Research Article

Structure and Magnetic Properties of $Y_{3-x}Er_xFe_5O_{12}$ ($x = 0.2, 1.0$, and 2.0) Thin Films Prepared by Sol-Gel Method

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Nanoparticles $Y_{3-x}Er_xFe_5O_{12}$ ($x = 0.2, 1.0$, and 2.0) thin films were prepared by sol-gel method and treated at 800, 900, and 1000°C, respectively, for 2 h. The films have single phase garnet structure and the sizes of particles are in the range of 44 to 83 nm. The magnetic measurements show that the saturation magnetization decreased with increasing of Er concentration for all samples treated at different annealing temperatures. The saturation magnetization increased with the particle size due to the enhancement of the surface spin effect. The coercivity initially decreased for $x = 1.0$ and then increased for $x = 2.0$ with increasing annealing temperature.

1. Introduction

The rare-earth iron garnets (RIGs) have the general unit formula as $R_3Fe_5O_{12}$, where R is either a trivalent rare-earth ion or yttrium. The garnets have eight formula units in a cubic unit cell. The cubic unit cells of RIGs have approximately the same lattice constant of the order of 12 Å [1], due to similar ionic radii of R^{3+} ions. Ionic distribution in garnet is represented as $\{R_3^{3+}\}[Fe_2^{3+}](Fe_3^{3+})O_{12}$. The interaction between the Fe^{3+} ions in [a] and (d) sites is strongly antiferromagnetic due to a strong superexchange interaction. The magnetic moment of the rare-earth ions in the {c} sublattice couples antiparallel with the resultant moment of Fe^{3+} ions. YIG ($Y_3Fe_5O_{12}$) is one of the common RIGs, which has attracted much attention in telecommunications and data storage industries due to their interesting magnetic and magneto-optic properties [2]. The resulting magnetic moment in YIG is due to the unequal distribution of Fe^{3+} ions in two different sublattices of [a] and (d). YIGs are also of scientific importance because of the wide variety of magnetic properties that can be obtained by substituting yttrium with a rare-earth (RE) metal [3–9]. Most of the previous studies have concentrated on the preparation of Bi- and Ce-doped YIG powders and films because of their high

Faraday rotation coefficient [10–17]. Some studies have been carried out on Er-YIG powder nanoparticles [18–27].

In this paper erbium is chosen because its ionic radius (1.03 Å) is slightly less than ionic radius of yttrium (1.04 Å). Also, it has an extremely high Verdet constant ($\sim -11 \times 10^{-2}$ min/Oe·cm) at ($\lambda = 600$ nm) and large Bohr magneton ($9.6 \mu_B$) [28]. This paper reports the influence of low and high concentration of Er^{3+} on the structure and magnetic properties of YIG thin films.

2. Experimental Method

The YIG precursor sol was prepared by a sol-gel method using reagent grade nitrates purchased from Aldrich, Milwaukee, Wis, USA. Yttrium nitrate hexahydrate ($Y(NO_3)_3 \cdot 6H_2O$, 99.95% purity), iron(III) nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$, 98% purity), and Erbium nitrate pentahydrate ($Er(NO_3)_3 \cdot 5H_2O$) were used as the raw materials. 2-methoxyethanol and acetic acid were used as solvents. $Fe(NO_3)_3 \cdot 9H_2O$ and $Y(NO_3)_3 \cdot 6H_2O$ were dissolved in the 2-methoxyethanol and refluxed at 80°C for 3 hours. The $Er(NO_3)_3 \cdot 5H_2O$ dissolved in acetic acid was added gradually into the Fe-Y solution. Then the refluxing

FIGURE 1: XRD patterns of $Y_{3-x}Er_xFe_5O_{12}$ films heated from 800 to 1000°C (a) $x = 0.2$, (b) $x = 1.0$, and (c) $x = 2.0$.

process was continued for 3 hours. The pH value was adjusted in the range of 2-3. After cooling down to room temperature, the solution was stirred for 3 days. The gel was transformed into film on a quartz substrate using the spin coating technique. The rate of the spinning process was 3500 rpm, and it was done for 30 seconds. After the spinning process, the film was dried at room temperature. Then the

FIGURE 2: Particle size dependence on the heating treatment for $Y_{3-x}Er_xFe_5O_{12}$ films.

heat treatment was carried out: initial heating at 350°C for 15 min to burn off the organic materials followed by heating at 800°C, 900°C, and 1000°C for 2 hours to crystallise the films.

The characterizations were carried out using an X-ray diffractometer (Philips model Pw 3020 MRD x'pert pro) with a $CuK\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$) to identify the phases and field emission scanning electron microscopic (FE-SEM model Zeiss Supra 55 vp) to determine the particle size and films thicknesses. The magnetic properties of the films were measured at room temperature using a vibrating sample magnetometer (VSM, LakeShore Cryotronics and 7400 Series).

3. Results and Discussion

3.1. Structural Properties. Figure 1 shows the spectra for all samples. The XRD patterns reveal a single phase garnet structure and the crystallization had completely occurred at 800°C due to the good homogeneity of the gel prepared at pH = 2-3. This temperature is lower than that reported by Xu et al. [29]. However, increasing the temperature up to 1000°C does not give great influence to the sample crystallization. This is proved by the intensities ratio calculation shown in Table 1.

The average crystallite size was calculated according to the Scherrer's formula

$$D = \frac{k\lambda}{\beta \cos \theta}, \quad (1)$$

where D is the mean crystallite size, k (0.89) is the Scherrer constant, λ is X-ray wavelength (0.154252 nm), and β is the relative value of the full width at half maximum (FWHM) of the diffraction peak (420).

