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Effect of Mn$^{3+}$ doping on the loss of Li$_{0.37}$Zn$_{0.26}$Ti$_{0.12}$Fe$_{2.37}$O$_{4}$ ferrite

Aya Li ©
Westa College, Southwest University, Chongqing, People’s Republic of China
E-mail: liaya000201@163.com

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Abstract
In this paper, a series of the gyromagnetic ferrite Li$_{0.43}$Zn$_{0.26}$Ti$_{0.12}$MnxFe$_{2.19}$O$_{4}$ (x = 0–0.14) samples were prepared with the solid-phase reaction sintering method. The influences of Mn$^{3+}$ doping on the microscopic morphology, ferromagnetic resonance linewidth, and microwave dielectric loss of LiZnTi ferrite were investigated. Doping in an appropriate amount of Mn$^{3+}$ will reduce the saturation magnetization of the sample and the magnetocrystalline anisotropy of the ferrite. It also inhibited the generation of Fe$^{2+}$ and reduced the porosity, to the benefit of keeping the ferromagnetic resonance linewidth ($\Delta H$) of the material and microwave dielectric loss at a low level. The results suggested that when the doping amount of Mn$^{3+}$ is 0.08, the ferromagnetic resonance linewidth of the material is $27.8 \times 10^{-5}$ A m$^{-1}$, the microwave dielectric loss tangent $\tan \delta$, equals to 0.001, and the B-H hysteresis loop remanence ratio of the sample reaches 0.87, which is a beneficial application in lock-type microwave ferrite devices.

1. Introduction

LiZn ferrite has been widely used in ferrite devices and self-locking microwave iron, for instance, ferrite microwave phase shifters, microwave ferrite switches, and so on, taking the advantage of its high gyromagnetic properties, low loss, good temperature stability, and high hysteresis loop remanence ratio [1–3]. In the past decades, the use of LiZn ferrite was dramatically developed in microwave electronic systems, such as radar and communication systems. Currently, reducing magnetic loss and keeping a high hysteresis loop squareness ratio are still challenges in putting forward on the electromagnetic properties of LiZn ferrite materials in lock-type microwave ferrite devices.

The loss of LiZn ferrite in microwave devices generally includes microwave magnetic loss, electrical loss, and low field loss. Among them, the magnetic loss is characterized by ferromagnetic resonance linewidth ($\Delta H$), which mainly consists of magnetocrystalline anisotropy field-induced linewidth, stomatal-induced linewidth, and intrinsic linewidth [4]. To reduce the microwave loss of materials, a two-step sintering method under the oxygen atmosphere is employed in the preparation process to obtain a larger grain size [5]. The sintering temperature of the material can be reduced by adding low melting point fluxes such as Bi$_2$O$_3$. This procedure not only suppresses the volatilization of Li$^+$, but also adds low melting point fluxes for increasing the sintering density of the material, assisting the growth of the grain, and reducing the porosity of the material [6, 7]. Thereby, the ferromagnetic resonance linewidth and side effects of component segregation of the dielectric properties are reduced [8]. The reduction of the linewidth of material ferromagnetic resonance benefits from the application of iron-deficiency formula and lithium-rich formula [9, 10]. Meanwhile, these formulae promote the densification of the material and increase the grain size for inhibiting the production of Fe$^{2+}$ and lowering the dielectric loss of the material to a certain extent [11, 12]. For the sake of cutting down the electrical loss of the material, in the process, the sample after the second sintering is annealed in an oxygen atmosphere to oxidize the Fe$^{2+}$ to Fe$^{4+}$ in the material decreasing the electronic transition from Fe$^{3+}$ to Fe$^{4+}$ [13]. LiZn ferrite is working in a remanence state in a self-locking microwave device, and only in a saturated magnetization state, the material can avoid the low field loss. Consequently, the low field loss of the material is restrained by heightening the
hysteresis loop squareness ratio, which makes the residual magnetization close to the saturation magnetization of the material.

