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Influence of bismuth substitution on yttrium orthoferrite thin films preparation by the MOD method

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ABSTRACT

Yttrium orthoferrite thin films with a thickness of about 0.4 μm were prepared on glass substrates by using a metal-organic decomposition method. Our studies reveal that it is possible to reduce the crystallization temperature of the yttrium orthoferrite by the substitution of the yttrium ion with bismuth. For the samples $Bi_xY_{1-x}FeO_3$ with $x=0.3$ and $x=0.4$, orthorhombic yttrium orthoferrite characteristic peaks in the X-ray diffraction spectra have been detected. The lattice constants of the $Bi_{0.3}Y_{0.7}FeO_3$ film were $a=5.905$ Å, $b=7.66$ Å, $c=5.256$ Å with an average grain size of about 40 nm. The magnetization data indicate that the film has in-plane easy axis and weak coercivity which might be explained by a possible secondary garnet phase crystallization. Faraday rotation angle of the sample was measured to be about 0.3°/μm.

1. Introduction

The rare-earth orthoferrites with a general formula $RFeO_3$, where R is the rare-earth ion has attracted great research attention due to their magnetic, magneto-optical properties and transparency in the visible and near-infrared regions [1–3]. Particularly, yttrium orthoferrite (R=Y, $YFeO_3$) which has a distorted perovskite crystalline structure is an interesting material because of its wide application in sensors [4,5], magneto-optical devices [6,7], and photocatalysis [8]. However, there are several difficulties concerning synthesis of $YFeO_3$: the formation of secondary phases like $Y_3Fe_5O_{12}$ (yttrium iron garnet) [9], crystallization in either orthorhombic (o-$YFeO_3$) or hexagonal (h-$YFeO_3$) structures depending on preparation conditions [10–12].

Most of the researches have been carried on the bulk form of these materials because of the difficulties encountered in preparation of thin films [13]. To the best of our knowledge, there are few reports available on the preparation of $YFeO_3$ thin films [13–15]. Schmool et al. in Ref. [13] described the preparation of the orthoferrite thin films on quartz substrates using the pulsed-laser deposition method which requires high temperature (860 °C) post-deposition annealing treatment. In Ref. [14], the sol–gel synthesis method has been used. We used the metal-organic decomposition (MOD) method [16,17] for the preparation of thin films because this method is inexpensive and consists of simple steps: preparation of metal-organic solution, which can be obtained by using commercially available or in house synthesized precursors. Then the MOD solution is deposited on the substrate using any of the liquid phase film growth techniques, for example, spin, spray or dip coating. After deposition, wet films are dried in an oven at moderate temperatures to evaporate the solvent. The dried compound is then pre-annealed to bring the film to the amorphous condition. These steps are repeated until the film has the desired thickness. Finally, the amorphous film is post-annealed in a furnace at the crystallization temperature. As substrate we used glass but the problem with the preparation of o-$YFeO_3$ thin films on such substrates is that the crystalline structure of o-$YFeO_3$ which requires a relatively high temperature of crystallization [14]. High temperature or long time annealing process will cause the deformation of glass substrate. As we will show, MOD is a promising method for o-$YFeO_3$ thin films preparation on glass substrates because it does not require high temperatures or long time annealing to produce the desired materials. Our results indicate that by substitution of yttrium with different concentration of bismuth the crystallization of the orthorhombic phase of $YFeO_3$ becomes possible.

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In the present paper, we report the preparation conditions of $YFeO_3$ thin films by the MOD method and discuss the impact of substitution of yttrium by different concentration of bismuth on crystallization conditions of thin films. We also investigated the magnetic, optical and magneto-optical properties of the prepared films.

2. Experiment

Metal-organic solutions for film preparation were purchased from Kojundu Chemical laboratory. We prepared $YFeO_3$ thin films by spin coating of a metal-organic solution at 3000 rpm for 30 s on an Eagle XG borosilicate glass substrate with 0.5 mm thickness and 10×10 mm^2 surface area. The substrates were cleaned using standard cleaning procedures: ultra-sonication in acetone, detergent, distilled water, and isopropanol for 15 min. The deposited solution was dried at 70 °C for 30 min. After drying it was pre-annealed at 450 °C for 30 min. These processes, i.e., spin coating, drying, and pre-annealing, were repeated to obtain an appropriate thickness. Then samples were post-annealed in a furnace at 650–750 °C for 1–4 h in order to obtain crystallized films (Fig. 1). The typical thicknesses of the films obtained in the present study were about 0.4 μm. All thermal treatments were done in air. Table 1 shows preparation conditions and thin-film properties of prepared samples.

