Influences of Ti$^{4+}$ and Mg$^{2+}$ substitutions on the properties of lithium ferrites

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Abstract. The Ti$^{4+}$ and Mg$^{2+}$ co-substituted lithium ferrites with different compositions of Zn$_{0.1}$Li$_{0.45}$Mn$_{0.1}$Fe$_{2.35-2x}$ (TiMg)$_x$O$_4$ (x=0.0-0.5) were prepared by the ceramic standard processing. The magnetic properties and microstructure of the samples were investigated. A single phase spinel structure was confirmed by XRD in substituting range. Sintering densities continuously decreased with the increase at $x$ value, which was attributed to the fact that the heavier Fe$^{3+}$ ions were replaced by the relatively lighter Ti$^{4+}$ and Mg$^{2+}$ ions. However, relative density of the samples had no obvious relationship with the substituting value. Saturation magnetization continuously decreased with $x$ value, which was attributed to the decrease of resultant magnetic moment between A and B sub-lattice. Remanence decreased monotonously with $x$ value due to the decrease of saturation magnetization and magnetocrystalline anisotropy constant. But the effect of Ti$^{4+}$ and Mg$^{2+}$ substitutions on the Br/Bs ratio values was not obvious. Coercive force was mainly determined by the microstructure and magnetocrystalline anisotropy constant of the ferrites. In this research, with the increase of Ti$^{4+}$ and Mg$^{2+}$ substitutions, the advantageous influence by the decrease of magnetocrystalline anisotropy constant was more significant than the disadvantageous influence caused by the increase of closed pores. As a result, coercive force of the ferrites also decreased monotonously with the increase at $x$ value.

1. Introduction

Li-based spinel ferrites have been widely used in high frequency magnetic applications, such as circulators, phase shifters and isolators, due to their high Curie temperature, high saturation and hysteresis loop properties offer performance advantages over other spinel structure [1-5]. The properties desired for specific applications have been provided by controlling the preparation conditions or by adopting appropriate substitutions. Till now, the conventional way of producing these ferrite materials is by the solid state reaction of oxide/carbonate and calcined at high temperature. Furthermore, some different soft-chemic methods, such as coprecipitation, sol-gel synthesis, alkoxide hydrolysis, hydrothermal reaction and citrate route have also been reported to prepared lithium ferrites [6-8]. As for the influences of substitutions, probably the substitutions of Zn and Mn are best known to improve the magnetization and electrical resistivity respectively [9]. In addition, some sintering aids [10-11], such as cordierite glass, which can lower sintering temperature, have also been introduced with beneficial influences on magnetic properties. To meet requirements of different microwave magnetic devices, which possibly work at different frequency band, properly adjusting the saturation magnetization of the ferrites is necessary. At the same time, other magnetic properties, such as Br/Bs.
(remanence/Saturation flux density) ratio, Hc (coercive force), can’t be depressed. In this paper, we substituted the Fe$^{3+}$ ion with the Ti$^{4+}$ and Mg$^{2+}$ ions synchronously to adjust saturation magnetization of the lithium ferrites, and prepared Zn$_{0.1}$Li$_{0.45}$Mn$_{0.1}$Fe$_{2.35-2x}$(TiMg)$_{x}$O$_4$ (x=0.0, 0.1, 0.2, 0.3, 0.4 and 0.5) ferrites by the conventional ceramic processing. To lower sintering temperature and prevent lithium element volatilizing, 0.5wt% Bi$_2$O$_3$ additive was added in all samples. And the influences of Ti$^{4+}$ and Mg$^{2+}$ co-substitution on the magnetic properties and microstructure of the lithium ferrites were studied in detail.

2. Experimental details

The lithium ferrite samples were prepared by the solid state reaction method. Analytical grade Fe$_2$O$_3$, ZnO, Li$_2$CO$_3$, MnCO$_3$, TiO$_2$ and MgO were weighed following the compositions of Zn$_{0.1}$Li$_{0.45}$Mn$_{0.1}$Fe$_{2.35-2x}$(TiMg)$_{x}$O$_4$ (x=0.0, 0.1, 0.2, 0.3, 0.4 and 0.5). The oxides were wet-mixed in planetary mills firstly. After drying, the mixtures were calcinated at 800$^\circ$C in air. Then the calcinated powders were mixed with 0.5wt% Bi$_2$O$_3$ and wet-milled in planetary mills again. Following the addition of polyvinyl alcohols (PVA), the milled powders were granulated and pressed into toroidal shaped samples, which were finally sintered at varying temperatures from 900$^\circ$C to 1000$^\circ$C in 50$^\circ$C intervals, and left to cool inside the electric furnace.

Phase purity were checked by X-ray diffraction (XRD), using Cu K$_\alpha$ radiation. Densities of the sintered specimens were calculated by mass/volume ratio. Relatively density values were obtained by comparing sintering density and X-ray density of the samples. Microstructures were obtained using scanning electron microscopy (SEM). Saturation magnetization (4$\pi$M$_s$), remanence (Br) and coercive force (Hc) of the samples were tested by a B-H analyzer (IWATSU, SY8232).

3. Results and discussion

The diffraction patterns of the 900$^\circ$C sintered samples with x=0.0, 0.3, 0.5 are presented in Figure 1. A single phase spinel structure is observed for all samples, no second phase is detected. So it can be concluded that the Ti$^{4+}$ and Mg$^{2+}$ substitutions fully enter into the spinel lattice in the substituting range.

