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# STRUCTURAL AND MAGNETIC CHARACTERISTICS OF ER DOPED YTTRIUM IRON GARNET NANO-PARTICLES

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# ABSTRACT

Polycrystalline ER  $_xY_{3-x}Fe_5O_{12}$ nano-particleshave been prepared by conventional ceramic method. The structural parameters and Phase purity were investigated using X-ray diffractometer (XRD) and Scanning Electron Microscopy (SEM), which indicates the single-phase Er-YIG having well defined intensity peaks. The lattice constant was decreased from 12.29<sup>0</sup>Ato 12.27<sup>0</sup>A, in accordance with Vegard's law and comparatively less than the reported results by Sol gel method due to increased heat treatment in conventional method. The crystallite size varies from 45.9nm-48.6nm with increase in Er-concentration relates to internal stresses caused by the addition of dopant which creates substitutional defects, that hinders the growth of the crystallite size. SEM micrograph was in support of XRD results with varied average grain size in the range of  $4.21\mu$ m- $3.85\mu$ m with increasing ER. The magnetic characteristics investigated by Vibrating Sample Magnetometer (VSM) confirmed the soft magnetic nature of all the samples. Decrease in saturation magnetization and increase in coercivity were observed with increase in ER doping. The Remanent magnetization was about (2 emu/g) for all the reported compositions.

Keywords: nano crystalline materials, structural properties, magnetic properties, chemical synthesis.

# **1. INTRODUCTION**

The demand of rare-earth iron garnets (RIGs) is greatly increased due to their use in magneto-optical and microwave communication devices. Properties of RIGs such as low dielectric loss, high electrical resistance, changeable saturation magnetization, small anisotropy constant and high Faraday rotation enabled their use in circulators, gyrators, oscillators, phase shifters and tuneable filters [1,2]. The general formula for rare-earth garnets is M<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub>, where M is mostly Yttrium ion or a trivalent rare-earth ion of nearly equivalent effective ionic radius as a replacement for Yttrium. Single unit cell of Yttrium iron Garnet (YIG) possesses three types of lattice sites, includes tetrahedral[A], octahedral [B] and dodecahedral [C] Sites. Iron ions have smaller ionic radius as compare to Yttriumasa result ironi on occupy smaller sites [A-sites and B-sites] and larger dodecahedral sites are occupied by larger Yttrium or other rare-earth ion in substituted Garnets. A unit cell of Garnet has 24 A-sites, 16 B-sites, 24 C-sites having 8 formula units of M<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub>. The ionic distribution in general formula of RIGs is  $\{M_3^{3+}\}^{dodeca}$   $[Fe_3^{3+}]^{tetra}$   $(Fe_2^{3+})^{octa}O_{12}$ , where the moments of iron ions on A-sites are oppositely aligned to the magnetic moments of iron ions on B-sites such magnetic behaviour is referred as antiferromagnetic coupling, the moments of rare earth ionson C-sites are also antiferromagnetically coupled with remaining magnetic moments of A-sites such coupling determines the net magnetization of associated sub-lattice [2,3].

The reported research is focused to study the effect of Erbium addition on the structural andmagneticcharacteristicsofYIGpreparedbyconventionalc eramicmethod. The prepared samples were characterized and discussed by using X-ray diffractrometer (XRD), Scanning Electron Microscope (SEM) and Vibrating Sample Magnetometer (VSM) in comparison with the reported results of Sol gel method.

## 2. EXPERIMENTAL DETAILS

The Erbium substituted YIG( $Er_x Y_{3-x}Fe_5O_{12}$ ) with variation of Ercontentasx =0.1, 0.3, 0.6 were prepared by conventional ceramic method using Stoichiometric mixture of  $Y_2O_3$  powder, iron oxide  $Fe_2O_3$  powder and Erbium Oxide  $Er_2O_3$  powder, all with99.99% purity (Sigma Aldrich). The general chemical equation used to get Stoichiometric mixture of Erbium substituted Yttrium Iron Garne t( $Er_x Y_{3-x}Fe_5O_{12}$ ) is;

$$\frac{(3-x)}{2} \operatorname{Y}_2\operatorname{O}_3 + \frac{x}{2} \operatorname{Er}_2\operatorname{O}_3 + \frac{5}{2} \operatorname{Fe}_2\operatorname{O}_3 \to \operatorname{Er}_x\operatorname{Y}_{3-x}\operatorname{Fe}_5\operatorname{O}$$

The Stoichiometric mixtures were initially grinded for 2 hours to increase the homogeneity in automatic grinder with 30 minutes of intermediate relaxation after each 25 minutes of grinding. The whole mixture was appeared as reddish powder for each composition, was than calcinated at1100<sup>o</sup>C in automatic box furnace (CY-M1700-21C) in air for 1 hour with 5<sup>o</sup>C/min of increment and decrement of temperature. All the samples were appeared as dark greenish after calcinations and re-grinded for half an hour in Automatic grinder to speed up the reaction between chemicals due to the contact between new surfaces.

