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Effect of Bi-substitution on the microstructure and electromagnetic properties of YCaZrVIG with low sintering temperature☆

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Abstract

Bi substituted YCaZrVIG ferrites, $Y_{2.3-x}Bi_xCa_{0.7}Zr_{0.3}V_{0.2}Fe_{4.42}O_{12}$ (x=0.1, 0.25, 0.4, 0.5, 0.75) ferrites were prepared by conventional oxide method. The addition of Bi_2O_3 promoted the sintering performance and lowered the sintering temperature from 1420–1230 °C. However, it also resulted in the formation of minor second phases and the decrease of grain size. With the increase of Bi concentration, the dielectric constant increases linearly and then remains unchanged. The dielectric loss decreased firstly and then increased. The saturation magnetization ($4\pi M_s$) almost retained unchanged as the Bi concentration increased except for the sample with 0.75. The coercivity (H_c) decreased firstly and reached the minimum of 1.32 Oe at 0.25, and then rose when $x>0.25$, which was related to the facility of magnetic domain wall motion and magnetic moment reverse. Moderate addition of Bi also can increase the remanence (B_r) by improving sintering process. Additionally, we got the optimum electromagnetic properties in the samples with $x=0.25$ at 1230 °C: RD > 97%, $\varepsilon_r=15.7$, tan $\delta_e=2.48\times10^{-4}$, H_c=1.32Oe, $4\pi M_S$=1663 Gs, B_r=583.91 Gs.

Keywords: Conventional oxide method; Microstructure; Electromagnetic properties; Low temperature sintering

1. Introduction

YIG and substituted YIG ceramic materials have been applied widely in microwave devices, such as circulators, oscillators and phase shifters, due to their excellent electromagnetic properties at microwave frequencies: low dielectric loss tangent (tan δ) and small linewidth (ΔH) in ferromagnetic resonance [1]. A high density and saturation magnetization, as well as uniform microstructure, are essential for these materials to minimize the energy loss at high frequencies [2].

Recently, research indicated that YCaZrVIG ferrites showed more excellent magnetic and microwave properties compared with other YIG ferrites [3]. However, in order to synthesize high-density YCaZrVIG ferrites, a high sintering temperature up to 1420 °C is needed [4]. Low sintering temperature ferrites are needed for the development of materials co-firable with electrode materials, which is necessary for the miniaturization of RF modules in microwave communication system. Moreover, lowering sintering temperature is of great significance to the decrease of the manufacturing cost.

The effects of many additives have been investigated in an attempt to improve the density and electromagnetic properties of garnet materials at low sintering temperatures. Recently, it has been reported that the sintering temperature of YIG system was reduced to 1020 °C × 6 h for (Y_2Bi) Fe_5O_{12} doped with Bi_2O_3 [5]. Subsequently, Bi-substituted YIG ceramics were prepared at a lower temperature of 1050 °C × 6 h with a relative density of above 96% [6].

In this work, the YCaZrVIG ferrites doped with Bi_2O_3 are synthesized successfully by conventional oxide method

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and the density, microstructure and electromagnetic properties of the Bi doped YCaZrVIG materials are investigated.

2. Experiment

2.1. Sample preparation

The raw materials were Y_2O_3 (99.9% purity), Fe_2O_3 (98% purity), Bi_2O_3 (99% purity), $CaCO_3$ (99% purity), ZrO_2(99.9% purity) and V_2O_5 (99.9% purity) powders. They were mixed according to the chosen stoichiometry of $Y_{2.3-x}Bi_xCa_{0.7}Zr_{0.3}V_{0.2}Fe_{4.42}O_{12}$ (YBiCaZrVIG) with x=0.1, 0.25, 0.4, 0.5 and 0.75, and then wet milled in a planetary mill for 6 h with ethanol and ZrO_2 balls. The slurries were dried and then calcined at 1150 °C for 2 h, which was followed by re-milling for 6 h. After being dried, the powders were pulverized, prilled, screened and pressed into cylindrical specimens of ∅12.25 mm × 5 mm and ring tablets of ∅18 mm × 9 mm × 4.5 mm. Isostatic pressing technology was also used to improve the density and uniformity of green bodies. Finally, the samples were sintered at a temperature range from 1170 °C to 1290 °C for a fixed soaking time of 4 h in air atmosphere with a heating rate of 100 °C/h and then furnace cooled to room temperature.

