Effects of La$_2$O$_3$-B$_2$O$_3$-ZnO additions on the low temperature sintering and microwave dielectric properties of (Ca$_{0.61}$La$_{0.26}$)TiO$_3$ ceramics

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Abstract. The influence of La$_2$O$_3$-B$_2$O$_3$-ZnO (LBZ) additions on the sintering behavior, microstructure, phase composition, and the microwave dielectric properties of (Ca$_{0.61}$La$_{0.26}$)TiO$_3$ (CLT) ceramics have been investigated. The results indicate that the LBZ additions could efficiently lower the sintering temperature of the CLT ceramics from 1400°C to 950°C, and excellent microwave properties remain. Small amount of LBZ glass promotes the densification of the CLT ceramics and enhances the microwave dielectric properties. However, excess amount of LBZ glass deteriorates the dielectric properties because of the increasing glass phase. The CLT ceramic with 3 wt. % LBZ additions, sintered at 950°C, exhibit excellent properties: $\varepsilon_r = 103.12$, $Q \times f = 8826$ GHz ($f = 3.312$ GHz) and $\tau_f = 299.52$ ppm/°C.

1. Introduction

Low temperature co-fired ceramics (LTCC) technology plays an important role in the integration of the electronic device, which reduces the fabrication expenditure by using cost-effective electrodes Ag or Cu relative to the traditional Pt electrode and simplifies the manufacture process of electronic components [1,2]. In normal conditions, the firing temperature of the LTCC materials is limited below 950°C[3]. High relative permittivities are necessary since the size of the dielectric device is inversely proportional to the square root of the dielectric constant $\varepsilon_r$. While the result should not be achieved with the decrease of the quality factor ($Q \times f$), where $Q \sim 1/\tan\delta$ ($\tan\delta$ is the dielectric loss tangent and $f$ is the resonant frequency)[4–8].

The dielectric properties of the CaTiO$_3$ ceramics were first reported by Kell et al. [9] in 1970s. They reported that CaTiO$_3$ had a high permittivity, $\varepsilon_r = 170$, and a temperate dielectric losses, $Q \times f = 3500$ GHz, which provides a valuable reference for microwave components [9]. Then many studies about the advance of the microwave dielectric properties of CaTiO$_3$-based ceramics have been conducted for the last 20 years [10–13]. Moreover, the substitution of Ca$^{2+}$ by other trivalent lanthanide ions, such as La$^{3+}$, Sm$^{3+}$ and Nd$^{3+}$, has also been investigated by several research groups. Kim et al. [14] reported that the partial substitution of Ca$^{2+}$ by La$^{3+}$ led to forming of the phase Ca$_{1-x}$La$_{2x/3}$TiO$_3$; And when $x = 0.4$, the microwave dielectric properties ($\varepsilon_r = 109$, $Q \times f = 17,600$ GHz and $\tau_f = +213$ ppm/°C ) of Ca$_{0.6}$La$_{0.267}$TiO$_3$ ceramics were reached at 1400°C[15]. As mentioned above, the CaTiO$_3$-based ceramics are generally fired above 1100°C, which is too high to apply in actual application. So the important thing is to lower the sintering temperatures of ceramics without the decrease of dielectric properties. And the study about the low temperature firing of the CLT ceramics with high $\varepsilon_r$ and high $Q \times f$ value has not been reported so far. Usually, there are two
common methods to reduce the firing temperature: low melting temperature sintering aids, the use of ultrafine powders prepared by chemical routes as the starting material of ceramics. And the addition of low melting temperature glasses is the most inexpensive and effective method to get dense ceramics at a low sintering temperature. [16-18].

La$_2$O$_3$-B$_2$O$_3$-ZnO (LBZ) glass has a low glass transition point[19], and in the previous study[20], the CNT ceramics with 3 wt% LBZ could be fired at 975°C and exhibited good properties: $\varepsilon_r = 87.8$, $\tau_f = +244$ ppm/°C, $Q \times f = 8132$ GHz. Hence, in this work, the LBZ glass was also selected as the sintering addition agent of the CLT ceramic. And the low temperature firing behavior with the firing addition agents and the dielectric properties were systematically discussed.

