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A Novel Magneto-Dielectric Solid Solution Ceramic $0.25LiFe_5O_8$–$0.75Li_2ZnTi_3O_8$ with Relatively High Permeability and Ultra-Low Dielectric Loss

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In this study, a $0.25LiFe_5O_8$–$0.75Li_2ZnTi_3O_8$ solid solution ceramic was developed via the solid-state reaction method. Its phase evolution, microstructure, and sintering behavior were investigated and it was found that the 25 mol.% $LiFe_5O_8$ phase is almost fully soluble in $Li_2ZnTi_3O_8$, and only the $Li_2ZnTi_3O_8$ type spinel phase was formed in the $0.25LiFe_5O_8$–$0.75Li_2ZnTi_3O_8$ ceramic. The ceramic sample sintered at 1050°C for 2 h was found to possess both good magnetic properties and dielectric properties in the frequency range from 1 to 10 MHz, with permeability between 38.2 and 15 and magnetic loss tangent between 0.25 and 0.75, permittivity between 19.6 and 19.3 and dielectric loss tangent between 8×10^{-3} and 2×10^{-3}. The sample also possesses good microwave dielectric properties with a relative permittivity of 19.1, a high quality factor (*Qf*) ~11,770 GHz (at 6.84 GHz). The ceramic is a novel magneto-dielectric ceramic with both high permeability and good dielectric properties, which might be a good candidate for the applications in novel electronic devices.

I. Introduction

Owing to the rapid development of the information and wireless technologies, the multifunctional materials to meet the requirements of circuit dimension shrinking and high level passive integration are needed.[1,2] Among them, the magneto-dielectric materials have received much attention recently. However, the traditional ferrites (Mn–Zn, Ni–Zn ferrite, for example) with high permeability always show high dielectric loss from low-frequency range to microwave region.[3,4] Moreover, although the popular magneto–dielectric composites in polymer matrix possess lower dielectric and magnetic loss, their permittivity and permeability are also very low, which are limited by the low volume fraction of the magnetic ceramic powders.[5,6] Meanwhile, these composites can hardly be used at a high temperature above 200°C. Hence, the search for new magneto-dielectric ceramics with a wide range of dielectric permittivity, low dielectric loss (high *Qf* value), and high permeability has always been a popular research topic.[7–9]

Recently, the spinel-structured $Li_2ZnTi_3O_8$ ceramic in cubic phase (lattice constant a = 8.394 Å) has been studied a lot due to its high microwave dielectric performance with a permittivity of 25.6, a *Qf* value of ~72,000 GHz and a temperature coefficient of resonant frequency (TCF) value of −11.2 ppm/°C.[10,11] Furthermore, studies show that lithium ferrite $LiFe_5O_8$ ceramic, with the same structure, similar lattice constant (a = 8.331 Å), and close sintering temperature as the $Li_2ZnTi_3O_8$, possessed high initial permeability (μ' = 34) and relatively low dielectric tangent loss (tanδ = 0.1 at 10 MHz).[12] This indicates that the adequate solid solution ceramics $x$$LiFe_5O_8$–$(1-x)$$Li_2ZnTi_3O_8$ might be a good option for the development of a magneto-dielectric material which possesses both the high permeability and permittivity in a relative wide frequency range from 100 Hz to 1 GHz, combined with the excellent microwave performance of the two above-mentioned ceramics.

In this study, the $0.25LiFe_5O_8$–$0.75Li_2ZnTi_3O_8$ ceramic was developed via the solid-state reaction method and its phase evolution, microstructure, magnetic properties, and microwave dielectric properties were studied.

II. Experimental Procedure

Reagent-grade starting materials of Li_2CO_3 ($\geq$98%), TiO_2 ($\geq$99%), ZnO ($\geq$99%) and Fe_2O_3 ($\geq$99%; Sinopharm Chemical Reagent Co., Ltd, Shanghai, China) were weighed in proportionate amounts according to the stoichiometric proportion of $0.25LiFe_5O_8$–$0.75Li_2ZnTi_3O_8$. Powders were mixed and milled for 4 h using a planetary mill by setting the running speed at 150 rpm with the ZrO_2 milling media. The mixed oxides were then calcined in air at temperatures 900°C for 4 h. Then the powders were remilled for 4 h to obtain homogeneous pure $0.25LiFe_5O_8$–$0.75Li_2ZnTi_3O_8$ powders. After drying, the powders were pressed into cylinders and rings after adding 5 wt% polyvinyl alcohol. Samples were sintered in the temperature range of 1000°C–1150°C for 2 h with a heating rate of 3°C/min.

