IR SPECTROSCOPIC INVESTIGATION OF THE GARNET MATERIALS USED IN THE MICROWAVE ELECTRONICS

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Summary

For the possible application of the IR spectroscopy in the production and research of magnetic materials based on YIG (yttrium-iron garnet) IR spectra of YIG and substituted YIG crystals were investigated and also the formation of polycrystalline YIG from $3Y_2O_3:5Fe_2O_3$ powder mixture at different temperatures.

Introduction

The magnetic garnets are of great interest because of the wide variety of their composition. $Y_3Fe_5O_{12}$ (yttrium-iron garnet, YIG) is regarded as the prototype of these magnetic garnets. It is used in the microwave electronics either as a polycrystalline material or in single-crystal form. Its magnetic properties can be well influenced by substituting the Fe^{3+} ions by diamagnetic ions as gallium or scandium and the Y^{3+} by rare-earth ions.

YIG is considered as a member of the group of rare-earth garnets having the general formula $R_3A_5O_{12}$. These crystals have got several other applications in optics, acoustics and electronics. $Y_3Al_5O_{12}$, a laser material and $Gd_3Ga_5O_{12}$, the substrate material for the bubble memories are other well-known members of this group.

The crystalline structure of the rare-earth garnets consists of oxygen tetrahedra, octahedra and dodecahedra with three A^{3+} ions per formula unit in the tetrahedral sites, two of them in octahedral sites and the rare-earth ions or Y^{3+} in the dodecahedral sites. All the magnetic moments of the tetrahedral Fe^{3+} ions in YIG stand parallel to each other and antiparallel to those in the octahedral sites. So YIG possesses spontaneous magnetization. The magnetic properties can be influenced by substituting the Fe^{3+} ions with diamagnetic ones.

The composition and structure of the magnetic garnets are investigated by analytic chemical, AES or AAS methods and by X-ray diffraction, respectively. For the identification of the magnetic phases the DTGM method [1] is the most sensitive one. By Mössbauer spectroscopy, the relative amount of the tetrahedral and octahedral iron ions can be determined [2]. In addition to these methods, IR spectroscopy also can yield some information about the garnets [3, 4]. As it is a non-specific method first it has to be known how the changes in composition or structure influence the IR spectra.

In this paper, IR spectra of YIG and substituted garnet crystals are investigated. We measured the transmittance spectra of polycrystalline samples and of single-crystal powders in KBr pellet and the transmittance and specular reflectance of single crystal slices, polished on both sides. The spectra were measured with a PE-580A IR spectrophotometer. For the reflectance measurements, a Perkin-Elmer specular reflectance unit was used. The angle of incidence in the unit was 6.5°.

The optical properties of the YIG in the infrared

The absorption edge of the YIG crystal is at about 9000 cm^{-1}. It is due to the electronic transition between the crystal-field splitted d levels of the octahedral Fe^{3+} ions. Below the absorption edge down to 2300 cm^{-1} the YIG is fairly transparent. It has a weak absorption band at 4800 cm^{-1}. From 2300 to 1300 cm^{-1} the absorption gradually increases and below 1300 cm^{-1} the YIG is opaque. The lattice spectrum of the YIG consists of two groups of bands, centred at 600 cm^{-1} (group "A") and at 400 cm^{-1} (group "B") both of them are followed by a very deep reflection minimum (Fig. 1).

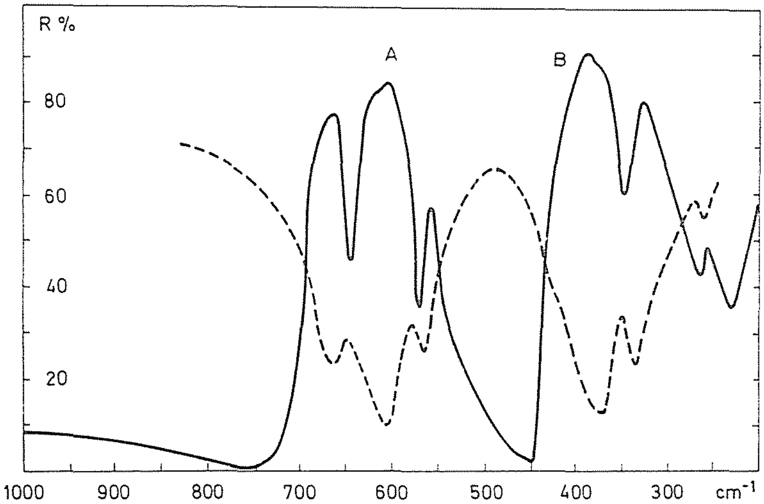

Fig. 1. Specular reflectance spectrum of the single crystal YIG measured at 6.5° angle of incidence (full line) together with the transmittance spectrum of the same material measured in KBr pellet (dashed line)

