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Temperature stable microwave dielectric ceramic $0.3Li_2TiO_3$–$0.7Li(Zn_{0.5}Ti_{1.5})O_4$ with ultra-low dielectric loss

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ABSTRACT

In the present work, the $0.3Li_2TiO_3$–$0.7Li(Zn_{0.5}Ti_{1.5})O_4$ ceramic was prepared via the conventional solid state reaction route, and the phase composition, microstructure, and sintering behavior were investigated. The ceramic sample sintered at 1100 °C for 2 h demonstrated high microwave dielectric performance with a relative permittivity of 23.5, a high quality factor (Qf) ~88,360 GHz (at 7.4 GHz), and near zero temperature coefficient of resonant frequency about −0.8 ppm/°C. These results indicate that the $0.3Li_2TiO_3$–$0.7Li(Zn_{0.5}Ti_{1.5})O_4$ ceramic might be a good candidate for dielectric resonators, filters and other microwave electronic device applications.

1. Introduction

In recent years, with the rapid development of wireless and mobile communication, the high performance microwave dielectric ceramics have been extensively studied for the microwave device applications, such as dielectric resonator, dielectric filter, dielectric substrates, etc. Hence, the search for new microwave dielectric ceramics with a series of dielectric permittivities, high Qf values (low dielectric loss), near zero temperature coefficients of resonant frequency (TCF/τ_f= 0 ppm/°C), has attracted much attention [1–3].

Recently, much research is focused on the Li_2TiO_3 ceramic due to its high performance microwave dielectric properties with dielectric permittivity about 20~24, high Qf value about 23,600~70,000 GHz and a TCF value about +20~+39 ppm/°C [4,5]. Its sintering temperature can be lowered to around 900 °C by addition of B_2O_3–CuO and ZnO–B_2O_3 frits, which made it a candidate for low temperature co-fired ceramic (LTCC) technology [6,7]. The $Li(Zn_{0.5}Ti_{1.5})O_4$ ceramic sintered at 1075 °C was reported to possess a permittivity of 25.6, a Qf value ~72,000 GHz and a TCF value of −11.2 ppm/°C [8]. The opposite sign of TCF values of Li_2TiO_3 ceramic and $Li(Zn_{0.5}Ti_{1.5})O_4$ ceramic offers an opportunity to design a temperature stable composite ceramic. In the present work, the $0.3Li_2TiO_3$–$0.7Li(Zn_{0.5}Ti_{1.5})O_4$ ceramic was fabricated by the conventional solid state reaction method. The phase composition, microstructure and microwave dielectric properties were studied.

2. Experimental procedure

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 weighed according to the stoichiometric proportion of $0.3Li_2TiO_3$–$0.7Li(Zn_{0.5}Ti_{1.5})O_4$. Powders were mixed and milled for 5 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 a temperature of 900 °C for 4 h. Then the powders were re-milled for 5 h using the ZrO_2 milling media and ethanol to increase reactivity and better homogeneity. After drying, the powders were pressed into cylinders (10 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. Samples were sintered at temperatures of 1100~1160 °C for 2 h in air with a heating rate of 3 °C/min, a cooling rate of 1 °C/min to 900 °C, and a natural cooling below 900 °C.

The crystalline structures of samples were investigated using X-ray diffraction with CuKα radiation (Rigaku D/MAX-2400X-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 apparent densities of sintered ceramics were measured by Archimedes' method. The dielectric behaviors at microwave frequency were measured with the $TE_{01\delta}$ shielded cavity method using a network analyzer (8720ES,

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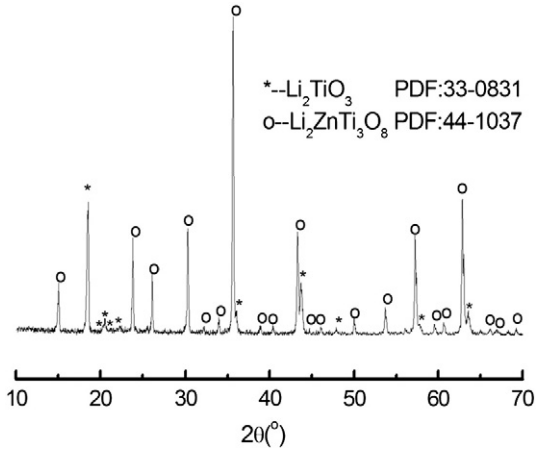

Fig. 1. XRD result of $0.3Li_2TiO_3$–$0.7Li(Zn_{0.5}Ti_{1.5})O_4$ ceramic sintered at 1100 °C/2 h.

