# A comparative study of the structure, magnetic properties of Terbium and Erbium doped Yttrium Iron Garnet thin films

**Ramadan E. Shaiboub[1] and Ftema W. Aldbea[2]**
1Physics Department, Faculty of Education, Nalut University, Nalut, Libya
2Physics Department, Faculty of Science, Sabah University, Sabah, Libya
Email address: shaiboubr@yahoo.com

## Abstract

The structure and magnetic properties of ($Tb_{0.4}Y_{2.6}Fe_5O_{12}$) and ($Er_{0.4}Y_{2.6}Fe_5O_{12}$) thin films were fabricated onto quartz substrate by a sol–gel method followed by spin coating process. Heat treatment of the films was processed at 900 °C in air for 2-3hrs. The crystalline structures and magnetic properties of samples were investigated by X-ray diffraction (XRD), the field emission scanning electron microscope (FESEM) and vibrating sample magnetometer (VSM). The XRD patterns of the ($Tb_{0.4}Y_{2.6}Fe_5O_{12}$) and ($Er_{0.4}Y_{2.6}Fe_5O_{12}$) films were consistent with single phase garnet structure. FE-SEM micrographs of films reveal that the particles were highly agglomerated. The grain size for the ($Tb_{0.4}Y_{2.6}Fe_5O_{12}$) film was about 50 nm, while for ($Er_{0.4}Y_{2.6}Fe_5O_{12}$) film found about 68 nm and the average thicknesses ranged from 180 - 245 nm. The magnetic measurements at room temperature show that the saturation magnetization ($M_s$) and the coercivity ($H_c$) of ($Tb_{0.4}Y_{2.6}Fe_5O_{12}$) film is about (67 emu/cm$^3$) and 14 Oe, while for ($Er_{0.4}Y_{2.6}Fe_5O_{12}$) film it's about (51 emu/cm$^3$) and 37 Oe respectively.

Keywords: structure, magnetic properties, Thin film, Er, Tb and YIG

## 1. Introduction

Yttrium iron garnets (YIG) is a ferrimagnetic material that has attracted a lot of attention because of its applications in microwave communication and magneto- optical devices [1,2]. Nowadays, despite the remarkable utility of small magnetic particles in magnetic recording media, permanent magnets, microwave devices and so on have been proved, their present applications and a full understanding of their magnetic properties remain a challenge. YIG has a cubic structure with a space group Ia3d with the general unit formula ($Y_3Fe_5O_{12}$). The magnetic ions are distributed over three crystallographic sites with sublattice magnetization *Ma* [octahedral site, 16 $Fe^{3+}$ ions in a], *Md* (tetrahedral site, 24 $Fe^{3+}$ ions in d), and *Mc* {dodecahedral site,24 $Y^{3+}$ ions in c}. Ionic distribution in garnet is represented as $\{Y_3^{3+}\}\ [Fe_2^{3+}\ ](Fe_3^{3+})O^{-2}_{12}$. The interaction between the $Fe^{3+}$ ions in [a] and (d) sites is strongly antiferromagnetic due to strong super exchange interaction.

The magnetic moment of the rare-earth ions in the {c} sublattice couples antiparallel with the resultant moment of $Fe^{3+}$ ions. The magnetic moment caused by two $Fe^{3+}$ ions in [a] site is aligned antiparallel to that caused by three $Fe^{3+}$ ions in (d) site, leaving a net moment from $Fe^{3+}$ in the d-site. Therefore, the saturation magnetization ($M_s$) of YIG is given by the magnetic $Fe^{3+}$ in the d-sites. The paramagnetic trivalent ($Tb^{3+}$, $Er^{3+}$) ions can be substituted for nonmagnetic $Y^{3+}$ ions in {c} sites, but not for $Fe^{3+}$ ions in [a] or (d) sites [3]. The magnetic moment of both ions can substituted for $Y^{3+}$ in {c} sites, which can be parallel to the magnetic moment of $Fe^{3+}$ in the d-sites, meaning that the saturation magnetization of Tb:YIG or Er:YIG is different from that of pure YIG. So, YIG is the most representative and well-known compound among the rare earth-iron garnets, and various magnetization can be achieved by substitution in the YIG [4]. A low-coercivity, high-remanence, soft magnetic material, having a hysteresis loop, is required for microwave operation. For a magnetic material to be applied in microwave devices, the most important static magnetic properties are the saturation magnetization ($M_s$), anisotropy constants, Neel temperature, remanent magnetization, coercivity ($H_c$). In general, $M_s$ and $H_c$ are required for applications [5].

