

THE SINTERING BEHAVIOUR, MICROSTRUCTURE AND MICROWAVE DIELECTRIC PROPERTIES OF $\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}$ CERAMICS DOPED BY LiF

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$\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}$ ceramics were prepared by the traditional solid-state reaction method. The sintering behaviour, microstructure and microwave dielectric properties of the LiF doped $\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}$ ceramics were studied by X-ray powder diffraction (XRD), Scanning Electron Microscopy (SEM) and a network analyser. When a small amount of LiF is added, LiF is a pure phase and the LiF and the $\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}$ phase coexisted under co-firing conditions, which reduced the sintering temperature to 900 °C without weakening its microwave dielectric properties. With an increase in the LiF content, the apparent density increased from 3.81 g·cm⁻³ to 4.17 g·cm⁻³, the dielectric constant decreased from 17.9 to 16.4, and the $Q \times f$ value firstly increased from 2800 GHz to 47 983 GHz and then decreased to 24 944 GHz. The temperature coefficient of the resonant frequency was slightly decreased from -48 ppm/°C to -54 ppm/°C. Excellent combined microwave dielectric properties were obtained for the LiF-added composition with $x = 1$ wt. % with an ϵ_r of 17.9, a $Q \times f$ of 47983 GHz and a τ_f of -48.3 ppm/°C when sintered at 900 °C for 4 h.

INTRODUCTION

With the rapid development of electronics technology, electronic components tend to be miniaturised, integrated, highly reliable and low-cost today. Electronic products made by low-temperature co-firing ceramic technologies have been widely used in modern communications, automotive electronics, medical electronics, aerospace and other fields [1]. Microwave dielectric ceramics, the key materials of these electronic devices, are developing in the direction of low temperature co-firing. In this regard, a Low Temperature Co-Fired Ceramics (LTCC) technology strongly requires microwave ceramics to have a sintering temperature below 950 °C without affecting the properties so that the ceramic material can be co-fired with the electrode material. Therefore, the search for microwave dielectric materials at a low sintering temperature and having a chemical compatibility with Ag electrodes has become a hot spot for researchers.

Recently, a series of lithium-based microwave dielectric ceramics with good microwave dielectric properties have attracted wide attention, Zhou et al. [2] reported a $\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}$ (LZT) ceramic sintered at 1075 °C exhibits microwave dielectric properties of $\epsilon_r = 20.6$, $Q \times f = 106,700$ GHz and $\tau_f = -48$ ppm/°C and does not react with the electrode material (Ag, Cu), but its sintering temperature is 1075 °C, which limits the application

in the LTCC technology. Generally, there are three methods to reduce the sintering temperature of microwave dielectric ceramics: low melting-temperature oxides or a glass addition, chemical processing and the use of smaller particles as the starting materials. The chemical method is time-consuming and expensive. The addition of low melting glasses for the liquid-phase sintering has been known to be the most effective and inexpensive method to achieve dense sintered ceramics at a low sintering temperature [3-5]. At present, attempts are being made to make glass-ceramic composite materials [6-9], and the sintering temperature of the ceramics is lowered by adding glass or low melting-temperature oxides, but often at the expense of reducing the ceramic original microwave dielectric properties. It has been reported that the addition of a small amount of $\text{Li}_2\text{O}-\text{ZnO}-\text{B}_2\text{O}_3$ glass [10] can reduce the sintering temperature of a $\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}$ ceramic from 1075 °C to 900 °C, but it also reduces the microwave dielectric properties. As a widely used sintering aid, LiF has successfully reduced the sintering temperature of $\text{Li}_3(\text{Mg}_{0.95}\text{Ca}_{0.05})_2\text{NbO}_6$ and $\text{BaFe}_{0.5}\text{Nb}_{0.5}\text{O}_3$ ceramics respectively, and has not deteriorated the ceramic microwave dielectric properties [11, 12]. Furthermore, appropriate amounts of LiF additives were added to $\text{Ca}[(\text{Li}_{0.33}\text{Nb}_{0.67})\text{Ti}_{0.1}]\text{O}_{3-6}$ ceramics to reduce the sintering temperature and obtain a good $Q \times f$ value [13]. Therefore, in order to further improve the sintering character and microwave dielectric

properties of LZT ceramics, a low-melting-point LiF was chosen as a sintering aid to co-fire with silver in this study. Moreover, the effects of the LiF on the sintering behaviour, phase composition, microstructure and microwave dielectric properties of the LZT ceramic were investigated. Furthermore, the chemical compatibility of the glass-added ceramics with an Ag electrode was investigated.

