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The synthesis and the magnetic properties of $Sm_xBiY_{2-x}Fe_5O_{12}$ nanoparticles

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Abstract $Sm_xBiY_{2-x}Fe_5O_{12}$ ($x = 0$, 0.1, 0.2, 0.4, 0.6, 0.8) nanocrystals were fabricated by sol–gel method. Samples were characterized by powder X-ray diffraction (XRD), thermal gravity analysis (TGA) and differential thermal analysis (DTA), transmission electron microscopy (TEM), vibrating sample magnetometer(VSM). The samples were calcined at 850 °C and 1000 °C and the average size of the particles were determined by Scherrer's formula . In this paper, we discussed the effect of Sm^{3+} substitution for Y^{3+} on magnetic properties of $BiY_2Fe_5O_{12}$. The magnetic properties of Sm_xBiY_{2-x} Fe_5O_{12} are decreased with increasing content of Sm ion.

Introduction

Rare-earth iron garnet ($R_3Fe_5O_{12}$) is one of a well-known family of ferromagnetic material. These materials have a uniquely defined cation distribution and do not present any site inversion problems which can arise in other ferrites. From an industrial viewpoint, they are applicable to media for high-density magnetic or magneto-optical information storage. Among the magnetic material, polycrystalline yttrium iron garnets and substituted ones have received a great deal of attraction in laser, microwave devices and magneto-optics.

Recently, the bismuth–yttrium iron garnet (Bi–YIG) was found that it has enhanced Faraday rotation effect of one order of magnitude larger than that of yttrium iron garnet (YIG) [1]. Furthermore, the crystallization temperature of preparing BiY2Fe5O12 is lower than that of Y3Fe5O12 because the Bi ion is doped to the YIG.

Replacement of Y^{3+} ions by Bi^{3+} ions can decrease the crystallization temperature for 100–300 °C in contrast to YIG. These properties make the bismuth–yttrium iron garnet much more promising for applications in magneto-optical discs and magneto-optical display devices [2–4].

In this paper, single-phase polycrystalline BiY_{2-} Fe_5O_{12} was synthesized by sol–gel method. Basing on the well properties of $BiY_2Fe_5O_{12}$, we further substituted Y^{3+} ions by Sm^{3+} ions to obtain Sm_xBiY_{2-x} Fe_5O_{12} ($x = 0$, 0.1, 0.2, 0.4, 0.6, 0.8) single-phase nanocrystals and studied the effect of different x value on magnetic properties.

Experimental

Polycrystalline samples with the general formula $Sm_xBiY_{2-x}Fe_5O_{12}$ ($x = 0$, 0.1, 0.2, 0.4, 0.6, 0.8) were prepared via sol-gel method. The initial compounds are analytically pure grade $Bi(NO_3)_2 \cdot 5H2O$, $Fe(NO_3)_3 \cdot 9H_2O$, $Y(NO_3)_2$, $Sm(NO_3)_3$ and polyethylene glycol (PEG, molecular weight 20000) which form a solution in appropriate stoichiometric ratios. Gels were dried at 100 °C for 36 h to form the precursors which were further preheated at 450 °C for 1 h and calcined at 850 °C for 3h.

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Differential thermal analysis (DTA) and thermal gravity (TG) of the samples were carried out with a Thermal Analyser (TGA/SDTA851e METTLER TOLEDO) in the temperature range 25–1000 °C, in air.

The structure and the crystallite sizes were tested by X-ray diffractometer in the 2θ range 25–55° using CuKα radiation ($\lambda = 0.15405$ nm). The type of X-ray diffractometer is SHIMADZU Co.Tokyo Japan. The crystallite sizes are calculated using Scherrer's relationship $D = k\lambda/B\cos\theta$, where 'D' is the average diameter in nm, 'k' is the shape factor, 'B' is the broadening of the diffraction line measured half of its maximum intensity in 'radians', 'λ' is the wave length of X-ray and 'θ' is the Bragg's diffraction angle. The crystallite sizes of the samples are estimated from the line width of the (422) XRD peaks.

