Influence of surfactants on co-precipitation synthesis of Bi–YIG particles

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A B S T R A C T

In this study bismuth substituted yttrium iron garnet (Bi1.8Y1.2Fe5O12) particles were prepared by co-precipitation. The influence of surfactants on the properties of Bi–YIG particles were studied by using different kind of surfactants, particles obtained were characterized by thermal gravity-differential thermal analysis, X-ray powder diffraction, transmission electron microscopy and vibrating sample magnetometer, respectively. Moreover, optical and magneto-optical (MO) properties of the particles modified PMMA slices were investigated by ultraviolet and visible spectrophotometer and Faraday rotation meter. Results suggest that the particles obtained using cationic surfactant (CTAB) as surfactant show the best properties with respect to particle size and magneto-optical applications.

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1. Introduction

Yttrium iron garnet (YIG, Y3Fe5O12) has been widely used in electronic devices, such as circulators, isolators, phase shifters for microwave and magneto-optical (MO) devices based on its magneto-optical properties. Yttrium iron garnets and substituted ones have been extensively studied for decades [1–4]. Since 1975, Wittekoek et al. [5] reported that Faraday rotation effects can be further enhanced when yttrium ions in the garnet were partially substituted with bismuth ions. Bismuth substituted yttrium iron garnet (Bi–YIG) has received much attraction for their use in magneto-optical discs and also magneto-optical display devices [6,7]. Many efforts have been made by dispersing Bi–YIG particles in polymer to prepare modified polymer films and the modified films show good MO properties. Kuroda et al. [8] prepared Bi–YIG (Bi1.5Y1.5Fe5O12) composite films by dispersing Bi–YIG in epoxy binder and investigated their MO properties, the figure of merit (θf/λc) of the composite film is as high as 2.6°. Lee et al. [9] reported that in the region of the wavelength 410–520 nm the figure of merit of the modified PMMA films was ranged 0.5–3.2°.

A variety of techniques have been used to prepare YIG powders, including ball milling [10], co-precipitation [11–13], microemulsion [14], hydrolysis of metal alkoxides and amorphous citrate gel [15–17]. Among them, co-precipitation shows some special advantages. In co-precipitation, precipitates are generated simultaneously and uniformly dispersed throughout the solution. To prevent them from agglomeration, generally surfactants are employed. Many efforts have been made to study the influence of surfactants on the properties of nanoparticles [18,19]. However, few studies have been done to the preparation of YIG nanoparticles [20].

In this study, bismuth substituted yttrium iron garnet particles were prepared by co-precipitation and the influences of surfactants on the properties of Bi–YIG particles were studied by using anionic surfactant (SDS), nonionic surfactant (PEG-20000) and cationic surfactant (CTAB) as surfactants, respectively. Moreover, magneto-optical properties of the nanoparticles modified PMMA slices were investigated.

2. Experimental

2.1. Materials

Ferric nitrate (Fe(NO3)3·9H2O), yttrium nitrate (Y(NO3)3·6H2O), bismuth nitrate (Bi(NO3)3·5H2O), polyethylene glycol 20000 (PEG-20000), sodium dodecyl sulfate (SDS), cetyltrimethylammonium bromide (CTAB), nitric acid, ethanol and other materials were all analytical grade. Methyl methacrylate (MMA) monomer and azobisisobutyronitrile (ABN) were all chemical grade. 25%-ammonia aqueous solution was used as precipitant. Deionized water was used throughout the experiments. All materials mentioned above were employed directly except that the ABN was
recrystallized with ethanol and MMA monomer was purified by distillation under reduced pressure.

2.2. Synthesis of Bi–YIG nanoparticles

Bismuth substituted yttrium iron garnets (Bi$_{1.8}$Y$_{1.2}$Fe$_5$O$_{12}$) were prepared by co-precipitation. Fe(NO$_3$)$_3$·9H$_2$O, Y(NO$_3$)$_3$·6H$_2$O and Bi(NO$_3$)$_3$·5H$_2$O as raw materials and 25%-ammonia aqueous solution as precipitant were utilized. Different agents of dispersion such as anionic surfactant, cationic surfactant and nonionic surfactant (PEG-20000) were used to reduce the size and improve the dispersibility of Bi–YIG nanoparticles. Table 1 describes precipitation conditions of Bi$_{1.8}$Y$_{1.2}$Fe$_5$O$_{12}$.

The starting solution is a mixture of bismuth nitrate, iron nitrate and yttrium nitrate in adequate proportions. These nitrates were mixed, according to the ratio of Bi, Y and Fe equal to the compositions of Bi$_{1.8}$Y$_{1.2}$Fe$_5$O$_{12}$. Afterwards, 1 wt.% of surfactants was added to avoid agglomeration. Such solution was added into the ammonia aqueous solution (pH 11) dropwise under vigorous stirring at room temperature, and some more ammonia aqueous solution was added to keep the pH constant during the co-precipitation. The obtained slurry was washed by deionized water for five times and ethanol for three times, respectively. The powder was then dried in a desiccator under vacuum and calcined in air at 700 °C for 1 h.

