

A Novel Magnetodielectric Solid Solution Ceramic $0.4\text{LiFe}_5\text{O}_8\text{--}0.6\text{Li}_2\text{MgTi}_3\text{O}_8$ with Excellent Microwave Dielectric Properties

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In this study, a novel spinel solid solution ceramic of $0.4\text{LiFe}_5\text{O}_8\text{--}0.6\text{Li}_2\text{MgTi}_3\text{O}_8$ (0.4LFO–0.6LMT) has been developed and investigated. It is found that the 40 mol% LiFe_5O_8 and 60 mol% $\text{Li}_2\text{MgTi}_3\text{O}_8$ are fully soluble in each other and a disordered spinel phase is formed. The ceramic sample sintered at $1050^\circ\text{C}/2\text{ h}$ exhibits both good magnetic and dielectric properties in the frequency range 1–10 MHz, with a permeability between 29.9–14.1 and magnetic loss tangent between 0.12–0.67, permittivity between 16.92–16.94 and dielectric loss tangent between 5.9×10^{-3} – 2.3×10^{-2} . The sample also has good microwave dielectric properties with a relative permittivity of 16.1, a high quality factor ($Q \times f$) ~28 500 GHz (at 7.8 GHz). Furthermore, 3 wt% $\text{H}_3\text{BO}_3\text{--CuO}$ (BCu) addition can effectively lower the sintering temperature to 925°C and does not degrade the magnetodielectric properties. The chemical compatibility with silver electrode indicates that this kind of ceramics is a good candidate for the low-temperature cofired ceramic (LTCC) application.

I. Introduction

THE magnetodielectric materials have been attracting increasing interest due to their multifunctionality and practicality in developing the advanced communication devices.^{1,2} In general, there are two methods which are commonly used in preparation of the magnetodielectric materials, i.e., the polymer-based composite method and the multiphase cofired ceramic method.^{3,4} And the materials prepared by these two methods have been studied, applied, and developed in recent years.^{5,6}

The solid solutions method, as another important way to improve the performance of materials through compositional design, is gaining an increasing concern in the field of materials.^{2,7} Thus, this method can also be very helpful in designing single-phase magnetodielectric ceramics, which may combine both high permeability and good dielectric properties. Starting from this idea, a ferrite with simple phase structure can be chosen as the basis and other materials with similar structure and excellent dielectric properties can be introduced into it proportionally by solid solution process.

Generally speaking, spinel, garnet, and hexaferrite are the three most important crystal structures of the ferrite magnetic materials, among which spinel has the simplest structure with a general formulation of AB_2O_4 and crystallizes in the cubic crystal system. There are 8A, 16B, and 32 oxygen atoms in

each unit cell, and the oxygen ions form a cubic close-packed array with tetrahedrally (T_d) and octahedrally (O_h) coordinated interstices, whereas the A and B can be divalent, trivalent, or quadrivalent cations and can be occupied in some or all of the tetrahedral and octahedral sites in the lattice.⁸ In addition to the magnetic ferrite, the spinel structure materials also can be frequently found in the use of making the radio-frequency and microwave dielectric materials.^{8–10} Therefore, the solid solution method with the spinel structure will provide an opportunity to develop the novel single-phase ceramics, which possess both the high magnetic and dielectric properties and the excellent microwave performance.

More recently, a magnetodielectric solid solution ceramic of cubic spinel $0.25\text{LiFe}_5\text{O}_8\text{--}0.75\text{Li}_2\text{ZnTi}_3\text{O}_8$ with relatively high microwave dielectric properties has been reported in our previous work.¹¹ It is really a great encouragement to our efforts; however, the $Q \times f$ value is still low (~11 740 GHz). And in order to enhance the quality factor, the content of Fe^{3+} is limited to a very low level, which also has negative influence on its magnetic properties.

In this study, the 0.4LFO–0.6LMT ceramic with better magnetodielectric properties, and much higher $Q \times f$ value was developed and investigated. To lower the sintering temperature, a small amount of BCu was added to the ceramic, and its beneficial effect was also studied.

