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Effect of B_2O_3 on the sintering and microwave dielectric properties of M-phase $LiNb_{0.6}Ti_{0.5}O_3$ ceramics

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Abstract

The effect of B_2O_3 addition on the sintering, microstructure and the microwave dielectric properties of $LiNb_{0.6}Ti_{0.5}O_3$ ceramics have been investigated. It is found that low-level doping of B_2O_3 ($\leq$2 wt.%) can significantly improve the densification and dielectric properties of $LiNb_{0.6}Ti_{0.5}O_3$ ceramics. Due to the liquid phase effect of B_2O_3 addition, $LiNb_{0.6}Ti_{0.5}O_3$ ceramics could be sintered to a theoretical density higher than 95% even at 880 °C. No secondary phase was observed for the B_2O_3-doped ceramics. There is no obvious degradation in dielectric properties for the ceramics with B_2O_3 additions. In the case of 1 wt.% B_2O_3 addition, the ceramics sintered at 880 °C show good microwave dielectric properties of $\varepsilon_r = 70$, $Q \times f = 5400$ GHz, $\tau_f = -6.39$ ppm/°C. It represents that the ceramics could be promising for multilayer low-temperature co-fired ceramics (LTCC) applications.

Keyword: Dielectric properties; Microwave dielectrics; Sintering; B_2O_3; Li(Nb,Ti)O_3

1. Introduction

Recently, much attention has been paid to the development of multilayer microwave devices due to the rapid progress on the satellite and mobile communications such as cellular phone, phasers and GPS.[1,2] Several layers of dielectric ceramics and internal electric metal conductors constitute these microwave components. For the fabrication of miniature multilayer devices involving the co-firing of dielectric and highly conductive metal, such as silver or copper, the development of low-temperature co-fired ceramics (LTCC) has been received increasing attention and represented a key position in a high frequency application.[3,4] Generally, low sintering temperature co-fired ceramics (LTCC) can be realized through developing new materials, chemical processing method and using additives which was nowadays an effective and low-cost method in fabricating LTCC. This paper reports on a new family of low sintering temperature dielectric compositions based on the M-phase $LiNb_{0.6}Ti_{0.5}O_3$ system.

In the case of the so-called M-phase compounds, Villafuerte-Castrejón et al.[5] have first described them as forming a series of a solid solution, $Li_{1+x-y}Nb_{1-x-3y}Ti_{x+4y}O_3$, with $0.05 \leq x \leq 0.3$, $0 \leq y \leq 0.182$. Since the excellent microwave dielectric properties of the $Li_{1+x-y}Nb_{1-x-3y}Ti_{x+4y}O_3$ system ($\varepsilon_r = 78$–55, a tunable τ_f, $Q \times f$ up to 9000 (6 GHz)) reported by Borisevich and Davies,[6] the $Li_{1+x-y}Nb_{1-x-3y}Ti_{x+4y}O_3$ solid solutions have been known as potential candidate materials for LTCC applications. Although this materials could be sintered to essentially full density at 1100–1150 °C without sintering aids, further investigations are still required for lowering their sintering temperature to about 900 °C so that they could be co-fired with Cu or Ag electrode. Borisevich and Davies[7] first reported that the V_2O_5-doped $Li_{1.0}Nb_{0.6}Ti_{0.5}O_3$ ceramic could be sintered at 900 °C, and showed the microwave dielectric properties of $\varepsilon_r = 66$, $Q \times f$ value = 3800 GHz, $\tau_f = 11$ ppm/°C. Recently, Kang et al.[8] lowered the sintering temperature of $Li_{1.0}Nb_{0.6}Ti_{0.5}O_3$ ceramic to 850 °C by adding 0.5 wt.% of 0.17 Li_2O–0.83V_2O_5, and obtained better dielectric properties of $\varepsilon_r = 64.5$, $Q \times f$ value = 5933 GHz, and $\tau_f = 9.4$ ppm/°C.

