Effect of TiO_2 Ratio on the Phase and Microwave Dielectric Properties of $Li_2ZnTi_{3+x}O_{8+2x}$ Ceramics

YINGXIANG LI,[1,3,4] HAO LI,[1] JUNSHAN LI,[2] BIN TANG,[1]
SHUREN ZHANG,[1] HETUO CHEN,[1] and YA WEI[1]

1.—State Key Laboratory of Electronic Thin Films and Integrated Devices, University of Electronic Science and Technology of China, Chengdu 610054, China. 2.—Department of Chemistry, Center for Materials Science and Nanotechnology, University of Oslo, Blindern, P.O. Box 1033, 0315 Oslo, Norway. 3.—e-mail: 408960349@qq.com. 4.—e-mail: lisi68mei@163.com

Low-loss materials $Li_2ZnTi_{3+x}O_{8+2x}$ (LZT) (x = 0, 0.10, 0.17, 0.25, 1.00) were prepared by the conventional solid-state route. The effect of TiO_2 ratio on phase composition, microstructure, and the microwave dielectric properties of $Li_2ZnTi_{3+x}O_{8+2x}$ ceramics were investigated using x-ray diffraction, scanning electron microscopy, energy-dispersive x-ray spectroscopy, and Vector Network Analyzer. The results revealed that a two-phase system $Li_2ZnTi_3O_8$-TiO_2 was formed. The appropriate content of TiO_2 ratio can effectively adjust the temperature coefficient of the resonant frequency (τ_f) value from -14.5 to 0 ppm/ °C without obvious degradation of the microwave dielectric properties. The microwave dielectric properties of the $Li_2ZnTi_{3+x}O_{8+2x}$ materials were characterized at microwave frequencies. Typically, the $Li_2ZnTi_{3+x}O_{8+2x}$ (x = 0.17) ceramic sintered at 1,160 °C for 5 h showed excellent microwave dielectric properties with ε_r = 28.51, $Q \times f$ = 58,511 GHz, and τ_f = + 2.3 ppm/ °C.

Key words: Microwave ceramics, dielectric properties, microstructure, TiO_2

INTRODUCTION

With the explosive growth in wireless communication technology, microwave dielectric ceramics have been widely used for microwave device applications, such as resonators, filters, and oscillators.[1,2] To meet the demands of microwave circuit designs, microwave dielectric resonator materials with a high dielectric constant ($\varepsilon_r > 20$), a high-quality factor ($Q > 2,000$), and a near zero temperature coefficient of the resonant frequency are required.[3–6] $Li_2ZnTi_3O_8$ ceramic sintered at 1,075 °C exhibits excellent microwave dielectric properties of ε_r of 26.2, $Q \times f$ value of 62,000 GHz, and τ_f value of -15 ppm/ °C.[7] Chemical compatibility with the Ag electrode and good microwave dielectric properties have led to many studies of glass-added $Li_2ZnTi_3O_8$ ceramics for low-temperature co-fired ceramics (LTCC) in the last decade. Most of the studies have focused on lowering the sintering temperature of $Li_2ZnTi_3O_8$ ceramics.[8–10]

Recently, Chen et al.[9] studied the dielectric properties of 1.5 wt.% $BaCu(B_2O_5)$-added $Li_2ZnTi_3O_8$ ceramics sintered at 925 °C with ε_r = 23.1, $Q \times f$ = 22,732 GHz and τ_f = -17.6 ppm/ °C. Li et al.[11] reported the sintering behaviors and microwave dielectric properties of $Li_2ZnTi_3O_8$ ceramics doped with ZnO-B_2O_3 frit, and the properties were $\varepsilon_r \sim 25.34$, $Q \times f \sim 61,660$ GHz, and $\tau_f \sim -12.98$ ppm/ °C. However, the high absolute value of τ_f cannot ensure thermal stability for commercial dielectric materials. Thus, a new method has been developed to tune the temperature coefficient of the resonant frequency to around 0 ppm/ °C, thereby maintaining the excellent microwave properties. In the 1990s, Kim et al.[12] investigated the $ZnTiO_3$+$xTiO_2$ system. Recently, Yoon et al.[13] reported the microwave dielectric properties of $LiNb_3O_8$ ceramics with TiO_2 additions. More recently, Hou et al.[14] studied Li_2O-B_2O_3-SiO_2 (LBS) glass-added $Li_2ZnTi_3O_8$ ceramics with different contents of TiO_2 to adjust the value of τ_f. The τ_f of ceramics can be modified to near 0 ppm/ °C by

