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Journal of the European Ceramic Society 32 (2012) 261–265

www.elsevier.com/locate/jeurceramsoc

Short communication

# $ZnLi_{2/3}Ti_{4/3}O_4$: A new low loss spinel microwave dielectric ceramic

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Received 5 April 2011; received in revised form 29 August 2011; accepted 30 August 2011
Available online 19 September 2011

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## Abstract

A new low loss spinel microwave dielectric ceramic with composition of $ZnLi_{2/3}Ti_{4/3}O_4$ was synthesized by the conventional solid-state ceramic route. The ceramic can be well densified after sintering above 1075 °C for 2 h in air. X-ray diffraction data show that $ZnLi_{2/3}Ti_{4/3}O_4$ ceramic has a cubic structure [*Fd*-3*m* (227)] similar to $MgFe_2O_4$ with lattice parameters of $a = 8.40172$ Å, $V = 593.07$ Å$^3$, $Z = 8$ and $\rho = 4.43$ g/cm$^3$. The best microwave dielectric properties can be obtained in ceramic with relative permittivity of 20.6, $Q \times f$ value of 106,700 GHz and $\tau_f$ value of −48 ppm/°C. The addition of $BaCu(B_2O_5)$ (BCB) can effectively lower the sintering temperature from 1075 °C to 900 °C and does not induce much degradation of the microwave dielectric properties. Compatibility with Ag electrode indicates that the BCB added $ZnLi_{2/3}Ti_{4/3}O_4$ ceramics are good candidates for LTCC applications.

*Keywords:* A. Firing; B. X-ray methods; C. Dielectric properties; D. Spinels

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## 1. Introduction

Low temperature cofired ceramics (LTCC) are essential for the miniaturization of microwave devices in mobile communications.[1–5] For the LTCC, the firing temperature should be less than 950 °C because the common internal electrode material, Ag, will melt at 961 °C. Unfortunately, many commercial microwave dielectric ceramics, such as $Ba(Mg_{1/3}Ta_{2/3})O_3$, $CaTiO_3$–$NdAlO_3$, BaO–$Nd_2O_3$–$TiO_2$, usually have high sintering temperature (>1300 °C), which can not be directly applied as LTCC materials.[6,7]

To solve this problem, several methods are pursued, including addition of low melting point additives such as $V_2O_5$, $Bi_2O_3$ and glass,[8–10] chemical processing for starting powders with smaller particle sizes[11] and searching for new material systems with low sintering temperatures (normally below 1100 °C). The first method can effectively lower the sintering temperature of microwave dielectric materials. However, large amounts of liquid phase-forming will degrade the microwave dielectric properties of the dielectrics. The second method leads to higher cost and longer processing time due to a complicated procedure. Thus, with the increasing requirements for the low temperature firing materials, the search for new materials with intrinsic low sintering temperatures is in rapid progress. Some low sintering materials, such as $TeO_2$-rich compounds, $Bi_2O_3$-rich compounds, $MoO_3$-rich compounds, have intrinsic low sintering temperatures (below 950 °C), but they are ease to react with Ag electrode and hence not suitable for LTCC devices.[12–17] Therefore, it is necessary to search new low temperature cofiring ceramics which have chemical compatibility with the Ag electrode.

In the $Li_2O$–ZnO–$TiO_2$ ternary system, the phase structure of $ZnLi_{2/3}Ti_{4/3}O_4$ (JCPDS #044-1038) was first reported by Porotnikov. However, to the best of our knowledge, the microwave dielectric properties of this composition have not been reported to date. In present study, the microwave dielectric properties, phase structure and microstructure of $ZnLi_{2/3}Ti_{4/3}O_4$ ceramic were investigated. $BaCu(B_2O_5)$ has been reported as a good flux former to lower the sintering temperature for many materials.[18–20] So, in order to reduce the sintering temperature to below 900 °C, small amount of $BaCu(B_2O_5)$ is added to the ceramic.

## 2. Experimental procedure

Specimens of the $ZnLi_{2/3}Ti_{4/3}O_4$ ceramic were prepared by a conventional mixed oxide route from the high-purity oxide

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doi:10.1016/j.jeurceramsoc.2011.08.036

