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Microstructure and densification mechanism of low temperature sintering Bi-Substituted yttrium iron garnet

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Abstract The low temperature sintering and densification mechanism of Bi-substituted yttrium iron garnet (Bi:YIG) polycrystalline samples were studied in this paper. The Bi:YIG polycrystalline samples, with the composition of $Y_{3-x}Bi_xFe_5O_{12}$ (x=0–1.2), were prepared by the solid-state reaction method. The X-ray diffraction (XRD) patterns show that Bi-substitution can lower the formation temperature of garnet phase from about 1200 to 900 °C and the thermo-mechanical analysis (TMA) indicates that the sintering temperature of ceramics can be decreased from over 1350 °C to below 1000 °C. The microstructure of grains and grain boundaries was observed by high resolution electron microscopy (HREM). The bismuth distribution in grains and grain boundaries was performed by X-ray energy dispersive spectroscopy (EDS). The occurrence of liquid phase with Bi-contained oxide in the sintering process caused the decrease in sintering temperature.

Keywords Yttrium iron garnet · Bi-substitution · Low temperature sintering

1 Introduction

As a new type of chip electronic components, multilayer ceramic microwave devices have attracted extensive attention due to the necessity for the miniaturization of microwave communication equipments. Yttrium iron garnet (YIG) is an important material commonly used as circulators, oscillators and phase shifters for microwave applications, because it possesses small linewidth in ferromagnetic resonance, high DC resistance, low dielectric loss and controllable saturation magnetization in microwave region [1]. However, YIG garnet is hardly used in multilayer microwave components because its sintering temperature (>1350 °C) is generally higher than the melting points of highly conductive metals like Ag–Pd alloy (1145 °C) [2]. Previous investigations have shown that the Bi-substituted (YIG:Bi) powders can be prepared at a lower temperature (<1100 °C), and the sintering temperature of relevant ceramics is much lower than that of pure YIG polycrystalline ceramics [3, 4].

It is well known that the bismuthous oxide has a low melting point of 700 °C and can remarkably lower sintering temperature of NiZn [5], MnZn [6] and hexagonal ferrites [7] due to the presence of liquid phase during sintering process. The aim of this work was to study the influence of Bi-substitution for Y on the sinterability and densification process of polycrystalline YIG ferrites. The possible sintering mechanism is discussed according to thermo-mechanical analysis (TMA), high resolution electron microscopy (HREM) as well as X-ray energy dispersive spectroscopy (EDS).

2 Experimental procedure

YIG:Bi ferrite powders of $Y_{3-x}Bi_xFe_5O_{12}$ where x=0, 0.8, 0.9, 1.0, 1.1 and 1.2, were prepared by the solid-state reaction method. The raw materials, Fe_2O_3 (A.R.), Bi_2O_3 (A.R.) and Y_2O_3 (99.99% purity) were mixed in a ball mill with ethanol for 24 h. The mixed powders were calcined in the air at 900 °C ($0.8 \leq x \leq 1.2$) and 1200 °C (x=0) respectively,

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and then milled again for 24 h. The resulting powders were pressed in a stainless-steel die under a pressure of 40,000 N/m^2 with 5 wt% polyvinylalcohol as lubricant. The pressed discs specimens were sintered in the air at 1050 °C for YIG: Bi and 1340 °C for YIG, respectively, and then cooled in the furnace. All the calcined powders were investigated by X-ray diffraction, using Cu K_α radiation to characterize phase formation. The sintering shrinkage was performed by TMA and the microstructures of sintered ceramics were characterized by HREM and EDS.

3 Results and discussion

3.1 Phase formation and ceramics density

Figure 1 shows the XRD patterns of samples for different Bi contents. It is found that Bi-substituted samples ($0.8 \leq x \leq 1.0$) can form a single garnet phase at a lower temperature (900 °C) than the formation temperature of YIG (1200 °C). But a secondary phase seems to be formed when $x \geq 1.0$, which can be attributed to the Bi-contained oxides separated out of YIG:Bi matrix.

High density (≥97% theoretical density, T.D.) can be obtained at 1050 °C for 6 h from YIG:Bi powders as shown in Table 1. As we know, the pure YIG ceramics with a high relative density should usually be achieved above 1350 °C. Substitution of Bi for Y can decrease the sintering temperature of YIG from above 1350 °C to below 1050 °C, at which the magnetic garnet medium can be co-sintered with low melting point metal electrodes like Ag–Pd alloy in monolithic structure.

