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Crystallization kinetics of $Bi_{0.25}Y_{2.75}Fe_5O_{12}$ prepared from coprecipitation process under non-isothermal conditions

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Abstract

The non-isothermal crystallization kinetics of $Bi_{0.25}Y_{2.75}Fe_5O_{12}$ powder prepared by the coprecipitation process has been investigated. The activation energy of crystallization was calculated by differential scanning calorimetry (DSC) at different heating rates. From non-isothermal DSC data presented values in the range of 712–772 kJ/mol and 2.90–3.46 for the activation energy of crystallization and the Avrami exponent, respectively at specific temperature ranging form 750.0 to 757.5 °C. This value for the Avrami exponent indicates that the controlling mechanism of crystallization is three-dimensional interfacial growth.

Keywords: A. Powder; C. Chemical properties; C. Thermal properties; E. Soft magnets

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1. Introduction

Yttrium iron garnet (YIG) was extensively studied owing to its interesting physical properties. For example, this material possesses the highest quality factor in microwave regime, and the smallest linewidth in magnetic resonance among magnetic materials [1,2]. YIG materials are important components of electronic 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) for YIG. Since the sintering temperature of YIG is generally higher than the melting point of highly conductive metals such as Ag–Pd alloy (1145 °C) [3]. Previous investigations have shown that Bi-substituted and 2Ca–V-substituted YIG powders can be prepared at much lower temperatures (<1100 °C) than that of pure YIG due to their lower melting temperature of substitution, and the sintering temperature of these materials is much lower than that of YIG polycrystalline ceramics [4–6].

Magnetic fine particles are very attractive for magnetic ceramic research. This is because they have a single magnetic domain and their mutual interaction can be studied without magnetic domain effects. Polycrystalline YIG and substituted YIG have attracted much attention for microwave device and magneto-optical applications [7]. The conventional method of producing these materials is by the solid-state reaction with oxide/carbonate and then calcined at a high temperature (≧1200 °C). The solid-state reaction has some inherent disadvantages as follows: (1) chemical inhomogeneity, (2) coarser particle size, and (3) introduction of impurities during ball milling. 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 reaction.

There have been many investigations on the microwave and magneto-optical properties, and they have focused on correlations between the microstructure, composition, and magnetic properties of Bi-YIG. However, there seem to be almost no report on the crystallization characterization of these materials. Therefore, in this study, we used coprecipitation process to produce as-prepared $Bi_{0.25}Y_{2.75}Fe_5O_{12}$ powder and studied its non-isothermal crystallization kinetics.

2. Experimental procedures

Fig. 1 plots the preparation process of Bi-YIG particles by coprecipitation. The preparation details are described as follows. According to the stoichiometric composition of

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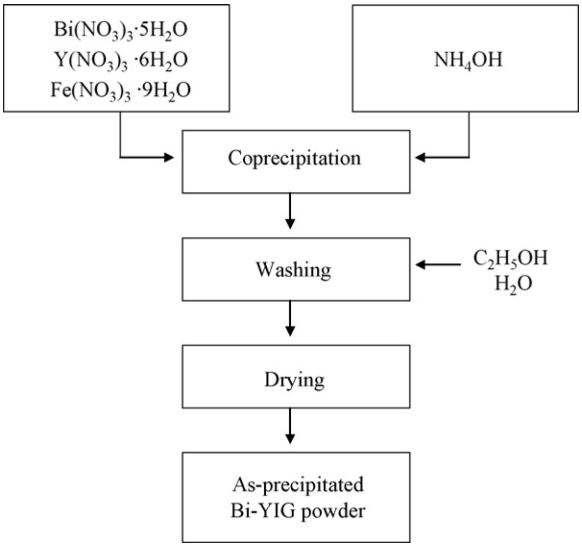

Fig. 1. Flowchart for the preparation of as-precipitated $Bi_{0.25}Y_{2.75}Fe_5O_{12}$ powder by coprecipitation.

