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Microwave dielectric properties and low temperature sintering of $Li_2Zn(Ti_{1-x}Sn_x)_3O_8$ ($x \leq 0.20$) ceramics with B_2O_3–CuO addition

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Abstract In the present work, the influence of Sn substitution for Ti on the phase composition and microwave dielectric properties of the $Li_2Zn(Ti_{1-x}Snx)_3O_8$ ($x \leq 0.20$) ceramics was studied. It was found that the Sn did not occupy the Ti site in the $Li_2Zn(Ti_{1-x}Sn_x)_3O_8$ system but existed in the form of SnO_2 as a secondary phase. With the increase of Sn amount, the best microwave dielectric properties with $\varepsilon_r = 23.3$, $Q \times f = 71{,}000$ GHz and TCF = −21.7 ppm/°C were obtained in the $Li_2Zn(Ti_{0.9}Sn_{0.1})_3O_8$ ceramic sintered at 1,120 °C. The sintering temperature of $Li_2Zn(Ti_{0.9}Sn_{0.1})_3O_8$ ceramic can be can effectively lowered to below 960 °C by the addition of $0.4B_2O_3$–0.6CuO and this materials is chemically compatible with silver. This makes the $Li_2Zn(Ti_{1-x}Sn_x)_3O_8$ ceramics good candidates for low temperature co-fired ceramics technology.

1 Introduction

In the past decades, with the rapid development of the mobile communication, global positioning system and other wireless communication, the microwave electronic devices are required to be developed and fabricated for miniaturization and integration. To meet these developments, low temperature co-fired ceramic (LTCC) technology was widely used in fabrication of many kinds of electronic devices. The materials used in LTCC are required to have low sintering temperatures (below the melting point of silver), wide range of dielectric permittivity, low dielectric losses (high Qf values) and near-zero temperature coefficient (τ_f). In these requirements, the low sintering temperature is hardly satisfied because for many commercial microwaves dielectric ceramics, the sintering temperature is higher than 1,000 °C. One of effective approaches to lower the sintering temperature is adding the low melting point additives [1–3].

Recently, many researches have been done on the Li_2O-ZnO-TiO_2 ternary ceramic system for its excellent microwave dielectric properties. The $Li_2ZnTi_3O_8$ ceramic has a primitive cubic structure [$P4_332$] with lattice parameters of $a = 8.3{,}710$ Å, $V = 586.59$ Å^3, $Z = 4$ and $\rho = 3.94$ g/cm^3. The best microwave dielectric properties can be obtained with a relative permittivity of 25.6, a $Q \times f$ value of 72,000 GHz and a τ_f value of −11.2 ppm/°C when the ceramic was sintered at 1,075 °C [4–6]. With Li_2O–B_2O_3–SiO_2 (LBS) or ZnO–B_2O_3 frit addition, its sintering temperature could be lowered to around 900 °C, which makes it a suitable material for LTCC. However the τ_f value of $Li_2ZnTi_3O_8$ ceramic is not near zero. By adding tetragonal rutile TiO_2 ($\tau_f \sim$ 465 ppm/°C), the temperature stable composite ceramic $(1-x)Li_2ZnTi_3O_8$–$xTiO_2$ can be obtained [7, 8]. SnO_2 was a well-known semiconductor sensor material and it has a tetragonal structure similar to rutile TiO_2. The ionic radius of Sn^{4+} (0.69 Å) is a little larger than that of Ti^{4+} (0.605 Å) [9]. Hence, it is interesting to investigate the

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microwave dielectric properties of $Li_2Zn(Ti_{1-x}Sn_x)_3O_8$ system.

In this work, the phase structure, microstructure and microwave dielectric properties of $Li_2Zn(Ti_{1-x}Sn_x)_3O_8$ ceramics, fabricated via the conventional solid state reaction method, were investigated. The effects of the addition of $0.4B_2O_3$–0.6CuO (BCu) frits on the phase composition, sintering behavior, and microwave dielectric properties of $Li_2Zn(Ti_{1-x}Sn_x)_3O_8$ ceramics were also studied.

