Microwave dielectric properties and microstructure of (Li\textsubscript{2}Zn\textsubscript{3-x}Ti\textsubscript{4-x}O\textsubscript{12-3x})\textsubscript{x}CaTiO\textsubscript{3} ceramics (x = 0 to 0.32)

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In this paper, we investigated the effects of calcium contents on the sintering behaviors, phase composition, microstructure and microwave dielectric properties of Li\textsubscript{2}Zn\textsubscript{3}Ti\textsubscript{4}O\textsubscript{12} (LZT) ceramics to find temperature stable and high quality factor (Qxf) microwave ceramics. The X-ray diffraction (XRD) results indicated the LZT and CaTiO\textsubscript{3} co-existed with each other and formed a stable composite system when the calcium was added. Scanning electron microscopy photographs also demonstrated the existence of CaTiO\textsubscript{3} phase, which were consistent with the XRD results. With the increasing calcium content, the apparent density decreased from 4.38 to 4.28 g/cm\textsuperscript{3}, the dielectric constant (\(\varepsilon_r\)) increased from 19.3 to 23.9, Qxf decreased from 74344 to 42264 GHz, and the temperature coefficient of resonant frequency (\(\tau_f\)) was significantly improved from -48 to +9.12 ppm/°C due to the increasing amount of CaTiO\textsubscript{3} phase. At last, the (Li\textsubscript{2}Zn\textsubscript{2.72}Ti\textsubscript{3.72}O\textsubscript{11.16})\textsubscript{0.28}CaTiO\textsubscript{3} ceramics sintered at 1200°C for 4 h displayed the excellent comprehensive properties of \(\varepsilon_r = 23.5, \quad Qxf = 55604\) GHz and \(\tau_f = 0\) ppm/°C.

Key-words: Microwave dielectric ceramic, (Li\textsubscript{2}Zn\textsubscript{3-x}Ti\textsubscript{4-x}O\textsubscript{12-3x})\textsubscript{x}CaTiO\textsubscript{3}, Temperature stable, High Q

1. Introduction

Microwave dielectric materials play a key role in the communication industry ranging from terrestrial and satellite communications, such as Internet of Things, software radio, GPS and DBS TV, to environmental monitoring through satellite, etc. Among the large number of materials, the microwave dielectric ceramics are widely used for the production of passive microwave components like substrates for integrated circuits, mounting, dielectric filters, dielectric antennas and dielectric resonators.\textsuperscript{1,2} The essential characteristics of microwave dielectric ceramics used in microwave telecommunication systems are: (a) high relative permittivity (\(\varepsilon_r\)) for miniaturization; (b) high Qxf or low dielectric loss (Q = 1/tan δ) for better selectivity and (c) near zero temperature coefficient of resonant frequency (\(\tau_f\)) for frequency stability.\textsuperscript{3} To meet the specifications of future systems, there is an increasing requirement of new designs or improved microwave dielectric ceramics that satisfies the three properties simultaneously.