$Bi_{0.25}Y_{2.75}Fe_5O_{12}$, specified amounts of bismuth nitrate pentahydrate [$Bi(NO_3)_3{\cdot}5H_2O$], yttrium nitrate hexahydrate [$Y(NO_3)_3{\cdot}6H_2O$], and iron nitrate nonahydrate [$Fe(NO_3)_3{\cdot}9H_2O$] were dissolved in a certain quantity of water. The 28% ammonia solution (NH_4OH) was added rapidly into the stirred solution at room temperature. In the pH range of more than 8.7, the ratio of the cations in the powders was the same as that in the nitrate solution. In this study, the pH of the solution was controlled to be above 12. The obtained slurry was washed with alcohol to remove the alkaline ions and obtain a weak agglomeration of Bi-YIG powders. This slurry was filtered and dried at 90 °C for 24 h.

A computer-interfaced X-ray powder diffractometer (XRD) with Cu Kα radiation ($\lambda = 1.5418$ Å) (Model Rigaku D/Max-II, Tokyo, Japan) was used to identify the crystalline phase during crystallization process. BET surface area measurements were made by nitrogen adsorption employing a Micromeritics ASAP 2000 instrument and calculated using the five point Brunauer-Emmit-teller (BET) theory. Mean particle size (D_{BET}) was calculated from the BET data according to the following equation assuming that the particles are closed sphere with smooth surface and uniform size: $D_{BET} = 6 \times 10^3/(\rho_{th}\ S_{BET})$, where D_{BET} (nm) is the average particle size, S_{BET} is the measured specific surface area expressed in m^2/g and ρ_{th} is the theoretical density of the compound (g/cm^3) [8]. Differential scanning calorimetry (DSC; Model TG-DTA/DSC Setaram, Caluiro, France) was used to carry out the crystallization characterization of as-precipitated Bi-YIG powders. A heating rate of 10–25 °C/min was used in DSC up to 900 °C in air. Thermal analysis was carried out under flowing air at 100 ml/min. A constant sample weight of 12.0 ± 0.2 mg was used for all measurements.

3. Results and discussions

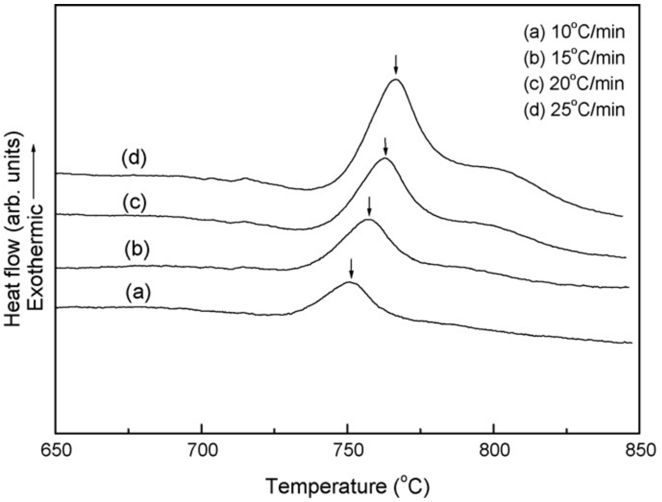

Fig. 2. Differential scanning calorimetry curves of as-precipitated $Bi_{0.25}Y_{2.75}Fe_5O_{12}$ powder at different heating rates of 10, 15, 20, and 25 °C/min, respectively.

Crystallization characterization of the Bi-YIG powder was estimated by non-isothermal DSC analysis. Fig. 2 shows the DSC curves of a sample with different heating rates ranging from 10 to 25 °C/min. With increasing heating rate, the exothermic peak shifts to a higher temperature. Phase development of as-precipitated Bi-YIG specimen during heat treatment was measured by XRD. The XRD results for specimen annealed from 650 to 725 °C for 2 h are shown in Fig. 3. The Bi-YIG specimen was primarily amorphous due to the broad low-intensity peak that appeared at 32° diffraction angle. When the annealing temperature reached 675 °C, the specimen showed (420) and (422) low-intensity peaks. With increasing annealed temperature, the number of broad hump associated with the amorphous phase decreased, and the intensity of XRD peaks increased as the amorphous phase got transformed into the crystalline phase, i.e. the garnet phase. The volume fraction of the crystallized phase increases with increasing annealed temperature. These results are consistent with the DSC results. The specific surface area and mean particle size of Bi-YIG powders calcined at different temperatures is listed in Table 1. The result indicates that

