

Microwave dielectric properties and low temperature firing of $(1 - x)\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12-x}\text{Li}_2\text{TiO}_3$ ($0.2 \leq x \leq 0.8$) ceramics with B_2O_3 – CuO addition

Ying Wu · Di Zhou · Jing Guo · Li-Xia Pang

Received: 22 August 2012 / Accepted: 29 October 2012 / Published online: 5 November 2012
© Springer Science+Business Media New York 2012

Abstract In the present work, the $(1 - x)\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12-x}\text{Li}_2\text{TiO}_3$ ($0.2 \leq x \leq 0.8$) ceramics were prepared via the solid state reaction method. The $0.8\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}-0.2\text{Li}_2\text{TiO}_3$ ceramic sample sintered at 1,160 °C for 2 h demonstrated high microwave dielectric property with a relative permittivity of 18.0, a high quality factor ($Q \times f$) $\sim 100,000$ GHz (at 7.2 GHz), and a temperature coefficient of resonant frequency about -47.8 ppm/°C. With 2.0 wt% $0.4\text{B}_2\text{O}_3-0.6\text{CuO}$ addition, a relative permittivity of 17.5, a $Q \times f$ value of 71,000 GHz and a temperature coefficient of resonant frequency of -44.4 ppm/°C can be obtained in $0.8\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}-0.2\text{Li}_2\text{TiO}_3$ ceramic sintered at 925 °C for 5 h and the chemical compatibility with silver electrode indicates that the ceramics may be a suitable candidate for the low temperature co-fired ceramic technology application.

1 Introduction

To meet the requirement of miniaturization and integration for wireless communication devices, the low temperature co-fired ceramic technology (LTCC) has become an important fabrication technology due to its advantage in

integrating electronic components and devices in a multi-layer ceramic structure [1, 2]. A range of dielectric constant (ϵ_r), high quality factor ($Q \times f$), near-zero temperature coefficient (τ_f), and low sintering temperature are a critical requirement for LTCC technology. However, most well-known commercial microwave ceramic materials cannot co-fire with the Ag electrode due to the high sintering temperatures above 1,000 °C [3–5]. Hence, the search for the novel low temperature firing microwave dielectric ceramic materials has always been a research hotspot [6, 7].

Recently, many studies have been focused on the Li_2TiO_3 ceramic due to its high performance of microwave dielectric properties with dielectric permittivity about 20–24, high $Q \times f$ value about 23,600–70,000 GHz and a τ_f value about +20 to +39 ppm/°C [8]. Its sintering temperature can be lowered to about 900 °C by addition of B_2O_3 – CuO frits, which made it a candidate for LTCC technology [9]. The $\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}$ ceramic sintered at 1,075 °C was reported to possess a permittivity of 20.6, a $Q \times f$ value $\sim 106,700$ GHz and a τ_f value of -48 ppm/°C [10]. The compensating τ_f values offer the opportunity to design $(1 - x)\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12-x}\text{Li}_2\text{TiO}_3$ composite ceramics, which might be temperature stable. In the present work, the influence of the B_2O_3 – CuO addition on the phase structure, microstructure and microwave dielectric properties of $(1 - x)\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}-\text{Li}_2\text{TiO}_3$ ceramic were investigated.

2 Experimental

Proportionate amounts of reagent-grade starting materials of Li_2CO_3 (≥ 98 %, Sinopharm Chemical Reagent Co., Ltd, Shanghai, China), TiO_2 and ZnO (≥ 99 %, >99 %, Sinopharm Chemical Reagent Co., Ltd, Shanghai, China) were

Y. Wu · D. Zhou (✉) · J. Guo
Electronic Materials Research Laboratory, Key Laboratory
of the Ministry of Education and International Center for
Dielectric Research, Xi'an Jiaotong University,
Xi'an 710049, Shaanxi, China
e-mail: zhoudi1220@gmail.com

