

MÖSSBAUER AND INFRARED SPECTRA
OF GERMANATE GARNETS*R. HŘÍCHOVÁ^a and J. LIPKA^b^a Department of Mineralogy,
Institute of Chemical Technology, 166 28 Prague 6,^b Department of Nuclear Physics and Engineering,
Slovak Institute of Chemical Technology, 809 33 Bratislava

Received March 6th, 1973

Mössbauer and infrared spectra of germanate garnets of the type $\text{Me}_3\text{FeRGe}_3\text{O}_{12}$ and the infrared spectra of the garnets of the general formula $\text{Me}_3\text{R}'_x\text{R}_{2-x}\text{Ge}_3\text{O}_{12}$ (where Me are bivalent ions of Ca, Cd, or Mn and R and R' are trivalent ions of Al, Cr, Fe, Ga, Sc, In and their mutual combinations with $x = 0, 1, 2$) were measured and analyzed. The data obtained were used for the study of the effect of isomorphous exchange of ions in the octahedral and cubic positions on the symmetry of the octahedron and on the bonding relations in the garnet lattice.

Samples of garnets were prepared by the reaction in the solid phase under the conditions reported by the authors¹⁻⁴, who were concerned with the synthesis of various germanate garnets. The X-ray structural analysis was carried out on an instrument Geigerflex using the powder technique (FeK_α , CuK_α); the lattice parameters a_0 were measured with the accuracy $\pm 0.005 \text{ \AA}$. The infrared spectra were scanned on a spectrophotometer Perkin-Elmer 325 in the region of $250 - 1100 \text{ cm}^{-1}$ with the accuracy $\pm 5 \text{ cm}^{-1}$, employing the KBr disk technique (some of the spectra were measured in Nujol mulls in addition for comparison). The Mössbauer spectra were measured on a spectrometer with the moving equipment of the electrodynamical type, working at a constant acceleration and connected to a 1024-channels analyzer. The maximum velocity of the source (Co^{57} in Pd) was 1.71705 mm/s . The measurements were performed at the temperature 298°K , with the surface density of the sample 5 mg Fe/cm^2 . The spectra obtained were evaluated by using the least squares method on a computer Minsk 22.

RESULTS AND DISCUSSION

The experimental values of the lattice constants a_0 and the infrared spectral data are given in Table I. In Table II the results obtained from the measurements of the Mössbauer spectra are listed.

* Part VI in the series Crystallochemical Behaviour of Ions in Garnet Lattice; Part V: This Journal 37, 3352 (1972).

In agreement with our previous paper⁵ the Fe^{3+} ions were confirmed to occupy only the octahedral positions in all the germanate garnets studied (Fig. 1). From the values of quadrupole splitting or the line widths (Γ_{exp}) of Table II it follows that the degree of distortion in the environment of the Fe^{3+} ion increases with the size of the ion R^{3+} — not only on the exchange of the ions in the octahedral positions (Al, Cr, Ga, Sc, In), but also on the exchange in the cubic positions (Mn, Cd, Ca). For some garnets with the Ga^{3+} ions, values Δ lower than those corresponding to the ionic

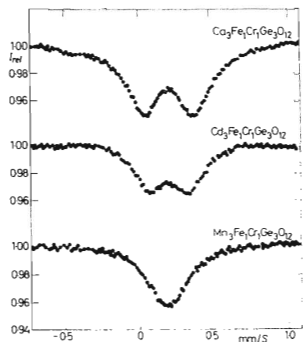


FIG. 1
Mössbauer Spectra of Garnets

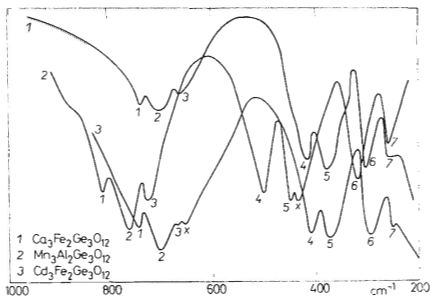


FIG. 2
Infrared Spectra of Germanate Garnets

radius were obtained. Similarly, an anomalous behaviour of some d^{10} ions in the garnet lattice has been observed during the study of the infrared and X-ray spectra⁶⁻⁸. An increase of the ionic radius in the cubic position proves to affect the symmetry of the octahedron to a higher extent than an equal increase of that of the ion R^{3+} ; this can be attributed to the fact that in the garnet lattice the octahedra share their