Based on the formula of Li_{0.43}Zn_{0.26}Ti_{0.12}Fe_{2.19}O_{4+} and the relatively excellent sintering temperature of 1050 °C [14], this study aimed to investigate the influence of Mn^{3+} doping and sintering temperature adjusting on the magnetic and electrical properties of the material, for further cutting down microwave magnetic loss and electrical loss of LiZn ferrite material. Sequentially, optimize the doping amount and material sintering temperature, and provide a material basis for the development of high-performance microwave ferrite devices.

2. Experiment

According to the molar ratio of Li_{0.43}Zn_{0.26}Ti_{0.12}Mn_{x}Fe_{2.19}O_{4+} (x = 0, 0.04, 0.08, 0.12, 0.14) for compounding, the raw materials were high-active analytically pure Li_{2}CO_{3}, ZnO, TiO_{2}, Mn_{3}O_{4}, and Fe_{2}O_{3}. Those mixtures were divided into different control groups according to varied Mn^{3+} doping amount. After the raw materials were weighed according to the standard formula, each group of samples was ball-milled for the first time at a speed of 260 r min^{-1} for 6 h. The mixtures were dried and sieved into powder and were placed in a muffle furnace at 1000 °C for 2 h. Then they were mixed with 0.5 wt% Bi_{2}O_{3} as a flux to the pre-fired material for 6 h of secondary ball milling. When the ball mill slurries were dried, 9 wt% polyvinyl alcohol was added as a binder to granulate before pressing them into a strip under the pressure of 10 Mpa. The products were sintered at a temperature of 980 °C, 1000 °C, 1020 °C, 1050 °C, 1070 °C, and kept warm in the air for 2 h. The sintered samples were processed into rod shape (diameter of 1.6 mm; length of 22 mm) and a ring (outer diameter of 18 mm; inner diameter of 8 mm; thickness of 5 mm) to measure the dielectric loss and the B-H curve of the material, respectively. Finally, part of the sample was blown into small spherical samples with a diameter of 0.5 mm for ferromagnetic resonance linewidth measurement.

(DX2700, Cu target, Kα radiation, 40 Kv, 40 mA) X-Ray diffractometer was chosen to analyze the phase formation and lattice constant (a) of the powder sample and the XRD characterization scans at a speed of 2.5 degrees per minute; use Quanta FEG250 scanning electron microscope to characterize the microscopic morphology of the cross-sectional surface of the sample and average it. The average grain size of the material was calculated with the intercept method. The B-H curve of the material was measured by using Linkjoin MATS-2010SD B-H analyzer. The M-H curve of the bulk sample was measured with the BHV525 vibrating sample magnetometer, and the saturation magnetization (M_s) of the sample was derived from the curve. The theoretical density of the sample was obtained from the formula (1); the density d of the annular sample was measured with the drainage method, and the porosity P of the sample was determined with the formula (2). The ferromagnetic resonance linewidth (∆H) of the sample was measured at the resonance frequency of 9.375 GHz. According to IEC 60556:2006, once the rod sample was placed in the TM_{010} mode at 10.7 GHz, a magnetic field was simultaneously applied to the cylindrical resonant cavity to determine the microwave complex permittivity and dielectric loss tangent (tanδ_e) of the rod-shaped sample.

\[
d_{t} = \frac{8m}{na^3}
\]

Where m is molecular weight, and n is Avogadro constant.

\[
P = \left(1 - \frac{d}{d_{t}}\right) \times 100\%
\]

Where P is the porosity of the material, d is the density of the material measured with the drainage method, and \(d_{t}\) was the theoretical density of the material.

3. Results and discussion

Figure 1 shows the XRD pattern of the Mn^{3+} doped samples sintered at 1050 °C. It presents in figure 1(a) that the XRD patterns corresponding to the samples with different doping levels all have the same characteristic peaks as the standard card: (220), (311), (222), (400), (422), (511), (440), indicating that the sample formed a pure spinel phase. Figure 1(b) is a partially enlarged view of the diffraction peaks in the range of 35° to 35.8° for Mn^{3+} doped samples. As we can see, the (311) reflection shifts to a higher angle (from x = 0 to x = 0.04), it can be explained that there can be some reflection of lattice distortion caused by macroscopic residual stress in sample x = 0.04. Further analysis of figure 1(b) illustrated that the characteristic diffraction peaks of the samples (from x = 0.04 to x = 0.14) shifted to a small angle with the increase of Mn^{3+} doping. The shift of diffraction peaks was the result of the alteration of crystal structure after doping. As a spinel ferrite, the unit cell of LiZn ferrite has oxygen tetrahedral voids (A site) and octahedral voids (B site). Mn^{3+} with an ionic radius is about 0.072 nm preferred to
occupy B site which was larger than that of Fe$^{3+}$ (0.069 nm). Therefore, the B-site gap caused by the entry of doped ions became larger, which contributed to the increase of the lattice constant and the shift of diffraction peak of the material with a small angle.

