and showed that the amount of the separation  $\Delta\nu$  of the lower frequency pair of bands 3 and 4 (Fig. 2) provided a measure of the  $S_4$  distortion of the tetrahedral site. Table 3 lists accurate band frequencies of synthetic garnets.

The shift of the three sharp bands 2, 3, and 4 with lattice constants in the cadmium garnet series is illustrated in Figure 3. Band frequencies, except for the manganese phases, decrease almost linearly with increase in  $a_0$  and the separations  $\Delta\nu$  are found to be almost equal. Accordingly, the degrees of distortion of  $\text{SiO}_4$  tetrahedra are suspected to be almost equal except in  $\text{Cd}_3\text{Mn}_2\text{Si}_3\text{O}_{12}$ . This speculation is consistent with the tendency that the degree of the distortion of the  $\text{SiO}_4$  tetrahedron decreases with the radius of eight-fold-coordinated cation but is independent of the radius of six-fold-coordinated cation (Novak and Gibbs, 1971). However, the separation  $\Delta\nu$  in both garnets,  $\text{Cd}_3\text{Mn}_2\text{Si}_3\text{O}_{12}$  and  $\text{Ca}_3\text{Mn}_2\text{Si}_3\text{O}_{12}$ , is abnormally large. Therefore, the  $\text{SiO}_4$  tetrahedra in these silicate garnets are suspected to be highly distorted.

### Discussion

Since the X-ray diffraction pattern of the high-pressure product with the composition  $\text{Ca}_3\text{Mn}_2\text{Si}_3\text{O}_{12}$  resembled that of andradite ( $\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$ ), its structure was classified as a cubic garnet type. Although the X-ray data were carefully examined,

TABLE 3. Infrared Data for Synthetic Garnets

	Wavenumber of Absorption Band in $\text{cm}^{-1}$			
	1	2	3	4
$\text{Ca}_3\text{Mn}_2\text{Si}_3\text{O}_{12}$		919	818	780
$\text{Cd}_3\text{Al}_2\text{Si}_3\text{O}_{12}$		920	860	840
$\text{Cd}_3\text{Cr}_2\text{Si}_3\text{O}_{12}$		895	836	820
$\text{Cd}_3\text{Ga}_2\text{Si}_3\text{O}_{12}$		905	850	828
$\text{Cd}_3\text{V}_2\text{Si}_3\text{O}_{12}$		890	832	812
$\text{Cd}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$		890	835	810
$\text{Cd}_3\text{Mn}_2\text{Si}_3\text{O}_{12}$	950	905	833	793

there was no evidence for other phases nor evidence for a distorted crystal structure.  $\text{Cd}_3\text{Mn}_2\text{Si}_3\text{O}_{12}$  with the garnet structure was also synthesized under high temperature and pressure. If all manganese ions in  $\text{Ca}_3\text{Mn}_2\text{Si}_3\text{O}_{12}$  and  $\text{Cd}_3\text{Mn}_2\text{Si}_3\text{O}_{12}$  are in the trivalent state and located on octahedral sites, these lattice constants should be close to those of the garnets in which Fe ions are substituted for Mn ions, as seen in the perovskite and the bixbyite structures (Geller, 1967). As indicated in Figure 1 and Table 2,  $\text{Ca}_3\text{Mn}_2\text{Si}_3\text{O}_{12}$  has almost the same lattice constant as  $\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$ , and the cell edge of  $\text{Cd}_3\text{Mn}_2\text{Si}_3\text{O}_{12}$  is only slightly smaller than that of  $\text{Cd}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$ . The garnet mineral containing Mn ions in the six-coordinated site has scarcely been found (Strens, 1965), but the present results suggest the possibility that such a garnet occurs in nature as a relatively high-pressure mineral.

X-rays could not detect noncubicity for the synthesized silicate garnets containing Mn ions. But, from the infrared spectra data, the degree of distortion of  $\text{SiO}_4$  tetrahedra in the silicate garnets with Mn ions was estimated to be considerably larger than that in the other garnets. In the garnet structure, alternating  $\text{SiO}_4$  tetrahedra and  $\text{BO}_6$  octahedra share corners and form a continuous three dimensional framework (Novak and Gibbs, 1971). The  $\text{SiO}_4$  tetrahedra in the silicate garnets

with Mn ions are strongly affected by the Jahn-Teller distortion of  $\text{MnO}_6$  octahedron and so are highly distorted, but these polyhedral distortions do not change the whole cubic structure in the synthesized silicate garnets  $\text{Ca}_3\text{Mn}_2\text{Si}_3\text{O}_{12}$  and  $\text{Cd}_3\text{Mn}_2\text{Si}_3\text{O}_{12}$ .

### Acknowledgments

The authors express their thanks to Drs. M. Shimada, N. Kinomura, and S. Kume at Osaka University. The expense of this study was partly defrayed by a Scientific Grant from the Ministry of Education, to which the authors wish to express their thanks.

### References

- GAUDEFRY, P. C., M. ORLIAC, F. PERMINGEAT, AND A. PARFENOFF (1969) L'henritermierite, une nouvelle espece minerale. *Bull. Soc. Franc. Mineral. Crystallogr.* **92**, 185-190.
- GELLER, S. (1967) Crystal chemistry of the garnets. *Z. Kristallogr.* **125**, 1-45.
- GENTILE, A. L., AND R. ROY (1960) Isomorphism and crystalline solubility in the garnet family. *Am. Mineral.* **45**, 701-711.
- NOVAK, G. A., AND G. V. GIBBS (1971) The crystal chemistry of the silicate garnets. *Am. Mineral.* **56**, 791-823.
- MILL, B. H. (1964) Hydrothermal synthesis of garnets containing  $\text{V}^{3+}$ ,  $\text{In}^{3+}$ , and  $\text{Sc}^{3+}$ . *Dokl. Akad. Nauk. (USSR)*, **156**, 814-816.
- MOORE, R. K., W. B. WHITE, AND T. V. LONG (1971) Vibrational spectra of the common silicates: I. The garnets. *Am. Mineral.* **56**, 54-70.
- SHANNON, R. D., AND C. T. PREWITT (1969) Effective ionic radii in oxides and fluorides. *Acta Crystallogr.* **B25**, 925-946.
- SHIMADA, M., S. KUME, AND M. KOIZUMI (1968) Possible existence of dense ferrimagnetic perovskite allotropic form of yttrium iron garnet. *J. Am. Ceram. Soc.* **51**, 713-715.
- STRENS, R. G. J. (1965) Instability of the garnet  $\text{Ca}_3\text{Mn}_2\text{Si}_3\text{O}_{12}$  and the substitution  $\text{Mn}^{3+} \rightleftharpoons \text{Al}$ . *Mineral. Mag.* **35**, 547-550.
- WICKERSHEIM, K. A., R. A. LEFEVER, AND B. M. HANKING (1960) Infrared absorption spectrum of the silicate ion in the garnet structure. *J. Chem. Phys.* **32**, 271-276.

Manuscript received, March 29, 1974; accepted for publication, August 2, 1974.