

$\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}\text{-Ba}_3(\text{VO}_4)_2$ microwave dielectric ceramics sintered at a low temperature without glass addition

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Abstract The microstructure and microwave dielectric properties of the $(1-x)\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}\text{-xBa}_3(\text{VO}_4)_2$ composite ceramics prepared via a solid-state reaction method have been investigated systematically by using an X-ray diffractometer (XRD), a scanning electron microscope equipped with an energy dispersive spectrometer and a microwave network analyzer. The XRD results exhibited that the $\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}$ and $\text{Ba}_3(\text{VO}_4)_2$ ceramic could coexist well in the sintered bodies, and no other secondary phase was detected. The microstructure and microwave dielectric properties of the composite ceramics were found to be obviously dependent on the sintering temperature and phase composition. With the addition of the $\text{Ba}_3(\text{VO}_4)_2$ phase, the sintering temperature of the $\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}$ ceramic could be reduced effectively and its temperature coefficient of resonant frequency (τ_f) value could also be adjusted to near zero together with a comparable quality factor ($Q \times f$) value. Excellent microwave dielectric properties of dielectric constant $\epsilon_r \sim 16.9$, $Q \times f \sim 51,322$ GHz and $\tau_f \sim +3.3$ ppm/°C were obtained in the $0.4\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}\text{-}0.6\text{Ba}_3(\text{VO}_4)_2$ composite ceramic, when sintered at 950 °C for 4 h. The good chemical compatibility between the $0.4\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}\text{-}0.6\text{Ba}_3(\text{VO}_4)_2$ composite ceramic and silver electrode indicates that the as-prepared composite ceramic is suitable for low-temperature cofired ceramic (LTCC) applications.

1 Introduction

The wireless and mobile communication industry have been developing rapidly in two decades, the miniature and portable electronic devices are become the main trend in consumption markets. To meet the requirement of miniaturization and integration of modern communication devices, the low-temperature cofired ceramic (LTCC) technology is an important approach to make it come true. The microwave dielectric ceramics used in the LTCC field usually have the following requirements: high relative permittivity (ϵ_r), high quality factor (Q) and near-zero temperature coefficient of resonant frequency (τ_f) [1]. The most important demand is that the sintering temperature should not exceed 950 °C so that it can be cofired well with silver electrode (the melting point ~ 961 °C). However, most commercial microwave dielectric ceramics can not be cofired with silver due to the relative high sintering temperature, such as $\text{MgTiO}_3\text{-CaTiO}_3$ ($\sim 1,350$ °C) [2]. Hence, the search for new low temperature sintering ceramic materials or practical methods to lower the sintering temperature is a significative issue for the future development of communication systems.

Recently, a number of new novel microwave dielectric ceramics have been developed. Among them, Zhou et al. [3] reported that the $\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}$ (LZT) ceramic possesses excellent microwave dielectric properties of $\epsilon_r \sim 20.6$, $Q \times f \sim 106,700$ GHz and $\tau_f \sim -48$ ppm/°C, when sintered at 1,075 °C for 2 h. Disappointedly, the large negative τ_f value and relative high sintering temperature are a huge obstacle for it to be further applied in LTCC. Thus, several researchers made use of TiO_2 ($\sim +465$ ppm/°C) or Li_2TiO_3 ($\sim +20.3$ ppm/°C) to modify the τ_f value of LZT ceramic to near-zero firstly, and then added low-melting point oxides (e.g. B_2O_3 , CuO) or glass phase (e.g. $\text{Li}_2\text{O-ZnO-B}_2\text{O}_3$) to it

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for reducing the sintering temperature below 950 °C [4–7]. It was obvious that the additives also brought about the deterioration of microwave dielectric properties seriously, although the sintering temperature was dropped apparently. Therefore, if there was a ceramic material that possessed above two characters (namely, positive τ_f value and low sintering temperature), the microwave dielectric properties of the final composite ceramics could be improved or comparable at least.

