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LETTER

Microwave dielectric properties of the $5.7Li_2O–Nb_2O_5–7.3TiO_2$ ceramics

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Low-firing microwave dielectrics are essential for the miniaturization of microwave devices in mobile communications. Particularly for the fabrication of a multi-chip module (MCM), a simple cofiring process of microwave dielectrics with an internal electrode is highly desirable. For this purpose, low-temperature cofired ceramics (LTCC) have been widely investigated [1–5]. In LTCC, firing temperature lower than 950 °C is favorable since Ag with the melting point of 960 °C can be used instead of more expensive electrodes such as Ag–Pd binary or Pt–Pd–Au ternary alloys.

Unfortunately, although most of the well-known commercial microwave dielectric ceramics could have good microwave dielectric properties, they could not be used as LTCC materials for high sintering temperatures. So, how to reduce their sintering temperatures to lower than the melting point of the electrode conductors has aroused worldwide interest. Up to now, three kinds of methods have been commonly used for reducing the sintering temperatures: (1) adding low melting point additives such as V_2O_5, Bi_2O_3, and glass [6–8]; (2) chemical processing for starting powders with smaller particle sizes [9]; and (3) searching for new material systems with low sintering temperatures (normally below 1,100 °C) [10]. The first method is the easiest method and widely used to lower their sintering temperatures. However, the microwave dielectric properties of the dielectric materials will be degraded if large amounts of liquid-phase-forming additives are added. And the second method requires a complicated procedure, which means that higher cost and longer processing time would be inevitable. So, with the increasing requirements for the low-temperature firing materials, there is always much interest in searching for new material systems.

In this study, we report the synthesis, characterization, and dielectric properties of a new sort of LTCC composition based on $Li_2O–Nb_2O_5–TiO_2$ system. To lower the sintering temperature to 900 °C and below, small amount of B_2O_3 is added to the LNT ceramic.

Specimens of the LNT ceramics were prepared by conventional mixed oxide route from the high-purity oxide powders (≥99%) of Li_2CO_3, Nb_2O_5, and TiO_2. Stoichiometric proportions of the above raw materials (5.7:1:7.3, by mole) were milled in alcohol medium using zirconia balls for 4 h. The mixtures were dried and calcined at 900 °C for 8 h with subsequent ball milling. After drying and sieving, the powders were uniaxially pressed under the pressure of about 150 MPa into pellets measuring 10 mm in diameter and 5 mm in thickness. Then the ceramic pellets were sintered at 1,050–1,150 °C for 2 h in air.

The crystal structures of the specimens were analyzed by an X-ray diffractometer (Rigaku D/MAX-2400 X-ray diffractometry, Japan) with Cu Ka radiation generated at 40 kV and 100 mA. The bulk densities of the sintered samples were measured by the Archimedes method. The microstructure observation of well-polished and etched surfaces of the samples was performed using scanning electron microscopy (JEOL JSM-6460LV, Japan).

Dielectric behaviors in microwave frequency were measured by the $TE_{01\delta}$-shielded cavity method using a Network Analyzer (8720ES, Agilent, U.S.A.) and a temperature chamber (DELTA 9023, Delta Design, U.S.A.). The temperature coefficients of resonant frequency τ_f values were calculated by the following formula:

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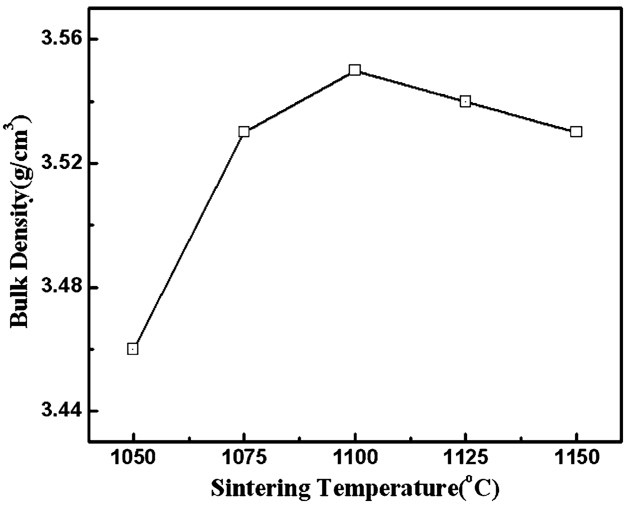


