

# Combinatorial Processing Study for 0.7(Bi<sub>0.95</sub>La<sub>0.05</sub>)FeO<sub>3</sub>-0.3BaTiO<sub>3</sub> Ceramics Produced by an Aqueous Tape Casting Method

He Zhu<sup>1</sup> and Guoxi Jin<sup>2,a</sup>

<sup>1</sup>Hockaday School, 75229 Dallas, Texas, USA

<sup>2</sup>Shanghai University, 200444 Shanghai, China

<sup>a</sup> Corresponding author

**Abstract.** 0.7(Bi<sub>0.95</sub>La<sub>0.05</sub>)FeO<sub>3</sub>-0.3BaTiO<sub>3</sub> (0.7BLF-0.3BT) ceramics with pure perovskite structure were produced and packed from an aqueous tape casting method. The effects of pressure and temperature, during the tapes lamination process, on the bulk density and dielectric were systematically investigated to obtain a proper lamination technique for further multilayer structure ceramic devices. The dielectric loss,  $\tan\delta$  decreased with the rising of lamination temperature from 20 to 110 °C due to the stronger combination between the gaps of ceramic tapes and relative higher bulk density. On the contrary, with the rising of lamination pressure from 40 to 160 MPa, The dielectric loss increased due to the serious inner structural broken. The results show that the laminated ceramics derived from tapes casting method exhibit comparable dielectric properties to those prepared by conventional technique, which is the basic step for the continuous developing for piezoelectric devices with multilayered structure.

## 1 Introduction

These Pb(Zr,Ti)O<sub>3</sub> (PZT) is the most widely used piezoelectric and ferroelectrics ceramics due to their high piezoelectric response in morphotropic phase boundary (MPB). However, conventional PZT ceramics have serious depoling and ageing problems at temperature above 200 °C which significantly limits their further applications as high-temperature devices [1-3]. Besides, the high lead concentration in PZT ceramics is potential harm to environment and ecosystem. Therefore, researchers are looking for a new alternative material with better electronic properties and higher depoling temperature with lower Pb content to eventually replace the PZT.

Recently, materials based on the BiFeO<sub>3</sub>-BaTiO<sub>3</sub> (BF-BT) system have drawn considerable attentions because of their high Curie temperature and larger piezoelectric constant exhibiting potential applications in sensors, actuators and especially high temperature devices [4-6]. With 5 at.% La doping in BF-BT modification, the ceramics were greatly enhanced with the Curie temperature  $T_c$ , dielectric constant  $\epsilon_r$ , dielectric loss  $\tan\delta$ , remnant polarization  $P_r$  and piezoelectric constant  $d_{33}$  of 0.7(Bi<sub>0.95</sub>La<sub>0.05</sub>)FeO<sub>3</sub>-0.3BaTiO<sub>3</sub> ceramics are 350 °C, 700, 5.2 %, 20  $\mu\text{C}/\text{cm}^2$  and 168 pC/N, indicating promising candidates for high temperature piezoelectric devices application [7,8].

Tape casting method is capable of fabricating flexible and low-cost thick films with widest thickness range showing great advantages in forming large-area, thin and flat ceramic parts and excellent convenience in multilayered structure design. And it has been widely used for several decades in MLCC, LTCC industry and so on [9]. The single tape can be controlled at the micrometer level by adjusting the gap of the blade. Hence, tape casting method is considered to be used for BLF-BT ceramics based high temperature devices preparation. The casting slurry usually consists of ceramic powders, solvents, plasticizers, dispersants and binders [10]. So the green sheets are flexible and easy to be shaped. Appropriate temperature and pressure during the molding

process is needed to make the elastic sheets be strongly combined, and the lamination parameters show great effect on the bulk density and electrical properties.

In consideration of the health problems of the workers and environmental protection, aqueous tape casting has been paid great attention and it has substituted for non-aqueous tape casting in many fields [11].