The crystalline structures of samples were investigated using X-ray diffraction with Cu*K*α radiation (D/MAX-2400 X-ray diffractometer, Rigaku, Tokyo, Japan). Microstructures of sintered ceramics were observed on the thermally etched fractured surfaces using scanning electron microscopy (SEM) (JSM-6460; JEOL, Tokyo, Japan). The low-frequency dielectric properties of the ceramics were measured from 100 Hz to 1 MHz, 1MHz to 100 MHz by impedance analyzers of 4980A, 4294A (Agilent, CA), respectively. The dielectric measurement frequency was extended from 10 MHz to 1 GHz by an impedance analyzer (4291B; Agilent, Palo Alto, CA) with a dielectric material test fixture (16453A; Agilent,

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CA). The magnetic measurements in the high-frequency range 1 MHz–1.8 GHz were conducted by an impedance analyzer (4291B) with a magnetic material test fixture (4291B; Agilent, CA). Dielectric behaviors at microwave frequency were measured with the $TE_{01\delta}$ shielded cavity method using a network analyzer (8720ES; Agilent, CA). The magnetic hysteresis loops of the composites were measured using a vibrating sample magnetometer (VersaLab; Quantum Design, San Diego, CA).

III. Results and Discussion

Figure 1 shows the XRD patterns of the $0.25LiFe_5O_8$–$0.75Li_2ZnTi_3O_8$ ceramic calcined at different temperatures. It can be seen that at 600°C, the raw materials have not completely reacted with each other, and the diffraction peaks of several starting materials, TiO_2, ZnO, and Fe_2O_3, can be observed in the XRD patterns. When the calcination temperature increases to 900°C, only the diffraction peaks of the cubic spinel phase (PDF 44-1037) are formed. The ceramic sintered at 1050°C also shows pure spinel phase, which indicates that the 25 mol.% $LiFe_5O_8$ phase is almost fully soluble in $Li_2ZnTi_3O_8$.

The BES image of thermally etched fractured surfaces of $0.25LiFe_5O_8$–$0.75Li_2ZnTi_3O_8$ ceramic sintered at 1050°C for 2 h is shown in Fig. 2. Dense and homogeneous microstructure with few pores and one kind of grains can be observed. The grain size lies between 1 and 5 μm, which is comparable, but a little smaller than both the fractured surface grain size of $LiFe_5O_8$ ceramic sintered at 1150°C[12] and the surface grain size of $Li_2ZnTi_3O_8$ ceramic sintered at 1075°C.[11]

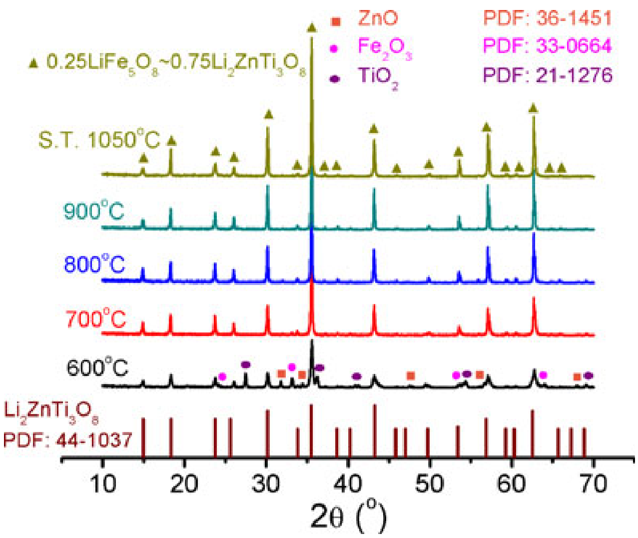

Fig. 1. The XRD patterns of the $0.25LiFe_5O_8$–$0.75Li_2ZnTi_3O_8$ ceramic calcined from 600°C to 1050°C.

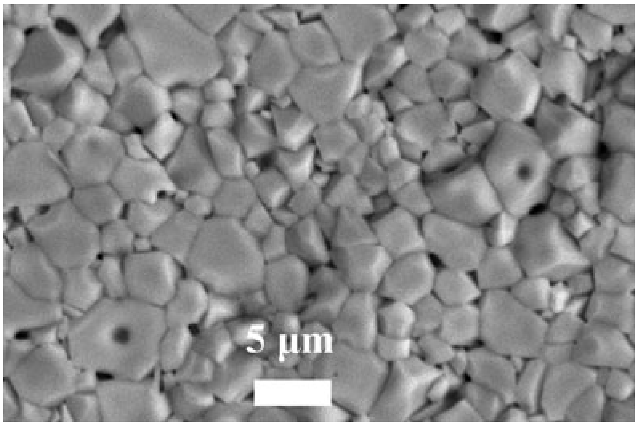

Fig. 2. BES image of the $0.25LiFe_5O_8$–$0.75Li_2ZnTi_3O_8$ ceramic sintered at 1050°C for 2 h.

