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A novel temperature stable microwave dielectric ceramic with low sintering temperature and high quality factor

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ABSTRACT

A new low-temperature sintering microwave dielectric ceramic with the composition of $Li_4Ti_5O_{12}$ was prepared by a solid-state reaction method. The ceramic was well densified at ~925 °C and possessed excellent microwave dielectric properties with a moderate relative permittivity of ~30.1, a $Q \times f$ value of 29,530 GHz (at ~7 GHz), and a negative temperature coefficient of resonant frequency of −15.0 ppm/°C. When the sintering temperatures increased from 875 °C to 1050 °C, the τ_f values of ceramics changed from −16.7 ppm/°C to +5.9 ppm/°C. X-ray diffraction (XRD) patterns and scanning electron microscopy (SEM) were employed to study the phase composition and microstructure of the ceramic. Especially, the ceramic presented good chemical compatibility with silver powders, indicating that $Li_4Ti_5O_{12}$ ceramic was a promising candidate for low temperature cofired ceramic devices.

1. Introduction

Low temperature co-fired ceramic (LTCC) has become an important fabrication technology because of the benefits for multilayer integrated circuits (MLICS) [1–3]. For LTCC applications, the material system should have good dielectric properties with appropriate relative permittivity (ε_r), low dielectric loss ($\tan\delta = 1/Q$) and small temperature coefficient of the resonant frequency (τ_f). The other requirement is the low sintering temperature (Ts) because the LTCC dielectrics needed to be co-fired with low-melting point conductors, such as silver (961 °C), copper (1064 °C) and their alloys. However, most of commercial materials need higher sintering temperatures (≥1300 °C) [4–5]. Recently, much attention has been paid to searching for new series of LTCC materials, such as Bi-based, Li-based and Te-based compounds [6–8].

The spinel compounds with general formula of AB_2O_4 have been reported for their excellent microwave dielectric performance, such as $MgAl_2O_4$ [9], $ZnAl_2O_4$ [10], but high sintering temperatures restricted their further application in LTCC devices. In previous works, many compounds with spinel structure were investigated, such as $Li_2MgTi_3O_8$ [11], $Li_2CoTi_3O_8$ [12], $ZnLi_{2/3}Ti_{4/3}O_4$ [13], $CoLi_{2/3}Ti_{4/3}O_4$ [14]. These materials could be well sintered at low temperatures (≤1075 °C), and exhibited good microwave dielectric properties with relative permittivities (ε_r) of 20–29, $Q \times f$ values of 35,000–106,700 GHz, and temperature coefficients of the resonant frequency (τ_f) of −48.0 to +7.4 ppm/°C. In addition, the addition of small amount of $BaCu(B_2O_5)$ (BCB) could reduce the sintering temperatures of these ceramics to 900 °C and did not induce much degradation of properties. They are easily compatible with Ag electrode and could be applied in LTCC devices. So it is concluded that Li-based spinel compounds not only have low sintering temperatures, but also exhibit ideal properties for LTCC application.

The spinel lithium titanate ($Li_4Ti_5O_{12}$) is well known as anode material for lithium-ion batteries because of its good performance [15]. However, the microwave dielectric properties of this composition have not been reported to date. In present work, phase evolution, microstructure and microwave dielectric properties of $Li_4Ti_5O_{12}$ ceramic were investigated. In addition, chemical compatibility with Ag electrode of the ceramic was explored to evaluate its application in LTCC devices.

2. Experimental procedures

Specimens of $Li_4Ti_5O_{12}$ ceramics were prepared by the conventional mixed oxide route. The analytical pure (≥99%, Guo-Yao Co. Ltd., Shanghai, China) Li_2CO_3 and TiO_2 were used as the raw materials. Stoichiometric proportion of the above raw materials was mixed in the high-purity alcohol (≥99.5%) medium using zirconia balls for 4 h. And then the mixtures were dried and calcined at 850 °C for 4 h. Subsequently, the calcined powders were milled in the same way as the raw materials. After dried, the powders were mixed with 5 wt % polyvinyl alcohol (PVA) and

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pressed into the cylinders with 12 mm in diameter and 6–7 mm in thickness by uniaxial pressing under a pressure of 200 MPa. Finally, the samples were sintered at 875–1050 °C for 4 h in air at a heating rate of 5 °C/min and then cooled to room temperature in furnace.