Most of the previous studies focused on the preparation of YIG substitution rare earth (RE) metals [6-12] in the formulation of ($Y_{3-x}R_xFe_5O_{12}$ powder or films) with varying concentrations (x=0,0.1,0.2,0.4,0.6, …etc), or co- substitution of (RE) [13]. Here in this paper, we try to gain more understanding about the effect of low concentration of $Tb^{3+}$, $Er^{3+}$ ($x = 0.4$) for some non-magnetic $Y^{3+}$ ions in YIG nanoparticles and study the structural, magnetic properties of the samples prepared under the same conditions using the sol–gel method, which may lead to new developments in the selection and purification of materials used in new techniques. $Tb^{3+}$ and $Er^{3+}$ ions are chosen for their high verdet constant, beside that larger values of Bohr magneton (9.59 µB for $Tb^{3+}$ and 9.72 µB for $Er^{3+}$) [14]. In recent years, great interest has been focused on the study of the dependence of the physical and chemical properties on the particle size. For this reason, there is renewed interest in the development of new techniques to produce particles of different sizes, sufficiently monodispersed and with a good grade of homogeneity. The sol–gel process offers considerable advantages such as better mixing of the starting materials and excellent chemical homogeneity in the final product [15].

## 2. Experimental

The (Er:YIG) precursor sol was prepared by sol-gel method. Yttrium nitrate hexahydrate [$Y(NO_3)_3{\cdot}6H_2O$], Iron (III) nitrate nanohydrate [$Fe(NO_3)_3{\cdot}9H_2O$], Erbium nitrate pentahydrate [$Er(NO_3)_3{\cdot}5H_2O$] were used as 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- methaxythanol and refluxed at 80°C for 3 hours. The $Er(NO_3)_3{\cdot}5H_2O$ dissolved in acetic acid added gradually into the yttrium and iron solution. Then the refluxing process was carried out for 3 hours. A small quantity of diethylamine was added to the mixture solution, while 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 thin film form (onto quartz

substrates) using the spin coating technique. The rate of the spinning process was 3500 rpm and it was done for 30 second. After the spinning process, the films were heated at 90 $^oC$ for 2 h to remove the residual solvents and then at 350$^oC$ for 15min at a heating rate of 3$^oC$/min to burn off the organic materials, followed by heat treatment process at 900 $^oC$ for 2 h at a heating rate of 4$^oC$/min to crystallize them.

For (Tb:YIG) precursor sol, Terbium (III) acetate hydrate ($Tb (COOCH_3)_3.H_2O$) was first dissolved in 1 ml of acetic acid. Then, 1 ml of distilled water was added to the terbium solution followed by 10 µl of nitric acid. Tb solution was added to the yttrium and iron solution. The pH of precursor solution can affect the formation temperature of the garnet phase [16], thus the precursor solution was maintained at pH 3 by adjusting the amount of diethylamin ($C_4H_{11}N$) in the solution. The resulting solution was refluxed again for 3 h at (80 ± 1) $^oC$ followed by stirring for 48 h to obtain a homogenous gel. To prepare the films, 25 µl of the gel was dropped onto a clean quartz substrate. The substrate was spin coated first at 500 rpm for 15 s, then at 3,500 rpm for 30 s. The film was heated at 90 $^oC$ for 2 h to get rid of residual solvent, and followed by 350 $^oC$ for 15 min at heating rate of 3 $^oC$ /min to burn-off the organic, then also, heat treatment process at 900 $^oC$ for 2 h at a heating rate of 4 $^oC$/min to crystallize them. The X-ray diffractions (XRD) were done at $2\theta = 20^o$ to $80^o$ to investigate the structural properties of the films. Magnetic measurements were carried out at room temperature using a vibrating sample magnetometer (VSM). The field emission scanning electron microscope (FESEM) was carried out to examine the surface quality of the films.