mixing with TiO_2 which exhibits a high $\tau_f \geq$ +400 ppm/ °C.[13–17] In this paper, we will present and discuss the effect of TiO_2 content on phase, microstructure, and characterization of $Li_2ZnTi_{3+x}O_{8+2x}$ (LZT) ceramics.

EXPERIMENTAL

The samples of $Li_2ZnTi_{3+x}O_{8+2x}$ (x = 0, 0.10, 0.17, 0.25, 1.00) were prepared by the solid-state route. Stoichiometric amounts of high-purity powders of Li_2CO_3 (99 %), ZnO (99.9 %), and TiO_2 (99.9 %) were weighed and ball-milled in an alcohol medium for 6 h in a plastic bottle using zirconia balls. The mixture was dried and calcined at 870 °C for 5 h, then re-milled again for 3 h. The dried powder was mixed with a 6 wt.% PVA as a binder, then again dried and ground well. The obtained fine powder was axially pressed into cylindrical disks with a thickness of 4–6 mm and 11 mm in diameter under an isostatic pressure of 25 MPa. These pellets were sintered at a high sintering temperatures ranging from 1,100 to 1,190 °C for 5 h in air.

After completion of sintering, the bulk densities of the samples were measured using the Archimedes method. The theoretical density of the LZT ceramics was calculated using the equation,

$$D = \frac{D_1V_1 + D_2V_2}{V_1 + V_2}$$

where V_1 and V_2 were the volume percentage of $Li_2ZnTi_3O_8$ and TiO_2 with densities D_1 and D_2, respectively. The phase composition and crystal structure of the ceramics were examined by conventional x-ray diffraction (XRD) technique using monochromatized Cu Kα radiation (DX–1000 CSC; Japan). Scanning electron microscopy (SEM) (JSM-6460LV; Jeol, Tokyo, Japan) coupled with energy-dispersive x-ray spectroscopy (EDS) was employed to study the surface morphology of the specimens. The microwave dielectric properties were measured by a Vector Network Analyzer (E5071C; Agilent Technologies) and a temperature chamber (DELTA 9023; Delta Design, USA.). The sintered samples used for this measurement had the ratio of diameter/length = 2–2.5. In addition, the temperature coefficients of resonant frequency τ_f values were calculated by the equation: $\tau_f = (f_{t_2} - f_{t_1})/ (f_{t_1} \times (t_2 - t_1))$, where f_{t_1} and f_{t_2} were the resonant frequencies at the measuring temperatures t_1 (25 °C) and t_2 (85 °C) respectively.

RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of the Li_2Zn-$Ti_{3+x}O_{8+2x}$ (x = 0.10, 0.17, 0.25, 1.00) ceramics sintered at 1,160 °C in air for 5 h. In order to analyze the phase compositions of the ceramics with the best properties, the XRD patterns of the LZT ceramics as a function of different x sintered at 1,160 °C were

studied. There were two phases in this system: the main phase was $Li_2ZnTi_3O_8$ and the secondary phase was TiO_2. These two phases coexist to form a stable $Li_2ZnTi_3O_8$-TiO_2 system. It was interesting that the behavior of this system was not the same as the $ZnTiO_3$+TiO_2 and $ZnNb_2O_6$+TiO_2 systems. For example, with the addition of TiO_2 in $ZnTiO_3$, Zn_2TiO_4 and $Zn_2Ti_3O_8$ were formed besides $ZnTiO_3$ and TiO_2.[12] And in the $ZnNb_2O_6$+TiO_2 system, phase composition also changed with the increasing content of TiO_2.[1] However, in this study, the increasing content of TiO_2 did not affect the phase composition of the ceramic to form a stable Li_2Zn-Ti_3O_8-TiO_2 system.

