MÖSSBAUER AND INFRARED SPECTRA OF SUBSTITUTED Y‑FE(III) GARNETS*

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Mössbauer and infrared spectra of substituted Y—Fe(III) garnets (YIG) of the type $Y_{3-x}Ca_x$ . . $Sn_xFe_{5-x}O_{12}$, $Y_{3-x}Ca_xZr_xFe_{5-x}O_{12}$, and infrared spectra of garnets of the type $Y_{3-x}Ca_x$ . . $Si_xFe_{5-x}O_{12}$, $Y_{3-x}Ca_xGe_xFe_{5-x}O_{12}$, $Y_3Fe_{2-x}Sc_xFe_3O_{12}$, and $YCa_2TiZrFe_3O_{12}$ were measured. From the measured data conclusions are drawn about the distribution of individual ions into the coordination polyhedrons. To study the position of the ions, use was made also of magnetic parameters (the dependence of H_{eff} on the degree of substitution and on the temperature) obtained by Mössbauer spectroscopy.

EXPERIMENTAL

Garnet samples were prepared both by a solid state reaction and synthesis from a PbF_2—PbO melt under conditions given in the literature[1–5]. The lattice parameters of the garnets were measured by the powder method on a Geigerflex apparatus (Japan) using the FeK_α and CoK_α lines with an accuracy of ± 0.5 pm. Infrared spectra were recorded on a Perkin Elmer 325 spectrometer by the KBr pellet technique in the range 250—1000 cm^{-1} with an accuracy of ± 5 cm^{-1}. Mössbauer spectra were measured on the nuclei Fe^{57} and Sn^{119} on a spectrometer with an electrodynamic type motion apparatus working at a constant acceleration and combined with a 1024 channel analyser. The maximum speed of the source (Co^{57} in Pd and SnO_2) was 1·71705 mm/s. The measurements were done in the temperature range 80—530 K, the surface density of the sample was 5 mg/cm². The measured spectra were evaluated by the least squares method on a Minsk 22 computer.

RESULTS AND DISCUSSION

The measured values of the lattice constants a_0 are summarized in Table I. In Table II are shown the measured wave numbers of the stretching vibrations.

The studies of the IR spectra of the garnets revealed that these spectra are characterized by pronounced vibration bands v_3 of tetrahedral XO_4 groups which are manifested usually as triplets in the regions 800—950 cm^{-1} (SiO_4 tetrahedrons), 680 to 730 cm^{-1} (GeO_4 and TiO_4), and 550—670 cm^{-1} (FeO_4). The bands of the stretching

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TABLE I

Lattice Constants for Substituted YIG

Substitution degree x	Ca + Sn a_0, pm	Ca + Zr a_0, pm	Ca + Ge a_0, pm	Ca + Si a_0, pm	Ca + (Zr + Ti) a_0, pm	Sc a_0, pm
0	1 237·6	1 237·6	1 237·6	1 237·6	1 237·6	1 237·6
0·2	1 239·7	1 239·2	—	—	—	—
0·3	1 240·9	1 242·3	—	—	—	—
0·5	1 243·5	1 245·5	1 237·0	1 233·0	—	1 241·8
0·7	1 245·8	1 248·6	—	—	—	—
0·9	1 248·2	1 251·7	—	—	—	—
1·0	1 249·6	1 253·3	1 236·2	1 228·6	—	1 245·8
1·2	1 252·0	1 256·5	—	—	—	—
1·5	1 255·2	1 261·1	1 235·9	1 223·4	—	—
2·0	1 261·3	1 269·0	1 235·5	1 219·0	1 265·0	—

TABLE II

Wave Numbers of Stretching Vibrations, v_3, for Tetrahedral Groups of Substituted YIG

Substitution degree x	Ca + Sn cm^{-1}	Ca + Zr cm^{-1}	Ca + Ge cm^{-1}	Ca + Si cm^{-1}	Sc cm^{-1}	Ca + (Zr + Ti) cm^{-1}
0	655 600 565	655 600 565	655 600 565	655 600 565	655 600 565	655 600 565
0·2	655 605 560	655 603 555	—	—	—	—
0·3	655 610 562	650 600 560	—	—	—	—
0·5	655 612 565	645 600 550	630 590 550	600 560	650 600 560	—
0·7	660 615 565	650 600 550	—	—	—	—
0·9	660 615 570	645 595 545	—	—	—	—
1·0	668 625 570	635 595 545	625 585 545 700	650 595 550 918 850	645 595 550	—
1·2	670 620 575	645 595 545	—	—	—	—
1·5	665 628	590 545	580 740 695 660	640 590 540 918 840	—	—
2·0	670 630 600	635 587 535	600 570 730 690 660	590 890 820	—	650 585 540 730 686

vibrations of the FeO_4 tetrahedrons in the studied garnets are shifted from 600 cm^{-1} for the pure $Y_3Fe_5O_{12}$, where all octahedral positions are occupied also with iron ions, toward lower values depending on the radius of the ion which replaces iron

in these octahedral positions; however the compound $Y_{3-x}Ca_xSn_xFe_{5-x}O_{12}$ is an exception[3,6,9].