B_2O_3 has been reported as a good flux former to lower the sintering temperature for many materials. With 0.3 wt.% B_2O_3, the 0.84 $Ba_5Nb_4O_{15}$–0.16 $BaNb_2O_6$ ceramics sintered

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at 900 °C showed excellent dielectric properties of $\varepsilon_r = 42$, $Q \times f = 28{,}000$ GHz, and $\tau_f = 0$ ppm/°C.[9] In the present work, B_2O_3 has been added to lower the sintering temperature of $LiNb_{0.6}Ti_{0.5}O_3$ ceramics. The influence of B_2O_3 additions on the densification, microstructure and microwave dielectric properties of $LiNb_{0.6}Ti_{0.5}O_3$ ceramics have been investigated.

2. Experimental

The ceramics were prepared using the conventional mixed oxide route. High-purity oxide powders (>99.5%) of Li_2CO_3, Nb_2O_5 and TiO_2 were used as starting materials. They were mixed according to the desired stoichiometric composition $LiNb_{0.6}Ti_{0.5}O_3$ and ball-milled in enthanol using zirconia balls as milling media for 24 h. The wet mixture was dried and pre-annealed at 700 °C to expel CO_2, then reground and calcined at 850 °C for 8 h. The calcined powder was then divided into two parts. One part was ball-milled without additives in enthanol. After drying and sieving, the powder was uniaxially pressed into disks measuring 16 mm in diameter and 6–8 mm in thickness. The disks were covered with crucibles and sintered at 1100 °C. Another part was re-milled with different amounts of B_2O_3.Then, following the same drying and forming procedures, the B_2O_3-contaning pellets were sintered at temperatures at 840–920 °C.

The bulk densities of the sintered ceramics were measured by Archimedes method. The crystalline phases of sintered samples were examined by X-ray diffraction (XRD) analysis with Rigaku RINT2000 (Cu Kα radiation generated at 40 kV and 40 mA). The well-polished and etched surfaces of the samples were investigated by the electron probe X-ray microanalyser (EPMA) (JXA-8100) and energy dispersive spectra (EDS). The dielectric constant (ε_r) and the quality values Q at microwave frequency were measured using the Hakki–Coleman's dielectric resonator method, as modified and improved by Courtney.[10,11] An Advantest E8363 network analyzer was employed in the measurement. The temperature coefficient of resonant frequency (τ_f) was measured in the temperature range of −25 to +85 °C. The τ_f value was defined as follows:

$$\tau_f = \frac{(f_{85} - f_{-25}) \times 10^{-6}}{110 \times f_{25}} (\text{ppm/°C}) \quad (1)$$

where f_{85}, f_{-25}, and f_{25} are the resonant frequencies at 85, −25 and 25 °C, respectively.

3. Results and discussions

Fig. 1 shows the bulk densities of $LiNb_{0.6}Ti_{0.5}O_3$ with various contents of B_2O_3 as a function of sintering temperature from 840 to 920 °C. As shown in Fig. 1, the samples with 0.5 wt.% B_2O_3 achieve a relatively high density only when the sintering temperature reached 920 °C. When the B_2O_3 content increased to above 1 wt.%, the samples could reach high densities even at 840 °C. The highest density could be obtained for the 1.5 wt.% B_2O_3-doped ceramic. There is an obvious decrease in the density as the B_2O_3 content increased to 2 wt.%, which means this

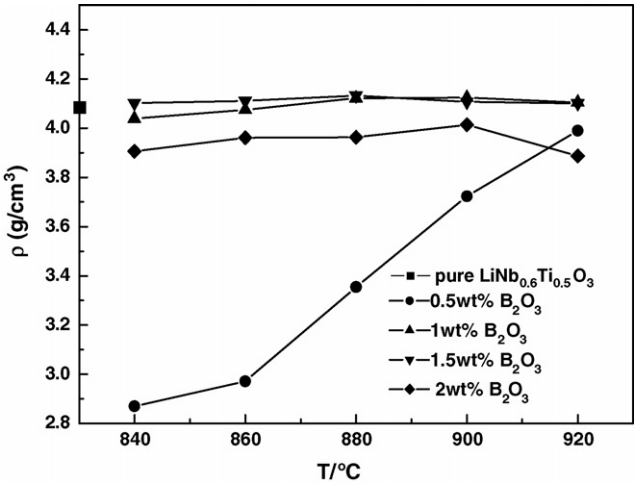

Fig. 1. The bulk density values of the $LiNb_{0.6}Ti_{0.5}O_3$ ceramics with B_2O_3 additions as a function of sintering temperature.

