

## Sintering of titanate based dielectrics doped with lithium fluoride and calcium borosilicate glass\*

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The effect of LiF and CBS glass additives on the microstructure and dielectric property of BaTiO<sub>3</sub> (BT) ceramics was studied. The phase of BaLiF<sub>3</sub> was observed from the interaction between BT and LiF when the samples were sintered at 900 °C for 1 h. Crystal grains with Ba and F in atomic ratios of 1:3 were observed from the SEM and TEM analysis of the microstructures. Abnormal grain growth (AGG) was observed to occur in the BT ceramics sintered at 950 °C. Further improvement to the composition was achieved by employing a two-stage process. This included CBS glass shell coating of the BT particles in the first stage, and the addition of LiF in the second stage. The composition thus formed had very good permittivity (1725) and an extremely low dielectric loss value (0.008).

Keywords: *dielectrics, low sintering temperature, barium titanate, two stage process*

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### 1. Introduction

Titanate-based dielectrics are widely used in multi-layer ceramic capacitors (MLCC), electro-optic devices and thermistors, because of their good dielectric characteristics. However, the conventional MLCC process, e.g. for BaTiO<sub>3</sub> dielectric, requires sintering temperatures above 1000 °C and utilization of expensive silver-palladium electrodes [1], both meaning that the production costs of multi-layer ceramic are high. This is one of the main reasons why low temperature co-fired ceramics (LTCC) are the subject of much recent research. These materials enable embedding of inexpensive, highly conductive silver electrodes at about 900 °C. Additionally, the capacitors made of LTCC mate-

rial can be integrated with other passive components, such as resistors and inductors [2, 3].

To realize the LTCC process, numerous kinds of glasses have been used to introduce liquid phase into BaTiO<sub>3</sub> ceramic, in order to lower its sintering temperature [4–6]. Lithium fluoride is also utilized to generate liquid phase for promoting the sintering of BaTiO<sub>3</sub> ceramic [7, 8]. However, when a large amount of glass is added to a dielectric, it generally decreases the relative permittivity, due either to the dilution effect caused by the presence of an additive having a low dielectric constant, or to the chemical reaction between the glasses and the BaTiO<sub>3</sub>, resulting in the formation of phase that has a low dielectric constant. The addition of Bi<sub>2</sub>O<sub>3</sub>–B<sub>2</sub>O<sub>3</sub> [9] and ZnO–B<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> [6] glass systems decreased the sintering temperature of BaTiO<sub>3</sub> to 850 °C, but at the same time the relative permittivity was reduced to below 1000. Lee et al. [10] found that BaTi<sub>4</sub>O<sub>9</sub> dielectrics sintered at 1050 °C with a B<sub>2</sub>O<sub>3</sub> additive level of ≤ 5 wt% maintained consis-

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Table 1. The relative permittivity and dielectric loss of the BT samples at 1 kHz for the samples doped with different amounts of CBS glass and LiF and sintered under different conditions

Item	Compositions	Sintering Conditions		$\epsilon_r$	$\tan \delta$
1	BT	1350 °C	2 h	2196	0.015
2	BT	1350 °C	4 h	2029	0.010
3	BT + 1 wt%LiF	900 °C	1 h	3921	0.020
4	BT + 4 wt%LiF	900 °C	1 h	4657	0.10
5	BT + 5 wt% glass	900 °C	1 h	556	0.015
6	BT + 20 wt% glass	900 °C	1 h	264	0.013
7 <sup>a</sup>	BT + 2 wt% glass + 4 wt% LiF	850 °C	1 h	1725	0.008
8 <sup>a</sup>	BT + 2 wt% glass + 4 wt% LiF	900 °C	1 h	2228	0.185

<sup>a</sup>two stage process (\*\*)

tent relative permittivity values similar to the undoped samples. By contrast, if the level of B<sub>2</sub>O<sub>3</sub> additive was larger than 5 wt%, it greatly decreased the relative permittivity of the compound.

