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Effect of Er^{3+} ions on structure, surface morphology, optical and magnetic properties of Tb-YIG nanocrystalline films

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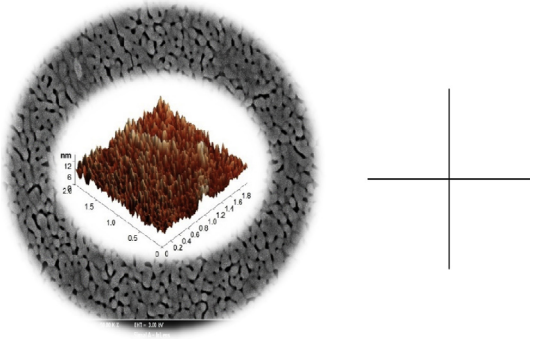
HIGHLIGHTS

- The pure phase of $Y_{2.8-x}Tb_{0.2}$ Er_x Fe_5 O_{12} films was grown by a sol-gel method.
- The Tb^{3+} ions effect could be compensated by adding Er^{3+} ions.
- Er ions reduces the saturation magnetization and increases the coercivity.
- An improvement in optical transparency with an increment of Er content was observed.

GRAPHICAL ABSTRACT



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ABSTRACT

Nanocrystalline $Y_{2.8-x}Tb_{0.2}$ Er_x Fe_5 O_{12}, ($x = 0.0–2.6$) films are successfully prepared under an annealed temperature of 900 °C in ambient oxygen using a sol-gel method. Structural investigations, using an X-ray diffractometer, confirmed that all films have a crystallographic cubic phase of pure garnet. An increment of lattice constant was observed at lower concentrations ($x \leq 0.8$), which then linearly decreased with higher concentrations; thus indicating a complete incorporation of Er^{+3} ions into the Tb: YIG structure. The surface morphology, obtained using field emission scanning electron microscopy and atomic force microscopy, showed a grain size nanostructure formation, a good adhesion of the film to the quartz substrate, and a smooth surface roughness. All samples showed high transparency in visible and near-infrared regions, with absorption edges below 500 nm. Vibrating sample magnetometer results at 29 °C revealed a formation of a soft ferrimagnetic material. Adding Er^{+3} ions reduced the saturation magnetization, M_s but, remarkably, increased the magnetic coercivity H_c. Based on a low absorption coefficient and saturation magnetization, the obtained films are a promising material for magneto-optical devices, such as optical isolators in visible and near-infrared regions.

1. Introduction

Ferrimagnetic garnets have suitable magnetic and electrical properties that are required for microwave communications and magneto-optical devices [1–3]. A typical magnetic garnet, $\{Y_3\}[Fe_2](Fe_3)O_{12}$, belongs to the space group Ia3d (O_h^{10}), with eight

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formula units in a body-centred cubic unit cell [4]. In this formula, all metal cations are in special three crystallographic sites; 24 Y^{3+} in c-site (2.40 Å), 16 Fe_2^{3+} in a-site (2.01 Å) and 24 Fe_3^{3+} in d-site (1.87 Å). This loose structure can accommodate an enormous variety of trivalent cations. The Y^{3+} ion is partially or completely replaceable by most rare earth elements (REs). This replacement allows the magnetic and magneto-optical properties of garnets to be enhanced by changing their composition. The magnetic moments in a YIG structure come from unpaired magnetic electrons in an incomplete d shell in the Fe^{3+} ions that occupy both a and d-sites. The interaction between individual magnetic moments is strongly antiferromagnetic through a super-exchange interaction [5].

Heavy REs (R = Eu, Gd, Tb …, Lu) have a large magnetic moment that comes from unpaired electrons in the 4*f* shell. Unlike transition metals (TMs), REs also has an orbital angular momentum L (except for Gadolinium) in addition to the large spin momentum S. The contributions of L and S, on the total angular momentum J, where J= (L + S), are different from one atomic structure to another. Thus, the total magnetic moment, as well as several intrinsic magnetic properties, such as a magnetization, will be affected [6]. However, the lattice constant of a unit cell of garnet is found to be influenced by preparation method, stress and strain, and the film-substrate lattice expansion [7]. This lattice expansion is mainly caused by the large ionic radii of some REs that occupy a c-site in the garnet structure. In fact, it is hard to substitute some REs into the YIG structure at high concentrations, because their ionic radii are bigger than the ionic radius of yttrium (Y), such as Ce, Tb, and Pr for example. Therefore, such ions doped onto the YIG structure will increase lattice distortion in a crystal, compared to pure YIG. Ibrahim [8], reported that the lattice parameters of Ce: YIG films, prepared by a sol-gel method, increase with the increment of Ce content up to ($x = 0.25$). They then found that, for $x \geq 0.3$, the solubility limit of Ce in YIG was reached due to the large ionic radius of Ce compared to the Y ion. In fact, the replacement of none magnetic Y^{+3} by heavy magnetic REs, such as Tb^{+3} or Er^{+3} ions, had received considerable attention due to their variety of magnetic properties. In this regard, the number of reports on the form of thin films is limited [9–12]. The terbium ion exhibits a larger Faraday effect that comes from a high value of its Verdet constant [13]. It also shows a strong paramagnetic effect, due to the transition between $4f^8 - 4f^7 5d$[14]. This effect becomes stronger when Tb ion is doped onto the YIG structure at low concentrations. Geller [15] reported that some rare earth elements, which have large ionic radii, could be substituted for Y^{3+} ion if it is combined with proper quantities of the smaller ions. However, the lattice distortion in a crystal caused by many Tb^{3+} ions could be relaxed by adding other R^{3+} ions that have smaller ionic radii than Y^{3+}, such as Er, Tm, and Lu; without degradation of other properties, such as Faraday rotation [16].

