The effect of MgO doped on the microstructural and dielectric properties of (Bi1.5Zn0.5)(Ti1.5Nb0.5)O7 ceramics

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Dense ceramics of the pyrochlore (Bi1.5Zn0.5)(Ti1.5Nb0.5)O7 can be prepared at 1100 °C and exhibit a high permittivity (\(\varepsilon_r = 200\)) and low dielectric loss (tan \(\delta < 1 \times 10^{-4}\)) at 1 MHz and room temperature. In this study, the effect of MgO addition on the phase evolution, sintering behaviour, microstructures and dielectric properties of (Bi1.5Zn0.5)(Ti1.5Nb0.5)O7 (BZTN) ceramics are investigated. The ceramics were sintered in air at temperatures ranging from 850° to 1000 °C. BZTN ceramics with small amount of MgO addition can significantly increase the density and improve the dielectric properties. It is found that MgO doped BZTN ceramics can be sintered at 900 °C to obtain a density higher than 94 % of the theoretical density. Scanning electron microscope (SEM) observations show that the BZTN grain sizes increase with increasing amounts of MgO. No secondary phases in the MgO doped BZTN ceramics were observed using X-ray diffraction (XRD) analysis. A high dielectric constant of 220, a low dielectric loss of 0.02 % and a stable temperature coefficient of capacitance (TCC) of \(\Delta C/C \approx \pm 12\%\) in the temperature range from −55 to 125 °C were obtained for 0.5 mol.% MgO-doped BZTN ceramics sintered at 900 °C for 2 h.

Key-words : (Bi1.5Zn0.5)(Ti1.5Nb0.5)O7 (BZTN), Pyrochlore, Dielectric constant, Dielectric loss

[Received May 19, 2022; Accepted July 25, 2022]

1. Introduction

Rapid development in wireless communication systems has increased the demand for the miniaturization of components such as band pass filters and local oscillators. Low-temperature cofired ceramic technology offers significant benefits over other established packaging technologies for high density, high RF, and fast digital applications requiring hermetical packaging and good thermal management.1,2) Microwave dielectric materials with low sintering temperature, high dielectric constant (\(\varepsilon_r\)), low dielectric loss (tan \(\delta\)), and near-zero temperature coefficient of resonant frequency TCF (\(\tau_f\)) are needed to cofire with low loss, low-melting-point conductors such as Ag, Cu, Au, or Al.3) Pyrochlore compounds exhibit a wide variety of physical properties such as semiconducting properties, dielectric properties, ionic conductivity, etc. In general, pyrochlore materials have the formula \(A_2B_2O_7\) indicating the existence of two different crystallographic sites, namely a relatively larger eight-coordinate A site and a smaller six-coordinate B site within the structure.4) Valant et al. performed a detailed investigation on the synthesis and dielectric properties of Bi2O3-ZnO-Nb2O5-TiO2.5) (Bi1.5Zn0.5)-(Ti1.5Nb0.5)O7 has a high dielectric constant (\(\varepsilon_r = 200\)), low dielectric loss (tan \(\delta < 1 \times 10^{-4}\)) at 1 MHz, and a temperature coefficient of the permittivity, 1300 ppm/K.

\(\text{Bi}_1.5\text{ZnNb}_1.5\text{O}_7\) (BZN) ceramics can be sintered at \(\sim 1000{\degree}\text{C}\) for microwave application, because it exhibits high dielectric constant and low-temperature coefficient of resonance frequency (\(\tau_f\)).6) (Bi1.5Zn0.5)(Ti1.5Nb0.5)O7 ceramic has a sintering temperature of \(\sim 1100{\degree}\text{C}\).7) When materials are sintered at this temperature, Ag electrode materials (\(\sim 961{\degree}\text{C}\)) cannot be employed moderately due to their low-evaporation temperatures. Therefore, studies of (Bi1.5Zn0.5)(Ti1.5Nb0.5)O7 ceramics have focused on decreasing the sintering temperature and improving the dielectric properties by controlling the sintering conditions and microstructure and by adding sintering aids.8-11) In this article, we report a systematic study of the microstructure and dielectric properties of \((\text{Bi}_1.5\text{Zn}_0.5)(\text{Ti}_1.5\text{Nb}_0.5)\text{O}_7\) ceramics with MgO doping levels ranging from 0 to 2.0 mol.%. The temperature coefficient of capacitance (TCC) of \((\text{Bi}_1.5\text{Zn}_0.5)(\text{Ti}_1.5\text{Nb}_0.5)\text{O}_7\) was attempt to be improved by substituting selected Mg cation into the pyrochlore structure. Because a near-zero TCC value is critical for several applications.
2. Experimental procedure

