SUBSTITUTIONAL EFFECT OF RARE EARTH ELEMENT HO³⁺ ON STRUCTURAL AND MAGNETIC PROPERTIES OF YTTRIUM IRON GARNETS

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Holmium (Ho^{3+}) substituted Yttrium Iron Garnets (YIGs) $Y_{3-x}Ho_xFe_5O_{12}$ (x = 0.1, 0.3, 0.6, 0.9, 1.5) prepared by conventional ceramic technique are reported in this article. X-rays diffraction data showed well-defined peaks of Holmium-YIG. The crystallite size calculated by Scherer formula increased from 66 nm to 123 nm with the addition of Holmium (Ho) contents. SEM micrographs show that the small crystallites agglomerated to make a big grain and the grain size lies in the range of (1.25 – 6.00 µm) for all the samples. The saturation magnetization (Ms) and remanance (Mr) enhanced withadditives. A noticeable decrease in the coercivity with the increase of Ho composition is also observed. It is worth noting that the substitution of Ho^{3+} makes the YIG better soft magnetic material which may be used in electronic devices like guided wave oscillators. These magnetic garnets have high utilization in magnetic bubble domain type memories. Furthermore, these substituted magnetic garnets have wide applications in optical devices like magneto-optical disks and displaying optical instruments. High technological utilization of this Ho-YIG series in telecommunication and defense industry can also be explored and apprehended.

1. Introduction

Rare-earth Iron Garnets (RIGs) are ferrimagnetic insulators and are being used in information technology, magneto optical applications and magnetic resonance devices. RIGs have the general unit formula as $R_3Fe_5O_{12}$, where R represents Yttrium (Y) or rare earth ions. The garnets have eight formula units in a cubic unit cell. Ionic distribution in garnet is represented as ${R_3^{+3}}[Fe_2^{+3}](Fe_3^{+3})O_{12}$. The magnetic structure for garnet formula is ${R_3^{+3}\uparrow}[Fe_2^{+3}\uparrow](Fe_3^{+3}\downarrow)O_{12}$. The magnetic properties of a magnetic material depend largely on the sintering temperature, particle size distribution, domains structure and magnetization process. Yttrium Iron Garnet (YIG), with chemical composition $Y_3Fe_5O_{12}$, is a synthetic garnet having cubic crystal structure. The non-magnetic Y^{+3} ions are located on the dodecahedral 24 (c) sites and 5 Fe^{+3} ions, which are strongly magnetic are oriented on the octahedral 16 (a) sites and tetrahedral 24 (d) sites and oxygen ions occupy 96 (h) sites [1-7].

Many researchers have reported the structural and magnetic properties of rare earth elements substituted garnets.The citrate precursor gel method was adopted to synthesize the Gadolinium iron garnet (GdIG) nanoparticles by Nguyet et al [8]. The mean particle size of the material measured by TEM analysis was about 37 nm. The magnetization increases with the increase in temperature from 5 K to 286.5 K and then decreases beyond the 286.5 K. The coercivity also decreased by elevating the temperature further than 286.5. Caffarenaet al [9] studied the microstructural and Hysteresis curves of Samarium-Holmium Garnets. High values of hysteresis losses, maximum magnetization

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and magnetic remanence were observed at $1400°C$. Many other researchers studied the structural and magnetic properties of YIG and substituted YIG. They concluded that saturation magnetization (Ms) decreased with the substitution of non-magnetic ions and increased with the substitution of magnetic ions [10-11]. However, Holmium substituted YIG (Ho-YIG) fabrication by conventional ceramic technique is not common in literature. Therefore, fabrication of Ho-YIG was decided for present investigation. Holmium having strong magnetic moment (10.6 μ_B), is substituted at Yttrium having (0 μ_B) magnetic moment, this substitution of Holmium has tremendously increased the saturation magnetization of YIG.

The aim of the present research is the fabrication of highly densified Holmium-YIGs and to understand the substitutional effect of rare earth element Ho^{3+} on YIG.