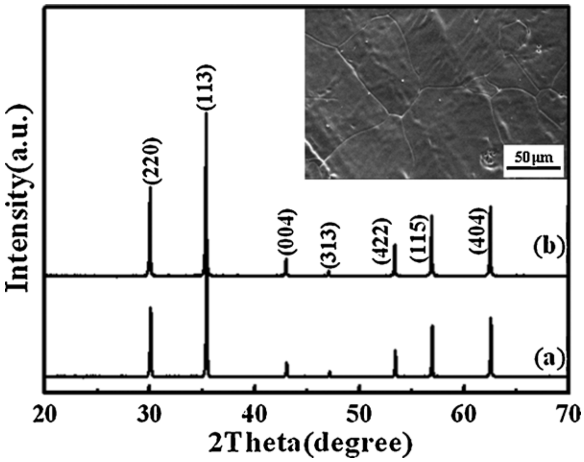

Fig. 1. XRD of $ZnLi_{2/3}Ti_{4/3}O_4$ (a) powders calcined at 900 °C and (b) ceramic sintered at 1075 °C for 2 h. Inset is the SEM of ceramic sintered at 1075 °C for 2 h.

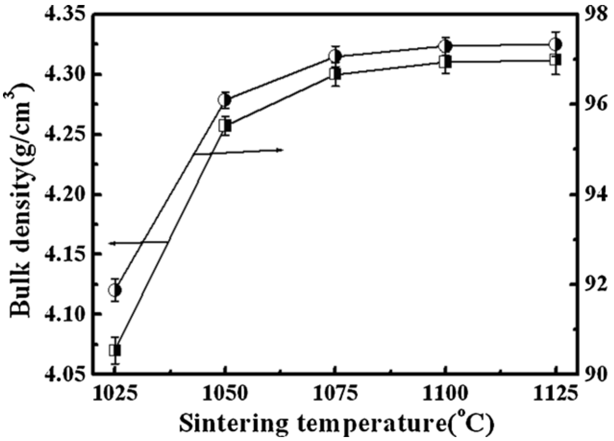

Fig. 2. Bulk density and relative density of $ZnLi_{2/3}Ti_{4/3}O_4$ ceramics as a function of the sintering temperature.

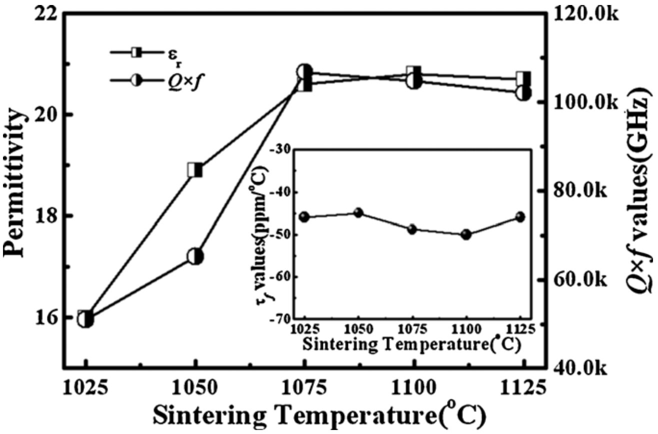

Fig. 3. The relative permittivity, $Q \times f$ values, and temperature coefficient of resonant frequency values of $ZnLi_{2/3}Ti_{4/3}O_4$ ceramics as a function of the sintering temperature.

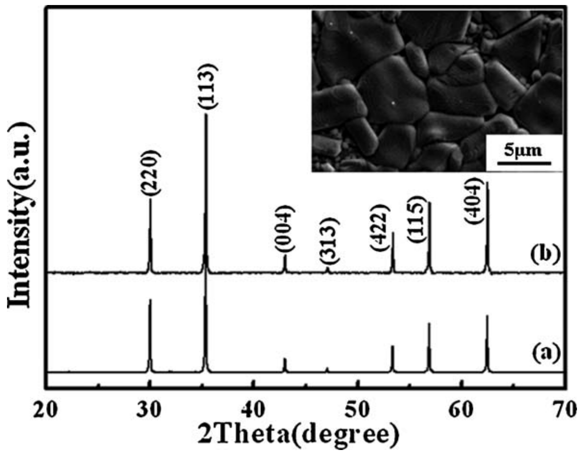

Fig. 4. XRD of $x$ wt% BCB added $ZnLi_{2/3}Ti_{4/3}O_4$ ceramics: (a) $x = 0$ sintered at 1075 °C and (b) $x = 1.5$ sintered at 900 °C for 2 h. Inset shows SEM photograph of 1.5 wt% BCB added $Li_2ZnTi_3O_8$ ceramic sintered at 900 °C for 2 h.