In this research, calcium borosilicate (CBS) glass flux, LiF and BaLiF<sub>3</sub> were added to BaTiO<sub>3</sub> to accelerate the densification and to lower its sintering temperature. The samples were formed by the dry pressing method and sintered in air. Samples prepared by a two stage process introduced in the previous investigation [11] were also studied. Furthermore, the effects of CBS glass and LiF addition on the microstructure and electrical properties of the samples were investigated.

## 2. Experimental procedure

A calcium borosilicate (CBS) glass was prepared using reagent grade chemicals having a composition of 46.5 wt% CaO, 27.6 wt% B<sub>2</sub>O<sub>3</sub>, 20.1 wt% SiO<sub>2</sub>, 2.6 wt% ZnO, 1.7 wt% Al<sub>2</sub>O<sub>3</sub> and 1.5 wt% BaO. The chemicals were mixed and melted in a platinum crucible at 1500 °C for 2 h and quenched in water to form amorphous glass that was subsequently dried and pulverized into a powder form. The glass transition and softening temperatures of CBS glass were observed to be 585 °C and 650 °C, respectively. The crushed powder was ball milled in a PVC jar using yttrium stabilized zirconia balls. A commercial BaTiO<sub>3</sub> (BT) powder (BTP-HT, Prosperity Dielectric, Taiwan) with an average particle size of 1 µm was used as the dielectric material. The BT material had a relative permittivity ( $\epsilon_r$ ) and loss tangent ( $\tan \delta$ ) of 2029

and 0.010 at 1 kHz, respectively, when sintered at 1450 °C for 4 h. The BT powders were mixed with different amounts of CBS glass and LiF, and sintered under various conditions. The two stage sintering process used in the previous investigation [11] was used to prepare the CBS glass added BT dielectric ceramics.

Differential thermal (DTA, PerkinElmer, U.S.A.) and thermal-mechanical (TMA7, PerkinElmer, U.S.A.) analysis experiments were conducted at a heating rate of 10 °C/min. Surface and cross-section microstructures of the sintered samples were analysed by scanning electron microscopy (FE-SEM, JSM6700-F, JEOL, Japan). The sample compositions were examined using energy dispersive X-ray spectroscopy (EDS, Oxford-6587, England) equipped with SEM. Thin foils for cross-sectional transmission electron microscopy (TEM) analysis were prepared by the conventional technique. The sintered sample was sliced to a thickness of ~200 µm using a diamond-embedded saw, followed by mechanical polishing of the disks to a thickness of ~30 mm and ion-beam thinning to electron transparency. Chemical microanalysis was performed using an energy-dispersive X-ray spectrometry (EDS) system attached to TEM equipment (Model TEM3010, JEOL) operating at an accelerating voltage of 300 kV. The crystalline phases of the sintered dielectrics were determined by X-ray diffractometry (XRD, D/MAX-2200, Rigaku, Japan). The dielectric properties of the sintered compacts were measured by using a LCR meter (Agilent E4980A) at 1 kHz.

### 3. Results and Discussions

The commercial BT powders sintered at 1350 °C for 2 and 4 hours had relative permittivities of 2196 and 2029, respectively, as listed in Table 1. The dielectric losses of the sintered BT were lower than 0.015. When LiF was added to the BT dielectric, samples with density  $\geq 95\%$  were obtained after sintering at 900 °C for 1 hour. The permittivity values for 1 and 4 wt% levels of LiF additive were 3921 and 4657, respectively; these values were approximately twice as large as those for the undoped samples. However, the corresponding dielectric loss values of 0.02 and 0.1 were higher than those measured for undoped BT. By adding 5 wt% CBS glass into the BT dielectric and sintering at 900 °C for 1 h, the permittivity and dielectric loss were 556 and 0.015, respectively. Increasing the glass content to 20 wt% showed permittivity and dielectric loss values of 264 and 0.013, respectively. Since the results clearly indicated that the addition of LiF enhances the permittivity while the addition of CBS glass does not dramatically increase the dielectric losses, their combination was researched using the two-stage process. The results showed that only 2 wt% CBS glass was necessary for 4 wt% LiF-added BT ceramic to samples with high permittivity (1725) and low dielectric loss (0.008), after sintering at 850 °C. However when this composition was sintered at 900 °C for 1 h, the permittivity of the sample increased to 2228, but the value for the dielectric loss increased substantially.