content is overweighed to the ceramics. From Fig. 1 it could be also observed that the sintering curves of 1–2 wt.% B_2O_3-added samples are similar, i.e., their densities slightly increase initially and then decrease with increasing temperature. All these results show that B_2O_3 is very effective in enhancing the sintering ability of $LiNb_{0.6}Ti_{0.5}O_3$ ceramics.

The SEM micrographs of $LiNb_{0.6}Ti_{0.5}O_3$ ceramics doped with (a) 0 wt.% B_2O_3 sintered at 1100 °C and (b) 1 wt.%, (c) 1.5 wt.%, and (d) 2 wt.% B_2O_3 sintered at 880 °C are shown in Fig. 2. Long-platelet shaped grains could be observed in all these micrographs, but due to the much lower sintering temperatures, the grain sizes of the B_2O_3-doped samples are much smaller than those of pure $LiNb_{0.6}Ti_{0.5}O_3$ ceramic. Besides, uniform microstructures with grains densely connected could be found in the samples doped with 1 and 1.5 wt.% B_2O_3 (Fig. 2(b) and (c)). However, in Fig. 2(d) it could be seen that when the B_2O_3 content increases to 2 wt.%, some abnormally-grown large grains would exist, which is probably the main reason for the low density of these samples shown in Fig. 1. Moreover, the EDS results show that no secondary phase could be detected in all these samples.

Fig. 3 shows the X-ray diffraction patterns of $LiNb_{0.6}Ti_{0.5}O_3$ ceramics with (a) 0 wt.% B_2O_3 sintered at 1100 °C and (b) 1 wt.%, (c) 1.5 wt.%, and (d) 2 wt.% B_2O_3 sintered at 860 °C for 4 h. A series of distinctive satellite reflections originated from the superstructure of the M-phase solid-solution are observed, which are agreed with the previous reports.[12,13] And no secondary phases could be detected for the B_2O_3-doped ceramics presumably because of its low mass fraction, which is coincident with the EDS results. In addition, it is found that the diffraction peak positions of the B_2O_3-doped ceramics have small shift compared with the pure $LiNb_{0.6}Ti_{0.5}O_3$ ceramic. With the B_2O_3 content increasing from 0 to 1.5 wt.%, the peak positions shift to lower 2θ angles. This phenomenon is similar with that reported by Kang et al.[8] However, the peak positions shift towards higher diffraction angles when 2 wt.% B_2O_3 added. For the specimens sintered at other temperatures, the similar tendency of XRD patterns has also been observed.