Conventional ceramic fabrication processes were used to prepare the present (Bi1.5Zn0.5)(Ti1.5Nb0.5)O7 ceramics from commercial Bi2O3, ZnO, TiO2 and Nb2O5 powders. The Bi2O3, ZnO, TiO2 and Nb2O5 powders were weighed and mixed according to the composition (Bi1.5Zn0.5)-(Ti1.5Nb0.5)O7 using deionized water and zirconia balls milling media for 24 h. The particle size of the starting powder was controlled at 1.0 ± 0.1 μm. The mixture powders were dried at 120 °C for 1 h, and calcined at 1000 °C for 6 h in air, and then crushed into a powder. Different amounts of MgO (0.2, 0.5, 1.0, and 2.0 mol %) was mixed with the (Bi1.5Zn0.5)(Ti1.5Nb0.5)O7 powders using the same procedure. The powders were mixed with the binder (PVA) additive and then were pressed into disk-shaped samples. The pellets were sintered in air at temperatures ranging from 850 to 1000 °C for 2 h.

The bulk density of the sintered pellets was measured using the Archimedean method. Particle size was measured using a particle size analyzer (Malvern, Mastersizer 2000, UK). The crystalline phases of the samples were detected by X-ray diffraction (XRD, Bruker D8A) pattern analysis using Cu-Kα radiation for 2θ value which ranged from 20 to 60°. The diffraction spectra were collected at a scan rate of 2.5°/min. The DIFFRAC plus TOPAS version 3.0 program was used to determine the lattice parameters. The sample microstructures were observed using a scanning electron microscope (SEM, JEOL, JEL-6400 Japan) equipped with energy-dispersive spectroscopy. The capacitance and dissipation factor were measured at 1 MHz and 23 °C (HP4278A). The dielectric properties of the samples were measured as a function of temperature using a HP 4284A LCR meter and programmable temperature chamber interfaced to a PC for automated measurements, and the samples were measured at temperatures ranging from −55 to 125 °C.

3. Results and discussion

3.1 Physical properties, phase and microstructural evolution in the BZTN ceramics

The (Bi1.5Zn0.5)(Ti1.5Nb0.5)O7 (BZTN) ceramics with different dopant levels of MgO (0.2, 0.5, 1.0, and 2.0 mol %) were sintered in air at temperatures ranging from 850° to 1000 °C for 2 h. The bulk density of the (Bi1.5Zn0.5)(Ti1.5Nb0.5)O7 ceramics as a function of different sintering temperatures and MgO addition as shown in Fig. 1. It found that the bulk density of BZTN ceramics increased with increasing of the sintering temperature, and they can be reached a saturation value at 900 °C for the 1.0 mol % MgO additions and at 950 °C for the 0.5 mol % MgO additions, respectively. However, the BZTN ceramics with 1.0 mol % MgO additions can be sintered to about 97% of the theoretical density (i.e. 6.7 g/cm³, at 900 °C for 2 h), since the theoretical density of the (Bi1.5Zn0.5)-(Ti1.5Nb0.5)O7 ceramic is 6.89 g/cm³. It can be found that the effect of the sintering temperature on the bulk density of the BZTN ceramics depends upon the amounts of the MgO addition. As is well known, pure BZTN ceramic has to be sintered at ~1000 °C for several hours, therefore a small amount of MgO addition can increase the density of BZTN ceramics which is sintered at lower than 950 °C.