2. Experimental procedure

The CLT ceramics were prepared by the solid-state reaction method. CaCO$_3$, La$_2$O$_3$, TiO$_2$, H$_3$BO$_3$ and ZnO with purity higher than 99% were adopted as raw chemicals. Firstly, the powders were weighed as the ratio of (Ca$_{0.61}$La$_{0.26}$) TiO$_3$ and then milled with zirconium balls in the de-ionized water for 8 h. Then the mixtures were calcined at 1100°C for 5 h after drying. To synthesize the LBZ glass, the chemical formula was designed to be 1La$_2$O$_3$-2B$_2$O$_3$-0.5ZnO, and the above materials were ball milled for 2 h and then melted in a platinum crucible at 1400°C for 2 h. Then the melting glass was poured into the copper plate to quench, triturated in mill for about 4 h. After that, the calcined CLT powder and LBZ glass were weighed as CLT+ x wt. % LBZ where x=1, 3, 5, 7 and re-milled together for 7 h. Subsequently, the powders were dried and pressed into cylindrical samples of 15 mm in diameter and 8 mm in thickness under a pressure of 20 MPa. After heating from the ambient temperature with a rate of 5°C /min, all samples were sintered from 875°C to 975°C, for 4 h.

The bulk densities of the samples were measured by the Archimedes method. The shrinkage during heat treatment was measured by the dilatometer with alumina rams and boats (Model DIL402C, Netzsch Instruments, Germany). Melting behavior of LBZ glass with CLT was investigated by placing LBZ on the surface of CLT substrate, then heated from 21°C to 950°C with a rate of 5 °C /min, at the same time, changes of the glass of LBZ and CLT were recorded by sintering point testing facility. Identification of crystalline phases was identified by X-ray diffractometry (XRD, Rigaku Industrial Corporation, Japan). The permittivity $\varepsilon_r$ and the quality factor ($Q \times f$) were determined by Hakki-Coleman dielectric resonator method with the network analyzer (HP83752A, the United States). The microstructure was determined by scanning electron microscope (SEM, JSM-6490LV, Japan). And the temperature coefficient of the resonant frequency $\tau_f$ value could be measured using the formula:

$$\tau_f = \left(\frac{f_{85} - f_{25}}{f_{25} \times 60}\right) \times 10^4 \text{ (ppm/°C)}$$

where $f_{25}$ and $f_{85}$ are the resonant frequencies at the temperature of 25°C and 85°C, respectively.

The temperature measurement was using the temperature chamber (HLT6003P, China).

3. Results and discussion

The linear shrinkage variations of the pure CLT and CLT +3wt. % LBZ during heating process were studied in Figure 1. The shrink of the pure CLT occurs at around 1140°C, while a great shrink takes place at around 850°C with 3 wt. % LBZ glass added, it means that the LBZ glass efficiently promotes the firing process of the CLT ceramics.

Fig. 2 reveals the melting behavior of CLT ceramic with LBZ glass at different temperatures. It can be found that no obvious melting is observed at temperatures below 640°C, while the LBZ shows a significant shrinkage at around 745°C, which agrees with the previous research result of DSC [20] that the endothermic peak at 742°C shows the melting temperature point of the LBZ glass. Then the volume expansion of LBZ appears and stays the same with the temperature increasing. It shows that a certain amount of LBZ can melt and penetrate the CLT substrate, while the thermal expansion of the remaining LBZ occurs during the further heating process. These results indicate that there is a good
chemical compatibility between LBZ glass and CLT at around 745°C which the low temperature densification probably owes to the formation of the liquid phase.

Fig. 3 shows the XRD patterns of CLT ceramics with 3 wt. % LBZ fired at different temperatures from 900 °C to 975°C. The XRD results illustrate that all samples contain three phases: the main phase CaTiO₃ (JCPDS No.82-0231), a small amount of LaBO₃ (JCPDS No.12-0762) and some excess TiO₂ (JCPDS No.87-0920) phase. The LaBO₃ ceramics sintered at 1300°C exhibit excellent microwave properties with a relative permittivity of εᵣ∼11.8, a quality factor of Q×f value~76,869 GHz (at~15 GHz), and a negative τₖ~−52 ppm/°C[21]. These results explain that liquid phases which caused by La-B-Zn mixture were formed during the heating procedure. As the liquid enter into the space between the crystal grains, then fills the pores and pulls the particles together via the capillary attraction, accelerates the grow of the grains. And the mixture exists in amorphous state and the LaBO₃ phase around the grains in the chilling process.

The SEM photographs of the CLT specimens with 3 wt. % LBZ glass fired at different temperatures (875°C to 1000°C) are shown in Figure 4. With the firing temperature increasing, a dense microstructure with hardly any pores is observed and the grains of the ceramic samples gradually grow more completely from Fig. 4(d)–(f), owing to the fluid phase which created by LBZ melting (with a fusion point of 750°C) fills the holes then attract the grains gather. This liquid-
assisted interaction facilitates the arrangement of particles and expedites the mass transportation. Thus, the glass of LBZ improve the sintering process and accelerate the shrinkage of the ceramics, which is accordance with the results of Fig. 1. When further raise the temperature, Fig. 4(e) and (f) shows that higher temperature results in the more glass phase separate out which damages the dielectric properties.