The DTA data showed an endothermic peak at 766 °C for the BT sample with of 4 wt% LiF (Fig. 1), which was the temperature for the formation of the liquid phase. Since this temperature was lower than the melting point of pure LiF, the liquid phase formed at 766 °C was supposed to be a mixture of LiF and BT. This formation of liquid phase was also observed to enhance the densification of the BT compacts. A dense microstructure with an average grain size of  $\sim 1.5\ \mu\text{m}$  was obtained with the 4 wt% LiF addition when sintered at 900 °C for 1 h (Fig. 2(a)). However the microstructure had some areas with very small particle agglomerates, as is indicated by the white ar-

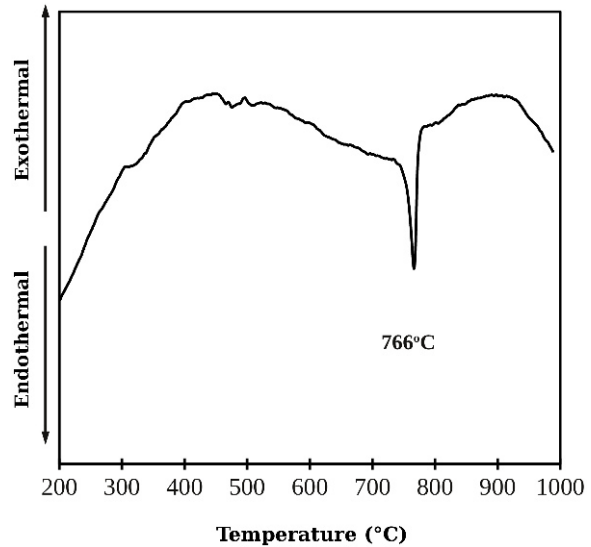


Fig. 1. DTA analysis of BT with 4 wt% LiF addition

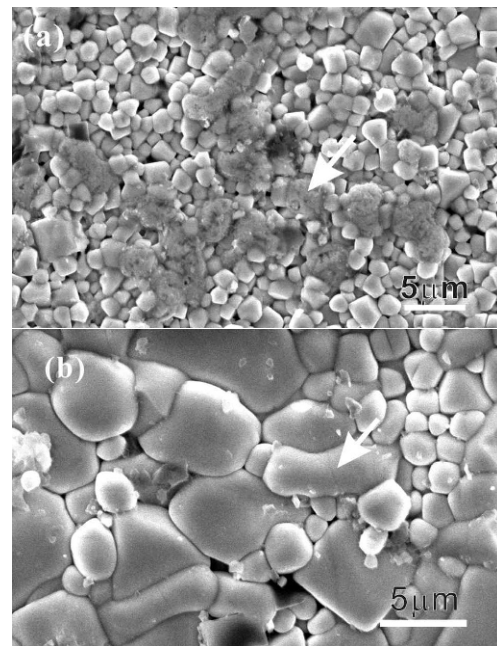


Fig. 2. Microstructures of the BT dielectric with 4 wt% LiF after sintering for 1 h at (a) 900 °C and (b) 950 °C.

row in Fig. 2(a). Analysis of the chemical composition of these areas showed high Ba and F content with a Ba/F ratio of 1/2.75, with relatively low content of Ti. This result indicates that the liquid phase forming at 766 °C according to the DTA data could be  $\text{BaLiF}_3$ . Unfortunately with diffraction analysis