The crystal structures of ceramics were measured by an X-ray diffractometer (XRD) ($CuK_{\alpha 1,}$ 1.54059 Å, Model X'Pert PRO, PANalytical, Almelo, Holland) operated at 40 kV and 40 mA. The microstructural observation of the samples was performed using a scanning electron microscopy (SEM) (Model JSM6380-LV, JEOL, Tokyo, Japan). The apparent densities of the sintered samples were measured by the Archimedes method using the distilled water as a medium.

Dielectric behaviors in microwave frequency were measured by the $TE_{01\delta}$ shielded cavity method [16] in the frequency range of 6–7 GHz using a Network Analyzer (Model N5230A, Agilent Co., CA, 10 MHz to 40 GHz) and a temperature chamber (Model DELTA 9039, Delta Design, USA) with an open invar cavity. The temperature coefficients of the resonant frequency (τ_f) were calculated by the formula as follows:

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

where f_T, f_0 were the $TE_{01\delta}$ resonant frequencies at the measuring temperature T (85 °C) and T_0 (25 °C), respectively.

3. Results and discussion

3.1. Phase evolution and microstructure of $Li_4Ti_5O_{12}$ ceramic

Fig. 1 shows the room-temperature XRD patterns of $Li_4Ti_5O_{12}$ samples sintered at 875–1050 °C. The results demonstrated that the diffraction peaks of samples could be indexed as a cubic structure (Fd-3m E), which agreed well with $Li_4Ti_5O_{12}$ (PDF code: 00-049-0207). Some diffraction patterns of TiO_2 were observed at 1025–1050 °C, implying the precipitation of TiO_2 at higher

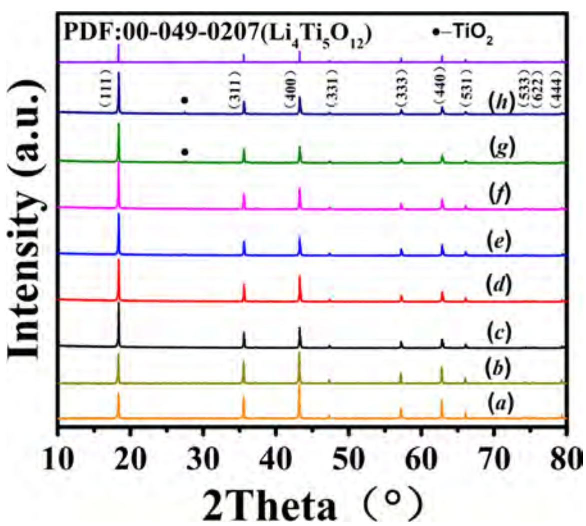

Fig. 1. Room-temperature XRD patterns of $Li_4Ti_5O_{12}$ ceramic sintered at: (a) 875 °C, (b) 900 °C, (c) 925 °C, (d) 950 °C, (e) 975 °C, (f) 1000 °C, (g) 1025 °C, (h) 1050 °C.

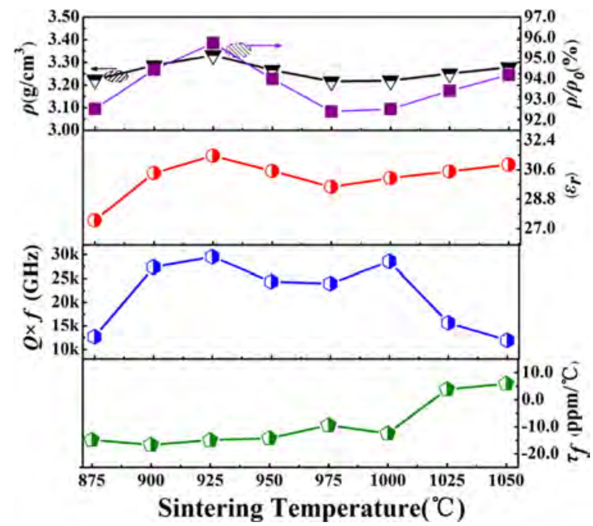

Fig. 3. The apparent density (ρ), relative density (ρ/ρ_0), permittivity (ε_r), $Q \times f$ and τ_f values of $Li_4Ti_5O_{12}$ ceramic as a function of the sintering temperatures.