Among the excellent ceramic materials, the Li\textsubscript{2}Zn\textsubscript{3}Ti\textsubscript{4}O\textsubscript{12} (LZT) ceramic has a cubic structure and lattice parameters of \(a = 8.3980\ \text{Å}, \quad V = 592.28\ \text{Å}^3, \quad Z = 4\) and \(\rho = 4.43\ \text{g/cm}^3\), which is a promising candidate in critical components of a microwave circuit system due to its excellent properties of \(\varepsilon_r = 20.6, \quad Qxf = 106700\) GHz, and \(\tau_f = -48\) ppm/°C.\textsuperscript{4} However, the large negative \(\tau_f\) of \(-48\) ppm/°C makes it quite unstable at microwave frequencies. It is easy and effective to obtain the near zero temperature coefficient by combining two chemical compounds with opposite temperature coefficients to form composite ceramics.\textsuperscript{5} Thus, several researchers have made use of TiO\textsubscript{2} (\(\sim +465\) ppm/°C), Li\textsubscript{2}TiO\textsubscript{3} (\(\sim +20.3\) ppm/°C), or Ba\textsubscript{0.8}(VO\textsubscript{4})\textsubscript{2} (\(\sim +52\) ppm/°C) to modify the \(\tau_f\) value of LZT ceramic firstly.\textsuperscript{6,7} It was obvious that the additives also brought about the serious deterioration of microwave dielectric properties. The mixing rule of \(\tau_f\) could be described as: 
\[
\tau_f = X_1\tau_{f1} + X_2\tau_{f2}, \quad \text{where} \quad X_1 \quad \text{and} \quad X_2 \quad \text{are the volume fractions of two phase,} \quad \tau_{f1} \quad \text{and} \quad \tau_{f2} \quad \text{are the} \quad \tau_f \quad \text{values of the two ceramics, respectively.} \textsuperscript{7}
\]
To get temperature stable and high Q microwave ceramics, it is better to dope less amount of material with a higher positive \(\tau_f\) value. CaTiO\textsubscript{3}, in which \(\varepsilon_r \sim 170, \quad Qxf \text{ value } \sim 3600\) at 7 GHz and \(\tau_f \text{ value } \sim 4800\) ppm/°C, could be a potential material to modify the \(\tau_f\) of LZT.\textsuperscript{9} Therefore it is logical to speculate that the LiZnCaTiO composite ceramics have adjustable \(\tau_f\) values. The sintering behavior, phase composition, microstructure and microwave dielectric properties of (Li\textsubscript{2}Zn\textsubscript{3-x}Ti\textsubscript{4-x}O\textsubscript{12-3x})\textsubscript{x}CaTiO\textsubscript{3} ceramics have been investigated in detail.

2. Experimental procedures

To prepare the (Li\textsubscript{2}Zn\textsubscript{3-x}Ti\textsubscript{4-x}O\textsubscript{12-3x})\textsubscript{x}CaTiO\textsubscript{3} powders, the starting raw materials were Li\textsubscript{2}CO\textsubscript{3}, ZnO, CaCO\textsubscript{3} and TiO\textsubscript{2} with at least 99.0% purity. The powders were
were calculated by the equation:
\[ \Delta_9023 = \Delta_9023(\text{DELTA}_9023, \text{Delta Design, USA}). \]

The temperature characteristics at microwave frequencies were measured by the Hakki–Coleman dielectric resonator method (Agilent Technologies E5071C, USA) and temperature chamber in the TE011 mode using a network analyzer (Agilent). The pellets of (Li\(_2\)Zn\(_{3-x}\)Ti\(_4-x\)O\(_{12-3x}\))\(-x\)CaTiO\(_3\) were sintered at 1150, 1175, 1200, and 1225°C for 4 h in air with a temperature-ramp rate of 3 °C/min. After sintering, the apparent densities of the samples were measured using the Archimedes’ method. The powder phase composition was examined by X-ray diffraction (XRD) using CuK\(_{α}\) radiation (Philips x’pert Pro MPD, Netherlands). The lattice parameters values were calculated by Jade software. Scanning electron microscopy (SEM) (FEI Inspect F, United Kingdom) coupled with energy dispersive spectrometer (EDS) was employed to study the thermally etched surface morphology of the specimens. The dielectric characteristics at microwave frequencies were measured by the Hakki–Coleman dielectric resonator method in the TE011 mode using a network analyzer (Agilent Technologies E5071C, USA) and temperature chamber (DELTA 9023, Delta Design, USA). The temperature coefficients of resonant frequency measured at 7–9 GHz were calculated by the equation: \[ \tau_r = (f_{m} - f_{l})/(f_{m} \times (t_{2} - t_{1})), \]
where \( f_{m} \) and \( f_{l} \) are the resonant frequencies at \( t_{1} = 25°C \) and \( t_{2} = 85°C \), respectively.

3. Results and discussion

Figure 1(a) shows the XRD profiles of (Li\(_2\)Zn\(_{3-x}\)Ti\(_4-x\)O\(_{12-3x}\))\(-x\)CaTiO\(_3\) \((x = 0.00–0.32)\) ceramics sintered at 1200°C for 4 h in air. Pure LZT (JCPDS# 44-1038), which belongs to a cubic structure in space group of P4\(_{3}\)32 (208), has the lattice parameter of \( a = 8.3980 \AA, V = 592.28 \AA^3, Z = 4 \)