2. Experimental procedure

A series of Holmium substituted Yttrium Iron Garnets ($Y_{3-x}Ho_xFe_5O_{12}$), where (x=0.1, 0.3, 0.6, 0.9, 1.2, 1.5) was synthesized by conventional ceramic technique. Stoichiometric mixture of Y_2O_3 (Alfa Aesar Case # 1314-36-9, 99.999%), Fe_2O_3 (Sigma Aldrich Case # 12342, 99.00%) and Ho_2O_3 (Alfa Aesar 1255-62-8, 99.99%) were mixed and milled manually. Holmium substituted garnets ($Y_{3-x}Ho_xFe_5O_{12}$) with six varying composition of Holmium were prepared. The powder samples were annealed at $1000°C$ for 1 hour in Lindberg box furnace (Model B51524C) and green powders were characterized by D8 Discover Diffractometer (Bruker, Germany). There were mixed peaks of Fe_2O_3, Ho_2O_3, Y_2O_3 and ortho ferrite. Green powders for different samples were ground for one hour individually in agate mortar. Cylindrical pallets of diameter (13mm) and thickness (3mm - 3.6 mm) were made using Carver Hydraulic Press and Carver Die by applying the pressure of 6 tones. The final sintering was carried out at $1300°C$ for 2 hours in a box furnace in air atmosphere and all samples were furnace cooled.

The structure and crystallite size were studied by D8 Discover Diffractometer working at 40kv and 40 mA, 2θ range (20°-60°) and increment of 0.40° using CuKα radiation (λ = 1.5405Å). Single phase peaks of Holmium-YIGs were obtained which confirmed the completion of solid state reaction. Confirmation of these peaks was done by standard YIG JCPDS Card No (43-0507). The crystallite size was calculated using Scherer's formula. The crystallite sizes of the samples are estimated from the full width at half maximum (FWHM) of the (420) XRD peaks. These pellets were characterized by SEM (Hitachi S-3400) for microstructural analysis. Magnetic measurements and Hysteresis Loops (M-H) were done with VSM (lake shore Model 7407) by using magnetic field of 4 K Gauss at room temperature(32°C). Special samples were prepared on Teflon tape for magnetic study. The slowly sweeping of the applied field was done from the maximum field (+4000 Gauss), through zero, to the maximum negative field (- 4000 Gauss) and again to the maximum positive field. Saturation Magnetization (Ms), Remanence Magnetization (Mr), Squarness ratio (Mr/Ms) and Coercivity (Hc) were calculated by applying different formulae on the data derived from magnetometer LakeShore (7407).

3. Results and discussion

3.1 Crystallographic Analysis
The XRD patterns for all the samples have been shown in Fig. 1. The XRD patterns indicate the single phase for all the samples, were confirmed by standard YIG JCPDS card No (43-0507), with the absence of any extra peak due to unreacted material and secondary phase. Maximum intensity peaks (420) for various compositions were observed between 2θ range 33°-34°. These peaks are narrower and sharper, which confirmed the enhanced crystalline behavior. The physical parameters of $Y_{3-x}Ho_xFe_5O_{12}$ obtained from XRD data are shown in Table 1.
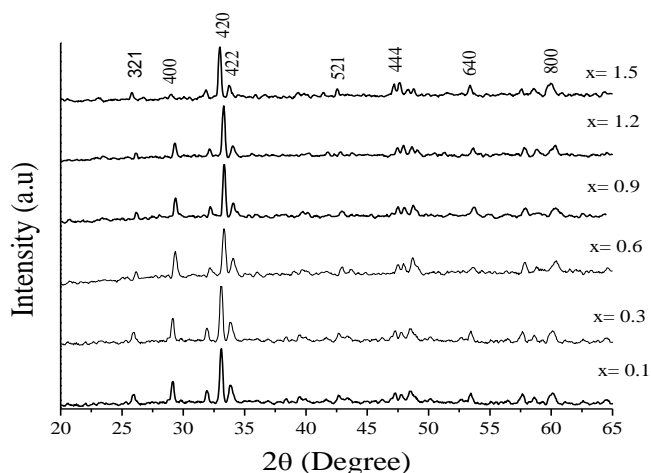
Fig. 1 XRD patterns for all the Ho-YIG samples

Table 1. Molecular weight, lattice parameters, X-rays density, Bulk density, porosity, crystallite size anddislocation density of $Y_{3-x}Ho_xFe_5O_{12}(x=0.1, 0.3, 0.6, 0.9, 1.2, 1.5)$ Holmium substituted Yttrium Iron Garnets.