powders of $Li_2CO_3$ (≥99%), ZnO (≥99%) and $TiO_2$ (≥99%). Stoichiometric proportion of the above raw materials was mixed in the high-purity alcohol (≥99.7%) medium using zirconia balls for 4 h. The mixtures were dried and calcined at 900 °C for 8 h. To synthesize the $BaCu(B_2O_5)$ (BCB) powders, $Ba(OH)_2·8H_2O$ (>99%), CuO (>99%) and $H_3BO_3$ (>99%) were mixed for 4 h in a nylon jar with zirconia balls, then dried and calcined at 800 °C for 4 h with a heating rate of 7–8 °C/min. After subsequent ball-milling with 0–2.0 wt% BCB, the resultant powders were mixed with 5 wt% of polyvinyl alcohol and pressed into pellets of 12 mm in diameter and 6 mm in height by uniaxial pressing under a pressure of 200 MPa. The pure $ZnLi_{2/3}Ti_{4/3}O_4$ samples were sintered at 1025–1125 °C for 2 h in air and the BCB doped ceramic pellets were sintered at 900 °C for 2 h in air.

The crystal structures of the samples were analyzed by an X-ray diffractometer (Model X'Pert PRO, PANalytical, Almelo, Holland) with Cu Kα radiation generated at 40 kV and 100 mA. The bulk densities of the sintered samples were measured by the Archimedes method. The microstructural observation of the samples was performed using scanning electron microscopy (Model JSM6380-LV SEM, JEOL, Tokyo, Japan). Specimens for transmission electron microscopy were prepared from sintered pellets by conventional polishing, dimpling, and ion milling. The specimens were examined using a Phillips FEI Tecnai G2 F20 S-TWIN TEM operated at 200 kV. Dielectric behaviors in microwave frequency were measured by the $TE_{01\delta}$ shielded cavity method using a Network Analyzer (Model N5230A, Agilent Co., CA) and a temperature chamber (DELTA 9039, Delta Design, USA). The temperature coefficients of resonant frequency $\tau_f$ values were calculated by the formula as follows:

$$\tau_f = \frac{f_T - f_0}{f_0(T - T_0)} \qquad (1)$$

where $f_T$, $f_0$ were the resonant frequencies at the measuring temperature $T$ and $T_0$ (25 °C), respectively.

## 3. Results and discussion

The room-temperature X-ray diffraction patterns recorded for the $ZnLi_{2/3}Ti_{4/3}O_4$ powders calcined at 900 °C and ceramic

Table 1
Sintering temperature, bulk density and microwave dielectric properties of BCB added $ZnLi_{2/3}Ti_{4/3}O_4$ ceramics.

| $ZnLi_{2/3}Ti_{4/3}O_4 + x$ wt% BCB | Relative density (%) | Sintering temperature | Microwave dielectric properties | | | |
|---|---|---|---|---|---|---|
| | | | $\varepsilon_r$ measured | $\varepsilon_r$ corrected for porosity | $Q \times f$ (GH) | $\tau_f$ (ppm/°C) |
| $x = 0$ | 97.1 | 1075 | 20.6 | 21.1 | 106,700 | −48 |
| $x = 0.5$ | 94.4 | 900 | 18.0 | 19.6 | 34,900 | −47.2 |
| $x = 1.0$ | 96.2 | 900 | 19.1 | 20.2 | 47,600 | −45.3 |
| $x = 1.5$ | 97.5 | 900 | 19.4 | 20 | 57,600 | −39.5 |
| $x = 2.0$ | 95.7 | 900 | 18.5 | 19.7 | 31,050 | −36.6 |

