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Influence of Li_2CO_3 and ZnO Nanoparticle on Microstructure and Magnetic Properties of Low-Temperature Sintering LiZnTiBi Ferrites for High-Frequency Applications

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Abstract: LiZnTi ferrite ceramics with high saturation flux density (Bs), large remanence ratio (Br/Bs) and high saturation magnetization (4πMs) is a vital material for high frequency devices. In the present work, we prepared uniform and compact LiZnTiBi ferrite with large average grain size (>30μm) at 900°C. Firstly, the hybrid materials, including Li_2CO_3, ZnO, TiO_2, Bi_2O_3 and Fe_2O_3, were pre-sintered at 850°C at O_2 atmosphere. Next, composite additives composited of Li_2CO_3 and ZnO nanoparticles were added to control grain growth. The influences of the Li_2CO_3 and nano-ZnO (LZ) on the microstructure and magnetic properties of LiZnTiBi ferrite, especially for grain size, have been analyzed. SEM images demonstrated that moderate LZ additives (x=0.75 wt%) can prevent abnormal grains. Also, the ferrite samples possess compact microstructures. The phenomenon indicated that the LZ additive is a good sintering aid for low-temperature sintering LiZnTiBi ferrites. XRD patterns showed that all samples have a pure spinel phase. The magnetic properties, including Bs, Br/Bs and 4πMs, have weak change when LZ additives were added. However, due to smaller average grain size, the coercivity (Hc) gradually increased. Thus, a low-temperature sintering LiZnTiBi ferrite with high saturation flux density (Bs=311.10 mT), large remanence ratio (Br/Bs=0.86), low coercivity (Hc=244.6 A/m) and high saturation magnetization (Ms=75.40) was obtained when 1.00 wt% LZ additive was added. More important, the LiZnTiBi ferrite possessed uniform average grain. Such a sintering method (i.e., adding composite additive to control abnormal grain) should also promote synthesis of other advanced ceramics for practical applications.

Keywords: LiZnTiBi Ferrite, Low Temperature Sintering, Li_2CO_3, ZnO Nanoparticle, Microstructure, Magnetic Properties

1. Introduction

Recent developments and progresses in low temperature co-fired ferrite (LTCF) are attracting widely interests for miniaturized and integrated microwave devices, such as antenna, phase shifter, circulator and filter [1-5]. For instance, as a vital passive device for phased array radar array antenna, phase shifter has urgent requirement for miniaturization and integration [6]. Therefore, to develop miniaturized, high power capacity and high-frequency phase shifter, ferrite phase shifter has attracted more attentions from researchers in recent years [7]. Due to high resistivity and great magnetic properties, ferrite ceramics with low sintering temperature have been widely studied, such as LiZn ferrite [8-11].

LiZn ferrite is a good and optional material for high-frequency microwave devices because of its high Curie temperature (T_c), high remanence ratio (B_r/B_s) and large saturation magnetization ($4\pi M_s$) [12]. However, high sintering temperature of the LiZn ferrite don't meet requirement of low temperature co-fired ceramic (LTCC) technology. In addition, the high temperature can lead to Li element volatilization and cause composition segregation of the ferrite. Thus, lower sintering temperature of LiZn ferrite is vital for expanding application filed. However, when the

sintering temperature of the LiZn ferrite ceramics decreased to ~900°C, insufficient grain growth and overmuch pores of the ferrite samples resulted in reduction of magnetic performances and increase of magnetic loss. In order to realize low temperature sintering, nanoparticle, low-melting point oxides or glasses are selected as sintering additives [13-14]. In our previous work, Bi_2O_3 was proved to be a great additive, which can promote grain growth at ~920°C because of reduction of activation energy [12]. Also, to obtain uniform and compact ferrite materials, various additives, such as LBSCA, BBSA glass and V_2O_5, have been widely studied in recent years [15-17]. However, overmuch additive was added, the magnetic properties of ferrite ceramics become worse.

