Effect of ZnO and B_2O_3 on the sintering temperature and microwave dielectric properties of $LiNb_{0.6}Ti_{0.5}O_3$ ceramics

Huan-fu Zhou, Hong Wang [*], Di Zhou, Li-Xia Pang, Xi Yao

Electronic Materials Research Laboratory, Key Laboratory of the Ministry of the Education,
Xi'an Jiaotong University, Xi'an 710049, China

Abstract

Dielectric ceramics $LiNb_{0.6}Ti_{0.5}O_3$ (LNT), containing $ZnO–B_2O_3$ (ZB) as sintering aids were prepared and investigated on microstructures and microwave dielectric properties. With addition of low amount of ZB (up to 3.0 wt%), the sintering temperature of the LNT ceramics could be lowered down to around 875 °C. A secondary phase was observed at the 3 wt% ZB addition. The addition of ZB does not induce much degradation on the microwave dielectric properties but adjusts the τ_f value to near zero. Typically, the excellent microwave dielectric properties of $\varepsilon_r = 70$, $Q \times f = 5900$ GHz, and $\tau_f = -4.5$ ppm/°C were obtained for the 1 wt% ZB-doped sample sintered at 875 °C. Silver powders were co-fired with the dielectric under air atmosphere at 900 °C. The XRD and EDS analysis show no reaction between the dielectric ceramic and silver powders. This result shows that the $Li_{1.0}Nb_{0.6}Ti_{0.5}O_3$ dielectric materials are good candidates for LTCC applications with silver electrode.
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1. Introduction

Development of communication systems such as mobile systems requires the miniaturization of device size. Recently, low temperature co-fired ceramic (LTCC) multilayer devices have been investigated to reduce device size [1–4]. As a metallic electrode, Ag has been widely used because of its high conductivity and low cost. The melting temperature of Ag is low, about 961 °C. Therefore, for the fabrication of the multilayer devices, it is important to develop microwave dielectric ceramics, which have a low sintering temperature and can be co-fired with Ag.

In the case of $Li_{1+x-y}Nb_{1-x-3y}Ti_{x+4y}O_3$ systems, Villafuerte-Castrejon et al. [5] have first described that a series of so-called M-phase solid solutions, which form an extended phase field in the center of the ternary section ($Li_2O–Nb_2O_5–TiO_2$), have structures related to $LiNbO_3$. Since their microwave dielectric properties have been reported by Borisevich and Davies [6], $Li_{1+x-y}Nb_{1-x-3y}Ti_{x+4y}O_3$ ($x = 0.1$, $y = 0.05–0.175$) solid solution was known as potential candidate materials for LTCC application with high dielectric constant, low loss and sta-

ble temperature coefficient of resonance frequency. Although this series of 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 Ag electrode. Borisevich and Davies [7] first reported that the V_2O_5-doped $LiNb_{0.6}Ti_{0.5}O_3$ 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 $LiNb_{0.6}Ti_{0.5}O_3$ ceramic to 850 °C by adding 0.5 wt% of $0.17Li_2O–0.83V_2O_5$, and obtained better dielectric properties of $\varepsilon_r = 64.5$, $Q \times f$ value = 5933 GHz, and $\tau_f = 9.4$ ppm/°C. However, the interaction between V and Ag limited the LTCC applications.

$ZnO–B_2O_3$ has been reported as a good flux former to lower the sintering temperature for many materials. With 4.0 wt% $ZnO–B_2O_3$, the $Ba_3Ti_5Nb_6O_{28}$ ceramics sintered at 925 °C showed excellent dielectric properties of $\varepsilon_r = 38$, $Q \times f = 24900$ GHz, and $\tau_f = 1$ ppm/°C [9]. In the present work, ZnO and B_2O_3 as flux materials were added to the $LiNb_{0.6}Ti_{0.5}O_3$ ceramics to decrease the sintering temperature for LTCC applications. Microstructure and microwave dielectric properties of low-fired $LiNb_{0.6}Ti_{0.5}O_3$ ceramics with ZnO and B_2O_3 additions were investigated.

[*] Corresponding author. Tel.: +86 29 8266 8679; fax: +86 29 8266 8794.
E-mail address: hwang@mail.xjtu.edu.cn (H. Wang).