Figures 2(a)–(d) are the SEM images of the cross-sections of the Mn$^{3+}$-doped samples ($x = 0.08$) at different sintering temperatures. In figure 2, as the amount of Mn ions doping increases, the grain size was no longer raised notably. The grain boundaries were decreased, and the density of material was further improved. At the same time, figure 3 suggests that the porosity of the material also decreased remarkably with the increased grain size.

Figures 4(a)–(e) are the SEM images of the cross-sections of the Mn$^{3+}$-doped samples ($x = 0$–0.14) at the sintering temperature of 1000 °C, respectively. In figure 4, as the amount of Mn ions doping increases, the grain

**Figure 1.** (a) XRD patterns of Li$_{0.43}$Zn$_{0.26}$Ti$_{0.12}$MnxFe$_{2.19-x}$O$_4$ (x = 0, 0.04, 0.08, 0.12, 0.14) ferrites at 1050 °C. (b) the diffraction peaks are indexed to (311) of the spinel structure of samples.

**Figure 2.** SEM images of Li$_{0.43}$Zn$_{0.26}$Ti$_{0.12}$MnxFe$_{2.19-x}$O$_4$ (x = 0.08) at different sintering temperatures.
size of sample increases. At the same time, as shown in figure 5, the porosity of the material also decreases and Mn ion doping increases the density of the sample.

The gyromagnetic properties of LiZn ferrite are related to saturation magnetization ($M_s$). The higher the $M_s$ is, the stronger the gyromagnetic properties will be. However, the increment in $M_s$ makes the material more likely to resonate naturally under the action of microwave signals and increases the low field loss. Meanwhile, an excessively high level of $M_s$ leads to a large amount of excitation of spin-wave while the material is working in a high-power device, and a higher loss of the device. To prevent the material from being affected by low field loss during work, $M_s$ and the operating frequency should satisfy the relationship of formula (3). Therefore, when the operating frequency does not match $M_s$, low field loss can be avoided by adjusting $M_s$.

After sintering at 1050 °C, the saturation magnetization of each sample doped with Mn$^{3+}$ is illustrated in figure 6. In figure 6, with the growth of Mn$^{3+}$ doping, the saturation magnetization of the material shows a downward trend. Because Mn$^{3+}$ likes to occupy the B site, it replaces the magnetic ion Fe$^{3+}$ as a non-magnetic ion, which reduces the total molecular magnetic moment of the material. Thereby, the magnitude of $M_s$ of the material drops. Hence, the purpose of adjusting $M_s$ of the material can be achieved by doping an appropriate

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**Figure 3.** Porosity of Li$_{0.43}$Zn$_{0.26}$Ti$_{0.12}$Mn$_x$Fe$_{2.19-x}$O$_4$ (x = 0.08) at different sintering temperatures.

**Figure 4.** SEM images of Li$_{0.43}$Zn$_{0.26}$Ti$_{0.12}$Mn$_x$Fe$_{2.19-x}$O$_4$ (x = 0–0.14) sintering at 1000 °C.
amount of Mn$^{3+}$. At the same time, the additional Mn$^{3+}$ reduced the magnetostriction coefficient of the material, which was beneficial to increase the remanence squareness ratio of the hysteresis loop of the material.

Figure 7 shows the B-H curve of Li$_{0.43}$Zn$_{0.26}$Ti$_{0.12}$Mn$_x$Fe$_{2.19-x}$O$_4$ ($x = 0.08$), sintered sample at 1050 °C. The squareness ratio of the hysteresis loop of the material reaches 0.87.