## 3. Results and Discussion

### 3.1. XRD Measurements

The XRD patterns of ($Er_{0.4}Y_{2.6}Fe_5O_{12}$) and ($Tb_{0.4}Y_{2.6}Fe_5O_{12}$) thin films with the Philips model Pw 3020 MRD x'pert pro (a CuK$\alpha$ radiation $\lambda$ = 1.54056A° ) reveal a single phase garnet structure and the crystallization had completely occurred at 900 $^oC$ due to the good homogeneity of the gel prepared at pH = 2-3. The peaks position illustrates a slight shift to the lower 2θ angles as shown in figure 1, indicating that Er and Tb atoms have been incorporated into garnet structure [17].

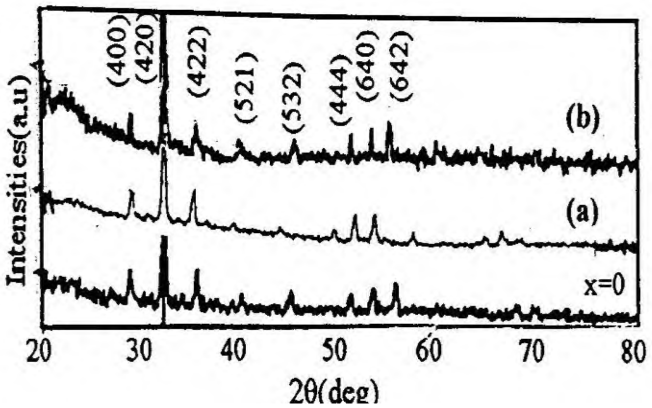

Fig. 1: XRD patterns of (a) $Er_{0.4}Y_{2.6}Fe_5O_{12}$ and (b) $Tb_{0.4}Y_{2.6}Fe_5O_{12}$ films at 900 °C

### 3.2. Microstructural Properties

Figure 2,3 shows the microstructure of the $Tb_{0.4}Y_{2.6}Fe_5O_{12}$ and $Er_{0.4}Y_{2.6}Fe_5O_{12}$ thin films obtained from (FE-SEM) at magnification of 300, 000X. In general, for these samples, the particle size increases with the annealing temperature increased. Most of the particles stuck to each other when the annealing temperature is above 800 °C and this implies that the particles are highly agglomerated due to their high surface energy [18]. Agglomeration of fine particles is caused by the attractive van der Waals force and the driving force that tends to minimize the total surface energy of the system. The grains could not be seen clearly, and this may be because of masking caused by the gold coating on the film's surface. The cross section backscattered FE-SEM microstructure was used to measure the film thickness. The thickness values of obtained (Tb:YIG) , (Er:YIG) films and the average grain sizes were summarized in table 1.

Table 1 . Variations of the grain size and the thickness of the (Tb:YIG) and (Er:YIG) films .

| The film | Average grain size (nm) | Thickness (nm) |
|---|---|---|
| $Tb_{0.4}Y_{2.6}Fe_5O_{12}$ | 50 | 185 |
| $Er_{0.4}Y_{2.6}Fe_5O_{12}$ | 68 | 245 |