2. Experimental procedure

The $Li_{1.0}Nb_{0.6}Ti_{0.5}O_3$ powders were prepared using Li_2CO_3 (>99%, Shu-Du Powders Co. Ltd., China), Nb_2O_5 (>99%, Zhu-Zhou Harden Alloys Co. Ltd., China), TiO_2 (>99%, Shu-Du Powders Co. Ltd., China). The powders were ball-milled in a polyethylene bottle with ZrO_2 media for 4 h using alcohol as a medium. The mixtures were then rapidly dried and calcined at 900 °C for 8 h. The calcined powders containing an appropriate amount of ZnO (>99%, Shu-Du Powders Co. Ltd., China) and B_2O_3 (>99%, Shu-Du Powders Co. Ltd., China) were ball-milled for 4 h using ethanol as a medium. The milled powders were then dried, granulated, and pressed at 150 MPa to form pellets of 8 mm in diameter and 4 mm in thickness. The pellets were sintered at 825–950 °C with a heating rate of 5 °C min^{-1}. For compatibility tests, the silver powder was mixed with the calcined powders that contain 1 wt% ZB and then sintered at 900 °C for different periods of time.

The bulk densities of sintered specimens were measured by Archimedes method. The crystal structures of ceramics were investigated by a X-ray diffractometry (XRD) with Cu Kα radiation (Rigaku D/MAX-2400 X-ray diffractometry, Japan). The surface of the sintered specimen and broken surface of co-fired sample were observed by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) (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, USA) and a temperature chamber (DELTA 9023, Delta Design, USA). The temperature coefficients of resonant frequency τ_f values were calculated by the formula as following:

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

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

3. Results and discussion

3.1. Phase analysis of low-fired $Li_{1.0}Nb_{0.6}Ti_{0.5}O_3$

Fig. 1 represents the bulk densities of the LNT ceramics with the addition of 0.1–3 wt% ZB as a function of sintering temperature from 825 °C to 950 °C. The dot on the vertical axis shows the density of an undoped LNT ceramic sintered at 1100 °C. The density of the undoped LNT ceramic is about 4.04 g cm^{-3}. For the ZB-doped ceramics, the bulk densities firstly increase and then decrease with increasing ZB content. As shown in Fig. 1,
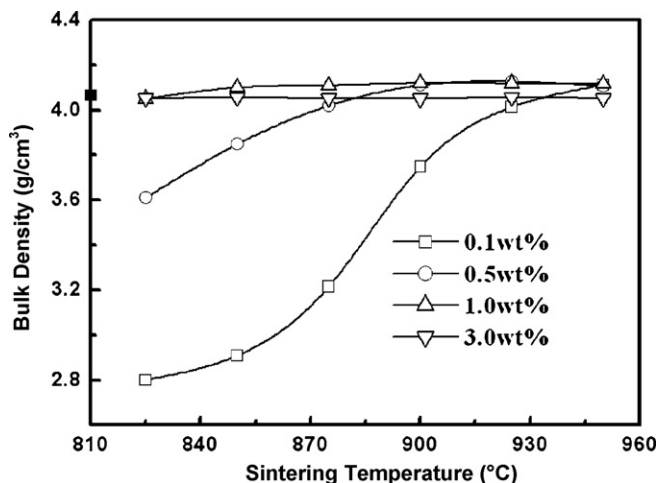

Fig. 1. Bulk density of the LNT samples with 0.1–3 wt% ZB additions as a function of sintering temperatures.
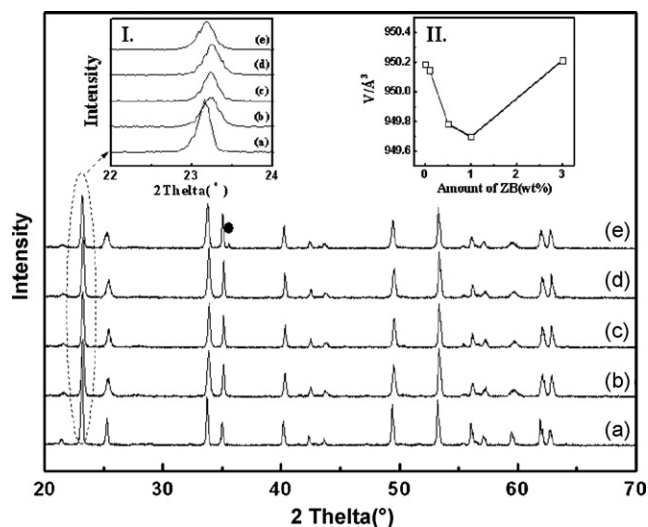