Pellet formation of each sample was done by hydraulic press using cylindrical die having 10mm dia and 5mm thickness under uniaxial pressure. Hydraulic press was maintained for about 10 minutes to avoid the breaking of pellets and final sintering of samples was carried out at  $1400^{\circ}$ C for 2 hrs in air with5°C/min of increment and decrement of temperature. The obtained nano-particles were characterized by XRD with Cu-Kαradiation and morphology was investigated by SEM. Magnetic properties were recorded by VSM.



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# 3. RESULTS AND DISCUSSIONS

The XRD data of the samples were collected from advanced D8 diffractometer by step scanning over the angular range of  $10^0 \le 2.8 \le 80^0$  at a step size of  $0.05^0$ . The data files were extracted by using Origin Pro 2016. The X-ray diffraction peaks of Erbium substituted YIG (Er<sub>x</sub>Y<sub>3-x</sub>Fe<sub>5</sub>O<sub>12</sub>) nanoparticles with x = 0.1, 0.3, 0.6 sintered at 1400<sup>o</sup>Care shown in Figure-1. The existence of major peaks associated with lattice planes (400), (420), (422), (521), (611),(444), (640), and (642) as shown in XRD patterns confirms the formation of a cubic Erbium doped YIG structure belong to space group of Ia-3d. No remarkable distortion was observed except a small peak of YFeO<sub>3</sub> (Yttrium Iron Perovskites) at about 20=33.15 in all the samples, due to the strong bonding between iron and yttrium.



**Figure-1.** XRD pattern of  $Er_X Y_{3-x} Fe_5 O_{12}$ sinteredat1400<sup>o</sup>C.

The lattice parameters of all the samples (x=0.1, 0.3, 0.6) for (420) plane were calculated from diffraction pattern of  $Er_xY_{3-x}Fe_5O_{12}$  by using equation (2) and mentioned in Table-1;

$$a = \sqrt{\{\frac{\lambda^2}{4\sin^2\theta} (h^2 + k^2 + l^2)\}} \qquad \dots \dots \dots \dots \dots (2)$$

X	Position (2 <del>0</del> )	Molecular Weight (g)	d-spacing ( <sup>0</sup> A)	Crystal Size (nm)	Latticecon stant ( <sup>0</sup> A)	X-Ray Density(g/ cm <sup>3</sup> )
0.1	32.33	745.766	2.766	45.945	12.2979	5.3257
0.3	32.34	761.436	2.766	48.656	12.2942	5.4426
0.6	32.39	784.942	2.761	45.952	12.2755	5.6362

**Table-1.**  $Er_X Y_{3-x} Fe_5 O_{12}$  Series for (420) plane Sinteredat 1400<sup>o</sup>C.

The decrease in lattice constant (12.297to 12.275A  $^{\circ}$ ) shown in Figure-2(a) was observed with an increase in Er concentration at a sinteringtemperature of 1400<sup>o</sup>C using conventional ceramic method compared to the pure YIG (12.376A  $^{\circ}$ ) [4, 5]. The obtained values of lattice constant were lower than already stated results [6, 7] using Sol gel method with Er doping. This further decrease in lattice constant with Er doping was due to the fact that lattice parameter decreases with increasing heat treatment temperature in addition to the replacement of Er with smaller ionic radius (1.03<sup>o</sup>A) by Yttrium with slightly larger ionic radius (1.04<sup>o</sup>A) at dodecahedral sites of YIGunitcell, which is in accordance with Vegard'slaw [8,

9]. Moreover, the Bond length  $(A^0)$  of Fe-O (both tetrahedral and octahedral) is larger in the case of yttrium than Erbium [10, 11].

Scherer's formula enabled to calculate the crystallite size for (420) peaks, shown in Figure-2(b) and Table-1. It was noted that the crystallite sizes vary with Er doping, first a decreased value 45.94nm was observed at x=0.1 which was increased to 48.65 for x=0.3 and then reduced to 45.95nm with an increased Er content of x=0.6. This relates to the internal stresses caused by the addition of dopant which formed a secondary phase and subsequently create substitutional defects that will hinder the growth of the crystallite size [12, 13].