L.-X. Pang
Micro-optoelectronic Systems Laboratories,
Xi'an Technological University, Xi'an 710032
Shaanxi, China

prepared according to the stoichiometric proportion of $(1-x)\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}-x\text{Li}_2\text{TiO}_3$ ($0.2 \leq x \leq 0.8$). Powders were mixed and milled for 4 h using a planetary mill (Nanjing Machine Factory, Nanjing, China) by setting the running speed at 150 rpm with the yttria-stabilized zirconia (2 mm in diameter) milling media. The mixed oxides were then sintered in air at temperatures 1,100 °C for 4 h. Then the powders were re-milled with different weight percentages 0.4B₂O₃–0.6CuO BCu addition (0–3 wt%) for 5 h using the ZrO₂ milling media and ethanol to increase reactivity and better homogeneity. After drying, the powders were pressed into cylinders (8 mm in diameter and about 5 mm in height) in a steel die with 5 wt% PVA binder addition under a uniaxial pressure of 250 MPa. The Samples were sintered in the temperature range of 1,160–1,240 °C and 850–950 °C for 2 h, respectively, for the pure $(1-x)\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}-x\text{Li}_2\text{TiO}_3$ and samples with the BCu additives. To investigate the chemical compatibility of $(1-x)\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}-x\text{Li}_2\text{TiO}_3$ ceramic with silver electrode, 20 wt% Ag powders were co-fired with the 0.8Li₂Zn₃Ti₄O₁₂–0.2Li₂TiO₃ samples added with BCu frits and held at 900 °C for 5 h.

The crystalline structures of samples were investigated using X-ray diffraction with CuK α radiation (RigakuD/MAX-2400 X-ray diffractometer, Tokyo, Japan). Microstructures of sintered ceramic were observed on the as-fired surface with scanning electron microscopy (SEM) (JSM-6460, JEOL, Tokyo, Japan). The dielectric behaviors at microwave frequency were measured with the TE₀₁₈ shielded cavity method using a network analyzer (8720ES, Agilent, Palo Alto, CA) and a temperature chamber (Delta 9023, Delta Design, Poway, CA). The TCF (τ_f) was calculated with the following formula

$$\tau_f = \frac{f_{85} - f_{25}}{f_{25} \times (85 - 25)} \times 10^6 \text{ ppm/}^\circ\text{C} \quad (1)$$

where f_{85} and f_{25} were the TE₀₁₈ resonant frequencies at 85 and 25 °C, respectively.

3 Results and discussions

Figure 1 shows the XRD patterns of the $(1-x)\text{LZT}-x\text{LT}$ ceramics ($0.2 \leq x \leq 0.8$) sintered at 1,200 °C/2 h, samples sintered at 900 °C/5 h with BCu addition and co-fired samples with 20 wt% Ag powders sintered at 900 °C/5 h. When $x \leq 0.2$, a LZT solid solution with a cubic structure [P4332] was formed. When x value increased to 0.4, the diffraction peaks of Li₂TiO₃ phase can be observed, which means that a composite ceramic was formed. The intensity of diffraction peaks of Li₂TiO₃ phase increased with the further increase of x value. Due to the small amount of BCu addition, no secondary phases can be revealed from the

XRD patterns. In the XRD pattern of co-fired sample, except the diffraction peaks of LZT solid solution and Li₂TiO₃ phase, the peaks of silver phase (Ag) can also be observed, which means that the silver did not react with the $(1-x)\text{LZT}-x\text{LT} + \text{BCu}$ system in 900 °C.

The microstructure of $(1-x)\text{LZT}-x\text{LT}$ ceramics sintered at 1,200 °C/2 h, samples with x wt% BCu additions and co-fired samples sintered at 900 °C/5 h are shown in Fig. 2. The grain size of $(1-x)\text{LZT}-x\text{LT}$ solid solution decreased from ~ 20 to ~ 8 μm with the increase of Li₂TiO₃ contents from $x = 0.2$ –0.8. The sintering temperature for pure LZT is around 1,075 °C. Hence, secondary growth of grains, segregation, and holes caused by the elements volatilization at the high temperature 1,200 °C can be observed from Fig. 2a–c. In the samples with BCu addition, the dense microstructure with two kinds of grains can be observed. According to the related EDS analysis, as shown in Fig. 3, the dark grains belong to the Li₂TiO₃ phase and the light grains belong to the $(1-x)\text{LZT}-x\text{LT}$ solid solution. The atom ratio of Ti and Zn was about 3:2 which was bigger than 4:3 in the pure Li₂Zn₃Ti₄O₁₂ ceramic. This might be attributed to the formation of solid solution in the $(1-x)\text{LZT}-x\text{LT}$ system. The grain size of the $(1-x)\text{LZT}-x\text{LT}$ ceramic with BCu addition, as shown in Fig. 2e,f. Was about 1–2 μm , which was much smaller than that of the pure $(1-x)\text{LZT}-x\text{LT}$ ceramic. Those results indicated that the addition of BCu effectively lowered the sintering temperature to around 925 °C.

