Production, characterization and magnetic properties of Bismuth-substituted Yttrium Iron Garnet layers prepared by sol–gel process

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Abstract. In this study, (BiY₂)Fe₅O₁₂ (Bi:YIG) magneto-optic layers were deposited on Si(100) and glass substrates using a sol-gel process. Bi, Y and Fe based-precursors were dissolved using methanol and glacial acetic acid as a solvent and chelating agent respectively. The turbidity, viscosity, gel point and pH values of the prepared solutions were determined using turbidimeter, rheometer and pHmeter. The prepared xerogels were dried and used for DTA/TG analysis to determine heat treatment regime in thin film production. Based on DTA/TG results, the deposited films were annealed at 800°C for 2 hours in air. Inasmuch as the magnetic and morphological properties are important for applications such as superconductive material vortex investigations, the produced films were investigated in details. The structural properties of the coatings were characterized by using XRD, SEM-EDS and AFM. The magnetic properties of the films were evaluated by the substitution of Bi and process conditions using VSM. The obtained results are presented.

Keywords: Thin films, Bi:YIG, Sol-gel, Magneto-optic properties

1. Introduction
With the development of microwave devices and magneto-optical (MO) integrated devices; the research of yttrium iron garnet (YIG) thin films is becoming more and more important because of properties that can be applied in both microwave and MO devices [1]. Artificial media providing the enhancement of magneto-optical MO effects attract much interest, due to the fact that they may advance functional capabilities of known optical devices such as isolators, magneto-optical memory systems, and magneto-optical spatial light modulators. Large angles of rotation, wide working spectral ranges, and nanosized or microsized dimensions of new MO media are essential properties demanded by applications [2]. To realize these applications, high-performance wide-band and temperature-stabilized optical isolators are essential, which in turn require Faraday rotators capable of ensuring a Faraday rotation stable against wavelength and temperature variation. Nevertheless, the Faraday rotation (θₑ) coefficient of YIG (approximately only 220 deg/cm at 1300 nm) is too small for practical use [3].

In order to improve the MO properties, the ions with +3 balance and suitable ionic radii to yttrium such as the Bi ion or Ce ions are usually substituted with yttrium in YIG films, which can increase the Faraday angle efficiently. Faraday rotation of Bi-substituted magnetic garnet reveals strong wavelength and temperature dependencies [3]. Produced YIG thin films serve as served as Faraday rotator for wide-band and temperature-stabilized optical isolators by the following reasons: (1) the Bi³⁺ and Y³⁺ ions offer the opposite contributes to the wavelength and temperature characteristic of Faraday rotation (2) doping Bi³⁺ ions on dodecahedral sites of garnet structure can enhance greatly the Faraday rotation and increases in proportion to Bi³⁺ ions concentration without increasing absorption loss.

In recent researches YIG or Bi-YIG films have been prepared by a variety of methods such as radiofrequency sputtering, liquid phase epitaxy, pyrolysis, sol–gel process, and pulsed laser ablation deposition on several substrates such as glass, Si(100) wafer or gadolinium gallium garnet (GGG). As
mentioned, several techniques can be employed to make YIG based materials such as RF magnetron sputtering, sol-gel and pulse laser deposition technique [4-9]. Of these techniques, the sol-gel processing has a number of advantages. To illustrate this, it is possible to synthesize quite good polycrystalline ferrites with the sol-gel method. The sol–gel process offers considerable advantages such as better mixing of the starting materials and excellent chemical homogeneity in the final product. Moreover, the molecular level mixing aids the structure evolution lowering the crystallization temperature [10] and the sol-gel layer can be deposited desired thickness in one step because this thickness depends only on precursor’s concentration. The available Bi-YIG material research has mainly on single thin film crystals. Here a polycrystalline Bi-YIG, studied infrequently, have been produced using the sol-gel method and eventually its magneto-optical properties are presented.