2.2. Sample characterization

The density of the sintered samples was measured using Archimedes' method. The crystalline structure of the sintered samples were examined by ARLX'TRA X-ray diffractometer using CuKα_1 radiation in the 2θ angle range from 20° to 80°. The fracture face of the sintered samples were observed by JEOL JSM-5900 scanning electron microscope (SEM). Permittivity ε_r and dielectric loss tangent tan δ_e were measured at a frequency between 8 GHz and 12 GHz in a network analyzer by the modified Hakki and Cole-man's method [7] under the TE011 mode. The magnetic properties (H_c, B_r and $4\pi M_s$) were measured using American SMT-600 hysteresiscope and magnetic balance.

3. Results and discussion

3.1. Phase analysis and sintering performance

Fig.1 shows the XRD patterns of the samples with different Bi addition. As can be observed from the figure, for all the sintered samples, almost all the peaks were identical to garnet phase ($Y_3Fe_5O_{12}$) and only minor of the second phases $YFeO_3$ and $Y_2Fe_4O_9$ appeared. It implies that the substituting of Fe^{3+} with Bi^{3+} does not change the primary crystal structure. The inset in Fig. 1 indicates that the strongest peak shifts gradually to lower angles with increasing Bi content, which can also be found for other peaks. Increase in Bi content leads to the variation in

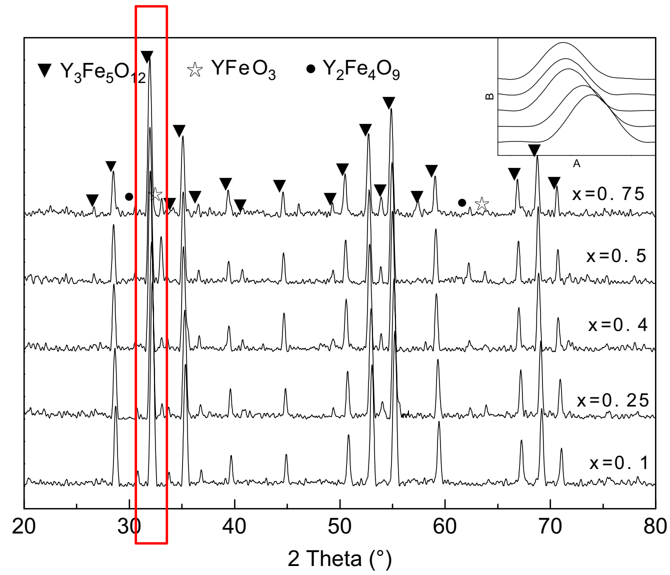

Fig. 1. XRD patterns of YBiCaZrVIG ferrites with different Bi_2O_3 concentration.

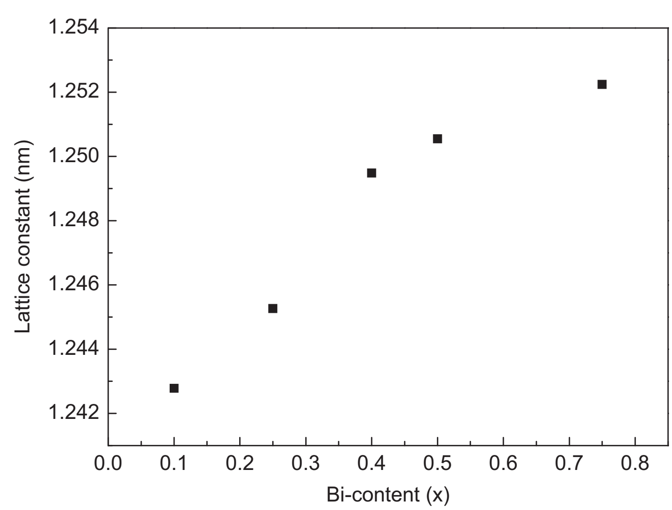

Fig. 2. Lattice constants of YBiCaZrVIG ferrites with different Bi_2O_3 concentration.

