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Formation enthalpy and magnetic properties of Bi-YIG powders

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Abstract

The formation enthalpy and magnetic properties of bismuth-doped yttrium iron garnet powders were investigated. The formation enthalpy and the crystallization temperature both decreased with increasing bismuth substitution for $Bi_xY_{3-x}Fe_5O_{12}$ ($0.25 \leqq x \leqq 1.25$) powders prepared by the coprecipitation process. Bi substitution for Y can significantly reduce crystallization temperature for bismuth-doped yttrium iron garnet powders, and the magnetic properties (saturation magnetization, remanence, and coercive force) are independent of Bi substitution amounts. The average particle size has been determined by the specific surface area. As Bi substitution for Y increased, the average particle size also increased, while the specific surface area decreased.

Keywords: A. Powder: chemical preparation; C. Thermal properties; C. Magnetic properties; D. Ferrites; E. Soft magnets

1. Introduction

Yttrium iron garnet (YIG) was extensively studied owing to its interesting physical properties; for example, among the magnetic materials, this material possesses the highest quality factor in microwave regime and the smallest linewidth in magnetic resonance, among the magnetic materials [1,2]. They are important components for electronics products, such as circulators, oscillators, and phase shifters. However, YIG is hardly used in multilayer microwave components because of its high sintering temperature (>1350 °C). The sintering temperature of YIG is generally higher than the melting point of highly conductive metal like Ag–Pd alloy (1145 °C) [3]. Previous investigations, however, have shown that Bi-substituted and 2Ca–V-substituted YIG powders can be prepared at much lower temperatures (<1100 °C) than pure YIG due to their lower melting temperature and the sintering temperature of these materials is much lower than YIG polycrystalline ceramics [4–6]. Magnetic fine particles are also very attractive objectives of magnetic research since they have a single magnetic domain and their mutual interaction can be studied without magnetic domain effects. Polycrystalline yttrium iron garnet and substituted yttrium iron garnets are considerably attractive in microwave devices and magneto-optical application with Bi-substituted garnets being especially suitable for magneto-optical display devices [7].

The conventional method for producing these materials is by solid-state reaction with oxide/carbonate and calcination at high temperature (≧1200 °C). This solid-state reaction method, however, has some inherent disadvantages: (1) chemical inhomogeneity, (2) coarser particle size, and (3) introduction of impurities during ball milling. In general, YIG-based powder can be prepared by several chemical approaches such as sol–gel [8–11], sol–gel auto-combustion method [12,13], spray pyrolysis [14], and the citrate method [15]. In previous works, there have been many investigations on the microwave and magneto-optical properties, focused on correlations between the microstructure, composition, and magnetic properties of Bi-substituted YIG. In order to improve the performance and quality of Bi-YIG magnetic ceramics, coprecipitation is an alternative method to overcome the deficiencies in the conventional solid-state method. In this study, we used the coprecipitation process to produce amorphous $Bi_xY_{3-x}Fe_5O_{12}$ ($0.25 \leqq x \leqq 1.00$) powders and investigated their formation enthalpy and magnetic properties.

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2. Experimental procedures

2.1. Preparation of Bi-YIG powders

Fig. 1 plots the preparation process of a Bi-YIG particle by coprecipitation. Stoichiometric $Bi_xY_{3-x}Fe_5O_{12}$ (x = 0.25, 0.50, 0.75, 1.00, and 1.25), needed amount of bismuth nitrate pentahydrate [$Bi(NO_3)_3{}^{\bullet}5H_2O$], yttrium nitrate hexahydrate [$Y(NO_3)_3{}^{\bullet}6H_2O$], and iron nitrate nonahydrate [$Fe(NO_3)_3{}^{\bullet}9H_2O$] were dissolved in water. A 28% ammonia solution (NH_4OH) was added rapidly into the stirred solution at room temperature. In the range of pH over 8.7, the ratio of the cations in the powders was the same as that of the nitrate solution. In the current study, the pH of the solution was controlled over 12. The obtained slurry was washed by alcohol to remove the alkaline ions and obtain a weak agglomeration of Bi-YIG powders, filtered and dried at 90 °C for 24 h. Subsequently, the coprecipitation of Bi-YIG was annealed at 700 °C for 2 h.

