

## Cationic Interdiffusion in Some Garnets

V. V. PAN'KOV AND L. A. BASHKIROV

*Institute of Physics of Solids and Semiconductors, P. Brovki 17, Minsk  
220726 USSR*

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The interdiffusion of Y, Fe, Ga, and Gd cations in diffusion couples of  $Gd_3Ga_5O_{12}$ - $Y_3Fe_5O_{12}$ ,  $Gd_3Ga_5O_{12}$ - $Gd_3Fe_5O_{12}$ , and  $Gd_3Fe_5O_{12}$ - $Y_3Fe_5O_{12}$  single crystals is investigated in the temperature range 1660-1810 K in air. The electron probe microanalysis method has been used in determining the cation diffusion profiles. The interdiffusion coefficients and their concentration dependences are determined and the activation energy values of the interdiffusion process are calculated. © 1985 Academic Press, Inc.

### Introduction

Most of the reported studies on cationic diffusion in garnets have been devoted to self-diffusion (1-3) and not to interdiffusion. Nevertheless, cationic interdiffusion is very important for understanding the transport processes in garnets, especially for developing a method for preparing thin garnet films by liquid-phase epitaxy. The films of mixed rare earth ferrites and garnets widely used in cylindrical magnetic domain devices are produced on single crystal substrates of transparent nonmagnetic garnets, in particular,  $Gd_3Ga_5O_{12}$ , using the liquid-phase epitaxy method. The temperature range of liquid-phase film epitaxy permits interaction of the film and the substrate that influences the characteristics of the material obtained. This interaction plays an essential role in preparing films with cylindrical magnetic domains, the diameter of which is less than 1  $\mu\text{m}$ . In this case the transition layer at the film-substrate interface makes up an appreciable

part of the film thickness (4). The films and single crystals of solid solutions of multi-component ferrogarnets grown by the flux method as a rule are complex in structure. Under thermal annealing, their composition becomes homogeneous. As shown in (5), films consisting of several iron-garnet layers of different composition are promising for new microelectronic devices. Thus, the investigation of cationic interdiffusion in garnets may favor the development of methods to produce both compositionally homogeneous and laminated epitaxial films.

To elucidate the mechanism of solid solution formation, the diffusion interactions of garnets with various cationic combinations in different sublattices have been investigated.

The  $Gd_3Fe_5O_{12}$ - $Y_3Fe_5O_{12}$  system was studied, where the diffusible Gd and Y ions occupy the dodecahedral (*c*) sites with eight-oxygen coordination. In the  $Gd_3Ga_5O_{12}$ - $Gd_3Fe_5O_{12}$  system the Ga and Fe ions diffuse through octahedral (*a*) and tetrahedral (*d*) sites with six- and four-oxy-

gen coordination, respectively. The third system studied,  $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ – $\text{Y}_3\text{Fe}_5\text{O}_{12}$ , is a combination of the two cases mentioned above.

### Experimental

The interdiffusion was studied using the method of diffusion couples composed of the  $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ ,  $\text{Gd}_3\text{Fe}_5\text{O}_{12}$ , and  $\text{Y}_3\text{Fe}_5\text{O}_{12}$  single crystals at 1660–1810 K in air. The single crystals were grown by the flux method and cut into rods ( $5 \times 5 \times 5$  mm). The diffusion couples were arranged in such a way that the direction of the diffusion flow coincided with that of [111] for the single crystals. During the annealing the contact between the crystals, constituting the diffusion couple, was kept constant by a special device. To find the initial interface a thin platinum line was precipitated on the crystals.

The distribution of the Ga, Gd, Fe, and Y content in the reaction zones was determined by electron probe microanalysis as was described in (6).

The electron beam moved continuously on the section surface. The characteristic irradiation intensities of the pure  $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ ,  $\text{Gd}_3\text{Fe}_5\text{O}_{12}$ , and  $\text{Y}_3\text{Fe}_5\text{O}_{12}$  were used as standards. The raw microprobe data were converted to the Gd, Ga, Y, and Fe atomic fractions by a computer program using the correction coefficients for the atomic number, absorption, and X-ray fluorescence.

The interdiffusion coefficients were calculated by the Boltzmann–Matano (7) method using the distribution curves of Ga, Gd, Fe, and Y in the diffusion zone.

