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Short communication

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

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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 [$Fd$-$3m$ (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

## 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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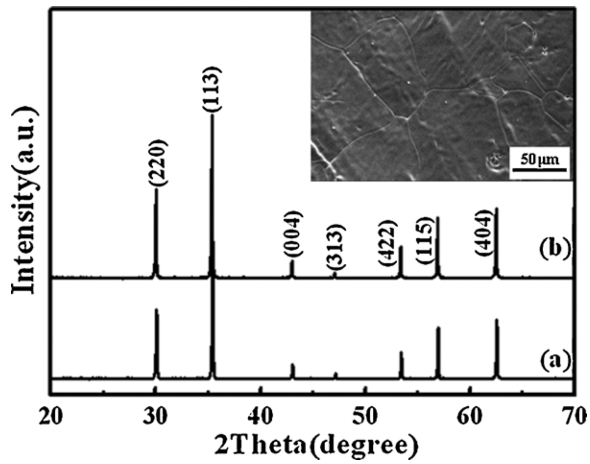


Fig. 1. XRD of $ZnLi_{2/3}Ti_{4/3}O_4$ (a) powders calcined at 900 °C and (b) ceramic sintered at 1075 °C for 2 h. Inset is the SEM of ceramic sintered at 1075 °C for 2 h.

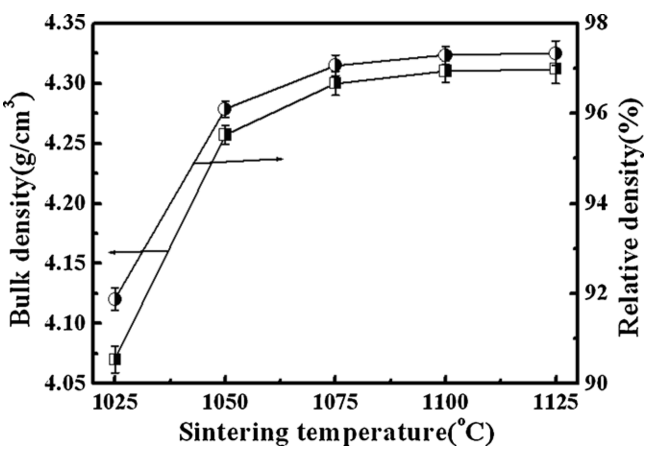


Fig. 2. Bulk density and relative density of $ZnLi_{2/3}Ti_{4/3}O_4$ ceramics as a function of the sintering temperature.

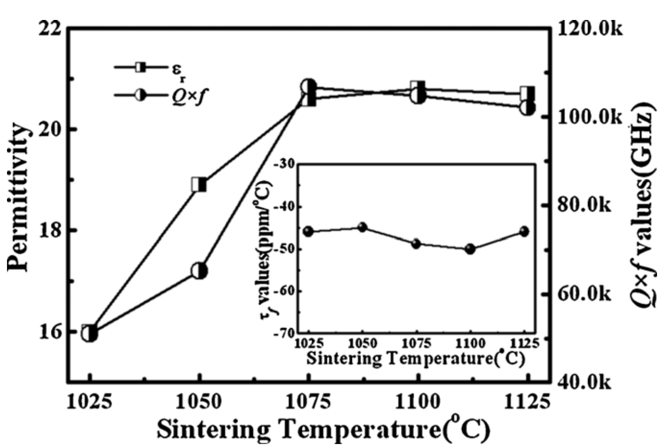


Fig. 3. The relative permittivity, $Q \times f$ values, and temperature coefficient of resonant frequency values of $ZnLi_{2/3}Ti_{4/3}O_4$ ceramics as a function of the sintering temperature.

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

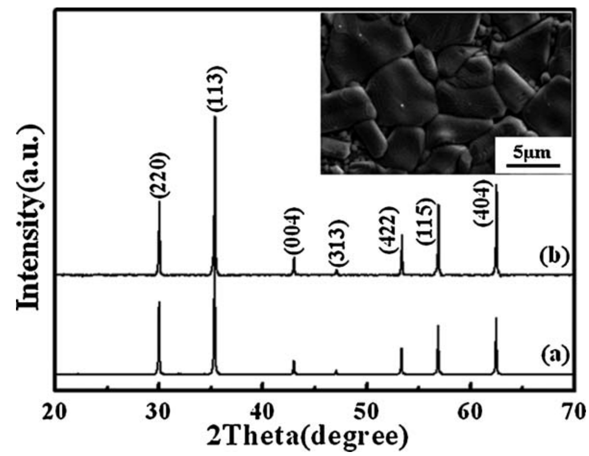


Fig. 4. XRD of $x$ wt% BCB added $ZnLi_{2/3}Ti_{4/3}O_4$ ceramics: (a) $x = 0$ sintered at 1075 °C and (b) $x = 1.5$ sintered at 900 °C for 2 h. Inset shows SEM photograph of 1.5 wt% BCB added $Li_2ZnTi_3O_8$ ceramic sintered at 900 °C for 2 h.

for 4 h. The mixtures were dried and calcined at 900 °C for 8 h. To synthesize the $BaCu(B_2O_5)$ (BCB) powders, $Ba(OH)_2{\cdot}8H_2O$ (>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:

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

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