Fig. 1 Bulk densities of the LNT ceramics as a function of sintering temperature

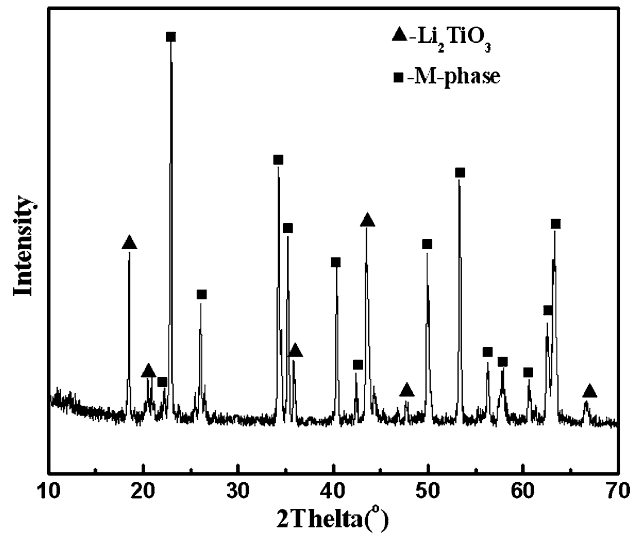


Fig. 2 The X-ray diffraction (XRD) patterns of the LNT sample sintering at 1,125 °C

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

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

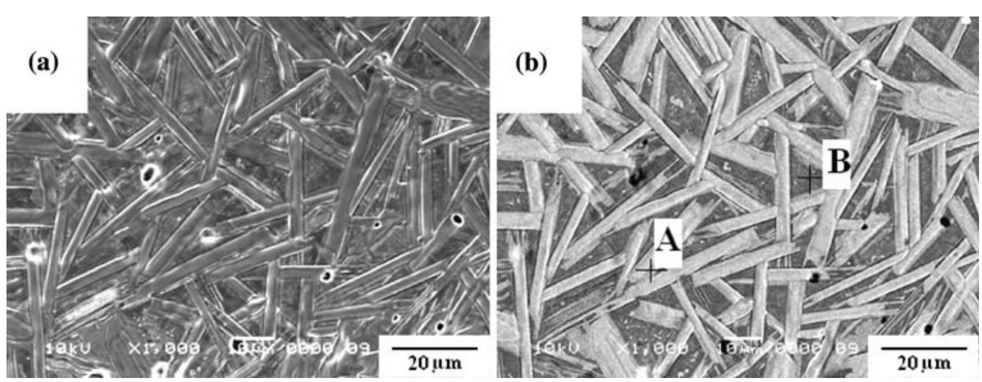
Figure 1 shows bulk densities of the ceramics as a function of sintering temperature. The fired densities of the LNT ceramics increase with increasing sintering temperature, reach a max value as the sintering temperature is 1,100 °C, then decrease slightly. The X-ray diffraction (XRD) patterns of the sample sintered at 1,100 °C for 2 h are shown in Fig. 2. The diffraction peaks indicate that all the ceramics are composed of two phases, the Li_2TiO_3 solid solution (Li_2TiO_3ss) (JCPDS file no. 33-0831) and M-phase. And no other phase has been found in the XRD spectrums.

Figure 3 is the SEM and backscattered electron images of LNT sample sintered at 1,100 °C for 2 h. Long-platelet-shaped grains have been observed (Fig. 3a). The ceramic has a relatively dense microstructure, and the grain sizes are in a range of 10–30 μm. Probably because of the fast growth of the grains, some pores are trapped in large grains. It can be observed that two detached phases connected densely in Fig. 3b. The EDS results of the two phases (denoted A and B) in LNT ceramic are presented in Fig. 4. From the EDS analysis and XRD results, the black grains (marked as A in Fig. 3) are identified as Li_2TiO_3ss structure and the gray grains (marked as B in Fig. 3) are M-phase structure.

Figure 5 shows the dielectric constant (ε_r) and quality factor value ($Q \times f$) of LNT ceramics as a function of sintering temperature. The relationship between ε_r values of LNT ceramics and sintering temperatures presents a trend similar to that between densities and sintering temperatures since a higher density means a lower porosity. The dielectric constant first increases, reaches the peak, and then decreases slightly with increasing sintering temperature. The quality factor value is changing in the same trend as the dielectric constant because a higher density means a low porosity and low loss.

Figure 6 illustrates the temperature coefficients of the resonant frequency (τ_f) of the LNT samples as a function of sintering temperature. The temperature coefficient of the

Fig. 3 SEM and Backscattered electron images of LNT ceramic sintering at 1,125 °C for 2 h