Ho Composition (x)	Molecular Weight (g)	Lattice Parameter (Aº)	X-RayDensity (g/cm³)	BulkDensity (g/cm³)	Porosity %	Crystal liteSize (nm)	DislocationDensity × 10^{14}linespmm
$Y_{2.9}Ho_{0.1}Fe_5O_{12}$	745.5376	12.300	5.3820	4.8860	9.21	66	2.990
$Y_{2.7}Ho_{0.3}Fe_5O_{12}$	760.7366	12.316	5.3881	4.9276	8.92	80	1.5625
$Y_{2.4}Ho_{0.6}Fe_5O_{12}$	783.5456	12.332	5.4450	4.9686	8.70	86	1.3520
$Y_{2.1}Ho_{0.9}Fe_5O_{12}$	806.3523	12.3482	5.4846	5.0253	8.37	99	1.0233
$Y_{1.8}Ho_{1.2}Fe_5O_{12}$	829.1594	12.366	5.6096	5.1851	7.56	106	0.883
$Y_{1.5}Ho_{1.5}Fe_5O_{12}$	851.9701	12.3863	5.7136	5.3630	6.13	123	0.787

The lattice parameters "a" for all the samples were calculated using the equation;

$$a = \sqrt{\frac{\lambda^2(h^2+k^2+l^2)}{4sin^2\theta}} \qquad (1)$$

The variation in lattice parameters with Holmium-contents is shown in Fig. 2. It is obvious that the lattice parameter "a" increases linearly with increasing Holmium contents. It varies from 12.3000Å to 12.3866 Å. This increase is attributed to the fact that Ho^{3+} has larger ionic radius (0.901Å) as compared to Y^{3+} ionic radius (0.890Å). Ho^{3+} is a rare earth ion and is substituted at dodecahedral site replacing the Y^{3+} ion. There is no substitution of Ho^{3+} on tetrahedral and octahedral sites [12]and hence there is no noticeabledistortion in the garnet crystal structure. Therefore, the Ho-YIGs almost show the same XRD patterns as that of pure YIG.
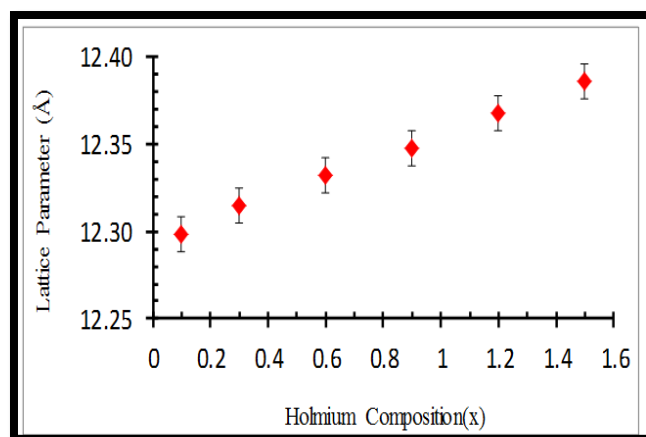
Fig. 2 Variation of lattice parameter of Holmium-YIG garnets with Holmium composition

The x-ray density was calculated using the formula;

$$D_x = 8M/Na^3 \qquad (2)$$

WhereM= Molecular Weight of the Sample, N= Avogadro number, A= Lattice constant of sample
The bulk density of all the samples was determined by using the following relation;

$$D_B = (W_a \times \rho_t) \ / \ (W_a - W_t) \qquad (3)$$

WhereD_B =Bulk density of sample, Wa =Weight of the sample in air, Wt = Weight of the sample in toluene, ρ_t = Density of the toluene
The percentage porosity of the prepared garnet samples was determined by using the formula;

$$\% \ Porosity = (1 - D_B / D_x) \times 100 \qquad (4)$$

D_B is the bulk density and D_x is the x-ray density. Porosity decreases with the increase of Holmium contents. The decrease in porosity was due to negative micro-strain which produces the compressive stresswithin the lattice [13].

