Infrared and Mössbauer Spectra of Synthetic Garnets $A_3Fe_2Si_3O_{12}$ (A: Mn, Cd, Ca)

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The garnet $Mn_3Fe_2Si_3O_{12}$ with $a_0=11.821$ Å was synthesized at high pressure and temperature. Infrared and Mössbauer spectra of the synthetic garnets $A_3Fe_2Si_3O_{12}$ (A: Mn, Cd, Ca) suggest that the distortion of SiO_4 tetrahedra in these garnets increases and that of FeO_6 octahedra decreases with increase in the radius of eight fold coordinated cation.

The garnets, general formula $A_3B_2C_3O_{12}$, contain metal ions in eight, six and four coordinated sites, affording a fruitful field for investigation of the influence of ionic substitution and excellent models for crystal chemical studies.

Infrared absorption spectra of garnet group minerals $A_3B_2Si_3O_{12}$ were studied by Wickersheim and Tarte.[1–4] They found that the major absorption bands for 800 to 1100 cm^{-1} arise from the site group splitting of ν_3 due to the distortion of the isolated SiO_4 tetrahedron. Moor and White[5] explained the distortion of tetrahedra in the crystal lattice of natural garnet series by using group theory.

Recently considerable attention has been paid to the chemical application of the Mössbauer effect. The two parameters, the chemical shift and the electric quadrupole splitting obtained from Mössbauer spectra, vary not only with oxidation state and electronic configuration and coordination number of iron atoms in crystal structure, but also with marked changes in geometry of the ligand environment.

We have measured infrared and Mössbauer spectra for synthetic garnet series $A_3Fe_2Si_3O_{12}$ (A: Mn, Cd, Ca). The effects of the substitution of ions in the eight coordinated site on the geometry of SiO_4 tetrahedra and FeO_6 octahedra are discussed.

Experimental

For the synthesis of $A_3Fe_2Si_3O_{12}$ (A: Mn, Cd, Ca), starting materials were prepared by mixing oxides, nitrates or carbonates of the cations with colloidal silica in stoichiometric proportions. They were then dried and heated at 750 °C in most cases for at least four hours. The temperature was varied somewhat with material since it had to be high enough to decompose the starting material without causing any volatilization. After the heating, the starting materials were ground and mixed.

Piston-cylinder type and cubic type apparatus were used for high temperature and pressure experiments. The starting materials were packed into a platinum capsule and compressed. After treatment at 10—60 kbar and 1000—1200 °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.

The Mössbauer spectra were measured at room temperature using radiation from ^{57}Co in Pd, with a 400 channel multichannel analyzer. Velocity scale was calibrated with iron foil as a standard absorber. Infrared spectra were obtained using a Hitachi Model 225 Spectrophotometer and the Nujol mull technique.

Results

Single phases of garnets $Ca_3Fe_2Si_3O_{12}$ and $Cd_3Fe_2Si_3O_{12}$ were synthesized at 15 kbar and 1000 °C. They have a cubic structure with $a_0=12.06$ and 12.01 Å, respectively. Geller and Miller[6] attempted to synthesize the solid solution of $Mn_3(Al_{1-x}Fe_x)_2Si_3O_{12}$ in air and succeeded in synthesizing garnets containing up to 20 per cent of Fe^{3+}. High pressure was necessary to synthesize the single phase of garnet $Mn_3Fe_2Si_3O_{12}$ which is the last member in the above solid solution series. The products synthesized below 35 kbar at 1000 °C consist of mixtures of two or more phases such as $(Mn, Fe)_2O_3$, spinel phases and SiO_2 (quartz or coesite). Even under high pressure conditions of 40 kbar, traces of these phases were found when the temperature was above 1100 °C. The single phase garnet $Mn_3Fe_2Si_3O_{12}$ was synthesized under the conditions of 1000 °C and 60 kbar. No evidence was found for the other phases mentioned above by means of X-ray data. The garnet $Mn_3Fe_2Si_3O_{12}$ obtained has a cubic structure with $a_0=11.821$ Å. X-Ray diffraction data are given in Table 1.

TABLE 1. X-RAY POWDER DATA OF $Mn_3Fe_2Si_3O_{12}$

h	k	l [a]	d_{obsd}	I_{obsd}
4	0	0	2.96	45
4	2	0	2.65	100
3	3	2	2.52	25
4	2	2	2.416	65
5	1	0	2.320	15
5	2	1	2.160	10
6	1	1	1.918	25
6	2	0	1.870	5
4	4	4	1.707	10
6	4	0	1.640	25
7	2	1	1.608	5
6	4	2	1.580	60
8	0	0	1.478	15

a) Indexed on the basis of $a_0=11.821$ Å.