\( (Z \text{ denotes the number of unit cell molecules in } a \text{ unit cell}) \). For \( x = 0.00 \), the peaks were in accordance with that of LZT. In the region of \( x \geq 0.04 \), all the samples exhibited the mixture phases of LZT and CaTiO\(_3\) (JCPDS# 89-6949), and this finding indicated that the CaTiO\(_3\) phase could coexist with the LZT phase. Figure 1(b) illustrates that intensities of the diffraction peaks for CaTiO\(_3\) phase gradually increased with increasing Ca\(^{2+}\) contents. The formation of the second phase was attributable to the difficulty in the relatively large calcium ions \((R = 1.34 \AA)\) as substitution for zinc ions \((R = 0.74 \AA)\), thus formed a stable composite phase system. Figure 1(c) shows the lattice parameters values of Li\(_2\)Zn\(_{3-x}\)Ti\(_4-x\)O\(_{12-3x}\) \((x = 0.00–0.32)\) sintered at 1200°C for 4 h, and the samples showed a cubic structure with no big changes for lattice parameters. It is also confirmed that Ca ions were not loaded into the cation sites.

Figure 2 shows the SEM of thermally etched surface images of (Li\(_2\)Zn\(_{3-x}\)Ti\(_4-x\)O\(_{12-3x}\))\(-x\)CaTiO\(_3\) ceramics sintered at 1200°C for 4 h with (a) \( x = 0.00 \), (b) \( x = 0.04 \), (c) \( x = 0.08 \), (d) \( x = 0.12 \), (e) \( x = 0.16 \) (f) \( x = 0.20 \), (g) \( x = 0.24 \), (h) \( x = 0.28 \), (i) \( x = 0.32 \). Sample presented the dense and compact microstructures, and little porosity was observed for the well-sintered samples. The pure LZT ceramic [Fig. 2(a)] had a dense microstructure with the average grain size of about 15 μm. The second phase, which was randomly distributed on the surface, was firstly observed in Fig. 2(b) at \( x = 0.04 \). The second phase presented a small round-like shape and had an average size of about 1.5 μm. The amount of the small grains increased with increasing calcium ion concentration. The large grains and small grains should be considered as LZT and
CaTiO$_3$ phase, respectively. EDS was employed to identify the chemical composition of two shaped grains shown in Fig. 2. Figure 3 presents the EDS spectra of marked areas (A–D) of (Li$_2$Zn$_{1-x}$Ti$_{4-x}$O$_{12-3x}$)$_x$CaTiO$_3$ ceramics corresponding to Fig. 2. Table 1 lists the testing data. It is difficult to detect lithium ions by EDS due to its detection limit. As shown in Table 1 and Fig. 3, the large grains A and D, contained the elements Zn, Ti and O. However, the small grains B and C, consisted of the elements Zn, Ca, Ti and O. According to Table 1, the ratios of Zn:Ti were close to 3:4, and the ratios of Ca:Ti were approximately 1:1. Thus the large grains should be the LZT phase, and
small grain should be the CaTiO₃ phase. The co-existence of two phases in this system is consistent with the XRD results. Because the sintering temperature of the pure CaTiO₃ ceramic was about 1300-1400°C, the small CaTiO₃ grain size could be attributable to the relatively low sintering temperature. The optimal sintering temperature of the (Li₂Zn₃₋ₓTi₄₋₀₁₂₋₃₋ₓCaTiO₃) ceramics was about 1200°C in this experiment.

Figure 4 displays the apparent density of (Li₂Zn₃₋ₓ Ti₄₋₀₁₂₋₃₋ₓCaTiO₃) (x = 0.00–0.32) as a function of the sintering temperature and Ca content. As shown in Fig. 4, the apparent densities decreased remarkably from 4.38 to 4.28 g/cm³ with increasing CaTiO₃ content, which was caused by a low density of 4.04 g/cm³ of the new CaTiO₃ phase and the appearance of pores. Meanwhile, there was an increasing trend of apparent densities with increasing sintering temperature at a given Ca concentration, however, this increase was followed by a decrease, which was attributable to the over-sintering process. Thus, the optimal sintering temperature of (Li₂Zn₃₋ₓTi₄₋₀₁₂₋₃₋ₓCaTiO₃) samples was 1200°C, and the optimal density of the sample was 4.31 g/cm³.

