

# X-Ray Diffraction and Cation Distribution Studies on Eu Substituted Yttrium Iron Garnet

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## Abstract

Eu substituted yttrium iron garnet (YIG) with generic formula  $Y_{3-x}Eu_xFe_5O_{12}$  where  $x = 0.0, 0.1, 0.3, \text{ and } 0.5$  have been prepared by standard ceramic technique using AR grade oxides. Structural characterization of  $Y_{3-x}Eu_xFe_5O_{12}$  was performed by X-ray diffraction (XRD) technique at room temperature. The single phase cubic garnet structure of the prepared samples was confirmed through X-ray analysis. The particle size was obtained from the XRD data using Scherrer's formula. The lattice parameter calculated from XRD data found to increase with Eu substitution. The X-ray diffraction method was used for the determination of cation distribution in  $Y_{3-x}Eu_xFe_5O_{12}$  garnet system. Here, we report the studies on X-ray diffraction and cation distribution of  $Y_{3-x}Eu_xFe_5O_{12}$

**Keywords:** Garnet, Ceramic technique, X-ray diffraction, Cation distribution.

## 1. Introduction

The garnets and their derived compounds are known as important class of magnetic materials due to their magnetic, magneto-optical, magneto-resistive, thermal, electrical and mechanical properties such as ferrimagnetism, high thermal conductivity, high electrical resistivity, controllable saturation magnetization, etc. These properties lead them to employ into several applications such as electronic devices like phase shifters, circulators, oscillators for microwave frequencies, sensors, magneto-optic sensors, anode materials for batteries, catalysts, and magneto-optical devices [1-3]. Garnet materials of different shapes and sizes have found considerable interest due to their technological promising applications in the microwave frequencies, magnetic data storage, for high speed digital tape or disk recording etc. Many methods have been used to prepare garnet material especially  $Y_3Fe_5O_{12}$ . The conventional way of synthesizing this material is by solid state reaction of oxide/carbonate powders and calcinations at high

temperature ( $>1200^\circ\text{C}$ ) [4]. The electrical and magnetic properties of  $Y_3Fe_5O_{12}$  garnet are strongly affected by the composition and microstructure and cation distribution which are sensitive to the preparation methodology used in their synthesis.

Recently, polycrystalline YIG also find its application in magneto-optical recording media devices [5, 6]. However, to improve their present applications and develop new uses, a full understanding of their structural, magnetic properties along with cation distribution is essential.

In the present work, studies on the synthesis, structural and cation distribution of  $Eu^{3+}$  substituted yttrium iron garnet have been reported.

## 2. Experimental Details

The samples of  $Y_{3-x}Eu_xFe_5O_{12}$  where  $x = 0.0, 0.1, 0.3, \text{ and } 0.5$  were prepared by using ceramic technique. The raw materials used for the synthesis of  $Y_{3-x}Eu_xFe_5O_{12}$  where  $x = 0.0, 0.1, 0.3, \text{ and } 0.5$  high purity oxides of  $Y_2O_3, Eu_2O_3, Fe_2O_3$  were used. The oxides were mixed thoroughly in stoichiometric proportion to yield the desired composition. The mixture was dried and pre-sintered at  $1050^\circ\text{C}$  for 24 h in air and cooled to room temperature.

### 2.1 Characterizations

The powders X-ray diffractograms for all the samples were recorded at room temperature using Philips X-ray diffractometer (Model PW-3710). XRD pattern were obtained in the range of  $20^\circ$  to  $80^\circ$  with  $Cr-K\alpha$  radiation.

### 2.2 Cation distribution

Cation distribution in  $Y_{3-x}Eu_xFe_5O_{12}$  garnet system was estimated by using X-ray diffraction method. X-ray intensities of selected planes were calculated using

Berger's formula and compared them with the observed intensities. A close match of the two intensities for a given possible combination of cations residing at interstitial sites is taken as correct cation distribution

### 3 RESULTS AND DISCUSSION

#### 3.1 X-Ray Diffraction

Typical diffraction pattern X-ray diffraction (XRD) pattern of  $Y_{3-x}Eu_xFe_5O_{12}$  where  $x=0.1$  recorded at room temperature is shown in the Figure 1.

