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Microstructure and microwave magnetic properties of Low-Firing $Li_{0.42}Zn_{0.27}Ti_{0.11}Mn_{0.1}Fe_{2.1}O_4$ ferrite

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Abstract. Low firing temperature and excellent gyromagnetic properties such as high remanence square ratio and narrow ferromagnetic resonance line width are required for the application in nonreciprocal microwave ferrite devices based on low temperature cofired ceramics (LTCC) technology. In this research, Bi_2O_3-Li_2CO_3 mixture was introduced as the sintering agent to lower the sintering temperature of $Li_{0.42}Zn_{0.27}Ti_{0.11}Mn_{0.1}Fe_{2.1}O_4$ ferrite. The influence of Bi_2O_3-Li_2CO_3 mixture upon the phase composition, composite microstructures and gyromagnetic properties of LiZnTiMn ferrite sintered at low temperature has been investigated for LTCC integration applications. With a proper amount of Bi_2O_3-Li_2CO_3 mixture, the sintering temperature of LiZnTiMn ferrite successfully reduced to below 900^{o}C from 1100^{o}C without degradation of magnetic properties, meanwhile, both of saturation flux density and remanence square ratio were increased.

1. Introduction

Ferrites, having been studied for several decades, are very important magnetic materials and are widely used in RF application due to its excellent magnetic properties, good chemical stability and high electrical resistivity [1]. With the advancement of low temperature cofired ceramic (LTCC) and rapid development of microwave devices towards miniaturization, lightweight and integration, developing suitable ferrite materials become a key factor for the preparation of LTCC systems [2, 4]. Among various ferrites, spinel phase lithium ferrite has received considerable attention and been extensively studied for its remarkable magnetic and dielectric properties. The excellent temperature stability, high remanence square ratio and high Curie temperature make lithium ferrite a suitable candidate for high frequency application and other new concept devices [5-8]. However, lithium ferrite with superior property have high firing temperature (1100^{o}C), which cannot be cofired with Ag electrode. In the past decade, a mountain of work has been implemented to reduce the sintering temperature of high temperature fired traditional material systems such as low melting oxide or glass additions and ultra-fine initial powders [9, 10].

Generally, adding low-milting oxide additions such as Bi_2O_3, V_2O_5, CuO, B_2O_3 and Li_2CO_3 is known to be practical method to reduce the sintering temperature of the LTCC material systems [11-15]. Particularly, there has been proved that using combined sintering agent rather than a single sintering agent is an effective way for lowing sintering temperature of many microwave materials [16， 17]. Hence, in this study, we introduced the addition of Bi_2O_3-Li_2CO_3 mixture as a combined sintering agent to LiZnTiMn ferrite. The phase composition, composite microstructures and gyromagnetic properties of LiZnTiMn ferrite with different amount of Bi_2O_3-Li_2CO_3 mixture has been studied in detail.

2. Experimental Procedure

2.1. Sample preparation
In this experiment, to synthesize the LiZnTiMn ferrite, stoichiometric amounts of reagent-grade Fe_2O_3, Mn_3O_4, ZnO, TiO_2, and Li_2CO_3 were weighted as the mole ration of $Li_{0.42}Zn_{0.27}Ti_{0.11}Mn_{0.1}Fe_{2.1}O_4$ and mixed homogeneously with steel balls in distilled water for 4 h using a planetary mill. After drying, the mixture was then calcined in alumina crucible at 800^{o}C for 2h. The resultant powders containing a proper amount of Bi_2O_3-Li_2CO_3 mixture (x wt.% Bi_2O_3-y wt.% Li_2CO_3, x+y=0.5) ball-milled 6 h. The mixtures were then pressed into toroidal bulks (φ18mm×φ8mm×h3mm) at 8 Mpa of pressure. Finally, sintering was carried out in air for 2 h in the temperature range from 880^{o}C to 920^{o}C with an interval of 20^{o}C.

2.2. Sample characterization
Phase conposition of ferrite were analyzed by an X-ray diffractometer (XRD; DX-2700) using a CuKα radiation. Surface morphologies were investigated by scanning electron microscopy (SEM; JOEL JSM6490LV). The Archimedes method was applied to estimate the bulk density. The remanence square ratio (B_r/B_s), saturation induction (B_s) and coercive force (H_c) were tested using an Iwatsu B-H analyzer (SY8232). The microwave magnetic loss (ΔH) was measured by the perturbation method in TE_{106} model.

