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Low-temperature sintering and magnetic properties of MABS glass doped $Li_{0.35}Zn_{0.30}Mn_{0.05}Ti_{0.1}Fe_{2.05}O_4$ ferrites

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ABSTRACT

In this study, the crystal structure and magnetic properties (B_s, ΔH, and $4\pi M_s$) of $Li_{0.35}Zn_{0.30}Mn_{0.05}Ti_{0.1}Fe_{2.05}O_4$ (LiZnMnTi) ferrites sintered at low temperature doped with MgO-Al_2O_3-B_2O_3-SiO_2 (MABS) glass were investigated. The results indicated that a spinel phases LiZn ferrite was obtained at low temperatures (from 880 °C to 920 °C), which is very advantageous for LTCC technology. Moreover, additive of MABS glass can promote grain growth, improve densification and enhance gyromagnetic properties. In addition, for the LiZnMnTi ferrites sintered at 920 °C, when amounts of MABS glass reached 0.5 *wt %*, saturation magnetization increased from 141 mT to 304 mT, coercivity decreased from 512 A/m to 189 A/m, and FMR line width (ΔH) reduced from 749 to 262 Oe at ~9.5 GHz. These findings confirmed that MABS glass had positive effects on low temperature co-fired ferrites.

1. Introduction

Low temperature co-fired ferrites received worldwide concern because of the development of miniaturization of phase shifters [1–3]. LiZnMnTi ferrites have widely been studied in recent years due to their satisfactory magnetic properties, such as high remanence square ratio, low coercivity (H_c), high saturation magnetization ($4\pi M_s$), far-infrared spectral, elastic and thermal properties [4–8]. Synthetic methods include hydrothermal, sol-gel, co-precipitation, combustion synthesis or solid-state reaction method [9–11]. In general, to yield high densification, sintering temperature of Li-Zn-Mn-Ti ferrites need to exceed 1100 °C [12–14]. However, for LTCC technology, it is crucial to decrease the sintering temperatures to allow Li-Zn-Mn-Ti ferrites co-firing with low-melting-point silver electrodes (around 860 °C) [15]. Up to now, numerous methods have been proposed, including the addition of glass, found practical and effective [16].

For Li-Zn-Mn-Ti ferrites, B_2O_3 could effectively enhance the densification properties and promote grain growth [17]. On the other hand, Al_2O_3 is an effective material for stimulating the interaction in raw materials to form ferrites [18]. Since MgO-Al_2O_3-B_2O_3-SiO_2 (MABS) glass contains both B_2O_3 and Al_2O_3, we hypothesized that MABS glass could reduce sintering temperatures of co-fired ferrites. In this work, $Li_{0.35}Zn_{0.30}Mn_{0.05}Ti_{0.1}Fe_{2.05}O_4$ ferrites doped with 0.0 *wt %*~3.0 *wt %* MABS glass were successfully synthesized at relatively low sintering temperatures. The crystal structure and magnetic properties of $Li_{0.35}Zn_{0.30}Mn_{0.05}Ti_{0.1}Fe_{2.05}O_4$ ferrites were investigated and the results were discussed.

2. Experimental

2.1. Synthesis of ferrite and MABS glass

The solid-state reaction method was utilized to synthesize LiZnMnTi ferrites ($Li_{0.35}Zn_{0.30}Mn_{0.05}Ti_{0.1}Fe_{2.05}O_4$). First, high purity raw materials (Li_2CO_3, ZnO, TiO_2, Mn_3O_4, and Fe_2O_3) were weighed and mixed to form a mixture powder, which was then ball-milled in a planetary mill for 4 h (milling media: steel balls) and calcined at 800 °C for 2 h. MABS glass was added to the resulting mixture powder and wet-milled for 6 h. The composite mixture was then dried and granulated with the binder (10 *wt%* polyvinyl alcohol), sieved though a 100 μm mesh, and pressed into toroidal samples (⌀18 mm × 8 mm) at 10 MPa. Finally, toroidal samples were sintered by the conventional sintering process in an oxygen atmosphere and temperatures of 880 °C, 900 °C, and 920 °C.