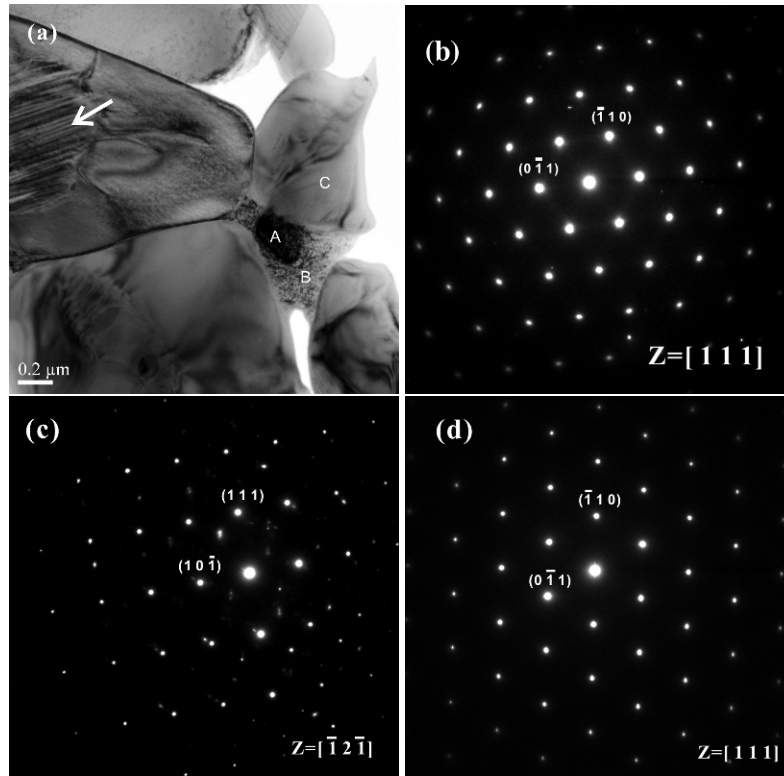


Fig. 3. Transmission electron microscopy (a) bright field image of BT dielectric mixed with 4 wt% LiF after sintering at 900 °C for 1 h. Selected area diffraction pattern (SADP) of location marked A, white arrow points to the core-shell structure formed in BaTiO<sub>3</sub> grain. (b) in the micrograph indexed as BaTiO<sub>3</sub> phase (JCPD 05-0626) with a zone axis of [111], location marked B (c) in the micrograph is indexed as BaLiF<sub>3</sub> phase (JCPD 18-0715) with zone axis of [121], and location marked C (d) in the micrograph is indexed as BaTiO<sub>3</sub> phase (JCPD 05-0626) with a zone axis of [111].

this could not be verified, since the BT and BaLiF<sub>3</sub> have the same crystal structure with similar lattice parameters, and thus their diffraction peaks overlap. However, with a higher sintering temperature (950 °C), abnormal grain growth was observed and grains with a Ba/F ratio of 1/3.02 were detected (Fig. 2(b)).

The TEM data for the samples with 4 wt% LiF addition after sintering at 900 °C showed three different kinds of grains. The grain type which, according to EDS analysis, had a composition of Ba 21 atom%, Ti 13 atom%, F 24 atom%, and O 41 atom%, was marked as grain A. The electron diffraction pattern (see Fig. 3(b)) indicated grain A to be small BT grain on the top of BaLiF<sub>3</sub> phase. The B grain had a Ba/F ratio of 2.53 (Fig. 3(a)) and although the Ba and O atoms were not detectable in this grain, the electron diffraction pattern of this

grain was consistent with a BaLiF<sub>3</sub> structure having a zone axis of [121] (Fig. 3(c)). The C grain in the TEM micrograph, on the other hand, had a low F content of about 3 atom%, and could be considered to be pure BT (Fig. 3(d)). Additionally, the core-shell structure was also observed in the micrograph (pointed to by white arrow). There was no liquid phase detected in the TEM data for this 4 wt% LiF added BT ceramic.

The addition of LiF produced high density microstructures, when sintered at 900 °C, which had higher permittivities than those microstructures obtained without LiF addition. This result is consistent with the ones reported by Walker et al. [7], who were able to achieve a relative density higher than 98 % with 0.5 ~3 wt% levels of LiF additive. However, the dielectric loss of LiF added BT ceramic increased as the level of LiF additive increased.