II. Experimental Procedure

Reagent-grade starting materials of Li_2CO_3 ($\geq 98\%$), MgO ($\geq 98.5\%$), Fe_2O_3 ($\geq 99\%$; Sinopharm Chemical Reagent Co., Ltd, Shanghai, China) and TiO_2 ($\geq 99.9\%$; Linghua Co. Ltd, Zhaoqing, China) were weighed according to the stoichiometric proportion of $0.4\text{LiFe}_5\text{O}_8\text{--}0.6\text{Li}_2\text{MgTi}_3\text{O}_8$ composition. Powders were mixed and milled in ethanol with ZrO_2 as the milling media using a planetary mill (Nanjing Machine Factory, Nanjing, China). The mixed oxides were dried and calcined at 900°C for 4 h. Then, some powders were remilled and the others were remilled with 0.5–5 wt% $\text{H}_3\text{BO}_3\text{--CuO}$ addition (with 4:3 mol ratio). After drying, the powders were pressed into different cylinders and rings according to the testing requirement. The samples of 0.4LFO–0.6LMT ceramic and that with BCu addition were sintered at 1000°C – 1100°C and 900°C – 1000°C for 2 h, respectively. The chemical compatibility tests with silver were taken by adding 20 wt% Ag to the 0.4LFO–0.6LMT ceramic with BCu addition.

The structure analysis and the property measurement of the samples are using the same methods, as described in detail in another work.¹¹

III. Results and Discussion

The XRD patterns of the calcined 0.4LFO–0.6LMT ceramic are shown in Fig. 1. It can be seen that the raw materials have not completely reacted at 600°C and the diffraction

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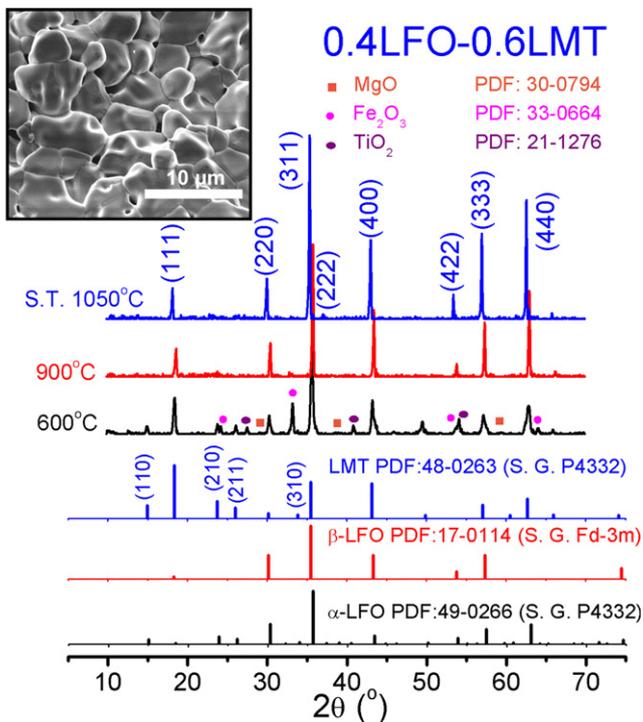


Fig. 1. The XRD patterns of the calcined 0.4LFO–0.6LMT ceramics and the SEM micrographs of 1050°C sintered 0.4LFO–0.6LMT ceramic.

peaks of several starting materials (MgO , Fe_2O_3 , and TiO_2) still exist. When the calcination temperature increases to 900°C, only the diffraction peaks of the cubic spinel phase are found. The ceramic sintered at 1050°C also shows pure spinel phase, which indicates that the 40 mol% LiFe_5O_8 phase and 60 mol% $\text{Li}_2\text{MgTi}_3\text{O}_8$ are fully soluble in each other.