$\gamma \frac{4\pi M_r}{\omega_{\text{work}}} = 0.4 - 0.75$  \hspace{1cm} (3)

Among them, $\gamma$ is the gyromagnetic ratio and $\omega_{\text{work}}$ is the working angular frequency of the material.

The microwave magnetic loss of the material is characterized by the ferromagnetic resonance linewidth. The main component of $\Delta H$ of LiZn ferrite is given by formula (4), where the magnetocrystalline anisotropy field-induced linewidth ($\Delta H_a$) can be calculated using the formula (5). $\Delta H_a$ is related to the magnetocrystalline anisotropy constant ($|K_1|$) and $M_r$. According to the law of approaching saturation [15], the value of $|K_1|$ is derived and then given in figure 8. When the sintering temperature is 1050 °C, the value of $|K_1|$ of each sample is between 3.5 KJm$^{-3}$ and 4.8 KJm$^{-3}$, which is similar to the value of $|K_1|$ of the formula Li$_{0.5-0.5x}$Zn$_x$Ti$_{0.5-0.5x}$Fe$_{2.5-0.5x}$O$_4$ ($x = 0.2-0.64$) [16]. What could be derived from figure 8 is that $|K_1|$ decreases observably with the increase of the Mn$^{3+}$ doping amount. The rationale behind this is that Mn$^{3+}$ replaces Fe$^{3+}$, which reduces the super-exchange between A and B sites, resulting in a decrease in $|K_1|$. Given in figure 9 is the $\Delta H_a$ value of the sample sintering at 1050 °C. It can be seen from the figure that $\Delta H_a$ does not change notably with the increase of Mn$^{3+}$ doping amount, which can be attributed to the fact that the doping of Mn$^{3+}$ leads to the drop in the value of $|K_1|$. At the same time, $M_r$ also decreased, resulting in the variation of the Mn$^{3+}$ doping amount without causing the change of $\Delta H_a$. 

Figure 5. Porosity of Li$_{0.43}$Zn$_{0.26}$Ti$_{0.12}$Mn$_x$Fe$_{2.19-x}$O$_4$ ($x = 0-0.14$) sintering at 1000 °C.

Figure 6. Saturation magnetization of Mn$^{3+}$ doped samples at sintering temperature of 1050 °C.
Figure 7. B-H curve of Li_{0.43}Zn_{0.26}Ti_{0.12}Mn_{x}Fe_{2.19-x}O_4 (x = 0.08) sample at sintering temperature of 1050 °C.

Figure 8. Magnetocrystalline anisotropy constant of Li_{0.43}Zn_{0.26}Ti_{0.12}Mn_{x}Fe_{2.19-x}O_4 (x = 0–0.14) samples sintering at 1050 °C.

Figure 9. Magnetocrystalline anisotropy field-induced linewidth constant of Li_{0.43}Zn_{0.26}Ti_{0.12}Mn_{x}Fe_{2.19-x}O_4 (x = 0–0.14) samples sintering at 1050 °C.
The porosity broadening ($\Delta H_p$) of ferromagnetic resonance linewidth can be determined with the formula (6). The magnitude of $\Delta H$ for each Mn$^{3+}$ doped sample at different sintering temperatures is shown in Figure 10. With the increase of sintering temperature, $\Delta H$ decreases significantly. When the doping amount of Mn$^{3+}$ is 0.08, and the sintering temperature is 1050 °C, $\Delta H$ of the material is $27.8 \times 10^3$ A m$^{-1}$. With the increase of the sintering temperature, the grains grow sufficiently and get bigger. Meanwhile, Mn$^{3+}$ doping is beneficial to increase the density and reduce the porosity of the material, thereby effectively lessening the $\Delta H_p$ of material. Table 1 shows $\Delta H_p$ of the material calculated by the size of $P$. Looking at table 1 below, it is apparent that when the Mn$^{3+}$ doping amount is 0.08, $\Delta H_p$ decreases from $34.9 \times 10^3$ A m$^{-1}$ to $17.3 \times 10^3$ A m$^{-1}$ with the increase of sintering temperature. Compared with the ferromagnetic resonance linewidth caused by the magnetocrystalline anisotropy, the porosity widening effect of the sample has a greater impact on the ferromagnetic resonance linewidth of the material.