TABLE I
Lattice Constants and Wavenumbers ν_3 (cm^{-1})

Garnet	$a_0, \text{Å}$	ν'_3	ν_3	ν''_3
$\text{Ca}_3\text{Al}_2\text{Ge}_3\text{O}_{12}$	12.120	775	730	695
$\text{Ca}_3\text{Cr}_2\text{Ge}_3\text{O}_{12}$	12.271	755	710	670
$\text{Ca}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$	12.271	755	716	675
$\text{Ca}_3\text{Fe}_2\text{Ge}_3\text{O}_{12}$	12.320	740	699	660
$\text{Ca}_3\text{Sc}_2\text{Ge}_3\text{O}_{12}$	12.500	741	700	671
$\text{Ca}_3\text{In}_2\text{Ge}_3\text{O}_{12}$	12.590	748	710	680
$\text{Ca}_3\text{CrAlGe}_3\text{O}_{12}$	12.195	750	717	680
$\text{Ca}_3\text{GaAlGe}_3\text{O}_{12}$	12.195	768	725	690
$\text{Ca}_3\text{FeAlGe}_3\text{O}_{12}$	12.215	760	712	675
$\text{Ca}_3\text{CrGaGe}_3\text{O}_{12}$	12.270	750	712	676
$\text{Ca}_3\text{FeCrGe}_3\text{O}_{12}$	12.295	740	700	665
$\text{Ca}_3\text{FeGaGe}_3\text{O}_{12}$	12.296	750	710	670
$\text{Ca}_3\text{FeScGe}_3\text{O}_{12}$	12.412	735	695	655
$\text{Ca}_3\text{FeInGe}_3\text{O}_{12}$	12.455	735	690	655
$\text{Ca}_3\text{ScGaGe}_3\text{O}_{12}$	12.384	750	712	678
$\text{Ca}_3\text{ScInGe}_3\text{O}_{12}$	12.544	744	705	679
$\text{Ca}_3\text{GaInGe}_3\text{O}_{12}$	12.430	750	712	685
$\text{Cd}_3\text{Al}_2\text{Ge}_3\text{O}_{12}$	12.072	785	735	700
$\text{Cd}_3\text{Cr}_2\text{Ge}_3\text{O}_{12}$	12.213	755	715	680
$\text{Cd}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$	12.192	775	722	685
$\text{Cd}_3\text{Fe}_2\text{Ge}_3\text{O}_{12}$	12.260	750	705	660
$\text{Cd}_3\text{Sc}_2\text{Ge}_3\text{O}_{12}$	12.440	755	712	679
$\text{Cd}_3\text{In}_2\text{Ge}_3\text{O}_{12}$	12.510	755	712	680
$\text{Cd}_3\text{CrAlGe}_3\text{O}_{12}$	12.143	760	725	690
$\text{Cd}_3\text{GaAlGe}_3\text{O}_{12}$	12.130	780	735	700
$\text{Cd}_3\text{FeAlGe}_3\text{O}_{12}$	12.166	760	715	670
$\text{Cd}_3\text{CrGaGe}_3\text{O}_{12}$	12.201	760	720	685
$\text{Cd}_3\text{FeCrGe}_3\text{O}_{12}$	12.237	750	710	675
$\text{Cd}_3\text{FeGaGe}_3\text{O}_{12}$	12.225	760	713	670
$\text{Cd}_3\text{FeScGe}_3\text{O}_{12}$	12.353	750	704	670
$\text{Cd}_3\text{FeInGe}_3\text{O}_{12}$	12.390	755	710	670
$\text{Cd}_3\text{GaInGe}_3\text{O}_{12}$	12.350	760	718	690