In our previous studies, it was found that the $\text{Ba}_3(\text{VO}_4)_2$ (BV) ceramic has good microwave dielectric properties ($\epsilon_r \sim 14$, $Q \times f \sim 42,000$ GHz and $\tau_f \sim +52$ ppm/°C) with relatively low sintering temperature ($\sim 1,100$ °C) [8]. In the study of $\text{BV-LiMg}_{0.9}\text{Zn}_{0.1}\text{PO}_4$, the sintering temperature of $\text{LiMg}_{0.9}\text{Zn}_{0.1}\text{PO}_4$ ceramic was found to be reduced to 800 °C after 55 vol % BV addition [8]. Meanwhile, the τ_f value of $\text{LiMg}_{0.9}\text{Zn}_{0.1}\text{PO}_4$ ceramic could be adjusted to ~ -2.1 ppm/°C and the final properties were also very good. Thus, in present work, the BV ceramic was also employed to modify the LZT ceramic. The microstructure and microwave dielectric properties of the (1-x)LZT-xBV composite ceramics were investigated systematically.

2 Experimental procedure

The LZT and BV ceramics were synthesized through a conventional solid-state reaction method. The LZT and BV powders were obtained by mixing the high-purity (>99.9 %) powders of Li_2CO_3 , ZnO , TiO_2 , BaCO_3 and V_2O_5 as the stoichiometric ratio strictly and then calcined at 900 °C for 8 h and 800 °C for 4 h, respectively. Then, (1-x)LZT-xBV ($x = 0.3-0.6$) were prepared by mixing the pure LZT and BV powders at several volume ratios. The mixtures were ground again by planetary ball milling for 6 h in the alcohol medium using zirconia balls. The slurries were then dried, mixed together with an appropriate amount of 5 wt% poly vinyl alcohol (PVA) as a binder. The granulated powders were subsequently pressed into cylinders with dimensions of 10 mm in diameter and 7–8 mm in height. The specimens were first heated at 550 °C for 4 h at 3 °C/min to burn out the organic binder, and then sintered in the temperature range of 925–1,025 °C for 4 h at 5 °C/min in air. In order to suppress the lithium evaporation loss, the pellets were muffled with the powders of the same composition. The bulk densities of the sintered pellets were measured by the Archimedes method. The theoretical densities of the compounds are calculated by the following formula:

$$\rho_{theo} = \frac{W_1 + W_2}{W_1/\rho_1 + W_2/\rho_2} \tag{1}$$

where, ρ_1 , ρ_2 and W_1 , W_2 are the theoretical densities and weight fractions of LZT and BV, respectively. The relative densities of the composite ceramics are calculated by the equation of $\rho_{measured}/\rho_{theoretical}$.

The crystal structure of the sintered ceramics was examined by an X-ray diffractometer (XRD, D/Max2500V, Rigaku, Japan) using $\text{CuK}\alpha$ radiation. The grain morphology was analyzed by a scanning electron microscope (SEM, JSM-6490LV, JEOL, Tokyo, Japan) equipped with an energy dispersive spectrometer (EDS). Microwave dielectric properties of the sintered samples were measured by a network analyzer (N5230C, Agilent, Palo Alto, CA) in the frequency range of 8–10 GHz. The dielectric constant was measured by the Hakki-Coleman method [9, 10] modified by Courtney, and the unloaded Q values were measured by the cavity method [11]. The τ_f value of the samples was measured in the temperature range from 20 to 80 °C. It can be calculated by the following relationship:

$$\tau_f = \frac{f_{80} - f_{20}}{f_{20} \times (80 - 20)} \times 10^6 (\text{ppm}/^\circ\text{C}) \tag{2}$$

where f_{80} and f_{20} represent the resonant frequencies at 80 and 20 °C, respectively.

3 Results and discussion

Figure 1 shows the XRD patterns of (1-x)LZT-xBV ceramics sintered at optimal temperatures for 4 h. It is clearly seen that all of the peaks could be indexed in terms of the MgFe_2O_4 (+) and BV (*), whose crystal structures are cubic (JCPDS #36-0398) belonging to the space group of $\text{Fd-3 m}(227)$ and hexagonal (JCPDS #29-0211)

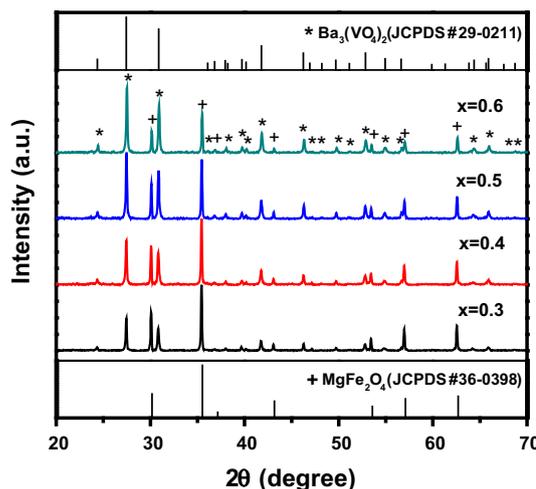


Fig. 1 The XRD patterns of (1-x)LZT-xBV composite ceramics sintered at optimal temperatures for 4 h