The bulk density, $Q \times f$ values and relative permittivity of the pure $(1-x)\text{LZT}-x\text{LT}$ samples as a function of the sintering temperatures are shown in Fig. 4. Due to the

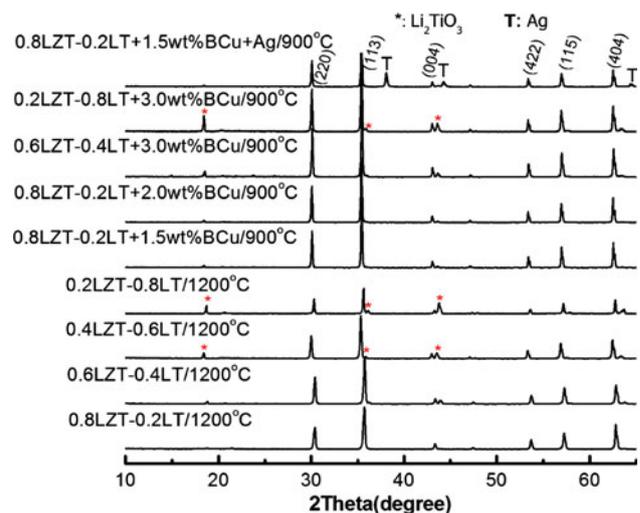


Fig. 1 The XRD profile for the pure $(1-x)\text{LZT}-x\text{LT}$ ceramic sintered at 1,200 °C/2 h, samples with x wt% BCu additive sintered 900 °C/5 h and co-fired sample with 20 wt% Ag powder sintered at 900 °C/5 h

Fig. 2 The SEM micrographs of the $(1 - x)\text{LZT} - x\text{LT} + y \text{ wt\% BCu}$: **a–d** for $x = 0.2 - 0.8, y = 0$; **e** $x = 0.2, y = 1.5$; **f** $x = 0.2, y = 2.0$; **g** $x = 0.6, y = 3.0$; **h** $x = 0.8, y = 3.0$; **i** $0.8\text{LZT} - 0.2\text{LT} + 1.5 \text{ wt\% BCu} + 20 \text{ wt\% Ag}$

