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# Sintering behavior and microwave dielectric properties of $B_2O_3$-$La_2O_3$-MgO-$TiO_2$ based glass-ceramic for LTCC applications

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ABSTRACT

A new low temperature co-fired ceramic is fabricated from $B_2O_3$-$La_2O_3$-MgO-$TiO_2$ (BLMT) glass with ZnO, $ZrO_2$ and $TiO_2$ ternary fillers, and the sintering behavior, crystalline phases, microstructures and microwave dielectric properties of the glass-ceramics is investigated. The results show that its sintering process starts at about 640 °C and ends up mostly at higher than 710 °C. During the process, BLMT glass crystallizes forming $LaBO_3$ and the filler ZnO reacts with and gets into the residue glass phase, while $TiO_2$ and $ZrO_2$ are stable. With increasing sintering temperature, dielectric constant and temperature coefficient of resonant frequency of the glass-ceramic decrease, while the quality factor firstly increases and then decreases. Typically, the glass-ceramic sintered at 860 °C for 20 min reaches a maximum density of 4.25 g/cm$^3$ and has an excellent microwave dielectric properties with the dielectric constant of 14.08, quality factor of 41,600 GHz (at 8 GHz), and temperature coefficient of resonant frequency of −2.78 ppm/°C.



## 1. Introduction

Low-temperature co-fired ceramics (LTCC) technology has played a more and more important role in the development of mobile communications, satellite communications, radar systems, global positioning systems (GPS) and wireless area network (WLAN) technology since it can meet the requirements of miniaturization, integration and high reliability of electronic devices [1]. There are several features for ideal LTCC materials such as low sintering temperature (below 900 °C), appropriate dielectric constant ($\varepsilon_r$), high quality factor ($Q \times f$) and near-zero temperature coefficient of resonant frequency ($\tau_f$) [2].

Nowadays, the commercially available LTCC materials are divided into two major categories: glass/ceramic systems such as lead borosilicate glass/$Al_2O_3$ system of Dupont and glass–ceramic systems including MgO-$Al_2O_3$-$SiO_2$ system from IBM and CaO–$B_2O_3$–$SiO_2$ system from Ferro [3–5]. Nevertheless, these silicate-based LTCC materials are generally with low dielectric constant (less than 10) because the main crystalline phase of these systems is silicate phase, for example $CaSiO_3$ with $\varepsilon_r = 5$, $Mg_2Al_4Si_5O_{18}$ with 6.2 and $CaAl_2Si_2O_8$ with 7.4 [6,7]. Although LTCC materials with low dielectric constant are required to diminish signal propagation delay, it is also important to study the glass-ceramic LTCC materials with $\varepsilon_r$ higher than 10 for the fulfilling the potential application. Besides, there are few papers about the study of glass-ceramic LTCC materials with $\varepsilon_r$ higher than 10 [1,8].

According to our previous report, $60B_2O_3$-$12La_2O_3$-18MgO-$10TiO_2$ in mol% glass is with low $T_g$ (661 °C), and exhibits great potential as candidates for LTCC applications [9]. The main crystal phases formed from the BLMT glass is $LaBO_3$, which shows optimum dielectric properties: $\varepsilon_r = 12.5$, $Q \times f = 76000$ GHz as reported by Chen [10]. In this paper, a new LTCC glass-ceramic based on BLMT glass with ZnO, $ZrO_2$ and $TiO_2$ ternary fillers is fabricated, and the sintering process and the effects of the temperature on the microstructure and microwave dielectric properties of the material are investigated.

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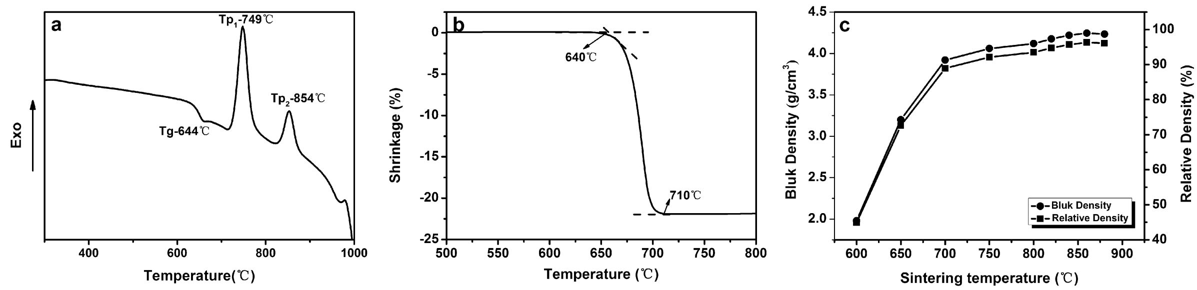


**Fig. 1.** DTA curves (a) of the BLMT glass, shrinkage curve (b) and bulk and relative density (c) of the glass-ceramic.