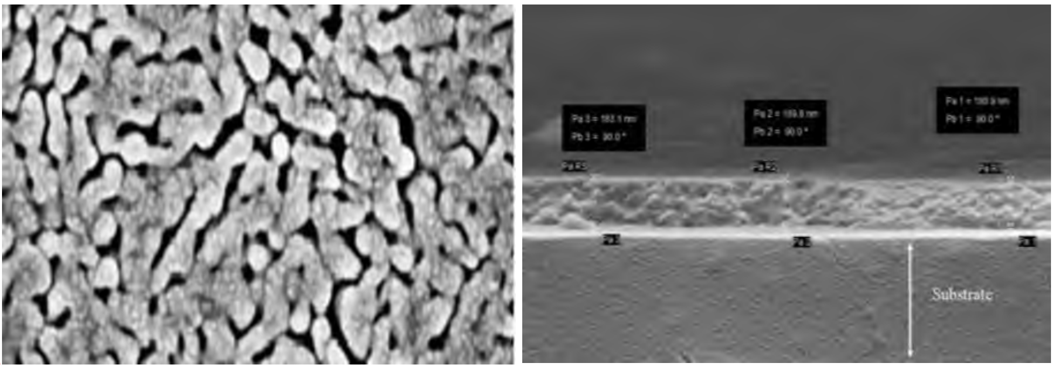

Fig 2: FE-SEM micrograph and image of cross-section of $Tb_{0.4}Y_{2.6}Fe_5O_{12}$ films at 900 °C.

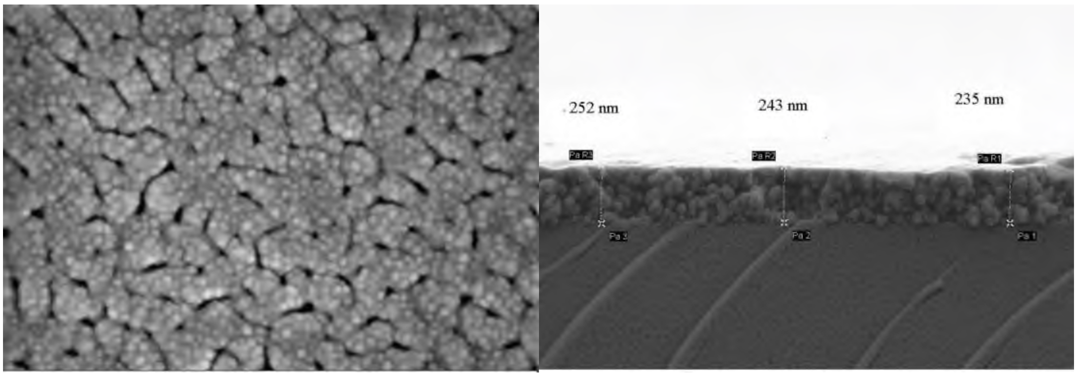

Fig 3: FE-SEM micrograph and image of cross-section of $Er_{0.4}Y_{2.6}Fe_5O_{12}$ films at 900 °C.

### 3.3. Magnetic Measurements

The magnetic properties of the (Tb:YIG) and (Er:YIG) films were measured using the vibrating samples magnetometer (VSM) at room temperature (25 °C). Figure 4,5 shows the hysteresis loops for these films measured with a 15kOe field step. The magnetic measurements at room temperature show that the saturation magnetization ($M_s$) of the films and the curves revealed soft magnetic nature of ($Tb_{0.4}Y_{2.6}Fe_5O_{12}$) film than that of ($Er_{0.4}Y_{2.6}Fe_5O_{12}$) film. The saturation magnetization of the ($Tb_{0.4}Y_{2.6}Fe_5O_{12}$ = 67emu/cm$^3$) is somewhat higher than the ($Er_{0.4}Y_{2.6}Fe_5O_{12}$ = 51emu/cm$^3$), this could be due to the difference in synthesis route, the higher purity of the sample and related to the magnetic structure of the films . While the coercivity ($H_c$) of ($Tb_{0.4}Y_{2.6}Fe_5O_{12}$ = 14 Oe) is less than the coercivity ($H_c$) of ($Er_{0.4}Y_{2.6}Fe_5O_{12}$ = 37 Oe). The largest coercivity for (Er:YIG) film is probably due to the different ionic radius of $Er^{3+}$ (1.004 Å) and $Tb^{3+}$ (1.044 Å) substituted $Y^{3+}$ (0.892 Å).