2.2. Characterization

Differential scanning calorimetry (DSC; Model TG-DTA/DSC, Caluiro, France) was used to study the exo–endo temperature and formation enthalpy for the as-prepared Bi-YIG powders. A heating rate of 10 °C/min was used in DSC measurement up to 1000 °C in air. A constant sample and standard reference weight of 12.0 ± 0.2 mg were used for all measurement, and thermal analysis was done under flowing air at 100 ml/min. In order to estimate the formation enthalpy, we calibrate the energy scale of the instrument with standard reference material whose formation enthalpy is well characterized. The detailed process is described as follows. By calibration a certain peak area corresponds to a known formation enthalpy and under identical experimental conditions from the area of the sample peak, the formation enthalpy can be estimated. The peak area can be measured by a software option that automatically calculates the peak area. In addition, a computerized X-ray powder diffractometer (XRD; Model Rigaku D/Max-II, Tokyo, Japan) with Cu Kα radiation was used to identify the crystalline phase, and the magnetic properties of Bi-YIG powders at room temperature were measured by a vibrating sample magnetometer (VSM; Model 7407 Lake Shore, Westerville, OH). Specific surface areas of the annealed powders, S_{BET} were measured by the Brunauer–Emmit–Teller (BET) method on an atomic surface area analyser (Model Quantachrome Instruments Autosorbs-1, Boynton Beach, FL) and calculated using the five-point theory. The average particle sizes, D_{BET} (nm) were calculated from the BET data according to $D_{BET} = 6 \times 10^3/\rho th\, S_{BET}$, where S_{BET} is the measured surface area (m^2/g) and ρth is the theoretical density of the compound (g/cm^3).

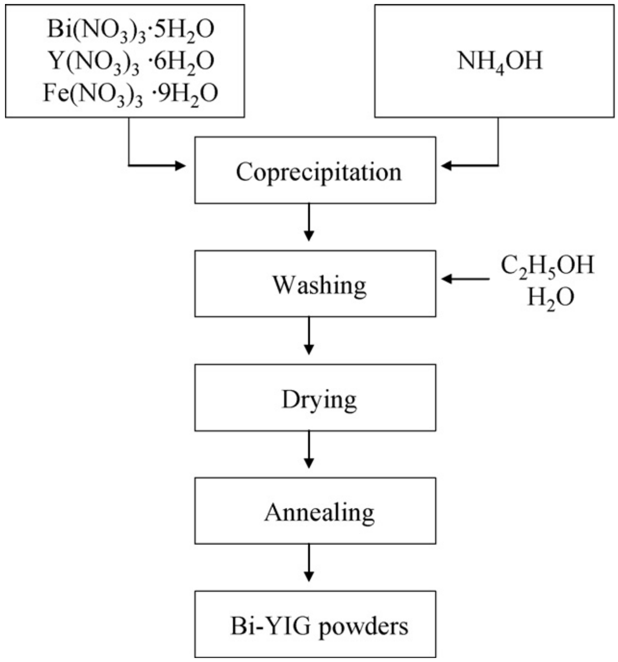

Fig. 1. Flowchart for the preparation of Bi-YIG particle by coprecipitation.

3. Results and discussion

X-ray diffraction patterns of the as-received Bi-YIG powder annealed at 700 °C for 2 h are shown in Fig. 2. It is found that Bi-substituted specimens ($0.75 \leqq x \leqq 1.25$) can form a single garnet phase at lower temperature (700 °C) than formation temperature of YIG (1200 °C). On the contrary, lower the Bi-substituted specimen ($0.25 \leqq x \leqq 0.50$) could not form the garnet phase at such low temperature (700 °C), which indicates that the amount of Bi substitution can significantly affect the formation of garnet phase. In order to prove Bi-substitution can reduce the formation temperature for the Bi-YIG powder, we further investigate the formation enthalpy for Bi-YIG. It is well known that the area of a DSC peak can be used to estimate the formation enthalpy. The most common method is to calibrate the energy scale of the instrument with standard reference materials whose enthalpies of melting are well characterized and whose melting temperatures extend over a wide temperature range [16]. In this study, we used KNO_3 as a reference standard, whose melting temperature (T_m) is 128 °C