The relation between lattice constants and the ionic radii of eight fold coordinated cations in the synthetic garnets are shown in Fig. 1 on the basis of Shannon and Prewitt's effective radii.[7] The same relationship for the pyralspite series $A_3Al_2Si_3O_{12}$ was also found.[8] Parallelism was found in both garnet series.

The infrared spectra for the synthetic garnets are

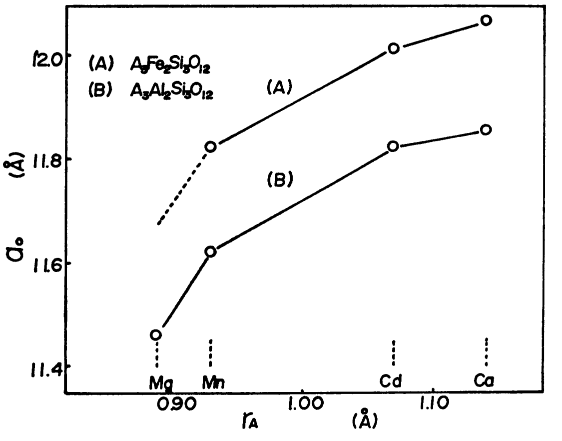

Fig. 1. Lattice constants a_0 vs. ionic radii of divalent dodecahedrally coordinated cations.

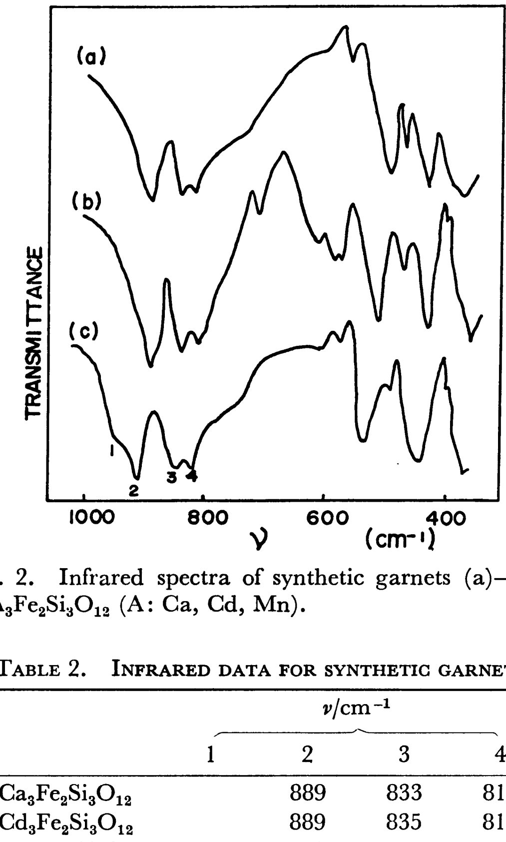

Fig. 2. Infrared spectra of synthetic garnets (a)—(c): $A_3Fe_2Si_3O_{12}$ (A: Ca, Cd, Mn).

Table 2. Infrared data for synthetic garnets

	ν/cm^{-1}			
	1	2	3	4
$Ca_3Fe_2Si_3O_{12}$		889	833	814
$Cd_3Fe_2Si_3O_{12}$		889	835	810
$Mn_3Fe_2Si_3O_{12}$	949	913	848	822

qualitatively similar in the region 800—1000 cm^{-1}. There are three strong and sharp bands (2, 3, 4 in curve c) with almost equal intensity (Fig. 2). The band frequencies decrease almost linearly with increase of a_0. They are assigned to the ν_3 vibration of SiO_4. Splitting of ν_3 vibration into three bands due to the distortion of SiO_4 tetrahedron in the garnet structure is in line with the results of site group and factor group analyses.[5] The origin of band 1 is not clear but it may result from a combination of internal and/or external mode.[10] The magnitude of band splitting of ν_3, Band 2—(Band 3—Band 4)/2, is known to be correlated with the distortion of SiO_4 tetrahedron.[11] From the band splitting of ν_3, the distortion of SiO_4 tetrahedron seems to increase with decrease in the radius of eight fold coordinated cation.