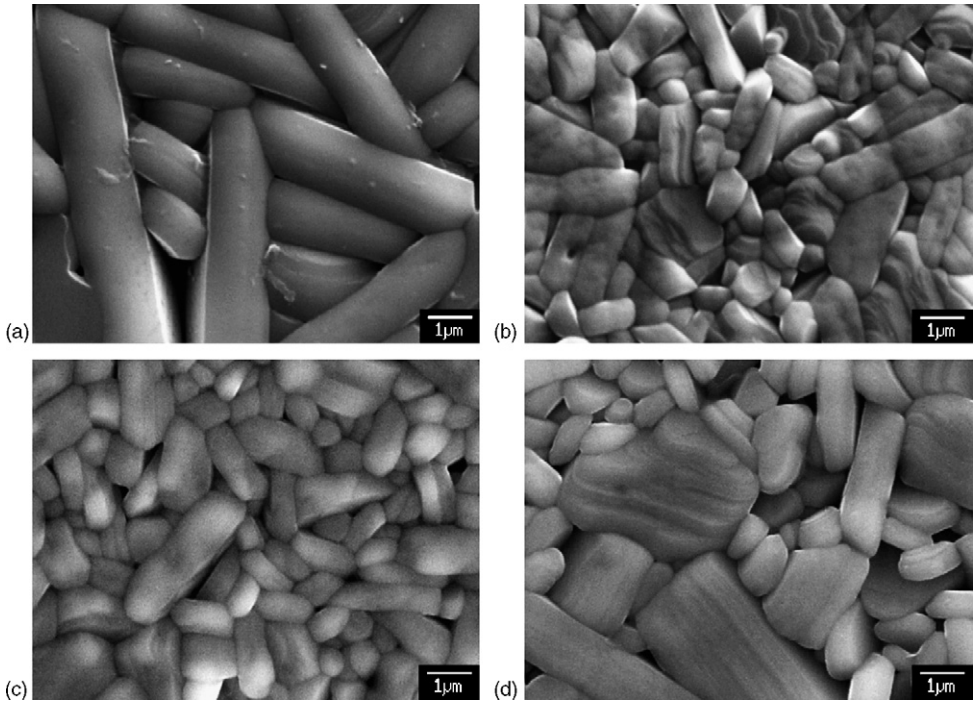

Fig. 2. The SEM micrographs of $LiNb_{0.6}Ti_{0.5}O_3$ ceramics doped with (a) 0 wt.% B_2O_3 sintered at 1100 °C and (b) 1 wt.%, (c) 1.5 wt.%, and (d) 2 wt.% B_2O_3 sintered at 880 °C.

The microwave dielectric properties of $LiNb_{0.6}Ti_{0.5}O_3$ ceramics doped with B_2O_3 as a function of sintering temperature are shown in Figs. 4–6. In these figures, plots on the vertical axis show the properties of undoped $LiNb_{0.6}Ti_{0.5}O_3$ ceramic sintered at 1100 °C. The relationship between ε_r values and sintering temperature show the similar trend as that between densities and sintering temperature. This result suggests that the bulk density of the sintered ceramics determine, to an extent, the dielectric constant of the sintered ceramics. Probably due to the uniform microstructures and high densities, higher dielectric constant than that of the undoped $LiNb_{0.6}Ti_{0.5}O_3$ ceramic sintered at 1100 °C could be obtained for 1 and 1.5 wt.% B_2O_3-doped specimens sintered at 840–880 °C.

Fig. 5 shows the $Q \times f$ values of B_2O_3-doped $LiNb_{0.6}Ti_{0.5}O_3$ ceramics as a function of sintering temperature. The $Q \times f$ values of all the samples with B_2O_3-doped had some decrease than that of undoped $LiNb_{0.6}Ti_{0.5}O_3$ ceramic. With 1–2 wt.% B_2O_3 addition, the $Q \times f$ value variation revealed similar tendency with the apparent density and dielectric constant as shown in Figs. 1 and 4. In Fig. 5 it could also be found that the $Q \times f$ values of $LiNb_{0.6}Ti_{0.5}O_3$ ceramics with 2 wt.% B_2O_3 is much

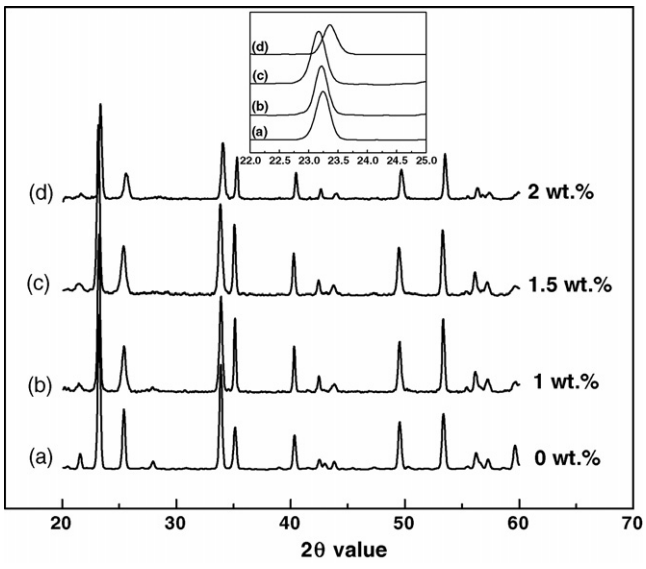

Fig. 3. X-ray diffraction spectra of (a) the undoped $LiNb_{0.6}Ti_{0.5}O_3$ ceramic sintered at 1100 °C and the ceramics with (b) 1 wt.%, (c) 1.5 wt.%, and (d) 2 wt.% additions sintered at 860 °C.