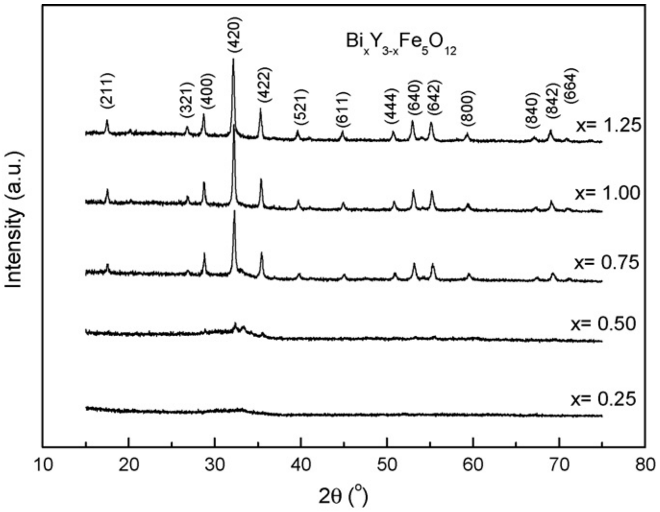

Fig. 2. XRD patterns of as-received Bi-YIG powder annealed at 700 °C for 2 h.

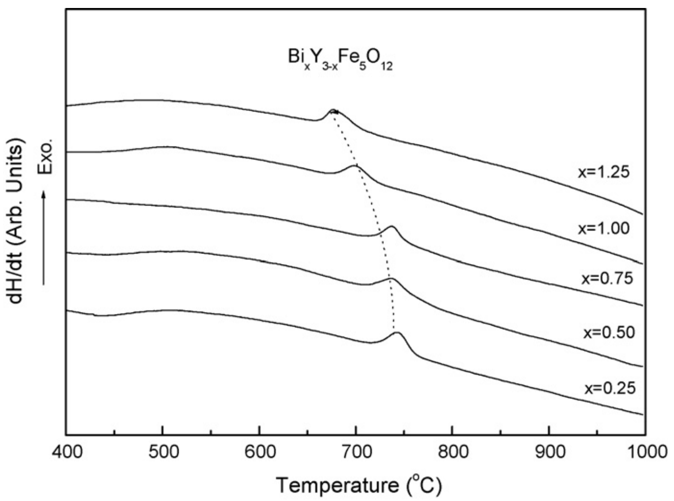

Fig. 3. DSC curves of the Bi-YIG powders at a heating rate of 10 °C/min.

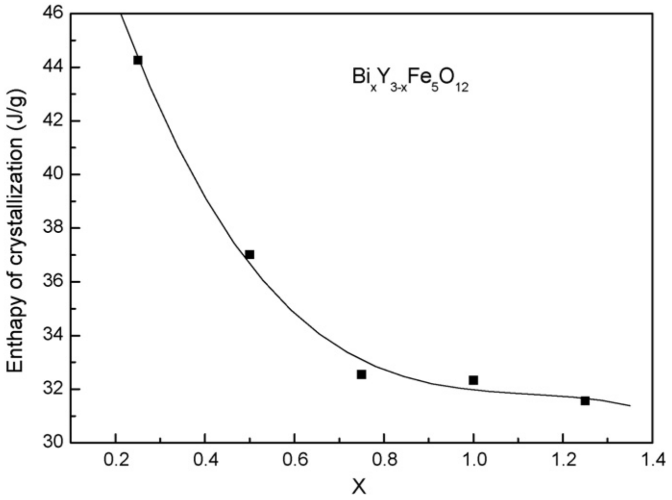

Fig. 5. Formation enthalpy as a function of Bi substitution for Bi-YIG powders.

and enthalpy of fusion (ΔH_{fus}) is 53.5 J/g. The enthalpy of crystallization can be calculated by using the following equation:

$$\Delta H = \frac{\mathrm{ABT}}{W}\frac{\Delta H_{\mathrm{s}} W_{\mathrm{s}}}{A_{\mathrm{s}} B_{\mathrm{s}} T_{\mathrm{s}}}$$

where ΔH_{s} is the enthalpy of melting of the standard reference material (J/g), A and A_{s} are the peak area of the sample and standard reference (cm^2), W and W_{s} are the weight of the sample and standard reference (mW/cm) and B and B_{s} are the horizontal sensitivity of the sample and standard reference (cm/min), respectively [16].