The garnets have body-centered cubic lattice with 8 formula units in the crystallographic unit cell. They belong to the O_h^{10} space group. Part of the unit cell is shown in Fig. 2 and the description in the unit cell is found in Table 1.

Each of the oxygen ions is connected to one tetrahedral and to one octahedral A^{3+} ions and to two dodecahedral ions. For the YIG, the bond distances and bond angles are shown in Table 2.

The factor group analysis predicts 18 IR active lattice vibration modes; each of them belong to the F_{1u} symmetry species. One of the species corresponds to the acoustic vibrations so 17 IR bands ought to be found in the spectra of the garnets. Because of the high ionicity of the garnet crystals, some of the vibrational modes are accompanied by high dipole-moment changes; these bands are broad so some of the bands cannot be resolved. Measuring also in the far infrared, McDevitt [3] found only 11 lattice bands of the YIG.

As the group-theoretical method was not of much use for the explanation of the garnet spectrum, it is more usual to assign the bands in the IR to the Me—O stretching vibrations of the polyhedra. Tarte [6] collected the absorption ranges of the metal-oxygen tetrahedra and octahedra in different compounds. He observed that the absorption range is higher if the polyhedra are condensed (in the sense that they are connected with other polyhedra of the same kind) than in the case when they are isolated, that is, only polyhedra of different kind are connected. Tarte considered the polyhedra in the garnet structure as isolated ones [7]. The isolated FeO_4 tetrahedra absorb in the range of 550–650 cm^{-1} and the isolated FeO_6 octahedra in the range of 300–400 cm^{-1}. In this sense, the bands of group "A" in the spectrum can be assigned to the vibrations of the tetrahedra and the higher wavenumber bands of the group "B" to those of the octahedra. The Y–O stretching vibrations in the yttrium garnets can appear at around 300 cm^{-1} [7].

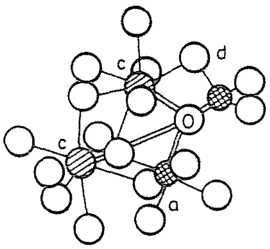

Fig. 2. Part of the unit cell of YIG showing the four cations nearest to the oxygen ion "O" together with their coordinated oxygen ions. "a": Fe^{3+} at tetrahedral site, "d": Fe^{3+} at octahedral site, "c": Y^{3+} at dodecahedral site

This assignation might be not quite correct, but it helps to explain the effects of the substituents on the spectra. It is expected that a substituent causes

Table 1

Description of the unit cell of $R_3A_5O_{12}$ garnet crystals [3]

Site position	16a	24c	24d	96a
Ion in site	A^{3+}	R^{3+}	A^{3+}	O^{2-}
Point symmetry	S_6	D_2	S_4	C_1
Number of nearest neighbours	6	8	4	
Polyhedra generated	octahedron	dodecahedron	tetrahedron	

Table 2

Bond distances and bond angles between nearest neighbours in YIG [5]

Bond	Bondlength (nm)	Bond angle	Degrees
O – Fe(d)	0.188	Fe(a) – O – Fe(d)	126.6
O – Fe(a)	0.202	Fe(a) – O – Y*	102.8
O – Y*	0.243	Fe(a) – O – Y⁺	102.7
O – Y⁺	0.237	Fe(d) – O – Y*	122.2
		Fe(d) – O – Y⁺	92.2

the major changes (splitting, new bands and band shifts) in the bands of those polyhedra where the substitution took place, and only broadening and shift of the bands of the other polyhedra.