The effect of MgO addition on the microstructural characteristic and phase evolution of BZTN ceramics were analyzed. Figure 2 shows the XRD patterns of the BZTN ceramics with 0, 0.2, 0.5, 1.0 and 2.0 mol % MgO additions sintered at 900 °C for 2 h. For the undoped BZTN ceramic sintered at 900 °C as shown in Fig. 2, it was determined that there is a single crystalline phase of BZTN present in the specimen. For BZTN ceramics with 0.2, 0.5, 1.0 and 2.0 mol % MgO addition sintered at 900 °C, it is found that the crystalline phase is the same as those of the undoped BZTN ceramics, without the presence of a secondary phase. Figure 3 shows the XRD patterns of the BZTN ceramics with 0, 0.2, 0.5, 1.0 and 2.0 mol % MgO additions which were sintered at 1000 °C for 2 h. For all the samples, the XRD results clearly indicated that the pyrochlore structure was the unique crystallized phase. Furthermore, XRD spectra with 2θ scale ranging from 29 to 31° only were analyzed. It can be observed that the (222) peak of BZTN phase has shifts to a higher angle when MgO was added. This is probably due to substitution of Mg2+ with Ti4+ and Nb5+ cations that oxygen vacancy has formed. It means that the decrease of lattice constants lead to peaks shift to a higher angle.

The formula of a pyrochlore structured A2B2O7 is able to be written as A2B2O7 which distinguishes the oxygen atoms (or anions) in the two different networks. The A and B cations occupy the 16d (1/2, 1/2, 1/2) and 16e (0, 0, 0) sites, respectively, and the O and oxygen anions are in 48f (x, 1/8, 1/8) and 8b (3/8, 3/8, 3/8) sites, respectively. The ionic radii of Bi, Zn, Ti, Nb, O, and Mg are summarized as follows: Bi3+ = 1.40 Å, Zn2+ = 0.88 Å, Nb5+ = 0.64 Å, Ti4+ = 0.605 Å, and Mg2+ = 0.72 Å. O2− = 1.40 Å. Accordingly, the Mg2+ would occupy the B-sites of the pyrochlore structure because Mg2+ is too small for the A site. When Mg2+ substitutes into the B site, a double ionized oxygen vacancy is formed simultaneously, i.e.
MgO $\rightarrow$ Mg$^{2+}$$_{Ti}$ + Vo$^{**}$ + O$_o$
MgO $\rightarrow$ 2Mg$^{2+}$$_{Nb}$ + 3Vo$^{**}$ + O$_o$

The lattice parameter is found to be decreasing with the stoichiometric increase of Mg concentration. These may be attributed to the ionic radius of Mg$^{2+}$ (0.72 Å), which is larger than that of Ti$^{4+}$ (0.605 Å). When Mg substitutes into Ti or Nb sites in the pyrochlores A$_2$B$_2$O$_7$ structure, it will create lattice strain and oxygen vacancies. The Mg$^{2+}$ ion acts as an acceptor in the BZTN ceramics.

The grain growth kinetics of the MgO-doped BZTN specimens was investigated by measuring the average grain size of the sintering product. SEM micrographs of the BZTN specimens with 0.5 mol % MgO addition sintered at different temperatures are shown in Fig. 4. The microstructures of the sintered ceramics were significantly different. The grain sizes of the specimens sintered at different temperatures are compared, the grain size increased with increasing of sintering temperatures. The grain sizes for 900, 950 and 1000 °C are 0.8, 1.5, and 6 μm, respectively. The results show that the grain size of the specimen increased with sintering temperature. It found that the densification of BZTN ceramics is not sufficient at 850 °C. However, it is widely accepted that pure BZNT ceramic has to be sintered at $\geq$1000 °C for several hours. Therefore this result shows that a small amount of MgO dopant can increase the density of BZTN ceramics at 900 °C. This result is consistent with the relative density of Fig. 1. SEM micrographs of the BZTN specimens with MgO addition sintered at 900 °C are shown in Figs. 5(a)–5(d), for 0, 0.2, 0.5 and 1.0 mol % MgO, respectively. It can be seen that many pores in the undoped specimens have formed, as shown in Fig. 5(a). Significant densification occurred as the MgO content increased as shown in Figs. 5(b)–5(d). The grain sizes of the specimens with different MgO levels are compared, it is found that the
grain size increased with increasing of MgO amounts. For example, the grain sizes for 0, 0.2, 0.5 and 1.0 mol % MgO addition are 0.95, 1.28, 1.52, and 2.03 μm, respectively.