DSC curves for as-received Bi-YIG powders at a heating rate of 10 °C/min are plotted in Fig. 3. It is found that the crystallization temperature decreased steadily with increasing Bi substitution for the Bi-YIG powder. The crystallization temperature as a function of Bi substitution for Bi-YIG is shown in Fig. 4. The crystallization temperature decreases from 743 °C for $Bi_{0.25}Y_{2.75}Fe_5O_{12}$ to 677 °C for $Bi_{1.25}Y_{1.75}Fe_5O_{12}$. Obviously, the crystallization temperature decreases gradually with increasing Bi substitution. As the Bi substitution increases, the crystallization temperature (°C) decreases as $T(x) = 745.4 + 24.38095x - 129.14286x^2 + 53.33333x^3$ for $Bi_xY_{3-x}Fe_5O_{12}$($x = 0.25$–1.25). Fig. 5 presents the formation enthalpy as a function of Bi substitution for Bi-YIG powders. This plot indicates that the formation enthalpy decreased with increasing Bi substitution. The formation enthalpy decreases from 44.26 (J/g) for $Bi_{0.25}Y_{2.75}Fe_5O_{12}$ to 31.56 (J/g) for $Bi_{1.25}Y_{1.75}Fe_5O_{12}$. As the Bi substitution amount increases, the formation enthalpy (J/g) decreases as $E(x) = 57.822 - 67.64876x + 59.50629x^2 - 17.70667x^3$ for $Bi_xY_{3-x}Fe_5O_{12}$($x = 0.25$–1.25). The results on formation enthalpy and the crystallization temperature are in agreement with XRD analysis. The formation enthalpy and crystallization peaks are summarized in Table 1.

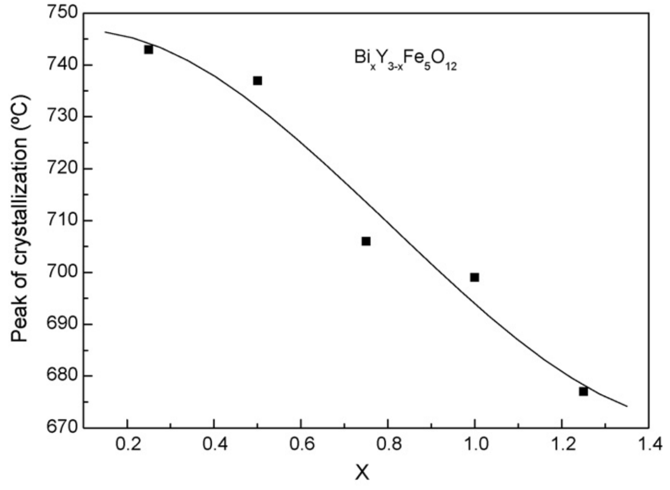

Fig. 4. Crystallization temperature as a function of Bi substitution for Bi-YIG powders at a heating rate of 10 °C/min.

As shown in Fig. 6, specific surface area and average particle size is as a function of Bi substitution for the $Bi_xY_{3-x}Fe_5O_{12}$ powders. This figure revealed that the average particle size increases with rising Bi substitution amount from $x = 0.25$ to $x = 1.25$, and the average particle size increases from 46 nm to 271 nm. Noticeably, the average particle size dramatically increased with Bi substitution amount from $x = 1.00$ to $x = 1.25$. This is ascribed to the fact that the heating treatment temperature (700 °C) is over-annealing, as such high annealing temperature may lead to grain growth, coarsening, and necking for $Bi_{1.00}Y_{2.00}Fe_5O_{12}$ and $Bi_{1.25}Y_{.1.75}Fe_5O_{12}$ powders. These results also proved that Bi substitution for Y can effectively

Table 1
Crystallization peak temperature and formation enthalpy for $Bi_xY_{3-x}Fe_5O_{12}$ powders

Composition	Crystallization peak temperature (°C)	Formation enthalpy (J/g)
$x = 0.25$	743	44.262
$x = 0.50$	737	37.022
$x = 0.75$	706	32.546
$x = 1.00$	699	32.334
$x = 1.25$	677	31.566