2. Experimental Procedures

The solutions were prepared by dissolving Bi-, Y- and Fe-based alkoxide based precursors in glacial acetic acid as a chelating agent and methanol as solvent respectively. The transparent solutions were formed through the hydrolysis of Bi, Y and Fe alkoxides after stirring in an ultrasonic cleaner at room temperature for 30 minutes. The obtained transparent solutions can remain stable approximately for a month. Four solutions, as listed in Table 1, were prepared and differ from each other depending on their concentrations since we aimed a research on the effect of concentration to film thicknesses and magneto-optical properties in this study. The solutions were called as BM1, BM2, BM3 and BM4 (see Table 1 for more details).

| Solvent | BM1  | BM2  | BM3  | BM4  |
|---------|------|------|------|------|
| Fe-alkoxide (g) | 0.7063 | 0.3532 | 0.2648 | 0.1765 |
| Y- alkoxide (g)  | 0.308  | 0.154  | 0.1155 | 0.077  |
| Bi- alkoxide (g) | 0.152  | 0.076  | 0.057  | 0.038  |
| Glacial acetic acid (ml) | 10 | 10 | 10 | 10 |
| Methanol (ml) | 2 | 2 | 2 | 2 |
| C.R | 1 | 2 | 3 | 4 |

C.R Concentration Rate. If the concentration of BM1 is the unit concentration. The rate of other solution to unit solution is concentration rate.

To determine solution characteristics which affect thin film structure, turbidity, pH values and rheological properties of the prepared solutions were respectively measured using turbidimeter, pH meter and rheometer machines before coating processes. Turbidity properties of the solutions were measured using standard solutions for coating process by TB 1 Velp Scientifica Model turbidimeter according to ISO 7027 nepheometric method. The sample was placed in a vessel with a dimension of Ø25 mm and height of 50 mm. Formazin has been recognized throughout the world as a primary standard. Thus formazin solution was used to calibrate the turbidity in the range of 0 and 1000 ntu (nephelometric turbidity unit). Having prepared transparent solutions, we measured pH values of the solutions to check their acidic and basis characteristics using a standard pH meter with Mettler Toled electrode. Besides pH and turbidity measurements, rheological behaviour of the solutions including viscosity was determined by CVO 100 Digital Rheometer (Bohlin Instrument).

Commercial Pyrex glass and Si (100) were used as substrates. The substrate surface was cleaned with acetone just before coating process. The solutions were used for coatings on the Pyrex glass and Si (100) substrates by spin coating system at ambient conditions. The spin coating system has been used for several decades in thin film preparation process. A typical process entails depositing a small puddle of a sol or gel onto the centre of a substrate and then spinning the substrate at high speed.
Centripetal acceleration causes the gel to spread to, and eventually off, the edge of the substrate leaving a thin film of gel on the surface. Hence the film thickness and their properties depend on the nature of the gel (viscosity, drying rate, percent solids, surface tension, etc.) and the parameters chosen for the spin process. Factors such as final rotational speed, acceleration, and fume exhaust contribute to how the properties of coated films are defined. For the most resin materials the final film thickness will be inversely proportional to the spin speed and spin time. Final thickness will be also be proportional to the exhaust volume although uniformity will suffer if the exhaust flow is too high since turbulence will cause non uniform drying of the film in the spin process [11]. Bi-YIG solutions were spin coated on the glass and Si (100) substrates with 3000 rpm for 20 s at room temperature. After spin coating process, the obtained gel coating was dried up to 500 °C with a heating rate 15°C/ min, at this temperature of the calcined films for 30 minutes in air. Same processes were applied for two times to obtained three layered Bi-YIG film. After coating and drying of three layers, the films were annealed at 800 °C for 2 hours in air to obtain Bi-YIG film structure in an electric furnace according to obtained DTA/TG result.