3.2 SEMmicrographs
The SEM micrographsfor all the Holmium-YIGssamples are shown in Fig. 3. SEM studies of Holmium-YIG samplesshowed the minimum pore size distribution, small necking phenomenon, aggregation and agglomeration process and grain boundaries development. The platelet like structure of all the grains can easily be seen. This platelet like structure grains arrange themselves in order to enhance the permeability in response of externally applied magnetic field hence these samples can be used in microwave absorbing devices [13]. The grain size measured by line-intercept method lies in the range of 1.25 – 6.00 μm for all the samples.
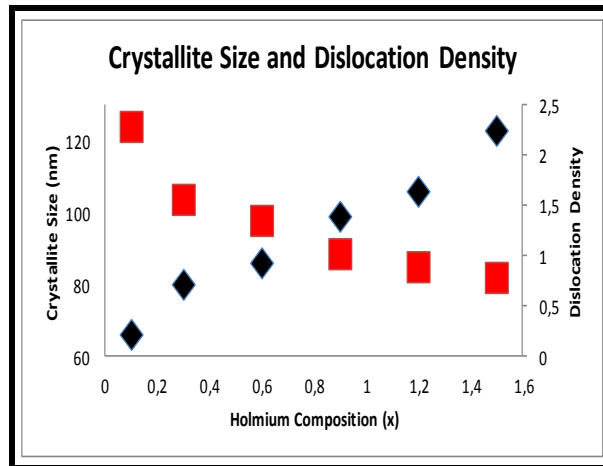
Fig. 3. Variation of crystallite size and dislocation density with Holmium composition

3.3 Magnetic Properties

Magnetic properties of this Holmium-YIG series are described by two factors; the high sintering temperature and substitution of highly magnetic Holmium ions on non-magnetic Yttrium ions. High sintering temperature favors grain growth process which increases the magnetization process remarkably. The domain wall movements become easy and resultantly high increase in saturation magnetization and decrease in coercivity was observed. At high sintering temperature (1300°C)grain growth occurred, resultantly grain size increased. The enhancement of crystalline nature and increased grain size has made the domain walls movement easy [12].The hysteresis loops of all the samples with magnetic field applied from -4 kG to +4 kG are shown above in Fig. 5.
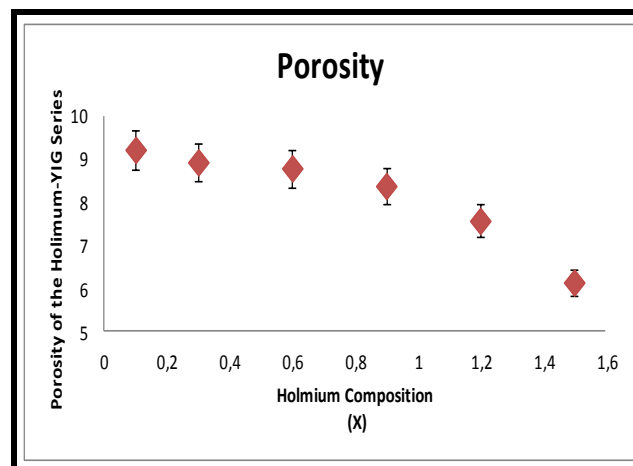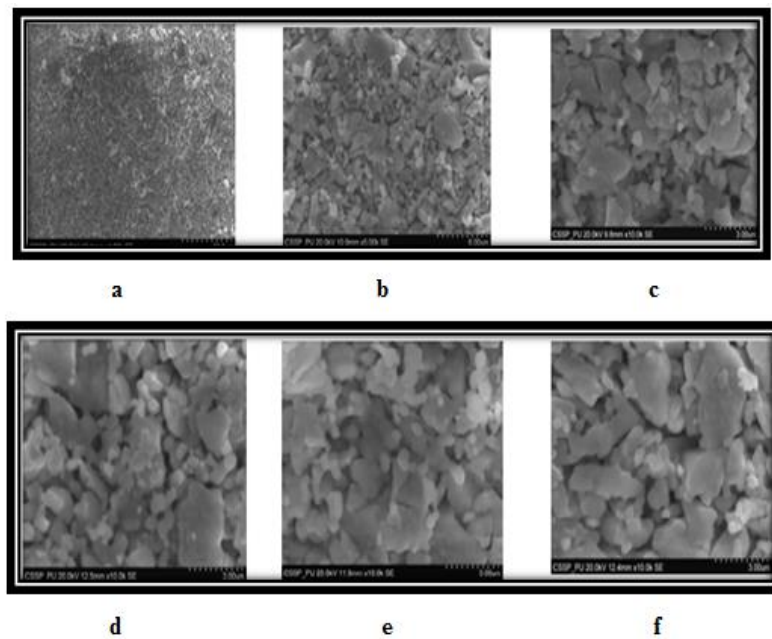