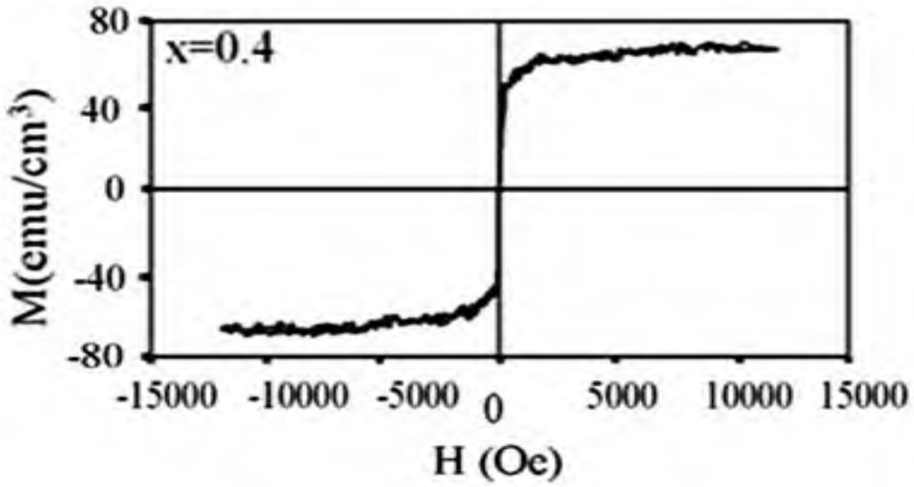

Fig. 4: Hysteresis loop of the $Tb_{0.4}Y_{2.6}Fe_5O_{12}$ film at 900 °C

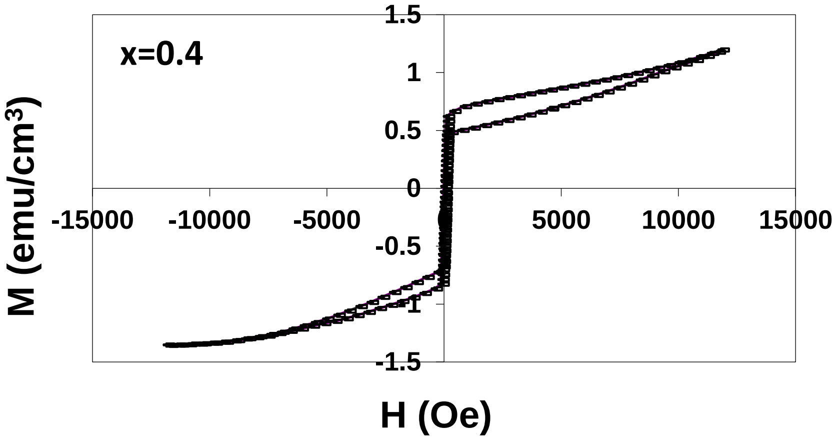

Fig. 5: Hysteresis loop of the $Er_{0.4}Y_{2.6}Fe_5O_{12}$ film at 900 °C

## 4. Conclusion

The structure and magnetic properties of the (Tb:YIG) and (Er:YIG) thin films were prepared using a sol–gel method. The films can be crystallized into a single phase garnet structure at 900 °C for 3 h. The grain size was measured to be in the range of 50 –70 nm. These films heated at same temperature 900 °C exhibited almost the same trend, only differing in saturation magnetization ($M_s$) and coercivity ($H_c$) values. The films have normal shape of hysteresis loops, the saturation magnetization ($M_s$) of the (Tb:YIG) film was somewhat higher than the (Er:YIG) film and the $Tb_{0.4}Y_{2.6}Fe_5O_{12}$ film have low coercivity and exhibit soft magnetic nature compared with $Er_{0.4}Y_{2.6}Fe_5O_{12}$ film. This study reported further understanding of the effect of $Tb^{+3}$ and $Er^{+3}$ in $Y^{+3}$ ions of YIG thin films, which may lead to the development of new materials for new technologies. So, this results indicate that (Tb:YIG) and (Er:YIG) films could be suitable for devises of microwave and memory applications respectively. Based on this study, it can also be suggested that the small amount of Tb and Er into YIG have strong effect on the magnetic structure of the films. The annealing temperature films and different concentrations are of further interest and would prove very useful as an integrated sensor and electronics industry .