## 2 Experimental Procedures

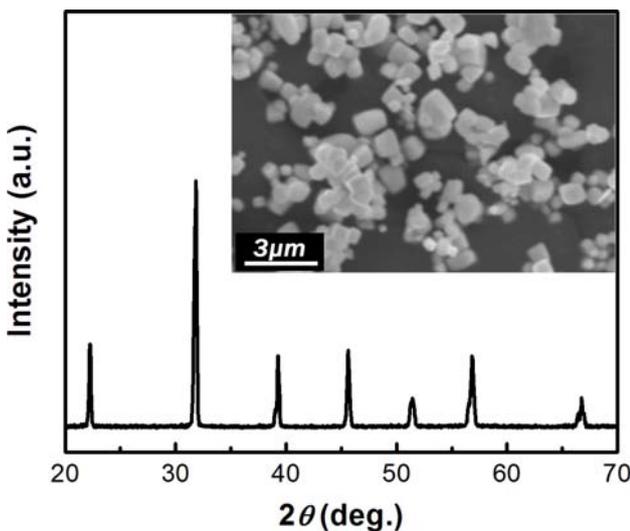
In the present work, BLF-BT lead-free ceramics was firstly developed by an aqueous tape casting method. This research is the basis for developing composite and device structure ceramics. Analytical-grade powders of Bi<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, BaCO<sub>3</sub> and TiO<sub>2</sub> were used to produce 0.7(Bi<sub>0.95</sub>La<sub>0.05</sub>)FeO<sub>3</sub>-0.3BaTiO<sub>3</sub> (0.7BLF-0.3BT) via solid reaction. The mixture of oxides was dried and calcined at 850 °C for 3 h to obtain powder with pure phase structure. The prepared powders were then mixed with polyacrylic acid (PAA) as dispersant, polyvinyl alcohol (PVA) as binder and polyethylene glycol (PEG) as plasticizer in deionized water. After being ball-milled for 24 h, the slurry was sieved and de-aired by using a vacuum system. The gap height of the blade was controlled at 500  $\mu\text{m}$ . The casting speed is 10 mm/s. The tapes were left to dry at room temperature for 72 h. The dried green sheets were cut into dozens of disk pieces of 10 mm in diameter, then the tapes were packed for 30 layers at different temperature (of 20, 50, 80 and 110 °C) and pressure (of 40, 80, 120 and 160 MPa), then being cold isostatic pressed at 200 MPa for 2 minutes. Following a 600 °C binder burnout to remove all organic additives, the pressed tablets were sintered at 1100 °C in air for 2 h.

The crystallographic phases of the prepared 0.7BLF-0.3BT ceramics were characterized by X-ray diffraction (Bruker D8 Advanced, Germany). The fracture surface morphology of the ceramics and fresh powder was observed by scanning electron microscopy (Hitachi S3400, Japan). The rheological properties of the slurries were carried out using a shear controlled rheometer

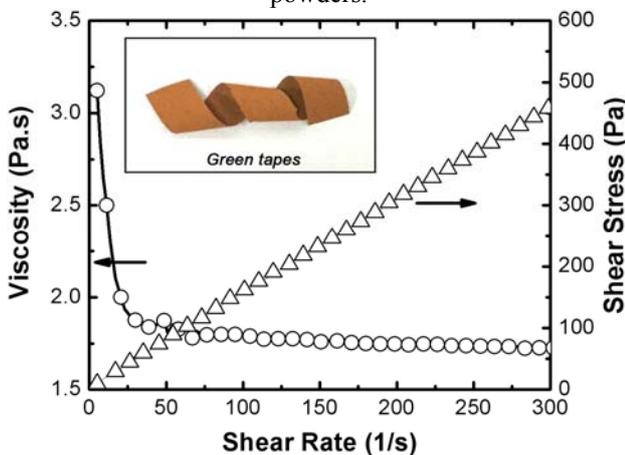
(Physica MCR301, Germany). Dielectric properties were measured by a precision impedance analyzer (Agilent HP4294A, USA).

### 3 Results and Discussion

Fig. 1 shows the XRD and the SEM patterns of synthesized  $0.7(\text{Bi}_{0.95}\text{La}_{0.05})\text{FeO}_3\text{-}0.3\text{BaTiO}_3$  (0.7BLF-0.3BT) powders respectively. It is obvious that the powders are crystallized into pure perovskite phase structure. In addition, the relevant peaks in XRD results are narrower and stronger indicating excellent grain growth during the preparation calcination process. Moreover, for the same test on sintered ceramics produced from casting tapes, there is no phase change or peaks position shift occurrence, reveals no structure damage during the casting tapes lamination and ceramic sintering process. Furthermore, SEM pattern here displays the morphology of the 0.7BLF-0.3BT powders. It is noted that all the powders are fine uniform and cubic shaped with the average size of 1~2  $\mu\text{m}$ . However, after being sintered in later process the grain size will enlarge to 6~10  $\mu\text{m}$ .