The morphology and the particle sizes of the samples were observed from the Hitactli H-800 TEM. For this measurement, the sample was deposited on copper grids and the microscope was operated at an accelerating potential of 175 KV.

Magnetic measurements are carried out at room temperature using a vibrating sample magnetometer (VSM) (Digital Measurement System JDM–13) with a maximum magnetic field of 10000 Oe.

Results and discussion

X-ray diffraction

Several sets of X-ray powder diffraction data at various temperatures were collected for structural analysis. Figure 1 shows the X-ray diffraction pattern of sample $BiY_2Fe_5O_{12}$ obtained by increasing the temperature from 600 °C to 1000 °C for 3 h. Figure 1a shows that at 600 °C all the peaks can be attributed to $Bi_{1/3}Y_{2/3}FeO_3$ and the small amount of Fe_2O_3 which are the intermediates compounds. They will proceed the further reaction to format $BiY_2Fe_5O_{12}$ which is confirmed by the appearance of peaks of $Bi_{1/3}Y_{2/3}FeO_3$, Fe_2O_3 and $BiY_2Fe_5O_{12}$ at 750 °C (Fig. 1b). The process of transaction is completed at 850 °C and a single garnet phase is obtained (Fig. 1c). The crystallite size of $BiY_2Fe_5O_{12}$ increased apparently from 43 nm at 850 °C to 57 nm at 1000 °C (Fig. 1d) [1, 5] (Fig 2).

The X-ray diffraction patterns of $Sm_xBiY_{2-x}Fe_5O_{12}$ ($x = 0$, 0.1, 0.2, 0.4, 0.6, 0.8) nanoparticles calcined at 850 °C are shown in Fig. 3. It is shown that the structures of $Sm_xBiY_{2-x}Fe_5O_{12}$ nanoparticles are all single garnet phases. Table 1 is the dependence of crystalline size of $Sm_xBiY_{2-x}Fe_5O_{12}$ nanoparticles

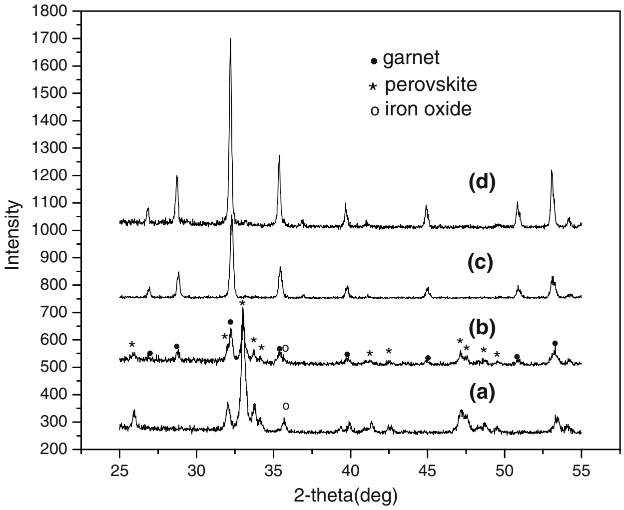

Fig. 1 XRD patterns of $BiY_2Fe_5O_{12}$ nanoparticles calcined at: (**a**) 600 °C, (**b**) 700 °C, (**c**) 850 °C, (**d**) 1000 °C

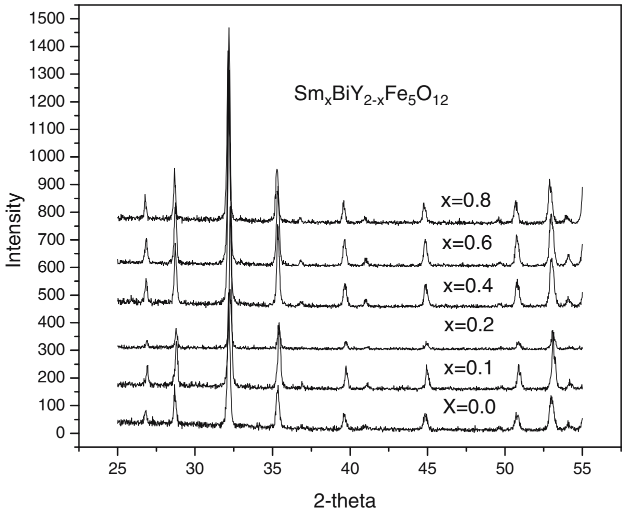

Fig. 2 XRD patterns of $Sm_xBiY_{2-x}Fe_5O_{12}$ ($x = 0$, 0.1, 0.2, 0.4, 0.6, 0.8) nanoparticles calcined at 850 °C for 3h