## References

**1-** P. Vaqueiro, M.A. Lopez, J. Rivas and J.M. Greneche (1997) "*Annealing dependence of magnetic properties in nanostructural particles of yttrium iron garnet prepared by citrate gel process*". J. Magn. Magn. Mater. 169: 56-68.

**2-** M.J. Jafelicei and R.H. Godoi (2001) "*Preparation and characterization of sperical yttrium iron garnet via coprecipitation*". J. Magn. Magn. Mater. 226-230: 1421-1423.

**3-** M. S. Lataifeh and A. al-sharif (1995) "*Magnetization measurements on some rare-earth iron garnets*" . Applied Physics A: Materials Science & Processing, vol. 61, no. 4, pp. 415–418.

**4-** S. Mandal, S. Phadtare, Curr. Appl. Phys. 5, 118 (2005).
**5-** Y.B. Lee, K.P. Chae, J. Phys. Chem. Solids 62, 1335 (2001).

**6-** M. J. Geselbracht, A.M. Cappellari, A. B. Ellis,M. A. Rzeznik, and B. J. Johnson, "Rare earth iron garnets: their synthesis and magnetic properties," *Journal of Chemical Education*, vol. 71, no. 8, pp. 696–703, 1994.

**7-** M. S. Lataifeh and A. Al-sharif, "Magnetization measurements on some rare-earth iron garnets," *Applied Physics A*, vol. 61, no. 4, pp. 415–418, 1995.

**8-** H.Xu, H. Yang, and L. Lu, "Effect of erbium oxide on synthesis and magnetic properties of yttrium-iron garnet nanoparticles in organic medium," *Journal of Materials Science: Materials in Electronics*, vol. 19, no. 6, pp. 509–513, 2008.

**9-** Zhongjum Cheng HY, Cui Y, Yu L, Zhao X, Feng S (2007) Synthesis and magnetic properties of Y3-xDyx Fe5O12 nanoparticles. J Magn Magn Mater 308:5–9.

**10-** Zhongjum C, Hau Y (2007) Synthesis and magnetic properties of Sm-Y3Fe5O12 nanoparticles. Physica E 39:198–202.

**11-** Xu H, Yang H, Xu W, Yu L (2008) Magnetic properties of Bi doped Y3Fe5O12 nanoparticles. Curr Appl Phys 8:1–5.

**12-** T. Shintaku and T. Uno, "Preparation of Ce-substituted yttrium iron garnet films for magneto-optic waveguide devices," *Japanese Journal of Applied Physics*, vol. 35, no. 9A, pp. 4689–4691, 1996.

**13-** Suleiman M. Elhamali, N.B. Ibrahim* and S.Radiman," Structural, Optical and Magnetic Properties of YIG Doped with Erbium and Terbium Nanofilms using Sol-Gel Method". Journal of Advances in Nanomaterials, V1, No 1. https://dx.doi.org/10.22606/jan.2016.11002.

**14-** C. Kittel, P. McEuen, and P. Mc Euen (1976 ) " *Introduction to solid state physics vol. 8*". Wiley New York.

**15-** J.C. Rehspringer, J. Bursik, J. Magn. Magn. Mater. 211, 291(2000).

**16-** Guillot M, Gall LE, Marchand A, Desvignes JM, Artinian M (1990) "*Contribution of the terbium ion to the Faraday rotation of terbium yttrium ferrite garnets*". J Magn Magn Mater 83:25–26.

**17-** Toledo JA, Valenzuela MA, Bosch P, Armenda´riz H, Montoya A, Nava N, Vazquer A (2000) "*Effect of* $Al_3^+$ *introduction into hydrothermally prepared* $ZnFe_2O_4$" . Appl Catal A 198:235–245.

**18-** S. Verma, S. D. Pradhan, R. Pasricha, S. R. Sainkar, and P. A. Joy (2005) "*A novel low-temperature synthesis of nanosized NiZn ferrite*". Journal of the American Ceramic Society, vol. 88,no. 9, pp. 2597–2599.