**Figure 1.** XRD and SEM patterns of 0.7BLF-0.3BT powders.



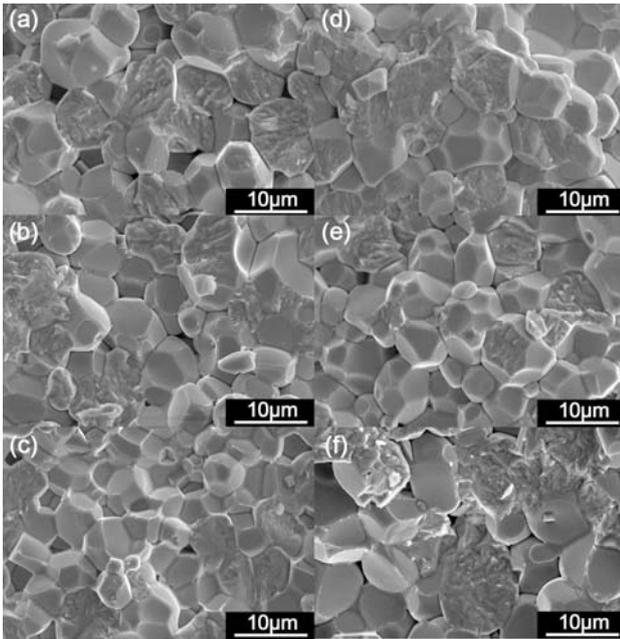
**Figure 2.** Rheological properties of the slurry and photo of the green tape sample.

Fig. 2 is the rheological curves of the slurry prepared from the mixture of 40 wt.% 0.7BLF-0.3BT powders, 6

wt.% PVA, 8 wt.% PEG and 1 wt.% PAA. From the relationship between shear stress and shear rate, it can be seen that the slurry exhibits shear thinning behavior. The shear stress begins from 0 Pa. The value of shear stress increases with the shear rate while the viscosity decreases. Both the shear stress curves and the viscosity curves show the slurry are important characteristic for pseudo plastic fluid of tape casting slurry. It is distinct that over 15 wt.% volatilizable component existing in the casting tapes. So the densification forming process during the tapes lamination is more difficult and complicated compared with the conventional craft. Besides, the actual photograph of the tapes is also given. The tapes were cut into disk slices and single slices were laminated with 20 layers to form a pressed bulk. The green bodies underwent the organic additives removal, cold isostatic pressing procedures and sintering process. As a result, the bulk diameter shrunk from 10 mm to about 9.5 mm with the single tape layer of 60  $\mu\text{m}$ .

The bulk density distribution of the ceramics laminated in different temperature (of 20, 50, 80 and 110  $^{\circ}\text{C}$ ) and pressure (of 40, 80, 120 and 160 MPa) are calculated according to Archimedes law. It is noted that the bulk density of the ceramics laminated at 20  $^{\circ}\text{C}$  with 40 MPa is only 6.99  $\text{g}/\text{cm}^3$ . And with the lamination temperature increasing, the bulk density reaches the maximum value of 7.87  $\text{g}/\text{cm}^3$  at 110  $^{\circ}\text{C}$ . Besides the temperature, the pressure also shows a great effect on the bulk density. It can be observed that the bulk density first slightly increased with the pressure rising from 40 MPa to 120 MPa, then decreased rapidly to about 6.66  $\text{g}/\text{cm}^3$  when the pressure further increased to 160 MPa. These results above indicate the densest ceramics are able to obtain at the lamination temperature of 110  $^{\circ}\text{C}$  with the pressure of 40 MPa. It may be attributed to the inside binder of PVA melting made a well wetting of the interface between the layers and a stronger junction for layers during the cooling with appropriate pressure. However, when the lamination pressure increased over 120 MPa, the melt binder fluid tended to seep inward which damaged the green body structure and reduced the bulk density.