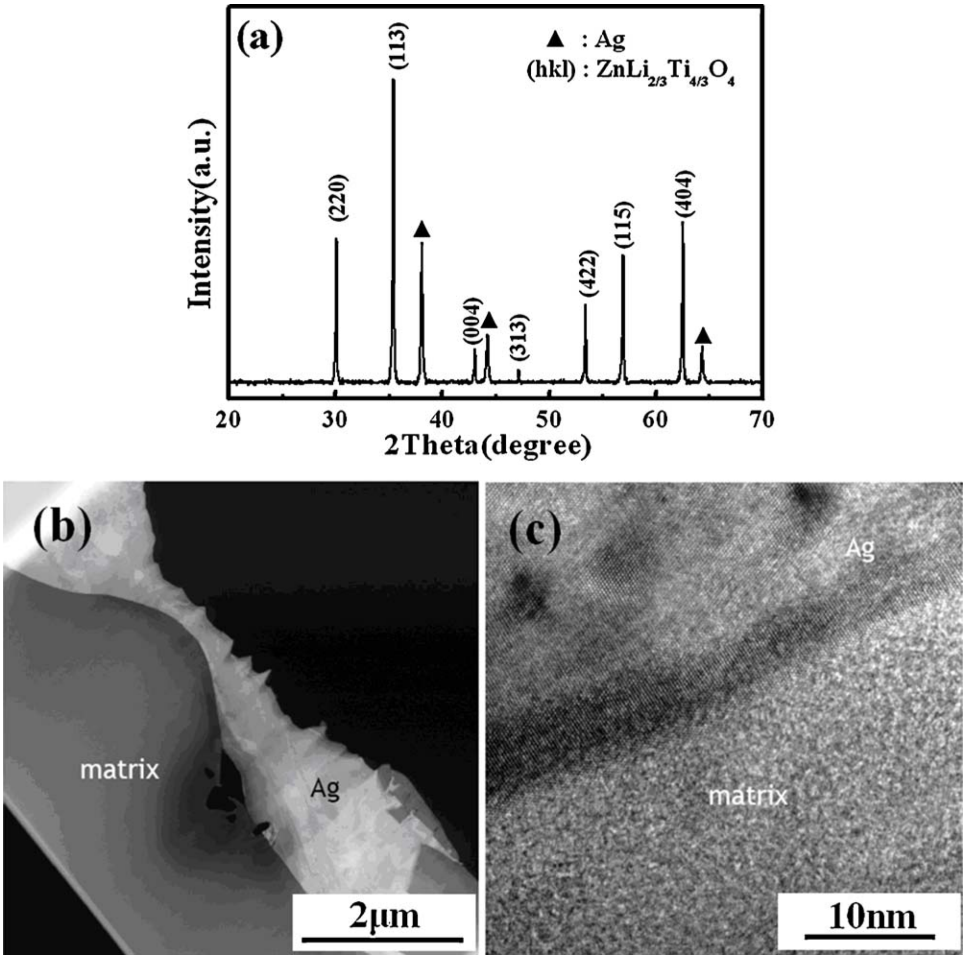

Fig. 5. Chemical compatibility tests of 1.5 wt% BCB doped $ZnLi_{2/3}Ti_{4/3}O_4$ samples mixed with 20 wt% Ag sintered at 900 °C: (a) powder X-ray diffraction data, (b) STEM/HAADF image, and (c) HRTEM image.

sintered at 1075 °C for 2 h are shown in Fig. 1. In Porotnikov's work (JCPDS #044-1038), $ZnLi_{2/3}Ti_{4/3}O_4$ has a cubic structure [$P4_232$ (208)] with lattice parameters of $a = 8.3980$ Å, $V = 592.28$ Å$^3$, and $Z = 4$. However, in our study, $ZnLi_{2/3}Ti_{4/3}O_4$ has a cubic structure [$Fd$-$3m$ (227)] similar to $MgFe_2O_4$ with lattice parameters of $a = 8.40172$ Å, $V = 593.07$ Å$^3$, $\rho = 4.43$ g/cm$^3$ and $Z = 8$ ($Z$ denotes the number of unit cell molecules in a unit cell), which does not agree well with Porotnikov's work. The SEM micrograph of the $ZnLi_{2/3}Ti_{4/3}O_4$ ceramic surface is also shown in Fig. 1. The dense microstructure with only few pores of $ZnLi_{2/3}Ti_{4/3}O_4$ ceramic sintered at 1075 °C for 2 h can be confirmed by the SEM result. The grain size is found to be in the range of 50–100 μm.

Fig. 2 presents the relative and bulk densities of $ZnLi_{2/3}Ti_{4/3}O_4$ ceramics as a function of the sintering temperature. As the sintering temperature increases from 1025 to 1050 °C, the bulk density increases from 4.0 to 4.25 g/cm$^3$. When the sintering temperature further increases, the density of $ZnLi_{2/3}Ti_{4/3}O_4$ ceramics reaches saturation (bulk density of 4.3 g/cm$^3$ and relative density of 97.1%). This result indicates that the densification temperature of the $ZnLi_{2/3}Ti_{4/3}O_4$ ceramic is around 1075 °C.

The microwave dielectric properties of $ZnLi_{2/3}Ti_{4/3}O_4$ ceramics as a function of the sintering temperature are shown in Fig. 3. The relationship of relative permittivity versus sintering temperature of $ZnLi_{2/3}Ti_{4/3}O_4$ ceramics has a trend similar to that of the densities. When the sintering temperature increases to 1075 °C, the relative permittivity reaches to a saturated value of 20.6. The $Q \times f$ value of $ZnLi_{2/3}Ti_{4/3}O_4$ ceramics reaches the maximum with a value of 106700 GHz (at 8.4 GHz). Thereafter, the $Q \times f$ values decrease with further increasing temperature, which may be due to extrinsic factors, such as the increase of liquid phase, and the abnormal grain growth.[21] Moreover, the volatile Li has a deleterious effect on dielectric properties.[7] The $\tau_f$ values do not change remarkably with increasing the sintering temperature and remain stable about −48 ppm/°C. In general, the $ZnLi_{2/3}Ti_{4/3}O_4$ ceramic sintered at 1075 °C for 2 h has good microwave dielectric properties of $\varepsilon_r = 20.6$, $Q \times f = 106{,}700$ GHz, $\tau_f = -48$ ppm/°C.