The present study reports on the effect of low and high concentrations of Er ions on the nanostructure, surface morphology, optical and magnetic properties of sol-gel Tb doped YIG films. To the best of our knowledge, the preparation a series of $Y_{2.8-x}Tb_{0.2}$ Er_x Fe_5 O_{12} ($0 \leq x \leq 2.6$) nanofilms, annealed in an oxygen ambient environment, has not been previously reported. The presence of an oxygen atmosphere could not reduce Fe^{3+} to Fe^{2+} ion, or change the oxygen content of YIG enough during the annealing process [17]. Kang [18] prepared amorphous YIG films that were crystallized by ex situ post-annealing (600–900 °C) in oxygen and air atmospheres. They proved that an oxygen annealing atmosphere was an effective environment to yield high-quality films with narrower ferromagnetic resonance FMR, ΔH values and smoother surfaces. In addition, it was reported that the presence of oxygen during the annealing process of $Bi_{0.85}$ $Pr_{0.15}Fe_{0.9}$ $Co_{0.1}$ O_3 (BPFCO) thin film suppressed the double hysteresis loop phenomenon, which was associated with the oxygen vacancy [19]. However, Er^{+3} ions were chosen in this work due to their small ionic radii (1.00 Å) compared to Y (1.015 Å) [20], a high Verdet constant at visible wavelength [12], and a high magnetic moment (9.72 μB) [21]. The objectives of this work were to prepare sol-gel $Y_{2.8-x}Tb_{0.2}$ Er_x Fe_5 O_{12} nanocrystalline films and study the effect caused by different Er ion concentrations; ranging from $x = 0$ to 2.6 on the physical properties of these films. A Tb content of $x = 0.2$ was chosen because it was found that a Tb content of less than 0.8 prevented Y ions from occupying the octahedral sites; which may give rise to distortion of lattice parameters [9,22]. The performance of the magneto-optical materials (MO) is evaluated by the figure of merit: $F_1 = (\theta_f/M_s)^2$ and $F_2 = (\theta_f/\alpha)$, where θ_f is the Faraday rotation angle, M_s is the saturation magnetization and α is the optical absorption coefficient of material, respectively [23,24]. Decreasing the material absorption and the M_s value, therefore, is highly required for better performance of ferrite materials in the MO applications. This study reports low absorption coefficient besides a low M_s value of the $Y_{2.8-x}$ $Tb_{0.2}$ Er_x Fe_5 O_{12} nanofilms. The findings should make an important contribution to developing a more compact optical isolator and circulator in the visible and NIR regions.

2. Experimental procedure

A series of $Y_{2.8-x}Tb_{0.2}$ Er_x Fe_5 O_{12} samples, with atomic weight ratios of $x = 0$, 0.4, 0.8, 1.4, 1.8, 2.2, and 2.6, respectively, were prepared by a sol-gel method using high purity raw materials (99.9%) from Sigma Aldrich company-USA. Stoichiometric mixtures of Yttrium (III) Y $(NO_3)_3.6H_2O$ and Iron (III) Fe $(NO_3)_3.9H_2O$ were dissolved in 2 mL of 2-methaoxythanol, then stirred by a magnetic stirrer for 15 h at room temperature (~29 °C). The Y-Fe solution was refluxed at 80 ± 2 °C for 3hr. The terbium (III), Tb $(NO_3)_3.5H_2O$ and erbium (III), Er $(NO_3)_3.5H_2O$ were dissolved separately in 2 mL of acetic acid, then stirred for 3hr before being added gradually to the Y-Fe solution. Then, the mixture solutions were refluxed at 80 ± 2 °C for 3hr. The resulting solution was stirred for two days to obtain a homogenous gel. It was then filtered using a 0.45 μm syringe filter to get rid of any unwanted particles before the deposition process began. The clean quartz substrate was heated to 75 ± 2 °C for 1 min to enhance the adhesion of the films onto the substrate. In order to achieve well-coated nanofilms on quartz substrates, 20 μL of the gel was put onto the quartz glass followed by spin coating at 500 ± 3 rpm for 15 s followed by 3500 ± 5 rpm for 30 s. The resulting films were dried at 70 °C for 25 min in an oven to get rid of all organic solvents. All samples were annealed at 900 °C for 2hr in a pure oxygen ambient environment at 100 kPa pressure with a gas flow rate of 30 sccm. The samples were annealed in an oxygen atmosphere to avoid oxygen deficiency during the crystallization process of the films.

Crystallographic properties were analysed by X-ray diffractometer (XRD) using CuKα radiation (λ = 0.15406 nm) in the 2θ range 20–60°. Field emission scanning electron microscopy (FE-SEM; ZEISS Supra 55VP) was used for surface morphology and to measure the film's thickness. Surface roughness measurements were carried out using an Atomic Force Microscope (AFM). Energy dispersive X-ray spectroscopy (EDX), coupled with the FE-SEM, was used for the elemental analysis. A UV–Vis spectrophotometer (Perkins Elmer- Lambda 950) was used to measure the optical properties in a wavelength range of 300–900 nm. A vibrating sample magnetometer (VSM), with a maximum magnetic filled with 5000 Oe, was used for in-plane magnetic measurements at room temperature.