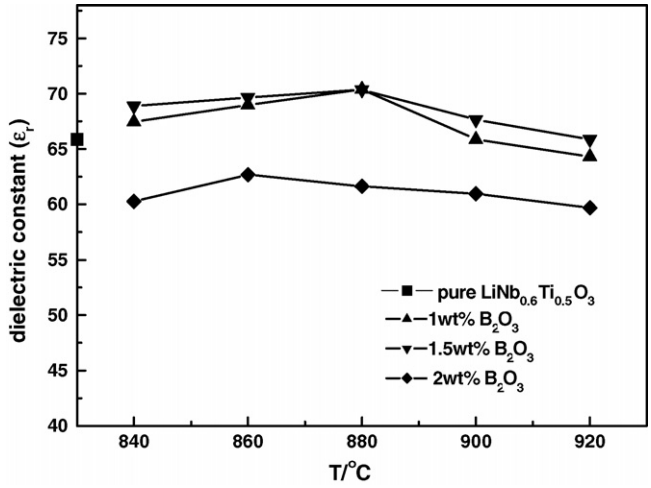

Fig. 4. The dielectric constant values of $LiNb_{0.6}Ti_{0.5}O_3$ ceramics with B_2O_3 additions as a function of sintering temperature.

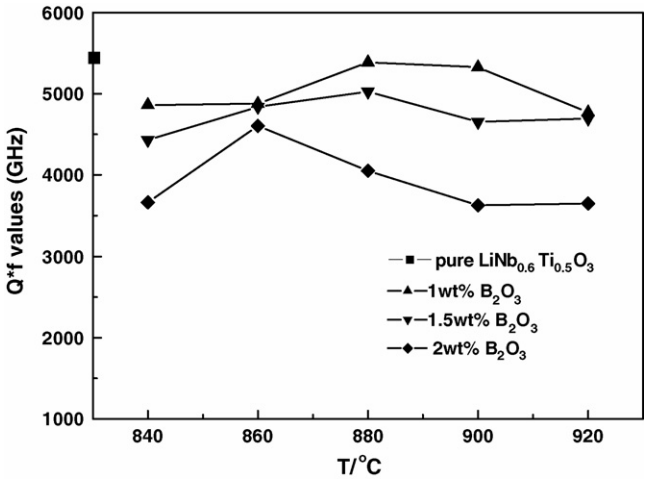

Fig. 5. The $Q \times f$ values of $LiNb_{0.6}Ti_{0.5}O_3$ ceramics with B_2O_3 additions as a function of sintering temperature.

lower than that with 1 and 1.5 wt.% B_2O_3 additions. As we know, the microwave dielectric loss includes not only intrinsic losses which were mainly caused by the lattice vibrational modes but also extrinsic losses dominated by densification/porosity, the secondary phases, grain sizes and oxygen vacancies.[14] Some investigations[15,16] also reported that the $Q \times f$ value is independent of the density and the porosity for a theoretical density higher than 90%. As for the 1–2 wt.% B_2O_3-doped $LiNb_{0.6}Ti_{0.5}O_3$ ceramics, the densities are all higher than 90%, and the secondary phase and charge unbalance are also not possible, so the grain morphology is suggested to dominate the $Q \times f$ values. More uniform grain morphology for 1 and 1.5 wt.% B_2O_3 addition than that for the 2 wt.% B_2O_3 addition in Fig. 2 may mean reductions in lattice imperfection as well as dielectric loss.[14] From Figs. 4 and 5, it could be seen that the good dielectric properties of $\varepsilon_r = 70$ and $Q \times f = 5400$ GHz could be obtained at 880 °C when 1 wt.% B_2O_3 added, which is superior to that of pure $LiNb_{0.6}Ti_{0.5}O_3$ ceramic ($\varepsilon_r = 66$, $Q \times f = 5432$ GHz) sintered at 1100 °C.