TABLE I
(Continued)

Garnet	$a_0, \text{Å}$	ν'_3	ν_3	ν''_3
$\text{Mn}_3\text{Al}_2\text{Ge}_3\text{O}_{12}$	11.896	805	755	720
$\text{Mn}_3\text{Cr}_2\text{Ge}_3\text{O}_{12}$	12.049	770	730	695
$\text{Mn}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$	12.053	790	740	705
$\text{Mn}_3\text{Fe}_2\text{Ge}_3\text{O}_{12}$	12.084	765	725	680
$\text{Mn}_3\text{CrAlGe}_3\text{O}_{12}$	11.973	796	737	702
$\text{Mn}_3\text{GaAlGe}_3\text{O}_{12}$	11.976	806	750	708
$\text{Mn}_3\text{FeAlGe}_3\text{O}_{12}$	11.989	785	740	700
$\text{Mn}_3\text{CrGaGe}_3\text{O}_{12}$	12.051	777	735	700
$\text{Mn}_3\text{CrFeGe}_3\text{O}_{12}$	12.067	770	729	690
$\text{Mn}_3\text{GaFeGe}_3\text{O}_{12}$	12.068	785	735	690

Ionic radii (Å)

Ca^{2+}	0.995	Al^{3+}	0.558	Fe^{3+}	0.628	Si^{4+}	0.420
Ce^{2+}	0.945	Cr^{3+}	0.608	Sc^{3+}	0.686	G_2^{4+}	0.530
Mn^{2+}	0.800	Ga^{3+}	0.613	In^{3+}	0.714	O^{2-}	1.400

TABLE II
Quadrupole Splitting and Experimental Line Widths

Garnet	$\text{Ca}_3\text{FeRGe}_3\text{O}_{12}$	$\text{Cd}_3\text{FeRGe}_3\text{O}_{12}$	$\text{Mn}_3\text{FeRGe}_3\text{O}_{12}$
R	$\Delta \pm 0.0025 \text{ mm/s}$	$\Delta \pm 0.0025 \text{ mm/s}$	$\Gamma_{\text{exp}}, \text{ mm/s}$
Al	—	—	0.3592
Cr	0.3285	0.2558	0.3687
Ga	0.3331	0.2559	0.3682
Fe	0.3591	0.2641	0.3811
Sc	0.4264	0.2918	—
In	0.4510	0.3142	—

edges with the cubes. The chemical shift (IS) exhibits a slightly ascending trend with the increase of the size of the central ions (*e.g.*, in the group $\text{Mn}_3\text{FeRGe}_3\text{O}_{12}$, $\text{IS}_{\text{AlFe}} = 0.1811 \text{ mm/s}$ and $\text{IS}_{\text{Fe}_2} = 0.1895 \text{ mm/s}$).

The evaluation of the IR spectra of the garnets showed a group of seven principal absorption bands in the region of 250–850 cm^{-1} to be typical of the germanate garnets (Fig. 2). In analogy with the IR spectra of natural silicate garnets^{9,10} the bands can be assigned to the vibrations as follows:

1 $S_4 \nu_3 \text{XO}_4$, 2 $S_4 \nu_3 \text{XO}_4$, 3 $S_4 \nu_3 \text{XO}_4$, 4 $S_4 \nu_2 \nu_4 \text{XO}_4$, 5 $S_4 \nu_2 \nu_4 \text{XO}_4$, 6 $S_6 \text{XO}_6$, 7 $D_2 \text{XO}_8$

The absorption bands accounted for by the tetrahedral groups GeO_4 are shifted parallel to the changing lattice parameter (Table I).