2 Experimental procedure

Proportionate amounts of reagent-grade starting materials of Li_2CO_3, TiO_2, SnO_2^- and ZnO (≥98, ≥99, >99, >99 %, Sinopharm Chemical Reagent Co., Ltd, Shanghai, China) were prepared according to the stoichiometric proportion of $Li_2Zn(Ti_{1-x}Sn_x)_3O_8$ ($0.05 \leq x \leq 0.20$). 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 1,050 °C for 4 h. Then the powders were re-milled with different weight percentages of $0.4B_2O_3$–0.6CuO (BCu) addition (0 ~ 2 wt%) for 5 h using the ZrO_2 milling media and ethanol. 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 pure $Li_2Zn(Ti_{1-x}Sn_x)_3O_8$ ($0.05 \leq x \leq 0.20$) ceramics and samples with the BCu additives were sintered in the temperature range of 1,080 ~ 1,160 °C and 850 ~ 950 °C for 2 h, respectively. To investigate the chemical compatibility of $Li_2Zn(Ti_{1-x}Sn_x)_3O_8$ ceramics with silver electrode, 20 wt% Ag powders were co-fired with the $Li_2Zn(Ti_{1-x}Sn_x)_3O_8$ 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 CuKα radiation (RigakuD/MAX-2400 X-ray diffractometer, Tokyo, Japan). Microstructures of sintered ceramics were observed on the as-fired surfaces with scanning electron microscopy (SEM) (JSM-6460, JEOL, Tokyo, Japan). The dielectric behaviors at microwave frequency were measured with the $TE_{01\delta}$ 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:

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

where f_{85} and f_{25} were the $TE_{01\delta}$ resonant frequencies at 85 and 25 °C, respectively.

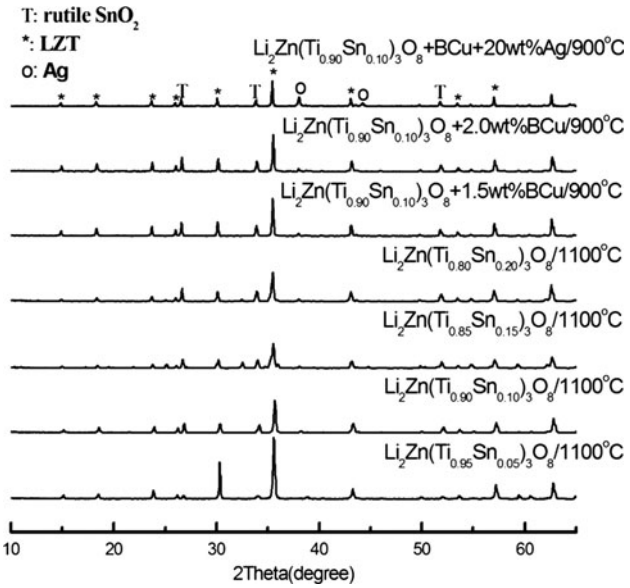

Fig. 1 The XRD profile for the pure $Li_2Zn(Ti_{1-x}Sn_x)_3O_8$ ceramic sintered at 1,100 °C/2 h, samples with x wt% BCu additive sintered 900 °C/5 h and co-fired sample with 20 wt% Ag powder sintered at 900 °C/5 h

3 Results and discussions

Figure 1 shows the XRD patterns of the $Li_2Zn(Ti_{1-x}Sn_x)_3O_8$ ($0.05 \leq x \leq 0.20$) ceramics sintered at 1,100 °C/2 h, samples with the x wt% BCu sintered at 900 °C/5 h and the co-fired sample with 20 wt% Ag powders sintered at 900 °C/5 h. In the XRD patterns of pure $Li_2Zn(Ti_{1-x}Sn_x)_3O_8$ ceramics and samples with BCu addition, only the SnO_2 phase and $Li_2ZnTi_3O_8$ phase were observed. For the co-fired samples, in addition to a set of diffraction peaks of Ag, the sample's diffraction pattern was the same with that of the pure $Li_2Zn(Ti_{1-x}Sn_x)_3O_8$ ceramic. This means that the silver does not react with the $Li_2Zn(Ti_{1-x}Sn_x)_3O_8$ + BCu system at 900 °C.