### Results and Discussion

#### $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ – $\text{Y}_3\text{Fe}_5\text{O}_{12}$ System

In the reaction zone only a layer of the  $(\text{Gd}_x\text{Y}_{1-x})_3(\text{Ga}_y\text{Fe}_{1-y})_5\text{O}_{12}$  solid solution is

formed, with  $x$  and  $y$  varying from 0 to 1. The interdiffusion profiles (Fig. 1) show that various cations are probably transported only through the corresponding garnet structure sublattices: Ga and Fe, through  $(a, d)$  sublattices; Gd and Y, through  $(c)$  sublattices. It was established that the diffusion zone on the  $\text{Y}_3\text{Fe}_5\text{O}_{12}$  plate is larger than that on the  $\text{Gd}_3\text{Ga}_5\text{O}_{12}$  one.

The Matano plane, coinciding with the initial interface in case of gadolinium at all temperatures, passes through the composition containing 0.075 atomic fraction of gadolinium. This corresponds to the solid solution composition with a Gd : Y concentration ratio of 1 : 1. In the case of the Ga concentration profile, the Matano plane position varies with temperature from 0.125 to 0.075 atomic fraction of gallium, which indicates an increase in asymmetry of the concentration profile with temperature.

While calculating the interdiffusion coefficients for the same area of the diffusion zone from the concentration curves of gallium and iron the difference proved to be quite small. For instance, at 1780 K the interdiffusion coefficient containing 0.125 and 0.200 atomic fraction of Ga is  $1.07 \times 10^{-11}$  and  $0.53 \cdot 10^{-11}$   $\text{cm}^2/\text{sec}$ , respectively. The corresponding values calculated from the Fe curve were  $1.11 \times 10^{-11}$  and  $0.56 \times 10^{-11}$   $\text{cm}^2/\text{sec}$ . However, the correction-co-

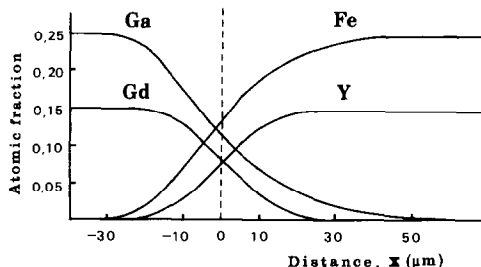


FIG. 1. Distribution of the Gd, Y, Ga, and Fe concentrations in the reaction zone for the  $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ – $\text{Y}_3\text{Fe}_5\text{O}_{12}$  diffusion couple annealed at 1780 K for 31 hr.  $x = 0$  is the initial interface.

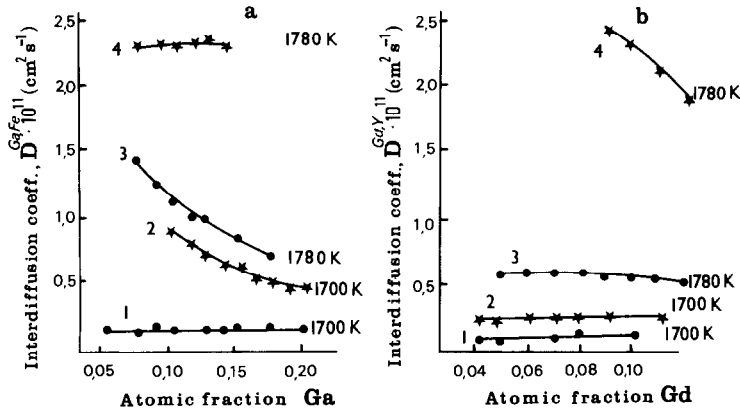


FIG. 2. Interdiffusion coefficients  $D^{Ga,Fe}$  (a) and  $D^{Gd,Y}$  (b) vs Ga and Gd concentrations for  $Gd_3(Ga_y, Fe_{1-y})_5O_{12}$  (a-2.4);  $(Gd_xY_{1-x})_3Fe_5O_{12}$  (b-2.4),  $(Gd_xY_{1-x})_3(Ga_y, Fe_{1-y})_5O_{12}$  (a-1.3, b-1.3) solid solutions at 1780 and 1700 K.