The MABS glass (MgO-Al_2O_3-B_2O_3-SiO_2) materials were prepared by means of the solid-state reaction. Precisely, 29 *wt%* MgO, 16 *wt%* Al_2O_3, 42 *wt%* H_3BO_3 and 13 *wt%* SiO_2 were mixed and wet-milled for 6 h (milling media: zirconia balls). The mixed material

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was oven-dried at 100 °C for 24 h, melted at 1200 °C for 4 h, then quenched and crushed into powder.

2.2. Characterization

The phase of $Li_{0.35}Zn_{0.30}Mn_{0.05}Ti_{0.1}Fe_{2.05}O_4$ ferrites was detected by X-Ray diffraction (Cu Kα radiation, Rigaku, Japan). The volume densities were detected by the Archimedes method. The coercivity and remanence square ratios were measured by Iwatsu B-H analyzer (SY8232, IWATSH, and Japan). The microstructures of the ferrites were analyzed by scanning electron microscopy (SEM, JSM-6490, JEOL, and Japan). The FMR linewidth were measured by TE106 perturbation method cavity at 9.3 GHz. The M-H loop was tested by a vibrating sample magnetometer (VSM, BHV-525, IWATSH, and Japan). All measurements were performed at room temperature.

3. Results and discussion

The XRD results of $Li_{0.35}Zn_{0.30}Mn_{0.05}Ti_{0.1}Fe_{2.05}O_4$ (LiZnMnTi) ferrites sintered at different temperatures (880 °C, 900 °C and 920 °C) with various MABS glass additives are shown in Fig. 1. In Fig. 1, XRD results indicated that all diffraction peaks were found to match pure spinel ferrites, which demonstrated the successful preparation of spinel structure LiZnTi ferrites. It indicated that adding MABS glass has no effect on crystal structure. Moreover, XRD patterns of the ferrites sintered at 920 °C in log y-scale format were presented in Fig. S1 (Supplementary Information). Similarly, there is no any impurity peak for all samples sintered at the temperature. In our previous study, we demonstrated that Mn^{2+} and Mn^{3+} of Mn_3O_4 substituted Fe^{3+} in A, B sites of LiZn ferrites, respectively [19]. Thus, in this work, the manganese ion of Mn_3O_4 enters into ferrites. In addition, no high energy γ-irradiation was used in our experimental process. Thus, there is no second phase in the LiZnMnTi ferrites, which is different with previous studies [20–24]. In a word, a spinel phases LiZn ferrite was obtained at low temperatures (from 880 °C to 920 °C) when MABS glass was introduced, which is very advantageous for LTCC technology.

The SEM images of LiZnMnTi ferrites doped with different MABS glass contents sintered at 920 °C are presented in Fig. 2. When compared to samples without MABS glass, the increase in MABS glass content promote grain growth. The grain sizes of samples prepared in presence of MABS significantly increased from 1 μm to 8 μm (Fig. 2 (a)-(d)). In Fig. 3, we noted that MABS glass liquid phase formed in the crystal boundary when amounts of MABS exceeded 0.25 wt%. Also, the activation energy of sold-melt interface was low and rate of solid-phase reaction increased. This resulted in some larger crystalline grains formed by devouring smaller crystalline grains. Excess MABS glass induced grain boundaries and pinholes with filled glass phase, resulting in restricted crystal growth (Fig. 2(e) and (f)). MABS glass contents of 0.00 *wt%*~1.00 *wt%* induced irregular grain boundaries. As MABS glass content further increased, hackly edge embossments were dissolved in the liquid glass during sintering to form relatively smooth grain edges. In brief, the addition of MABS glass obviously affected the grain growth of $Li_{0.35}Zn_{0.30}Mn_{0.05}Ti_{0.1}Fe_{2.05}O_4$ ferrites.