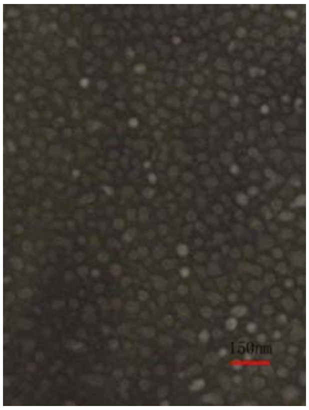

Fig. 3 Transmission electron micrograph images for $Sm_{0.2}BiY_{1.8}Fe_5O_{12}$

Table 1 The crystallite sizes of $Sm_xBiY_{2-x}Fe_5O_{12}$ nanocrystals calcined at 850 °C and 1000 °C

$x(Sm_xBiY_{2-x}Fe_5O_{12})$	0.0	0.1	0.2	0.4	0.6	0.8
D(nm)						
850 °C	43.3	50.4	49.5	52.6	48.8	48.9
1000 °C	54.7	54.64	55.95	54.88	50.04	53.54

calcined at 850 °C and 1000 °C on the content of doped Sm^{3+}. When Y^{3+} ions in $Sm_xBiY_{2-x}Fe_5O_{12}$ garnet nanoparticles are substituted by Sm^{3+} ions, the crystallite sizes of samples calcined at 850 °C increase slightly compare to $BiY_2Fe_5O_{12}$, but they don't increase further as x added, which maybe relate to the reason that the ionic radius of Sm^{3+}(0.964Å) is larger than that of Y^{3+}(0.892 Å) [6]. The crystallite sizes of the nanoparticles don't change apparently, and the average size is 54 nm. It also can be seen that the crystallite sizes of the nanoparticles increase with the increasing temperature.

Figure 3 shows the TEM images of the $Sm_{0.2}BiY_{1.8}Fe_5O_{12}$ nanoparticles calcined at 850 °C. It is shown that the average particle size is about 45 nm and the particles are dispersed uniformly [7]. The result is in good agreement with XRD analysis. The XRD result is consisted with that of TEM image.

DTA and TG

DTA and TG curves of dried precursor sample of $BiY_2Fe_5O_{12}$ are shown on Fig. 4. DTA plot shown an endothermic peak at 105 °C which is the desorption peak of adsorption water on the precursor. There are two exothermic peaks in the DTA curve at 240 °C and 375 °C, respectively and TG curve shows that both the exothermic peaks are accompanied with the apparent weight loss. The first exothermic peak appears to be due to the decomposition of nitrates, which may occur according to the following reaction:

$$M(NO_3)_3 \rightarrow M_2O_3 + 12\ NO_2 + O_2 \qquad (1)$$

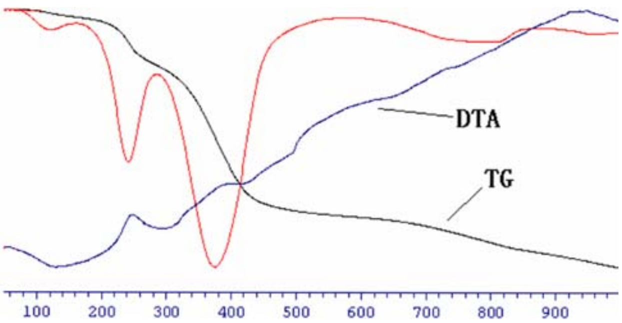

Fig. 4 TG and DTA plots of $BiY_2Fe_5O_{12}$ precursor

And the exothermic peak at 375 °C which is accompanied with large weight loss is probably due to decomposition of surfactant (PEG). The process of decomposition of PEG at 440 °C, and accordingly we preheat the samples at 450 °C for 1 h to burn out the surfactant. Following the exothermic peaks, a broad hump appear in the DTA curve between 500 °C and 600 °C which can be due to formation of the $Bi_{1/3}Y_{2/3}FeO_3$ as the XRD data (Fig. 1a) shows the presence of the perovskite phase and Fe_2O_3 in the sample sintering at 600 °C. It can be expressed by the following chemical reaction:

$$Fe_2O_3 + 1/3Bi_2O_3 + 2/3Y_2O_3 \rightarrow 2Bi_{1/3}Y_{2/3}FeO_3 \qquad (2)$$

The small exothermic peak at 730 °C may be attributed to the crystallization of $BiY_2Fe_5O_{12}$ which can be expressed by the following chemical reactions:

$$3Bi_{1/3}Y_{2/3}FeO_3 + Fe_2O_3 \rightarrow BiY_2Fe_5O_{12} \qquad (3)$$

This is identified by the XRD patterns of the sample sintering at 750 °C and 850 °C (Fig. 1b and c). The TG curve shows that there is a continuous and gradual weight loss up to 1000 °C, which may be due to the further crystallization [8].

XRD patterns and DTA/TG curves indicate that the post-annealing above 850 °C is necessary to obtain a single garnet phase of samples.

Magnetic measurements

The magnetic hyteresis of $BiY_2Fe_5O_{12}$ and $Sm_{0.8}BiY_{1.2}Fe_5O_{12}$ samples are shown in Fig. 5. The saturation magnetization (Ms) at room temperature was obtained from the hysteresis curve for each sample, and the value of coercivity (Hc) and remanence saturation magnetization (Mr) are all zero. The dependence of saturation magnetization on the Sm^{3+} content is plotted in Fig. 6. Saturation magnetization (Ms) of $Sm_xBiY_{2-x}Fe_5O_{12}$ nanoparticles calcined at both 850 °C and 1000 °C decreased apparently as *x* increases. This is obvious because of the effect of doped Sm^{3+} on the saturation magnetization (Ms), which is more dominant than the effect of the grain size. This in turn leads to lower saturation magnetization (Ms). Saturation magnetization (Ms) increase slightly as the crystallite sizes increase.

Garnet has the composition $A_3B_2B'_3O_{12}$ (cubic space group, Ia3d),with eight formula units per cell. In the case of $BiY_2Fe_5O_{12}$, the A = Y^{3+},Bi^{3+} site is

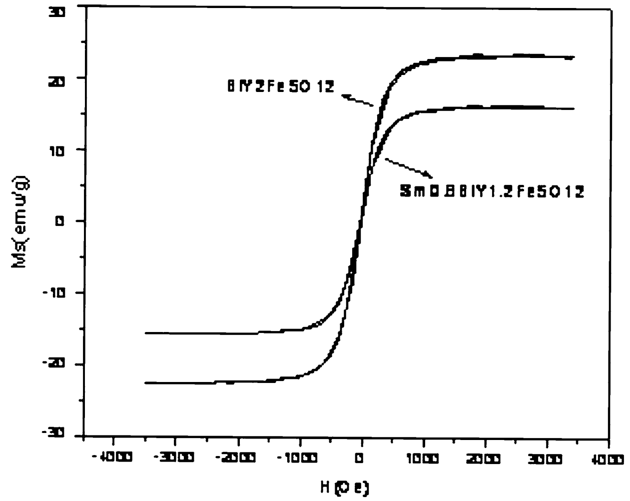

Fig. 5 The hysteresis loop of $BiY_2Fe_5O_{12}$ and $Sm_{0.8}BiY_{1.2}Fe_5O_{12}$ nanoparticles calcined at 850 °C

eight-fold dodecahedrally coordinated(c site), The B = Fe^{3+} site six-fold octahedral(a site) and the B′ = Fe^{3+} site four-fold tetrahedral(d site). Y^{3+}, Bi^{3+} are diamagnetic and 5 μ_B (T = 0 K) per formula unit results from negative superexchange (antiferromagnetic) interactions are dominant to a–a and d–d interactions.