Fig. 2. XRD patterns and lattice parameters of the LNT samples with x wt% ZB addition sintered at 875 °C for 2 h: (a) 0 wt% (b) 0.1 wt%, (c) 0.5 wt%, (d) 1 wt% and (e) 3 wt%.

the densities of the samples doped with 0.1 wt% ZB remain relatively low, which indicates that 0.1 wt% ZB is not enough for densifying the ceramics efficiently at these low sintering temperatures. Then, when the ZB content increases to 0.5 wt%, the samples could reach high densities at around 900 °C. But when the ZB content increases to 1.0 wt%, the samples could reach high densities at around 825 °C It could be also observed that the sintering curves of 1.0–3.0 wt% ZB-doped samples are similar, i.e., their densities slightly increase initially with increasing sintering temperature and then decrease slightly after reaching its maximum value. All these results show that ZB is effective in enhancing the sintering ability of the LNT ceramic.

The X-ray diffraction (XRD) patterns and lattice parameters of the samples with different amounts of ZB additive are shown in Fig. 2, where the undoped ceramic was sintered at 1100 °C, and the ZB-doped ceramics were sintered at 875 °C. It is observed that all the compounds below 1.0 wt% ZB exhibit a single M-phase structure, and only for the specimens containing 3 wt% ZB, the secondary phase is detected in the ceramics. Compared with the pure LNT ceramic, one special phenomenon is observed: the diffraction peak shifts slightly to higher 2θ angles with increasing ZB content from 0.1 wt% to 1 wt%. But then, probably due to the formation of the secondary phase, the 2θ angles shift toward lower diffraction angles when 3 wt% ZB is added (inset I in Fig. 2). Pure $LiNb_{0.6}Ti_{0.5}O_3$ was indexed as a single M-phase structure with $a = 5.125(0)$ Å, $c = 13.924(8)$ Å and the cell volume $V = 950.1838$ Å^3. With ZB doping, the a parameter increased slightly, but the c parameter first decreased apparently and then increased, thus the cell volume first decreased and then increased (inset II in Fig. 2).

The SEM micrographs of the LNT ceramics doped with different amount of ZB sintered at 875 °C are illustrated in Fig. 3. From Fig. 3, platelet shaped grains could be observed in all these micrographs, but due to the much lower sintering temperatures, the grain sizes of the ZB-doped samples are much smaller than those of pure LNT ceramic. Besides, uniform microstructures
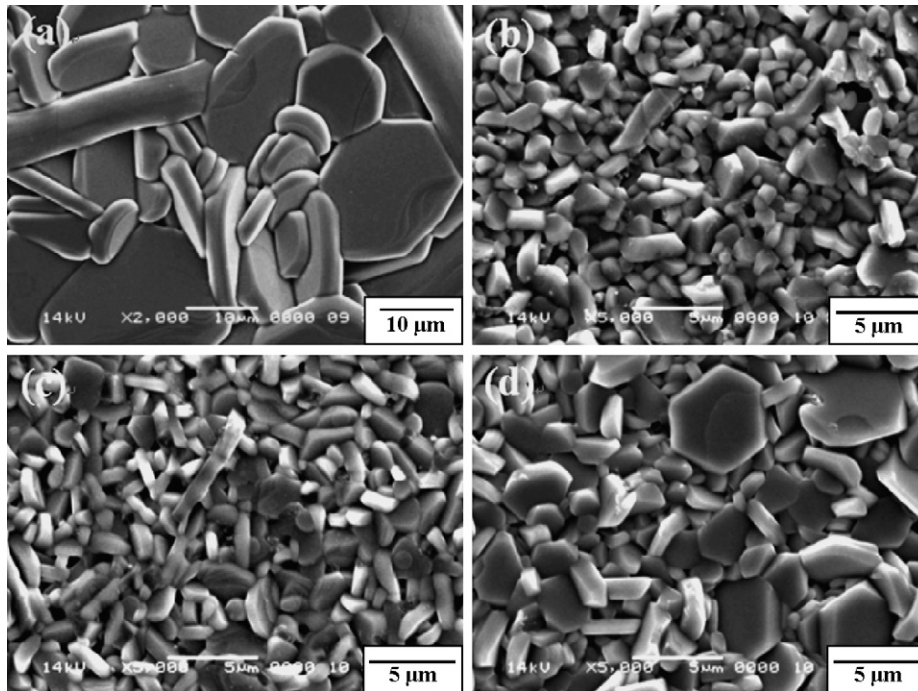
Fig. 3. SEM images of the LNT samples doped with different ZB: (a) 0 wt% sintered at 1100 °C (b) 0.5 wt%, (c) 1 wt% and (d) 3 wt% sintered at 875 °C.
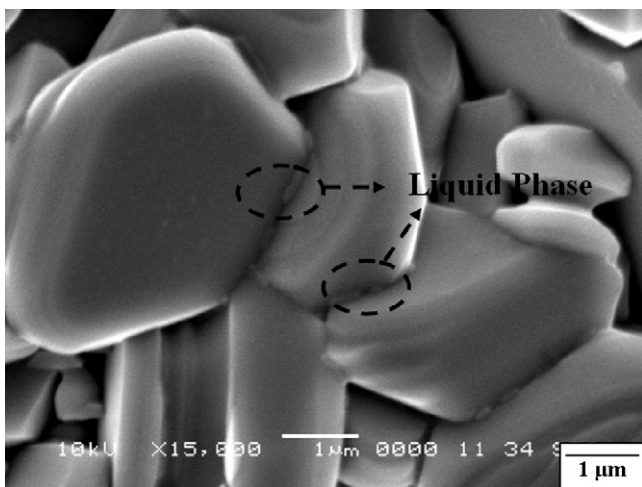