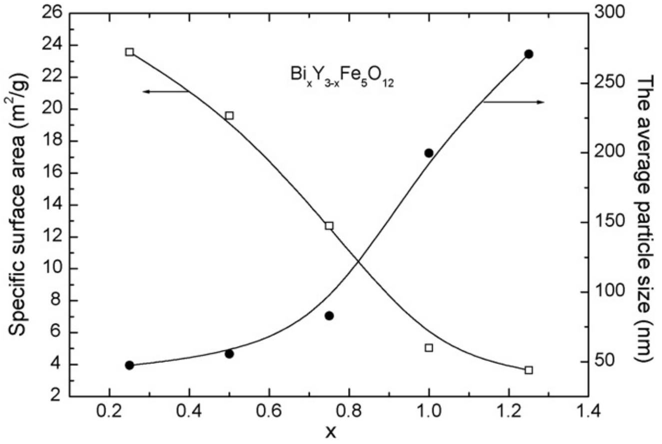

Fig. 6. Specific surface area and the average particle size of as-received Bi-YIG powders annealed at 700 °C for 2 h.

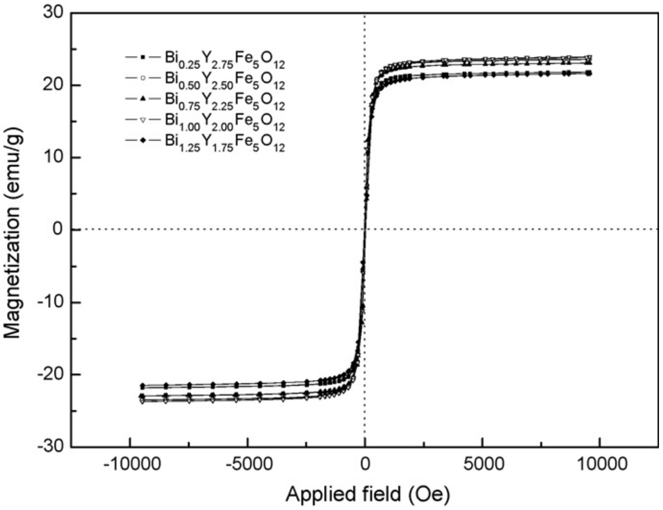

Fig. 7. Magnetization against applied field hysteresis for Bi-YIG powders annealed at 700 °C for 2 h.

decrease the heating treatment temperature for Bi-YIG powder. The magnetic properties are an important factor to evaluate Bi-YIG powders; as such, the magnetization measurements were carried out using a VSM at room temperature with an applied magnetic field of 10 kOe to reach saturation values. Fig. 7 shows a hysteresis curves for $Bi_xY_{3-x}Fe_5O_{12}$ powders. This figure indicates that Bi-YIG powders are soft magnetic materials. The variation of saturation magnetization (Ms), remanence (Mr), and coercive force (Hc) for $Bi_xY_{3-x}Fe_5O_{12}$ are shown in Table 2. This table indicates that Ms is in the range of 21.52–23.80 emu/g, Mr is in the range of 1.37–2.24 emu/g, and Hc is in the range of 17.72–27.21 Oe. It is found that Bi substitution seems to present unobvious tendency on magnetic properties for Bi-YIG powders.

Table 2
Magnetic properties of $Bi_xY_{3-x}Fe_5O_{12}$ powders annealed at 700 °C for 2 h

Sample	Ms (emu/g)	Mr (emu/g)	Hc (Oe)
$x = 0.25$	21.81	1.37	17.72
$x = 0.50$	23.54	1.87	23.78
$x = 0.75$	23.01	2.24	26.56
$x = 1.00$	23.80	1.77	21.90
$x = 1.25$	21.52	1.97	27.21

4. Conclusions

The influence of Bi substitution on formation enthalpy and magnetic properties was investigated in this study for $Bi_xY_{3-x}Fe_5O_{12}$ powders. A single garnet phase is formed under condition of Bi substitution (x) $\geqq$0.75, annealed at 700 °C for 2 h. According to the DSC analysis results, the crystallization temperature and the formation enthalpy were significantly decreased with increasing Bi substitution for the $Bi_xY_{3-x}Fe_5O_{12}$ powders. In fact, specific surface area decreased with increasing Bi substitution, and the average particle size increased with increasing Bi substitution for $Bi_xY_{3-x}Fe_5O_{12}$ powders. Therefore, the magnetic properties of Bi-YIG powders are not sensitive to Bi substitution.

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