Fig. 4 shows the saturation magnetization ($4\pi M_s$) of ferrite samples sintered at 920 °C with various contents of MABS glass. When no MABS glass was added, the solid-phase reaction was hard to react at the temperature. Thus, there are much small grain sizes and pores. It caused the ferrites possess low $4\pi M_s$. However, as MABS glass additive increased, the liquid phase can promote grain growth and reduce pores of the samples. As a result, the $4\pi M_s$ values obvious increased. In Fig. 4, the samples with 0.25 *wt %* MABS glass possessed maximum $4\pi M_s$ values (~4327 gauss). This

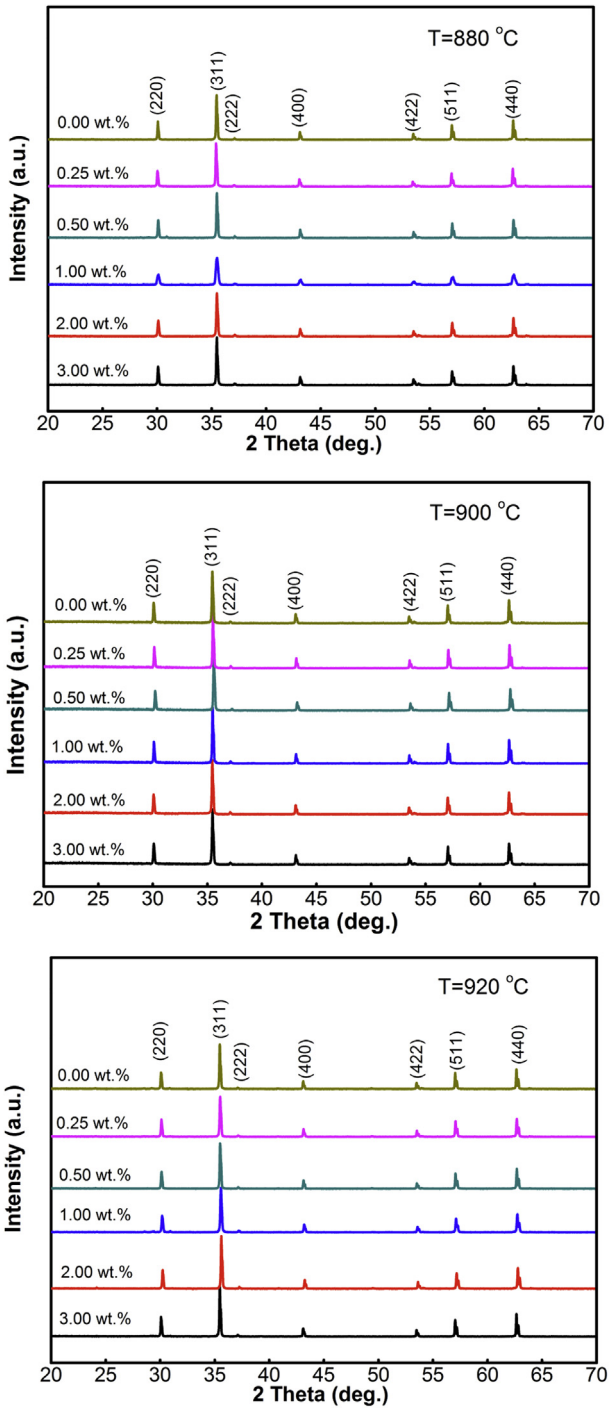

Fig. 1. XRD patterns of $Li_{0.35}Zn_{0.30}Mn_{0.05}Ti_{0.1}Fe_{2.05}O_4$ ferrites sintered at different temperatures with various MABS glass additives.

phenomenon can be explained by nonmagnetic MABS glass liquid phase. The liquid phase not only can dilute the samples, also hinder the solid-phase reaction [25]. Overall, the addition of moderate amounts of MABS glass improved the $4\pi M_s$ values.

Fig. 5 shows the coercivity (H_c) values of LiZnMnTi ferrites. As MABS glass content increased, H_c distinctly decreased to the minimum value (around 189.75 A/m at added MABS glass of 1.00 *wt %*) and then increased when x = 2 *wt %* and 3 *wt %*. The H_c value is inversely proportional to grain size. Smaller grain sizes often resulted in higher coercive force due to domain wall pinning, which