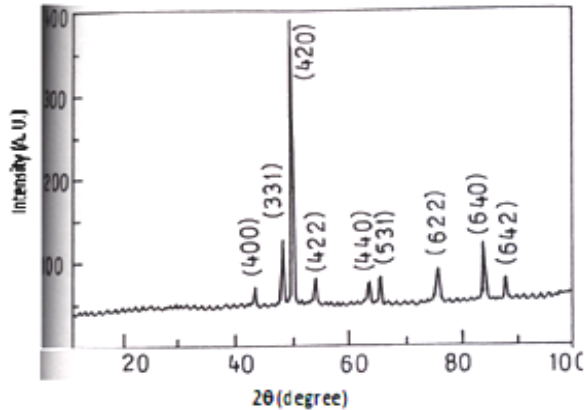


Fig. 1 Typical XRD pattern for  $x = 0.1$  of the series  $Y_{3-x}Eu_xFe_5O_{12}$

The XRD pattern shows well defined, intense reflections belonging to cubic structure. The XRD patterns analysis indicates that the samples under investigation were formed in a single phase with a cubic garnet structure. No impurity peaks were observed in the XRD patterns. All the peaks of the XRD patterns were indexed using Bragg's law. XRD data was used to determine the lattice constant 'a' using the following relation

$$a = d\sqrt{N} \quad (1)$$

All the notations have their usual meaning. The lattice constant increases linearly and obeys Vegard's law. The increasing behavior of lattice constant with Eu substitution can be understood from the knowledge of ionic radii of the constituent ions. Yttrium ions of smaller ionic radii ( $0.89\text{\AA}$ ) have replaced by  $Eu^{3+}$  of larger ionic radii ( $0.95\text{\AA}$ ) and therefore lattice constant increases with Eu substitution.

The particle size was calculated by using Scherrer's equation as follows;

$$t = \frac{0.9\lambda}{\beta \cos \theta} \quad (2)$$

where,  $t$  is particle size,  $\lambda$  is the wavelength and  $\beta$  is a full width half maximum (FWHM). The value of particle size

obtained from above relation for all the samples is almost same. It is of the order of 151-152 nm.

The X-ray density of the samples of the series  $Y_{3-x}Eu_xFe_5O_{12}$  where  $x= 0.0$  and  $0.1$  has been calculated from the molecular weight and volume of the unit cell. Using the formula,

$$d_x = \frac{8M}{Na^3} \quad (3)$$

where,  $M$  is molecular weight,  $N$  is Avogadro's no. and  $a$  is the lattice constant.

The values of X-ray density are listed in table 1. It is observed from table 1 that X-ray density increases with the substitution of Eu. In the present series  $Y_{3-x}Eu_xFe_5O_{12}$ , the lattice constant increases with Eu substitution. Therefore, naturally the X-ray density should decrease. However, in the present study, X-ray density increases instead of decrease. This is because of the fact that the increase in the mass overtakes the increase in volume of the unit cell. The values of the molecular weight for the samples of the series  $Y_{3-x}Eu_xFe_5O_{12}$  are given in table 1. The bulk density of the samples of the series  $Y_{3-x}Eu_xFe_5O_{12}$  was obtained using the values of mass and dimensions of pellets. The values of bulk density are presented in table 1. From table 1 it is clear that the bulk density is of the order of 95% to that of X-ray density.

The percentage porosity of the samples was calculated using the relation;

$$p = \left(1 - \frac{d}{d_x}\right) \times 100 \quad (4)$$

where,  $d$  is bulk density and  $d_x$  is the X-ray density.

The values of porosity of all the samples are listed in table 1. The porosity value indicates that the samples are dense and compact.

**Table 1:** Structural parameters (lattice constant  $a$  and particle size  $t$ ) and activation energy ( $E_g$ ) for the series  $Y_{3-x}Eu_xFe_5O_{12}$  ( $x= 0.0$  and  $0.1$ )

$x$	$a$ $\text{\AA}$	Mol. wt. gm	$d_x$ $\text{gm/cm}^3$	$d_B$ $\text{gm/cm}^3$	P %
0.0	12.331	738	5.222	5.339	2.23
0.1	12.334	744	5.272	5.193	1.50

#### Cation Distribution

The study of the distribution of cations among the available sites in ferrites is very much important in understanding the structural and magnetic behavior of ferrite. The cation distribution can be obtained from X-ray diffraction [7], Mossbauer spectroscopy [8], neutron diffraction [9] and magnetization [10] techniques. In garnets cations are distributed at three sub lattices namely

dodecahedral [c], octahedral (a) and tetrahedral (d). The total magnetic moments on the 'a' and 'd' ions are aligned anti-parallel and moments on the 'c' ions are anti-parallel to those on the 'd' ion. Thus, for the formula  $(3M_2O_3)^c(2Fe_2O_3)^a(3Fe_2O_3)^d$  the arrangement is  $6Fe^d$ ,  $4Fe^a$ ,  $6M^c$ . The net moment  $m$  (in Bohr magneton per unit formula) is