Figure 2 presents the SEM micrographs of the $Li_2ZnTi_{3+x}O_{8+2x}$ ceramics with (a) x = 0, (b) x = 0.10, (c) x = 0.17, (d) x = 0.25, and (e) x = 1.00 sintered at 1,160 °C for 5 h. Almost no porosity in compact microstructure was observed in the ceramics except for Fig. 2a. The decrease in the pores could be owing to the presence of TiO_2 in the $Li_2ZnTi_3O_8$ ceramic. The grain boundary became clear with increasing TiO_2 content. From the SEM micrographs, it can be easily detected that two kinds of crystal growth were co-exhibited. The grain size of the two crystals varied greatly in the microstructures. In order to identify the chemical composition of the different grains, EDS was employed, as shown in Fig. 2d and Table I, point B representing the large grains contained the element Zn. However, point A representing the small grains did not detect the element Zn. This was consistent with the results of XRD that two phases existed in this system. In addition, since the sintering temperature of the pure TiO_2 ceramic was about 1,500 °C, while the best sintering temperature of the $Li_2ZnTi_{3+x}O_{8+2x}$ ceramics was around 1,160 °C in our study. It was possible that the small TiO_2 grain size could be attributed to the
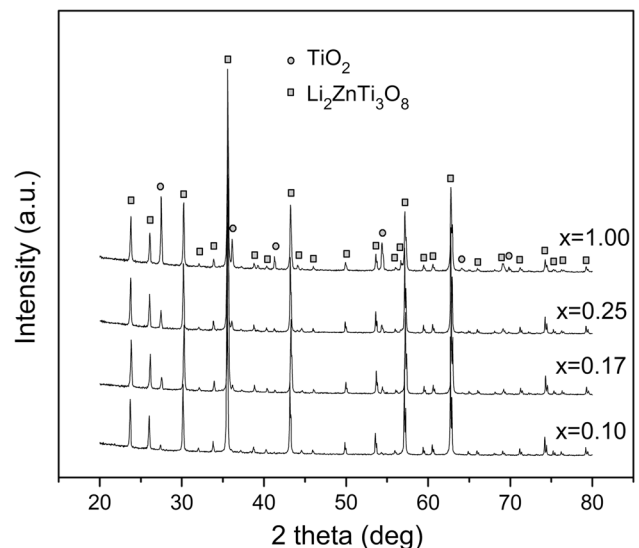

Fig. 1. The XRD patterns of the $Li_2ZnTi_{3+x}O_{8+2x}$ (x = 0.10, 0.17, 0.25, 1.00) ceramics fired at 1,160 °C in air for 5 h.

lower densification temperature. Thus it can be concluded that the large grains were most likely to be Li$_2$ZnTi$_3$O$_8$ and the small grains were TiO$_2$. As can be seen from the micrographs, it was obvious that the amount of TiO$_2$ grains increased with the increasing content of TiO$_2$.

Figure 3 shows the temperature coefficient of the resonant frequency of LZT ceramics sintered at 1,160 °C as a function of the TiO$_2$ content (x). When x was increased from 0 to 1.00, the τ_f value was observed to increase from -14.5 to $+61.35$ ppm/ °C. When x was 0.17, a near zero τ_f value in this system was obtained. As we know, the τ_f value of the composite ceramics is greatly related to the composition of the ceramic. According to previous studies, the Li$_2$ZnTi$_3$O$_8$ and TiO$_2$ ceramics possessed a negative τ_f value of -15 ppm/ °C and a positive τ_f value of about $+400$ ppm/ °C, respectively.[7,14,18] Therefore, the τ_f value in this system can be effectively adjusted from negative to positive by changing the content of TiO$_2$ because of its large positive τ_f value.