(C)

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Figure-2 (a, b). Variation of lattice parameterand Crystallite size (nm) of  $Er_X Y_{3-x} Fe_5 O_{12}$ 

The micro-structural study of samples was done by using Scanning Electron Microscopy (SEM). The magnified micrographsat  $10\mu$  mclearly confirmt hegrains of YI Gwithvarious substitutions of Erbium in Figure-3 (a, b, c) respectively. The mean grain size of each sample was measured by using Image J software along with their Histograms to show the count rate, mentioned in Table-2.

Sample No	Minimum size (µm)	Maximum size (µm)	Mean size (µm)
0.1	1.397	11.6	4.20951
0.3	1.366	11.616	4.62108
0.6	0.894	8.147	3.85462

**Table-2.** Variation in average grainsizeof $Er_xY_{3-x}Fe_5O_{12}$ .

SEM results confirmed the polycrystalline nature of Erbium-YIG, were in support of XRD results disclosed irregular shapes and diverse average grain size in the range of 4.209 $\mu$ m - 3.854 $\mu$ m for x = 0.1 to 0.6. The observed average grain sizes for each sample were slightly shifted toward lower size [12] may be attributed to the structural deformation due to decrease in Fe-Obond length with substitution of Er at higher sintering temperature of 1400 <sup>0</sup>C. The SEM results revealed that the Er doping in YIG resulted in reduced average grain size with narrow particle size distribution and uniform particle shape.



**Figure-3 (a, b, c).** Micrographs and his to grams of  $Er_xY_{3-x}Fe_5O_{12}$  with Erbium (x=0.1,0.3,0.6).

The magnetic properties were on served by Vibrating Sample Magnetometer (VSM) with maximum applied magnetic field of 0.5 Tesla at room temperature of 287 Kelvin. The variation in magnetic characteristics depends mostly on concentration of Er due to its large magnetic moment and was investigated at auniforms intering temperature of 1400<sup>o</sup>C. The magnetic hysteresis loops of samples as shown in Fig.4indicate the soft magnetic nature of all the samples.



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The decrease in saturation magnetization (20.66 emu/g to 19.22 emu/g) with increase in Er concentration as shown in Figure-4 can be attributed to the attained reduced particle size and progressive reduction of the super exchange interactions between sites of the iron ions with decreased magnetic dipole-dipole interaction [12, 14]. This behavior was due to the antiferromagnetic orientation of Erion's moments with net moments of iron ions. According to Neel's theory [8, 15] two iron sublattices having tetrahedral and octahedral sites are antiferromagnetically coupled with each other through oxygen ions.



Figure-4. Magnetic Hysteresis loops of  $\text{Er}_{x} Y_{3-x} \text{Fe}_{5} O_{12}$  with Erbium, variations in saturation magnetization, remanence and coercivity.

The sub lattice having Erbium ions at dodecahedral site is also coupled antiferromagnetically with net moment of ironios, therefore total magnetic moment decreases according to;

# Mnet=Mdodecahedral-[Mtetrahedral-Moctahedral (4)

The observed values of coercivity were small which indicate the soft ferrimagnetic nature of samples. Increase in coercivity is observed with increase in Er concentration as shown from Figure-5, because the coercivity depends on irreversible domain rotation according to equation;

$$H = \frac{2K_1}{\mu oMs}$$
(5)

where  $k_1$  is magneto-crystalline anisotropy constant. The equation 4 indicates that the decrease in saturation magnetization causes increase in coercivity, same results were obtained by [2, 14]. Remanent magnetization as

## 4. CONCLUSIONS

Polycrystalline Erbium-substituted Yttrium Iron Garnet,  $Er_x Y_{3-x} Fe_5 O_{12}$  (x = 0.1, 0.3 and 0.6) have been prepared at sintering temperature of 1400°C by conventional ceramic method. XRD patterns confirm the formation of cubic YIG structure belongs to space group of Ia-3d. No remarkable distortion was noticed. The decrease in lattice constant was observed with increase in Erbium concentration due to the decrease in Fe-O bond length, which is less than already reported results by Sol gel method. Crystallite sizes varies in the range of 45.94 nm - 48.65nm with increase in Er content from 0.1 to 0.6 at asintering temperature of 1400°C. The SEM result showed polycrystalline nature of Erbium-YIG with slight decrease in average grain size which is in agreement of XRD results. The VSM results in dicate the soft magnetic nature of Er-YIG. The decrease in saturation magnetization was observed with increase in Er concentration, which is in accordance of Neel's theory, whereas, the obtained values of coercivity shows soft ferrimagnetic nature of samples and increases with increase in Er concentration. Remanent magnetization is almost unchanged (2emu/g)due to almost identical crystallite size.

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### **Conflict of interest**

The authors declare that there is no conflict of interest regarding the publication of this article. Authors confirmed that the paper was free of plagiarism.

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