Fig. 4 Variation of porosity of Holmium-YIG garnets verses Holmium composition

Fig 5 SEM micrographs of Holmium YIG Samples (a=0.1, b=0.3, c=0.6, d=0.9, e=1.2, f=1.5) Holmium composition

The values of saturation magnetization, retentivity, coercivity (Hc), Bohr magnetons (μ_B) and squareness ratio (Mr/Ms) are shown in the Table 2. The saturation magnetization of the Holimum-YIG series increased from 32.5 – 139.00 emu/g for all the samples. While the pure YIG exhibits comparatively low value of saturation magnetization 21.3 – 26.5 emu/g [14]. This enhancement in magnetization is attributed to the substitution of the strongly magnetic Holmium ions having 10.6 μ_B on the non-magnetic Yttrium ions with zero magnetic moment. Therefore it is concluded that the magnetic Holmium has enhanced the magnetic behavior of this series. The remanence magnetization (Mr) also increased with the increase of Ho contents. High increase in the Bohr magnetons was also observed. It is worth noting that the value of coercivity decreases with the additives. This decrease in coercivity can be explained on the basis of inverse relation between grain size and coercivity $H_c \alpha$ 1/r [13]. It can be seen very clearly that the decrease in coercivity and increase in grain size completely satisfy the above mentioned inverse relation. The squareness ratio (Mr/Ms) of samples increased with the increase of Ho contents making this series highly useful for technological applications. These changes are due to grain growth and decrease in dislocation density. Grain growth phenomenon has contributed to the enhancement of saturation magnetization and reduction in coercivity. This Holmium-substituted YIG series has shown high grain growth process with enhanced saturation magnetization and low coercivity. These fundamental magnetic characteristics make the series highly efficient magnetic material which can be utilized in optical devices like magneto-optical disks and magneto-optical display instruments [15-17].

Table 2 . Saturation magnetization, retentivity, coercivity, Bohr magneton and squareness ratio of $Y_{3-x}Ho_xFe_5O_{12}$ (x=0.1, 0.3, 0.6, 0.9, 1.2, 1.5) Holmium substituted Yttrium Iron Garnets

