Optical absorption spectra of iron (III) and chromium (III) doped in synthetic yttrium-aluminium-garnets (YAG)

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ABSTRACT

Eleven weak absorption peaks of Fe^{3+} and two broad absorptions of Cr^{3+} doped in synthetic yttrium-aluminium-garnets, $Y_3Al_2Al_3O_{12}$, have been assigned to d–d transitions of the metal ions in octahedral and tetrahedral sites. All of these absorption peaks have 1 : 1 correspondence to transitions which are predicted to occur in lower energy region by energy level diagrams.

Intensity analysis of $Y_3Al_2Al_3O_{12}$: Fe (III) spectra reveals that the ratio of site occupancy of Fe^{3+} between octahedral and tetrahedral positions is approximately 100 : 1.

Introduction

The optical absorption spectra of natural garnets exhibit a number of overlapped peaks which are usually superimposed on a big charge-transfer band, and make the interpretation of the spectra very difficult. This is mainly due to the presence of more than one transition metal ions in different valence state in octahedral, tetrahedral, and hexahedral cube sites. Secondly it is due to the fact that the transitions predicted by crystal field theory are not always

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clearly observed in spectral patterns because some of the transitions are spin-forbidden and consequently have very weak intensities.

The spectra of synthetic garnets are somewhat easier to interpret because they are dominated by absorption peaks of known cations.

Wood and Remeika (1967) presented an interpretation of the spectra of Fe^{3+} in yttrium-iron-garnet (YIG) and in yttrium-gallium-garnet (YGG) on the basis of a comparison between the lines of the rare-earth orthoferrites where there is only an octahedral site, and those of the garnets, where both octahedral and tetrahedral sites exist. Manning (1972) discussed the optical spectra of Fe^{3+} in some natural garnets including some almandine spectra for which curve resolution was adapted, and he compared the results with those by Wood and Remeika.

In the present work, the optical spectra of yttrium-aluminium-garnet (YAG), $Y_3Al_2Al_3O_{12}$, doped by proper amount of Fe^{3+} are shown to give all peaks predicted by crystal field theory with better resolution, and are discussed and compared with results reported so far.

Experimental

Doped crystals have been grown by flux method. Component materials of oxide form and flux material (PbF_2+PbO) were put in Pt-crucible, and kept at 1300°C in an electric furnace for a couple of hours and then slowly cooled down to 900°C in the rate of 1°C/ hr. At this temperature the crucible was taken out of the furnace and kept in air down to room temperature. The crystals grown on the wall of the crucible were taken out and washed with hot 6N HNO_3. The size of the crystals obtained are about 0.3×0.5 cm in average. The colour of the Fe-doped YAG is pale yellow (1.3 wt. % Fe) or pale yellow with a tint of brown (3.0 wt. % Fe). Chro-

mium-doped YAG has pale green colour. Chemical analyses of the samples were made by usual wet method for Fe and Cr metals. The crystals were cut and polished into plates with the thicknesses of about tenths of a millimeter, for which optical spectra were recorded on Hitachi EPS–3T spectrophotometer in the range of 340 nm to 2000 nm at room temperature.

Results and discussion

$Y_3Al_2Al_3O_{12}$: Fe(III)

Absorption spectra of Fe^{3+}-doped YAG are shown in Fig. 1 (a) in the range of 15000-28000 cm^{-1} for sample A (1.3 % Fe) and in Fig. 1 (b) in the range of 5000-20000 cm^{-1} for sample B (3.0 % Fe). The sample B of higher Fe content (3.0 % Fe) does not give well re-