For garnets containing d^{10} ions (Cd^{2+} , Ga^{3+} , In^{3+}) values of ν_3 wavenumbers higher than those corresponding to the lattice constants of the garnets were obtained; this has been observed previously^{5,7,11,12} and a connection of that anomaly with the electron configuration of the d^{10} ions whose d -electrons participate in the π -bonds has been suggested. Thus the higher values of the wavenumbers of the stretching

TABLE III

Comparison of the Experimental Wavenumbers ν_3 (cm^{-1}) of Tetrahedra XO_4 in Garnets $\text{Me}_3\text{Me}'_2\text{X}_3\text{O}_{12}$ with Values Calculated from the Correlation Equation (2)

Me and Me' are cations with configurations d^0 to d^5 .

Garnet	ν_3 exp	ν_3 Eq. (2)	$\Delta\nu$
$\text{Ca}_3\text{Al}_2\text{Ge}_3\text{O}_{12}$	730	729	-1
$\text{Ca}_3\text{Cr}_2\text{Ge}_3\text{O}_{12}$	710	709	-1
$\text{Ca}_3\text{Fe}_2\text{Ge}_3\text{O}_{12}$	699	700	+1
$\text{Ca}_3\text{FeAlGe}_3\text{O}_{12}$	712	714	+2
$\text{Ca}_3\text{FeCrGe}_3\text{O}_{12}$	700	703	+3
$\text{Ca}_3\text{FeScGe}_3\text{O}_{12}$	695	687	-8
$\text{Ca}_3\text{CrAlGe}_3\text{O}_{12}$	717	718	+1
$\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$	855	860	+5
$\text{Ca}_3\text{Cr}_2\text{Si}_3\text{O}_{12}$	835	839	+4
$\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$	830	830	0
$\text{Mn}_3\text{Al}_2\text{Ge}_3\text{O}_{12}$	755	754	-1
$\text{Mn}_3\text{Cr}_2\text{Ge}_3\text{O}_{12}$	730	733	+3
$\text{Mn}_3\text{Fe}_2\text{Ge}_3\text{O}_{12}$	725	724	-1
$\text{Mn}_3\text{FeAlGe}_3\text{O}_{12}$	740	739	-1
$\text{Mn}_3\text{AlCrGe}_3\text{O}_{12}$	737	743	+6
$\text{Mn}_3\text{FeCrGe}_3\text{O}_{12}$	729	728	-1
$\text{Mn}_3\text{Al}_2\text{Si}_3\text{O}_{12}$	890	885	-5

vibrations could be interpreted in terms of a strengthening of the lattice and so the enhanced electron density at the germanium atoms.

During the study of the stretching vibration ν_3 of the germanate and silicate tetrahedra in dependence on the bulk of the central ions in the octahedral and cubic positions^{1,2} the lattice constant a_0 was found to depend additively on the ionic radii

TABLE IV

Comparison of Experimental Wavenumbers ν_3 (cm^{-1}) of Tetrahedra XO_4 in Garnets $\text{Me}_3\text{.Me}'_2\text{X}_3\text{O}_{12}$ with Values Calculated from the Correlation Equation (2) for Garnets with d^{10} Ions in the a and c Positions