The bulk density, dielectric constant, and quality factor of LZT ceramics as a function of the sintering temperature and TiO$_2$ content (x) are shown in Fig. 4. It can be observed that the bulk densities increased because of the elimination of pores at the
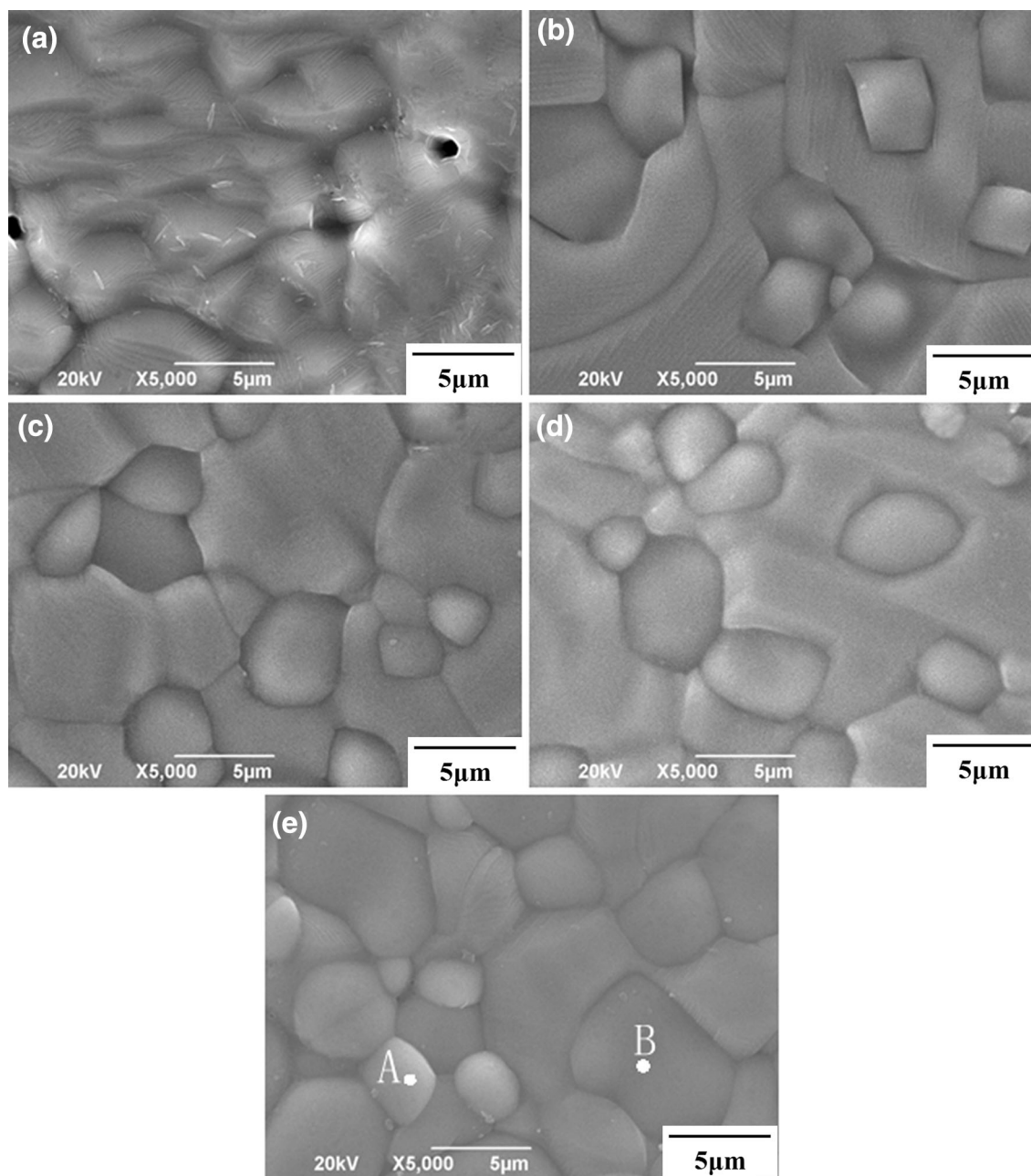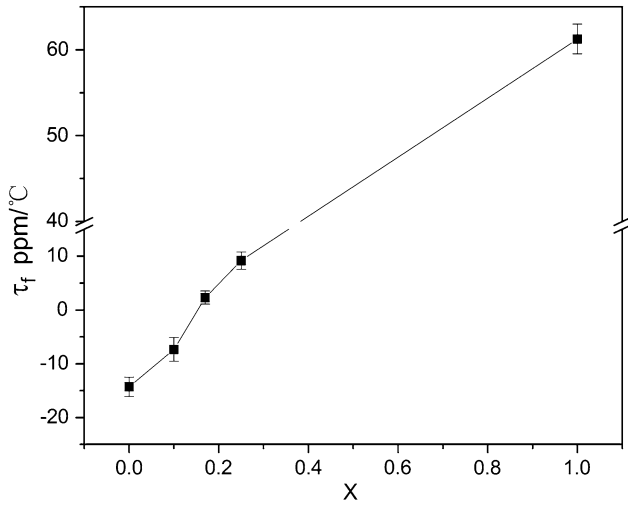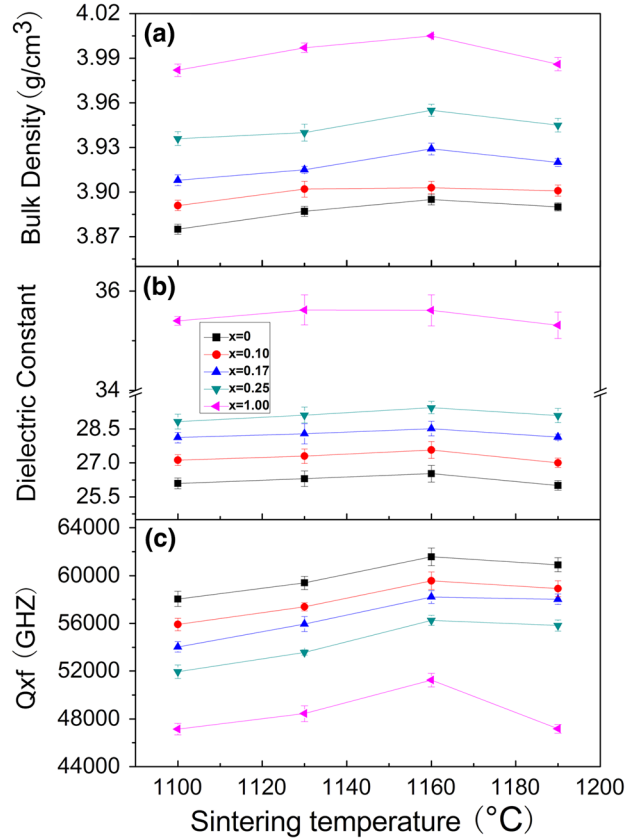