In the case of garnets where the combination of Y(III) with Fe(III) is replaced by the combination of Ca(II) with Sn(IV) or Zr(IV), the substitution concerns only the centers of the octahedrons and cubes. The Fe(III) ions in the centers of the tetrahedrons maintain their positions (Table II).

On the other hand, in the case of the group where the combination of Y(III) and Fe(III) is replaced by Ca with Ge(IV) or Si(IV), the IR spectra show besides the characteristic vibration bands of the FeO_4 tetrahedrons also those of GeO_4 or SiO_4, which suggest that Ge and Si enters preferentially the tetrahedral positions replacing the Fe(III) ions (Fig. 1).

With garnets substituted by Sc(III), the substitution concerns obviously Fe^{3+} ions only in the octahedral positions. Entering of Sc^{3+} into the tetrahedral positions in YIG was not observed, which is in accord with our earlier observations[7]. The entering of larger Sc^{3+} ions is manifested by a shift of the v_3 bands of the tetrahedral FeO_4 groups toward lower values (Table II).

With YIG substituted by a Ca—Zr—Ti combination, obviously the Fe^{3+} ions in the octahedron are replaced by Zr^{4+} whereas the Ti^{4+} ions go rather into the tetrahedron as evidenced by two new bands in the region about $685-780$ cm^{-1} (Table II). The preferential entering of the larger Ti^{4+} ion into the tetrahedron was proved by Mössbauer spectroscopy[4]. In our case of the garnet $YCa_2ZrTiFe_3O_{12}$ the ions could hence be distributed according to the formula $\{YCa_2\}[ZrFe]$ . . $(TiFe_2)O_{12}$.
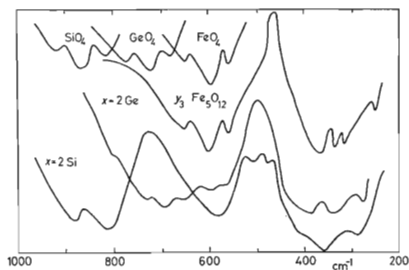

FIG. 1

Infrared Spectra of YIG Substituted by the Combination Ca + Si or Ca + Ge
    Constitution: $\{YCa_2\}$ $[Fe_2]$ $(FeSi_2)O_{12}$, $\{YCa_2\}$ $[Fe_2]$ $(FeGe_2)O_{12}$, $\{Y_3\}$ $[Fe_2]$ $(Fe_3)O_{12}$.

In Mössbauer spectra of garnets substituted by Ca and Sn, a superposition of two quadrupoles is apparent, which correspond to Fe^{3+} ions in octahedral and tetrahedral positions (Fig. 2); this is in accord with the results of IR spectroscopy. The doublet with a larger splitting and higher intensity in Fig. 2 corresponds to Fe^{3+} ions in tetrahedral positions and the other one with a smaller splitting to Fe^{3+} ions in octahedral positions[3,8]. The intensity corresponding to an octahedral position decreases with replacing Fe^{3+} by Sn^{4+} ions and for $x = 2$, when all octahedral positions are occupied by tin ions, this doublet entirely disappears.

An analogous situation is also in the second group of garnets (Fig. 3), where iron ions in octahedral positions are gradually replaced by zirconium ions, and also here the substitution is possible only up to $x = 2$, i.e., until all Fe^{3+} ions in octahedral positions are replaced by zirconium. The latter, similarly as tin, does not enter the tetrahedral positions[9].