the lattice constants of the samples (seen in Fig. 2), which were calculated by a Cohen canonical equation shown as follows [8]:

$$\sum a\sin^2\theta = A\sum a^2 + C\sum a\delta$$

$$\sum a\sin^2\theta = A\sum a\delta + C\sum a^2 \quad (1)$$

where $A=(\lambda^2/4a_0^2)$, $a=(h^2+k^2+l^2)$, $C=D/10$, $\delta = 10\sin^2 2\theta$ and D is the particle size.

It can be seen from Fig. 2 that the lattice constants increased linearly with the increase in Bi^{3+} content which can be explained by partial substitution of Y^{3+} ions with Bi^{3+} ions, since the ionic radius of Bi^{3+} ion (0.117 nm) is

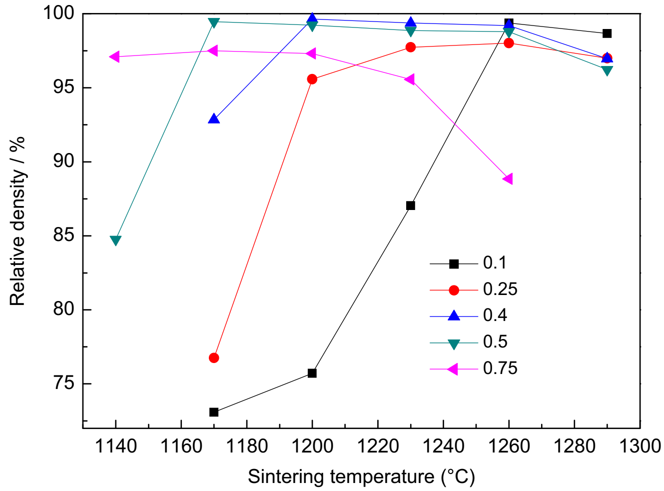

Fig. 3. Relative density of YBiCaZrVIG ferrites with Bi concentration x and the sintering temperature.

larger than that of Y^{3+} ion (0.102 nm) [9]. The XRD result suggests that Bi^{3+} ions do substitute Y^{3+} ions and enter into the lattice of the garnet.

Fig. 3 displays the variations in relative density of the sintered YBiCaZrVIG samples with Bi concentration x and the sintering temperature. As illustrated in this figure, firstly, the relative density of all specimens increases with sintering temperature and remains stable after their respective best sintering temperature, then it decreases slightly. At all concerned sintering temperature, the relative density also shows similar variation with the increase of Bi content x. Moreover, it can be seen that the best sintering temperature decreases with the increase of Bi content x. This result indicates that the Bi substitution with appropriate amount may promote the sintering behavior and decrease the sintering temperature. The samples with $x=0.25$–0.5 sintered at 1230–1290 °C show a high relative density with above 97%.