2.3. Preparation of modified PMMA slices

Bi–YIG nanoparticles were mixed with MMA monomer, then the mixtures were milled with a planetary milling machine operating at the speed of 40 rpm for 3 h. PMMA slices named S-P1, S-P2, S-P3 and S-P4 which was modified by samples S1, S2, S3 and S4, respectively, were prepared after polymerization and solidification. The content of the particles in PMMA is 0.2 wt.% and the thickness of the PMMA slice is about 2.5 mm.

2.4. Characterization

Thermal behavior of Bi–YIG precursors was measured by thermogravimetry (TG) (PerkinElmerTGA7) and differential thermo-analysis (DTA) (TA Instruments, SDT-2960). Bi–YIG (annealed at 700 °C) particle sizes were determined from transmission electron microscopy (TEM) images using H-600-II transmission electron microscope (Hitachi, Japan) and from analysis of the broadened major peak of XRD spectra. The structures of Bi–YIG particles were identified by X-ray powder diffraction (XRD) with a D/Max-III C, using Cu Kα radiation. Magnetic properties of Bi–YIG particles were measured on a BHV-55 vibrating sample magnetometer (VSM). Ultraviolet–visible (UV–vis) optical absorption spectrum was achieved by HITACHI U-2810 spectrophotometer and magneto-optical properties of the modified PMMA slices were measured by a Faraday rotation meter.

3. Results and discussion

3.1. Thermal analysis

TG–DTA curve of sample S3 is shown in Fig. 1. The TG curve shows an overall weight loss of 21.81%. The loss of mass is gradual and 83.72% of the mass loss occurs before 271.77 °C which corresponds to an endotherm peak at 61.99 °C in DTA. This event is the result of the dehydration process wherein significant amount of water is released from the gel matrix. The further 4.56% weight loss which gives rise to a broad endotherm peak around 340.28 °C in DTA is due to the decomposition reactions of the hydroxids. A constant mass is obtained at temperatures as low as 505.08 °C with a corresponding weak exotherm in the DTA. The sample isothermally heated at 505.08 °C has a constant weight upon heating to higher temperatures, revealing the fact that Bi–YIG is free from dispersant anions and hydroxyl groups. Two exothermic peaks (629.78 °C and 647.66 °C) in the DTA suggested that the formation of YIP and the phase transformation from YIP to YIG, respectively.

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surfactant</th>
</tr>
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<tbody>
<tr>
<td>S1</td>
<td>None</td>
</tr>
<tr>
<td>S2</td>
<td>SDS</td>
</tr>
<tr>
<td>S3</td>
<td>PEG-20000</td>
</tr>
<tr>
<td>S4</td>
<td>CTAB</td>
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</tbody>
</table>

3.2. Structure of Bi–YIG nanoparticles

Calcination temperature has been studied for the evolution of the crystalline phase. Fig. 2 shows the X-ray diffraction patterns of
sample S3 obtained by increasing the temperature from 600 °C to 750 °C. Through Fig. 2, powders calcined at 600 °C merely exhibit a very broad peak at diffraction angles from 25° to 40°, temperatures of phase transitions are identified beginning at 650 °C and after calcined at 700 °C for an hour, the sample gives broad XRD peaks, and all the prominent peaks (4 2 0), (4 0 0), (4 2 2), (6 4 0) and (6 4 2) are observed at the corresponding angles in the peak positions, which is in excellent accordance with the powder data of index card JCPDS-ICDD number 83-1027. The variation of X-ray diffraction patterns obtained by annealing the powders at 600 °C and 650 °C could be associated with the exothermic peaks (629.78 °C and 647.66 °C) in Fig. 1.

Fig. 3 shows the X-ray diffraction patterns of sample S2 annealed at 750 °C for 2 h which is almost the same with the patterns showed in Fig. 2, and it indicates the fact that surfactant was only used to improve the dispersibility and it will not influence on the structure of Bi–YIG phase. The crystallite sizes (showed in Table 2) were calculated using the X-ray broadening of the (4 2 0) diffraction peak by the well-known Scherrer equation: 

$$D = \frac{0.9 \lambda}{\beta \cos \theta}$$

where $D$ is

<table>
<thead>
<tr>
<th>Sample</th>
<th>XRD (nm)</th>
<th>TEM (nm)</th>
</tr>
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<tbody>
<tr>
<td>S1</td>
<td>50</td>
<td>80</td>
</tr>
<tr>
<td>S2</td>
<td>45</td>
<td>50</td>
</tr>
<tr>
<td>S3</td>
<td>40</td>
<td>45</td>
</tr>
<tr>
<td>S4</td>
<td>42</td>
<td>45</td>
</tr>
</tbody>
</table>

Table 2 Results obtained by XRD and TEM measurement

Fig. 4. TEM images of powders: (a) none surfactant, (b) SDS as surfactant, (c) PEG-20000 as surfactant, and (d) CTAB as surfactant.
the particle size in nm, $\lambda$ is the wavelength of the X-ray (0.15405 nm for Cu K$\alpha$), $\beta$ the corrected full width at half maximum and $\theta$ is the diffraction angle. From Fig. 2 it is clear that calcination at high temperature leads to the reduction in the full width at half maximum, which is due to the improvement in crystallinity and growth in particle size at high temperature.