EXPERIMENTAL

LiF-doped $\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}$ ceramics were synthesised by the conventional solid-state sintering method. Firstly, high purity powders of Li_2CO_3 (99 %, Aladdin, China), ZnO (99 %, Aladdin, China) and TiO_2 (99 %, Aladdin, China) were used as the raw materials and weighted according to the mixture of the $\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12} - x$ wt. % LiF, where $x = 0, 1, 2, 4, 6$, and then the powder mixtures were assisted in ethanol with a zirconia milling medium for 6 hours. The mixed slurry was dried and calcined at 800 °C for 4 hours, then the powders were mixed and granulated in a 10 % aqueous solution of polyvinyl acetate (PVA) and a cylindrical sample of $d = 15$ mm and $h = 7.5$ mm was uniaxially pressed under a pressure of 20 MPa. The pellets of $\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12} - x$ wt. % LiF were then sintered at 850 °C, 875 °C, 900 °C, 950 °C in an air atmosphere at a heating rate of 3 °C·min⁻¹ for 4 h and cooled in a furnace.

After sintering, the qualitative detection of the phase of the powdered sample was carried out by X-ray diffraction using $\text{CuK}\alpha$ radiation (XRD, Philips X'Pert Pro MPD). The microscopic morphology of the sample can be obtained by scanning electron microscopy (SEM, FEI Inspect F, United Kingdom). The microwave dielectric properties of the sintered samples were measured by using a network analyser (Agilent Technologies E5071C, USA) under the TE011 resonant mode by the Hakki-Coleman method. The ceramic resonant frequencies f_{t1} and f_{t2} are stabilised at 25 °C and 85 °C, and the τ_f value is calculated by the formula:

$$\tau_f = \frac{f_{t2} - f_{t1}}{f_{t1}(t_2 - t_1)} \times 10^6 \text{ ppm/}^\circ\text{C} \quad (1)$$

where f_{t1} and f_{t2} are the resonant frequencies of the ceramic at the temperature of t_1 and t_2 , respectively.

The apparent densities of the sample were measured by the Archimedes method at room temperature. The relative densities were equal to the ratio of the apparent densities to the theoretical densities, and the theoretical densities can be calculated by Equation 2:

$$\rho_{\text{theo}} = \frac{W_m \times Z}{V \times N_A} \quad (2)$$

where W_m , Z , V , and N_A represent the molar mass, atomic number, volume, and Avogadro's constant of a single unit cell, respectively.

RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of the different amounts of LiF-doped microwave dielectric $\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}$ ceramics sintered at 900 °C for 4 h. It can be seen from the X-ray diffraction pattern that the sample shows a single $\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}$ phase with a cubic spinel structure in the P4232 space group of x when $x \leq 1$ wt. %. This is because the F⁻ ions enter the lattice to replace O²⁻ ions, and the Li⁺ ions of the LiF replace the Li site of the matrix [14], so no impurity phase is formed. However, when $x \geq 2$ wt. %, the second phase of LiF (JCPDS#00-002-1111) is observed according to the diffraction peak. The diffraction peak intensity of LiF is significantly enhanced when $x = 4 - 6$ wt. %, indicating that a limited amount of LiF reacts with the $\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}$ ceramics, which may be caused by the excessive LiF. In addition, the diffraction peaks are not significantly shifted.

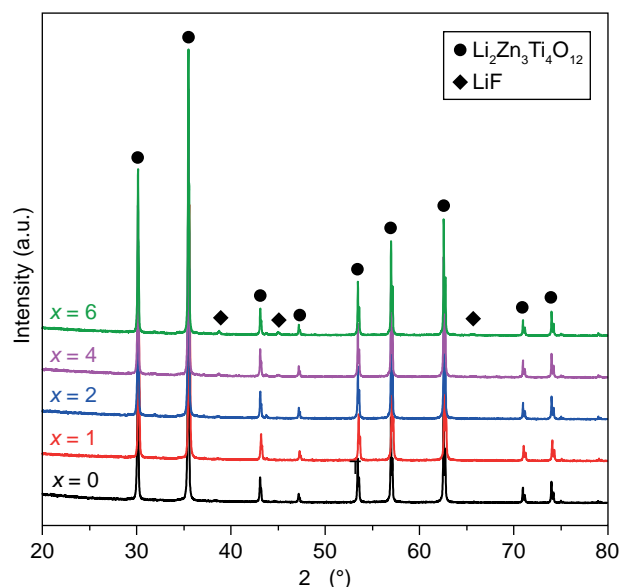


Figure 1. XRD patterns of the x wt. % LiF-doped $\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}$ ceramics sintered at 900 °C for 4 h.

