

Low temperature sintering and nonlinear dielectric properties of Li₂O doped Ba_{0.6}Sr_{0.4}TiO₃ ceramics derived from the citrate method

Xiaofei Zhang*, Xiangyi Deng, Yuting Ren

School of Mathematics and Physics, Hubei Polytechnic University, Huangshi, China

*Corresponding author e-mail: zhangxiaofei@whut.edu.cn

Abstract. A nominal composition of Ba_{0.6}Sr_{0.4}TiO₃ + 0.5 wt. % Li₂O ceramic specimen was prepared from the citrate method. The addition of Li₂O was found to be effective to reduce the sintering temperature of Ba_{0.6}Sr_{0.4}TiO₃ ceramics, which was attributed to the formation of transient liquid phase. The ceramic specimen sintered at 900 °C showed a fine-grained microstructure with considerable densification and attained the relative density of 97%. The diffusion of Li₂O into Ba_{0.6}Sr_{0.4}TiO₃ lattice was found to have an evident effect on the dielectric properties of the ceramics. The specimen exhibited a dielectric constant of 1997 and a dielectric loss 0.67% at 10 kHz and zero bias-field together with a tenability of 27.8% and a FOM of 41 at 10 kHz and 30 kV/cm.

1. Introduction

In the past decades, the dielectric nonlinearity of barium strontium titanate (Ba_{1-x}Sr_xTiO₃) under bias electric field has been the subject of extensive investigations [1, 2]. The outstanding dielectric nonlinearity of Ba_{1-x}Sr_xTiO₃ makes it a promising candidate material for electrically tunable microwave devices, such as filters, resonators, delay lines, variable capacitors and phase shifters [3]. Miniaturization and integration of the electrical devices are the currently developed trend, which necessitates the low temperature sintering of the dielectric materials. At present the sintering temperature of Ba_{1-x}Sr_xTiO₃ ceramics prepared from the conventional solid state method is approximately 1400 °C. Adopting superfine starting powders with high reactivity is a viable approach to enhance the sinter ability and reduce the sintering temperature of BST materials. In our previous work, we have proved the feasibility and made the sintering temperature decreased to be 1250 °C [4]. Adding sintering aids, such as glass frits and oxide additives, is an effective employed strategy to overcome the problem. By adding glass frits to the functional ceramics, the sintering temperature can be lowered drastically. However their dielectric properties were usually degraded by a large margin [5-6]. A small amount of lithium-based sintering aids such as LiF, Li₂O and Li₂CO₃ were reported to decrease the sintering temperature without sacrificing the electric properties of BaTiO₃-based materials [7-11]. While non-homogeneity is always the main problem for Li₂O doped BST materials produced by the conventional solid state method. In addition, fine grained ceramics prepared by chemical solution methods favor to obtain moderate dielectric constants, which contributes to the device matching.



The citrate method is essentially a polymeric precursor method, using citric acid and water as the complex agent and solvent, respectively. In this work, we produced a nominal composition of $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3 + 0.5 \text{ wt. } \% \text{ Li}_2\text{O}$ (abbreviated as BSTL) ceramics via the citrate precursor method. The structure and nonlinear dielectric properties of the ceramic specimens were investigated.

2. Experimental

All the raw materials used in this work were commercially available reagent grade chemicals (Sino pharm Chemical Reagent Co., Ltd.). BSTL powders were synthesized by a citrate method using reagent grade $\text{Ba}(\text{NO}_3)_2$, $\text{Sr}(\text{NO}_3)_2$, LiNO_3 , tetra butyl titivate and citric acid as starting materials. Tetra butyl titivate was first dissolved in a citric acid solution and various nitrates were then added, followed by stirring to yield a transparent aqueous solution. The mole ratio of citric acid to the total metal cation content was 1.5. A final doping level of 0.5 wt. % Li_2O was achieved by adding a corresponding molar fraction of LiNO_3 . The precursor solution was heated to form a foam-like solid precursor. The solid precursor was pulverized and calcined at 600 °C for 1 h in air. The calcined powder was uniaxial pressed under a pressure of 300 MPa into discs of 13 mm diameter and 1 mm thickness. The compacted discs were sintered at 900 °C for 2 h in air. Details of the synthesis and preparation processes have been described elsewhere [4].