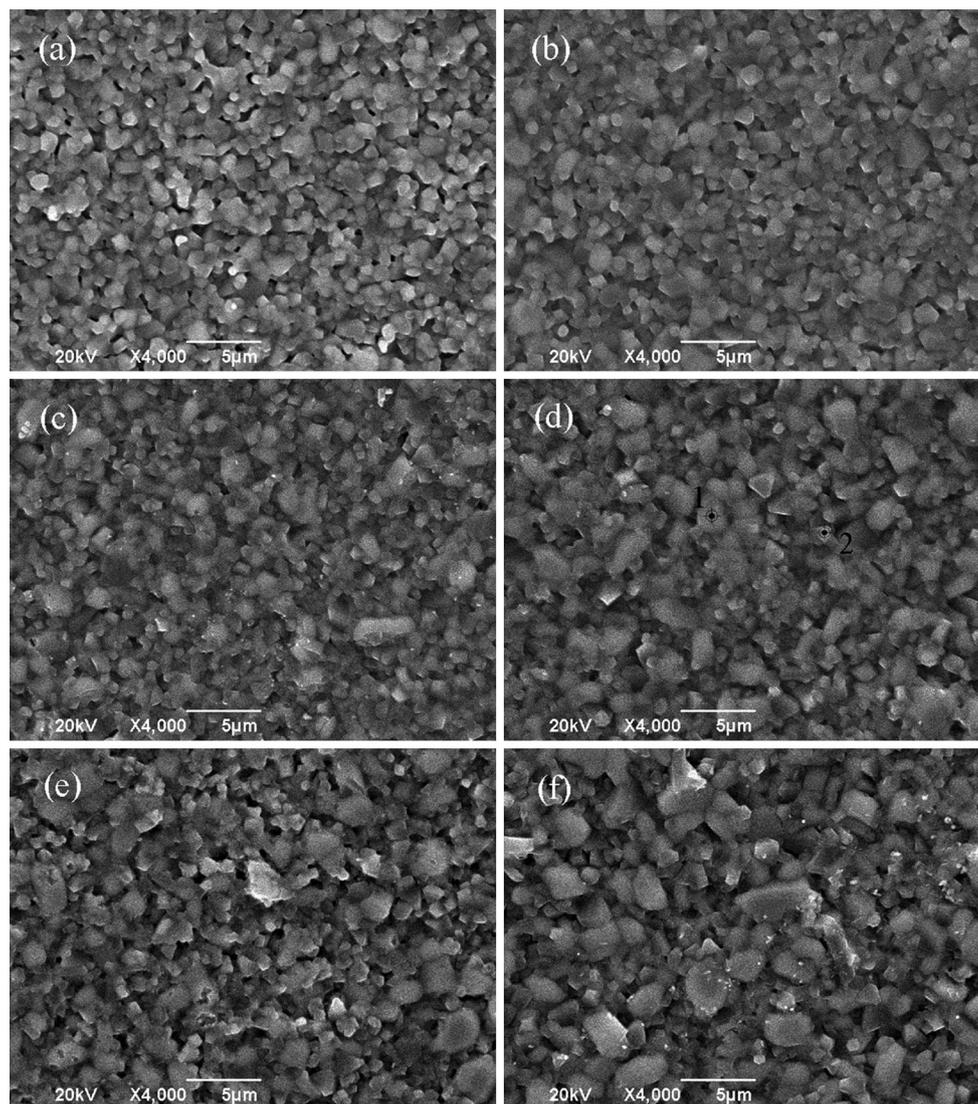


Fig. 2 The SEM images of $(1-x)\text{LZT}-x\text{BV}$ composite ceramics sintered at different temperatures for 4 h: **a** $x = 0.3$, at $950\text{ }^\circ\text{C}$; **b** $x = 0.4$, at $950\text{ }^\circ\text{C}$; **c** $x = 0.5$, at $950\text{ }^\circ\text{C}$; **d** $x = 0.6$, at $950\text{ }^\circ\text{C}$; **e** $x = 0.6$, at $925\text{ }^\circ\text{C}$ and **f** $x = 0.6$, at $975\text{ }^\circ\text{C}$