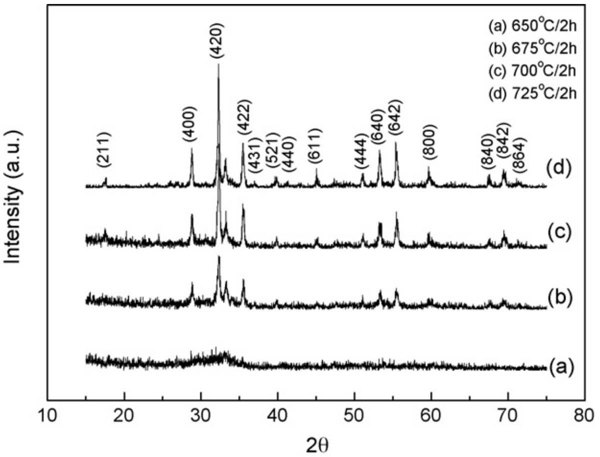

Fig. 3. X-ray diffraction results of as-precipitated $Bi_{0.25}Y_{2.75}Fe_5O_{12}$ powder annealed at various temperatures.

Table 1
Specific surface area and mean particle size for $Bi_{0.25}Y_{2.75}Fe_5O_{12}$ materials after calcination at different temperatures

Calcination temperature (°C)	Surface area (m^2/g)	Mean particle size[a] (nm)
650	51.14	21.89
675	30.29	36.96
700	15.35	72.94
725	8.26	135.54

[a] Mean particle size measured from specific surface area.

the particle size increased with annealing temperature. Compared XRD with BET results, we can conclude that when garnet crystalline phase appears, the mean particle size requires larger than 37 nm prepared by coprecipitation process.

The crystallization peaks depending on different heating rates can be used to estimate the activation energy of crystallization. The activation energy of crystallization can be estimated by using the following Kissinger analysis [9]. Through the change in the peak crystallization temperature (T_p) with respect to heating rate, the activation energy of crystallization could be determined by using the Kissinger equation as follows:

$$\ln\left(\frac{T_p^2}{\Phi}\right) = \frac{E}{RT_p} + \text{constant} \tag{1}$$

where, E is the activation energy of crystallization. T_p is the temperature corresponding to the maximum of the DSC crystallization peak, R is the gas constant (8.314 J/mol), and Φ is the heating rate, which is 10, 15, 20, and 25 °C/min. The slope of the plot of $\ln(T_p^2/\Phi)$ versus $1/T_p$ should be a straight line, the slope should be E/R, and the activation energy of the crystallization process could be estimated. Fig. 4 shows the Kissinger plot of the as-precipitated $Bi_{0.25}Y_{2.75}Fe_5O_{12}$ powder. The activation energy of crystallization is determined using the Kissinger from the slope and is equal to 492 kJ/mol.

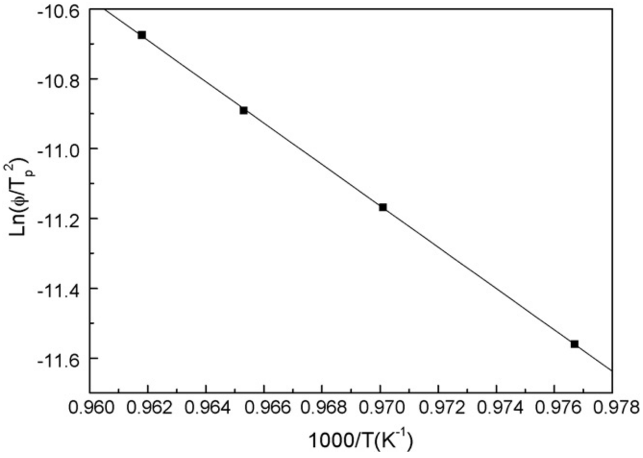

Fig. 4. Plot of $\ln(T_p^2/\Phi)$ against $1000/T_p$ for determining the value of crystallization activation energy for $Bi_{0.25}Y_{2.75}Fe_5O_{12}$.