![Figure 1. X-ray diffraction patterns of the samples with different substitutions](image)

Figure 2 shows the sintering density and relative density values as a function of the x value for the samples sintered at 900$^\circ$C, 950$^\circ$C and 1000$^\circ$C. It is seen that both sintering densities and relative densities gradually increase with increasing sintering temperature for all samples. Furthermore, with increasing content of Ti$^{4+}$ and Mg$^{2+}$ substitutions, sintering densities decrease monotonously. This fact
is attributed to that the heavier Fe$^{3+}$ ions are replaced by the relatively lighter Ti$^{4+}$ and Mg$^{2+}$ ions in the present case. However, the relative densities have no obvious relationship with the substituting values, which means that the Ti$^{4+}$ and Mg$^{2+}$ substitutions don’t markedly influence the sintering characteristic of the samples.

Relationship between saturation magnetization and x value for the samples sintered at different temperatures is shown in Figure 3. It clearly indicates that the saturation magnetization values present an approximatively linear decrease with the increase of x value. On the basis of site preference energy, it is known that Ti$^{4+}$ and Mg$^{2+}$ ions preferably occupy the octahedral site by replacing Fe$^{3+}$ ions. In view of this, the cation distribution of the ferrites can be written as

\[
(Zn_{0.1}^{2+}Fe_{0.9}^{3+})_x[Li_{0.45}Mn_{0.5}^{3+}Ti_{1-x}^{4+}Mg_x^{2+}Fe_{1.45-2x}^{3+}]_yO_{4}^{2-}
\]

Both Ti$^{4+}$ and Mg$^{2+}$ are non-magnetic ions. With increasing x value, the resultant magnetic moment between A and B sub lattice gradually decreases. As a result, saturation magnetization values of the lithium ferrites decrease. However, the saturation magnetization values show no significant dependence with the sintering temperature, especially for the samples sintered at 950°C and 1000°C. This fact is attributed to that with increasing sintering temperature; the advantage influence of increased density on saturation magnetization may be counteracted by the disadvantage influence of lithium volatilization on saturation magnetization.
Influences of the Ti$^{4+}$ and Mg$^{2+}$ substitutions on Br and Br/Bs ratio properties of the samples are shown in Figure 4. It can be seen that remanence values also continuously decrease with increasing $x$ value, despite different sintering temperature. First reason leaded to this fact is due to the decrease of saturation magnetization; the other reason is attributed to that non-magnetic Ti$^{4+}$ and Mg$^{2+}$ substitutions decrease the magnetocrystalline anisotropy constant of the lithium ferrites. Furthermore, remanence first increases and then decreases with the increase of sintering temperature. The highest remanence values are obtained when sintered at 950$^\circ$C, regardless different $x$ value. This fact may be attributed to that the volatilization of lithium element enhances when sintered at higher temperature and leads to the increase of closed pores in grains. And the 950$^\circ$C sintered samples also obtain the highest Br/Bs ratio. But the effect of Ti$^{4+}$ and Mg$^{2+}$ substitutions on the Br/Bs ratio is values not obvious.

![Figure 4](image)

**Figure 4.** Br and Br/Bs ratio values of the samples. The curves with open circles are the Br/Bs ratio values. The curves with solid circles are Br values

The coercive force values of the samples sintered at different temperatures versus Ti$^{4+}$ and Mg$^{2+}$ substitutions are plotted in Figure 5. With increasing sintering temperature, coercive force decreases monotonously, in spite of different $x$ value. This fact is attributed to that coercive force tends to be inversely proportional to the density and grain size. With increasing sintering temperature, both sintering density and grain size increase, so the coercive force decreases. To further determine the influence of Ti$^{4+}$ and Mg$^{2+}$ substitutions on the coercive force characteristic of the lithium ferrites, SEM photos of several samples sintered at 900$^\circ$C were examined and presented in Figure 6.

![Figure 5](image)

**Figure 5.** Coercive force of the samples with different content of substitutions and sintering temperatures
Figure 6. SEM photos of the samples with different substitutions

It is found that average grain size has no obvious connection with the Ti⁴⁺ and Mg²⁺ content. However, when the substitutions increase too much, closed pores in big grains increase obviously. As expected, coercive force is inversely proportional to grain size and directly proportional to magnetocrystalline anisotropy constant [10]. With increasing Ti⁴⁺ and Mg²⁺ substitutions, average grain size has no prominent change, but magnetocrystalline anisotropy constant gradually decreases, which is in favor of decreasing coercive force. It is also known that closed pores lead to increase of coercive force. From Figure 5, we can conclude that the advantageous influence led by the decrease of magnetocrystalline anisotropy constant is more predominant than the disadvantageous influence led by the increase of closed pores. As a result, coercive force also gradually decreases with increasing x value.

To sum up, Ti⁴⁺ and Mg²⁺ co-substitution is an effective method to adjust the saturation magnetization of the lithium ferrites, which also doesn’t obviously influence the sintering and Br/Bs ratio characteristics of the ferrites. At the same time, some magnetic properties, such as coercive force, can be improved.

4. Conclusions
In this experiment, sintering density, microstructure and magnetic properties of the Ti⁴⁺ and Mg²⁺ co-substituted lithium ferrites were investigated, and the following conclusions were drawn:

1. Sintering density values of the lithium ferrites gradually decreased with increasing Ti⁴⁺ and Mg²⁺ substitutions, which was attributed to that the heavier Fe³⁺ ions were replaced by the relatively lighter Ti⁴⁺ and Mg²⁺ ions in the present case. However, the relative densities of the ferrites had no obvious relationship with the substituting value.

2. Saturation magnetization decreased with increasing x value, which was attributed to the decrease of resultant magnetic moment between A and B sub lattice.

3. Remanence decreased monotonously with x value due to the decrease of saturation magnetization and magnetocrystalline anisotropy constant. But the influence of Ti⁴⁺ and Mg²⁺ substitutions on the Br/Bs ratio values was not obvious.

4. Coercive force decreased monotonously with increasing x value due to the predominant influence of the decrease of magnetocrystalline anisotropy constant.
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