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.

3. Results and discussions

Fig. 1 shows the XRD pattern of the $0.3Li_2TiO_3$–$0.7Li(Zn_{0.5}Ti_{1.5})O_4$ ceramic sintered at 1100 °C. It is seen that only the diffraction peaks of the Li_2TiO_3 phase and the $Li(Zn_{0.5}Ti_{1.5})O_4$ phase were observed, which indicates that at 1100 °C these two phases can be formed and they are chemical compatible with each other.

The BEI image of as-fired surface of $0.3Li_2TiO_3$–$0.7Li(Zn_{0.5}Ti_{1.5})O_4$ ceramic sintered at 1100 °C for 2 h is shown in Fig. 2. Dense and homogeneous microstructure with almost no pores with two kinds of grains can be observed. According to the related EDS analysis, the minor grains with dark color belong to the Li_2TiO_3 phase with relative smaller equivalent element number and the major grains with light color belong to the $Li(Zn_{0.5}Ti_{1.5})O_4$ phase. According to our previous work, the Li_2TiO_3 ceramic can only achieve a relative density of about 91% at 1200 °C [6]. The $Li(Zn_{0.5}Ti_{1.5})O_4$ ceramic was reported to reach a relative density of about 94.5% at 1075 °C [8]. The density of $0.3Li_2TiO_3$–$0.7Li(Zn_{0.5}Ti_{1.5})O_4$ ceramic sintered at 1100 °C was about 3.654 g/cm^3 as shown in Table 1. Considering a simple additivity rule for density of composite ceramic, the relative density of $0.3Li_2TiO_3$–$0.7Li(Zn_{0.5}Ti_{1.5})O_4$ reached 95% (3.511 g/cm^3 for Li_2TiO_3 and 3.974 g/cm^3 for $Li(Zn_{0.5}Ti_{1.5})O_4$), which indicates that the composite ceramic was well sintered [6,8]. In the present work, the composite $0.3Li_2TiO_3$–$0.7Li(Zn_{0.5}Ti_{1.5})O_4$ ceramic has a densification temperature between that of pure Li_2TiO_3 and $Li(Zn_{0.5}Ti_{1.5})O_4$ ceramics.

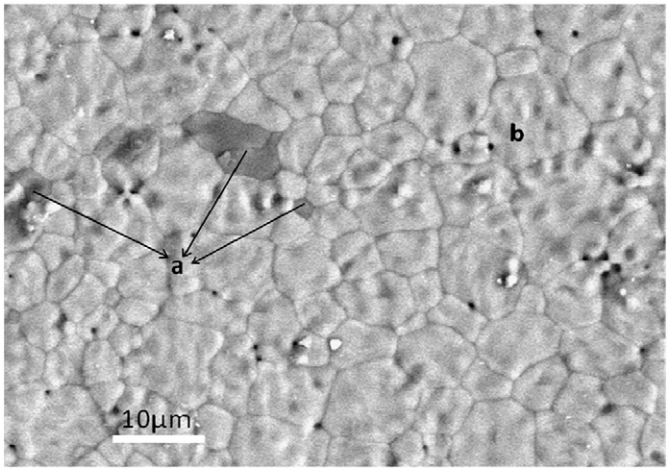

Fig. 2. BEI image of $0.3Li_2TiO_3$–$0.7Li(Zn_{0.5}Ti_{1.5})O_4$ ceramic sintered at 1100 °C/2 h. (a — Li_2TiO_3, b — $Li(Zn_{0.5}Ti_{1.5})O_4$).

Table 1
Microwave dielectric properties of $0.3Li_2TiO_3$–$0.7Li(Zn_{0.5}Ti_{1.5})O_4$ composite ceramic, Li_2TiO_3 ceramic and $Li(Zn_{0.5}Ti_{1.5})O_4$ ceramic.