Therefore, in the present work, to control grain growth and obtain great magnetic properties, low-melting-point Li_2CO_3 and ZnO nanoparticle (LZ additive) are selected as fluxing agent of $Li_{0.43}Zn_{0.27}Ti_{0.13}Bi_{0.003}Fe_{2.167}O_4$ (i.e., LiZnTiBi) ferrite ceramic with low sintering temperature (~900°C). During the sintering process, the Li_2CO_3 can offset Li loss. Importantly, the nano-ZnO particle can refine grain of the ferrite and control abnormal grains. In the work, the influences of the Li_2CO_3 and ZnO nanoparticle composite additives on phase structure, microstructure, and magnetic properties of the LiZnTiBi ferrite sintered at low temperature have been discussed in detailed.

2. Main Body

2.1. Experimental Section

Firstly, raw materials, including Li_2CO_3, ZnO, TiO_2, Bi_2O_3 and Fe_2O_3 (AR, >99%, Aladdin Reagent Co., Ltd., Shanghai, China) were weighed based on the chemical formula $Li_{0.43}Zn_{0.27}Ti_{0.13}Bi_{0.003}Fe_{2.167}O_4$ (LiZnTiBi). Next, the weighed powders were blended by ball-milling method for 4 hours. In the process, the deionized water is selected as mixed media. The dried powders were pre-sintered at 850°C for 2 hours at O_2 atmosphere to form spinel phase. According to molar ratio 0.43:0.27, the various Li_2CO_3 and nano-ZnO (LZ) (x=0.00, 0.50, 0.75, 1.00 and 1.50 *wt.* %) were added into the LiZnTiBi ferrite. Again, the mixtures were milled using planetary mill with a running speed of 250 rpm/min for 6 hours. After dried, the powders were granulated using PVA adhesive. And then, these particles were pressed into toroidal samples at ~10 MPa. At last, the samples were sintered at 875°C, 900°C, and 925°C, respectively.

2.2. Characterization

XRD peaks of LiZnTiBi ferrites with various Li_2CO_3 and ZnO nanoparticles were measured by X-ray diffractometer (Cu Kα radiation, Rigaku, Japan). Scanning electron microscopy (SEM) images of the ferrites sintered at 900°C were measured using a scanning electron microscope (SEM, Q-45, and FEI). Saturation magnetization (M_s) of the ferrites was measured by vibrating sample magnetometer (VSM) with ±5000 Oe magnetic field. Volume densities of sintered samples were measured by the Archimedes method in distilled water. The density of samples can be calculated by the formula:

$$\rho = \frac{m_0 \rho_0}{m_1 - m_2} \tag{1}$$

where m_0 is weighing mass of samples in the air. After filling the gap in the samples with distilled water, the mass was weighed again, marked m_1. The m_2 is mass of samples in the water. The saturation flux density (B_s), remanence (B_r), and coercivity force (H_c) of the samples were tested with an Iwatsu BH analyzer (SY8232) in an alternating field 1600 A/m at 1 kHz. And all the tests were carried out under room temperature.

2.3. Results and Discussions

The XRD patterns of the LiZnTiBi ferrite with different LZ additives sintered at 900°C are shown in Figure 1. In the Figure 1, for all the samples, a pure spinel phase is observed. And all diffraction peaks, including (220), (311), (222), (400), (422), (511), (440), (620), (533), (622) and (444), are marked in the figure. The results indicated that adding a small quantity of Li_2CO_3 and ZnO has no influence on formation of spinel phase polycrystalline LiZnTiBi ferrites at this calcination temperature (~ 900°C). The result was consistent with the previous studied [18].