To further decrease the sintering temperature of this new microwave dielectric ceramic, a small amount of BCB has been added into the samples. The sintering temperature, relative density and microwave dielectric properties of BCB doped $ZnLi_{2/3}Ti_{4/3}O_4$ ceramics are shown in Table 1. The experimentally obtained relative permittivity was corrected for porosity using the following equation.

$$\varepsilon' = \varepsilon_m \left[1 - \frac{3P(\varepsilon_m - 1)}{2\varepsilon_m + 1}\right] \tag{2}$$

where $\varepsilon_m$ is the relative permittivity corrected for porosity, $\varepsilon'$ is the experimental relative permittivity, and $P$ is fractional porosity.[22]

Due to the liquid phase effect, the addition of BCB can efficiently lower the sintering temperature of the ceramic from 1075 to 900 °C. The relative permittivity and $Q \times f$ values of BCB added $ZnLi_{2/3}Ti_{4/3}O_4$ ceramics are lower than that of pure ceramics because of the low permittivity and $Q \times f$ value of BCB liquid phase in ceramics. For BCB added $ZnLi_{2/3}Ti_{4/3}O_4$ ceramics, the permittivity and $Q \times f$ values first increase, reach a maximum as the content of BCB addition is 1.5 wt%, and decrease with further increasing the BCB addition. The $\tau_f$ values increase from −48 ppm/°C to −36.6 ppm/°C. The XRD patterns of the 1.5 wt% BCB-added ceramics sintered at 900 °C are very similar to that of the pure ceramic and no secondary phase could be detected (as shown in Fig. 4). The average grain size of 1.5 wt% BCB-added ceramics (~5 μm) is much smaller than that of the pure ceramic (~70 μm). For the 1.5 wt% BCB added ceramic, a relative high density of 4.32 g/cm$^3$ and good microwave dielectric properties of $\varepsilon_r = 19.4$, $Q \times f = 57600$ (8.72 GHz) GHz and $\tau_f = -39.5$ ppm/°C have been obtained by sintering at 900 °C for 2 h.

For chemical compatibility tests, the mixtures of 1.5 wt% BCB doped ceramic powders with 20 wt% Ag powders were cofired and analyzed to detect interactions between the low-fired samples and electrodes. Fig. 5 shows the XRD pattern, STEM/HAADF and HRTEM image of $ZnLi_{2/3}Ti_{4/3}O_4$ ceramics added with 1.5 wt% BCB cofired with Ag powders at 900 °C for 2 h. XRD analysis reveals no interaction to form new phases after firing, which indicate that the BCB doped ceramics can cofire with Ag powders. The STEM/HAADF and HRTEM images of the cofired samples reveal that the diffusion between low-fired $ZnLi_{2/3}Ti_{4/3}O_4$ ceramics and Ag electrodes did not occur. Therefore, $ZnLi_{2/3}Ti_{4/3}O_4$ ceramics with BCB additives could be selected as a promising candidate for LTCC application because of low sintering temperature, good microwave dielectric properties and chemical compatibility with Ag electrodes.

## 4. Conclusions

Microwave dielectric properties of the $ZnLi_{2/3}Ti_{4/3}O_4$ ceramic have been investigated. $ZnLi_{2/3}Ti_{4/3}O_4$ ceramic can be prepared by solid state reaction method and densified after sintering above 1075 °C for 2 h in air. The best microwave dielectric properties can be obtained in ceramic with relative permittivity of 20.6, $Q \times f$ value of 106,700 GHz and $\tau_f$ value of −48 ppm/°C. The addition of BCB can effectively lower the sintering temperature from 1075 °C to 900 °C and does not induce much degradation of the microwave dielectric properties. The BCB added $ZnLi_{2/3}Ti_{4/3}O_4$ ceramics have a good compatibility with silver electrode, which makes it a suitable candidate for low temperature-cofired ceramics (LTCC) devices.

## Acknowledgements

This work was supported by Natural Science Foundation of China (nos. 51102058, 50962004 and 21061004), Natural Science Foundation of Guangxi (no. 2011GXNSFB018012), Research start-up funds Doctor of Guilin University of Technology (nos. 002401003281 and 002401003282), and Program for NCET-06-0656, MOE, China.

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