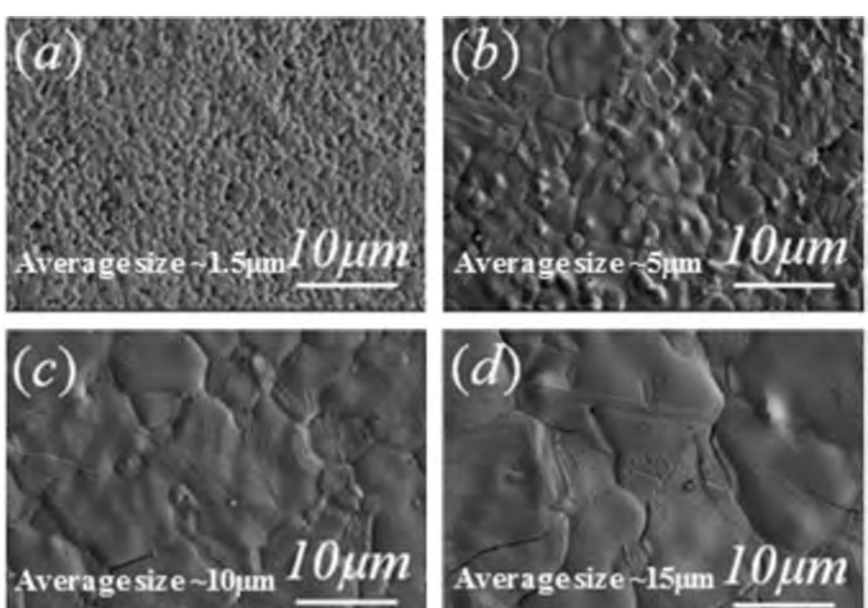

Fig. 2. SEM micrographs of $Li_4Ti_5O_{12}$ ceramic sintered at: (a) 875 °C, (b) 925 °C, (c) 1000 °C, (d) 1050 °C.

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sintering temperatures. SEM micrographs of the surface for ceramics sintered at different temperatures are demonstrated in Fig. 2. With increasing the sintering temperatures, the grains grew bigger and the microstructure became denser. The average grain size increased from ~1.5 μm to ~15 μm as the sintering temperature increased from 875 °C to 1050 °C. Dense microstructure of ceramic was obtained after sintered at 925 °C and 1000 °C, as shown in Fig. 2(b) and Fig. 2(c). However, the abnormal grain growth and some cracks appeared owing to higher sintering temperature, which was easily observed in Fig. 2(d).

3.2. Sintering ability and microwave dielectric properties of $Li_4Ti_5O_{12}$ ceramic

The apparent density (ρ), relative density (ρ/ρ_0) and permittivity (ε_r) of $Li_4Ti_5O_{12}$ ceramic as a function of sintering temperatures are shown in Fig. 3. The theoretical density (ρ_0) of $Li_4Ti_5O_{12}$ ceramic is 3.48 g/cm^3. With increasing the sintering temperatures, the apparent density and relative density increased to the maximum of 3.33 g/cm^3 and 95.7% at 925 °C, decreased with further increasing the sintering temperatures to 975 °C and increased thereafter. The variation of ε_r was consistent with that of the relative density and a maximum ε_r value of 31.5 was obtained at 925 °C. Moreover, the permittivity exhibited a slight change (27.5–31.5) over a wide sintering temperature range (875–1050 °C), indicating a wide process region, which benefits for application.