$$M = 6m_c - (6m_d - 4m_a) = 6m_c - 10\mu_B \quad (5)$$

Assuming a moment of  $5\mu_B$  per  $Fe^{3+}$  ion in terms of the unit formula  $M_3Fe_2Fe_3O_{12}$  equation (3) becomes

$$M = 3m_c - 5\mu_B \quad (6)$$

In general, cation distribution of yttrium iron garnet  $M_3Fe_2Fe_3O_{12}$  is expressed as,

$$\{Y_3\}^c[Fe_2]^a(Fe_3)^dO_{12} \quad (7)$$

Comparing the site preference energy of the constituent ions and assuming that  $Eu^{3+}$  has tendency to occupy dodecahedral C-sites, the cation distribution of the present garnet system  $Y_{3-x}Eu_xFe_5O_{12}$  can be written as,

$$\{Y_{3-x}Eu_x\}^c[Fe_2]^a(Fe_3)^dO_{12} \quad (8)$$

The obtained cation distribution is supported by magnetization data (not reported here). The average ionic radius of dodecahedral (c), octahedral (a) and tetrahedral (d) can be estimated using the relation [12]

$$r_d = [x(Fe^{3+}).r(Fe^{3+})] \quad (9)$$

$$r_a = 1/2[(xFe^{3+}).r(Fe^{3+}) + x(Fe^{2+}).r(Fe^{2+})] \quad (10)$$

$$r_c = [x(Y^{3+}).r(Y^{3+}) + x(Fe^{3+}).r(Fe^{3+})] \quad (11)$$

Where,  $x$  and  $r$  represents concentration and ionic radius of cation on the respective sites. Using above equations (8, 10 and 11), considering the ionic radii of yttrium ( $Y^{3+}$ ) as  $(0.89A^0)$ , Europium  $Eu^{3+}$  as  $(0.95 A^0)$  and the ferric ( $Fe^{3+}$ ) as  $(0.64 A^0)$  and the cation distribution formula given by eq. 6, the theoretical lattice constant of all the samples was also estimated using the following formula [11],

$$a_t = b_1 + b_2r_c + b_3r_d + b_4r_a + b_5r_c.r_d + b_6r_c.r_a \quad (12)$$

where,  $b_1 - b_6$  are exchange interaction in agreement with earlier report [12].

#### 4. Conclusions

The samples of the series  $Y_{3-x}Eu_xFe_5O_{12}$  ( $x = 0.0$  and  $0.1$ ) synthesized by ceramic technique possesses single phase

cubic garnet structure, which is evidenced by X-ray diffraction data. The lattice parameter of pure YIG is in good agreement with the reported data. The lattice constant increases with Eu substitution. Cation distribution data suggest that Y and Eu occupy dodecahedral site, whereas  $Fe^{3+}$  ions get distributed in remaining two sites i.e. tetrahedral [d] and octahedral (a) sites. The theoretical and experimental lattice parameter agrees closely with each other suggesting that the estimated cation distribution is correct.

#### References

- [1]. T. Y. Kim, Y. Yamazaki, T. Hirano, Phys. Status Solidi B 241 (7), 1601 (2004).
- [2]. Y. H. Jeon, J. W. Lee, J. H. Oh, J. C. Lee, S. C. Choi, Phys. Status Solidi A 201(8), 1893 (2004)
- [3]. S. Taketomi, C. M. Sorensen, K. J. Klabunde, J. Magn. Mater. 222, 54 (2000).
- [4]. H. Zhao, J. Zhou, Y. Bai, Z. Gui, L. Li, J. Magn. Mater. 280, 208 (2004).
- [5]. S. HosseiniVajargah, H. R. MadaahHosseini, Z. A. Nemati, Mater. Sci. Eng. B129, 211 (2006).
- [6]. Z. Cheng, Hua Yang, J. Physica E. 39, 198 (2007).
- [7]. D. S. Birajdar, Devatmal U. N. and Jadhav K. M., J. Matr. Sci. 21 (2002) 1443
- [8]. Jani N. N., Trivedi B. S., Joshi H. H., Bichile G. K., and Kulkarni R. G., Bull. Mater. Sci. 21 (1998) 639
- [9]. A. K. Ghatke, S. A. Patil, S. K. Paranjape, Sol. State Commun. 98 (1996) 885
- [10]. A. M. Shaikh, S. C. Watave, S. S. Bellad, S.A. Jadhav, B. K. Chougule, Mat. Chem. And Phys. 65 (2000) 46
- [11]. R. D. Shannon, and C. T. Orewitt, Acta. Cryst. B 25 (1969)
- [12]. Sung Ha Lee, KwangPyoChae, Seok Won Hong and YoundBae Lee, Solid State Comm. 83 (1992) 97