Table 1 The EDS data of $0.4\text{LZT}-0.6\text{BV}$ ceramics shown in Fig. 2d

Spots	Elements (Atom %)					Total (%)
	Zn K	Ti K	Ba L	V K	O K	
1	10.88	14.21	6.91	4.92	63.07	100.00
2	6.65	10.55	13.76	9.23	59.82	100.00

belonging to the space group of $R-3\ m(166)$, respectively. The crystal structure of LZT is similar to that of MgFe_2O_4 , which agreed well with what Zhou et al. reported³. The lattice parameters are $a = 8.40172\text{ \AA}$, $V = 593.07\text{ \AA}^3$, and $Z = 8$ (Z represents the number of unit cell molecules in a unit cell) [3]. The BV is composed of tetrahedral $[\text{VO}_4]$ units (which center is located by V^{5+} ion) linked by sixfold

or tenfold coordinated Ba^{2+} ions [12]. With increasing x , the intensities of the diffraction peaks of LZT phase decreased, whereas the intensities of BV phase increased. From the XRD pattern, it was concluded that both of the phases could coexist well in the sintered bodies, and no other phases were detected.

The SEM micrographs of $(1-x)\text{LZT}-x\text{BV}$ ceramics sintered at different temperatures for 4 h are illustrated in Fig. 2. It could be seen that all samples consisted of two types of grains, namely light grains and dim grains. In order to identify the compositions of these two types of grains, EDS analysis was used to distinguish each grain in $0.4\text{LZT}-0.6\text{BV}$ ceramic sintered at $950\text{ }^\circ\text{C}$, and the results are listed in Table 1. It revealed that the big and dim grains were the LZT phase (marked 1 in Fig. 2d), whereas the

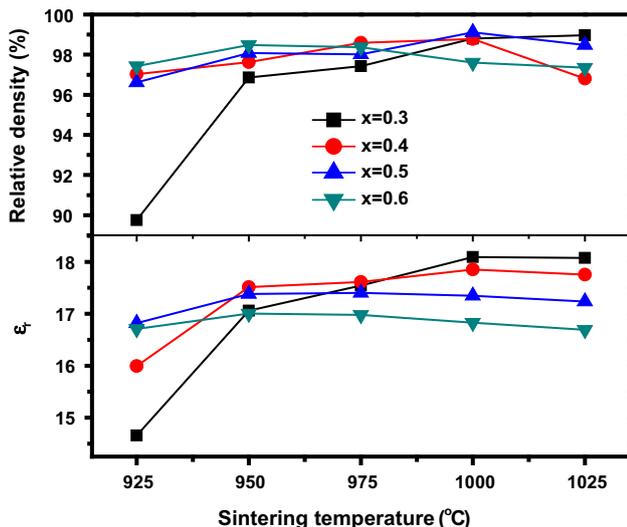


Fig. 3 The variation of relative density and ϵ_r of (1-x)LZT-xBV composite ceramics sintered at various temperatures for 4 h

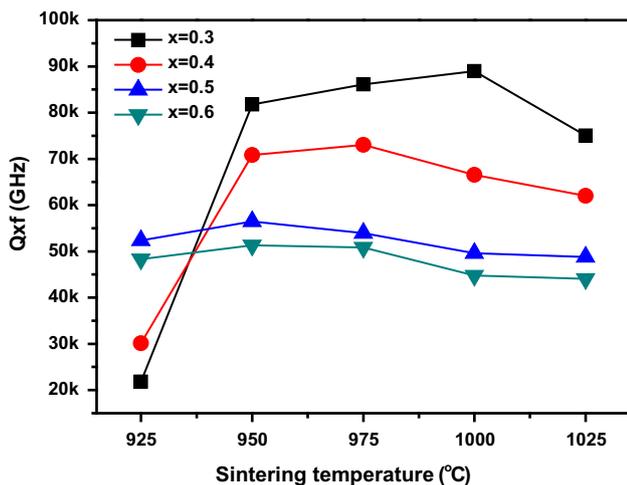


Fig. 4 The variation of $Q \times f$ values of (1-x)LZT-xBV composite ceramics sintered at various temperatures for 4 h

small and light ones were the BV phase (marked 2 in Fig. 2d). However, there was ionic diffusion between the two phases, because Ba^{2+} , V^{5+} could be detected in LZT phase, and Zn^{2+} , Ti^{4+} could be detected in BV phase (Li^+ is too light to be detected). For investigating the effect of BV content on the sintering behaviour, the grain morphologies of (1-x)LZT-xBV ceramics are shown in Fig. 2a-d. When x values were small ($x = 0.3$ or 0.4), the ceramics was not dense and the grain did not grow well. As x values increased, the pores were almost eliminated and the grain growth rapidly. Figure 2d-f show the effect of sintering temperature on the grain growth for the $x = 0.6$ sample. As the sintering temperature increased, the microstructure of 0.4LZT-0.6BV ceramic became dense,