3.2 Dielectric properties of the BZTN ceramics

The dielectric constant ($\varepsilon_r$) of MgO-doped BZTN ceramics with different sintering temperatures are shown in Fig. 6. The dielectric property was measured at 1 MHz. The $\varepsilon_r$ value of the undoped BZTN ceramic ranged from 178 at 900 °C to 202 at 1000 °C. (Bi1.5Zn0.5)(Ti1.5Nb0.5)O7 has a high dielectric constant ($\varepsilon_r$) ~ 200 and low dielectric loss (tan) < 1 × 10⁻⁴ at 1 MHz.¹⁸ In addition, the dielectric constant of the BZTN ceramics increased with increasing of amount of MgO. The $\varepsilon_r$ value of MgO-doped BZTN ceramics is 10% higher than undoped BZTN ceramics at 900 °C and $\varepsilon_r$ = 202 for undoped BZTN ceramics at 1000 °C. This is due to the replacement of Mg²⁺ for Ti⁴⁺ or Nb⁵⁺ will produce free electrons in the grains, the oxygen vacancies (Vo**) must be produced to remain neutral for compensating free electrons. These oxygen vacancies formed will create the lattice strain which could accelerate the mass transport process, further promoting grain growth will happen (Fig. 5). However, this is a typical of relaxor materials and is generally attributed to the presence of polar nanodomains within the crystal structure. From a physical point of view, a relaxor is defined as a material possessing a colossal, broad dielectric constant.¹² Much complex cases also exist where such substitution leads to some vacancy defects responsible of relaxor behaviour like Pb1-xLax(Zr1-yTi1-y)O3.¹⁹,²⁰ In this study, the dielectric constant of the sample with 1 mol % MgO sintered at 1000 °C was ~236, which is higher than all of samples. The reason for this is due to bigger grain size for 1 mol % MgO doped BZTN ceramics. The dielectric properties of the MgO-doped BZTN ceramics sintered at 900 °C were measured at different frequencies, as listed in Table 1. The permittivity of the MgO-doped BZTN ceramics sintered at 900 °C and measured at 1 GHz are 160, 191, 194 and 193, respectively. Unlike the permittivity at 1 MHz, this result shows that the MgO-doped BZTN ceramics have a higher dielectric constant than the other ceramics at microwave frequency. In fact, the dielectric constant decreases with increasing the frequency. This may probably due to the occurring of interfacial polarization.

Figure 7 shows the dielectric loss (tan $\delta$) of the MgO-doped BZTN ceramics at 1 MHz as a function of sintering temperatures. The dielectric loss of MgO-doped BZTN ceramics reached a minimum at 0.2 mol % at 1000 °C sin-
tering temperature, and then kept a constant with different MgO amount. However, the dielectric loss decreased gradually with increasing sintering temperatures. This is due to the liquid sintering formation when MgO is added in BZTN ceramics, it means that liquid sintering leads to dense BZTN structure. In addition, oxygen vacancies were the main intrinsic defects in pyrochlore oxides which were proved to affect electrical performance. Especially, oxygen vacancies related dielectric relaxation behavior was existed in high temperature and low frequency field. The higher dielectric loss at a specific temperature and the lower frequency was in good agreement with the high ionic conductivity in the high temperature electrical conductivity results. However, this result suggests that the BZTN ceramics with MgO addition can have good dielectric properties, which would be accompanied by an increase in the dielectric constant.