Garnets	ν_3 exp	ν_3 Eq. (2)	$\Delta\nu$
$\text{Cd}_3\text{Al}_2\text{Ge}_3\text{O}_{12}$	735	735	0
$\text{Cd}_3\text{Cr}_2\text{Ge}_3\text{O}_{12}$	715	714	- 1
$\text{Cd}_3\text{Fe}_2\text{Ge}_3\text{O}_{12}$	705	705	0
$\text{Cd}_3\text{FeAlGe}_3\text{O}_{12}$	715	720	+ 5
$\text{Cd}_3\text{FeCrGe}_3\text{O}_{12}$	710	709	- 1
$\text{Cd}_3\text{CrAlGe}_3\text{O}_{12}$	725	725	0
$\text{Cd}_3\text{FeScGe}_3\text{O}_{12}$	703	693	- 10
$\text{Cd}_3\text{Al}_2\text{Si}_3\text{O}_{12}$	870	866	- 4
$\text{Ca}_3\text{Ga}_3\text{O}_{12}$	716	706	- 10
$\text{Ca}_3\text{FeGaGe}_3\text{O}_{12}$	710	702	- 8
$\text{Ca}_3\text{FeInGe}_3\text{O}_{12}$	690	681	- 9
$\text{Mn}_3\text{CrGaGe}_3\text{O}_{12}$	712	707	- 5
$\text{Ca}_3\text{AlGaGe}_3\text{O}_{12}$	725	717	- 8
$\text{Ca}_3\text{ScGaGe}_3\text{O}_{12}$	712	690	- 22
$\text{Ca}_3\text{GaInGe}_3\text{O}_{12}$	712	687	- 25
$\text{Ca}_3\text{In}_2\text{Ge}_3\text{O}_{12}$	710	662	- 48
$\text{Ca}_3\text{ScInGe}_3\text{O}_{12}$	705	670	- 35
$\text{Mn}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$	740	731	- 9
$\text{Mn}_3\text{FeGaGe}_3\text{O}_{12}$	735	727	- 8
$\text{Mn}_3\text{CrGaGe}_3\text{O}_{12}$	735	732	- 3
$\text{Mn}_3\text{AlGaGe}_3\text{O}_{12}$	747	742	- 6
$\text{Cd}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$	722	712	- 10
$\text{Cd}_3\text{FeGaGe}_3\text{O}_{12}$	713	708	- 5
$\text{Cd}_3\text{CrGaGe}_3\text{O}_{12}$	720	713	- 7
$\text{Cd}_3\text{AlGaGe}_3\text{O}_{12}$	735	723	- 12
$\text{Cd}_3\text{FeInGe}_3\text{O}_{12}$	710	687	- 23
$\text{Cd}_3\text{ScGaGe}_3\text{O}_{12}$	721	697	- 24
$\text{Cd}_3\text{In}_2\text{Ge}_3\text{O}_{12}$	712	668	- 44
$\text{Cd}_3\text{GaInGe}_3\text{O}_{12}$	718	690	- 28

of the cations in the tetrahedral (r_d), octahedral (r_a), and cubic (r_c) positions according to the equation

$$a_0 = 7.970 + 1.250r_c + 2.800r_a + 2.550r_d. \quad (1)$$

This dependence suggested the idea that the wavenumber ν_3 also might depend additively on the functions of the ionic radii of the cations in the various coordination polyhedra. A starting model was adopted with the Me ions performing vibrational motions, which appear statistically quite disordered from the standpoint of an individual XO_4 tetrahedron. Since each of the Me cations represents in this case – in relation to the neighbouring XO_4 tetrahedra – a body of infinitely high mass with a fixed position of the center of gravity, we can assume the additivity of the force effect of the Me cation on the oxide ions in the XO_4 tetrahedron; this being expressed by the relation

$$\nu_3 = A - K_d r_d - K_a r_a - K_c r_c, \quad (2)$$

where A and K 's are parameters to be adjusted.

This equation, owing to the approximations involved, retains its physical validity

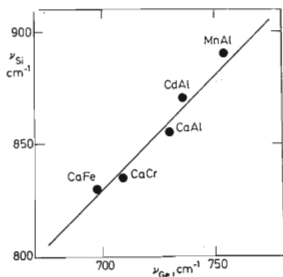


FIG. 3

Correlation of Wavenumbers ν_3 Measured for Germanate and Silicate Garnets with Equal Combinations of Cations in the Octahedral and Cubic Positions

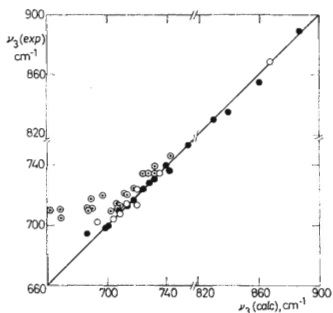


FIG. 4

Correlation of Experimental Wavenumbers ν_3 with the Wavenumbers Calculated from the Formula (2)

○ Cd, ⊙ Ga, In, ● others.