The crystallite size for samples with the same x but treated at different temperature increased with increasing

TABLE 1: The average intensity ratios calculations for $Y_{3-x}Er_xFe_5O_{12}$ films.

$x = 0.2$										
Temp. ($^{\circ}C$)	I^*	I_{o1}	I_{o2}	I_{o3}	I_{o4}	I_{o1}/I^*	I_{o2}/I^*	I_{o3}/I^*	I_{o4}/I^*	(I_o/I^*) average
800	1356	615	709	498	521	0.45	0.52	0.37	0.38	0.43
900	1464	613	711	501	585	0.42	0.49	0.34	0.40	0.41
1000	1047	488	558	406	423	0.47	0.53	0.39	0.40	0.45
$x = 1.0$										
Temp. ($^{\circ}C$)	I^*	I_{o1}	I_{o2}	I_{o3}	I_{o4}	I_{o1}/I^*	I_{o2}/I^*	I_{o3}/I^*	I_{o4}/I^*	(I_o/I^*) average
800	1082	478	516	397	387	0.44	0.48	0.37	0.36	0.41
900	1236	517	570	440	456	0.42	0.46	0.36	0.37	0.40
1000	1313	548	640	515	584	0.42	0.49	0.39	0.44	0.54
$x = 2.0$										
Temp. ($^{\circ}C$)	I^*	I_{o1}	I_{o2}	I_{o3}	I_{o4}	I_{o1}/I^*	I_{o2}/I^*	I_{o3}/I^*	I_{o4}/I^*	(I_o/I^*) average
800	1579	637	742	550	520	0.40	0.47	0.35	0.33	0.39
900	1178	486	589	441	422	0.41	0.50	0.37	0.36	0.41
1000	1966	743	804	633	602	0.38	0.41	0.32	0.31	0.36

I^* : highest intensity; I_{o1} , I_{o2} , I_{o3} , and I_{o4} : other peak intensities.

FIGURE 3: Particle size as a function of the Er concentration for $Y_{3-x}Er_xFe_5O_{12}$ films treated at different temperatures.

annealing temperature (Figure 2). It is observed that the films crystallites sizes are about the same at the same annealing temperatures as shown in Figure 3. The result is probably due to the similar ionic radii of Er^{3+} (1.03 Å) and Y^{3+} (1.04 Å) ions.

3.2. Magnetization

3.2.1. In-Plane Saturation Magnetization (M_s) versus Particle Size (D). Figure 4 shows the variation in M_s with the average particle size for all samples. The results show that the M_s decreases with decreasing particle size for samples with the same x . A similar reduction in the magnetization was also reported for small particles of iron [30], α - Fe_2O_3 [31], $BaFe_{12}O_9$ [32], and $MnFe_2O_4$ [33]. This reduction can be related to the higher surface-to-volume ratio in the smaller particles, which results in the existence of nonmagnetic surface layer. Therefore, the M_s of the particles decreased as the particle sizes is reduced.

FIGURE 4: Saturation magnetization with the average particle size for all films treated at different temperatures.

3.2.2. Saturation Magnetization (M_s) versus Er Concentration (x). The tetrahedral and octahedral cavities in YIG are occupied by Fe^{3+} ions and dodecahedral cavities are occupied by Y^{3+} ions. In this experiment, we substituted some Er^{3+} ions for Y^{3+} ions, so the ionic distribution can be written as $\{Y_{3-x}^{3+}Er_x^{3+}\}[Fe_2^{3+}](Fe_3^{3+})O_{12}^{2-}$, where, $\{ \}$ = c sub lattice, $[\]$ = a sub-lattice, and $()$ = d sub-lattice. Er^{3+} ion is magnetic (magnetic moment $9.6\mu_B$) and Y^{3+} ion is nonmagnetic (magnetic moment $0\mu_B$), so there are three magnetic sub-lattices: one (c) forms by the Er^{3+} ions occupying the dodecahedral sites, another [a] forms by Fe^{3+} ions occupying the octahedral sites, and the third (d) forms by the Fe^{3+} ions occupying the tetrahedral sites. The two iron sub-lattices are coupled antiferromagnetically by the superexchange interaction via the intervening O^{2-} ions. The {c} sub-lattice is coupled antiferromagnetically with the tetrahedral sub-lattice. At room temperature, the three sub-lattice moments align along the $[111]$ direction [34]. The net magnetic moment is $M = M_c - |M_d - M_a|$.

FIGURE 5: Saturation magnetization with Er concentration for all films treated at different temperatures.

FIGURE 6: Coercivity with Er concentration for all films treated at different temperatures.

The variation of M_s with the x is shown in Figure 5. At different temperatures, M_s decreased with increasing x , which could be related to the fact that the magnetic moment of Er^{3+} ions aligns opposite to the effective moments formed by Fe^{3+} ions. With decreasing annealing temperatures the coercivity is initially decreased for $x = 1.0$ and then increases for $x = 2.0$ as shown in Figure 6.

4. Conclusion

The structure and magnetic properties of $\text{Y}_{3-x}\text{Er}_x\text{Fe}_5\text{O}_{12}$ films ($x = 0.2, 1.0$ and 2.0) prepared by a sol-gel method have been reported. All the samples have only single phase garnet. The crystallization begins at 800°C , and as the heating temperature increases the obtained crystallite size is increased. At the same Er concentration, the saturation magnetization decreased as the particle size is reduced due to the influence of the magnetic domain structure and surface spin effect. The saturation magnetization decreased as the Er concentration is increased due to the opposite alignment between Er^{3+} ions and Fe^{3+} ions.

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