Experimental

Formation of polycrystalline YIG

The product of the solid-state reaction in $5Fe_2O_3 : 3Y_2O_3$ powder mixtures at different temperatures between 700 °C and 1400 °C was investigated by X-ray, diffraction, DTGM and infrared spectroscopic methods [8]. The mixtures were homogenized and then heat treated. After heating the mixtures at the rate of 200 °C/hour they were held at constant temperature for 6 hours and then cooled at the rate of 80 °C/hour.

The garnet spectrum, with the two well-separated groups of bands is very characteristic, so the garnet phase can easily be distinguished from the other oxides by its infrared spectrum (see Figs 3, 4).

Fe_2O_3 has corundum structure with condensed FeO_6 octahedra, which by Tarte [6] should have their stretching vibrations in the range of 400–500 cm^{-1}. Orthoferrite also contains condensed FeO_6 octahedra [5] so the

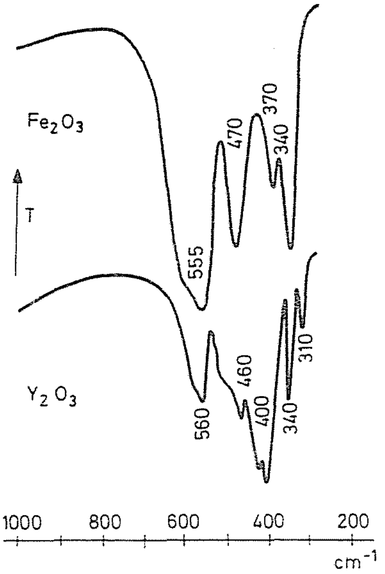

Fig. 3. Spectra of the primary materials in the solid-state reaction $3Y_2O_3+5Fe_2O_3\rightarrow YFeO_3\rightarrow 2Y_3Fe_5O_{12}$

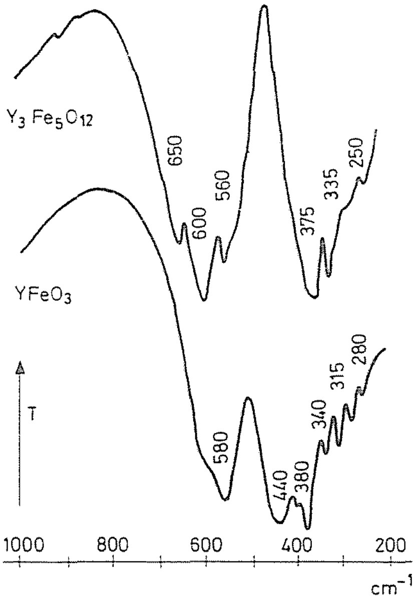

Fig. 4. Spectra of the products of the solid-state reaction above: Orthoferrite ($YFeO_3$) and yttrium-iron garnet ($Y_3Fe_5O_{12}$)

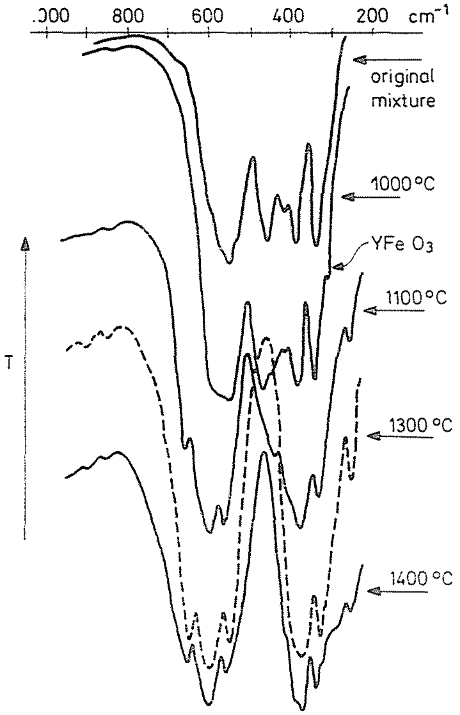

Fig. 5. Spectra of the powder mixture $3Y_2O_3:5Fe_2O_3$ after heat treatments at different temperatures. The peak which indicates the presence of orthoferrite is marked by an arrow

Fe-O vibrations appear at higher wavenumbers again. In the garnet, isolated FeO_4 tetrahedra appear which have Fe-O vibrations in the range of 550–650 cm^{-1} and the octahedra became isolated with absorption range 300–400 cm^{-1}. All these led to the clear separation of the tetrahedral vibrations from the vibrations involving the octahedra and the YO_8 dodecahedra.