$$\Delta H = \Delta H_a + \Delta H_p + \Delta H_i + \Delta H_{oth}$$  \hspace{1cm} (4)$$

Among them, $\Delta H_a$ is the field-induced linewidth of magnetocrystalline anisotropy; $\Delta H_i$ is the material intrinsic linewidth; $\Delta H_{oth}$ is the linewidth of the ball surface roughness. For LiZn ferrite, $\Delta H_i$ is less than 10Oe, and $\Delta H_{oth}$ is only a few Oersteds, which both can be ignored [17].

$$\Delta H_a = \frac{2.07 \times H_a^2}{4\pi M_s} G(\omega_i, \omega_i)$$  \hspace{1cm} (5)$$

Among them, $H_a$ is the magnetocrystalline anisotropy field, $H_a = 2|K_1|/M_s G(\omega_i, \omega_i)$ is a factor related to frequency, usually equals to 1 at high frequency [18].

$$\Delta H_p = \frac{0.56}{\cos \theta_a} \frac{4\pi M_s P(1 - P)}{P}$$  \hspace{1cm} (6)$$

Where $\theta_a$ is the polar angle of a magnetron with uniform precession of the same energy, and $\cos \theta_a$ is usually 0.33. The electrical loss of LiZn ferrite is characterized by dielectric loss, which is affected by factors such as material microscopic morphology and conductivity. Figure 11 shows the dielectric loss tangent ($\tan \delta$) for each sintering temperature and each Mn$^{3+}$ doping amount. It can be seen from the figure that when the doping amount $x = 0, 0.12, 0.14$, the $\tan \delta$ of the material decreases first and then increases with the growth of the
sintering temperature. It can be explained that the increase of the sintering temperature makes the material denser and reduces the \( \tan \delta \); when the sintering temperature continues to rise, from 1050 °C to 1070 °C, the easily volatile Li and Zn elements in the material become more volatilized and the material components segregate, resulting in an increase in Fe\(^{2+}\) in the material and a surge in the dielectric loss of the material. What can be obtained from the formula (7) is that the doping of Mn\(^{3+}\) cuts down the generation of Fe\(^{2+}\) to suppress the electron migration between Fe\(^{2+}\) and Fe\(^{3+}\). The results given in figure 11 demonstrates that when the sintering temperatures are 1000 °C and 1050 °C and the Mn\(^{3+}\) doping amount is 0.08, \( \tan \delta \) decreases to \( 9 \times 10^{-4}, 10 \times 10^{-4} \), respectively. Yet at the same sintering temperature, when the doped Mn content \( x = 0.12, 0.14 \), the dielectric loss of the material starts to increase. At this moment, excessive cations appear in the material, which makes most of the carriers in the material become free electrons that increase the probability of transition between ions greatly. As a result, the dielectric loss of the material starts to increase as the amount of Mn\(^{3+}\) doped increases. From the description above, the squareness ratio reaches 0.87 when the sintering temperature is 1050 °C, and the \( \Delta H \) is \( 27.8 \times 10^3 \) Am\(^{-1}\). To keep \( \tan \delta \) and \( \Delta H \) low, and a relatively high level of the hysteresis loop rectangle, 1050 °C is the best sintering temperature. Currently, the microwave complex dielectric constant of the sample is 14.5, and the \( \tan \delta \) equals to \( 1 \times 10^{-3} \).

\[ \text{Fe}^{2+} + \text{Mn}^{3+} \rightarrow \text{Fe}^{3+} + \text{Mn}^{2+} \]  

(7)

4. Conclusions

The present study was undertaken to investigate the preparation of Mn\(^{3+}\)-doped Li\(_{0.43}\)Zn\(_{0.26}\)Ti\(_{0.12}\)Mn\(_x\)Fe\(_{2.19-x}\)O\(_4\) ferrite and the influence of microwave magnetic loss and dielectric loss. The findings indicate that Mn\(^{3+}\) doping decreases the saturation magnetization and magnetocrystalline anisotropy of the sample, and increases the sintering density. The decrease of the ferromagnetic resonance linewidth of the sample is associated with Mn\(^{3+}\) doping that is effectively reduced the porosity. The incorporation of Mn\(^{3+}\) restrains the generation of Fe\(^{2+}\) and leads reduction of the microwave dielectric loss of the material. Overall, the optimal doping amount Mn\(^{3+}\) is 0.08, and the sintering temperature of the material is 1050 °C.