The SEM image of the x wt. % LiF ($x = 0, 1, 2, 4, 6$) doped $\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}$ microwave dielectric ceramic sintered at 900 °C for 4 h are shown in Figure 2. All the samples exhibited a closely packed grain morphology and discernible grain boundaries. The average grain size is small and a large number of pores are present for the undoped sample ($x = 0$), which indicated an insufficient grain growth at 900 °C for this sample as shown in Figure 2a. However, when the doping amount was increased to 1 wt. %, the grain sizes grow significantly and fewer porosities were observed. As the LiF content was increased further, from 2 wt. % to 6 wt. %, as shown in Figure 2c, d, e, the crystal grains grew significantly, but the grain sizes were not uniform, indicating that the crystal grains grow abnormally. Thus, an appropriate addition of LiF can achieve the densification of the

ceramics. Figure 2f shows the image of the 1 wt. % LiF-doped $\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}$ ceramic co-fired with Ag at 900 °C for 4 h, as can be seen from the image, the Ag layer was well bonded to the ceramic surface and had no permeation diffusion. Therefore, the 1 wt. % LiF-doped $\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}$ ceramic has a good chemical compatibility with Ag, so the system is well suited for LTCC material applications.

The variation in the apparent densities as a function of x ($x = 0, 1, 2, 4, 6$) for the LiF doped $\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}$ ceramics sintered from 850 °C to 950 °C for 4 h are presented in Figure 3. The apparent densities of the ceramics firstly increased and then decreased with an increasing LiF content. When 1 wt. % of the LiF was doped, the densities significantly increased, which was consistent with the SEM image of the microstructure. The samples sintered at 900 °C for 4 h showed a maximum apparent density of $4.17 \text{ g}\cdot\text{cm}^{-3}$ and a relative density of 96.98 %. However, as the temperature was raised to 950 °C, the density decreased due to the excessive sintering temperature. Under different doping levels, when the doping amount was 2–4 wt. %, the density decreased slowly with an increase in the doping amount. Moreover, the reasons for these decreases can be attributed to two aspects. On the one hand, since the doping amount

was increased, the crystal grains grew abnormally, and pores were generated, so that the density was lowered. On the other hand, the density of the resulting new LiF phase was $2.64 \text{ g}\cdot\text{cm}^{-3}$ (JCPDS#00-002-1111), which was much smaller than the density of $\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}$. When the doping amount was 6 wt. %, the ceramic density was further lowered, which was caused by the obvious

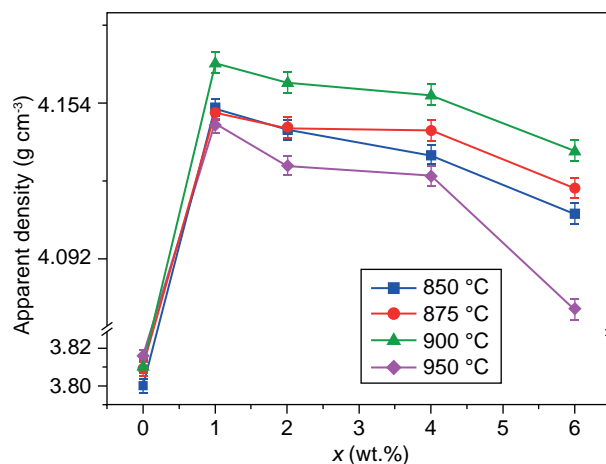


Figure 3. The densities of the x wt. % LiF doped $\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}$ ceramics sintered at the different sintering temperatures.