Table 2 The theoretical and measured microwave dielectric properties of (1-x)LZT-xBV composite ceramics sintered at optimal temperatures

x	ϵ_r	$Q \times f$ (GHz)	τ_f (theoretical) (ppm/°C)	τ_f (measured) (ppm/°C)	ST (°C)
0.3	18.1	88,982	-18	-25.4	1,000
0.4	17.5	73,053	-8	-15.8	975
0.5	17.4	56,462	2	-5.3	950
0.6	16.9	51,322	12	+3.3	950

ST sintering temperature

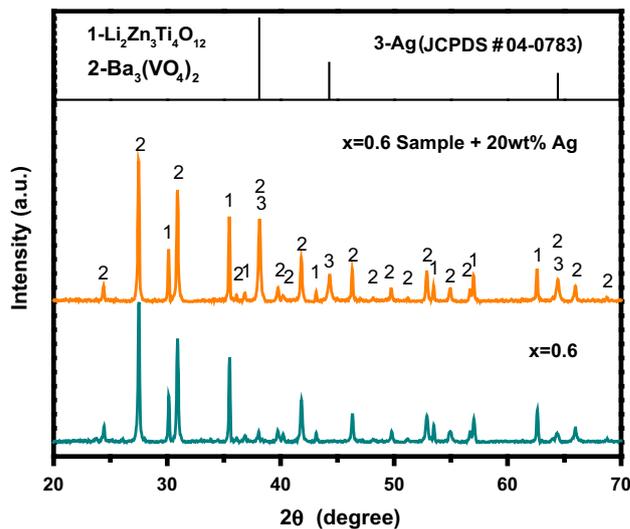


Fig. 5 The XRD patterns of the 0.4LZT-0.6BV sample mixed with 20 wt% Ag powders and sintered at 950 °C for 4 h

and no obvious pores could be observed at 950 °C. However, inhomogeneous grain growth occurred at 975 °C, which might degrade the microwave dielectric properties of the ceramics. As discussed above, the BV content and sintering temperature both played an important role in enhancing the densification of the ceramics, meaning that the BV could act as a low temperature sintering additive.

The relative densities and ϵ_r values of (1-x)LZT-xBV ceramics as a function of sintering temperature are shown in Fig. 3, through which the optimized sintering temperature can be determined. For all the samples, the relative densities increased firstly with increasing temperature, and then decreased after reaching their respective maximum values. It could be seen that the maximal relative density of each composition was very high ($\geq 97\%$), and the addition of BV could significantly reduced the sintering temperature of LZT by about 50 °C. The relationships between ϵ_r values and sintering temperatures revealed the same trend with those between relative densities and sintering temperatures since higher density results in a lower porosity.

Table 3 Comparison of LZT-based compounds between this work and the references

Compounds	ϵ_r	$Q \times f$ (GHz)	τ_f (ppm/°C)	ST (°C)	Ref.
0.4LZT–0.6TiO ₂	25.1	62,000	–5.2	1,075/4 h	[4]
0.3LZT–0.7Li ₂ TiO ₃	22.0	38,900	–1.3	1,100/2 h	[5]
0.2LZT–0.8Li ₂ TiO ₃ + 2.5 wt% Li ₂ O–B ₂ O ₃ –SiO ₂	22.0	28,407	–1.6	900/2 h	[5]
LZT + 1.5 wt% Li ₂ O–ZnO–B ₂ O ₃	19.1	63,751	–48.9	900/2 h	[6]
0.2LZT–0.8Li ₂ TiO ₃ + 3 wt% B ₂ O ₃ –CuO	18.5	42,000	–37.6	925/2 h	[7]
0.4LZT–0.6BV	16.9	51,322	+3.3	950/4 h	This work

ST sintering temperature, *Ref* references

The ϵ_r values varied in a narrow range from 18.1 to 16.9, and the ϵ_r value of the composite ceramics was generally decreased because of a lower ϵ_r value of the BV ceramic compared with that of the LZT ceramic.