The magnetic structure of $BiY_2Fe_5O_{12}$ can be understood with the framework of the sub-lattice magnetization model of Dionne [9]. According to this model, the magnetization of $BiY_2Fe_5O_{12}$,$\{BiY_2\}[Fe_2](Fe_3)O_{12}$($\{\ \}$ = c sub-lattice, [ ] = a sub-lattice, ( ) = d sub-lattice), is given by

$$M_{\text{total}}(T, H_{\text{app}}) = M_{\text{d}}(T, H_{\text{app}}) - M_{\text{a}}(T, H_{\text{app}})$$

where H_{app} is the applied magnetic field; T is the temperature; M_{d} and M_{a}, the sub-lattice magnetization of ‘d’ and ‘a’ sub-lattice.

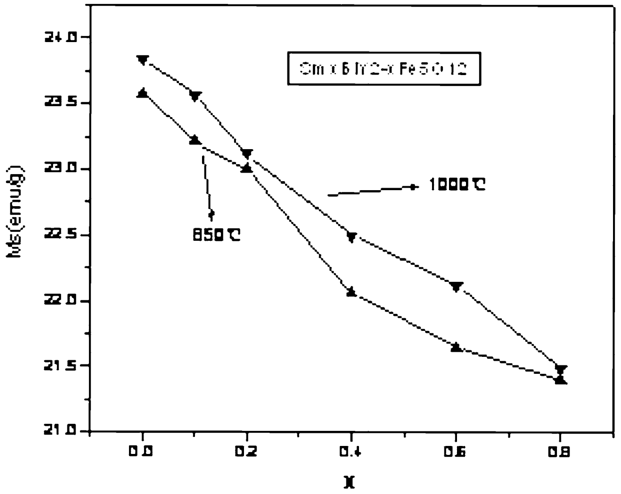

Fig. 6 The dependence of saturation magnetization of $Sm_xBiY_{2-x}Fe_5O_{12}$ nanocrystals on the Sm^{3+} content

Replacement of non-magnetic Y^{3+} ions by magnetic Sm^{3+} ions makes $Sm_xBiY_{2-x}Fe_5O_{12}$ have three magnetic sub-lattices, and the c sub-lattice is coupled antiferromagnetically with the resultant magnetic moments formed by the two iron sub-lattices. The magnetization of $\{Sm_xBiY_{2-x}\}[Fe_2](Fe_3)O_{12}$ is given by

$$M_{\text{total}}(T, H_{\text{app}}) = M_{\text{d}}(T, H_{\text{app}}) - M_{\text{a}}(T, H_{\text{app}}) - M_{\text{c}}(T, H_{\text{app}})$$

where M_{c} is the sub-lattice magnetization of ‘c’ sub-lattice. M_{c} (T, H_{app}) will increase with the increasing content of magnetic ions, which accordingly lead to the decrease of magnetization of $Sm_xBiY_{2-x}Fe_2Fe_3O_{12}$ samples [10–12].

Conclutions

Nanocrystalline $Sm_xBiY_{2-x}Fe_5O_{12}$ (x = 0, 0.1, 0.2, 0.4, 0.6, 0.8) samples were prepared via sol-gel method following by sintering at 850 °C and 1000 °C. XRD patterns show that $Sm_xBiY_{2-x}Fe_5O_{12}$ samples are all single garnet phase. We studied the process of crystallization of $BiY_2Fe_5O_{12}$ with DTA/TG and XRD analyses. Above 850 °C, nanocrystalline Bi–YIG with a single garnet phase are prepared.The saturation magnetization (Ms) of $SmxBiY_{2-x}Fe_5O_{12}$ calcined at 850 °C and 1000 °C are decreased with the increasing content of Sm^{3+} ions.

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