The $Q \times f$ and τ_f values of $Li_4Ti_5O_{12}$ ceramic sintered at different temperatures are also illustrated in Fig. 3. The microwave dielectric loss included not only intrinsic loss related to the lattice vibration modes, but also extrinsic contributions related to density, second phases, impurities, surface morphology, and lattice defect [17–18]. With increasing the sintering temperatures from 875 °C to 1000 °C, the variation of $Q \times f$ values presented a similar trend to that of the relative density, which suggested that the dielectric loss of the specimens was controlled by the density. The maximum $Q \times f$ value of 29,530 GHz was obtained at 925 °C. As the sintering temperature increased above 1000 °C, the $Q \times f$ values decreased because of the inhomogeneous grain distribution and elimination of cracks, as shown in Fig. 3(d) and Fig. 1. It is well known that the τ_f values are related to the composition and structure [19]. The τ_f values of the ceramic varied in the range from −16.7 to 5.9 ppm/°C as the sintering temperature increased from 875 °C to 1050 °C. Owing to no obvious composition variation, the τ_f values remained about −16.7–−9.4 ppm/°C at 875–1000 °C. But the τ_f values increased from 1025 °C to 1050 °C, which could be attributed to the elimination of TiO_2 phase. According to the mixing rule, larger positive τ_f value of TiO_2 leaded to positive τ_f value of the ceramic above 1025 °C [20].

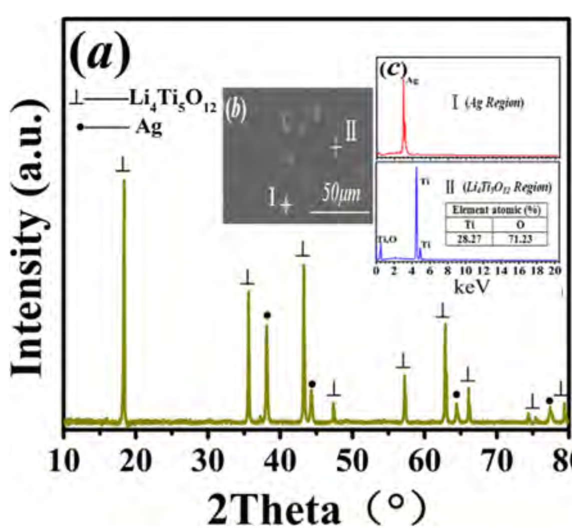

Fig. 4. XRD patterns (a) BEI micrograph (b) and EDS spectrums (c) of $Li_4Ti_5O_{12}$ sample cofired with Ag powders sintered at 925 °C for 2 h.

3.3. Chemical compatibility between the calcined $Li_4Ti_5O_{12}$ powders and Ag electrode

For chemical compatibility tests with silver electrode, mixtures of ceramic powders with 20 wt% Ag powders were cofired and analyzed to detect interactions between the low-fired samples and electrode. XRD patterns, backscattered electron imaging (BEI) and EDS of $Li_4Ti_5O_{12}$ ceramics cofired with Ag at 900 °C for 2 h are presented in Fig. 4. It can be seen that dense and homogeneous microstructure was observed from the as-fired surface. EDS analysis indicated that the co-fired ceramic consisted of both $Li_4Ti_5O_{12}$ and Ag grains, which agreed well with the XRD results, confirming that there was no intermediate phase and good chemical compatibility between $Li_4Ti_5O_{12}$ and silver powders was obtained. Therefore, $Li_4Ti_5O_{12}$ ceramic could be selected as a promising candidate for LTCC application.

4. Conclusions

$Li_4Ti_5O_{12}$ microwave dielectric ceramic has been prepared by the conventional solid state reaction method and well densified at 900–1050 °C. The best microwave dielectric performance with a moderate permittivity of 31.5, a high $Q \times f$ value of 29,530 GHz (at ~7 GHz) and a negative τ_f value of −15.0 ppm/°C was obtained in the ceramic sintered at 925 °C for 4 h. The $Li_4Ti_5O_{12}$ ceramic can be cofired with the silver electrode. Low sintering temperature, good microwave dielectric properties and chemical compatibility with Ag electrode indicate that the $Li_4Ti_5O_{12}$ ceramic can be a promising dielectric material for LTCC application.

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