3. Results and Discussion
The SEM micrographs of as-fired surfaces of LiZnTiMn ferrite with different amounts of Bi_2O_3-Li_2CO_3 mixture sintered at 900^{o}C for 2 h were illustrated in Fig.1. Clearly, the grain growth was sensitive to the addition content of Bi_2O_3-Li_2CO_3 mixture. Compared with 0.5 wt.% Li_2CO_3 doped sample [Fig. 1(a)], the crystallite dimension of the LiZnTiMn ferrite increased when no more than 0.1wt.% Bi_2O_3 was added [Fig. 1(b)], which indicated that a small amount of Bi_2O_3 made great contribution to grains growth of the sample. However, the pores in the ferrite were almost eliminated and the grain size obiously increased from ＜1 μm to 2 μm as Bi_2O_3 increased to 0.3 wt.% [Fig. 1(c)]. By contrast, we found that inhomogeneous grain growth could be clearly detected and the average grain size increased significantly when Bi_2O_3 content reached 0.4 wt.%, which also aroused the increase of intergranular and intergranular pores. Meanwhile, abnormal grain growth with huge grains (20 μm) and numerous intragranular pores was detected due to superfluous liquid on grain boundary.

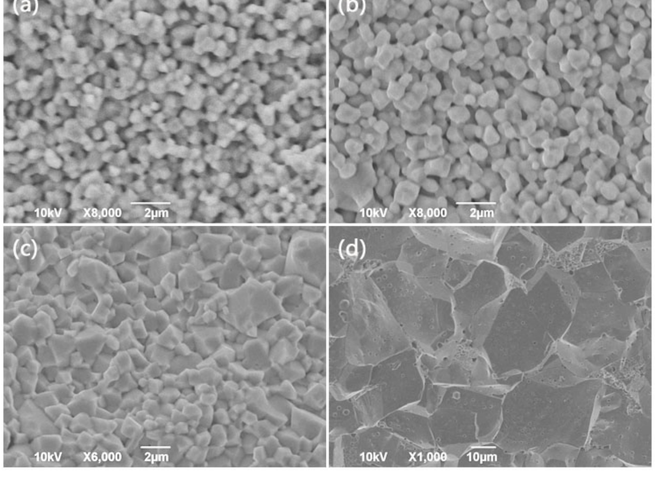

Fig. 1 SEM micrographs of LiZnTiMn ferrite sintered at 900^{o}C with Bi_2O_3-Li_2CO_3mixture of (a) x=0.0 wt.%, (b) x=0.1wt.%, (d) x=0.3wt.% and(e) x=0.4wt.%.

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The density value of LiZnTiMn ferrite was plotted as function of various content of Bi_2O_3-Li_2CO_3 mixture and sintering temperature, as shown in Fig. 2. It could be seen that the samples with no Bi_2O_3 had poorly densities. With further increase of Bi_2O_3 content, the density value for the sample sintered at 900°C achieved its maximum (4.78 g/cm^{-3}) when x=0.3, which met the basic requirements for LTCC applications. This proved that the addition of Bi_2O_3-Li_2CO_3 mixture could availably facilitate both grain boundary diffusion and grain boundary migration of LiZnTiMn ferrite, which led to both enhancement of densification and grain growth. However, when $x \geq 0.4$, the density value started to decrease, which can be ascribed to the holes increasing from the deterioration of uniformity. Therefore, appropriate addition of Bi_2O_3-Li_2CO_3 mixture was thought to play an essential role in promoting the densification of the composite ferrite.