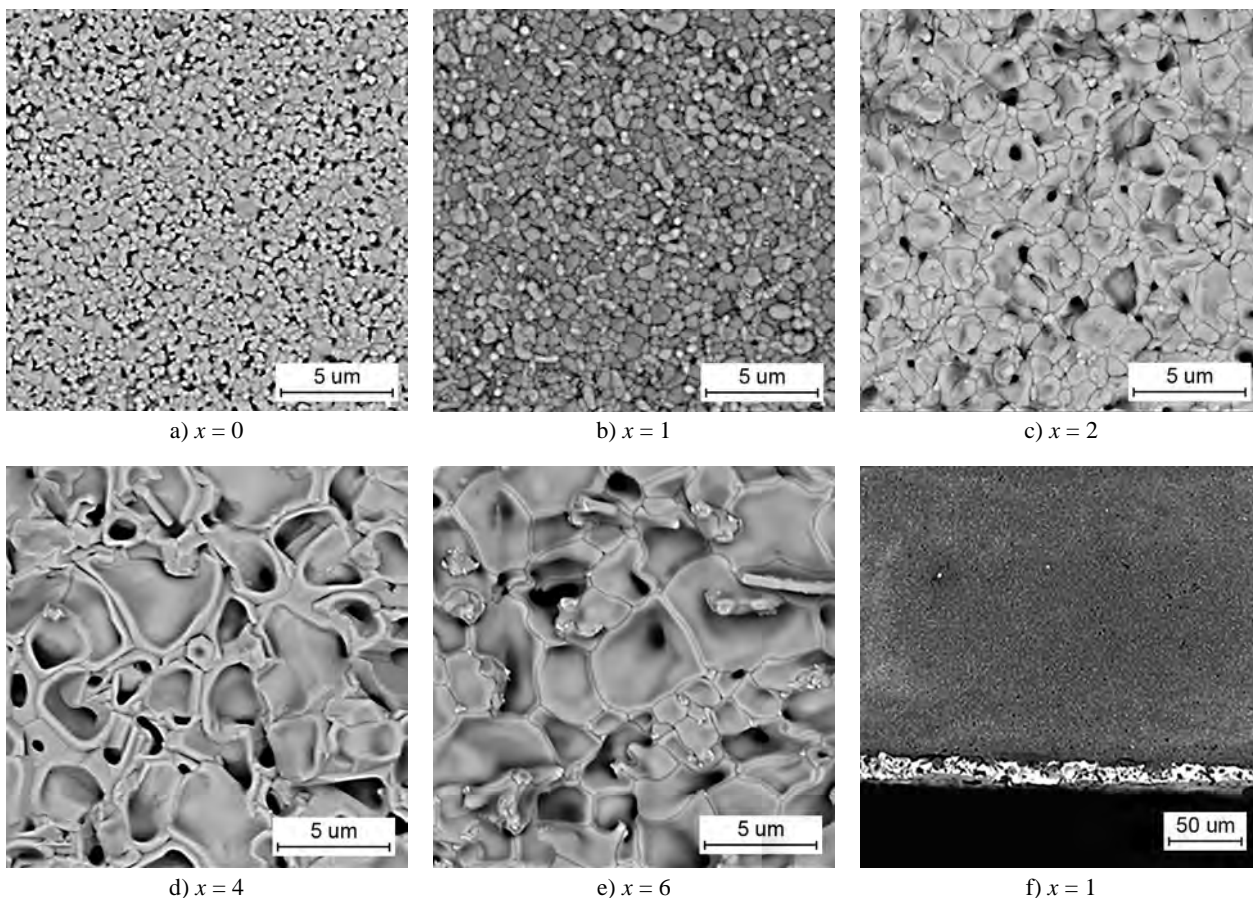


Figure 2. SEM image of the x wt. % LiF ($x = 0, 1, 2, 4, 6$) doped $\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}$ ceramics sintered at 900 °C for 4 h: a) $x = 0$; b) $x = 1$; c) $x = 2$; d) $x = 4$; e) $x = 6$; f) $x = 1$ at 900 °C with silver co-firing 4 h SEM image.

extrinsic defect, as seen in Figure 2e. It is concluded that an appropriate amount of doped LiF promoted the growth of ceramic grains, the elimination of pores and an increase in the ceramic density, thereby improving the microwave dielectric properties of the ceramics. Therefore, the optimum sintering temperature of the $\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}$ ceramic was 900 °C, and the optimum sample density was $4.17 \text{ g}\cdot\text{cm}^{-3}$ with $x = 1 \text{ wt. \%}$.