The phase purity of the calcined powder and crystal structure of the ceramic specimens were examined by a Philips X'pert PBO X-ray diffractometer using Cu K α radiation. The morphology of the calcined powder was observed at a Hitachi S-4700 field emission scanning electron microscope (FESEM). The microstructure of the powders and ceramic specimens was investigated at a Jeol JSM-5610LV scanning electron microscope (SEM). The dilatometry measurement of the compacted powder was conducted by a Nietzsche DIL 402C dilatometer at a heating rate of 5 °C/min between 20 and 1100 °C in air. The density of the ceramic specimens was measured by the Archimedes method with ethyl alcohol as the medium. The relative densities of the ceramic specimens were determined from the measured results and the theoretical densities calculated based on the X-ray diffraction (XRD) data of $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ ceramics using the Jade software. The ceramic specimens were painted with silver paste on both surfaces as electrodes for measuring electric properties. The temperature dependence of the dielectric constant and dielectric loss was measured by a HP4294 impedance analyzer and a JYT-800L environmental chamber between -60 and 110 °C at 1, 10 and 100 kHz, respectively. The nonlinear dielectric properties were measured at room temperature by a TH2818 impedance meter at 10 kHz under external bias electric fields rising from zero to 30 kV/cm.

3. Results and discussion

Figure 1 shows the XRD pattern of BSTL powder calcined at 600 °C. A pure perovskite structure was identified for the powder, indicating that a small amount of Li_2O didn't give rise to impurity phase at the temperature.

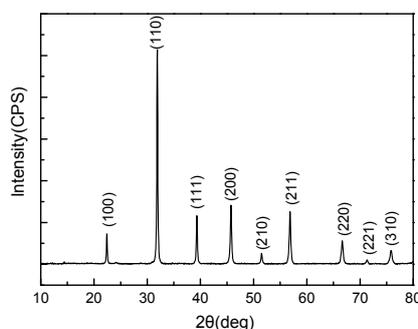


Figure 1. XRD pattern of BSTL powder calcined at 600 °C

Figure 2 shows SEM and FESEM images of BSTL powder calcined at 600 °C. The SEM image (Fig. 2a) offered a panoramic view of the powder morphology, displaying fine and relatively uniform. The FESEM image (Fig. 2b) further revealed that the size of preliminary particles was 30–40 nm and there exist slight agglomerations (around 150 nm) of the preliminary particles.

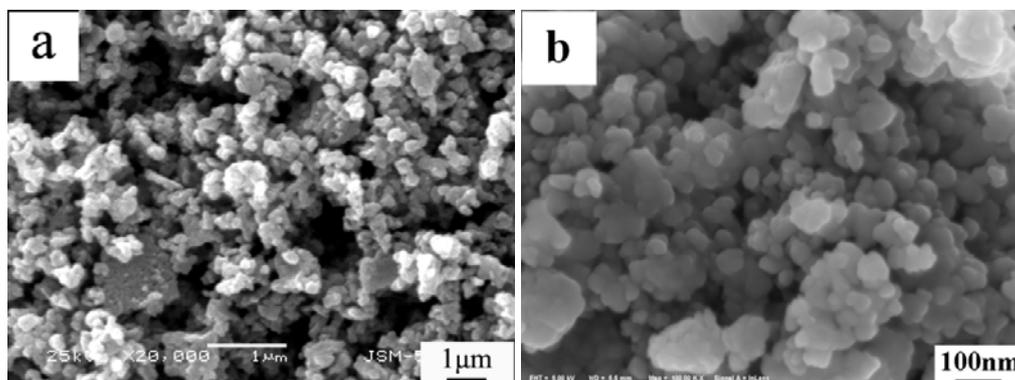


Figure 2. (a) SEM and (b) FESEM images of BSTL powder

Figure 3 shows the dilatometric curves of the BSTL compacted powder. One can see that an onset temperature of shrinkage occurred at around 780 °C and a maximum shrinkage rate at 800 °C. The shrinkage behavior tended to be saturated after 1100 °C. The onset temperature of shrinkage have been reported to be located at higher temperature (1060 °C) for $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ powder in our previous research [4]. The dilatometry results hint that the BSTL powders could be sintered to reasonable densification levels at relatively low temperatures. The sintering temperature for BSTL was reduced, which should be attributed to be the formation of liquid phase in the sintering process [8, 12].

Figure 4 shows the XRD pattern of BSTL ceramic specimen. A pure perovskite structure with a cubic symmetry was identified for the ceramic specimen. The result indicates that chemical reaction between $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ and Li_2O phase appears to be insignificant. The inset figure shows the SEM image of the specimen. It can be observed that the ceramic specimen has a fine-grained microstructure with considerable densification. The mean grain size of the specimen was estimated to be about 0.4 μm via an image analysis using the Image-Pro Plus software. The Archimedes measurement indicated that the ceramic specimen attained about 97% of the theoretical density. The relative density of the ceramic specimen is roughly comparable with those of $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ ceramics prepared by the conventional solid-state method at sintering temperature of 1400 °C or higher temperatures [13]. The comparison suggests Li_2O contributed to the sintering of the ceramic specimen, which is considered to be the formation of transient liquid phase. In addition, the explicit grain boundaries were observed to be quadrilateral, which should be attributed to the precipitation of BSTL phase from the eutectic liquid phase.