Figure 4 shows the $Q \times f$ values of (1–x)LZT–xBV ceramics at different sintering temperatures for 4 h. The contributions from various intrinsic and extrinsic parameters affect the $Q \times f$ values. Intrinsic effects are due to the interaction of phonon systems with the ac electric field [13]. Extrinsic parameters such as crystal imperfections, nonstoichiometry, grain boundaries, microstructural defects, porosity, and even crystallite orientation also effect the $Q \times f$ values [14–16]. It was observed that the $Q \times f$ values versus sintering temperature exhibited a trend similar to that of relative density versus temperature. The $Q \times f$ values increased with increasing temperature initially, which was attributed to the increase in the density as well as grain growth. After reaching the maximum values, the $Q \times f$ dropped or remain nearly unchanged because of the abnormal growth of partial grains. On the other hand, the deterioration of $Q \times f$ values might be due to the decreased densification caused by the evaporation of lithium at elevated temperatures.

In addition, the optimal microwave dielectric properties of each composition, and theoretical and measured τ_f values are listed in Table 2. For all samples sintered at optimal temperatures, the ϵ_r and $Q \times f$ values decreased from 18.1 and 88,982 to 16.9 and 51,322, respectively, with increasing the BV content. While the variation of τ_f values presents an opposite trend against the ϵ_r and $Q \times f$ values, which is due to the positive τ_f value of BV. The theoretical values of τ_f are calculated by the mixing rule described as following:

$$\tau_f = x_1 \tau_{f1} + x_2 \tau_{f2} \quad (3)$$

where x_1 and x_2 are the volume fractions of LZT and BV ceramics, τ_{f1} and τ_{f2} are the τ_f values of LZT and BV ceramics, respectively. From Table 2, it could be seen that the measured τ_f values showed a similar trend to the theoretical ones, although there was a small difference between them. This phenomenon might be ascribed to the ionic diffusion between the two phases as confirmed by the

EDS analysis. A near zero τ_f value ($\sim +3.3$ ppm/°C) could be obtained in 0.4LZT–0.6BV composite ceramic sintered at 950 °C for 4 h.

It is interesting to note that as the BV content increased to 0.6, the sintering temperature of LZT could be decreased to 950 °C, which was below the melting point of silver. So that it could be used for LTCC. To evaluate the chemical compatibility of the 0.4LZT–0.6BV composite ceramic with silver electrode, it was cofired with 20 wt% silver powder at 950 °C for 4 h, and the corresponding results are presented in Fig. 5. The XRD pattern did not show the formation of any other phases except for 0.4LZT–0.6BV and silver, suggesting that this composite ceramic had a chemical compatibility with silver. Table 3 shows a series of LZT-based compounds reported in the references, together with a comparison with the present study. It could be seen that the BV ceramic chosen in this work possesses both advantages of low sintering temperature and positive τ_f value, which reaches the target of the experimental design. Compared with other LZT-based ceramics, the composite ceramic prepared in this work has excellent microwave dielectric properties. Considering all other parameters such as the sintering temperature, microwave dielectric properties, and compatibility with silver electrode, it is reasonable to believe that the 0.4LZT–0.6BV composite ceramic could be selected as a suitable candidate for LTCC materials.

4 Conclusions

The microwave dielectric materials of the (1–x)LZT–xBV ($x = 0.3$ – 0.6) were investigated systematically in this study. All samples were sintered between 925–1,025 °C. The XRD and SEM patterns revealed that the (1–x)LZT–xBV was a composite ceramic with no secondary phases over the whole composition range. As x varied from 0.3 to 0.6, the ϵ_r values decreased from 18.09 to 16.98, the $Q \times f$ values decreased from 88,982 to 51,322, and the τ_f values shifted from -25.4 ppm/°C to $+3.3$ ppm/°C. Moreover, when x values were 0.5 and 0.6, the sintering temperature was reduced to 950 °C, and simultaneously good

microwave dielectric properties were obtained. The deviation between the measured ϵ_r values and the theoretical ones were probably attributed to the ionic inter-diffusion. As a result, excellent microwave dielectric properties of $\epsilon_r \sim 16.9$, $Q \times f \sim 51,322$ GHz and $\tau_f \sim +3.3$ ppm/°C were obtained in 0.4LZT–0.6BV composite ceramic sintered at 950 °C for 4 h. Also, this material is compatible with silver electrodes, which proves to be a promising candidate for the LTCC applications.

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