Fig. 4. Enlarged SEM image of the LNT samples doped with different ZB sintered at 875 °C.

with grains densely connected could be found in the samples doped with 0.5 and 1 wt% ZB (Fig. 3(b) and (c)). However, in Fig. 3(d) it could be seen when the ZB content increases to 3 wt%, some abnormally grown large grains would exist, which is probably the main reason for the low density of these samples (Fig. 2). Fig. 4 is enlarged SEM image of the LNT sample doped with 3.0 wt% ZB sintered at 875 °C. A liquid phase was found in the boundary of grains, which indicate that the $ZnO–B_2O_3$ forms liquid phases (such as ZnB_2O_4) and enhances the sintering ability of the LNT ceramic. The mechanism of liquid phase sintering is similar to that of $BaTiO_3$ doped with Li_2O [10,11].

3.2. Microwave dielectric properties of low-fired $Li_{1.0}Nb_{0.6}Ti_{0.5}O_3$

The microwave dielectric properties of ZB-doped LNT ceramics at different sintering temperatures are illustrated in
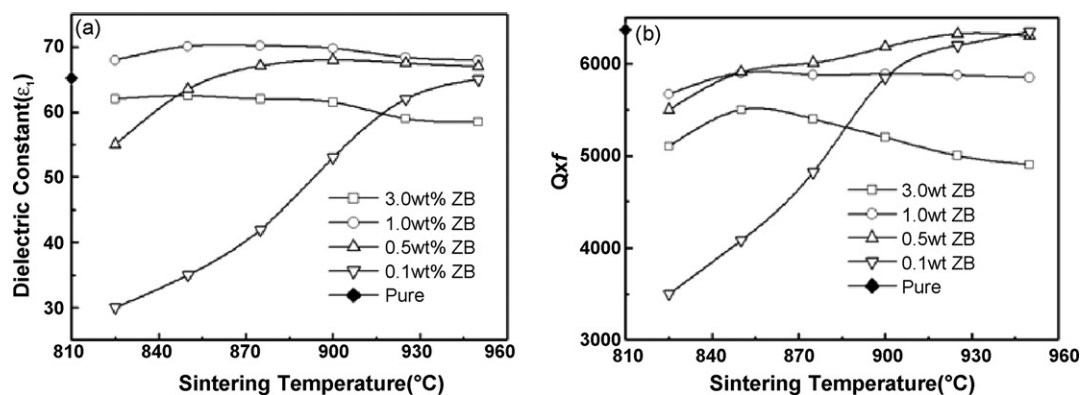