Figure 4 shows the dielectric constants of the $\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}$ ceramics sintered from 850 °C to 950 °C as a function of the LiF-doped contents. Generally, the dielectric constant depended mainly on the density of the ceramic, the grain size, the ionic polarizability and the second phase. The dielectric constant, in this paper, was mainly affected by the densities and the LiF content of the second phase. It can be seen from the figure that the change in the dielectric constant of the ceramic was basically the same as the change in the density as a function of the doping amount. When the doping amount of LiF was constant, the dielectric constant of the ceramic first increased to the maximum value and then decreased with an increase in the temperature. As the sintering temperature increased, the ceramic grains grew and became denser, which caused a large number of pores to be eliminated, and the dielectric constant increased. However, if the temperature was too high, the abnormal growth of the crystal grains caused the densification of the ceramic to decrease, and the porosity increased, thereby reducing the dielectric constant. Similarly, the dielectric constant value also increased firstly and then decreased as the LiF doping amount increased, wherein at $x = 1 \text{ wt. \%}$, the maximum dielectric constant of 17.9 was obtained when the sample was sintered at 900 °C for 4 h.

Figure 5 displays the relationship between the LiF doping amount and the $Q \times f$ value of the $\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}$ ceramic at different temperatures. The $Q \times f$ value of the undoped ceramic sample increased with the sintering

temperature, because the temperature was too low and it was not completely sintered, and the $Q \times f$ value is only a few thousand GHz. When 1 wt. % of the LiF was added, the $Q \times f$ value of the sample showed a tendency to increase firstly and then decrease as the sintering temperature increased, and reached a maximum at 900 °C. When the LiF doping amount was 2 wt. %, the sintering temperature had little effect on the $Q \times f$ value of the ceramic, and the $Q \times f$ value increased slightly with an increasing sintering temperature. When the LiF doping amount was more than 2 wt. %, the $Q \times f$ value of the ceramic sample increased firstly and then decreased with the increasing LiF doping amount. When the LiF doping amount was more than 2 wt. %, the $Q \times f$ value of the ceramic sample first increased and then decreased as the LiF doping amount increased. There are two main factors influencing the $Q \times f$ value of microwave dielectric ceramics. One is the lattice intrinsic loss of the crystal itself, and the other is the extrinsic loss. The extrinsic loss mainly included the grain boundary, defect, ceramic density, and the second phase. Therefore, for this phenomenon, as the LiF doping amount increased, a decrease in the density leads to a decrease in the $Q \times f$ value. On the other hand, when the doping amount was increased, a new LiF phase was generated. When the sintering temperature was 875 °C and 900 °C, the drop was drastic, which was understood to be that of the LiF and the ceramics, which promoted a better reaction at these two temperatures. Moreover, many micro-cracks appear on the grain boundary of the ceramics, which was the main reason for the decrease in the ceramic $Q \times f$ value. For the same temperature of 900 °C, as the amount of doping increased, the $Q \times f$ value of the ceramic first increased and then decreased, that is, from 2800 GHz to 47 983 GHz and then decreased to 24 944 GHz, and reached a maximum at a doping amount of 1 wt. %. The reason is that an appropriate amount of LiF dopant promotes ceramic growth, increases density,

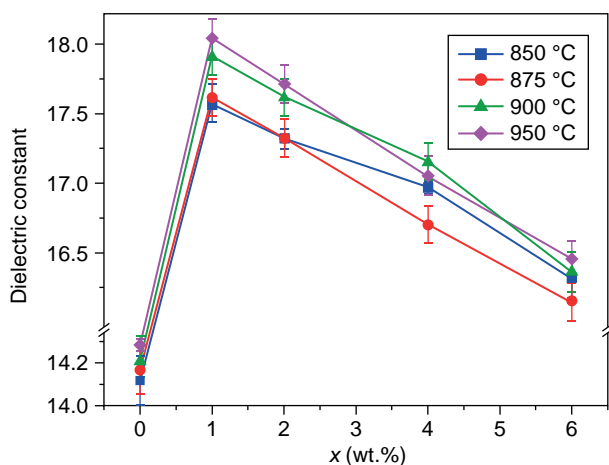


Figure 4. The dielectric constant value of the $x \text{ wt. \%}$ LiF doped $\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}$ ceramics sintered at the different sintering temperatures.

