

CRYSTALLOCHEMICAL BEHAVIOUR OF IONS IN GARNET LATTICE. V.*

STUDY OF DISTRIBUTION OF Ti^{4+} AND Fe^{3+} IONS BY MÖSSBAUER AND INFRARED SPECTROSCOPY

R. HŘÍCHOVÁ and J. LIPKA

Department of Mineralogy, Institute of Chemical Technology, Prague 6,

Department of Nuclear Physics and Techniques, Slovak Institute of Technology, Bratislava

Received July 7th, 1971

Mössbauer and infrared spectra of the garnets $Ca_3Zr_2Ti_1Fe_2O_{12}$ and $Ca_3Zr_{1.5}Ti_{1.5}Fe_2O_{12}$ were measured. Their evaluation has shown that all Fe^{3+} ions in the former garnet occupy tetrahedral positions, whereas in the latter they are partly replaced by Ti^{4+} ions and shifted into octahedral positions.

A number of papers concerning the study of the solid state¹⁻⁴ shows that Mössbauer spectroscopy is invaluable in solving certain crystallochemical problems, where it contributes to determining the coordination number, electron configuration, bonding energy, oxidation state and the position of ion or atom in the crystal lattice.

The mentioned method was used in the present work together with infrared spectroscopy to determine the distribution of Fe^{3+} and Ti^{4+} ions between octahedral and tetrahedral positions in the garnets $Ca_3Zr_2Ti_1Fe_2O_{12}$ and $Ca_3Zr_{1.5}Ti_{1.5}Fe_2O_{12}$. Both garnets were synthesized by Ito and Frondel⁵ who assume that the Fe^{3+} ions occupy only tetrahedral positions and the Ti^{4+} ions both octahedral and tetrahedral positions.

EXPERIMENTAL

Samples of garnets were prepared by the method of Ito and Frondel⁵; their X-ray analysis was made on a Japanese apparatus Geigerflex by the powder method ($Fe K_{\alpha}$; rate 2 cm/1°; lattice parameter measured from 12 lines). Infrared spectra were obtained on an apparatus Perkin-Elmer 325 in the range 200–1100 cm^{-1} . Mössbauer spectra were measured on a spectrometer with an electrodynamic type motion equipment operating in combination with a 1024-channel analyzer at a constant acceleration. The highest speed of the source was 5.4852 mm/s. Measurements were carried out at ambient temperature, surface density of sample was 5 mg Fe/cm². The spectra were evaluated by the least squares method on a Minsk 22 type computer.

* Part IV: *Kristallografija* 17, 1, 146 (1972).

RESULTS AND DISCUSSION

The results of X-ray analysis and data from infrared spectra are in Table I. Table II summarizes the results from Mössbauer spectra. Isomeric shifts are referred to sodium nitroprusside. As follows from Table I, the Ti : Fe ratio up to 3 : 4 is most favourable for obtaining a pure garnet. At a higher Ti content the starting mixture reacts unperfectly; from the lattice constants it follows that the garnet $\text{Ca}_3\text{Zr}_{1.5}\text{Ti}_{1.5}\text{Fe}_2\text{O}_{12}$ represents roughly the upper limit of the system. With a further increase of the Ti : Fe ratio, the perovskite type lattice is more stable. Titanium apparently does not enter into the garnets in which zirconium shares the cubic positions with calcium, since the results of X-ray analysis suggest that the garnet $\{\text{Ca}_{2.5}\text{Zr}_{0.5}\}[\text{Zr}_2](\text{Fe}_3)\text{O}_{12}$ is formed preferentially. Zirconium, in contrast to titanium, does not enter into tetrahedral positions; the corresponding mixtures give rise to the formation of the lattice of perovskite (CaZrO_3) rather than a garnet lattice. The Mössbauer spectra (Fig. 1) show that Fe^{3+} ions in the garnet $\text{Ca}_3\text{Zr}_2\text{Ti}_1\text{Fe}_2\text{O}_{12}$ occupy exclusively tetrahedral positions. With increasing ratio of Ti to Fe, the ions of iron are partly shifted into octahedral positions. Our results suggest that the ions in the garnets are distributed according to the formulas $\{\text{Ca}_3\}[\text{Zr}_2](\text{Ti}_1\text{Fe}_2)\text{O}_{12}$ and $\{\text{Ca}_3\}[\text{Zr}_{1.5}\text{Fe}_{0.5}]\cdot(\text{Ti}_{1.5}\text{Fe}_{1.5})\text{O}_{12}$. Replacing of iron by titanium in tetrahedral positions is with respect to small differences in ionic radii ($\text{Fe}^{3+}\dots 0.65 \text{ \AA}$, $\text{Ti}^{4+}\dots 0.68 \text{ \AA}$) obviously caused by the higher charge of Ti^{4+} ions, which are therefore directed preferentially into tetrahedral positions. The measured values of quadrupole splitting