To investigate magneto-optical properties of the films Faraday rotation (FR) angle have been measured. The experimental setup for FR measurements is schematically shown in Fig. 2. A semiconductor laser with 530 nm wavelength is used as a light source (L). The light, after passing the polarizer (P) traverses through the sample (S) under influence of the DC magnetic field which rotates the plane of polarization of light. The light exiting the sample passes through the rotatable analyzer (A) and finally is detected by a photodiode (D).

Table 1
Preparation parameters, crystal structure, and magneto-optical properties of synthesized samples. All samples were dried at 70 °C for 30 min and pre-annealed at 450 °C for 30 min.

Sample	Concentration of Bismuth $Bi_xY_{1-x}FeO_3$ ($x=$)	Post-annealing conditions (°C/h)	Phases observed by XRD	Faraday rotation (°/μm)
S1	0	650/3	Amorphous	–
S2	0	750/3	h-$YFeO_3$	–
S3	0.1	750/3	h-$YFeO_3$	–
S4	0.2	750/3	h-$YFeO_3$ + o-$YFeO_3$	–
S5	0.3	750/3	o-$YFeO_3$	0.3
S6	0.4	750/3	o-$YFeO_3$	0.3
S7	0.5	750/3	$Y_3Fe_5O_{12}$ + o-$YFeO_3$	0.58
S8	0.3	650/3	Amorphous	–
S9	0.3	700/3	h-$YFeO_3$ + o-$YFeO_3$	–
S10	0.3	700/4	h-$YFeO_3$ + o-$YFeO_3$	–
S11	0.3	750/2	h-$YFeO_3$ + o-$YFeO_3$	0.15
S12	0.3	750/4	h-$YFeO_3$ + o-$YFeO_3$	0.12

By using Jones calculus one can derive the light intensity equation measured by the photodiode

$$I = I_{off} + I_0 \sin^2(\theta + \theta_F) \cong I_{off} + I_0(\theta + \theta_F)^2, \quad (1)$$

where I_{off} is the intensity of offset (stray) light and I_0 is the initial intensity of light. As the rotation angle of the analyzer is correlated to the FR, we measured the intensity changes according to the rotation of the analyzer around the minimum where the principal axis of polarizer and analyzer were perpendicular to each other. Two intensity curves were recorded for each sample when the

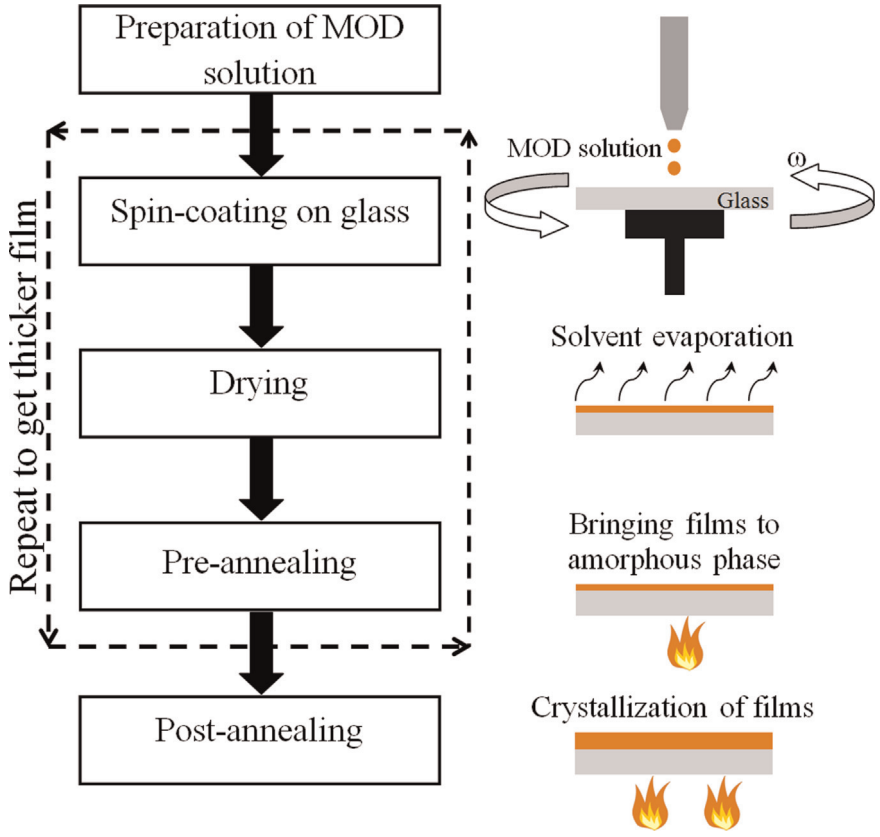

Fig. 1. The schematic of the MOD procedure.