Fig. 5 (a) manifests the volume of CLT with different contents (1wt.% - 7wt.% ) of LBZ as the change of sintering temperature (875°C - 975°C). For the pure CLT ceramic, the density maintains very low. But the densities of the samples with LBZ added elevate significantly and reach a peak value at 950°C, then decrease slightly as further increasing firing temperatures. At this point, the liquid phase formed by LBZ promotes effectively the firing process of CLT ceramics which is consistent with the previous conclusion. As the liquid draws the particles together in the sintering process, therefore, the density increase.

![Figure 4](image)

Figure 4. SEM of the CLT samples with 3 wt.% LBZ sintered at different temperatures for 4h: (a) 875°C (b) 900°C (c) 925°C (d) 950°C (e) 975°C (f) 1000°C.

Figure 5(b) and (c) indicate the εr and the Q×f of the CLT+ x wt.% LBZ(x=0 -7) ceramics at different fired temperature. It shows obviously that the LBZ glass effectively improves εr and Q×f value respectively. With 1 wt.% LBZ added, the εr of the samples reach the greatest values at 950°C. With more LBZ added (3wt.%, 5wt.%, 7wt.%), the εr enhance follow the increase of firing temperatures (Fig. 5(b)), which is accordance with the trends of density. While the Q×f of the CLT+ 1 wt.% LBZ sample changes smoothly at a relative low. When more LBZ is added (x= 3, 5), the Q×f value increases a lot, however, further increasing LBZ content (7 wt.%) results in the obvious diminution of the value (Fig. 5(c)). As we know, the dielectric loss contains intrinsic loss dominated by lattice vibrational and extrinsic loss affected by second phase, densification, crystallite dimension, the oxygen vacancy, etc. [22]. Consequently, microwave dielectric properties of CLT ceramic enhanced a lot at a low temperature since the glass of LBZ promoted the firing process and improved the microstructure. The dielectric properties of the CLT+ x wt.% LBZ samples are generalized in Tab1. Compared with the papers [14, 15], the addition of suitable LBZ efficiently decreases the firing temperature of the CLT ceramic without damaging the dielectric properties. And the enhance of the εr and Q×f values due to the densification of the samples induced by LBZ firing agent, but excess glass phase would damage the properties.
Figure 5. Density and dielectric property of CLT+ x wt.% LBZ (x=0,1,3,5,7) ceramics at different sintering temperatures for 4h (a) density (b) $\varepsilon_r$ (c) Q×f.

Figure 6. Temperature coefficient of resonant frequency of CLT+ x wt.% LBZ (x=1,3,5,7) ceramics sintered at 950°C for 4h.

Table 1. The properties of CLT + x wt. % (x =0, 1, 3, 5, 7) LBZ samples.

| Composition          | Sintering Temperature (°C) | $\varepsilon_r$ | Q×f (GHz) |
|----------------------|----------------------------|-----------------|-----------|
| CLT[18]              | 1400                       | 109             | 17600     |
| CLT+1wt%LBZ          | 950                        | 112.26          | 2298      |
| CLT+3wt%LBZ          | 950                        | 103.12          | 8826      |
| CLT+5wt%LBZ          | 950                        | 100.66          | 8098      |
| CLT+7wt%LBZ          | 950                        | 98.99           | 2391      |

Figure 6 shows the temperature coefficient of resonator frequent of CLT+ x wt. % LBZ (x=1, 3, 5, 7) samples sintered at 950°C. Since the $\tau_f$ value of LBZ glass is negative (~ -40 ppm/°C)[1], the $\tau_f$ value of CLT samples decreases with the increase of LBZ glass, from 324.19 ppm/°C to 267.1 ppm/°C.

4. Conclusions
The functions of LBZ glass on the dielectric properties and microscopic structure of the CLT ceramics were studied. LBZ glass is a good sintering additive, which can promote the firing process of the CLT ceramics and effectively reduce the temperature to 950°C. The appropriate amount of LBZ glass can form the liquid phase during sintering, leading to a densification microstructure, therefore enhances the dielectric properties. Typically, 3 wt.% LBZ-doped CLT ceramics sintered at 950°C present the best dielectric properties of $\varepsilon_r = 103.12$, Q×f = 8826 GHz, $\tau_f=299.52$ppm/°C, which are hopeful for the application of LTCC modules.

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