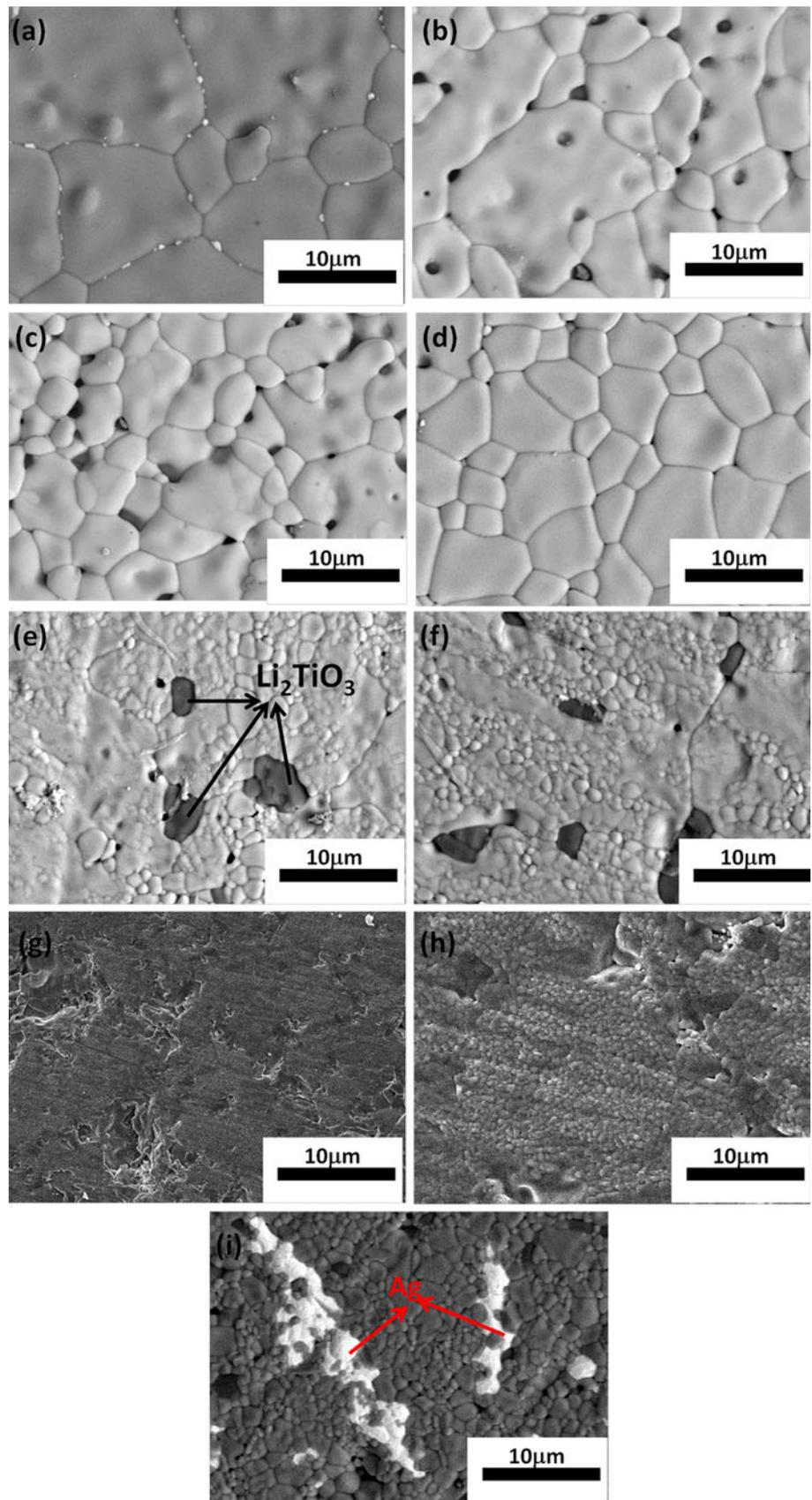


Fig. 3 EDS spectrum of 0.8LZT–0.2LT ceramic with 1.5 wt% BCu addition: **a** the light grains; and **b** the dark grains