Thermal behavior of Bi-, Y- and Fe-based xerogels, which were dried at 200 °C for 30 minutes in air, was evaluated at a heating rate of 10 °C/min under oxygen atmosphere by using DTA/TG machine (DTG-60H Shimadzu) in order to gain decomposition and phase formation, and to obtain an optimum heat treatment regime. The experiments were conducted in oxygen flow (60 ml/min) in the temperature range from ambient to 700 °C at a heating rate of 10 °C/min. XRD patterns of the coatings were determined to identify phase structure by means of a Rigaku (D/MAX-2200/PC) diffractometer with a CuKα irradiation (wavelength, λ=0.15418 nm) by both θ-2θ mode and 2θ scan mode. Thin-film XRD geometry where incident angle was fixed at 1° was used to collect data from only thin films. Thicknesses of the films were measured by spectrophotometer. The surface topographies of Bi-YIG coatings were examined by using SEM (JEOL JSM 6060) attached with energy dispersive spectroscopy (EDS). The magnetic properties of YIG films were measured at room temperature in a vibrating sample magnetometer (VSM, Lakeshore 736, 7400 Series) in a maximum applied field of 1000 Gauss. From the obtained hysteresis loops, the saturation magnetization ($M_s$) and coercivity ($H_c$) were determined.

3. Results and discussion
Turbidimetric measurements were performed to determine dissolution properties of solutions. It is interpreted that powder-based precursors are completely dissolved as turbidity value approaches to 0 ntu and they are not dissolved when some powder particles are suspended in a solution at near 1000 ntu. The fabrication of homogeneous and continuous thin film is directly related to turbidity value which is 0 ntu. According to these measurements results for solutions, BM1, BM2, BM3 and BM4 were obtained like; 280 ntu, 240 ntu, 200 ntu and 186 ntu respectively. Although we have homogenous and transparent solutions, the turbidity values are high because of iron colour. Due to the fact that iron has red colour, the turbidity values increase even if they are dissolved very well.

The pH values of BM1, BM2, BM3 and BM4 solutions were 5.20, 4.20, 3.38 and 3.19 respectively. Since the acidic content of BM4 is higher than that of the others, the pH value is lower. The pH value of the solution is an important factor influencing the formation of the polymeric three-dimensional structure of the gel during the gelation process; it should be taken into consideration during solution preparation.

A characteristic feature of many sol-gel solutions is the shear-rate or test time dependence of the viscosity. It was determined that the viscosity values of the BM1, BM2, BM3 and BM4 solutions were approximately equal to 2.8 mPa.s, 2.5 mPa.s, 2.3 mPa.s, and 2 mPa.s respectively. We have to point here that the viscosity values of the solutions are almost similar that shows a key factor in controlling film thickness. The obtained results are reasonable for sol-gel processing because the thicknesses of the films decrease from BM1 to BM4.

Due to optimisation of drying, heat treatment and annealing regimes, DTA/TG curves were obtained from the xerogel which was dried at 200 °C for 30 minutes. As shown in Figure 1, the
Exothermic and endothermic reactions occur in a temperature range between 30°C and 1000°C. It was determined that there are four different phenomena including removal of solvent-based materials, combustion of carbon-based content, formation of oxides and garnet formation. The first phenomenon is removal of solvent. In this case, physical water adsorbed in gel was evaporated occurs at 100°C. Secondly the combustion of carbon-based content occurs at 300°C. Thirdly oxidation occurs at 400°C and at last step formation of garnet phase starts at 700°C and reaches a maximum point at 800°C. According to TG results in Figure 1, weight loss of the Bi-YIG xerogel up to 500°C was determined as ~64%. Based on these results, a heat regime for coating process was determined at temperatures such as 500°C and 700-1000°C which indicate respectively combustion or drying, oxidation or heat treatment and annealing processes prior to not using a sol-gel coating processes.

Figure 1. DTA and TG curves of Bi-YIG xerogel.

Figure 2 shows XRD patterns of selected samples from Bi-YIG coatings. It is clear from Figure 2 that all produced samples contains YIG phase. However, there are FeYO₃ (YIP), Fe₂O₃ and orthorhombic YIG or Bi-YIG phases in our films (shown with circle symbols). According to XRD results, the patterns show that there is partially YIG phase in all films. Even though YIG phase partially presents in the films Fe₂O₃ (shown with diamond symbols) and FeYO₃ (shown with square symbols) phases present at all specimens from BM1 to BM4. As shown in Figure 2, lattice constant of YIG increases with Bi substitution causing the peaks of YIG slight shift since radius values of Bi³⁺ ion is different from that of Y³⁺. The radius of Bi³⁺ is 0.103 nm, whereas the radius of Y³⁺ is 0.09 nm. This results in a slight shift of YIG peak due to their characteristic properties. Studies of Haitao ve Shouhua [11] show that annealing process of Bi-YIG films at 800°C causes to obtain Fe₂O₃, FeYO₃ ve Bi-YIG together. They reported that they increased annealing temperature above 800°C and also Bi-YIG fraction was increased in the specimen. Similar results can be seen in our studies. X.W. Zhang [12] reported that YIG phase is not obtained at temperatures below 800°C. Increasing temperature accelerates the reaction of Fe₂O₃ with FeYO₃ to form YIG as shown in Equation 1.