The Powder Diffraction Standards cards of the α -LFO, β -LFO, and LMT are shown in Fig. 1. The superstructure peaks such as (110), (210), (211), (310) and so on can be observed in the XRD patterns of α -LFO and LMT. It has been reported that the α -phase LiFe_5O_8 has a FCC inverse spinel structure with the specific 1:3 ordering of Li^+ and Fe^{3+} at the octahedral B sites.¹² However, for the 0.4LFO–0.6LMT ceramic, with the increase in Li^+ , Mg^{2+} , and Ti^{4+} substitutions introduced into LiFe_5O_8 , a statistical disorder is induced within the structure, disrupting the ordered arrangement of Li^+ and Fe^{3+} in the octahedral B sites. According to the preference of the metal cations to take B site ($\text{Fe}^{3+} < \text{Mg}^{2+} < \text{Li}^+ < \text{Ti}^{4+}$),¹¹ the molecular formula 0.4LFO–0.6LMT can be rewritten as $[\text{Fe}_2]_{\text{T}}[\text{Mg}_{0.6}\text{Li}_{1.6}\text{Ti}_{1.8}]_{\text{O}_8}$ while the α -LFO equals to $[\text{Fe}_2]_{\text{T}}[\text{LiFe}_3]_{\text{O}_8}$, where T refers to the tetrahedron and O refers to the octahedron, respectively. It is obvious that Fe^{3+} ions all occupy A sites in 0.4LFO–0.6LMT, and the 1:3 ordering of Li^+ and Fe^{3+} at the B sites has been completely destroyed. Thus, the damage of the B sites ordering leads to the increase in crystal symmetry, which is corresponding to the disappearance of the superlattice X-ray diffraction peaks.

Figure 2 shows the SEM micrographs of thermal-etched fractured surfaces of 0.4LFO–0.6LMT ceramic added with a different amount of BCu and sintered at 925°C for 2 h. The grain size obviously increases with an increase in BCu additive content. Therefore, it is regarded that BCu has melted during sintering and aided the densification of 0.4LFO–0.6LMT ceramics. Comparatively speaking, the sample with 3 wt% BCu sintered at 925°C for 2 h has a relatively denser microstructure. The backscattered electron images show that the 0.4LFO–0.6LMT ceramic with 3 wt% BCu is chemically

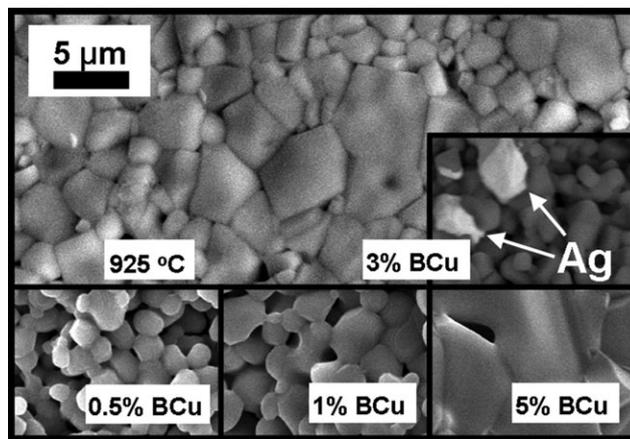


Fig. 2. The SEM micrographs of 0.4LFO–0.6LMT+(0.5, 1, 3, 5 wt%) BCu and the backscattered electron images of 0.4LFO–0.6LMT+3 wt% BCu+20 wt% Ag sintered at 925°C.

compatible with Ag, and therefore, the cofiring of 0.4LFO–0.6LMT ceramics with silver electrodes is feasible.

Figure 3(a) shows the magnetic hysteresis loops of the 0.4LFO–0.6LMT ceramic and the sample with 3 wt% BCu added. Their M_S values are much lower than that of the pure LiFe_5O_8 (58.8 emu/g).¹³ Previous studies have shown that both the total content and the A/B site occupation of the magnetic cations are the two main influencing factors to the magnetic properties of the ceramic samples.^{11,14} As mentioned, Fe^{3+} occupied the A site and this occupation could not be the main factor to influence the magnetic properties in this solid solution ceramic. Therefore, the only kind of magnetic cation of Fe^{3+} in LiFe_5O_8 is significantly diluted with the introduction of the large amount of $\text{Li}_2\text{MgTi}_3\text{O}_8$ and finally leads to the reduction in the M_S . Moreover, the sample sintered at 925°C shows higher M_S , which may be related to its larger grain size.¹⁵ The very low residual magnetism and coercivity indicate that it is also a kind of good soft magnetic material.