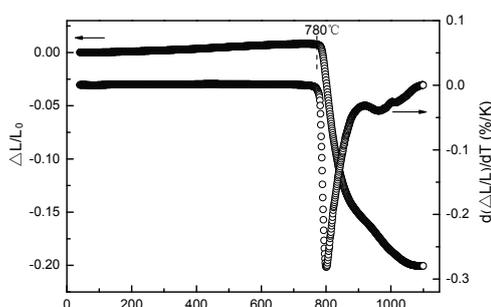


Figure 3. Dilatometry curves of the BSTL compacted powder

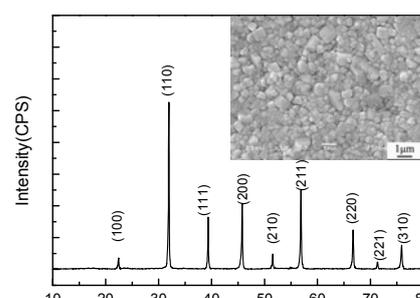


Figure 4. XRD pattern of BSTL ceramic specimen. The inset is SEM image of the specimen

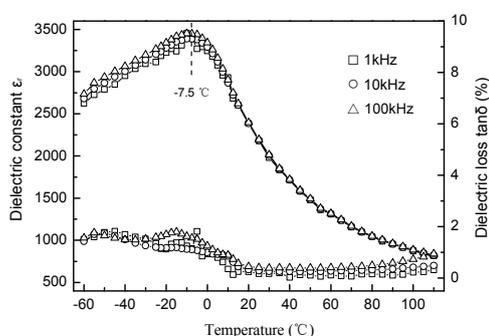


Figure 5. Temperature dependence of dielectric constant and dielectric loss at different frequencies for BSTL ceramic specimen

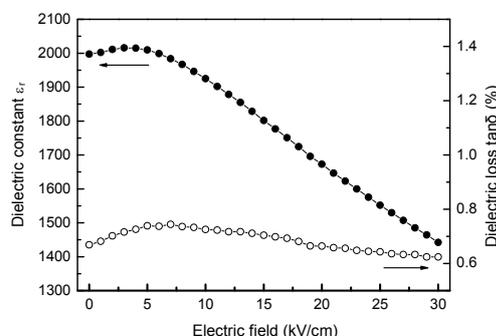


Figure 6. Bias electric field dependence of dielectric constant and dielectric loss for BSTL ceramic specimen

Figure 5 shows the temperature dependence of dielectric constant and dielectric loss at different frequencies for BST ceramic specimen. A slightly diffused peak of dielectric constant was observed at around $-7.5\text{ }^{\circ}\text{C}$, with a rather obscure frequency dispersion. A detectable peak of dielectric loss was also accompanied near the temperature. As well-known, the dielectric anomaly can be ascribed to a ferroelectric-Para electric phase transition. The dielectric behavior in Figure 5 is similar to previously reported results for $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ ceramics [14, 15]. The temperature of dielectric constant maximum (T_m) for BSTL specimen decreased compared to $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ ceramics in the literatures, which can be explained by the diffusion of lithium ions into the $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ lattice.

Figure 6 shows the dielectric constant and dielectric loss as a function of bias electric field for BSTL ceramic specimen. Generally speaking, the dielectric constant decreased with bias electric field, indicating the typical feature of nonlinear dielectrics. A careful inspection indicates a rather flat variation of the dielectric constant with electric field within 5 kV/cm and a rapid decline at the higher electric fields. Correspondingly, the dielectric loss increased with electric field through a maximum at 5 kV/cm and then tended to decrease slightly. The variation of the dielectric properties within low electric field was considered to be related with polar micro-regions [15]. The formation of polar micro-regions was believed to be caused partially by the substitution of Li^+ for Ti^{4+} in the perovskite structure [16].

The specimen exhibited a dielectric constant of 1997 and a dielectric loss of 0.67% at 10 kHz and zero bias-field. The tenability was determined as the percentage of dielectric constant change under 30 kV/cm . The figure of merits (FOM, defined as tenability/ $\tan\delta$) were determined from the results of the tenability and dielectric loss. The specimen attained a tenability of 27.8% and a FOM of 41 at 10 kHz and 30 kV/cm .

4. Conclusion

Superfine and uniform powders of $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3 + 0.5\text{ wt. } \%$ Li_2O with a pure perovskite phase was derived from the citrate method. The sintering temperature of the resulting ceramic specimen was reduced to $900\text{ }^{\circ}\text{C}$. The ceramic specimen showed a fine-grained microstructure and relative density of 97%. The variation of the dielectric constant and dielectric loss as a function of temperature and bias electric field was found to be related with the diffusion of Li^+ into $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ lattice. The ceramic specimen showed a dielectric constant of 1997 and a dielectric loss 0.67% at 10 kHz and zero bias-field together with a tenability of 27.8% and a FOM of 41 at 10 kHz and 30 kV/cm .