ORCID iDs

Aya Li © https://orcid.org/0000-0002-0835-8037

References

[1] Ziarati A et al 2017 Sonication method synergism with rare-earth-based nanocatalyst: preparation of NiFe\(_{2}\)-\(_x\)Er\(_{y}\)O\(_4\) nanostructures and its catalytic applications for the synthesis of benzimidazoles, benzoazoles, and benzothiazoles under ultrasonic irradiation J. Rare Earths 35 374–81
[2] White G O and Patton C E 1978 Magnetic properties of lithium ferrite microwave materials J. Magn. Magn. Mater. 9 299–317
[3] Van Hook H 1971 Microwave loss in low-magnetization polycrystalline garnets: a comparison of Ga and CA-V-In-substituted YIG Magnetics IEEE Transactions on 7 770–3
[4] Brower C J and Patton C E 1982 Determination of anisotropy field in polycrystalline lithium ferrites from FMR linewidths J. Appl. Phys. 53 2104–6
[5] Liao Y et al 2015 Low temperature firing of Li_{0.43}Zn_{0.27}Ti_{0.13}Fe_{2.17}O_{4} ferrites with enhanced magnetic properties J. Am. Ceram. Soc. 98 2556–60
[6] Liao Y et al 2017 Magnetic properties of low temperature sintered LiZn ferrites by using Bi_{2}O_{3}–Li_{2}O–CaO–SnO_{2}–B_{2}O_{3} glass as sintering agent Ceram. Int. 46 3357–64
[7] Xin L W et al 2019 Effects of La_{2}O_{3}–B_{2}O_{3}–ZnO glass additive on the gyromagnetic properties and microstructure of low temperature sintered LiZn ferrites Journal of Magnetic Materials and Devices 52 346–57
[8] Liu C et al 2008 Effects of sintering temperature and Bi_{2}O_{3} content on microstructure and magnetic properties of LiZn ferrites J. Magn. Magn. Mater. 320 1335–9
[9] Sun K et al 2016 Rietveld refinement, microstructure, and ferromagnetic resonance linewidth of iron-deficiency NiCuZn ferrites J. Alloys Compd. 681 139–45
[10] Spencer E G, Lepore D A and Nielsen J W 1968 Measurements on lithium ferrite crystals having Near-Zero defect concentrations J. Appl. Phys. 39 732–3
[11] Akhter S C 2013 Influence of In_{2}O_{3} addition on the magnetic and electrical properties of Iron—deficient Ni–Zn ferrite Journal of Bangladesh Academy of Ences 33 85–91
[12] Samuel D J 1967 Low-temperature nonlinear effects in High-Saturation magnetization ferrites J. Appl. Phys. 38 1417–8
[13] Teo M L S et al 2008 Development of magneto-dielectric materials based on Li–ferrite ceramics J. Alloys Compd. 459 557–66
[14] Yin Q et al 2019 Study of the microstructure and microwave magnetic characteristics of Ti-doped Li–Zn ferrite J. Mater. Sci.: Mater. Electron. 30 5430–7
[15] You J, Kim H J and Yoo S I 2017 Preparation of strontium W-type hexaferrite in low oxygen pressure and their magnetic properties J. Alloys Compd. 695 3011–7
[16] Dionne G F 1969 Magnetic–anisotropy and magnetostriction constants of substituted lithium ferrites at 300°K J. Appl. Phys. 40 4486–90
[17] Schlömann E 1959 Ferromagnetic resonance in polycrystals J. Phys. Radium 20 327–32
[18] Schlömann E 1958 Spin-wave analysis of ferromagnetic resonance in polycrystalline ferrites J. Phys. Chem. Solids 6 242–56