The permeability and magnetic loss factor of the sintered ceramics in the frequency range 1 MHz–1 GHz are shown in Fig. 3(b). Compared with the reported LFO ($\mu' = 34$, $f_c = 40$ MHz),¹⁶ the 0.4LFO–0.6LMT ceramic shows a similar initial permeability and the 3 wt% BCu addition has not caused obvious performance deterioration. The dielectric properties in a wide frequency range between 100 Hz and 1.8 GHz are shown in Figs. 3(c) and (d). For the general spinel ferrite, the dielectric permittivity is contributed mainly from the dipole orientation polarization near 1 MHz, and the permittivity always shows relaxation type dispersion characteristics and sharply declined with the increased test frequency.^{4,13} Therefore, the permittivity of this 0.4LFO–0.6LMT ceramic decreases quickly from 51.8 to 16.9 with the increased test frequency from 100 Hz to 1 MHz, and then becomes stable in the higher frequency range. The sample with 3 wt% BCu added shows similar permittivity tendency with the 0.4LFO–0.6LMT ceramic.

Figure 4 presents the bulk densities and the microwave dielectric properties of both the 0.4LFO–0.6LMT ceramic and the sample with 3 wt% BCu added as a function of the sintering temperature. For the 0.4LFO–0.6LMT, with the sintering temperature increasing from 1000°C to 1100°C, the bulk density increases from 3.62 to 3.75 g/cm³. And with the sintering temperature further increasing, the density of 0.4LFO–0.6LMT ceramics reaches saturation, which indicates that the densification temperature of the 0.4LFO–0.6LMT ceramic is around 1075°C. The relationship of relative permittivity versus sintering temperature of 0.4LFO–0.6LMT ceramics has a trend similar to that of the densities; however, its $Q \times f$ value reaches the maximum with a value of