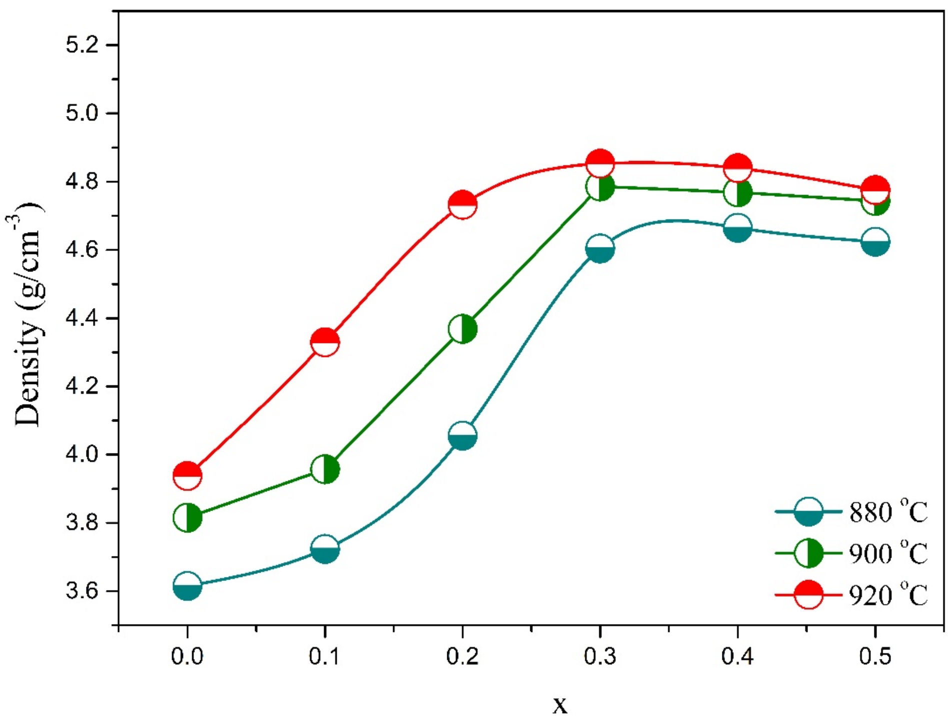

Fig. 2 Bulk density of LiZnTiMn ferrite with various Bi_2O_3-Li_2CO_3mixture.

Fig. 3 presented the X-ray diffraction of LiZnTiMn ferrite with different Bi_2O_3-Li_2CO_3 mixture sintered at 900°C. It was clearly observed that all the synthesized samples exhibited the characteristic peaks of cubic spinel structure. Meanwhile, there were no peaks of chemical components of Bi_2O_3 or Li_2CO_3 existed in all the samples. This proved that the phase formation of LiZnTiMn ferrite was not interfered by Bi_2O_3-Li_2CO_3 mixture. The results indicate that pure spinel phase was successfully obtained by Bi_2O_3-Li_2CO_3 mixture.

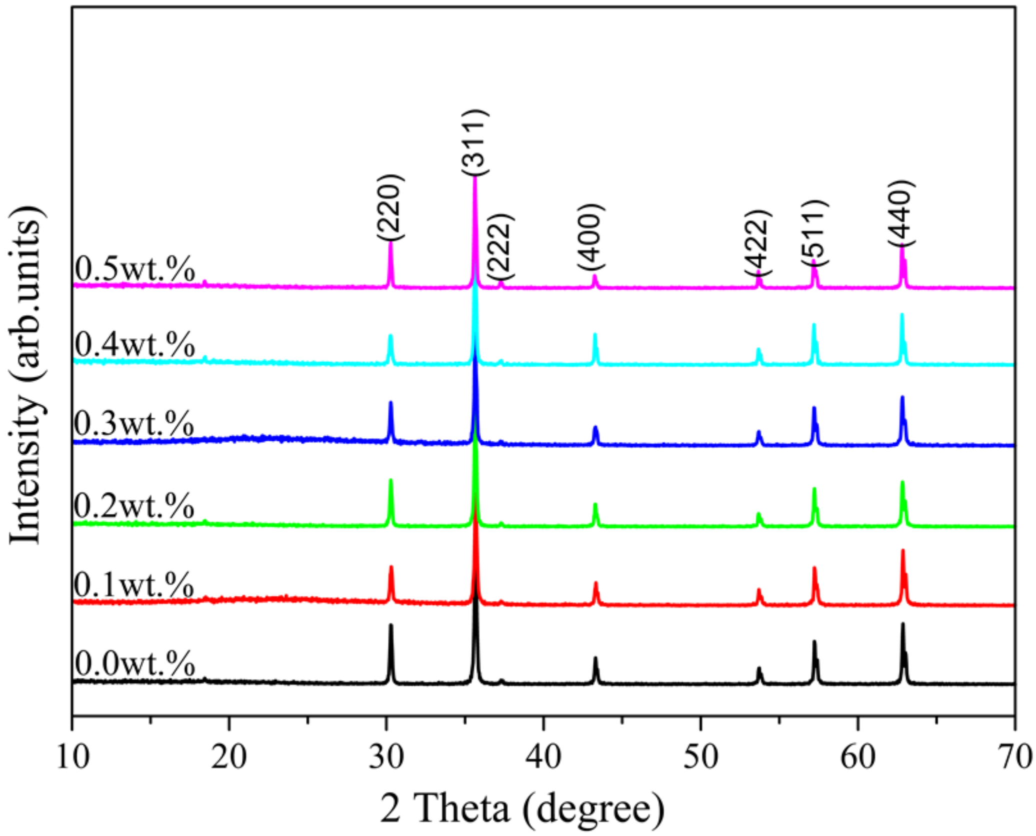

Fig. 3 X-ray diffraction of LiZnTiMn ferrite with different Bi_2O_3-Li_2CO_3 mixture.