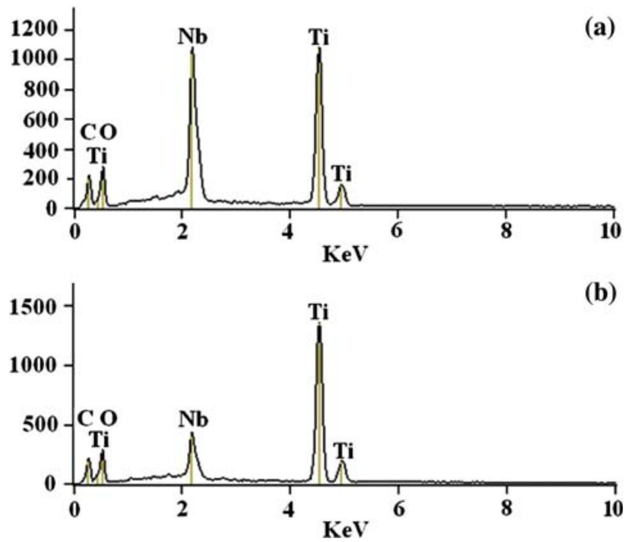


Fig. 4 EDS spectrums of LNT ceramic sintering at 1,125 °C for 2 h: (a) taken from the spot 1 and (b) taken from the spot 2

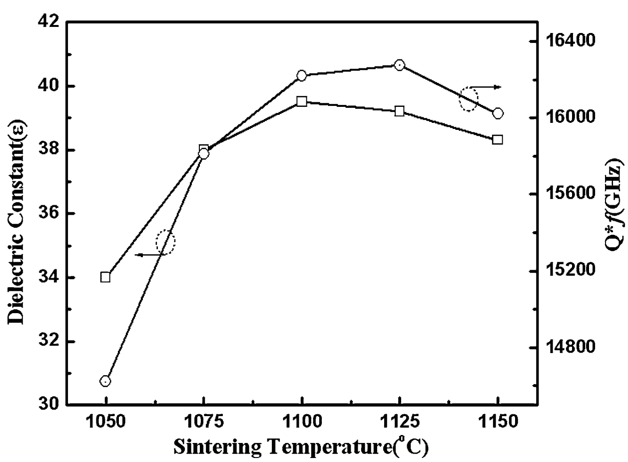


Fig. 5 The dielectric constant values and $Q \times f$ values of LNT ceramics as a function of sintering temperature

resonant frequency (τ_f) relates to the composition and the phases existing in the ceramics. Since the LNT ceramics are temperature stable and no second phase was detected in the ceramics, the τ_f values did not change significantly with different sintering temperatures in this experiment.

To further decrease the sintering temperature of this new kind of microwave dielectric ceramic, the amount of 1 wt% B_2O_3 has been doped into the samples. Due to the liquid-phase effect, the addition of 1 wt% B_2O_3 can efficiently lower the sintering temperature from 1,100 °C to 900°C. The XRD pattern of the B_2O_3-doped ceramic sintered at 900 °C is very similar to that of the undoped ceramic and no other secondary phase could be detected. For the 1 wt% B_2O_3-doped ceramic, a high density of 3.58 g/cm^3 and relatively good microwave dielectric properties of $\varepsilon_r = 40.5$, $Q \times f = 13{,}900$ GHz, and $\tau_f = 42.3$ ppm/°C have been

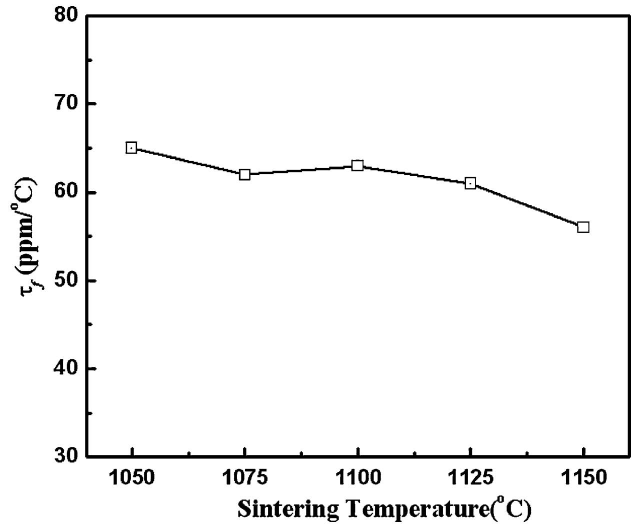


Fig. 6 Temperature coefficient of resonant frequency (τ_f) of LNT samples as a function of sintering temperature

obtained by sintering at 900 °C, which indicates that the new dielectric materials could be promising candidates for low-temperature cofired ceramics (LTCC) applications.

In summary, a new sort of low-firing temperature microwave dielectric ceramic, composing of Li_2TiO_3ss and M-phase phases, was found and investigated in the Li_2O–Nb_2O_5–TiO_2 system. This kind of microwave dielectric ceramic shows relatively high permittivity (39.5), high $Q \times f$ value up to 16,200 GHz, and temperature coefficient (63 ppm/°C), which has been obtained via sintering at 1,100 °C. The addition of B_2O_3 can effectively lower the sintering temperature of the ceramic from 1,100 °C to 900 °C and does not induce degradation of the microwave dielectric properties. Obviously, the new kind of microwave dielectric ceramic is a suitable candidate of low-temperature cofired ceramics for applications in wireless communication system.

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