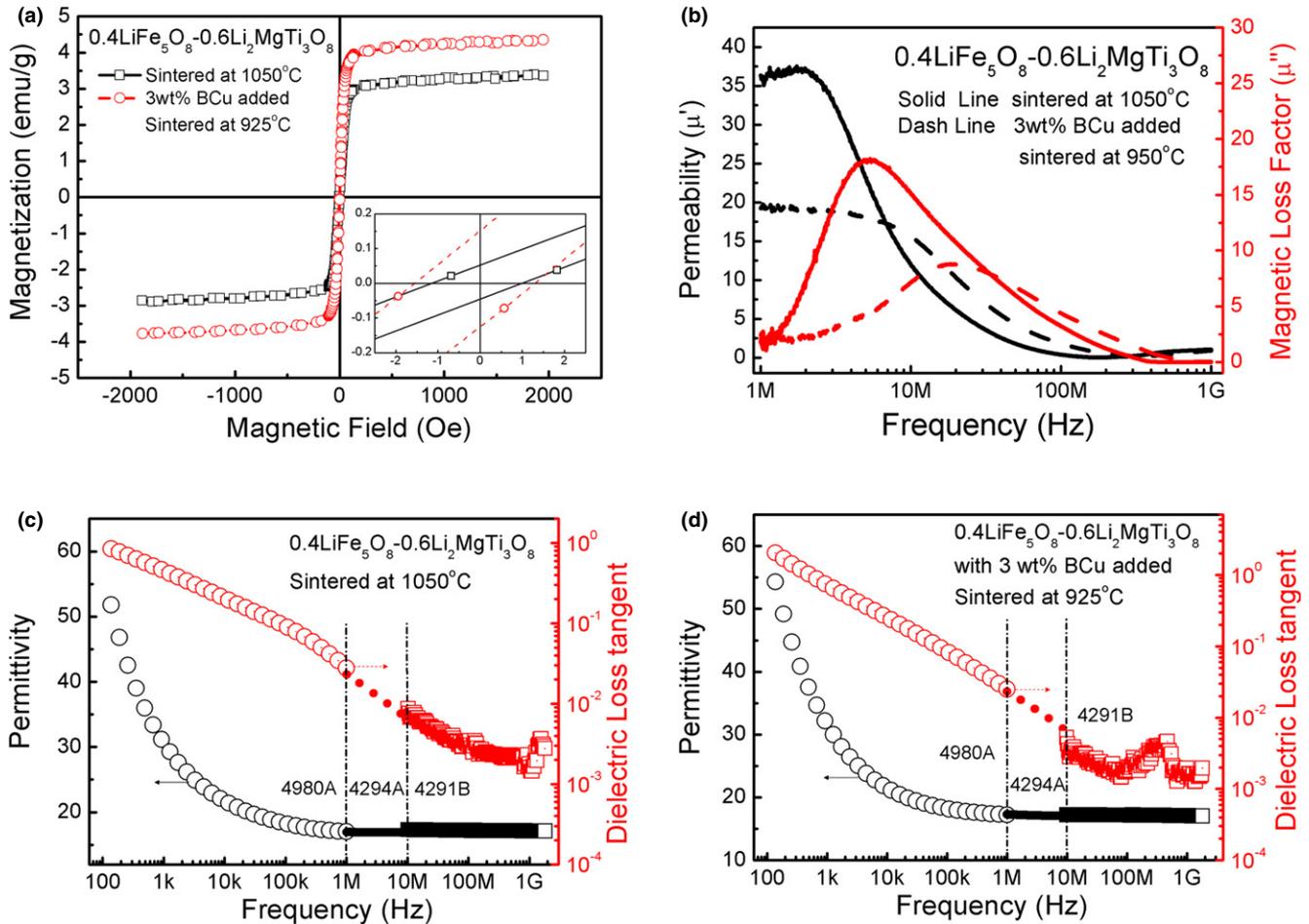


Fig. 3. The magnetic hysteresis loops (a), frequency dependence of permeability and magnetic loss factor at 1 MHz–1 GHz (b), frequency dependence of dielectric properties at 100 Hz–1.8 GHz (c) and (d) of the 0.4LFO–0.6LMT ceramic and that with 3 wt% BCu added.

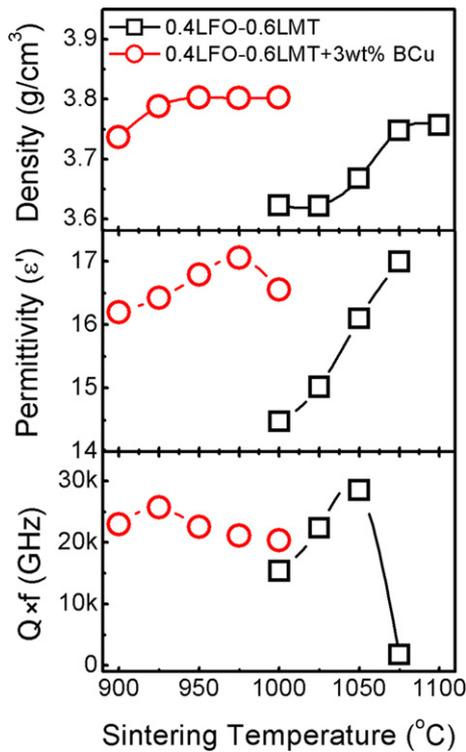


Fig. 4. Influence of the sintering temperature on the densities and microwave dielectric properties of the 0.4LFO–0.6LMT ceramic and that with 3 wt% BCu added.

28 500 GHz (at 7.8 GHz) at 1050°C and then decreases sharply to a very low level at 1100°C and can hardly be accurately measured. This decrease in $Q \times f$ values with further increasing temperature might be caused by some extrinsic factors, such as the increase in liquid phase, and the abnormal grain growth. Moreover, the volatile Li has some deleterious effect on the dielectric properties.^{8,9} It also can be observed, in Fig. 4, that the sample with 3 wt% BCu addition can be sintered at 925°C with a bulk density of 3.79, a permittivity of 16.4, and a relatively high $Q \times f$ value of 25 730 GHz.

IV. Conclusions

The 0.4LFO–0.6LMT solid solution ceramic sintered at 1050°C for 2 h is found to possess good magnetodielectric properties in the frequency range from 1 to 10 MHz. It also shows good microwave dielectric properties with a relative permittivity of 16.1, a high quality factor ($Q \times f$) of ~28 500 GHz (at 7.8 GHz). Furthermore, 3 wt% BCu additions can effectively lower the sintering temperature of the 0.4LFO–0.6LMT to 925°C, whereas its magnetodielectric properties are not substantially changed. The verified chemical compatibility with silver indicates that the 0.4LFO–0.6LMT ceramics with BCu additions are a potential for LTCC application. This kind of multifunctional magnetodielectric materials is also a good candidate for novel electronic devices.

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