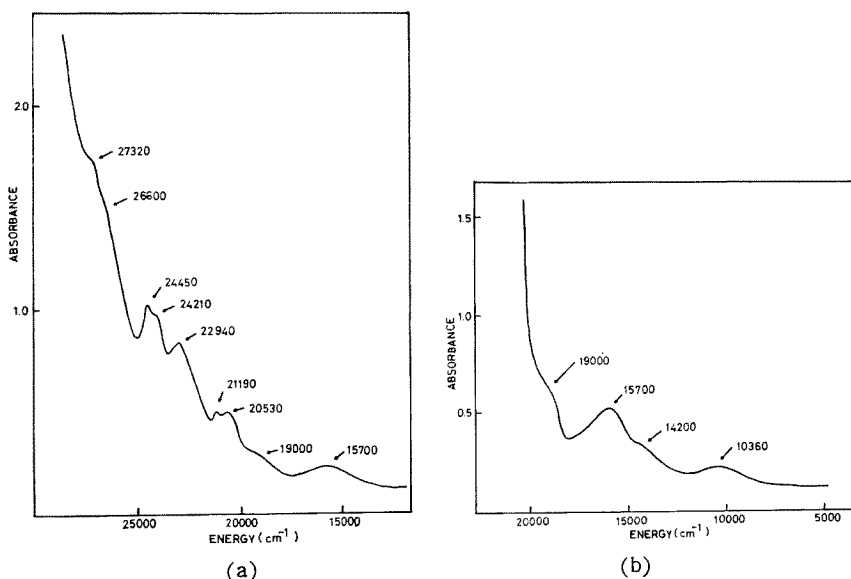Fig. 1. Absorption spectra of $Y_3Al_2Al_3O_{12}$: Fe(III) (a) in the range of 15000—28000 cm^{-1} for the sample A (thickness=0.3 mm, Fe content= 1.3%), (b) in the range of 5000—20000 cm^{-1} for the sample B (thickness= 0.4 mm, Fe content=3.0%).

solved peaks in the range of 20000-28000 cm^{-1} due to a big superimposed charge-transfer band. The difference of Fe content, however, does not give serious change in relative peak intensities except for total intensity and resolution. Eleven absorption peaks are found in the total range of 5000-28000 cm^{-1}. All of these weak lines suggest the spin-forbidden d-d transitions of Fe^{3+} with $3d^5$ configuration. In YAG, Fe^{3+} ions can replace Al^{3+} ions in octahedral and tetrahedral sites which in natural garnets are occupied by trivalent metal ions such as Al(III), Cr(III) and Fe(III), and by Si(IV) and Al (III), respectively. Cube sites are supposed to be occupied only by Y^{3+} ions, not by Fe^{3+} ions, as might be properly accepted.

Starting with the guide that the transitions to field-independent levels $^4A_1, ^4E$ should be sharp lines both for octahedral and tetrahedral sites (Manning, 1970), all of these peaks have been conclusively assigned as follows:

Octahedral

10360 cm^{-1}	$^6A_{1g} \rightarrow ^4T_{1g}(G)$
14200 cm^{-1}	$\rightarrow ^4T_{2g}(G)$
20530 cm^{-1}	$\rightarrow ^4A_{1g} {}^4E_g(G)$
22940 cm^{-1}	$\rightarrow ^4T_{2g}(D)$
24450 cm^{-1}	$\rightarrow ^4E_g(D)$

Tetrahedral

15700 cm^{-1}	$^6A_1 \rightarrow ^4T_1(G)$
19000 cm^{-1}	$\rightarrow ^4T_2(G)$
21190 cm^{-1}	$\rightarrow ^4A_1 {}^4E(G)$
24210 cm^{-1}	$\rightarrow ^4T_2(D)$
27320 cm^{-1}	$\rightarrow ^4T_1(P), {}^4E(D)$