Fig. 2. The SEM photographs of the Li₂ZnTi₃₊ₓO₈₊₂ₓ ceramics with (a) $x = 0$, (b) $x = 0.10$, (c) $x = 0.17$, (d) $x = 0.25$ and (e) $x = 1.00$ sintered at 1160 °C for 5 h.

Table I. The energy dispersive x-ray analysis (EDX) data of LZT ceramics corresponding to Fig. 2d

Atom (%)				
Spot	Li	Zn	Ti	O
A			45.45	54.55
B	–	13.81	39.46	46.73

Fig. 3. The temperature coefficient of the resonant frequency of LZT ceramics sintered at 1,160 °C as a function of the TiO_2 content (x).

Fig. 4. The (a) bulk density, (b) dielectric constant, and (c) quality factor of LZT ceramics as a function of the sintering temperature and TiO_2 content (x).

beginning of the sintering, followed by a slight decrease, which was attributed to the abnormal grain growth. The bulk density reached a relatively high value at 1,160 °C. Meanwhile, the bulk densities increased with increasing of TiO_2 content. Table II gives the measured bulk density, the theory density, and relative density of LZT ceramics sintered at 1,160 °C as a function of TiO_2 content (x). The relative density of LZT ceramics was found to increase with the increase in TiO_2 content. As the TiO_2 content increased from 0 to 1.00, the apparent relative density increased from 96.4 to 99.6 %. It can be demonstrated by comparing the SEM images that the increased densification could be due to the elimination of pores in the ceramics. The changing of dielectric constant was similar to that of the densities in a manner as illustrated in Fig. 4b, since higher bulk densities means lower porosity. The maximum dielectric constant was found at the point with the highest densification at 1,160 °C. As we know, the ε_r value was strongly determined by TiO_2 content which possesses a higher dielectric constant ($\varepsilon_r \approx 105$).[14] Therefore, it can also be understood that the ε_r value increased from 26.4 to 35.62 with the changing of x from 0 to 1.00. Figure 4c shows the $Q \times f$ value of this series of LZT ceramics. It can be

Table II. The bulk density, the theory density, and relative density of LZT ceramics sintered at 1,160 °C as a function of TiO_2 content (x)

x	Bulk density (g/cm^3)	Theory density (g/cm^3)	Relative density (%)
0	3.829	3.974	96.4
0.10	3.896	3.979	97.9
0.17	3.925	3.983	98.5
0.25	3.952	3.987	99.1
1.00	4.002	4.019	99.6

seen that the variation of $Q \times f$ value showed a similar tendency as the bulk density. On one hand, when increasing the sintering temperature, the $Q \times f$ value of the ceramics were first increased and reached a maximum at 1,160 °C, then declined as the sintering temperature further increased. These changes were believed to correlate with the compactness of the samples, and a higher $Q \times f$ value usually corresponded to a denser microstructure.[15,19] On the other hand, as the x value was

increasing from 0 to 1.00, a sustained downward trend in the $Q \times f$ value decreasing from 63,042 to 51,250 GHz was observed, as illustrated in Fig. 4c. The decrease of the $Q \times f$ value with increasing TiO$_2$ can be attributed to the relative lower $Q \times f$ value of TiO$_2$ (about 40,000 GHz) compared with Li$_2$ZnTi$_3$O$_8$ which has a $Q \times f$ value about 63,042 GHz.

CONCLUSIONS

The effects of TiO$_2$ ratio on phase, microstructure, and the microwave dielectric properties of the LZT ceramics were studied. The temperature coefficient of resonant frequency can be effectively modified to a near-zero ppm/ °C by changing the TiO$_2$ content in Li$_2$ZnTi$_{3+x}$O$_{8+2x}$ ceramics. A stable two-phase system Li$_2$ZnTi$_3$O$_8$-TiO$_2$ was formed. The chemical composition strongly determined the microwave dielectric properties. When the value of x was increased from 0 to 1.00, the ε_r was raised from 26.4 to 35.62, the $Q \times f$ value decreased from 63,042 to 51,250 GHz, and the τ_f value increased from -14.5 to $+62.25$ ppm/ °C. Typically, the Li$_2$ZnTi$_{3+x}$O$_{8+2x}$ ($x = 0.17$) ceramic sintered at 1,160 °C for 5 h exhibits good microwave dielectric properties of $\varepsilon_r = 28.51$, $Q \times f = 58,511$ GHz and $\tau_f = +2.3$ ppm/ °C, which is promising for LTCC applications with sintering glass-added aids.

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