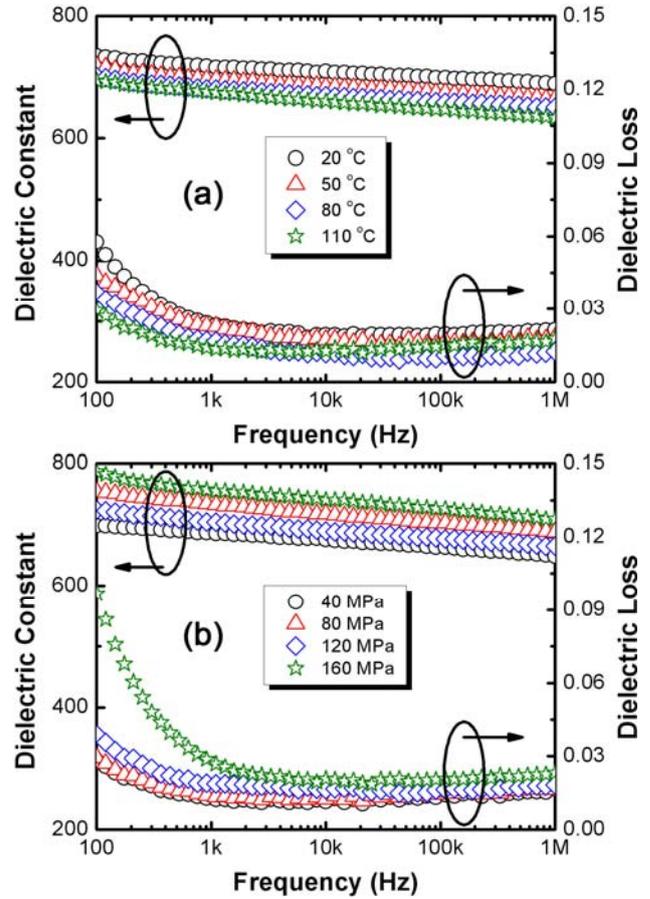
The SEM micrographs of fresh fracture surfaces of the laminated ceramics at various temperature and pressure



**Figure 3.** The SEM micrographs of fresh fracture surface of the laminated ceramics pressed at 60 MPa with various temperature of (a) 20 °C, (b) 50 °C and (c) 80 °C, and laminated at 110 °C with various pressure of (d) 40 MPa, (e) 80 MPa and (f) 160 MPa.

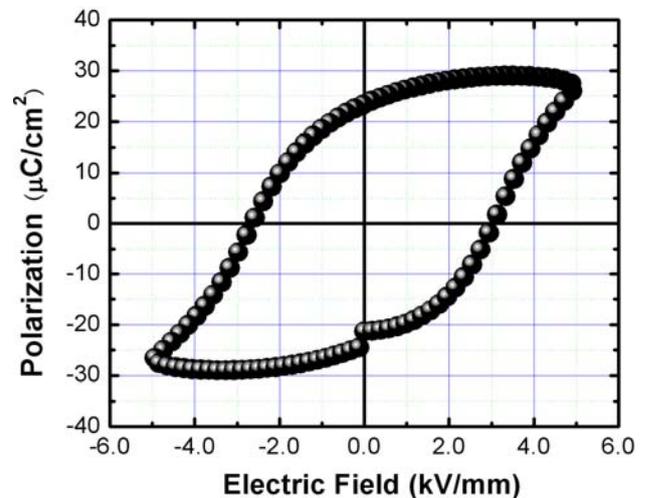
are given in Fig. 3. It is clearly shown in Fig. 3(a) to (c) that with the lamination temperature rising the samples are becoming considerably dense with a well developed microstructure that has an apparent grain boundary and uniform grain sizes while the lamination pressure rising also shows the same tendency below 160 MPa given in Fig. 3(d) to (f). As can be seen from the cross section, the grain sizes decreased with the increase of temperature and pressure from 20 °C to 110 °C and 40 MPa to 120 MPa respectively. However, when the lamination temperature and pressure are 20 °C, 80 MPa and 110 °C, 160 MPa, there appears an obviously increase of about twice larger grain size which can be attributed to the incompact green body caused by the weak conjunction between the layers and pressure driven binder fluid damage.