These assignments have been made on the basis of the energy level diagrams (Fig. 2) for $3d^5$ system which were originally given by Tanabe and Sugano (1954) and reproduced by Wood and Remeika
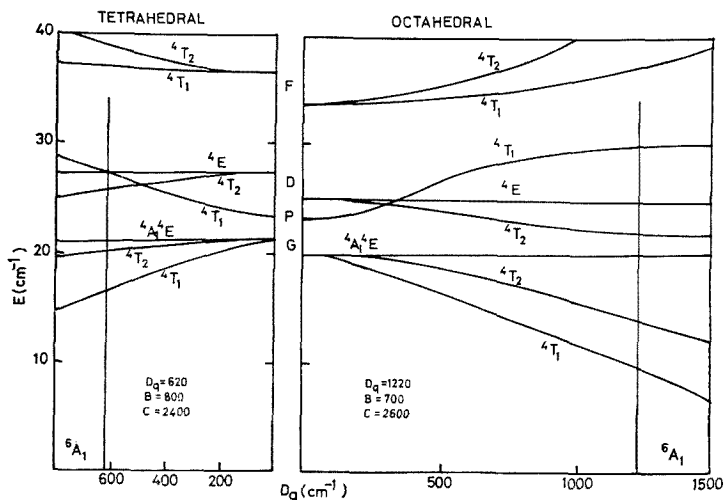
Fig. 2. Energy level diagrams for Fe^{3+} in octahedral (right) and tetrahedral (left) sites of $Y_3Al_2Al_3O_{12}$.

(1967) by computer calculation for the analysis of YIG and YGG: Fe(III). In Table 1, the results obtained here are listed comparing with those for YIG+YGG, andradite and grossular. In the spectra of YGG: Fe(III), Wood *et al.* reported only one peak at 20400 cm^{-1} around 20000 cm^{-1}, and they assigned this to transitions to octahedral $^4A_{1g}{}^4E_g(G)$ and to tetrahedral $^4T_2(G)$. In our spectra of YAG: Fe(III), however, two peaks are observed, a sharp peak at 20530 cm^{-1}, and a broad peak at 19000 cm^{-1}, which are assigned separately to octahedral $^4A_{1g}{}^4E_g(G)$ and to tetrahedral $^4T_2(G)$, respectively. Two peaks around 24000 cm^{-1} (24450 cm^{-1}, 24210 cm^{-1}) correspond to octahedral $^4E_g(D)$ and tetrahedral $^4T_2(D)$ levels. Energy level diagram suggests that transition to field independent octahedral $^4E_g(D)$ level is sharp, while that to field dependent tetrahedral $^4T_2(D)$ is less sharp or broad, so that the sharp peak at 24450 cm^{-1} is probably assigned to transition to $^4E_g(D)$ level and consequently the other peak at 24210 cm^{-1} to $^4T_2(D)$ level. On the other hand, Wood *et al.*

Table 1. List of assigned absorption peaks of Fe^{3+} in synthetic and natural garnets.

YAG : Fe (III)	Assignment	YIG+ YGG*	$Ca_3Fe_2Si_3O_{12}$** (andradite-93)	$Ca_3Al_2Si_3O_{12}$: Fe(III)** (grossular-87)
cm^{-1}		cm^{-1}	cm^{-1}	cm^{-1}
10360(0.03)	oct $^4T_{1g}$ (G)	11100	12453(0.12)	12635(0.02)
14200(0.06)	oct $^4T_{2g}$ (G)	14280	16650(0.07)	16800(0.01)
15700(0.3)	tet $^4T_1$(G)	16400		18200(0.01)
19000(0.2)	tet $^4T_2$(G)	} 20410		19228(0.01)
20530(0.5)	oct $^4A_{1g}{}^4E_g$ (G)		22701(1.50)	22861(0.05)
21190(0.3)	tet $^4A_1{}^4E$(G)	21050		21810(0.03)
			22999(0.86)	23300(0.06)
22940(0.8)	oct $^4T_{2g}$ (D)	23000	24000(0.09)	24000(0.01)
		23870	24509(0.14)	24449(0.03)
		24270	(Mn^{2+})	(Mn^{2+})
24210(0.9)	tet $^4T_2$(D)	26300		
24450(0.9)	oct ^4E_g (D)			27057(0.08)
26600(0.8)	}tet $^4T_1$(P) or			
27320(0.5)	}tet ^4E(D)	26670		26394(0.04)