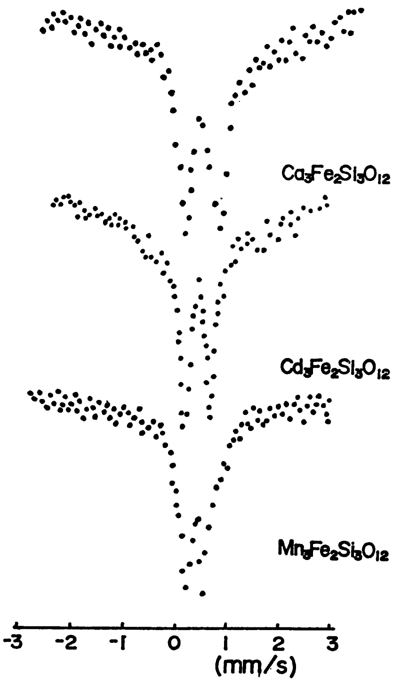

Fig. 3. Mössbauer spectra of synthetic garnets.

Table 3. Parameters of the Mössbauer spectra of ^{57}Fe nuclei for synthetic garnets

	Q.S. mm/s	I.S. mm/s
$Ca_3Fe_2Si_3O_{12}$	0.585	0.414
$Cd_3Fe_2Si_3O_{12}$	0.573	0.384
$Mn_3Fe_2Si_3O_{12}$	0.344	0.385

Figure 3 shows the Mössbauer spectra of synthetic garnets at room temperature. All the spectra are resolved symmetric doublets. The garnets are paramagnetic at room temperature and there is no hyperfine magnetic splitting. The doublet lines arise from the quadrupole interaction of the ^{57}Fe nuclei with the inhomogeneous electric field in the crystal. Table 3 shows the Mössbauer parameters for all the garnets synthesized. The values of the isomer shifts for all the garnets lie in the range characteristic of the trivalent high spin state of iron ion. The parameters indicate little contribution of covalent forces to the ionic chemical bond of iron with oxygen in the octahedral coordination. The quadrupole splitting due to the electric field gradient decrease with decrease in the radius of eight fold coordinated cation. This shows that the trivalent high spin state of iron ions in the garnet $Mn_3Fe_2Si_3O_{12}$ is in the most symmetrical octahedral environment.

Discussion

$Mn_3Fe_2Si_3O_{12}$ with a cubic garnet structure was synthesized under high temperature and high pressure conditions. The reason for the synthetic conditions under high pressure for $Mn_3Fe_2Si_3O_{12}$ being influenced by temperature thought to be due to the instability of Mn^{2+} ions in a high pressure vessel at elevated temperature. The parameter values of Mössbauer spectra for iron ions are typical for the trivalent high spin state of iron ions in an octahedral site. It is concluded that all manganese ions are divalent in the dodecahedral site and all iron ions are trivalent in the octahedral site. Although Mason reported the natural occurrence of a garnet with a probable composition of $Mg_3Fe_2Si_3O_{12}$, this compound could not be prepared under the experimental conditions employed in this study. From the similarity of both curves in Fig. 1, the lattice constant of $Mg_3Fe_2Si_3O_{12}$ is predicted to be 11.656 Å, which is a little higher than 11.515 Å reported by Mason.[9] Some of the Si^{4+} ions are presumed to be substituted for Fe^{3+} ions in the octahedral site of natural garnet $Mg_3Fe_2Si_3O_{12}$.

Usually, but not always, increase in the regularity of SiO_4 tetrahedron should allow the sp^3 hybrid orbitals on oxygen to be in a position for a more favorable overlap with those of Si, suggesting a decrease in the Si–O bond length. Novak showed by comparison of the refined structures of eight natural garnets that the Si–O bond length actually increases, as SiO_4 tetrahedron in pyralspite garnet series $A_3Al_2Si_3O_{12}$ (A: Ca, Mn, Fe, Mg) becomes more regular.[12] From the infrared spectra of synthetic garnets $A_3Fe_2Si_3O_{12}$, it seems that the regularity of SiO_4 tetrahedron also increases as the Si–O bond length increases due to a simple stretching of the $Fe_2Si_3O_{12}$ framework in response to the increase of radius of eight fold coordinated cation.

In pyralspite $A_3Al_2Si_3O_{12}$, the octahedral edge shared with triangular dodecahedron AO_8 is longer than the octahedron's unshared edge in A^{2+} ion's radius longer than 1.01 Å by weakening repulsive forces between A^{2+} and Al^{3+} (0.53 Å) cations. In the garnets $A_3Fe_2Si_3O_{12}$ with Fe^{3+} (0.645 Å) cations in octahedral site, the effect appears when the radius of A^{2+} ion is smaller than 1.01 Å. When the radius of the ion is near that of Mn^{2+} ion, shared and unshared octahedral edge lengths are statistically identical. $Mn_3Fe_2Si_3O_{12}$ garnet is thus considered to have an almost regular octahedron in line with the result of Mössbauer spectra.

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