Acknowledgments

This work was supported by Science and Technology Research Project of Hubei Provincial Department of Education (No. B2016277), Talent Project of Hubei Polytechnic University (No. 12xjz02R) and the National Natural Science Foundation of China (No. 51372077).

References

- [1] A.K. Tagatose, V.O. Sherman, K.F. Astafiev, J. Denktash, N. Setter, Ferroelectric Materials for Microwave Tunable Applications, *Journal of Electro ceramics* 11 (2003) 5–66
- [2] L.B. Kong, S. Li, T.S. Zhang, J.W. Zhai, F.Y.C. Boey, J. Ma, Electrically tunable dielectric materials and strategies to improve their performances, *Progress in Materials Science* 55 (2010) 840–893
- [3] C. Ang, Z. Yu, dc electric-field dependence of the dielectric constant in polar dielectrics: Multipolarization mechanism model, *Physical Review B* 69 (2004) 174109-1-8
- [4] X.F. Zhang, Q. Xu, Y.H. Huang, H.X. Liu, D.P. Huang, F. Zhang, Low-temperature synthesis of superfine barium strontium titanate powder by the citrate method, *Ceramics International* 36 (2010) 1405-1409.
- [5] D. Zhang, T.W. Button, V.O. Sherman, A.K. Tagantsev, T. Price, D. Iddles, Effects of glass additions on the microstructure and dielectric properties of barium strontium titanate (BST) ceramics, *Journal of the European Ceramic Society* 30 (2010) 407–412
- [6] H.T. Jiang, J.W. Zhai, J.J. Zhang, X. Yao, Dielectric Properties and Low-Temperature Sintering of the Ba_{0.6}Sr_{0.4}TiO₃ Ceramics with B₂O₃/CuO Additions, *International Journal of Applied Ceramics Technology* 10 (2013) 873–878
- [7] J.M. Haussonne, G. Desgardin, PH. Bajolet, B. Raveau, Barium Titanate Perovskite Sintered with Lithium Fluoride, *Journal of the American Ceramic Society* 66 (1983) 801-807
- [8] M. Valant, D. Suvorov, Low-temperature sintering of (Ba_{0.6}Sr_{0.4}) TiO₃, *Journal of the American Ceramic Society* 87 (2004) 1222-1226.
- [9] V.K. Pal kuru, J. Peräntie, M. Komulainen, T. Tick, H. Jantunen, Tunable microwave devices using low-sintering-temperature screen-printed barium strontium titanate (BST) thick films, *Journal of the European Ceramic Society* 30 (2010) 389–394
- [10] Y.S. Ham, S.W. Yun, J.H. Koh, Analysis on the temperature dependent structural properties of Li₂CO₃ doped (Ba, Sr) TiO₃ ceramics, *Journal of Electro ceramics* 26 (2011) 32–36.
- [11] S.H. Kim, J.H. Koh, The microwave properties of Li doped 0.7(Ba,Sr)TiO₃–0.3MgO thick film interdigital capacitors on the alumina substrates, *Microelectronic Engineering* 87 (2010) 79–82.
- [12] L. Zhao, B.P. Zhang, P.F. Zhou, L.F. Zhu, J.F. Li, Effect of Li₂O addition on sintering and piezoelectric properties of (Ba, Ca)(Ti, Sn)O₃ lead-free piezo ceramics, *Journal of the European Ceramic Society* 35 (2015) 533–540
- [13] B. Su, J.E. Holmes, B.L. Chen, T.W. Button, Processing Effects on the Microstructure and Dielectric Properties of Barium Strontium Titanate (BST) Ceramics, *J. Electro Ceram.* 9 (2002) 111-116.
- [14] A. Feteira, D.C. Sinclair, I.M. Rainey, Y. Somiya, M.T. Lanagan, BaTiO₃-Based Ceramics for Tunable Microwave Applications, *J. Am. Ceram. Soc.* 87 (2004) 1082-1087.
- [15] Q. Xu, X.F. Zhang, Y.H. Huang, W. Chen, H.X. Liu, M. Chen, B.H. Kim, Sinter ability and nonlinear dielectric properties of Ba_{0.6}Sr_{0.4}TiO₃ derived from a citrate method, *Journal of Alloys and Compounds* 485 (2009) L16–L20
- [16] L. Zhao, B.P. Zhang, P.F. Zhou, L.F. Zhu, N. Wang, Piezoelectric and ferroelectric properties of (Ba, Ca)(Ti, Sn)O₃ lead-free ceramics sintered with Li₂O additives: Analysis of point defects and phase structures, *Ceramics International* 42 (2016) 1086–1093