Table I shows the densities of the $0.25LiFe_5O_8$–$0.75Li_2ZnTi_3O_8$ ceramics sintered between 1000°C and 1150°C. In some previous studies, the densification temperature of $LiFe_5O_8$ ceramic is about 1200°C.[13–15] The $Li_2ZnTi_3O_8$ ceramic was reported to reach a relative density ~94.5% of 3.974 g/cm^3 at 1075°C.[11] In this study, judging from the measured density values, the $0.25LiFe_5O_8$–$0.75Li_2ZnTi_3O_8$ ceramic has almost the same densification temperature of 1075°C as that of the pure $Li_2ZnTi_3O_8$ ceramics.

The magnetic hysteresis loops and the frequency dependency of magnetic properties in the frequency range of 1 MHz–1.8 GHz are shown in Figs. 3(a) and (b), respectively.

Figure 3(a) shows that the saturation magnetization (M_S) is much lower (4.71 emu/g) than the M_S of the pure $LiFe_5O_8$ (58.8 emu/g).[10] It is reported that in the AB_2O_4 spinel structured ceramics, the net magnetic moment is given by the sum of the magnetic moments of A and B sublattices, i.e., $M_S = |M_B - M_A|$.[16] Among these metal cations, their preference to take A site can be sorted as $Zn^{2+} > Fe^{3+} > Li^{+} > Ti^{4+}$.[17] Therefore, if the molecular formula $0.25LiFe_5O_8$–$0.75Li_2ZnTi_3O_8$ is rewritten into $[(Zn_{0.375}Fe_{0.625})\ (Li_{0.875}Ti_{1.125})]O_4$, it is obvious that Fe^{3+} will all occupy A sites in this solid solution ceramic.

Thus, occupying the ion site is not the main influencing factor for the magnetic properties in this ceramic. Moreover, in this AB_2O_4 spinel structured solid solution, only the Fe^{3+} can cause the magnetic property of the ceramic. However, the introduction of the large amount of $Li_2ZnTi_3O_8$ will seriously reduce the concentration of the Fe^{3+}.

Therefore, the very low content of iron in this solid solution leads to the reduction in the M_S. This material also presents a very low residual magnetism (M_r = 0.08 emu/g) and coercivity (Hc = 0.83 Oe), which are much lower than the parameters of the pure $LiFe_5O_8$ (M_r = 1.57 emu/g, Hc = 25.07 Oe).[12]

It is reported that the initial permeability of the sintered pure lithium ferrite is 34 and the resonance frequency is ~40 MHz.[13,14] However, in Fig. 3(b), the solid solution bulk ceramic shows a comparable permeability ~38.2 ($\tan\delta_\mu$ = 0.25) at 1 MHz and a little lower resonance frequency at ~ 10 MHz.

The dielectric properties of the ceramic in wide frequency range (100 Hz–1 GHz) are shown in Fig. 4. The permittivity is 19.8 and the $\tan\delta_\varepsilon$ is very low, ~0.002 at 10 MHz. In Table I, it can be seen that the $Q \times f$ value reaches a maximum value of 11,770 GHz at 1050°C, with a relative permittivity of 19.1.

It can be inferred from the previous studies that the $Q \times f$ value measured via $TE01_\delta$ shielded cavity method may be

Table I. Influence of the Sintering Temperature to the Densities and Microwave Dielectric Properties of the $0.25LiFe_5O_8$–$0.75Li_2ZnTi_3O_8$ Ceramic

S. T. (°C)	Density (g/cm^3)	Permittivity	*Qf* (GHz)	TCF (ppm/°C)
1000	3.62	18.2	8800	–
1025	3.74	18.7	9798	−65.60
1050	3.85	19.1	11770	−60.48
1075	3.91	19.9	5838	−63.30
1100	3.93	20.2	2648	–
1125	3.93	20.2	2360	–
1150	3.93	20.3	1489	–