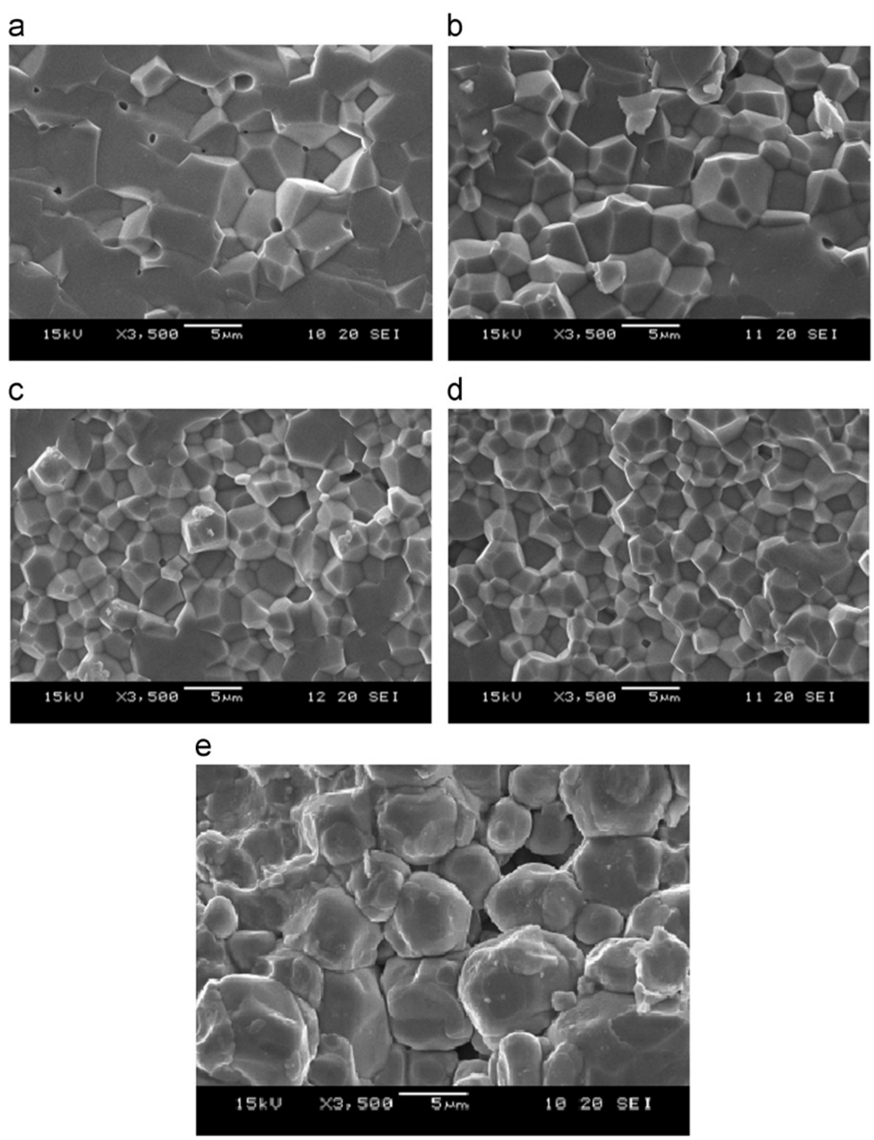

Fig. 4. SEM micrographs of YBiCaZrVIG ferrites with different Bi_2O_3 concentrations (a) $x=0.1$; (b) $x=0.25$; (c) $x=0.4$; (d) $x=0.5$; (e) $x=0.75$.

3.2. Microstructure analysis

Fig. 4 shows the SEM micrographs of the fracture face of the samples with different Bi concentration sintered at 1230 °C. As can be seen in the figure, the average grain size of the samples decreases gradually with Bi concentration increasing from 0.1–0.5. However, when the addition of Bi reached 0.75, the grains grew abnormally, which is probably the main reason for the low relative density of these samples. Obviously, both the relatively high porosity for the sample with $x=0.1$ and the fine grain size for the samples with $x=0.4$ and 0.5 are disadvantageous to the dielectric loss and coercivity. The sample with $x=0.25$ shows the optimum microstructure, i.e., well-developed grain, homogeneous grain-size distribution, clear grain boundary and high density.

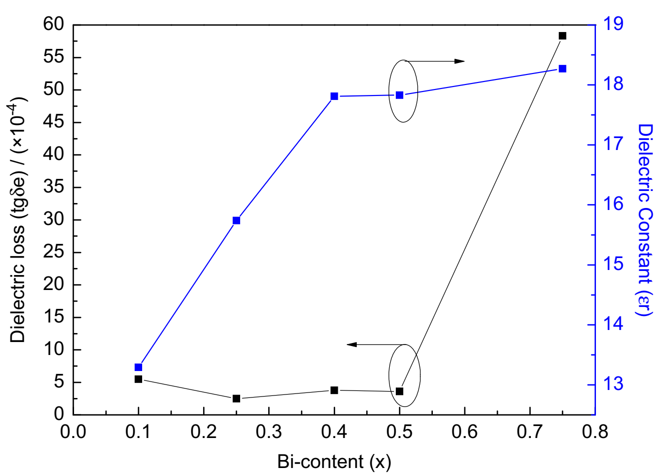

Fig. 5. Dielectric properties of YBiCaZrVIG ferrites (sintered at 1230 °C) with different Bi_2O_3 concentration.