That is supposed to be due to the formation of  $\text{BaLiF}_3$  phase, since no other phases were detected by TEM. Also, with a high level of LiF additive, high porosity could not be the reason for the high dielectric loss, since these samples had high relative density. The core-shell structure and high relative density of the LiF-added BT sintered ceramics clearly increased the permittivity. This is understandable since the formation of  $\text{BaLiF}_3$  phase, which has a permittivity of 16 and a dielectric loss of 0.08 [12], did not have significant influence on the permittivity of the BT ceramic when the level of LiF additive was less than 4 wt%.

Since the softening point of the CBS glass used in this study was 635 °C, it was expected to act as sintering aid for the BT ceramic. Actually, when the pure CBS glass was heated at 800 °C for 1 h,  $\text{CaSiO}_3$ ,  $\text{Ca}_2\text{B}_2\text{O}_5$ , and  $\text{Ca}_2\text{SiO}_4$  phases formed, but when the CBS glass was mixed with BT powder and heat-treated at 750 °C for 2 h,  $\text{CaTiO}_3$  and  $\text{Ba}_2\text{TiSi}_2\text{O}_8$  phases form as minor phases [11]. However the BT powder mixed with 5 wt% CBS glass and sintered at 900 °C for 1 h had a relative density lower than 60 %, as shown in Fig. 4. Because of the high porosity of this composition (Fig. 5(a)), the permittivity was lower than 600. The BT ceramic mixed with 20 wt% CBS glass and sintered at 900 °C for 1 h had a relative density higher than 95 % (Fig. 4) and it showed a permittivity of 264. Due to low value, the additive dilution effect of the second phases, such as  $\text{CaTiO}_3$  and  $\text{Ba}_2\text{TiSi}_2\text{O}_8$  phases, and residual glass phase, the 20 wt% CBS added BT ceramic had permittivity much lower than that of the pure BT ceramic.

In order to maintain the permittivity of the BT ceramic, the level of glass additive should be as low as possible. In the previous investigation a two-stage process was employed to prepare BT dielectric ceramic, where in the first stage the BT dielectric powder particles were coated with a thin layer of CBS glass, and then mixed with LiF and sintered at a temperature lower than 900 °C in the second stage. By using this two-stage process, dense BT ceramics were obtained from the 2 wt% CBS glass coated BT dielectric powder mixed with 2 or 4 wt% LiF and sintered at 900 °C for 1 h, as shown in Fig. 5(b) and 5(c). BT ceramic that had been pre-

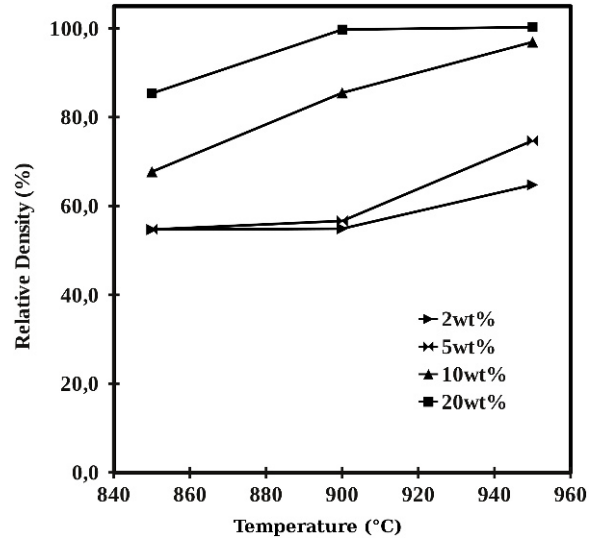


Fig. 4. Relative densities of BT dielectric ceramics mixed with different amounts of CBS glass after sintering at different temperatures for 1 h.

pared, via the two-stage process, with a 2 wt% CBS glass coating and mixed with 4 wt% LiF, had a permittivity of 1725 and a dielectric loss of 0.008, after sintering at a temperature of 850 °C for 1 h. A secondary phase of  $\text{LiTiO}_2$  was detected, by X-ray diffraction analysis, in the sample of BT ceramic that had been 2 wt% CBS glass coated, then mixed with 4 wt% LiF, and then sintered at 850 °C for 1 h. This phase was the main reason for the slightly lower permittivity compared with the pure BT samples.