3.3. Morphology of Bi–YIG particles

Fig. 4 shows micrographs of S1, S2, S3 and S4 (annealed at 700 °C), respectively. From Fig. 4a, the size of the crystallites is about 80 nm with severe aggregation. From Fig. 4b–d, particles with very slight aggregation can be observed, which are composed of irregular fine particles. The average size of particles is about 50 nm, 45 nm and 45 nm, respectively, which is accordance with the XRD analysis. Table 2 lists results obtained by XRD and TEM measurements. From Table 2, it is clear that the particles sizes obtained from XRD analysis are larger than that observed from TEM micrographs and the sample with more serious aggregation leads generally to larger difference between XRD and TEM measurements. It may be attributed to different degree aggregation of the samples.

Through comparison, it is clear that the addition of surfactants leads generally to smaller size particles, which is due to the stabilization properties of surfactants. As a result of addition of different kinds of surfactants during the co-precipitation, particles obtained exhibit different degree aggregation. The effect of CTAB surfactant is best, PEG-20000 take second place and finally is SDS. It maybe attribute to the different mechanisms of different kinds of surfactants. Ionic surfactants can be adsorbed on the surface of the particles to form a double electric layer to prevent the particles from agglomeration. According to the above results, we can draw a conclusion that Bi–YIG nanoparticles possess negative charges at the aqueous solution (pH 11). So cationic surfactant can easily be adsorbed on the surface of the precipitates and form a molecular film on the surface of the particles to keep them away from agglomeration. Macromolecular surfactants (such as PEG) can play a certain dimensional hindrance effect. There are two kinds of hydrophilic groups (hydroxy group and ether linkage) in PEG molecule, so it was a good water soluble surfactant. In aqueous solution, it looks like a snake, so it can easily be adsorbed on the surface of the particles to form a macromolecule protection layer. Due to the dimensional hindrance effect of PEG, Bi–YIG particles with smaller size and better dispersibility can be obtained.

3.4. Magnetic properties of Bi–YIG particles

Magnetic properties of the Bi–YIG nanoparticles were measured by VSM. Fig. 5 shows $M$–$H$ behavior of the samples at room temperature. The saturation magnetization of samples S1, S2, S3 and S4 is 19.70 emu/g, 14.78 emu/g, 12.73 emu/g and 12.35 emu/g, respectively, and magnetic saturations of all samples are attained at very low field, indicating that the soft magnetic nature of the samples. It is clear that the sample with smaller size exhibits a lower magnetization value.

3.5. Optical and magneto-optical properties of the modified PMMA

Absorption coefficient ($\alpha$) of the modified PMMA slice was measured with a spectrophotometer. The optical measurements were carried out in the region of the wavelength 400–800 nm. Fig. 6 shows the absorption coefficient curves of the modified PMMA slices in UV–vis range. All slices obtained exhibit high transparency and the PMMA slice (S-P1) modified by sample S1 exhibits the highest absorption coefficient than the others. It maybe attribute to the worst properties of sample S1, since, among these four samples, sample S1 with the largest size and highest agglomeration degree.

Magneto-optical properties were measured by a Faraday rotation meter. Table 3 lists values of $\alpha$, $\theta_F$ and figure of merit ($\theta_F/\alpha$) of the modified slices at the wavelength of 650 nm. The figure of merit of slices S-P1, S-P2, S-P3 and S-P4 observed at 650 nm is 1.21°, 1.57°, 1.74° and 1.83°, respectively. It is clear that the figure of merit of sample S1 modified PMMA slice is the lowest, magneto-optical properties of the slices are relate to the dimensions of the particles doped and the slice modified by the smaller size particles exhibits a better magneto-optical properties.
4. Conclusions

Bi$_{1.8}$Y$_{1.2}$Fe$_5$O$_{12}$ (40–100 nm) nanoparticles were prepared by co-precipitation. The YIG phase began to form at the temperature of 650 °C and accomplished at 700 °C. Different kinds of surfactants such as anionic surfactant, nonionic surfactant cationic surfactant were employed to reduce the size and improve the dispersibility of Bi–YIG particles. Among them, the effect of cationic surfactant is the best, nonionic surfactant (PEG-20000) takes second place and finally is anionic surfactant, Bi–YIG particles with the size of 40 nm were prepared using cationic surfactant as surfactant. Magneto-optical properties of PMMA slices modified by different particles were investigated. All slices obtained exhibit good magneto-optical properties. All results show that particles prepared using CTAB as surfactant exhibit the best properties with respect to particle size and magneto-optical applications.

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