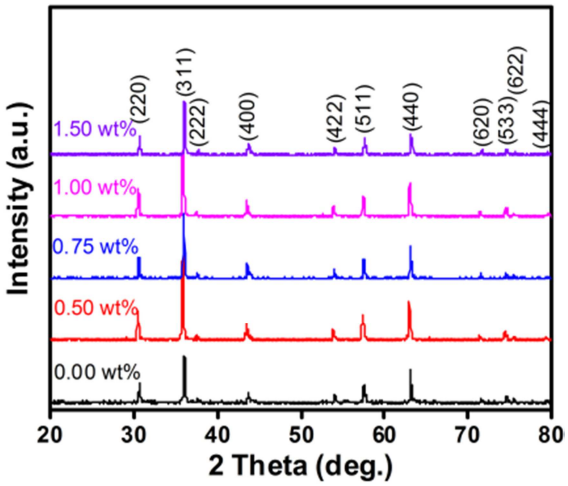

Figure 1. *XRD patterns for LZ doped LiZnTiBi ferrites.*

Microstructures of the LiZnTiBi ferrites with various LZ additives (x=0.50 wt% ~1.50 wt%) are shown in Figure 2. In the Figure 2, all sample ferrites sintered at 900°C possess big average grain size (more than 40 μm). This can attributed to introduction of Bi_2O_3, Li_2CO_3 and nano-ZnO. In the Fig. 2a, when 0.50 wt% LZ additives are added, there is some abnormal big grain (~ 100 μm). It can be explained by low activation energy and low-melting point Li_2CO_3. In addition, big grains resulted in appearance of small grains due to competitive relationship (Figure 2a). With more and more LZ additives are introduced, the LiZnTiBi ferrites possess uniform grains (see Figure 2c). This is due to increase of

ZnO nanoparticle, which can refine large grain. The phenomenon was similar with our previous work [18]. The moderate LZN nanoparticles can effectively control grain growth. However, when excessed LZ additives are added, many small grains start to appear (in the Figure 2d) because of overmuch nano-ZnO. In a word, the moderate LZ additives can promote grain growth of LiZnTiBi ferrite sintered at low temperature.

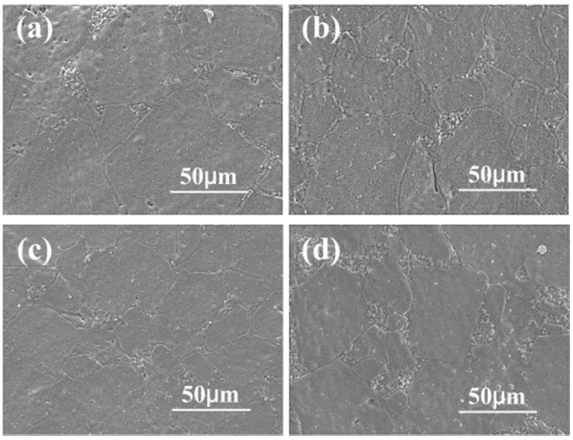

Figure 2. *SEM images of LZ doped LiZnTiBi ferrites: (a)x=0.50 wt%, (b)x=0.75 wt%, (c)x=1.00 wt% and (d)x=1.50 wt%.*

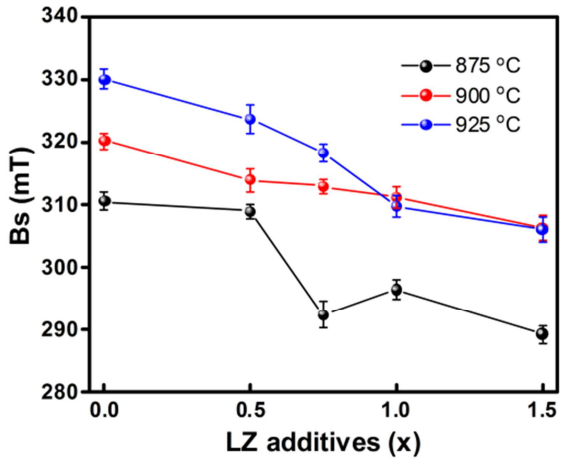

Figure 3. *Saturation flux density (Bs) of LiZnTiBi ferrites with various LZ additives sintered at different temperature.*

Figure 3 show that saturation flux density (B_s) of LZ doped LiZnTiBi ferrite sintered at different temperatures. It is apparent that the high sintering temperature can enhance B_s of the LiZnTiBi ferrite due to grain growth. When sintering temperature of samples is same, the ferrite sample with more LZ additives possesses low B_s value. However, the variation of B_s value is very small. For example, for ferrite samples sintered at 900°C, the value of B_s decrease from 320.2 mT to 306.2 mT, which is remain exceed 300 mT. The value was close to data reported by Liao et al. [19]. It was indicated that LZ is a selectable additive for the LiZnTiBi ferrite. The B_s value of samples sintered at 875°C have a large change when LZ additive more than 0.50 wt%, which can be explained by small grains (sintering temperature is too low). In a word, because of introduce of LZ additive, the abnormal grain size can be controlled (see Figure 2c), the B_s of samples slightly reduced.