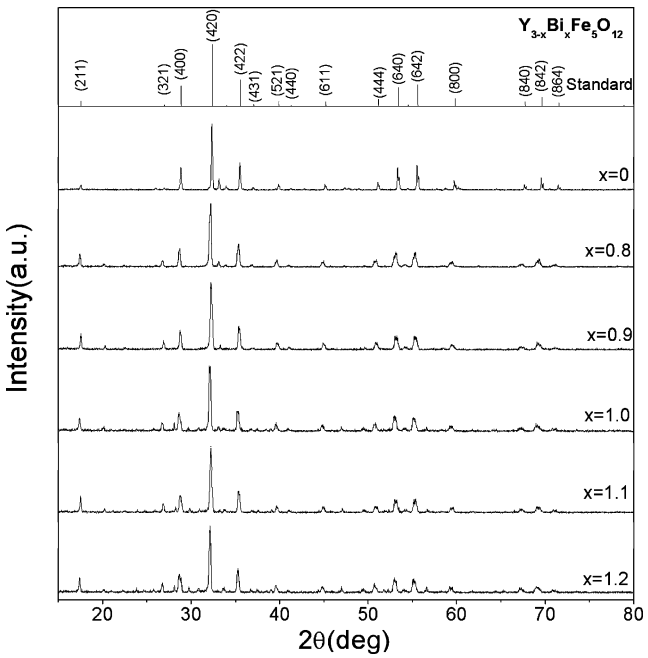

Fig. 1 X-ray diffraction patterns of $Y_{3-x}Bi_xFe_5O_{12}$ powders calcined at 900 °C ($0.8 \leq x \leq 1.2$) and at 1200 °C ($x=0$)

Table 1 Density of $Y_{3-x}Bi_xFe_5O_{12}$ specimens.

Specimens						
x	0	0.8	0.9	1.0	1.1	1.2
Density (g/cm^3)	4.98	5.54	5.65	5.72	5.77	5.84
Relative T.D. (%)	96.3	97.2	97.8	98.0	97.8	97.9

3.2 TMA analysis

Figure 2 shows the TMA curves of Bi-substituted YIG sample ($x=1.0$) and pure YIG sample ($x=0$). Compared to pure YIG sample (over 1300 °C), the temperature of beginning shrinkage for Bi-substituted sample was remarkably reduced (below 1000 °C). The decrease of the sintering temperature of Bi-substituted YIG can make co-sintering between garnet and metal internal electrodes like Ag–Pd alloy possible.

In addition, it is obviously shown that the shrinkage rate of Bi-substituted YIG sample is much larger than that of pure YIG sample. Therefore, the sintering time of Bi-substituted YIG can be shortened.

3.3 HREM and EDS

Microstructure characterization of a certain final material can reflect its formation process because the microstructure of the material usually indicates some specific information retained during its formation process. The densification mechanism of Bi-substituted YIG was supposed through HREM and EDS.

Figure 3(a) shows the microstructure morphology of the grains and the grain boundaries as well as the electron

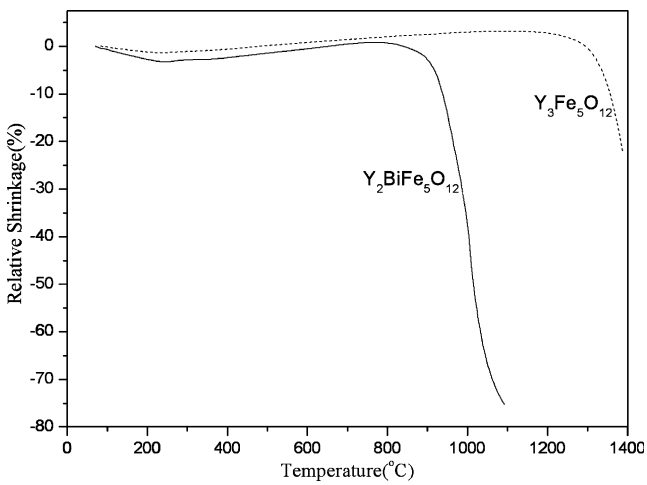

Fig. 2 TMA curves of Bi-substituted YIG sample ($x=1.0$) and pure YIG sample ($x=0$)