The spectra of the heat treated mixtures (Fig. 5) showed that the reaction began at 700 °C already. In spite of this, the spectra were very similar to that of the original mixture up to 1100 °C. At 900 °C new peaks were observable at 312 cm^{-1} and at 445 cm^{-1} which corresponded to the orthoferrite phase. It was proved by adding orthoferrite to the mixture, what made both peaks more pronounced.

At 1100 °C, the garnet phase formed, as it is shown by the spectrum with two well-separated bands. The separation became more pronounced at 1200 °C and at 1300 °C. At 1400 °C, however, such kind of garnet phase formed which had very similar absorption spectrum to that of the single crystal powder. This spectrum had broader bands than the lower-temperature phases. DTGM showed [1] that the phase formed at 1400 °C had more homogeneous structure and bigger grain size than those formed at lower temperatures. The difference in the spectra may correspond to differences in the short-range order in that sense that the formation of long-range order at 1400 °C led to the lowering of the rotational symmetry around the sites and thus to splitting and/or broadening of the bands.

Optical properties of the YIG and substituted YIG crystals in the transparent range

Single crystals of composition $Y_3Ga_xSc_yFe_{5-x-y}O_{12}$ were grown from a PbO—PbF_2—B_2O_3 flux. Planparallel slices of 1 mm thickness were cut from the crystals parallel to the (110) crystal faces and polished mechanically on both sides.

In the transparent range of the YIG in the IR (1300–4000 cm^{-1}) both the transmittance spectra and the reflectance spectra at 6.5° angle of incidence had been measured and both the refractive index, n, and the absorption coefficient, α were calculated using the following formulae for the transmittance and reflectance of a thick layer at normal incidence:

$$T=\frac{(1-R_0)^2e^{-\alpha d}}{1-R_0^2e^{-2\alpha d}}, \qquad R=R_0(1+Te^{-\alpha d})$$

where d is the layer thickness and R_0 is the surface reflectance. If $\alpha/4\pi\tilde{\nu}\ll n$

$$R_0=\left(\frac{n-1}{n+1}\right)^2 .$$

n and α were calculated with the following procedure:

$$\gamma=[(1-R)^2-T^2]/2T$$

$$\tau\equiv e^{-\alpha d}=-\gamma+\sqrt{1+\gamma^2}$$

$$\alpha=\frac{-1}{d}\ln\tau, \qquad R_0=\frac{R}{1+T\tau}, \qquad n=\frac{1+\sqrt{R_0}}{1-\sqrt{R_0}}.$$

Both n and α decreased with increasing substitution of the Fe^{3+} ions. The refractive index of the substituted crystals measured in the range of 3500–4000 cm^{-1} is shown in Table 3. In this range the absorption coefficient was less than the experimental error (0.05 cm^{-1})

In Figure 6 the refraction of the unit cell,

$$R=\left(\frac{n^2-1}{n^2+2}\right)V_c$$

Table 3

Refractive index (n) between 3500 cm^{-1} and 4000 cm^{-1} and lattice parameter of Ga- and Sc-substituted YIG crystals

Sample	Amount of Ga (x) and Sc (y) per formula unit		Lattice parameter (nm)	n
	x	y		
$Y_3Fe_5O_{12}$	0	0	1.2376	2.131
$Y_3Ga_xFe_{5-x}O_{12}$	0.45	0	1.2368	2.122
	0.54	0	1.2367	2.120
	0.70	0	1.2364	2.112
	0.78	0	1.2362	2.105
	0.82	0	1.2362	2.103
$Y_3Sc_yFe_{5-y}O_{12}$	0	0.1	1.241	2.116
	0	0.4	1.241	2.096
	0	0.5	1.242	2.077
$Y_3Ga_xSc_yFe_{5-x-y}O_{12}$	0.8	0.2	1.2376	2.085
	0.8	0.4	1.2384	2.063
	0.8	0.8	1.2410	2.039
	0.9	1.1	1.2436	2.050