Figure 4 shows that remanence ratio (B_r/B_s) of the ferrites. The change of B_r/B_s is opposite with B_s. In the Figure 3, the samples sintered at 875°C have larger saturation flux density. However, in the Figure 4, the remanence ratio is smallest. In addition, the introduction of LZ additives leads to reduction of B_r/B_s. But for all samples, the B_r/B_s value is more than 0.83. The results indicated that the LZ doped LiZnTiBi ferrite possesses high remanence ratio.

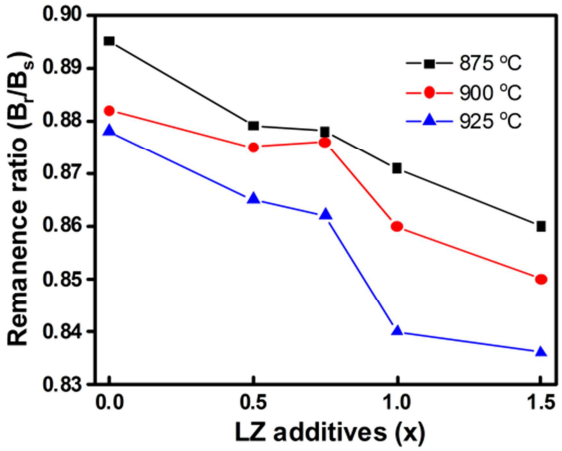

Figure 4. *Remanence ratio (B_r/B_s) of LZ doped LiZnTiBi ferrites.*

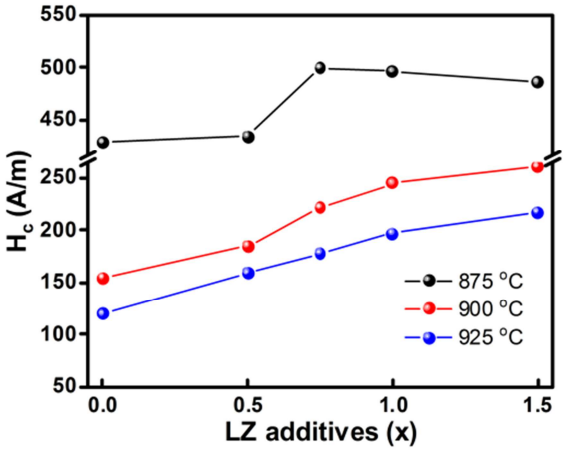

Figure 5. *Changes of coercivity value of LZ doped LiZnTiBi ferrites.*

The coercivity (H_c) of LZ doped LiZnTiBi ferrite sintered at low temperatures are displayed in Figure 5. In general, the coercivity (H_c) is inversely proportional to the grain size. Thus, in the Figure 5, the samples sintered at higher temperature have lower H_c value. Also, the change that H_c is consistent with grains size when various LZ additives were added. For the samples sintered at 875°C, the H_c value more than 400 A/m. The result is due to small grains. When sintering temperature more than 900°C, the H_c value obviously decreased.

The saturation magnetization of LZ doped LiZnTiBi ferrite sintered at 900°C is shown in Figure 6. In the Figure 6, all ferrite samples have similar magnetization curve. When

external magnetic field exceeds 2500 Oe, the samples are close to saturated state. The values of Ms are listed in Table 1. With the increase of LZ additives, the value of M_s gradually decreases. However, all samples have a high saturation magnetization (M_s >70 emu/g). Thus, adding LZ additives has a little influence on saturation magnetization of LiZnTiBi ferrite.