Sample	S. T. (°C)	Density (g/cm^3)	ε_r	Qf (GHz)	TCF (ppm/°C)	Ref.
0.3LT–0.7LZT	1100	3.654	23.6	88,360	−0.80	This work
$Li(Zn_{0.5}Ti_{1.5})O_4$	1075	3.795	25.6	72,000	−11.2	George and Sebastian [8]
Li_2TiO_3	1230	3.112	19.8	23,600	+38.5	Pang and Zhou [6]

S. T.: sintering temperature; TCF: temperature coefficient of resonant frequency; 0.3LT–0.7LZT represents $0.3Li_2TiO_3$–$0.7Li(Zn_{0.5}Ti_{1.5})O_4$ in this work.

Table 1 shows the microwave dielectric properties of $0.3Li_2TiO_3$–$0.7Li(Zn_{0.5}Ti_{1.5})O_4$ composite ceramic, Li_2TiO_3 ceramic and $Li(Zn_{0.5}Ti_{1.5})O_4$ ceramic. The theoretical permittivity (ε_r) of the composite ceramic was obtained from the well-known Lichtenecker empirical logarithmic rule [9],

$$1g\varepsilon = x_1 1g\varepsilon_1 + x_2 1g\varepsilon_2 \quad (2)$$

where x_1 and x_2 are the volume fractions. As known to all, the relationship between temperature coefficient of permittivity (τ_ε) and τ_f is

$$\tau_f = -\frac{1}{2}\tau_\varepsilon - \alpha_L \quad (3)$$

where α_L is the linear thermal-expansion coefficient.

Then the mixing rule of τ_f value could be described like this:

$$\tau_f = x_1\tau_{f1} + x_2\tau_{f2} \quad (4)$$

where the τ_{f1} and τ_{f2} are the τ_f values of the Li_2TiO_3 ceramic and $Li(Zn_{0.5}Ti_{1.5})O_4$ ceramic, respectively. The calculated dielectric permittivity and τ_f value of $0.3Li_2TiO_3$–$0.7Li(Zn_{0.5}Ti_{1.5})O_4$ composite ceramic is 24.2 and +1.5 ppm/°C, which are similar to the measured values. The Qf value is influenced by many complex aspects, such as grain size, grain size distribution, grain boundaries, pores etc. A very high Qf value about 88,360 GHz (at 7.4 GHz) was obtained in the $0.3Li_2TiO_3$–$0.7Li(Zn_{0.5}Ti_{1.5})O_4$ composite ceramic, which is larger than both the pure Li_2TiO_3 and $Li(Zn_{0.5}Ti_{1.5})O_4$ ceramics. Although the Qf value of pure Li_2TiO_3 was about 23,600 GHz, addition of B_2O_3–CuO can increase the Qf to about 46,300 GHz at 7.9 GHz, which means that the dielectric loss $\tan\delta = 1.7\ 10^{-4}$. The dielectric loss of pure $Li(Zn_{0.5}Ti_{1.5})O_4$ ceramic was about $\tan\delta = 6.9\ 10^{-5}$ at 5 GHz. The composite ceramic $0.3Li_2TiO_3$–$0.7Li(Zn_{0.5}Ti_{1.5})O_4$ has an understandable dielectric loss about $\tan\delta = 8.4\ 10^{-5}$ at 7.4 GHz, lying between that of Li_2TiO_3 and $Li(Zn_{0.5}Ti_{1.5})O_4$ ceramics. In addition to the simple additivity rule of dielectric loss, the chemical compatibility, similar chemical elements (Li and Ti) both help to improve the microwave dielectric properties, which is similar to the $Li_2Ca_2Mo_3O_{12}$ composite ceramic ($Li_2MoO_4 + CaMoO_4$) [10].

4. Conclusions

The $0.3Li_2TiO_3$–$0.7Li(Zn_{0.5}Ti_{1.5})O_4$ ceramic, prepared via the solid state reaction method, can be well densified at 1100 °C for 2 h

showing composite phases with both Li_2TiO_3 and $Li(Zn_{0.5}Ti_{1.5})O_4$ phases. As predicted by the empirical logarithmic rule, a near zero temperature coefficient of resonant frequency of about −0.8 ppm/°C was obtained in the composite ceramic sintered at 1100 °C with a dielectric permittivity of 23.5, a high Qf value of 88,360 GHz (at 7.4 GHz).

Acknowledgments

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