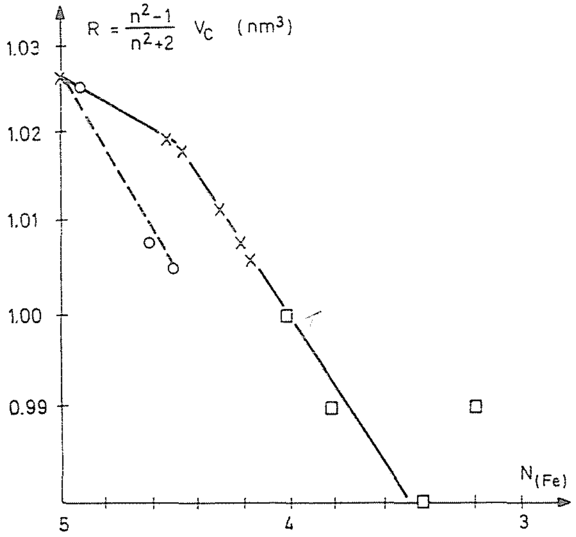

Fig. 6. Refraction of the unit cell of substituted YIG crystals (R) versus the number of iron atoms (N) per formula unit. ○: substitution by Ga, ×: substitution by Sc, □: substitution by Ga(x = 0.8) and by Sc

is plotted versus N, the number of the Fe^{3+} ions per formula unit. (V_c is the volume of the unit cell.) R decreased with the decreasing number of the iron ions. It is known that Ga^{3+} prefers tetrahedral sites but it can substitute also in the octahedra. It was proved by Mössbauer measurements [2] that Ga^{3+} substitution took place in the octahedral sites when the concentration exceeded $x = 0.5$.

The $R-N$ plot started with a smaller slope and it became steeper for $x > 0.5$ when considerable substitution into the octahedra took place. We got this higher gradient of the plot for the Sc- and for the Ga+Sc-substituted crystals up to $y = 0.8$. The parallel plots show that the same centers had been replaced by Sc^{3+} as by Ga^{3+} for $x > 0.5$ — octahedral iron ions. For $y = 1.1$ the refraction was higher than expected. The Mössbauer measurements had not indicated any Sc substitution in the tetrahedral sites. So the increased refraction might be due to some structural change which resulted in the increased polarizability of the remainig Fe^{3+} ions.

Spectra in the range of lattice absorption (1300 cm^{-1} – 200 cm^{-1})

In this range it is possible to measure the specular reflectance of a single-crystal face or the transmittance of powdered sample in KBr pellet. In Fig. 1 the transmission spectrum of YIG, measured in KBr pellet is compared to the reflection spectrum of the single crystal. As the figure shows the transmittance minima correspond to the maxima of the reflectance spectrum. The high reflectance maxima and very deep minima indicate the high ionicity and high perfection of the YIG crystal.

The lattice absorption spectra of the Ga-substituted samples of Table 3 did not change much compared to that of the pure YIG, only small shift of the bands were observable. The Sc substitution, however, caused marked changes in the bands of group "B". (See Fig. 7.)

The effect of a substituent on the spectrum is not clearly predictable. If the substitution is random in the equivalent sites, it does not alter the rotational symmetry so the structure of the spectrum does not change. On the other hand, if ordering takes place in the equivalent sites it may result in the lowering of the rotational symmetry and this involves the appearence of new bands or band splitting.

If the vibrational frequency of the substituent atom and its coordinated oxygens is similar to that of the replaced one then the structure of the spectrum remains the same, only shifts of the bands take place. Such "one-mode behaviour" is characteristic to the $Y_3Ga_xFe_{5-x}O_{12}$ series (Fig. 8).

A light substituent may cause localized modes in the spectrum. If the band of the localized mode is at higher wavenumber than any of those of the host material the substitution took place in those polyhedra which have the highest wavenumber bands.

The substitution of the Ga^{3+} ions in $Y_3Ga_5O_{12}$ by Al^{3+} caused such a localized mode at the high-wavenumber side of the group "A" showing that substitution took place into the tetrahedra (Fig. 9).