(with respect to the experimental accuracy) only in a not too high span of the ionic radii, up to 15% of the Me—O bond length in each position.

Regarding the anomalies found recently^{3,6-8,12} in the case of ions with the electron configuration d^{10} we have employed only those garnets, which do not contain such ions, for the adjustment of the parameters A and K 's. The numerical evaluation of the data according to Eq. (2) yielded the following values (mean deviations in parentheses):

$$A = 1729 (\pm 0.4) \text{ cm}^{-1}, \quad K_d = 1190 (\pm 0.9) \text{ \AA}^{-1} \text{ cm}^{-1},$$

$$K_a = 430 (\pm 0.5) \text{ \AA}^{-1} \text{ cm}^{-1}, \quad K_c = 130 (\pm 0.8) \text{ \AA}^{-1} \text{ cm}^{-1}.$$

The comparison of the experimental data with those calculated using these parameters is given in Table III.

For garnets with the d^{10} ions (Cd, Ga, In) an anomalous enhancement of the ν_3 wavenumbers with respect to the values calculated as mentioned was observed (Table IV); this confirms the assumption that the d^{10} ions form stronger bonds in the garnet lattice than ions with another electron configuration.

As the coefficients K include practically no characteristics of the central atoms X in the tetrahedra, a given exchange of the ions Me should result in the same change of the frequency of the stretching vibration of the tetrahedra XO_4 , independent of the nature of the central element X. This conclusion was verified by combining the experimental data on germanate and silicate garnets, as shown in Fig. 3. The straight line with the slope 1, drawn through the experimental points in the plot of ν_{Si} versus ν_{Ge} for garnets with equal cations Me, exhibits a maximum difference of $\pm 5 \text{ cm}^{-1}$ from the experimental points, which falls in the limits of accuracy with which the positions of the absorption band maxima can be red.

The calculated values of ν_3 for garnets not containing Ga^{3+} or In^{3+} (not excluding, however, cadmium-containing samples) agree with the measured wavenumbers in average to $\pm 3 \text{ cm}^{-1}$ (Fig. 4). With regard to the rather wide variety of composition of the garnets studied the agreement can be considered quite satisfactory; it amounts to approximately 2% of the interval of values of ν_3 occurring in this work ($\sim 700 - 850 \text{ cm}^{-1}$).

REFERENCES

1. Tauber A., Whinfrey C. C., Banks E.: *J. Phys. Chem. Solids* 21, 25 (1961).
2. Geller S., Miller C. E., Treuting R. G.: *Acta Cryst.* 13, 179 (1960).
3. Hřichová R., Feixová J.: *Sborník Vysoké školy chemicko-technologické v Praze G 13*, 29 (1971).
4. Hřichová R., Lašfovka R.: *Sborník Vysoké školy chemicko-technologické v Praze G 14*, 73 (1972).

5. Lyubutin I. S., Belyaev L. M., Hřichová R., Lipka J.: *Kristallografija* 17, 146 (1972).
6. Hřichová R.: *Kristallografija* 18, 847 (1973).
7. Hřichová R., Lipka J.: *Studium sloučenin $Mn_3Fe_xR_{2-x}Ge_3O_{12}$ granátového typu pomocí Mössbauerovy spektroskopie*. Proceedings of the XXVIII Congress of Czechoslovak Chemical Society, Pardubice 1972.
8. Marezio M., Remeika J. P., Dernier P. D.: *Acta Cryst. B* 24, 1670 (1968).
9. Moore R. K., White W. B., Long T. V.: *Am. Mineralogist* 56, 54 (1971).
10. Omori K.: *Am. Mineralogist* 56, 841 (1971).
11. Hřichová R., Lipka J., Círák J.: *Radiochem. Radioanal. Letters* 13, 63 (1973).
12. Hřichová R., Lašfovka R.: *Sborník Vysoké školy chemicko-technologické v Praze G* 15, 53 (1973).

Translated by P. Adámek.