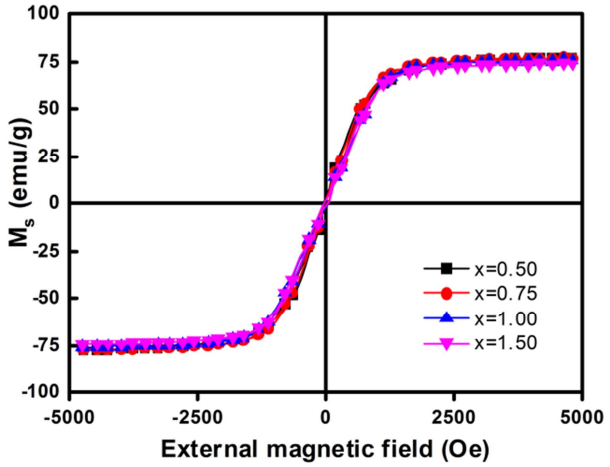

Figure 6. *Saturation magnetization (M_s) of different LZ doped LiZnTiBi ferrite ceramics sintered at 900°C.*

Figure 7 shows that density of the LZ doped LiZnTiBi ferrite sintered at different temperatures. As shown in Figure 7, high sintering temperature can improve density of the LiZnTiBi ferrite samples due to enhance of grain growth and reduction of pores. In addition, when the ferrite samples were sintered at same temperature, the density of sample start to increased and then decreased. The phenomenon that improved density can be attributed to reduction of abnormal grains and densification. However, due to lower density of LZ composite additives, the density of ferrite samples started to reduce when more LZ additives were added. At last, when 0.75 wt% LZ additives were added, the ferrite possessed highest density at every sintering temperature.

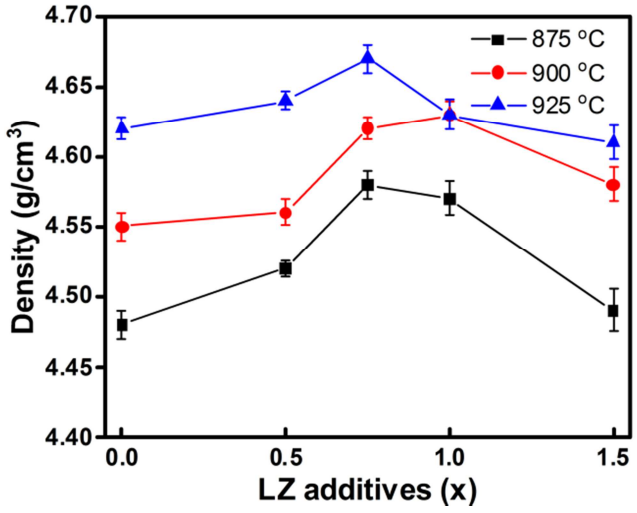

Figure 7. *Density of different LZ doped LiZnTiBi ferrite ceramics sintered at different sintering temperatures.*

Table 1 show important parameters of the LZ doped LiZnTiBi ferrite sintered at 900°C. The data of the table indicated that the LiZnTiBi ferrite with 1.00 wt% possesses high saturation flux density (B_s=311.1mT), high remanence ratio (B_r/B_s=0.86) and low coercivity (H_c=244.6 A/m). Moreover, the SEM image show the sample possesses uniform and compact grains.

Table 1. *Important parameters of LZ doped LiZnTiBi ferrite sintered at 900°C.*

LZ (wt%)	B_s	B_r/B_s	H_c	Density (g/cm^3)	M_s(emu/g)
0.00	320.2	0.88	154.6	4.55	78.64
0.50	313.9	0.87	185.2	4.56	76.74
0.75	312.9	0.87	221.3	4.62	76.72
1.00	311.1	0.86	244.6	4.63	75.40
1.50	306.2	0.85	260.5	4.58	73.79

3. Conclusion

In this work, low-melting point Li_2CO_3 and nano-ZnO were selected as a new composite additive (LZ), which was added to LiZnTiBi ($Li_{0.43}Zn_{0.27}Ti_{0.13}Bi_{0.003}Fe_{2.167}O_4$) ferrite ceramic to promote solid-phase reaction at low temperature. Results, including saturation flux density (B_s), remanence ratio (B_r/B_s) and saturation magnetization (M_s) indicate that the LZ is a good additive. The magnetic properties of the LiZnTiBi ferrite ceramic have a weak deterioration. For example, the B_s reduced from 320.2 mT to 311.1 mT when 1.00 wt% LZ was added. And the value of B_r/B_s reduced from 0.88 to 0.86. However, SEM image shows that the abnormal grains can be controlled by adding 1.00 wt% LZ additive. At last, a LiZnTiBi ferrite with great magnetic properties and uniform grains was obtained by using a new LZ additive when sintered at low temperature.

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