The SEI image of as-fired surfaces of pure $Li_2Zn(Ti_{1-x}Sn_x)_3O_8$ ceramics sintered at 1,100 °C, samples with BCu addition sintered at 950 °C and co-fire sample sintered at 900 °C are shown in Fig. 2. From the SEI image, it can be seen that there are two different grains in the $Li_2Zn(Ti_{1-x}Sn_x)_3O_8$ ceramics. According to the related XRD, Fig. 2 and EDS results, Fig. 3, the smaller grains distributing on the surface belong to SnO_2 phase and the bigger grains belong to $Li_2ZnTi_3O_8$ phase. From Fig. 2a–d, as the content of SnO_2 increased, the grain size of $Li_2ZnTi_3O_8$ decreases. This may be caused by the high sintering temperature of SnO_2. Fig. 2e, f show that, as the BCu addictives increased, the sintering temperature becomes lower and the grain size gets smaller. What's more, the Ag powders did not react with the ceramic, which agrees well with the XRD results.

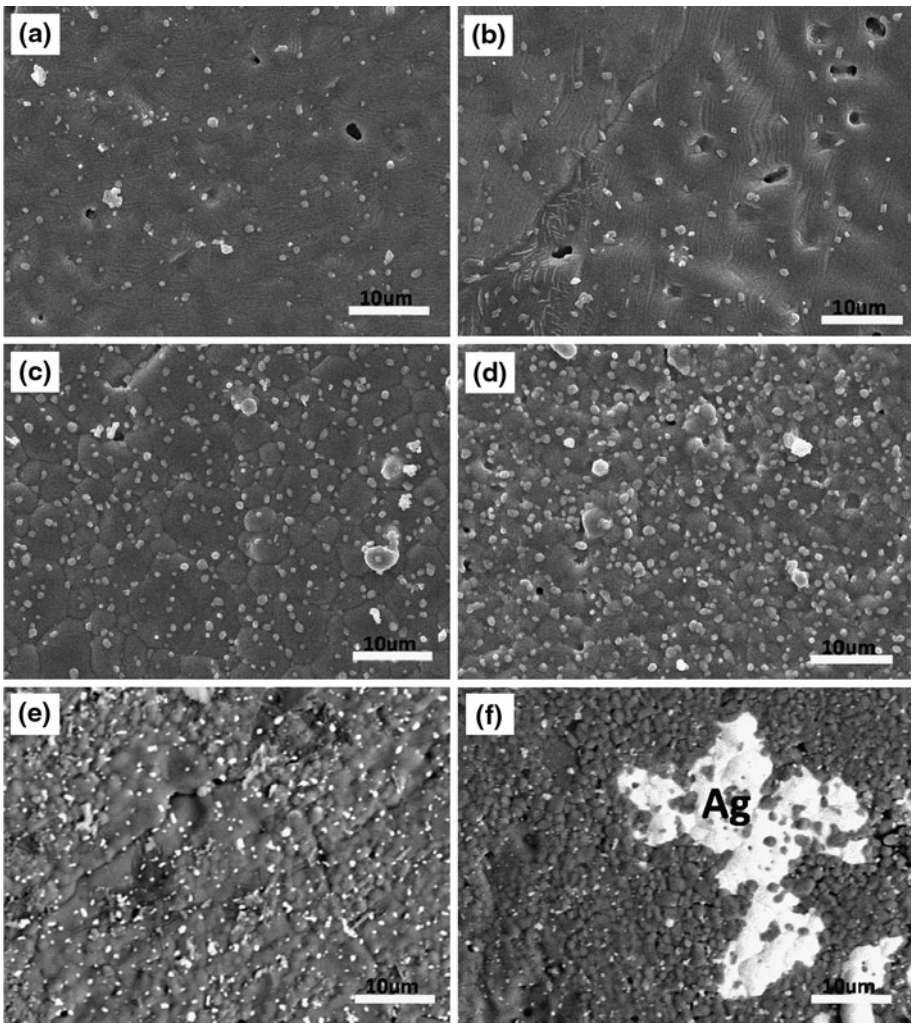

Fig. 2 The SEI micrographs of the $Li_2Zn(Ti_{1-x}Sn_x)_3O_8$ + y wt% BCu: **a**–**d** x = 0.05 ~ 0.20, y = 0; **e** x = 0.1, y = 2.0 and **f** $Li_2Zn(Ti_{0.9}Sn_{0.1})_3O_8$ + 1.5 wt% BCu + 20 wt% Ag