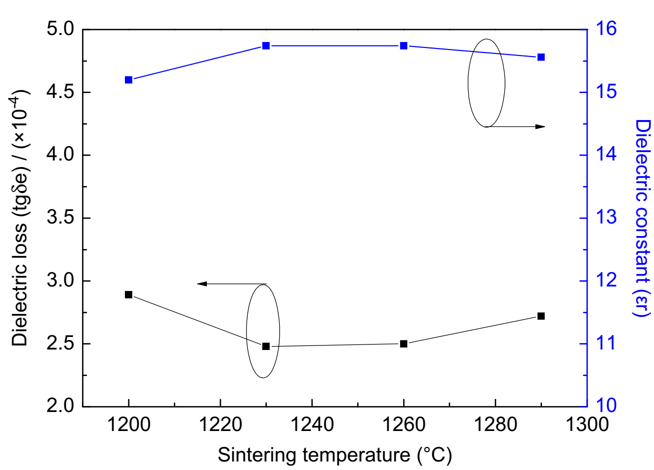

Fig. 6. Dielectric properties of YBiCaZrVIG ferrites ($x=0.25$) sintered at different temperatures.

3.3. Dielectric properties

Figs. 5 and 6 illustrate the variation of dielectric properties with sintering temperature and Bi concentration, respectively.

As can be seen in Fig. 5, the dielectric constant increases linearly with Bi concentration x up to 0.4 and then remains unchanged. The fact can be attributed to two reasons: (1) the densification promoted by Bi substitution is beneficial to the increase of ε_r; (2) Bi substitution changes polarization mechanism of YCaZrVIG, which leads to the increase of ε_r. Hong et al.[10] reveals that the dielectric loss of YIG doesn‘t change with the addition of Bi as the dielectric loss is mainly related to the amount of Fe^{2+} ions in the material and the substitution of Bi has no influence on the transformation between Fe^{3+} and Fe^{2+}. The dielectric loss shown in Fig. 5 exhibits a small fluctuation between 2×10^{-4} and 5×10^{-4} when x varies from 0.1–0.5, which may be related to the formation of the second phases $YFeO_3$ and $Y_2Fe_4O_9$ and the increase in the amount of grain boundary caused by Bi addition (shown in Fig. 4) [11]. When Bi concentration reached 0.75, the dielectric loss $tg\delta_e$ shows a sharp increase, which is attributed to the increase in the amount of deficiencies and the degree of lattice distortion caused by excessive addition and over-sintering [13].

Referring to Fig. 6, it is obvious that the sintering temperature shows little influence on the dielectric constant and the dielectric loss of the samples. The dielectric constant varies between 15.2 and 15.7, whose variation tendency is identical to that of the relative density. The dielectric loss is mainly influenced by the amount of Fe^{2+} ions. The appearance of Fe^{2+} ions, which may result from the deoxidation of Fe^{3+} ions at high sintering temperature (>1300 °C), will lead to the increase of dielectric loss [12]. The YBiCaZrVIG ferrites in this work were all prepared at temperature lower than 1300 °C. Therefore, it is easy to understand why the dielectric loss of the samples shows little variation with sintering temperature. It can be seen from Figs. 5 and 6 that the sample with $x=0.25$ sintered at 1230 °C shows the lowest dielectric loss of 2.48×10^{-4} companied with a dielectric constant of 15.7.