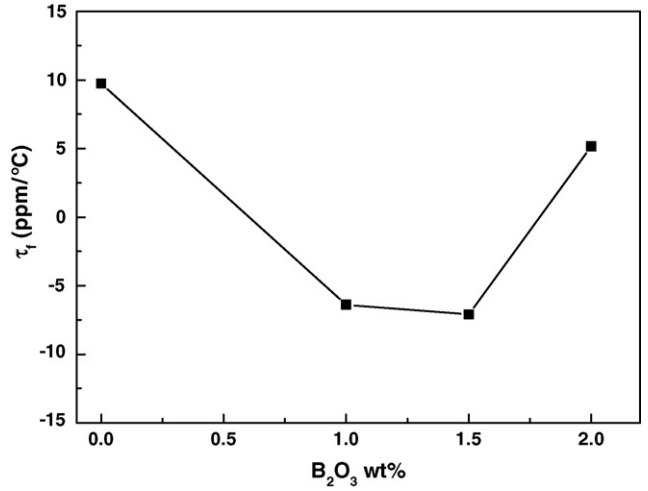

Fig. 6. The τ_f values of $LiNb_{0.6}Ti_{0.5}O_3$ ceramics doped with different amount B_2O_3 additions sintered at 880 °C.

The τ_f values of the B_2O_3-ceramics sintered at 880 °C are illustrated in Fig. 6. From Fig. 6 it could be found that the τ_f value was first decreased from 9.7 to −7.1 ppm/°C as the B_2O_3 content increased from 0 wt.% B_2O_3 to 1.5 wt.%, which is similar as the results when $0.17Li_2O$–$0.83V_2O_5$ was used as additives reported in Ref. 8. However, the τ_f value then increases to 6.5 ppm/°C when B_2O_3 content increases to 2 wt.%. These strange results could be attributed to the tendency of XRD peak shift which have been introduced in Ref. 8. Kang et al.[8] found that the τ_f value shifted to negative direction with the XRD peak shifting to lower angles. Combining Figs. 4 with 6, the similar consistency of the variation of τ_f values and the tendency of XRD peak shift could also be observed. Although the reasons for the variation of the τ_f values are unclear now, it could be reasonably believed that the liquid phase and distortion of crystal lattice should be responsible for the variation of the τ_f value. Moreover, it implies that the addition of appropriate B_2O_3 content could adjust the τ_f value of pure $LiNb_{0.6}Ti_{0.5}O_3$ ceramic close to zero. In general, the $LiNb_{0.6}Ti_{0.5}O_3$ ceramics with small amount of B_2O_3 additions such as 1 wt.% B_2O_3 addition have good dielectric properties of $\varepsilon_r = 70$, $Q \times f = 5400$ GHz, and $\tau_f = -6.39$ ppm/°C.

4. Conclusions

The sintering characteristics, microstructure and microwave dielectric properties of the M-phase $LiNb_{0.6}Ti_{0.5}O_3$ ceramic with different B_2O_3 additions have been investigated systematically in this study. By adding 1–2 wt.% B_2O_3, the $LiNb_{0.6}Ti_{0.5}O_3$ ceramic could be successfully sintered at low temperatures around 880 °C. These low-fired $LiNb_{0.6}Ti_{0.5}O_3$ ceramics exhibit good microwave dielectric properties. Typically, the good dielectric properties of $\varepsilon_r = 70$, $Q \times f = 5400$ GHz, $\tau_f = -6.39$ ppm/°C are obtained for the $LiNb_{0.6}Ti_{0.5}O_3$ ceramics with 1 wt.% B_2O_3 sintered at 880 °C, which are promising for the application of multiplayer microwave components using Ag as an inner electrode.

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