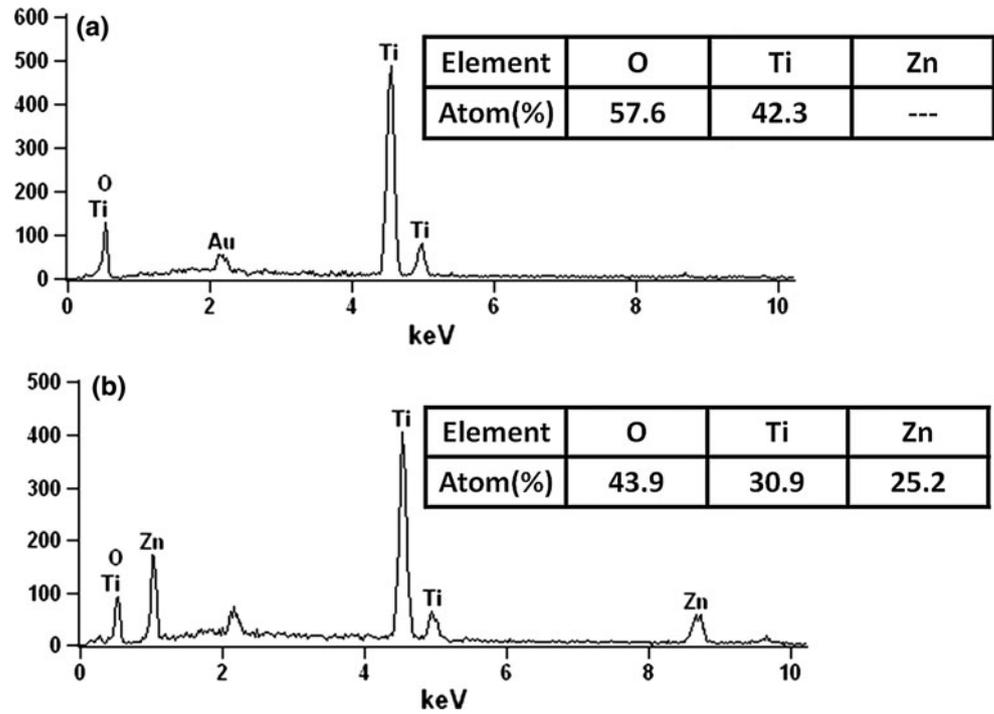
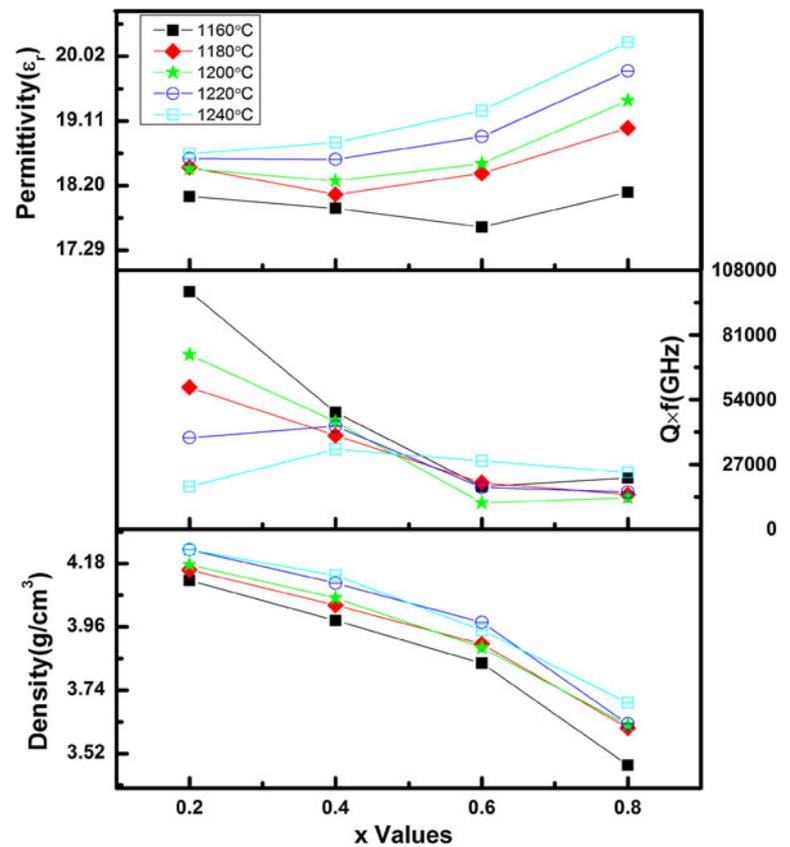


Fig. 4 The bulk density, $Q \times f$ and relative permittivity of $(1-x)\text{LZT}-x\text{LT}$ ceramics as a function of the sintering temperature



smaller density value of Li_2TiO_3 ($3.42 \text{ g}/\text{cm}^3$) than $\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}$ ($6.65 \text{ g}/\text{cm}^3$), it is understandable that the bulk densities almost linearly decrease about from 4.15 to

$3.58 \text{ g}/\text{cm}^3$ as x value increases from 0.2 to 0.8. For the same composition, the ϵ_r increases with the sintering temperature, which is consistent with the change trend of

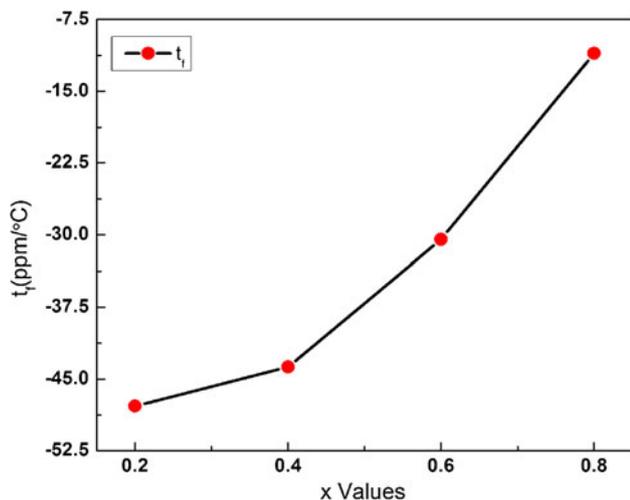


Fig. 5 Temperature coefficients of resonant frequency (τ_f) of the $(1 - x)$ LZT- x LT ceramics sintered at 1,160 °C