3.4. Magnetic properties

Fig. 7 displays the variation of the room temperature saturation magnetization $4\pi M_s$ and coercivity H_c with Bi concentration (x) for the YBiCaZrVIG ferrites. Fig. 8 describes the variation of $4\pi M_s$ and H_c with sintering temperature for the YBiCaZrVIG ferrites ($x=0.25$).

As can be seen from Fig. 7, the addition of Bi_2O_3 shows no influence on the saturation magnetization ($4\pi M_s$) of the samples with $x=0.1$–0.5 which varies between 1663 and 1689 Gs. The saturation magnetization ($4\pi M_s$) reflects the amount of magnetic moment in unit volume of the samples. This phenomenon can be ascribed to the substitution of Bi^{3+} for Y^{3+} at dodecahedron [$24Y^{3+}$] sites

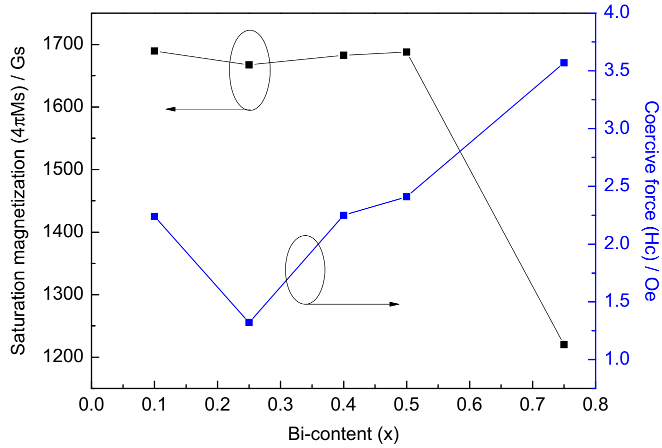

Fig. 7. Saturation magnetization ($4\pi M_s$) and coercivity (H_c) of YBiCaZrVIG ferrites (sintered at 1230 °C) with different Bi_2O_3 concentration.

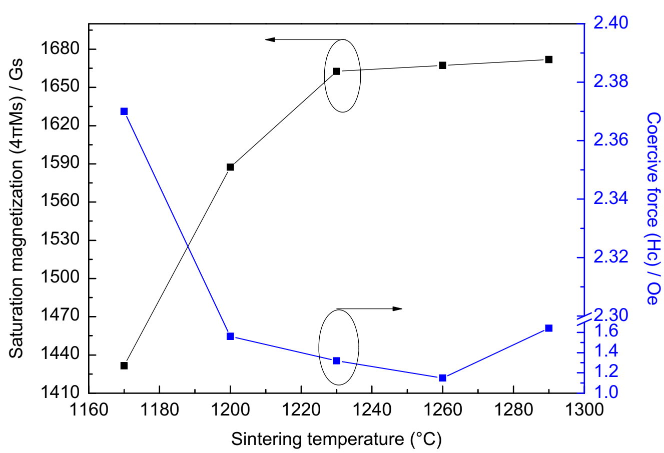

Fig. 8. Saturation magnetization $4\pi M_s$ and coercivity H_c of YBiCaZrVIG ferrites ($x=0.25$) sintered at different temperatures.

which would not change the original magnitude of magnetic moment in c, a, d sites because both Bi^{3+} and Y^{3+} are non-magnetic ions. However, when x is 0.75, the saturation magnetization shows an unusual decrease. The decrease of relative density and abnormal grain growth are probably the main reasons, which may introduce defects in the samples. The coercivity is decided by the facility of magnetic domain wall motion and magnetic moment reverse, which is very sensitive to the presence of pinning sites and the grain boundaries [13]. As can be seen in Fig. 7, it decreases firstly with the increasing Bi_2O_3 concentration and reaches the minimum of 1.32 Oe at $x=0.25$. This phenomenon can be explained by the improvement in the homogeneity of grain-size distribution and the decrease in pinning effect caused by the decrease in porosity, which are favorable for domain wall movement. The latter rise of coercivity when $x>0.25$ can be attributed to the increase in the amount of grain boundaries and the existence of the second phases, which increase the magnetocrystalline anisotropy to raise domain wall energies and impede wall motion [14].