Figure 5(c) shows the change in the dielectric constant of (Li₂Zn₃₋ₓTi₄₋₀₁₂₋₃₋ₓCaTiO₃) ceramics as a function of sintering temperature and calcium content. As sintering temperature increased, the dielectric constant changed slightly for the same composition. This finding could be explained by all samples with high densification, and the dielectric constant showed a limited dependence on the sintering temperature when samples were in high densification and compact microstructure. Especially, the εᵣ had a maximum value when sintering temperature was 1200°C. This result indicated that the densification temperature of the (Li₂Zn₃₋ₓTi₄₋₀₁₂₋₃₋ₓCaTiO₃) ceramic was around 1200°C. However, the dielectric constant was highly correlated to the calcium content. In general, the dielectric constant is affected by density and the secondary phase. Therefore, the increase in dielectric constant from 19.3 to 23.9 is reasonable owing to the increasing amount of CaTiO₃ phase (εᵣ = 170).

The Q×f values of (Li₂Zn₃₋ₓTi₄₋₀₁₂₋₃₋ₓCaTiO₃) samples as a function of sintering temperature and calcium content are shown in Fig. 6. The change in Q×f value were similar to that of apparent density at a given calcium content. The Q×f value increased with increasing sintering temperature, reached a maximum value at their optimal sintering temperature of 1200°C, and later declined as the sintering temperature increased further. These changes were considered to correlate with the compactness of the samples; a higher Q×f value was usually related to a denser microstructure. At the same time, however, a downward trend in the Q×f value from 74434 to 42264 GHz was observed as calcium content increased. The average grain sizes had effects on Q×f values. Larger grain sizes reduced the number of grain boundaries per unit volume, resulting in lower dielectric loss. However, for

### Table 1. The EDS data of the marked spots of A, B, C and D of Fig. 2

| Spot | Li | Zn | Ca | Ti | O |
|------|----|----|----|----|---|
| A    | —  | 18.1 | 0 | 19.1 | 62.7 |
| B    | —  | 1.4 | 15.1 | 18.4 | 65.1 |
| C    | —  | 1.3 | 14.5 | 18.6 | 65.6 |
| D    | —  | 11.5 | 0 | 12.4 | 76.1 |

Fig. 4. Apparent density of (Li₂Zn₃₋ₓTi₄₋₀₁₂₋₃₋ₓCaTiO₃) (x = 0.00–0.32) ceramics sintered at 1150–1225°C for 4 h.

Fig. 5. Dielectric constant of (Li₂Zn₃₋ₓTi₄₋₀₁₂₋₃₋ₓCaTiO₃) (x = 0.00–0.32) ceramics sintered at 1150–1225°C for 4 h.

Fig. 6. Quality factor of (Li₂Zn₃₋ₓTi₄₋₀₁₂₋₃₋ₓCaTiO₃) (x = 0.00–0.32) ceramics sintered at 1150–1225°C for 4 h.
The results showed the...tered at 1150°C.

(calcium content, which was consistent with the theory of wave dielectric ceramics with negative $\varepsilon_r$.)

The inset shows $\varepsilon_f$ values of the (Li$_{2}$Zn$_{2.72}$Ti$_{3.72}$O$_{11.16}$) ceramics sintered at 1150°C for 4 h.

$x \geq 0.24$, the change in grain size is small and all samples sintered at 1200°C for 4 h had average grains size of about 2 μm, but the $Q\times f$ values decreased from 57156 GHz to 48792 GHz. The grain size effect is not dominant factor determining the $Q\times f$ as well as microwave permittivity. Kawashima et al. also mentioned that the direct effect of grain boundary on $Q$ is extremely limited in Ba(Zn$_{1/3}$Ta$_{2/3}$)O$_3$ ceramics. The CaTiO$_3$ had a very low $Q\times f$ value of 3600 GHz as compared to LZT ceramics. Therefore, the low $Q\times f$ of CaTiO$_3$ phase was the main reason for the sharp decrease in the $Q\times f$ of the (Li$_{2}$Zn$_{1-x}$Ti$_{4-x}$O$_{12-3x}$) ceramics.