efficient variations for Ga and Gd are smaller than those for Fe and Y. Consequently, in this case it is possible to convert weight fraction to atomic fraction with great accuracy while calculating concentration. Thus the interdiffusion coefficients were calculated using the concentration curves of Ga and Gd. It appeared that the interdiffusion coefficient for Ga and Fe,  $D^{Ga,Fe}$  depends strongly on the  $(Gd_xY_{1-x})_3(Ga_y, Fe_{1-y})_5O_{12}$  solid solution composition and increases continuously with the decreasing y. In the case of interdiffusion in the rare earth sublattice the concentration

dependence of  $D^{Gd,Y}$  is negligible and the  $D^{Gd,Y}$  values are lower than the corresponding  $D^{Ga,Fe}$  values (Fig. 2). The activation energy values are calculated from the temperature dependence of  $D$ . The increase of x and y results in a decrease of the activation energy for the process of interdiffusion both between Ga and Fe and between Gd and Y cations. In the case of the interdiffusion between Ga and Fe the activation energy obeys the linear law and its values are almost a factor of 2 higher than those for the interdiffusion process in the case of Gd and Y (Table I).

TABLE I

THE ACTIVATION ENERGY  $Q$  VALUES AND THOSE OF PREEXPONENTIAL MULTIPLIER  $D_0$  OF THE INTERDIFFUSION COEFFICIENT IN THE SOLID SOLUTIONS  $(Gd_xY_{1-x})_3(Ga_y, Fe_{1-y})_5O_{12}$  IN THE CASE OF INTERDIFFUSION OF Gd AND Y AND OF Ga AND Fe

Ga (Atomic fraction)	Ga-Fe		Gd (Atomic fraction)	Gd-Y	
	$Q$ (kJ/mole)	$D_0$ (cm <sup>2</sup> /sec)		$Q$ (kJ/mole)	$D_0$ (cm <sup>2</sup> /sec)
0.075	596.5 ± 7.9	5.1 × 10 <sup>6</sup>	0.05	250.4 ± 6.3	116.0 × 10 <sup>-6</sup>
0.090	581.0 ± 2.1	1.6 × 10 <sup>6</sup>	0.06	232.4 ± 5.8	36.1 × 10 <sup>-6</sup>
0.100	567.6 ± 7.5	0.58 × 10 <sup>6</sup>	0.07	210.3 ± 4.2	8.0 × 10 <sup>-6</sup>
0.115	543.8 ± 8.4	0.11 × 10 <sup>6</sup>	0.08	183.5 ± 7.9	1.3 × 10 <sup>-6</sup>
0.125	528.8 ± 8.8	0.04 × 10 <sup>6</sup>	0.09	188.9 ± 2.1	1.7 × 10 <sup>-6</sup>
0.140	510.0 ± 4.2	0.98 × 10 <sup>4</sup>	0.10	191.0 ± 8.4	1.9 × 10 <sup>-6</sup>
0.150	505.8 ± 7.1	0.71 × 10 <sup>4</sup>			

*Gd<sub>3</sub>Ga<sub>5</sub>O<sub>12</sub>-Gd<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub> and  
Gd<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub>-Y<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub> Systems*

The concentration distribution of elements in the diffusion zone of the Gd<sub>3</sub>Ga<sub>5</sub>O<sub>12</sub>-Gd<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub> system is shown in Fig. 3a, with the diffusion zone consisting of Gd<sub>3</sub>(Ga<sub>y</sub>Fe<sub>1-y</sub>)<sub>5</sub>O<sub>12</sub> solid solution, where *y* varies from 0 to 1.

The peculiarity of the diffusion zone for the Gd<sub>3</sub>Ga<sub>5</sub>O<sub>12</sub>-Gd<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub> system is the presence of a comparatively large layer, consisting of a Gd<sub>3</sub>(Ga<sub>y</sub>Fe<sub>1-y</sub>)<sub>5</sub>O<sub>12</sub> solid solution with an almost constant *y* value. For instance, its composition at 1700 K is given as Gd<sub>3</sub>Ga<sub>2</sub>Fe<sub>3</sub>O<sub>12</sub> (Fig. 3a). A temperature rise leads to the shift in the composition of this layer with almost constant concentration toward Gd<sub>3</sub>Ga<sub>5</sub>O<sub>12</sub>, and to its displacement in the diffusion zone toward the Gd<sub>3</sub>Ga<sub>5</sub>O<sub>12</sub> plate. Thus, with a rise of the diffusion annealing temperature the composition of this layer varies in such a way that the Ga concentration increases, while that of Fe decreases (Table II).