As shown in Fig. 8, with the sintering temperature increasing to 1260 °C, the saturation magnetization $4\pi M_s$ obviously increases, but coercivity H_c remarkably reduces. When further increasing the sintering temperature, H_c increases gradually whereas $4\pi M_s$ maintains invariable, suggesting that the saturation magnetization for the densified samples only depends on the material itself and has less to do with the sintering temperature. Coercivity H_c is mainly related to the grain size of the samples, and the larger the grain size is, the smaller the coercivity is. It is generally acknowledged that increasing the sintering temperature is beneficial to the densification and grain growth [15–17]. So, the coercivity decreases as the sintering temperature increases up to 1260 °C. When the sintering temperature is above 1260 °C, the coercivity shows a weak increase. This phenomenon may be related to the increase in closed porosity, and the enhanced pinning effect.

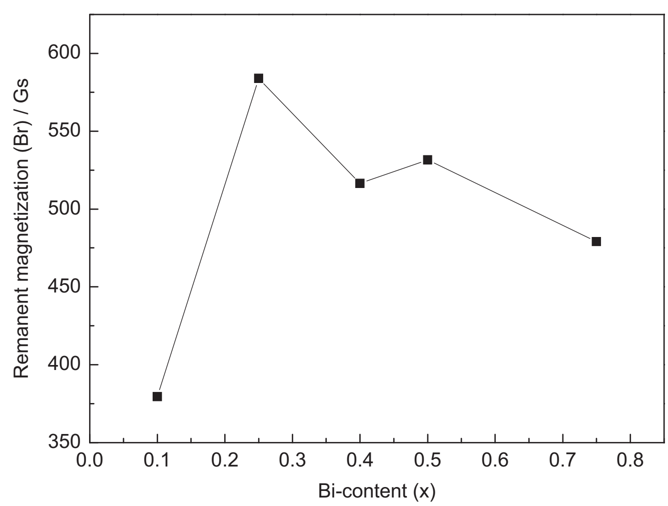

Fig. 9. Remanence (B_r) of YBiCaZrVIG ferrites (sintered at 1230 °C) with different Bi_2O_3 concentration.

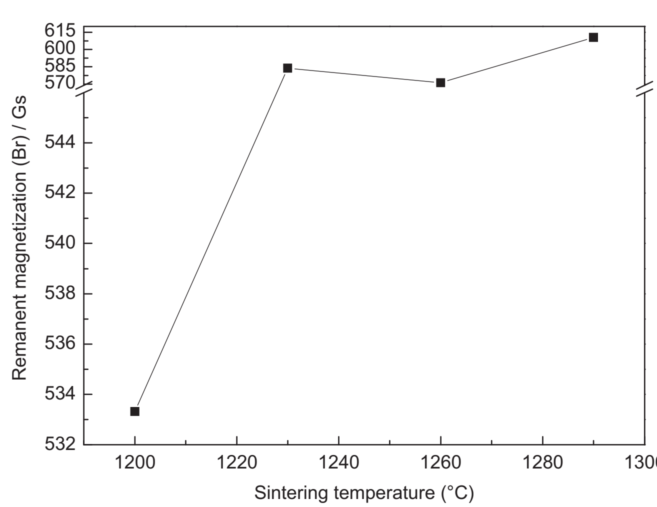

Fig. 10. Remanence (B_r) of YCaZrVIG ferrites ($x=0.25$) sintered at different temperatures.