Figure 7 depicts the $\varepsilon_f$ and $\tau_f$ of (Li$_{2}$Zn$_{3-x}$Ti$_{4-x}$O$_{12-3x}$) ceramics sintered at 1200°C, the top left insert figure shows the $\tau_f$ values of the (Li$_{2}$Zn$_{2.72}$Ti$_{3.72}$O$_{11.16}$) ceramics as a function of the sintering temperatures. The $\tau_f$ of (Li$_{2}$Zn$_{3-x}$Ti$_{4-x}$O$_{12-3x}$) ceramics increased significantly from $-48 \to +9.12$ ppm/°C. It is well-known that the CaTiO$_3$ has a large positive $\varepsilon_r$ value of +800 ppm/°C, and it is widely used to tune the microwave dielectric ceramics with negative $\varepsilon_r$. Hence, with increasing calcium content, the positive $\varepsilon_f$ of the CaTiO$_3$ phase was the primary reason for the increase in the $\tau_f$ of (Li$_{2}$Zn$_{3-x}$Ti$_{4-x}$O$_{12-3x}$) ceramics. Both of the $\tau_f$ and $\varepsilon_f$ were nearly linearly increased with increasing calcium content, which was consistent with the theory of

$$\tau_f = -[(1/2)\varepsilon_r \pm \alpha]$$

(α is coefficient of linear thermal expansion.) The results showed the $\alpha$ of (Li$_{2}$Zn$_{1-x}$Ti$_{4-x}$O$_{12-3x}$) ceramics was a constant and it approximately equaled to 8 ppm/°C. The $\tau_f$ values of the (Li$_{2}$Zn$_{2.72}$Ti$_{3.72}$O$_{11.16}$) ceramics at different temperatures have no obvious change and keep relatively steady. As a result, a zero $\tau_f$ value was obtained when $x$ was 0.28, which was of great significance for this system. As seen from Figs. 4 and 7, both $\varepsilon_f$ and $\tau_f$ increased linearly with increasing Ca content, which can be explained by linear addition theory.

In summary, for $x = 0.28$, the (Li$_{2}$Zn$_{3-x}$Ti$_{4-x}$O$_{12-3x}$) ceramics sintered at 1200°C for 4 h exhibited excellent comprehensive properties of $\varepsilon_f = 23.5$, $Q\times f = 55604$ GHz and $\tau_f = 0$ ppm/°C. Table 2 summarizes some typical compounds with high quality factor reported in the references. Compared with other LZT-based ceramics, it was clear that the (Li$_{2}$Zn$_{2.72}$Ti$_{3.72}$O$_{11.16}$) ceramics possessed both advantages of high $Q\times f$ and near zero $\tau_f$ value. However, although the Ba(Zn$_{1/3}$Ta$_{2/3}$)O$_3$ ceramic had a high $Q\times f$ of 168000 GHz, the tantalum content in Ba(Zn$_{1/3}$Ta$_{2/3}$)O$_3$ ceramics was very expensive. What’s more, it had to take at least 120 h to achieve a perfect hexagonally ordered structure at 1350°C. In conclusion, the composite ceramic in this work had excellent microwave dielectric properties and good prospect for application.

### 4. Conclusion

The influence of Ca contents on the sintering behaviors, phase structure, microstructure and microwave dielectric properties of (Li$_{2}$Zn$_{3-x}$Ti$_{4-x}$O$_{12-3x}$) ceramics were systematically investigated in this study. The XRD patterns indicated the LZT and CaTiO$_3$ co-existed with each other and formed a stable composite system when the calcium was added. The results of SEM photographs demonstrated the appearance of CaTiO$_3$ phase, which are consistent with the XRD results. The relative density and microwave dielectric properties were strongly dependent on the calcium content. As $x$ increased from 0 to 0.32, there was a decrease in the relative density due to the lower density of CaTiO$_3$. As the intensity of the CaTiO$_3$ phase increased, the $\varepsilon_f$ rose from 19.3 to 23.9, the $Q\times f$ decreased from 74344 to 42264 GHz, and the $\tau_f$ increased significantly from $-48 \to +9.12$ ppm/°C. At $x = 0.28$, the (Li$_{2}$Zn$_{3-x}$Ti$_{4-x}$O$_{12-3x}$) ceramics sintered at 1200°C for 4 h exhibited excellent comprehensive properties of $\varepsilon_f = 23.5$, $Q\times f = 55604$ GHz and $\tau_f = 0$ ppm/°C, which had an obvious advantage in microwave dielectric and sintering properties other high-Q ceramic systems.

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