Fig. 5. Microwave dielectric properties of LNT ceramics doped with ZB: (a) relative dielectric constant and (b) quality factor ($Q \times f$).
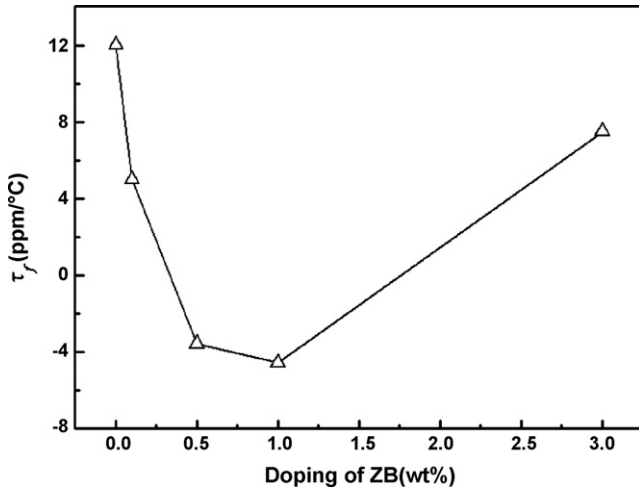
Fig. 6. Temperature coefficient of resonant frequency (τ_f) of LNT samples as a function of ZB doping.

Fig. 7. XRD patterns of LN ceramics doped with 1.0 wt% ZB co-fired with Ag at 900 °C for different time: (a) pure 2 h, (b) 2 h, (c) 4 h and (d) 8 h.

Figs. 5 and 6. In these figures, dots on the vertical axes show the properties of pure LNT ceramic sintered at 1100 °C. From Fig. 5(a), it can be observed that the relationship between ε_r values of ZB-doped ceramics and sintering temperatures presents a trend similar to that between densities and sintering temperatures. The dielectric constant increased owing to the higher density. The highest dielectric constant was obtained for 1.0 wt% ZB-doped LNT sintered at 875 °C. Moreover, the dielectric constant slightly decreased with increasing ZB content.

As we know, the microwave dielectric loss includes not only intrinsic losses which were mainly contributed by the lattice vibrational modes but also extrinsic losses caused by densification/porosity, the secondary phases, grain sizes and oxygen vacancies. Some investigations also reported that the $Q \times f$ value is independent of the density and the porosity for a theoretical density higher than 90%. With 0.1 wt% ZB addition, the $Q \times f$ values increase from 3500 GHz to 6350 GHz as the sintering
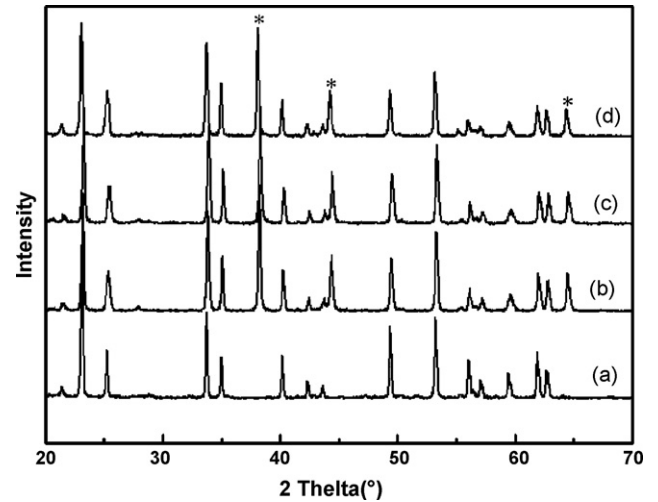
temperature increasing from 825 °C to 950 °C. Since porous specimens were obtained after sintering at low temperatures, the presence of the pores may caused the $Q \times f$ value to be diminished. On the other hand, with the increasing of sintering temperature, the $Q \times f$ increases to a maximum value and thereafter decreases as the increasing amount of ZB. The decrease in the $Q \times f$ value is due to the rapid grain growth, as observed in Fig. 5(b). Density plays an important role in controlling the dielectric loss, as has been shown for other microwave dielectric materials. High ZB content would degrade the $Q \times f$ value of LNT ceramics because grain boundary phases and abnormal grains are dominant products at higher sintering temperatures, as also observed in Fig. 5(b). Because the observed grains of LNT ceramics with 0.5 wt% ZB are more uniform than those of other samples and there is a reduction in lattice imperfections and dielectric loss, the decrease in the $Q \times f$ values for highly ZB-doped LNT ceramics could be related to the grain morphol-
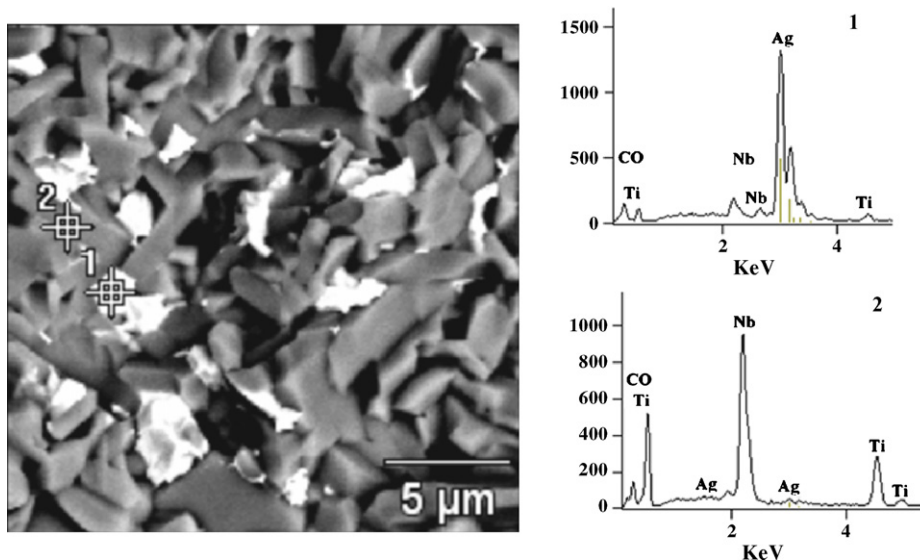