The frequency dependency of the dielectric and dielectric loss of the series specimens sintered at 900 °C and measured at room temperature are shown in Fig. 8. The curves of dielectric constant and dielectric loss remain flat with the frequency changing when MgO was added in the BZTN ceramics. This indicates that MgO doped BZTN ceramics with MgO addition sintered at 900 °C for 2 h.

Table 1. Relative density and dielectric properties for BZTN ceramics with MgO addition sintered at 900 °C

<table>
<thead>
<tr>
<th>MgO (%)</th>
<th>Bulk Density (g/cm³)</th>
<th>Permittivity (at 1 MHz)</th>
<th>Dielectric Loss (×10⁻⁴)</th>
<th>Permittivity (at 1 GHz)</th>
<th>Q value</th>
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<tr>
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<td>9</td>
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<td>6.75</td>
<td>228</td>
<td>2.0</td>
<td>193</td>
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</tr>
</tbody>
</table>

Fig. 6. Dielectric constant of (Bi₁.₅Zn₀.₅)(Ti₁.₅Nb₀.₅)O₇ ceramics as functions of sintering temperature and MgO addition.
ceramics sintered 900 °C have quite stable frequency dependence. When pure BZTN ceramics sintered 900 °C, both dielectric constant and dielectric loss were decreased with the increasing of frequency. It is similar to some papers for the behavior of dielectrics and ferroelectrics related to leakage conductance,23,24 which the decrease is rapid in low frequencies but becomes much slower in higher frequencies.

The dielectric constant at a temperature range of −55–125 °C was measured to be observed the possible effects of temperature variation. Figure 9 shows the temperature dependence of dielectric constant of BZTN series ceramics at a heating cycle, all the samples were sintered at 1000 °C. The dielectric behavior of undoped and MgO-doped BZTN ceramics is shown the paraelectric clearly, which is as a normal paraelectrics, exhibits a linear depression of dielectric constant. However, the overall $\Delta C/C$ of the MgO-doped BZTN ceramics sintered at 1000 °C are significantly decreased as the MgO concentration increases.

4. Conclusions

In this study, it was found that the addition of MgO to the BZTN ceramics can lower the sintering temperature from 1000 to 900 °C, and the bulk density of the sintered ceramics can reach to 6.7 g/cm³. The BZTN ceramics with MgO addition indicated that they consist mainly of a (Bi$_{1.5}$Zn$_{0.5}$)(Ti$_{1.5}$Nb$_{0.5}$)O$_7$ crystalline phase without a secondary phase by XRD examination. This is due to Mg$^{2+}$ substituting into the B-site, when Mg$^{2+}$ substitutes into Ti$^{4+}$ and Nb$^{5+}$ sites in the pyrochlores A$_2$B$_2$O$_7$ structure that oxygen vacancy has formed. It means that the decrease of lattice constants lead to peaks shift to a higher angle. A (Bi$_{1.5}$Zn$_{0.5}$)(Ti$_{1.5}$Nb$_{0.5}$)O$_7$ ceramic formed by adding 1.0 mol% MgO and sintering at 900 °C in air for 2 h exhibits dielectric properties of $\varepsilon_r = 227$, dissipation loss $= 3 \times 10^{-4}$, and relative density $\sim 97\%$ of theoretical density.

References

**Fig. 7.** Dielectric loss of (Bi$_{1.5}$Zn$_{0.5}$)(Ti$_{1.5}$Nb$_{0.5}$)O$_7$ ceramics as functions of sintering temperature and MgO addition.

**Fig. 8.** Frequency dependency of dielectric constant and dissipation factor of BZTN ceramics with MgO addition at room temperature.

**Fig. 9.** Temperature dependence of permittivity of (Bi$_{1.5}$Zn$_{0.5}$)(Ti$_{1.5}$Nb$_{0.5}$)O$_7$ ceramics sintered at 950 °C with different MgO addition. Permittivity was measured at 1 MHz.