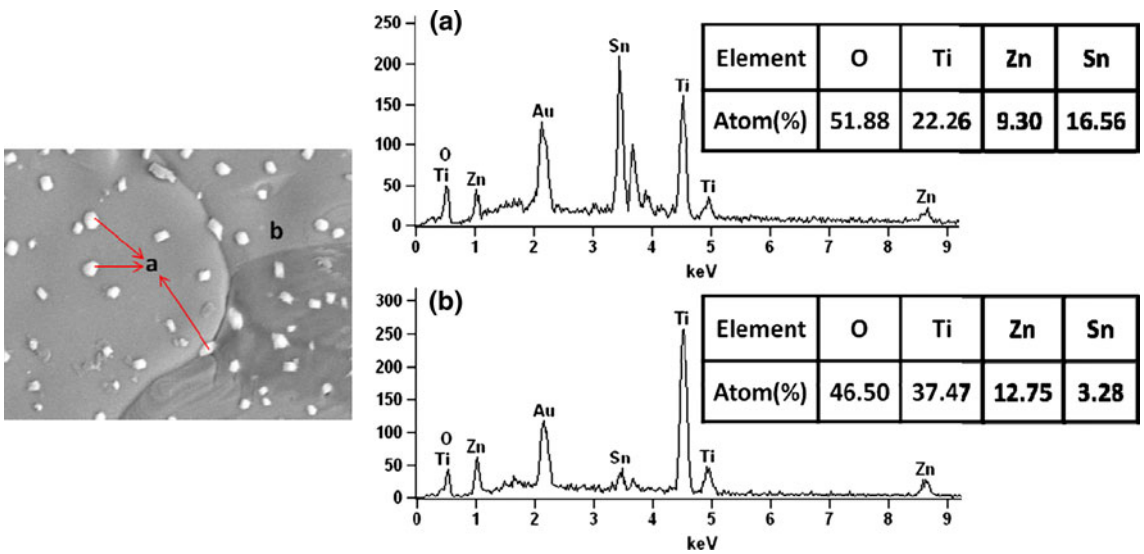

Fig. 3 The EDS spectrum of $Li_2Zn(Ti_{0.9}Sn_{0.1})_3O_8$ ceramic sintered at 1,100 °C/2 h **a** the smaller grains distributed on the surface; **b** the bigger grains

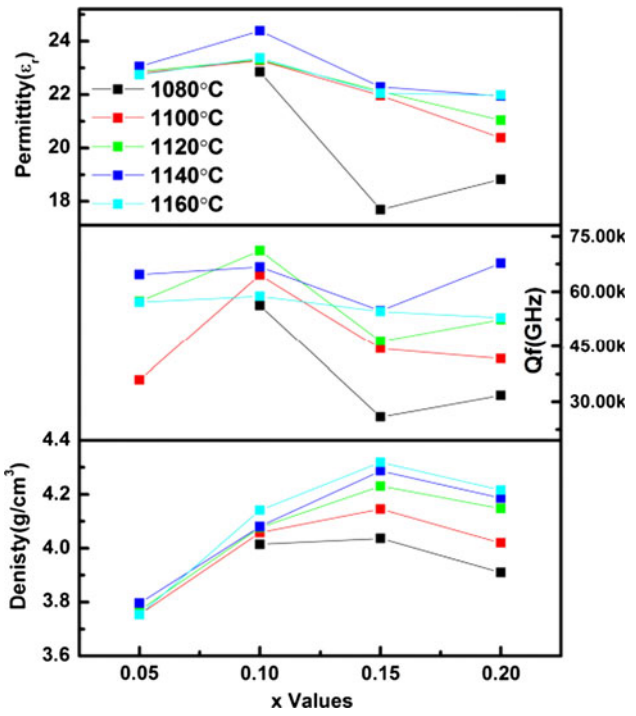

Fig. 4 The bulk density, Q × f and relative permittivity of $Li_2Zn(Ti_{1-x}Sn_x)_3O_8$ ceramics as a function of x value