\[3\text{FeYO}_3 + \text{Fe}_2\text{O}_3 \rightarrow \text{Y}_3\text{Fe}_5\text{O}_{12} \quad (T>800\, ^\circ\text{C})\]  

According to these results, it is obvious that time for transformation of YIG is not enough. Also many papers reports that Fe₂O₃ and FeYO₃ are inter-phases for YIG formation.
Figure 2. XRD patterns of the prepared specimens.

(a)  (b)  (c)  (d)

Figure 3. SEM micrographs of Bi-YIG film on Si(100) substrates deposited from (a) BM1, (b) BM2, (c) BM3 and (b) BM4 solutions. The scale bars are 10 µm.
Microstructural properties of Bi-YIG films are shown in Figure 3 from BM1 to BM4. Since the molar concentration of the solutions decreases from BM1 to BM4 according to C.R. values, the fraction of the cracks, pinholes and deposition islands also decreases too. The obtained structure is directly related with deposition process. Spin coating technique involves a well spreading of the film. In addition, their microstructures are directly affected from pH value, heat treatment regime, and viscosity. Decreasing viscosity causes crack free deposition which influences good magneto-optic properties.

![Graph showing M-H curves of the Bi-YIG film at room temperature on a Si(100) substrate produced from BM2 solution.](image)

**Figure 4.** M-H curves of the Bi-YIG film at room temperature on a Si(100) substrate produced from BM2 solution.

The magnetization M versus applied magnetic field H curves was obtained from a VSM device where diamagnetic contribution is not subtracted. We have measured for two configurations: the applied field parallel and perpendicular to the film plane. Since the results are similar for all our samples, we have shown here results for a selected sample. Prepared Bi-YIG specimens show magnetic properties in-plane and perpendicular configurations. Along with VSM results we should also regard XRD results: the XRD results indicate a small value of magnetization due to lower fraction of Bi-YIG is in comparison to other phases present. According to XRD result in Figure 2, the existing phases are \( \text{Fe}_2\text{O}_3 \), \( \text{YFeO}_3 \) and \( \text{Y}_3\text{Fe}_5\text{O}_{12} \). \( \text{Fe}_2\text{O}_3 \) has paramagnetic behaviour and also \( \text{YFeO}_3 \) and \( \text{Y}_3\text{Fe}_5\text{O}_{12} \) are ferrimagnetic materials but there is evidently a diamagnetic affect in our measurements dominating other phases. Si (100) was used as a substrate. Due to the fact that bulk Si is a diamagnetic material, the curve probably is affected from this condition as explained in Ref. [15]. However for perpendicular configurations diamagnetic effect is suppressed. This can be attributed to film perpendicular case has nonzero de-magnetization coefficient whereas for in plane case de-magnetization coefficient is almost zero.

4. Summary and Conclusions

Bi-YIG thin films were synthesized on Si(100) substrates from the solutions prepared from Bi, Y, and Fe based precursors, methanol, glacial acetic acid using sol–gel process for magneto-optical applications. The experiments were carried out at non-defined conditions just to obtain phase. At further studies we will perform experiments at refined conditions. The DTA-TG curve revealed that endothermic and exothermic reactions occur at temperatures between 30 °C and 1000 °C. The
formation of Bi:YIG phase was occurred in the range of 700 °C and 800 °C. We decided the heat treatment regime as temperature versus time but the reaction kinetics carried out slower than it was thought. To optimize the heat treatment and to obtain exact phase and good magnetic properties, different experiments will be performed at different regimes.

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