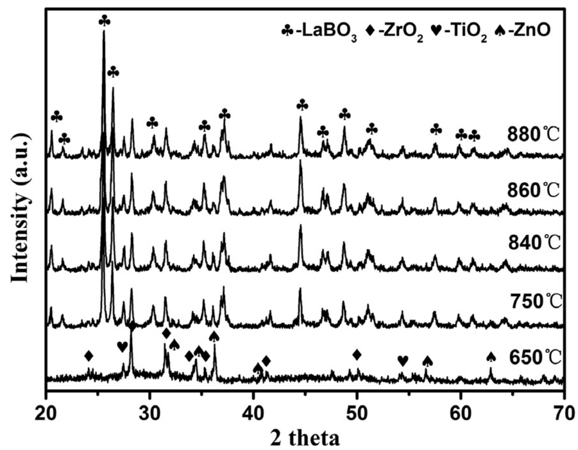


**Fig. 2.** XRD patterns of the glass-ceramic with the different sintering temperature for 20 min.

## 2. Experimental

Reagent-grade MgO, ZnO, $La_2O_3$, $H_3BO_3$, $ZrO_2$ and $TiO_2$ were chosen as the raw materials in the study. Glass of $42.8B_2O_3$-$17.2La_2O_3$-25.7MgO-$14.3TiO_2$ in mol% was prepared by melting the batch in a platinum crucible at 1350 °C for 1.5 h and then quenching in water. 70 wt% of the BLMT glass powder was mixed with 10 wt% of ZnO, 15 wt% of $ZrO_2$ and 5 wt% of $TiO_2$. The mixture of 100 g was first planetary ball-milled for 1 h. After that, the milled powders were dried at 110 °C and mixed with 3% PVB as binder to do manual granulation for getting the uniformity particle size and good fluidity power. Preformed pellets of 15 mm in diameter and 7–8 mm in height were obtained from the powder using a cylindrical steel mold, and then were pressed at 2 MPa by hydraulic pressing. The pellets were sintered at 600–880 °C for 20 min at a heating rate of 5 °C/min.

The bulk densities were measured by the Archimedes method. For DTA experiments, the glass powers was run on a computerized system (DSC 404C, Netzsch, Germany) at a heating rate of 10 °C/min. Shrinkage of the sample was measured with a horizontal-loading dilatometer with alumina ram and boat at a heating rate of 10 °C/min (DIL 402C, Netzsch, Germany). The crystalline phases of the sintered samples were identified using XRD (Uitima, Rigaku, Japan), and microstructures were studied by scanning electron microscopy (S-4800, Hitachi, Japan). The microwave dielectric properties in frequency range of 1–20 GHz were measured by using the TE011 mode of an Agilent E8363A PNA series network analyzer. Disks of 12 mm in diameter and 6 mm in height were used for this measurement. The temperature coefficient of resonant frequency was measured in the temperature range of 25–85 °C.

## 3. Results and discussion

Fig. 1a shows the DTA curve of the BLMT glass. It can be found that the glass transition temperature ($T_g$) of BLMT glass is 644 °C and the glass has two crystallization peaks ($T_p$) : 749 °C and 854 °C, which indicates that BLMT glass with low $T_g$ is suitable for LTCC application. In order to demonstrate the sintering behavior of the glass-ceramic, the shrinkage curve and bulk and relative density as a function of temperature are represented in Fig. 1b and c. The result in Fig. 1b suggests that sintering of glass-ceramic starts at about 640 °C and ends up mostly at higher than 710 °C, and the linear shrinkage is about 22%. Fig. 1c summarizes the bulk and relative density change for glass-ceramic sintered at 600–880 °C. It shows that the bulk and relative density of the glass-ceramic increase with the increase in sintering temperature and reaches their maximum value (about 4.25 g/cm$^3$ and 97%, respectively) at 860 °C, and then slightly decrease due to overfiring.

Fig. 2 shows the XRD patterns of the glass-ceramics for the different sintering temperature. It reveals that except for the filler phases, no other crystalline peaks are identified in the sample sintered at 650 °C. For the temperature above 750 °C, a new crystalline phase, $LaBO_3$ (JCPDS No. 12-0736), is found and becomes the main crystalline phase. At these temperatures, all fillers are found, but ZnO peaks became weaker. $LaBO_3$ is believed to be