Hence, in the Gd<sub>3</sub>Ga<sub>5</sub>O<sub>12</sub>-Gd<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub> system there exists the composition Gd<sub>3</sub>(Ga<sub>y</sub>Fe<sub>1-y</sub>)<sub>5</sub>O<sub>12</sub>, where the interdiffusion process between Ga and Fe accelerates when compared to that of the neighboring compounds. In this case the Ga concentration in the diffusion zone of Gd<sub>3</sub>Ga<sub>5</sub>O<sub>12</sub> decreases up to the value corresponding to its concentration in the above-mentioned solid solution.

The Ga and Fe ions diffuse in this solid

TABLE II  
THE Gd<sub>3</sub>(Ga<sub>y</sub>Fe<sub>1-y</sub>)<sub>5</sub>O<sub>12</sub> SOLID SOLUTION COMPOSITION FOR THE REACTION AREA WITH NEARLY CONSTANT *y* VALUES AS A FUNCTION OF ANNEALING TEMPERATURE

<i>T</i> <sub>annealing</sub> (K)	Composition
1660	Gd <sub>3</sub> Ga <sub>0.8</sub> Fe <sub>4.2</sub> O <sub>12</sub>
1700	Gd <sub>3</sub> Ga <sub>2.0</sub> Fe <sub>3.0</sub> O <sub>12</sub>
1740	Gd <sub>3</sub> Ga <sub>3.7</sub> Fe <sub>1.3</sub> O <sub>12</sub>
1780	Gd <sub>3</sub> Ga <sub>3.8</sub> Fe <sub>1.2</sub> O <sub>12</sub>

solution more rapidly than in the surrounding areas. A slower interdiffusion process occurring near both sides of the layer of the characteristic solid solution results in an accumulation of the ions at its boundaries and in an increase of the length of this layer. The concentration distribution of elements in the diffusion zone formed while annealing a diffusion couple Gd<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub>-Y<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub> shows the reaction zone to be the (Gd<sub>x</sub>Y<sub>1-x</sub>)<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub> solid solution with *x* changing from 0 to 1 (Fig. 3b). Unlike the Gd<sub>3</sub>Ga<sub>5</sub>O<sub>12</sub>-Gd<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub> system relative to the initial interface, nearly symmetric curves of concentration distribution Gd and Y are obtained in this case.

The interdiffusion coefficients (*D*<sup>Ga,Fe</sup> and *D*<sup>Gd,Y</sup>) for the Gd<sub>3</sub>Ga<sub>5</sub>O<sub>12</sub>-Gd<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub> and Gd<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub>-Y<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub> systems under identical thermal treatment conditions are found to be of the same order (Figs. 2a and b).

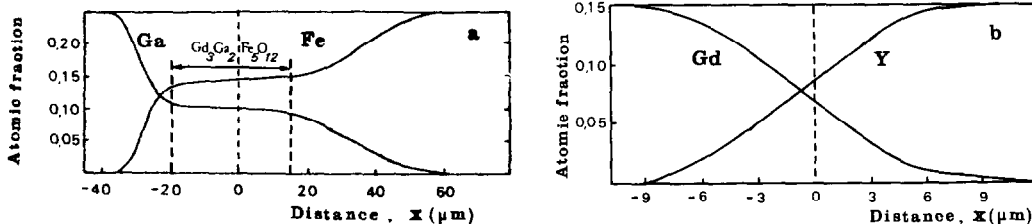


FIG. 3. Distribution of the Ga and Fe (a) and Gd and Y (b) concentrations in the reaction zones for the Gd<sub>3</sub>Ga<sub>5</sub>O<sub>12</sub>-Gd<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub> (a) and Gd<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub>-Y<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub> (b) diffusion couples annealed at 1700 K for 11 hr. *x* = 0 is the initial interface.