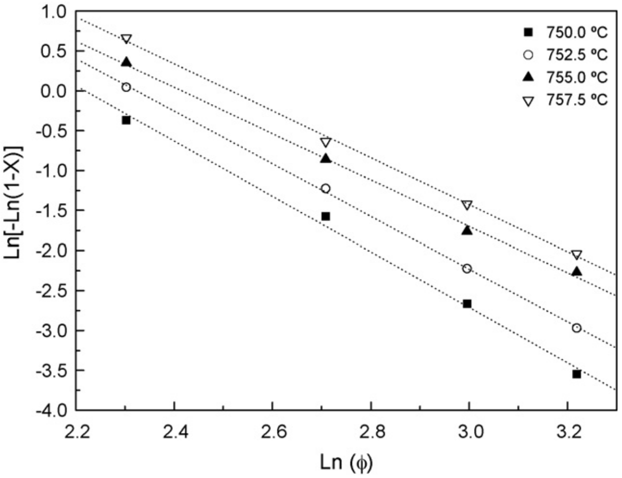

Fig. 5. Plot of $\ln[-\ln(1-X)]$ versus $\ln\Phi$ for the calculation of Avrami constant n values.

Moreover, the Avarami exponent n can be determined from the DSC results. The value of the Avrami parameter n, which is a measure of the dimensionality of transformation, is determined using the Ozawa equation [10]:

$$\frac{d\{\ln[-\ln(1-X)]\}}{d\ln\Phi} = -n \tag{2}$$

In this equation, Φ is the different heating rates, X is the volume fraction crystallized at a specified temperature T, X is given the ratio of the partial area crystallized at a certain temperature to the total area of the crystallization exotherm. Here, the total area of the crystallization exotherm is between the temperature T_i at which crystallization just begins and the temperature T_f at which the crystallization is complete. The partial area crystallized at a certain temperature is between T_i and T [11]. A plot of $\ln[-\ln(1-X)]$ versus $\ln\Phi$ should be a straight line. In this equation, n can be calculated from the slope. A value of n close to 3 indicates bulk or three-dimensional crystal growth and a value close to 1 indicates surface growth. Intermediate values of n between 1 and 3 indicate that the surface and internal crystallizations occur simultaneously [12]. The Ozawa plot of $\ln[-\ln(1-X)]$ versus $\ln\Phi$ is shown in Fig. 5. Here, the volume fraction crystallized was calculated at a specific temperature in range of 750.0–757.5 °C. The value of n is determined form the slope of the plot was 3.46, 3.30, 2.90, and 2.94 for 750.0, 752.5, 755.0, and 757.5 °C, respectively. These results indicated that the crystallization dominated by three-dimensional interfacial growth. Summary of crystallization parameters is listed in Table 2.

Matusita and Sakka proposed that the Kissinger model is only valid when crystal growth occurs on a specific number of nuclei [13,14]; otherwise, incorrect values for the activation energy are obtained. Therefore, they modified the Kissinger

Table 2
Crystallization parameters of $Bi_{0.25}Y_{2.75}Fe_5O_{12}$ at various temperatures

Temperature (°C)	Avrami constant (n)	E_a (kJ/mol)
750.0	3.46	712
752.5	3.30	725
755.0	2.90	772
757.5	2.94	766