## 4. Conclusion

BT ceramics of high relative density and high permittivity were prepared by adding a small amount of LiF, less than 4 wt%, to the BT ceramics. A very low amount of  $\text{BaLiF}_3$  phase formed at the BT grain boundary, but did not have much influence on the dielectric properties of the BT ceramic. For the core-shell structure formed with the addition of 4 wt% LiF to the BT ceramic, the permittivity was increased up to a value of about 4657 after sintering at 900 °C. However very advanced LTCC BT was achieved by the co-addition of only 2 wt% CBS glass and 4 wt% LiF and by applying the two stage process. This composition could

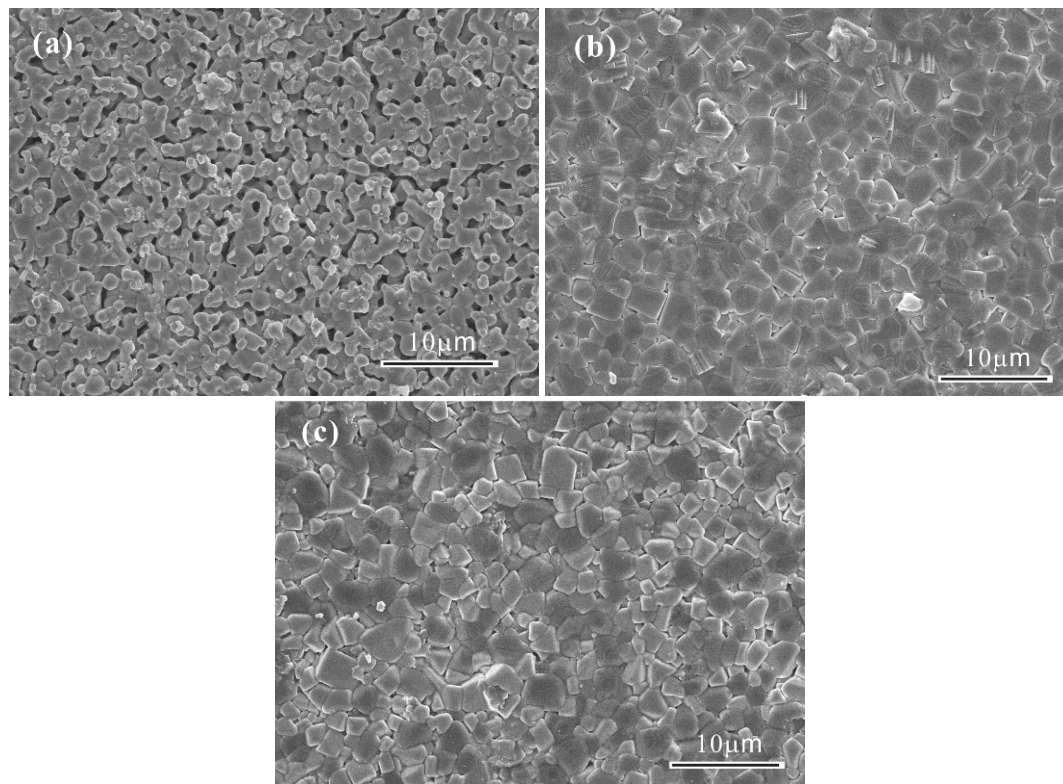


Fig. 5. Microstructures of BT dielectrics mixed with (a) 2 % CBS glass, (b) 2 % CBS glass and 2 wt% LiF, and (c) 2 % CBS glass and 4 wt% LiF after sintering at 900 °C for 1 h.

be sintered at 850 °C with a dwelling time of 1 h, forming a high density microstructure with dielectric properties that are very compatible with the dielectric properties of pure BT ceramics sintered at 1350 °C for 4 h.

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