Fig. 4 showed the coercive force (H_c) of the Bi_2O_3-Li_2CO_3 mixture modified LiZnTiMn ferrite sintered in the 880-920^{o}C temperature range. When the addition amount of Bi_2O_3-Li_2CO_3 mixture was around x=0.4, H_c value could be decreased from above 530 A/m to about 95 A/m at 920^{o}C, which due to the evident increase of average grain size. However, when more Bi_2O_3 was introduced into ferrite, the H_c value increased slightly. An accepted explanation is that bigger grains can form lesser grain boundaries, which is beneficial for the domain wall displacement and domain rotation. Thus, they are helpful to decrease the coercive force. Moreover, as indicated in Fig.4, H_c value was found reduced with the increase of sintering temperature. This could be contributed to the fact that higher sintering temperature can promote grain growth.

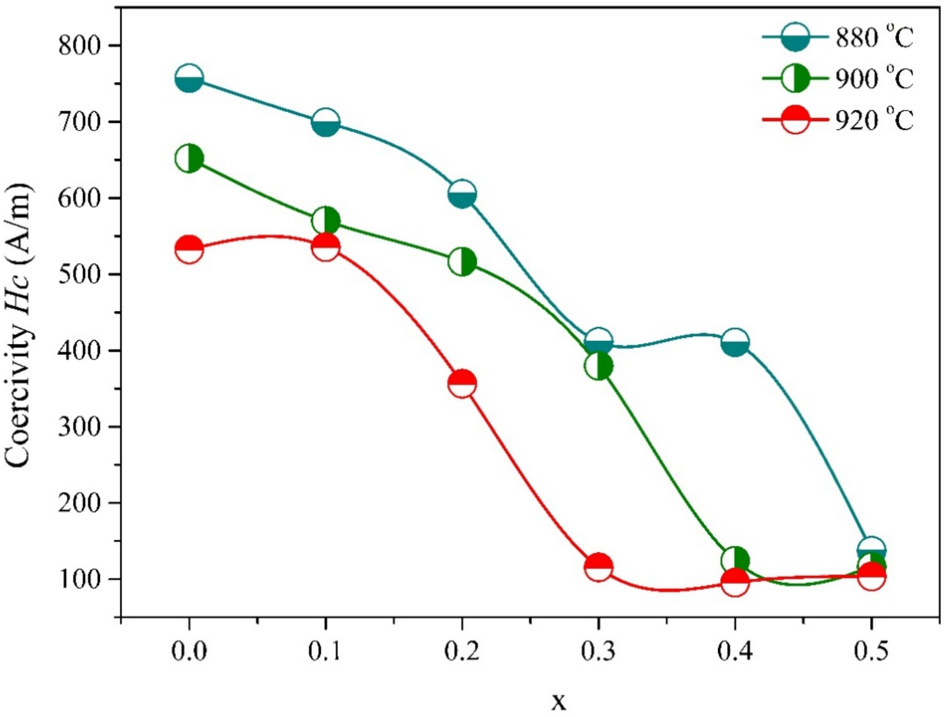

Fig. 4 Variation curves of coercive force (H_c) at different temperature.

The saturation induction (B_s) value of LiZnTiMn ferrite varying with the Bi_2O_3-Li_2CO_3 mixture content and sintering temperature were illustrated in Fig. 5. Usually, high sintering temperature could enhance the activity of the grains, which were conducive to form compact structure and produce higher B_s value. In Fig. 5, the B_s value increased even with a small fraction of Bi_2O_3. When the Bi_2O_3 content increased to 0.3 wt.%, the B_s value achieved the maximum, which was mainly contributed to grain growth and improved degree of densification, see Fig 1(c). However, the B_s value slightly decreased by the further increasing the Bi_2O_3 content. These observations suggested that excessive Bi_2O_3 in mixture led to increased nonmagnetic contents and a decreased relative density. Fig. 5 illustrates the remanence square ratio (B_r/B_S) of LiZnTiMn ferrite with different amounts of Bi_2O_3-Li_2CO_3 mixture with different temperature. It was found that remanence square ratio for all the samples exhibited similar trend of change with increasing sintering temperature. At a sintering temperature of 900^{o}C, remanence square ratio increased from 0.62 to 0.90 when x varied from 0.0 to 0.3 and then decreased. This could be proved from the SEM micrographs that the samples with x=0.3 possessed refined microstructure and small grains, which was beneficial for increasing the remanence square ratio.