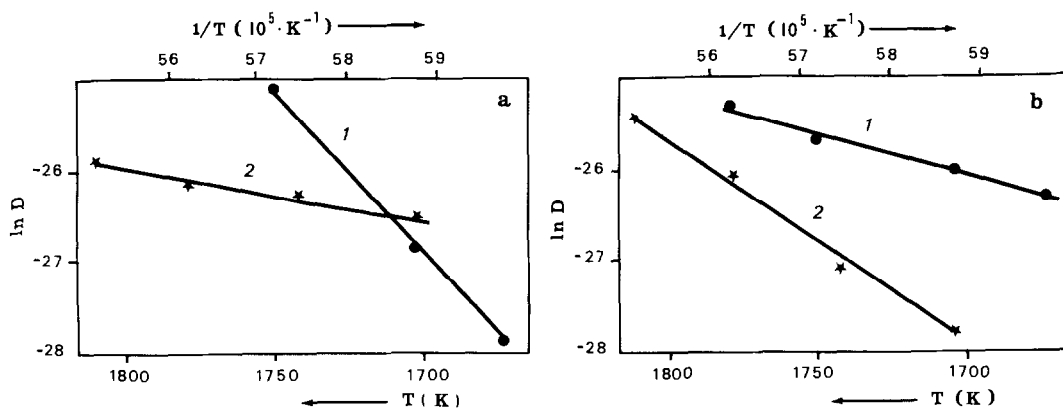


FIG. 4. Interdiffusion coefficients  $D$  of gadolinium and yttrium (a) and of gallium and iron (b), vs temperature of annealing for solid solutions of the following compositions:  $Gd_{1.7}Y_{1.3}Fe_5O_{12}$  for the  $Gd_3Fe_5O_{12}-Y_3Fe_5O_{12}$  (1a),  $Gd_3Ga_{2.5}Fe_{2.5}O_{12}$  for the  $Gd_3Ga_5O_{12}-Gd_3Fe_5O_{12}$  (1b), and  $Gd_{1.7}Y_{1.3}Ga_{2.5}Fe_{2.5}O_{12}$  for the  $Gd_3Ga_5O_{12}-Y_3Fe_5O_{12}$  (2a,b).

It is established that the presence of two pairs of ion flows moving in opposite directions ( $Gd_3Ga_5O_{12}-Y_3Fe_5O_{12}$  system) decreases the  $D$  values as compared to the case of only one pair of ion flows ( $Gd_3Ga_5O_{12}-Gd_3Fe_5O_{12}$  and  $Gd_3Fe_5O_{12}-Y_3Fe_5O_{12}$  system). This is observed for all annealing temperatures except 1700 K in the case of gadolinium-yttrium interdiffusion whenever the concentrations of these cations for the system of four and two different cations are similar. The interdiffusion coefficients then coincide.

It is noted that the difference in the  $D$  values above 1700 K increases sharply for the  $Gd_3Ga_5O_{12}-Y_3Fe_5O_{12}$  and  $Gd_3Fe_5O_{12}-Y_3Fe_5O_{12}$  systems.

The activation energy of the Ga and Fe interdiffusion process in  $(Gd_xY_{1-x})_3(Ga_yFe_{1-y})_5O_{12}$  for the composition  $Gd_{1.7}Y_{1.3}Ga_{2.5}Fe_{2.5}O_{12}$  is  $(528.8 \pm 8.8)$  kJ/mole. For the interdiffusion of these cations in a binary system, i.e.,  $Gd_3(Ga_yFe_{1-y})_5O_{12}$  with the same Ga and Fe concentrations, for  $Gd_3Ga_{2.5}Fe_{2.5}O_{12}$  it is equal to  $(224.5 \pm 8.4)$  kJ/mole (Fig. 4). For the interdiffusion in the rare earth sublattice of the system

$(Gd_xY_{1-x})_3(Ga_yFe_{1-x})_5O_{12}$  at the above-mentioned element amounts to  $(183.5 \pm 7.9)$  kJ/mole, which is much lower than the activation energy of the Ga and Y interdiffusion in the binary system  $(Gd_xY_{1-x})_3Fe_5O_{12}$ , which for the solid solution  $Gd_{1.7}Y_{1.3}Fe_5O_{12}$  is  $(873.6 \pm 41.8)$  kJ/mole.

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