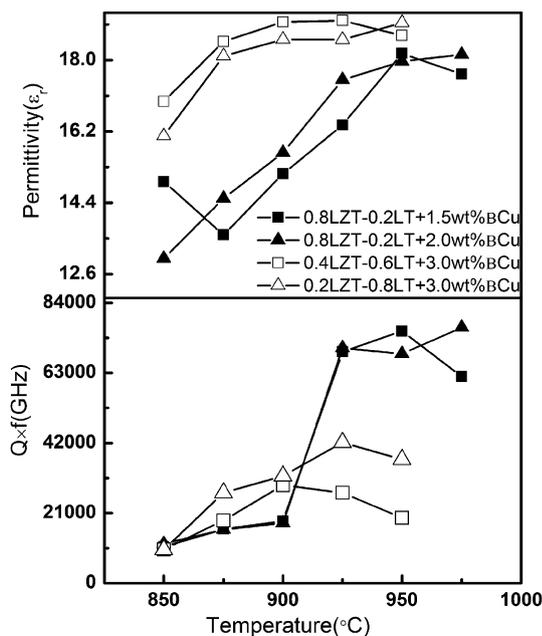


Fig. 6 Microwave dielectric constant and $Q \times f$ values of $(1 - x)$ LZT- x LT ceramics and samples with x wt% BCu addition as a function of sintering temperature

Table 1 Microwave dielectric properties of pure $(1 - x)$ LZT- x LT ceramic and $(1 - x)$ LZT- x LT ceramic with BCu addition

| Sample | ST (°C) | Permittivity | Qf (GHz) | TCF (ppm/°C) |
|----------------------------|---------|--------------|----------|--------------|
| 0.8LZT-0.2LT | 1,160 | 18.0 | 100,000 | -47.8 |
| 0.4LZT-0.6LT | 1,240 | 19.3 | 28,000 | -30.5 |
| 0.2LZT-0.8LT | 1,240 | 20.2 | 24,000 | -11.0 |
| 0.8LZT-0.2LT + 1.5 wt% BCu | 925 | 16.4 | 69,000 | -42.1 |
| 0.8LZT-0.2LT + 2.0 wt% BCu | 925 | 17.5 | 71,000 | -44.4 |
| 0.4LZT-0.6LT + 3.0 wt% BCu | 900 | 19.0 | 29,000 | -37.6 |
| 0.2LZT-0.8LT + 3.0 wt% BCu | 925 | 18.5 | 42,000 | -37.5 |

ST sintering temperature; TCF temperature coefficient of resonant frequency

the bulk density as a function of sintering temperature, and this phenomenon was attributed to the elimination of pores. The $Q \times f$ values generally decreased with x value and the largest $Q \times f$ values, about 100,000 GHz, was obtained in 0.8Li₂Zn₃Ti₄O₁₂-0.2Li₂TiO₃ ceramic sintered at 1,160 °C/ 2 h.

Figure 5 shows the temperature coefficients of resonant frequency (τ_f) of the $(1 - x)$ LZT- x LT ceramics sintered at 1,160 °C. The τ_f value of Li₂Zn₃Ti₄O₁₂, Li₂TiO₃ ceramic was about -48.0 ppm/°C and +38.5 ppm/°C, respectively. As x value increased from 0.2 to 0.8, the τ_f values of $(1 - x)$ LZT- x LT ceramic increased from -47.8 to -11.0 ppm/°C. However, when the τ_f value is close to zero the microwave dielectric property was deteriorated seriously. The 0.8LZT-0.2LT ceramic sintered at 1,160 °C shows the best microwave dielectric properties with $\epsilon_r = 28.0$, $Q \times f = 100,000$ GHz and $\tau_f = -47.8$ ppm/°C.

The microwave dielectric properties of the low-firing $(1 - x)$ LZT- x LT ceramic with BCu addition are shown in Fig. 6. With the increase of sintering temperature, the ϵ_r value increases gradually and then reaches saturated value. The saturated permittivity of 0.8LZT-0.2LT with 2.0 wt% BCu frits could be obtained at around 925 °C. For 0.4LZT-0.6LT and 0.2LZT-0.8LT with 3.0 wt% BCu additive the sintering temperature could be lowered to about 875 °C.