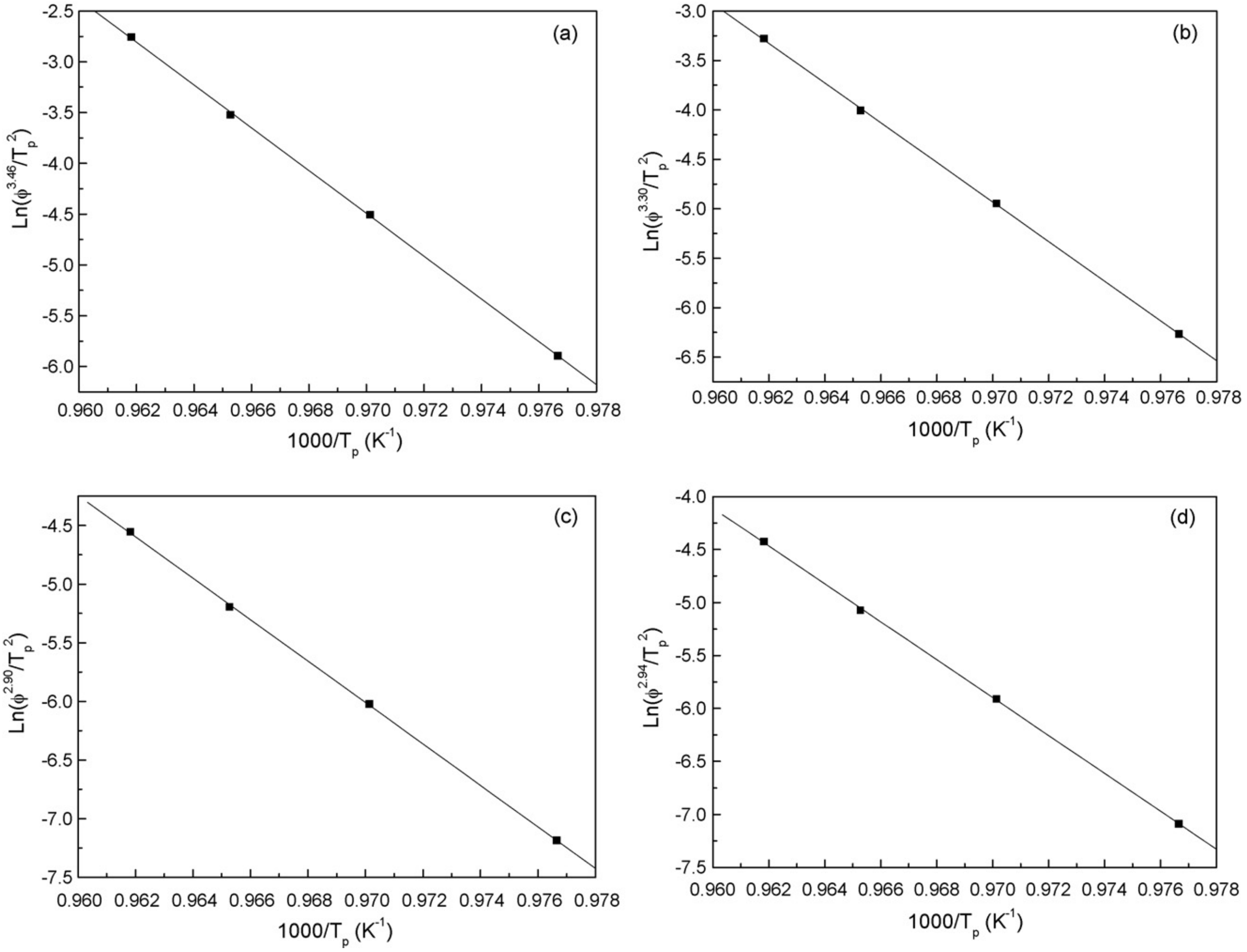

Fig. 6. Plot in accordance with the Matusita and Sakka equation for the determination of the activation energy for crystallization at specific temperature (a) 750.0 °C, (b) 752.5 °C, (c) 755.0 °C and (d) 757.5 °C.

equation to account for nucleation and crystallization growth occurring simultaneously to

$$\ln\left(\frac{\Phi^n}{T_p^2}\right) = \frac{-mE_c}{RT_p} + \text{constant} \tag{3}$$

where E_c is the activation energy of crystallization and m represents the dimensionality of the crystalline phase. n and m are correlated to each other through the relation $m = n - 1$. Fig. 6(a–d) shows the Matusita and Sakka plot for the determination of activation energy of crystallization. It is found that the values of n are in the range of 2.90–3.46 and activation energy in the range of 712–772 kJ/mol at a specific temperature ranging from 750.0 to 757.5 °C. The detailed n and activation energy values are shown in Table 2. Applying the modified Kissinger model, the activation energies of crystallization are obtained in the range of 712–772 kJ/mol for as-precipitated $Bi_{0.25}Y_{2.75}Fe_5O_{12}$ powder.

4. Conclusions

A non-isothermal study of the crystallization kinetics of coprecipitation $Bi_{0.25}Y_{2.75}Fe_5O_{12}$ was carried out by DSC measurement technique. The activation energy of crystallization is determined using the method proposed by Kissinger from the slope and is equal to 492 kJ/mol. The Avrami exponent n suggesting the dimensionality of crystal growth was determined using the Ozawa equation. The results revealed that the values of the n obtained experimentally are in the range of 2.90–3.46 for the specific temperature ranging from 750.0 to 757.5 °C. It is found that the controlling mechanism of crystallization is three-dimensional interfacial growth for a specific temperature ranging from 750.0 to 757.5 °C. By applying the modified Kissinger model, the activation energies of crystallization are obtained in the range of 712–772 kJ/mol.

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