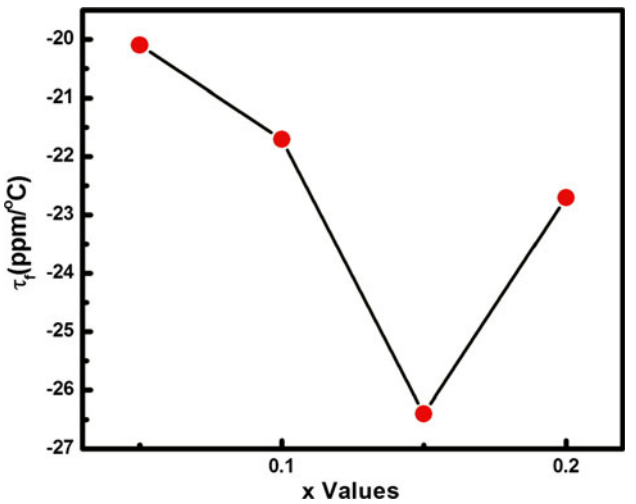

Fig. 5 The temperature coefficients of resonant frequency (τ_f) of the $Li_2Zn(Ti_{1-x}Sn_x)_3O_8$ ceramics sintered at 1,120 °C

The bulk density, Q × f values and relative permittivity of the pure $Li_2Zn(Ti_{1-x}Sn_x)_3O_8$ samples sintered at 1,080 ~ 1,160 °C/2 h as a function of x value are shown in Fig. 4. The bulk density of the ceramic first increased with x values and then slightly decreased at $x = 0.20$. The increase of the bulk densities is attributed to the large density value of SnO_2 (7.28 g/cm^3). Generally when the sintering temperature is above 1,080 °C, the effect of sintering temperature on the relative permittivity is not

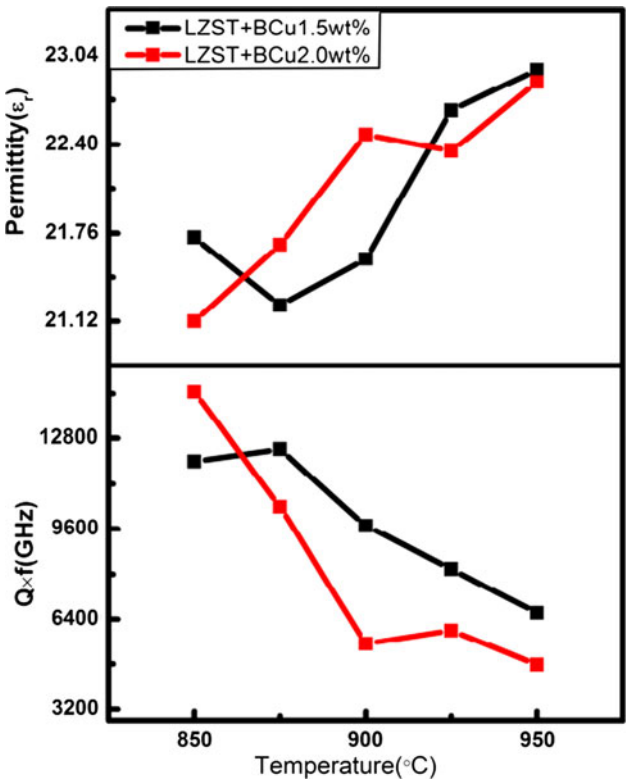

Fig. 6 The Q × f and relative permittivity of the $Li_2Zn(Ti_{0.9}Sn_{0.1})_3O_8$ sample with BCu addition as function of sintering temperature

obvious in the region $0.05 \leq x \leq 0.15$. And for $x = 0.15$, the permittivity increased gradually when the sintering temperature rised. When the sintering temperature was below 1,160 °C, the Q × f values of $Li_2Zn(Ti_{1-x}Sn_x)_3O_8$ increased with the sintering temperature. However, the Q × f values decreased with the further increase of sintering temperature. Figure 5 shows the temperature coefficients of resonant frequency (τ_f) of the $Li_2Zn(Ti_{1-x}Sn_x)_3O_8$ ceramics sintered at 1,120 °C. The τ_f is about −20 to −25 ppm/°C. Overall, the best microwave dielectric property with a relative permittivity of $\varepsilon_r = 23.3$, Q × f = 71,000 GHz and TCF = −21.7 ppm/°C can be obtained in $Li_2Zn(Ti_{0.9}Sn_{0.1})_3O_8$ ceramic sintered at 1,120 °C.