| Composition of Holmium-YIG series Samples	SaturationMagnetization (Ms)	RemanenceMagnetization (Mr)	Coercivity (Hc)	Bohr Magnetron μ_B	Squareness Ratio (Mr/Ms)
X	emu / g	emu /g	Gauss	A/m^2	
$Y_{2.9}Ho_{0.1}Fe_5O_{12}$	32.897	22.5306	341.3263	1.377×10^{27}	0.6910
$Y_{2.7}Ho_{0.3}Fe_5O_{12}$	57.849	41.1366	312.4363	4.050×10^{27}	0.7068
$Y_{2.4}Ho_{0.6}Fe_5O_{12}$	66.662	48.6103	280.2339	4.784×10^{27}	0.7273
$Y_{2.1}Ho_{0.9}Fe_5O_{12}$	77.540	56.4366	235.3439	5.580×10^{27}	0.7292
$Y_{1.8}Ho_{1.2}Fe_5O_{12}$	87.281	67.6999	178.7646	6.290×10^{27}	0.7819
$Y_{1.5}Ho_{1.5}Fe_5O_{12}$	139.264	126.3076	126.3636	9.946×10^{27}	0.9946
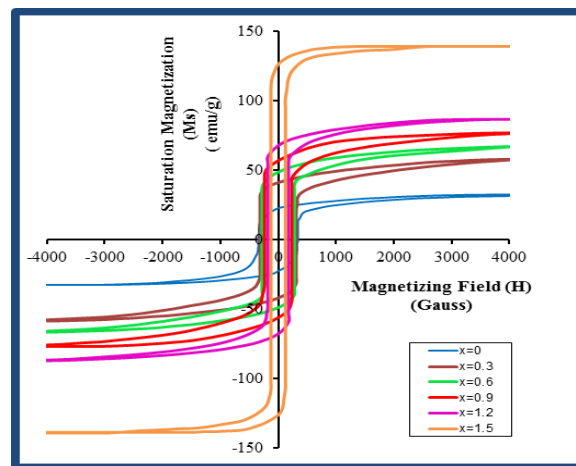
Fig. 6 M-H loops for all the Ho-YIG samples
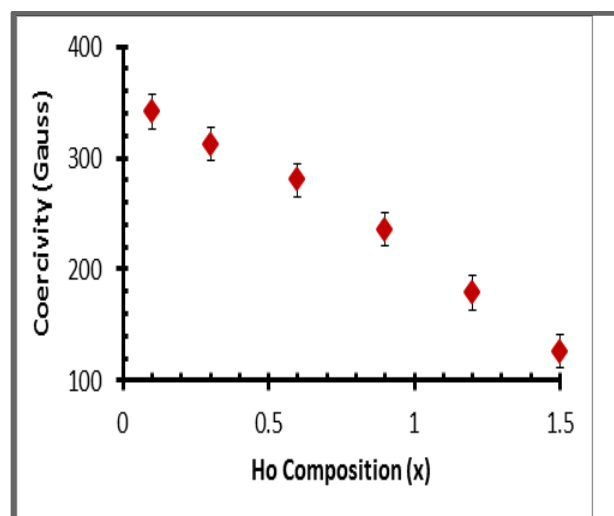

Fig. 7 Variation of coercivity with Ho concentration

4. Conclusions

Polycrystalline garnet series have been fabricated using conventional ceramic This technique inherits percentage purity and contamination free atmosphere.Crystallographic parameters like crystallite size, bulk density, x-ray density and molecular weight of the samples are found to be increased with increase in Holmium contents. SEMmicrographs showed the well-defined and arranged grains. The size of the grains increased with increasing amount of Holmium, this is due to the densification process and grain growth. Reduction of porosity occurred with the increase of Holmium contents. This reduction in porosity has caused the reduction in pinning centers of the domain wall movement. Therefore easy domain wall movement has caused the improved magnetization process. This series showed a ferromagnetic phase due to their large grain size and high volume fraction of the complete Holmium-YIG series. Further this Holmium-YIG series is in multi domain stage. Here the domain wall movement is much easier as compared to domain rotation. Less energy is required for domain wall movement in bigger grains as compared to rotation or twisting of domains in smaller grains. Therefore this grain growth process has reduced the coercivity. Saturation magnetization (Ms) increased with Holmium contents while coercivity decreasedmaking this fabricated series better than pure YIG with reference to magnetic properties.

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