S. T. sintering temperature; TCF temperature coefficient of resonant frequency.

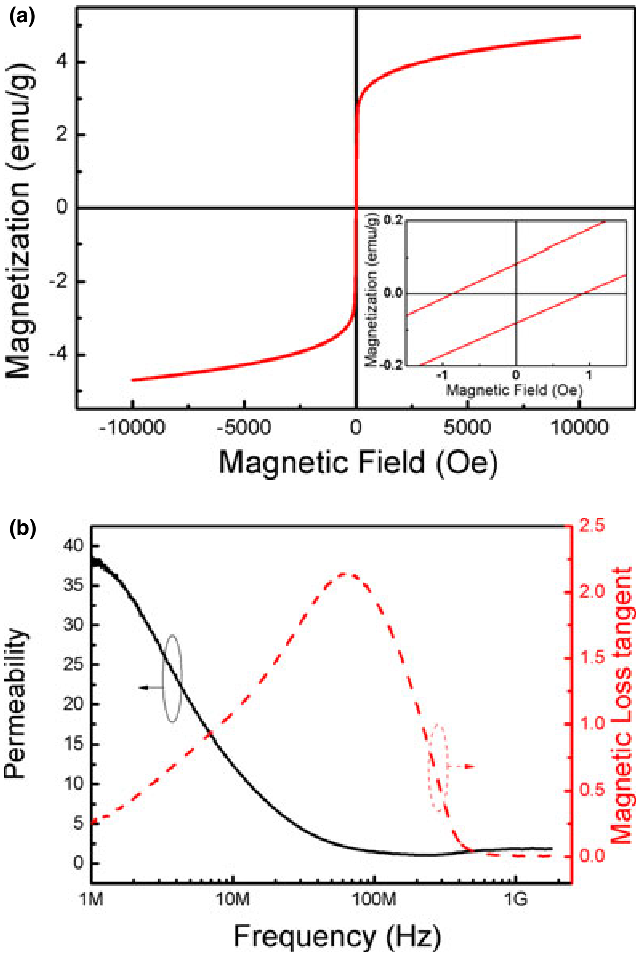

Fig. 3. (a) The magnetic hysteresis loops of the $0.25LiFe_5O_8$–$0.75Li_2ZnTi_3O_8$ ceramic in the magnetic field range of −10000–10000 Oe and −1.5–1.5 Oe, and (b) the frequency dependency of magnetic properties of the $0.25LiFe_5O_8$–$0.75Li_2ZnTi_3O_8$ ceramic in the frequency range of 1 MHz–1.8 GHz, respectively. The ceramic was sintered at 1050°C for 2 h.

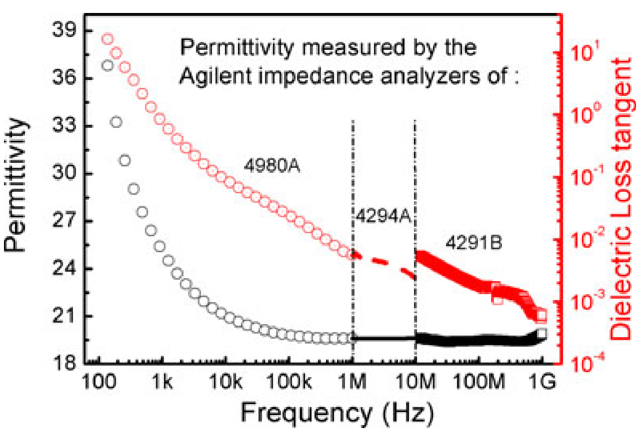

Fig. 4. The frequency dependency of dielectric properties of the $0.25LiFe_5O_8$–$0.75Li_2ZnTi_3O_8$ ceramic measured in a wide frequency range of 100 Hz–1 GHz. The ceramic was sintered at 1050°C for 2 h.

influenced by the magnetic property.[18] However, the $0.25LiFe_5O_8$–$0.75Li_2ZnTi_3O_8$ ceramic shows very weak magnetic properties at microwave frequency range (the resonant frequency did not vary in the presence of external magnetic field), and then a high $Q \times f$ value of 11,770 GHz can be measured. These results fit very well with the dielectric properties measured in the low-frequency range.

IV. Conclusions

The $0.25LiFe_5O_8$–$0.75Li_2ZnTi_3O_8$ solid solution ceramic, developed via the solid-state reaction method, shows a pure $Li_2ZnTi_3O_8$ phase at above 900°C. The ceramic sample sintered at 1050°C for 2 h was found to possess both good magnetic and dielectric properties in the frequency range from 1 to 10 MHz, with permeability between 38.2 and 15 and magnetic loss tangent between 0.25 and 0.75, permittivity between 19.6 and 19.3 and dielectric loss tangent between 8×10^{-3} and 2×10^{-3}. The sample also possesses good microwave dielectric properties with a relative permittivity of 19.1, a high Qf ~11,770 GHz (at 6.84 GHz).

Conclusively, this magneto-dielectric solid solution ceramic of $0.25LiFe_5O_8$–$0.75Li_2ZnTi_3O_8$ is a new soft magnetic-dielectric material possessing both high permeability and good dielectric properties and thus might be a good candidate for novel electronic devices.

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