Fig. 8. SEM and EDS of LN ceramics doped with 1.0 wt ZB co-fired with Ag.

ogy as well as the low $Q \times f$ of the liquid phase. This would explain the decrease in $Q \times f$ values for LNT ceramics with the increasing of ZB amounts.

Fig. 6 shows the temperature coefficient of resonant frequency (τ_f) values of the ZB-doped ceramics sintered at 875 °C as a function of the amount of ZB addition. As shown in Fig. 6, the τ_f values decrease slightly first with increasing ZB content from 0 wt% to 1.0 wt% and then increase when the ZB content increases from 1.0 wt% to 3.0 wt%. Combining Figs. 2 and 6, it reveals that the variation of τ_f values is similar to the tendency of XRD peak shift. It is reasonably believed that the liquid phase and distortion of crystal lattice could be responsible for the variation in the τ_f values.

3.3. Co-fire with Ag of low-fired $Li_{1.0}Nb_{0.6}Ti_{0.5}O_3$

For compatibility tests, mixtures of ceramic powder with Ag powders were co-fired and analyzed to detect interactions between the low-fired samples and electrodes. XRD patterns of $LiNb_{0.6}Ti_{0.5}O_3$ ceramics doped with 1.0 wt% $ZnO–B_2O_3$ co-fired with Ag at 900 °C for different periods of time are presented in Fig. 7. It was observed that all the compounds below 3.0 wt% $ZnO–B_2O_3$ exhibit a single M phase structure. SEM and EDS analysis reveal no interaction to form new phases after firing, as shown in Fig. 8 (The diameter of EDS analysis is several microns, which is larger than that of silver particles doped (~3 μm), so the EDS analysis contains some lines from Nb and Ti). This observation is also confirmed by the evidence of no difference between the XRD patterns before and after firing. It is obvious that the reaction of low-fired $LiNb_{0.6}Ti_{0.5}O_3$ ceramics with Ag electrodes did not occur. Therefore, $LiNb_{0.6}Ti_{0.5}O_3$ with $ZnO–B_2O_3$ can be suitable candidates for LTCC materials, because of low sintering temperature, good microwave dielectric properties, and compatibility with Ag electrodes.

4. Conclusion

For the $Li_{1.0}Nb_{0.6}Ti_{0.5}O_3$ ceramic, a small amount of ZB addition can lower the sintering temperature from 1100 °C to 875 °C. At a low addition level (<3 wt%), the ZB-doped ceramics remain single phase and present a secondary phase only when 3 wt% ZB is added. The low-firing LNT ceramics exhibit excellent microwave dielectric properties. For the 1 wt% ZB-doped samples, excellent microwave dielectric properties of $\varepsilon_r = 70$, $Q \times f = 5900$ GHz, and $\tau_f = -4.5$ ppm/°C could be obtained at 875 °C. The EDS analysis shows no reaction between the dielectric ceramic and silver powders. This result shows that the $Li_{1.0}Nb_{0.6}Ti_{0.5}O_3$ dielectric materials are good candidates for LTCC applications with silver electrode.

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