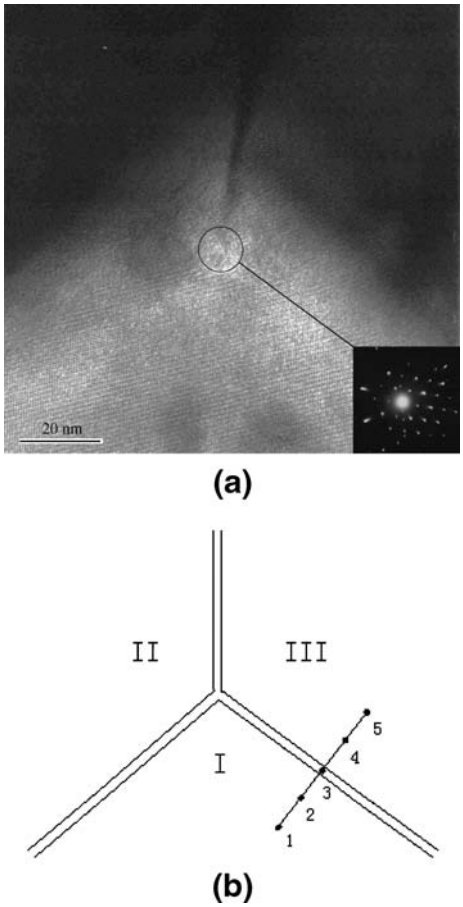

Fig. 3 HREM photograph (**a**) of Bi-substituted sample and its schema figure (**b**).

diffraction pattern at the triangular grain boundary from Bi-substituted sample. It can be clearly found that crystallization of the grains is quite satisfactory and only a few defects can be found at the grain boundaries. The triangular grain boundary seems to characterize crystalline state from the electron diffraction pattern of Bi-substituted sample as shown by Fig. 3(a).

Figure 3(b) is the triangular grain boundary's sketch corresponding to Fig. 3(a), where space of neighbour position is 20 nm and electron beam spot diameter is about 10 nm. The measured Bi contents at different positions by EDS were shown in Fig. 4. It can be observed that the Bi concentration at the grain boundary is much higher than that inside the grains. The Bi segregation and remains at grain boundaries can attribute to the occurrence of liquid Bi-contained oxides during the sintering process. Bi-contained oxides have a low melting point and become liquid phase at the sintering temperature (1050 °C). This liquid phase promoted the low-temperature sintering. After sintering the Bi-contained oxides recrystallized at grain boundaries during cooling process.

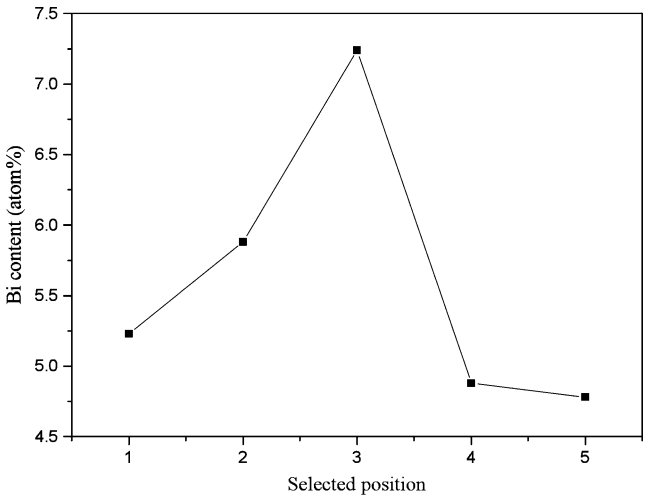

Fig. 4 Bismuth contents of Bi-substituted YIG sample (x=1.0) at different positions

4 Conclusions

The important conclusions of our work can be summarized as follows:

1. Substitution of Bi for Y can decrease the phase formation temperature and sintering temperature of YIG.
2. The rich-Bi grain boundary phase was observed, which can attribute to the occurrence of liquid phase during the sintering process. The sintering mechanism is proposed, with its core point that the occurred liquid in sintering process can promote densification of YIG.

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