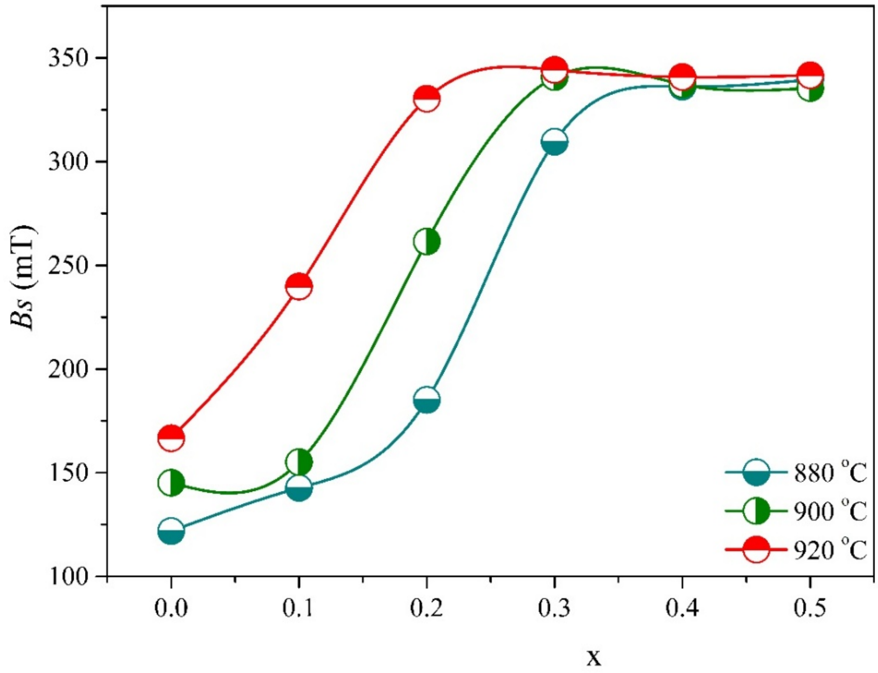

Fig. 5 Effect of Bi_2O_3-Li_2CO_3 mixture and sintering temperature on saturation induction.

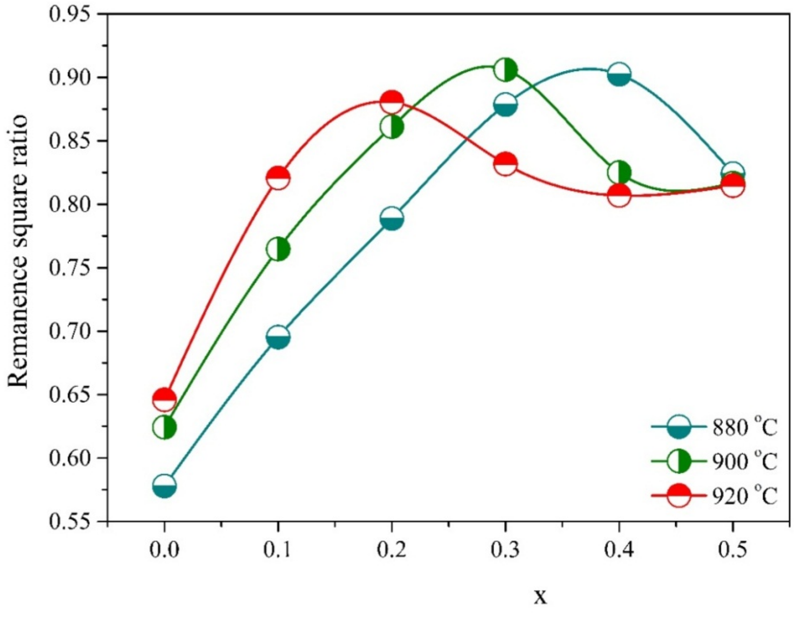

Fig. 6 Remanence square ratio of LiZnTiMn ferrite as a function of sintering temperature and content of Bi_2O_3-Li_2CO_3 mixture.