The series $Y_3Al_xGa_{5-x}O_{12}$ is an example for the "two-mode behaviour" when the spectrum of a solid solution is rather what one might expect from the

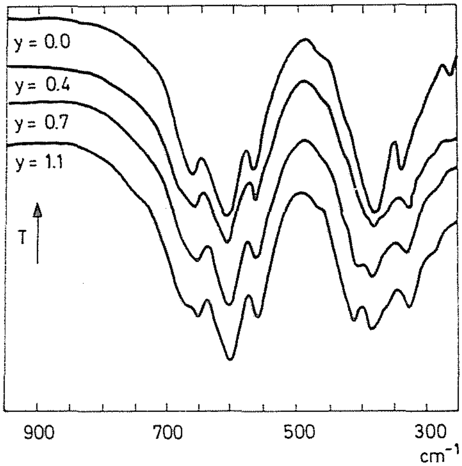

Fig. 7. The effect of Sc substitution on the lattice vibration spectrum of $Y_3Ga_{0.8}Sc_yFe_{4.2-y}$

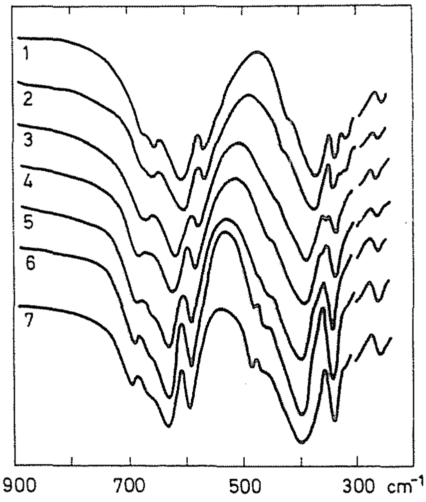

Fig. 8. Spectra of the solid solutions of composition $Y_3Ga_xFe_{5-x}O_{12}$. The amount of gallium in the compounds is as follows:
$1: x=0$, $2: x=0.8$, $3: x=1.75$, $4: x=3.0$, $5: x=4.6$, $6: x=5.0$

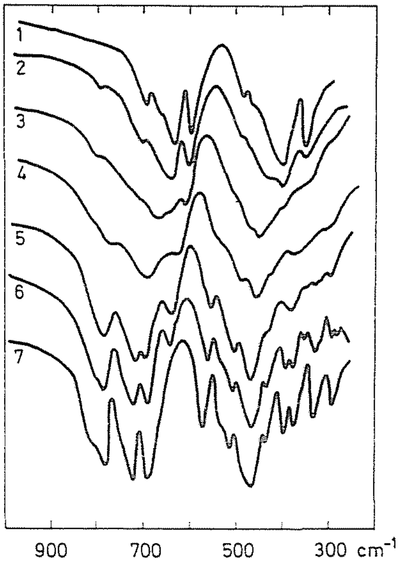

Fig. 9. Transmittance spectra of the solid solutions of composition $Y_3Al_xGa_{5-x}O_{12}$. The amount of Al is as follows:
1 : x = 0, 2 : x = 0.68, 3 : x = 2.07, 4 : x = 3.05, 5 : x = 3.96, 6 : x = 4.95, 7 : x = 5.0

mechanical mixture of the end members. Such behaviour occurs when the mass of the replaced atom is very different from that of the substituent.

Sc^{3+} is lighter than Fe^{3+} so if it substituted in tetrahedral sites a new band ought to appear at the higher-wavenumber side of the "A" bands. But the spectrum did not change in this range except for some broadening. In the range of the octahedral bands around 400 cm^{-1}, however, the Sc substitution caused splitting in the highest wavenumber band. This proves again that Sc substituted only in the octahedral sites.

Conclusion

The substitution of the Fe^{3+} ions in YIG by diamagnetic ones can improve its magnetic properties. The effect of the substitution is determined mainly by the place where the substitution happened. The substitution can cause characteristic changes in the wavenumber or/and shape of the IR bands. It also influences the refractive index in the transparent range. These changes, detectable by IR spectroscopy, can be used to estimate the composition of the crystal or sometimes to determine the location of the substituent. IR spectroscopy can also be used for the identification of the garnet phase or of such composite phases in a mixture whose concentration is more than a few percent. As the IR spectra are influenced mainly by the short-range order, they are usually more sensitive to those structural changes which took place inside the unit cell than the X-ray diffraction method.

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