TABLE I
Lattice Parameters and Stretching Vibrations for Garnets

Tablet composition 1200°C/5 h	X-ray analysis	Stretch. vibr. ν_3, cm^{-1}	
$\text{Ca}_3\text{Zr}_2\text{Ti}_1\text{Fe}_2\text{O}_{12}$	garnet a_0 12.73 Å	680	620, 580
$\text{Ca}_3\text{Zr}_{1.5}\text{Ti}_{1.5}\text{Fe}_2\text{O}_{12}$	garnet a_0 12.68 Å	680	630, 580
$\text{Ca}_3\text{Zr}_1\text{Ti}_2\text{Fe}_2\text{O}_{12}$	garnet $a_0 \approx 12.66 \text{ \AA}$ Fe_2O_3		—
$\text{Ca}_3\text{Ti}_3\text{Fe}_2\text{O}_{12}$	$\text{CaTiO}_3, \text{FeO}_3$		—
$\text{Ca}_3\text{Zr}_1\text{Ti}_1\text{Fe}_4\text{O}_{12}$	garnet $a_0 \approx 12.66 \text{ \AA}$ Fe_2O_3		—
$\text{Ca}_{2.5}\text{Zr}_{0.5}\text{Ti}_2\text{Fe}_3\text{O}_{12}$	garnet $a_0 \approx 12.67 \text{ \AA}$ $\text{Fe}_2\text{O}_3, \text{ZrO}_2$		—
$\text{Ca}_{2.5}\text{Zr}_{0.5}\text{Zr}_2\text{Fe}_3\text{O}_{12}$	garnet a_0 12.65 Å	565	—
$\text{Ca}_3\text{Zr}_{0.5}\text{Ti}_{2.5}\text{Fe}_2\text{O}_{12}$	$\text{CaTiO}_3, \text{Fe}_2\text{O}_3$		—
$\text{Ca}_3\text{Zr}_3\text{Fe}_2\text{O}_{12}$	$\text{CaZrO}_3, \text{Fe}_2\text{O}_3$		—

in tetrahedral positions (Δ_d , Table II) increase with increasing radii of ions in these positions analogously as with germanium(IV) garnets⁶. This dependence is still more marked with isomeric shift (IS_d) values, since in this case also the increase of charge in the polyhedron plays a role. Accordingly, the results from infrared spectra (Table I and Fig. 2) show an increasing frequency and splitting of stretching

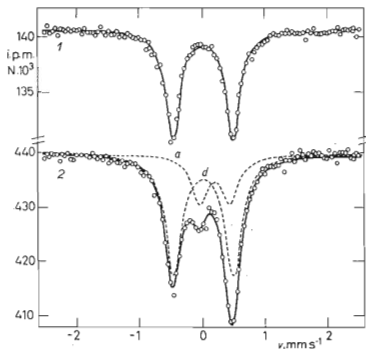


FIG. 1

Mössbauer Spectra of Garnets

1 $\text{Ca}_3\text{Zr}_2\text{Ti}_1\text{Fe}_2\text{O}_{12}$; 2 $\text{Ca}_3\text{Zr}_{1.5}\text{Ti}_{1.5}\text{Fe}_2\text{O}_{12}$.

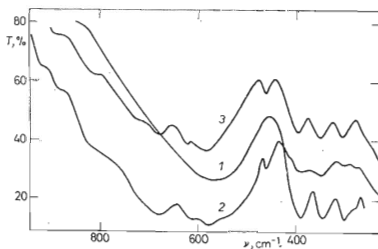


FIG. 2

IR Spectra of Garnets

1 $\text{Ca}_{2.5}\text{Zr}_{2.5}\text{Fe}_3\text{O}_{12}$; 2 $\text{Ca}_3\text{Zr}_2\text{Ti}_1\text{Fe}_2\text{O}_{12}$; 3 $\text{Ca}_3\text{Zr}_{1.5}\text{Ti}_{1.5}\text{Fe}_2\text{O}_{12}$.

TABLE II
Quadrupole Splitting and Isomeric Shift for Garnets

Measured quantity	$\text{Ca}_3\text{Zr}_2\text{Ti}_1\text{Fe}_2\text{O}_{12}$	$\text{Ca}_3\text{Zr}_{1.5}\text{Ti}_{1.5}\text{Fe}_2\text{O}_{12}$
Quadrupole splitting		
mm/s A_d	0.955 ± 0.004	0.957 ± 0.004
A_a	—	0.504 ± 0.004
Isomeric shift		
mm/s IS_d	0.455 ± 0.004	0.655 ± 0.004
IS_a	—	0.456 ± 0.004

vibrations, ν_3 , conditioned by the entrance of a Ti^{4+} ion into the FeO_4 tetrahedron. The increase of the frequency of stretching vibrations with increasing lattice parameter can be attributed to a heterovalent ion exchange in the tetrahedron similarly as found⁷ with garnets of the type $[\text{Y}_{3-x}\text{Ca}_x](\text{Sn}_x\text{Fe}_{5-x})\text{O}_{12}$.

REFERENCES

1. Bancroft G. M.: *Geochim. Cosmochim. Acta* 32, 547 (1968).
2. Bancroft G. M., Maddock A. G., Burns R. G.: *Geochim. Cosmochim. Acta* 31, 2219 (1967).
3. Ljubutin I. S., Mill B. V.: *Fizika Tverdogo Tela* 9, 3145 (1967).
4. Beljajev L. M., Ljubutin I. S., Mill B. V., Povickij V. A.: *Fizika Tverdogo Tela* 11, 795 (1969).
5. Ito J., Frondel C.: *Am. Min.* 52, 773 (1967).
6. Ljubutin I. S., Beljajev L. M., Hřichová R., Lipka J.: *Kristallografija* 17, 1, 146 (1972).
7. Círák J., Hřichová R., Lipka J.: *A Mössbauer and IR Study of Substituted YIG. 4th Internat. Conference on Applications of Mössbauer Spectroscopy*, Dresden, September 20—26th, 1971.

Translated by K. Míčka.