* Data from Wood and Remeika (1967).
** Data from Moore and White (1972).
Figures in parentheses are peak intensities in A_s/mm.

assigned the peaks of YIG around 24000 cm^{-1}, (23870 cm^{-1}, 24270 cm^{-1}) to transitions to tetrahedral $^4A_1{}^4E$(G), resulting in somewhat different assignments from ours in higher energy region.   Manning (1972) seems to have followed this in the study on andradite and kimzeite. In our spectra of YAG : Fe, the peak at 21190 cm^{-1} seems to be more properly assigned to tetrahedral $^4A_1{}^4E$(G).   Moore and White (1972) are on the same line with us for the interpretation of andradite and grossular spectra.

These our assignments lead to crystal field parameter D_q=1220 cm^{-1} for octahedral site and D_q=620 cm^{-1} for tetrahedral site.   The ratio of these values is 1.95, which is close to the theoretical ratio 9/4 and is considered as a support for our assignments.

Site preference of Fe^{3+} *in YAG*

On the basis of the assignments deduced, the site preference of Fe^{3+} between octahedral and tetrahedral sites in YAG can be discussed. To avoid the influence due to the overlapping of charge-transfer absorption, two absorption peaks in low energy region will be adopted, the peak at $15700 \ cm^{-1}$ for tetrahedral site and the peak at $10360 \ cm^{-1}$ for octahedral site. As seen in Table 2 and in Fig. 3, absorption intensities are approximately proportional to the doped

Table 2. Peak intensities (absorbance/mm) at $15700 \ cm^{-1}$ and $10360 \ cm^{-1}$ with some other data for the discussion of site preference.

| | Fe^{3+} content | Intensity | | tet/oct |
		$15700 \ cm^{-1}$ (tet)	$10360 \ cm^{-1}$ (oct)	
Sample A	1.3%	0.27	0.027	10
Sample B	3.0%	0.63	0.069	9.1
B/A	2.4	2.3	2.5	
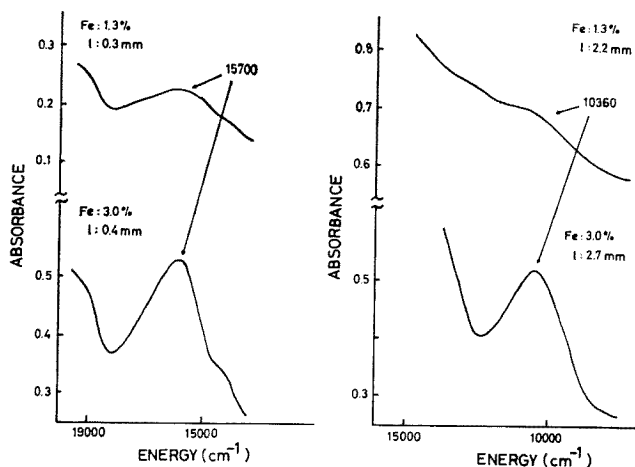
Fig. 3. Absorption peaks of $Y_3Al_2Al_3O_{12}$: Fe(III) at $15700 \ cm^{-1}$ and $10360 \ cm^{-1}$, showing the change of peak resolution depending on the thickness of the sample as well as its Fe content.

amount of Fe^{3+} ion within the doping extent of our experiment, so much as 3.0 %. This shows that Beer's law also holds for these samples studied, and consequently suggests that the doped Fe^{3+} ions are distributed between octahedral and tetrahedral sites in a certain ratio.