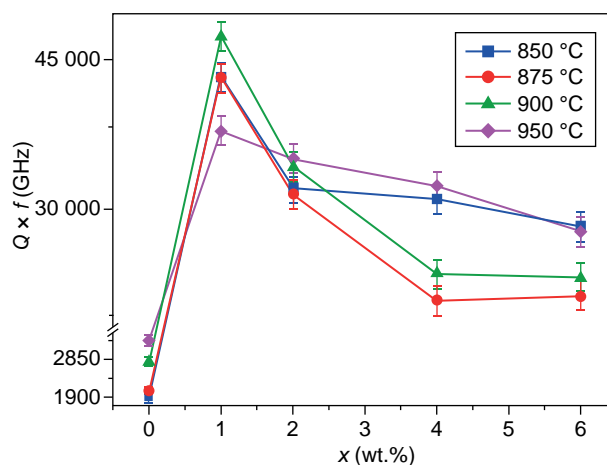


Figure 5. The variation in the $Q \times f$ value of the $x \text{ wt. \%}$ LiF doped $\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}$ ceramics at the different sintering temperatures.

and increases the $Q \times f$ value of the ceramic. However, the incorporation of excess LiF not only introduced a new phase, but also caused the abnormal growth of the crystal grains, which generated a large number of pores and reduced the density, which led to a decrease in the $Q \times f$ value of the ceramic; it also brought a large amount of liquid phase and absorbed the microwave's power, which reduced the $Q \times f$ value.

The temperature coefficient of the resonance frequency (τ_f) values of the x wt. % LiF doped $\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}$ ceramic after being sintered at 900 °C for 4 h are presented in Figure 6. When the amount of LiF increased from 0 to 6 wt. %, the τ_f value of the samples gradually decreased from -48 ppm/°C to -54 ppm/°C. Typically, the τ_f value of the ceramic is influenced by the primary ingredients, additives, and the second phase [15, 16]. In this study, the variation in the τ_f value was caused by the generation of the secondary phase of the LiF. Akinori Kan et al. [17] introduced LiF in MgO to lower the τ_f value. The LiF dopant also had a more negative τ_f value, which lowered the τ_f value of the $\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}$ ceramic. As discussed above, an LiF-doped $\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}$ ceramic with excellent microwave dielectric properties ($\epsilon_r = 17.9$, $Q \times f = 47\,983$ GHz, $\tau_f = -48.3$ ppm/°C) was obtained at $x = 1$.

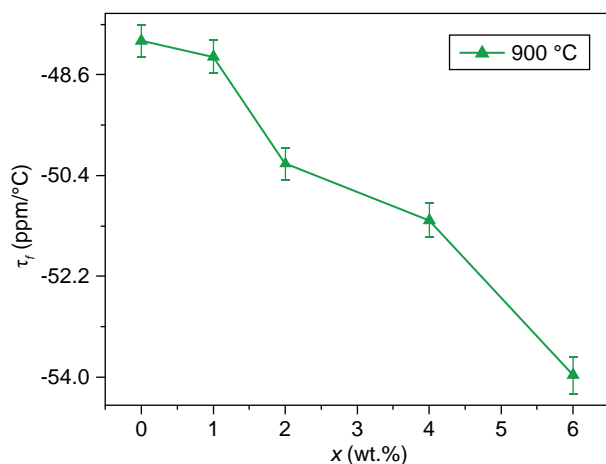


Figure 6. The τ_f values of the $\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}$ ceramics doped with different amounts of LiF sintered at 900 °C for 4 h.

CONCLUSION

In this paper, the effects of different LiF doping amounts on the sintering behaviour, microstructure and microwave dielectric properties of $\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}$ microwave dielectric ceramics were systematically investigated. The XRD patterns and the SEM images together demonstrated that the LiF and LZT coexisted and formed a stable composite system. The LiF doping amount largely affected the relative density and microwave dielectric properties of the ceramics. The results showed that the dielectric constant decreased from 17.9

to 16.4, and the $Q \times f$ value increased from 2800 GHz to 47 983 GHz and then decreased to 24 944 GHz with an increase in the LiF. The τ_f value decreased from -48 ppm/°C to -54 ppm/°C. The $\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}$ ceramic doped with 1 wt. % LiF presented a single-phase structure and excellent microwave dielectric properties with $\epsilon_r = 17.9$, $Q \times f = 47983$ GHz and $\tau_f = -48.3$ ppm/°C. This finding confirmed that LiF-doped $\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}$ microwave dielectric ceramics are good candidates in the application of LTCC manufacturing technologies.

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