Also the Mössbauerian measurements of the dependence of effective magnetic field on the Fe^{3+} nuclei in dependence on the degree of substitution show a decrease

Fig. 2

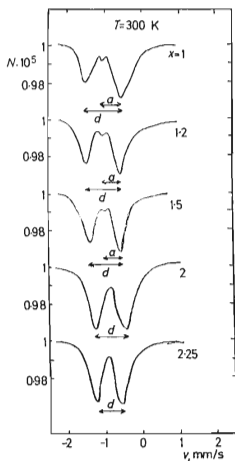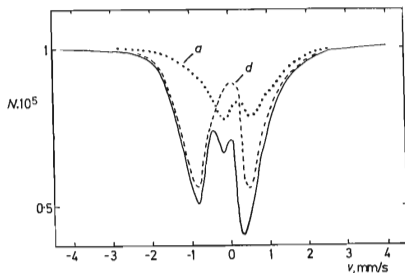Mössbauer Spectra of YIG Substituted by the Combination Ca + Sn

Fig. 3

Distribution of Ions in the Garnet $Y_{2,7}Ca_{0,3}Zr_{0,3}Fe_{4,7}O_{12}$

of H_{eff} in both the octahedron and tetrahedron with the increasing content of nonmagnetic ions. A decrease of H_{eff} in the tetrahedral positions was observed even when no substitution of iron in these positions took place. This can be attributed to a drop in the effective magnetic moment in the tetrahedrons as a result of a decrease of the number of possible interactions with magnetic ions in the octahedron, where Fe^{3+} ions are gradually replaced by nonmagnetic Sn^{4+} ions in the first group or Zr^{4+} ions in the second group. In both cases the covalent character of the bond becomes more pronounced, which again causes a decrease in H_{eff} on iron ions in the tetrahedron (Fig. 4).

The same result is obtained from the measurement of the content of octahedral iron in dependence on the substitution of iron by tin and zirconium (Fig. 5). The number of Fe^{3+} ions in octahedral positions decreases with increasing x until it becomes zero[10] at $x = 2$. At the same time, the number of Fe^{3+} ions in the tetrahedron
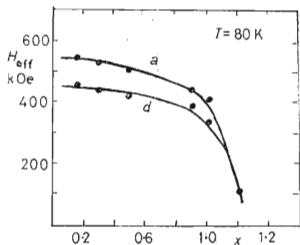

FIG. 4

Dependence of H_{eff} on Degree of Substitution for the Garnet Group $Y_{3-x}Ca_xZr_x$. $.Fe_{5-x}O_{12}$
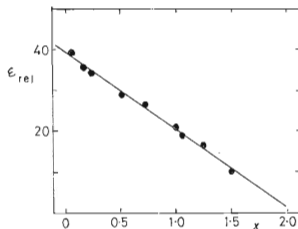
FIG. 5

Dependence of Iron Content, ε_{rel}, on the Degree of Substitution for the Garnet Group $Y_{3-x}Ca_xSn_xFe_{5-x}O_{12}$

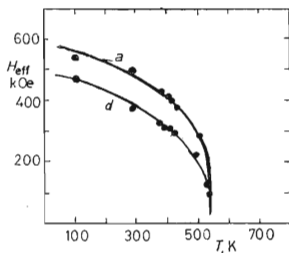FIG. 6

Dependence of H_{eff} on Temperature for Garnet $Y_{2,8}Ca_{0,2}Fe_{4,8}Sn_{0,2}O_{12}$

TABLE III

Relation between Curie Temperature and Substitution Degree for the Garnet Group $Y_{3-x}Ca_x$. $Zr_xFe_{5-x}O_{12}$

x	0·0	0·2	0·3	0·5	0·7	0·9	1·0	1·2	1·5
T_C, K	545	510	490	446	394	337	309	242	137

remains constant. Hence, it can be deduced that when YIG is substituted by the combination Ca + Sn or Ca + Zr, the Sn^{4+} or Zr^{4+} ions replace preferentially the octahedral iron whereas Y^{3+} ions in cubic positions are replaced by Ca^{2+} ions[9-11].

The temperature dependence of effective magnetic fields was followed at $80-530$ K with certain samples. For example, with the garnet $Y_{2.8}Ca_{0.2}Fe_{4.8}Sn_{0.2}O_{12}$ (Fig. 6) the effective magnetic fields decrease with increasing temperature up to 519 K (T_c for YIG = 545 K), at which they attain zero value both in the octahedron and tetrahedron. This temperature is equal to the Curie point of the mentioned garnet; it decreases with increasing substitution of iron ions by nonmagnetic ions as can be seen from the measurements on YIG substituted by zirconium (Table III).

Our measurements showed that with the studied groups of substituted yttrium--iron garnets the Y^{3+} and Ca^{2+} ions occupy cubic positions with the coordination number 8, Fe^{3+} ions occupy both octahedral and tetrahedral positions, Sc^{3+}, Sn^{4+}, and Zr^{4+} ions exclusively octahedral positions, and Ge^{4+} and Si^{4+} ions tetrahedral positions.

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