Although the BCu addition effectively lowered the sintering temperature and reduced the grain size, the increase of the grain boundaries, acting as two-dimensional defects, would bring much dielectric loss [9]. In other words, the grain sizes, grain shapes, and the pores would significantly affect the dielectric loss at microwave region. The $Q \times f$ value of 0.8LZT-0.2LT + 1.5 wt% BCu and 0.8LZT-0.2LT + 2.0 wt% BCu, ceramic sintered at 925 °C for 5 h were about 69,000 and 71,000 GHz respectively. For 0.4LZT-0.6LT + 3.0 wt% BCu and 0.2LZT-0.8LT + 3.0 wt% BCu ceramic, the $Q \times f$ values were around 29,000 and 42,000 GHz, respectively, which are a little higher than that of the ceramic without BCu addition. The sintering temperature and microwave dielectric property of well-densified $(1 - x)$ LZT- x LT + y wt% BCu ceramic are shown in Table 1. The τ_f value of 0.8LZT-0.2LT ceramic changed only a little with the BCu addition. For

0.4LZT–0.6LT and 0.2LZT–0.8LT, the τ_f value decreased to about -37.5 ppm/ $^{\circ}\text{C}$ with 3 wt% BCu addition.

4 Conclusion

The $(1-x)\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12-x}\text{Li}_2\text{TiO}_3$ ceramic prepared by the solid state reaction method can be densified above $1,160$ $^{\circ}\text{C}$ for 2 h. The best microwave dielectric property can be obtained in 0.8LZT–0.2LT ceramic with relative permittivity of 18.0, $Q \times f$ value of 100,000 GHz and τ_f value of -47.8 ppm/ $^{\circ}\text{C}$. With 2.0 wt% BCu addition, microwave dielectric properties with a relative permittivity of 17.5, a $Q \times f$ value of 71,000 GHz and a τ_f value of -44.4 ppm/ $^{\circ}\text{C}$ can be obtained in $0.8\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}-0.2\text{Li}_2\text{TiO}_3$ ceramic sintered at 925 $^{\circ}\text{C}$ for 5 h. With 3.0 wt% BCu addition, $0.2\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12}-0.8\text{Li}_2\text{TiO}_3$ shows good properties with a relative permittivity of 18.5, a $Q \times f$ value of 42,000 and a τ_f value of -37.6 ppm/ $^{\circ}\text{C}$. The $(1-x)\text{Li}_2\text{Zn}_3\text{Ti}_4\text{O}_{12-x}\text{Li}_2\text{TiO}_3$ ceramic with BCu addition also is chemical compatible with silver electrode, which makes it a suitable candidate for LTCC application.

Acknowledgments This work was supported by the National Science Foundation of China (51202182, 51202178), the Fundamental Research Funds for the Central University, the headmaster foundation of Xi'an Technological University (XAGDXJJ1001) and the Foundation of Shaanxi Educational Committee (12JK0432).

References

1. M.T. Sebastian, H. Jantunen, *Int. Mater. Rev.* **53**, 57 (2008)
2. R.J. Cava, *J. Mater. Chem.* **11**, 62 (2001)
3. L. Fang, D.J. Chu, H.F. Zhou, X.L. Chen, H. Zhang, B.C. Chang, *J. Alloys Compd.* **509**, 8840 (2011)
4. Y. Wu, D. Zhou, J. Guo, L.X. Pang, H. Wang, Y. Xi, *Mater. Lett.* **65**, 2680 (2011)
5. S. George, M.T. Sebastian, *J. Am. Ceram. Soc.* **93**, 2164 (2010)
6. L. Fang, D.J. Chu, H.F. Zhou, X.L. Chen, Z. Yang, *J. Alloys Compd.* **509**, 1880 (2011)
7. J. Guo, D. Zhou, H. Wang, Y.H. Chen, Y. Zeng, F. Xiang, Y. Wu, X. Yao, *J. Alloys Compd.* **509**, 5863 (2011)
8. Q. Zeng, W. Li, J.L. Shi, J.K. Guo, M.W. Zuo, W.J. Wu, *J. Am. Ceram. Soc.* **89**, 1733 (2006)
9. L.X. Pang, D. Zhou, *J. Am. Ceram. Soc.* **93**, 3614 (2010)
10. H.F. Zhou, X.B. Liu, X.L. Chen, L. Fang, Y.L. Wang, *J. Eur. Ceram. Soc.* **32**, 261 (2012)