The microwave dielectric properties of the low-firing $Li_2Zn(Ti_{1-x}Sn_x)_3O_8$ ceramics with BCu addition are shown in Fig. 6. The ε_r value increased gradually as the sintering temperature rised. The BCu addition lowered the sintering temperature and reduced the grain size as shown in Fig. 2. This seriously affects the microwave dielectric losses because the grain boundaries, related to the sizes and shapes of grains and pores, interrupt the perfect symmetry of the crystal and act as two-dimensional defects. In other words, the grain sizes, grain shapes, and the pores would significantly affect the dielectric losses at microwave region. The Q × f values of $Li_2Zn(Ti_{0.9}Sn_{0.1})_3O_8$ + 1.5

Table 1 Microwave dielectric properties of pure $Li_2Zn(Ti_{1-x}Sn_x)_3O_8$ ceramic and $Li_2Zn(Ti_{1-x}Sn_x)_3O_8$ ceramic with BCu addiction

S. T.: sintering temperature; TCF: temperature coefficient of resonant frequency

Sample	S. T. (°C)	Permittivity	Qf (GHz)	TCF (ppm/°C)
$Li_2Zn(Ti_{0.95}Sn_{0.05})_3O_8$	1,100	23.3	64,500	−20.1
$Li_2Zn(Ti_{0.9}Sn_{0.1})_3O_8$	1,120	23.3	71,000	−21.7
$Li_2Zn(Ti_{0.85}Sn_{0.15})_3O_8$	1,140	24.4	67,000	−26.4
$Li_2Zn(Ti_{0.8}Sn_{0.2})_3O_8$	1,160	23.4	59,000	−22.7
$Li_2Zn(Ti_{0.9}Sn_{0.1})_3O_8$ + 1.5 wt% BCu	875	21.2	12,000	−20.3
$Li_2Zn(Ti_{0.9}Sn_{0.1})_3O_8$ + 2.0 wt% BCu	875	21.7	10,000	−19.3

wt% BCu and $Li_2Zn(Ti_{0.9}Sn_{0.1})_3O_8$ + 2.0 wt% BCu ceramics decreased as the sintering temperature increased from 850 to 950 °C. The sintering temperatures and microwave dielectric properties of well-densified $Li_2Zn(Ti_{0.9}Sn_{0.1})_3O_8$–$xSnO_2$ + y wt% BCu ceramics are shown in Table 1. The $Li_2Zn(Ti_{0.9}Sn_{0.1})_3O_8$ ceramic sintered at 1,120 °C shows best microwave dielectric properties with a relative permittivity of $\varepsilon_r = 23.3$, $Q \times f =$ 71,000 GHz and TCF = −21.7 ppm/°C. With the BCu addition, the ceramic could be well sintered below the silver melting point and the Qf values were acceptable.

4 Conclusion

The Sn was supposed to occupy the Ti site in the $Li_2ZnTi_3O_8$ ceramic. However, the Sn was revealed to exist in the form of SnO_2 as a secondary phase. The addition of SnO_2 did not influence the temperature coefficient remarkably and high microwave dielectric performance with $\varepsilon_r = 23.3$, $Q \times f$ = 71,000 GHz and TCF = −21.7 ppm/°C were obtained in the $Li_2Zn(Ti_{0.9}Sn_{0.1})_3O_8$ ceramic sintered at 1,120 °C. With addition of 1.5 wt% $0.4B_2O_3$–0.6CuO, the $Li_2Zn(Ti_{0.9}Sn_{0.1})_3O_8$ ceramic could be well densified at 875 °C and good microwave dielectric properties with $\varepsilon_r = 21.2$, $Q \times f = 12{,}000$ GHz and TCF = −20.3 ppm/°C could be obtained. This series of microwave dielectric ceramics might be candidate for low temperature co-fired ceramics technology.

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