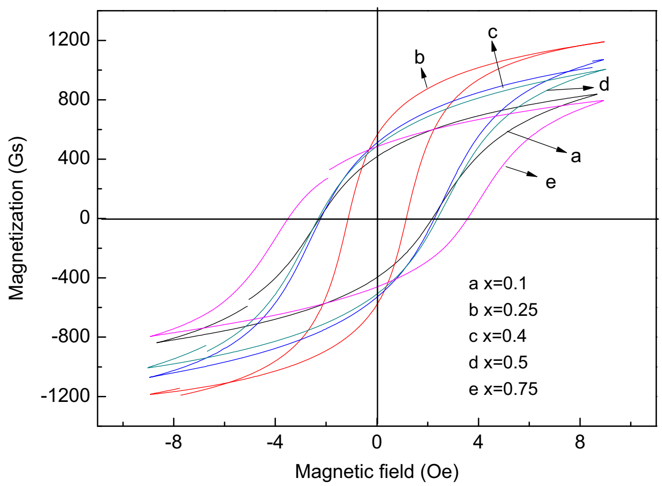

Fig. 11. Hysteresis loops of YBiCaZrVIG ferrites with different Bi_2O_3 concentration.

Figs. 9 and 10 demonstrate the variation of remanence (B_r) of YBiCaZrVIG ferrites with Bi concentration and sintering temperature, respectively.

Remanence of garnet ferrites is a structure sensitive parameter, which mainly depends on porosity and external phases and has little relation with grain size and its distribution [18,19]. As can be seen from Fig. 9, the remanence exhibits a sharp increase firstly and then a gradual decrease with the increase of Bi_2O_3 addition. The samples with $x=0.25$ show the highest remanence of 583.91 Gs, which can be explained by the closed porosity shown in Fig. 4. Due to the same reason as saturation magnetization ($4\pi M_s$), the remanence decreases markedly when $x=0.75$. As shown in Fig. 10, the variation of the remanence is identical to that of the relative density and has less to do with the sintering temperature after being densified.

In general, the substitution of Bi could improve the sinterability and lower the sintering temperature of YCaZrVIG from 1420 °C to 1230 °C, and the sample with $x=0.25$ sintered at 1230 °C i.e., $Y_{2.05}Bi_{0.25}Ca_{0.7}Zr_{0.3}V_{0.2}Fe_{4.42}O_{12}$ shows the optimum electromagnetic properties: $\varepsilon_r=15.7$, $\tan\delta_e=2.48\times10^{-4}$, $H_c=1.32$Oe, $4\pi M_S=1663$ Gs, $B_r=583.91$ Gs. Fig. 11 shows the hysteresis loops of the YCaZrVIG ferrites with different Bi concentration sintered at 1230 °C, from which it also can be found that the YBiCaZrVIG ferrite with $x=0.25$ owns the smallest coercivity and highest remanence.

4. Conclusions

High density (relative density higher than 97%) Bi-substituted YCaZrVIG ferrites were successfully prepared by conventional oxide method. The addition of Bi_2O_3 could promote the sinterability and lower the sintering temperature notably from 1420 to 1230 °C. However, it also resulted in the formation of minor second phases of $YFeO_3$ and $Y_2Fe_4O_9$ and the decrease of grain size. With the increase of Bi concentration, the dielectric constant increases linearly and then remains unchanged. The dielectric loss decreased firstly and then increased, which may be ascribed to the densification, the formation of the second phases and the increase in the amount of grain boundaries. The substitution of Bi^{3+} for Y^{3+} at dodecahedron [$24Y^{3+}$] sites would not change the original magnitude of magnetic moment in c, a, d sites. So, the saturation magnetization ($4\pi M_s$) almost retained unchanged as the Bi concentration increased except for the sample with 0.75. The coercivity (H_c) decreased firstly and then rose, which was attributed to the facility of magnetic domain wall motion and magnetic moment reverse. Moderate addition of Bi also can increase the remanence (B_r) by improving sintering process. The YBiCaZrVIG ferrite with $x=0.25$, i.e., $Y_{2.05}Bi_{0.25}Ca_{0.7}Zr_{0.3}V_{0.2}Fe_{4.42}O_{12}$ shows the optimum electromagnetic properties: RD > 97%, $\varepsilon_r=15.7$, $\tan\delta_e=2.48\times10^{-4}$, $H_c=1.32$ Oe, $4\pi M_S=1663$ Gs, $B_r=583.91$ Gs.

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