Fig. 4 shows the frequency dependence of the dielectric constant and loss for the laminated 0.7BLF-0.3BT ceramics from 100 Hz to 1 MHz. As can be seen that all the sample show a stable tendency to the rising frequency response. Moreover, the dielectric loss shifted from 5.8% to 2.9% at 100 Hz, indicating the enhanced insulativity with the increasing of the lamination temperature matching with the bulk density and the SEM micrographs results. It may be caused by the organic additives further melting at higher temperature leading to intense interfaces combination. In addition, with the lamination pressure increasing, dielectric loss reveals a small amplitude fluctuation but a rapid sharp when the pressure up to 160 MPa leading to the densification decreasing resulting from the development of pressure gradients and other defects at higher molding pressure.



**Figure 4.** XRD and SEM patterns of 0.7BLF-0.3BT powders.

The ferroelectric hysteresis loop of 0.7BLF-0.3BT produced by tape casting method is presented in Fig. 5. The remnant polarization  $P_r$  and coercive field  $E_c$  are of 22  $\mu\text{C}/\text{cm}^2$  and 27 kV/cm while the ceramics prepared by traditional solid state reaction share the dielectric and ferroelectric properties of  $\epsilon_r=720$  (1 kHz),  $\tan\delta=3.2\%$  (1 kHz),  $P_r=17 \mu\text{C}/\text{cm}^2$  and  $E_c=24 \text{ kV}/\text{cm}$ , respectively. Thus, specimens produced via tape casting method are comparable to those by conventional craft.



**Figure 5.** XRD and SEM patterns of 0.7BLF-0.3BT powders.

## 4 Conclusions

The effects of molding temperature and pressure on the structure and electric properties of laminated  $0.7(\text{Bi}_{0.95}\text{La}_{0.05})\text{FeO}_3\text{-}0.3\text{BaTiO}_3$  ceramics via aqueous tape casting method were studied in this work. The optimal lamination temperature and pressure are 110 °C and 40 MPa. In which, the dielectric constant  $\epsilon_r$ , dielectric loss  $\tan\delta$  at 1 kHz and remnant polarization  $P_r$ , were 690, 1.4% at 1 kHz and 22  $\mu\text{C}/\text{cm}^2$ , respectively. These good performances suggested that the laminated 0.7BLF-0.3BT ceramics was a promising candidate to replace the conventional ones, meanwhile they own the great convenience in multilayer structure design must be useful to the devices development in future.

## References

- [1] T. Shao, A. Scholl, F. Zavaliche, K. Lee, M. Barry, A. Doran, M.P. Cruz, Y.H. Chu, C. Ederer, N.A. Spaldin, R.R. Das, D.M. Kim, S.H. Baek, C.B. Eom, R. Ramesh, *Nature Materials* **5** (2006)
- [2] H. Fukumura, S. Matsui, N. Tonari, T. Nakamura, N. Hasuike, K. Nishio, T. Isshiki, H. Harima, K. Kisoda, *Acta Physica Polonica A* **116** (2009)
- [3] A.Z. Simoes, A.H.M. Gonzalez, L.S. Cavalcante, C.S. Riccardi, E. Longo, J.A. Varela, *Journal of Applied Physics* **101** (2007)
- [4] K. Singh, N. S. Negi, R. K. Kotnala, M. Singh, *Solid State Communication*, **148** (2008)
- [5] T. Leist, K. G. Webber, W. Jo, E. Aulbach, *ACTA Materails*, **58** (2010)
- [6] W. Eerenstein, N. D. Mathur, J. F. Scott, *Nature*, **442** (2006)
- [7] F.P. Gheorghiu, A. Ianculescu, P. Postolache, N. Lupu, M. Dobromir, D. Luca, L. Mitoseriu, *Journal of Alloys and Compounds* **506** (2010)
- [8] M.T. Buscaglia, L. Mitoseriu, V. Buscaglia, I. Pallecchi, M. Viviani, P. Nanni, A.S. Siri, *Journal of the European Ceramic Society* **26** (2006)
- [9] M. Hagymasi, A. Roosen, R. Karmazin, O. Dernovsek and W. Haas, *Journal of the European Ceramic Society* **25** (2005)
- [10] R. E. Mistler and E. R. Twiname, *Tape Casting: Theory and Practice*. Westerville, OH: The American Ceramic Society, 2000
- [11] B. Bitterlich, J.G. Heinrich, *Journal of the European Ceramic Society* **22** (2002)