Generally the oscillator strength (absorption intensity) of d-d transition concerning tetrahedral site is about 10^{-3}, while that of spin-forbidden d-d transition concerning octahedral site is about 10^{-6} (Kamimura, Sugano and Tanabe, 1969), so that the intensity of tetrahedral peak is roughly 1000 times larger than that of octahedral peak if Fe^{3+} ions are distributed in equal amounts between tetrahedral and octahedral sites. The experimental intensity ratios, however, are obtained as

$$\frac{0.27(\text{tet. } 15700\,\text{cm}^{-1})}{0.027(\text{oct. } 10360\,\text{cm}^{-1})}=10.0 \text{ for the sample A,}$$

and
$$\frac{0.63(\text{tet. } 15700\,\text{cm}^{-1})}{0.069(\text{oct. } 10360\,\text{cm}^{-1})}=9.1 \text{ for the sample B,}$$

showing that tetrahedral peaks have only about ten times of intensities for both samples. This means that Fe^{3+} ions are considered to be distributed between octahedral and tetrahedral sites in the ratio of about $100\left(\doteqdot\frac{\sim1000}{\sim10}\right):1$. Similar preference type and even larger preference to octahedral sites are found in natural garnets of various Fe^{3+} contents. For instance, a grossular (Moore and White, 1972) which contains 0.53 % of Fe_2O_3 is calculated to have the ratio of about 2000 : 1, and an andradite (Moore and White, 1972) which contains 32 % of total Fe ion shows only peaks of octahedral sites, indicating that almost all of Fe^{3+} ions occupy the octahedral sites. They used this result of octahedral occupation as a starting assumption in their interpretation of other garnet spectra. The character of site preference does not seem to be simply compared between the synthetic garnets and natural ones. The

former ones are oxides, while the latter ones are silicate minerals with many other metal ions contained. However, large preference to octahedral sites in the order of about 10^2 to 10^3 is common for both synthetic and natural garnets.

YAG: Cr(III)

The optical spectra of Cr^{3+} doped crystal of YAG show two broad bands at 16800 cm^{-1} and 23400 cm^{-1} which are characteristic of spin-allowed d–d transition of Cr^{3+} in octahedral coordination (Fig. 4). No additional splittings are observed for the crystal which contains 0.14 % of Cr^{3+}. D_q and B values are obtained by solving the matrices of Coulomb interaction for d^3 system. Results are listed in Table 3 together with those for chromium-pyrope (Poole, 1964) and for uvarovite (Manning, 1969). The agreement of these data is excellent, showing that the crystal field character around Cr^{3+} ions in YAG is similar to that of silicate garnets.
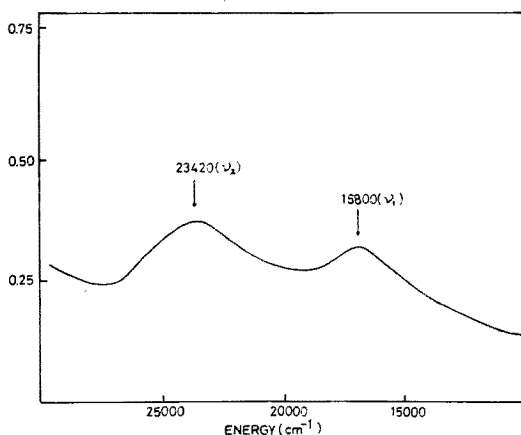

Fig. 4. Absorption spectrum of $Y_3Al_2Al_3O_{12}$: Cr(III) (thickness=1.40 mm, Cr content=0.14%).

Table 3. Crystal field data for YAG : Cr(III) compared with
those for natural garnets.

	YAG : Cr(III)	$Ca_3Cr_2Si_3O_{12}$* (uvarovite)	$Mg_3Al_2Si_3O_{12}$: Cr(III)** (chromium-pyrope)	Assignment
$\nu_1(cm^{-1})$	16800	16600	17600	oct $^4A_{2g} \rightarrow {}^4T_{2g}$ (F)
$\nu_2(cm^{-1})$	23420	23100	24130	oct $^4A_{2g} \rightarrow {}^4T_{1g}$ (F)
ε_{ν_1} (liter·mole^{-1} cm^{-1})	22		12	
ε_{ν_2}	31		20	
$D_q(cm^{-1})$	1680	1660	1760	
$B(cm^{-1})$	659	646	655	

  * Data from Manning (1969).
 ** Data from Poole (1964).

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