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Ferromagnetic resonance (FMR) linewidth (*ΔH*) is an important property of ferrite for characterization magnetic loss of gyromagnetic material. Fig. 7 showed *ΔH* value of the LiZnTiMn ferrite sintered at 900^{o}C as a function of Bi_2O_3-Li_2CO_3 mixture content. Firstly, it was observed that *ΔH* value of the ferrite was around 900 Oe when no Bi_2O_3 added, and the *ΔH* value was quickly decreased with adding of Bi_2O_3-Li_2CO_3 mixture and then reached its minimum value when *x*=0.3. Further increasing the Bi_2O_3 content, *ΔH* value started to increase. As we discussed above, for the 0.5 wt.% Li_2CO_3 doped sample (*x*=0.0), the grain size is less than 1μm with abundant pores in grain boundaries [Fig. 1(a)], which was beneficial for the increase of porosity broadened linewidth, resulting in a wide ferromagnetic resonance linewidth. With the increasing addition of Bi_2O_3, the grain size slightly increased and the microstructure became much more compact [Fig. 1(b)]. Particularly in the sample *x*=0.3, the sample of LiZnTiMn ferrite presented a compact microstructure with uniform grains [Fig. 1(c)] and its porosity decreased significantly while the B_s value increased, which finally caused the reduction of *ΔH.* However, when *x*⩾0.4, the ferromagnetic resonance linewidth display contrary tendency. One possible factor is that superfluous liquid phase results in the abnormal grain growth with huge grains (20μm) and the increase of intergranular and intragranular pores.

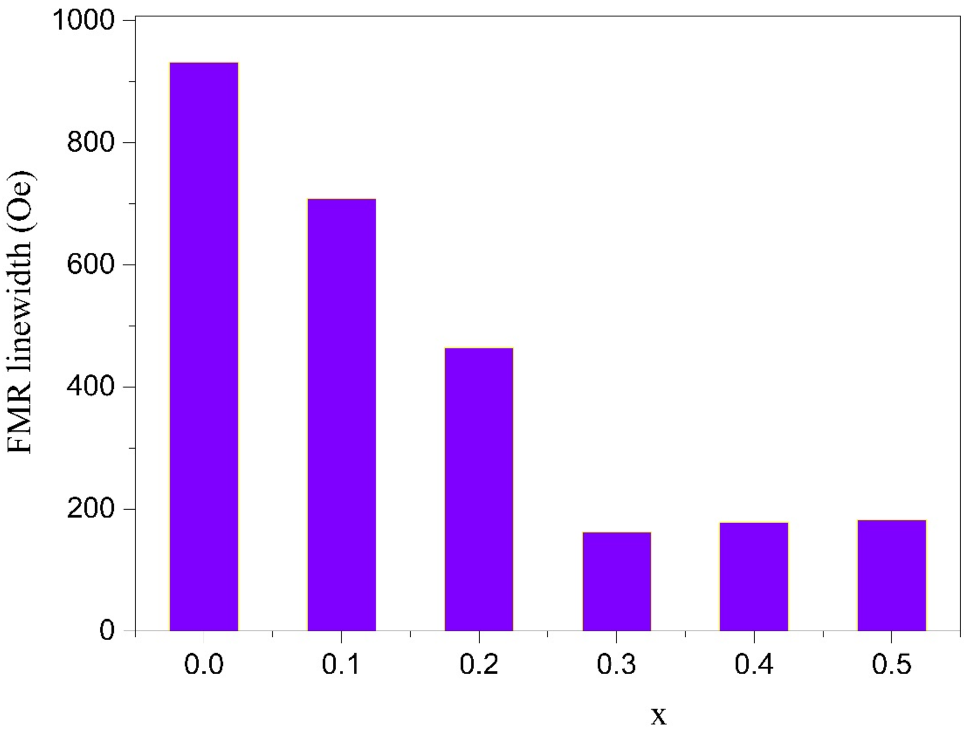

Fig. 7 The value of Ferromagnetic resonance (FMR) linewidth (*ΔH*) with various Bi_2O_3-Li_2CO_3mixture sintered at 900 ^{o}C

4. Conclusion

To summarize, the phase composition, composite microstructures and microwave gyromagnetic properties of LiZiTiMn ferrite was systematically investigated as a function of Bi_2O_3-Li_2CO_3 mixture content. Through the optimization of doping content, the increased and homogeneous grain size and dense microstructure could be obtained. More important, a relatively high remanence square ratio and as well as a narrow ferromagnetic resonance linewidth could be achieved in the LiZiTiMn ferrite.

Thus, these results have revealed that Bi_2O_3-Li_2CO_3 mixture is a good sintering aid for synthesis of LiZiTiMn ferrite, which make it a promising candidate for LTCC applications.

Acknowledgments
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