

Preparation and property of submicrometre-crystalline $\text{Ba}_{0.67}\text{Sr}_{0.33}\text{TiO}_3$ powders and ceramics

Jing Xu^a, Hanxing Liu^{a*}, Bo He^b, Yiqiu Li^a, Minghe Cao^a, Hua Hao^a and Zhiyong Yu^a

^aState Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, 122 Luo Shi Road, Wuhan 430070, China

^bSHU-Solar E PV Laboratory, Department of Physics, Shanghai University, Shanghai 200444, China

Submicrometre-particulate pure $\text{Ba}_{0.67}\text{Sr}_{0.33}\text{TiO}_3$ (BST) powders approximately 110 nm in size have been prepared by a solid-state reaction technique. BST ceramics derived from powder calcined at different temperatures were fabricated with various sintering conditions. High-density BST ceramics at all sintering temperatures were obtained at a calcination temperature of 950 °C with the highest 99.6% of the theoretical density. Calcining at 950 °C and sintering at 1300 °C for 2 h, BST ceramic samples with an average grain size about 250 nm were obtained, showing satisfying dielectric properties and ferroelectric properties, with high permittivity $\epsilon_r = 7676$, low loss factor $\tan\delta = 0.01$ and remanent polarization $P_r = 9.2 \mu\text{C}/\text{cm}^2$, coercive electric field $E_c = 1.58 \text{ kV}/\text{cm}$ at room temperature.

Key words: Submicrometre -particulate, BST Ceramics, Dielectric properties, Ferroelectric properties.

Introduction

In recent years, ferroelectrics have become increasingly important as materials for electronic devices. The most experimentally and theoretically investigated materials are perovskite-based SrTiO_3 , BaTiO_3 and the $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ alloys, because they are the prototype ferroelectrics and are used extensively in the capacitor industry [1-5].

Presently, industrial synthesis processes of fine BaTiO_3 -based dielectric powders include mainly the oxalate route [6], co-precipitation, a sol-gel method, and hydrothermal processing [7], typically resulting in an average particle size of the raw powders of a few hundred nanometre. Ultrafine BaTiO_3 powders only several tens of nanometre in size derived from the hydrothermal method have been reported by Ikawa *et al.* [8] and Tokita and Sato [9]. However, almost all of these methods are complex and require high-purity inorganic or organic chemicals as the starting materials, raising the cost above the conventional solid-state reactions that are more economical for large batch processing of these ferroelectric materials.

In this paper, we have prepared submicrometre sized BST powder and have obtained fine-grained BST ceramics by a conventional solid-state reaction method. We studied the effects of calcining and sintering conditions on the dielectric properties, ferroelectric properties and sintering behavior of BST.

Experimental

$\text{BST}(\text{Ba}_{0.67}\text{Sr}_{0.33}\text{TiO}_3)$ was synthesized using an established solid-state reaction method. $\text{Ba}(\text{NO}_3)_2$, $\text{Sr}(\text{NO}_3)_2$ and TiO_2 (19 nm) powders were used as starting materials. The raw materials were mixed in stoichiometric proportions, ball-milled with ethanol as a solution media for 30 h and dried in an oven. The powders were then calcined at 800, 850, 900, 950, 1000, and 1050 °C for 2 h. The calcined powders were pressed into disc-shaped pellets (1 mm thick and 10 mm diameter). No binder was used. The green pellets were sintered at different temperatures (1200, 1250, 1300, and 1350 °C) for 2 h. Pellets were cooled to room temperature slowly. The densities of the sintered pellet were determined using the Archimedes method. The crystalline structure of BST was analyzed by XRD (PANalytical Xpert PRO). The SEM (Akashi Seisakusho, Japan) microstructures of the samples were observed on polished sections followed by thermal etching. The dielectric properties were measured using a TH2818A LCR meter at 10 kHz-300 kHz over a temperature range from -63 °C to 150 °C.

Results and Discussion

The XRD patterns for the powders calcined at 800, 850, 900, 1000, and 1050 °C for 2 h are shown in Fig. 1. These results clearly show the effect of calcining temperature on the purity of the powder. It is found that BST structure is formed even at 800 °C, but with a barium-rich titanate phase of Ba_2TiO_4 in the calcined powder. The X-ray diffraction peaks, which are specific to the secondary phases Ba_2TiO_4 , firstly

*Corresponding author:
Tel : +86 27 87642079
Fax: +86 27 87651779
E-mail: lhxhp@whut.edu.cn

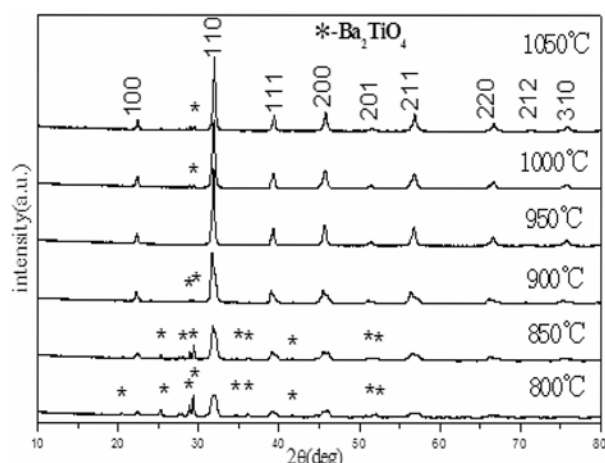


Fig. 1. XRD patterns of BST powders calcined at different temperatures for 2 h.

decrease and then increase with an increase in the calcination temperature. At a calcination temperature of 950 °C, the peaks of the Ba_2TiO_4 phase disappear and the calcined powders consist of the single perovskite BST phase. The crystallinity of the calcined powders is improved by increasing the calcining temperature, as indicated by the increase in intensity of the X-ray diffraction peaks.

Fig. 2 shows the SEM images of BST powders calcined at 900, 950, 1000 and 1050 °C for 2 h. It is noted that powder calcined at 950 °C presents homogeneous polyhedral well-facetted particles and the least aggregation compared with

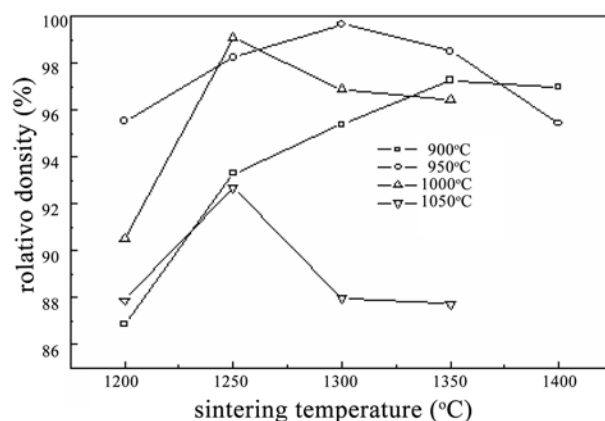


Fig. 3. Densities of BST ceramics for various calcination and sintering temperatures.

the other powders calcined at 900, 1000 and 1050 °C. Also the average particle size of the powder calcined at 950 °C is about 110 nm, which accords well with the effective diameter value 109.5 nm obtained by a Zeta potential analyzer. For the 900, 1000 and 1050 °C calcined BST powder, the effective diameter is 143.1 nm, 128.9 nm, and 134.3 nm, respectively. This also indicates that these powders have substantial aggregation and illustrates the beneficial effect of choosing a moderate calcination temperature.

Fig. 3 shows the relative densities of BST specimens prepared at different calcination and sintering temperatures as determined by the Archimedes method. The density

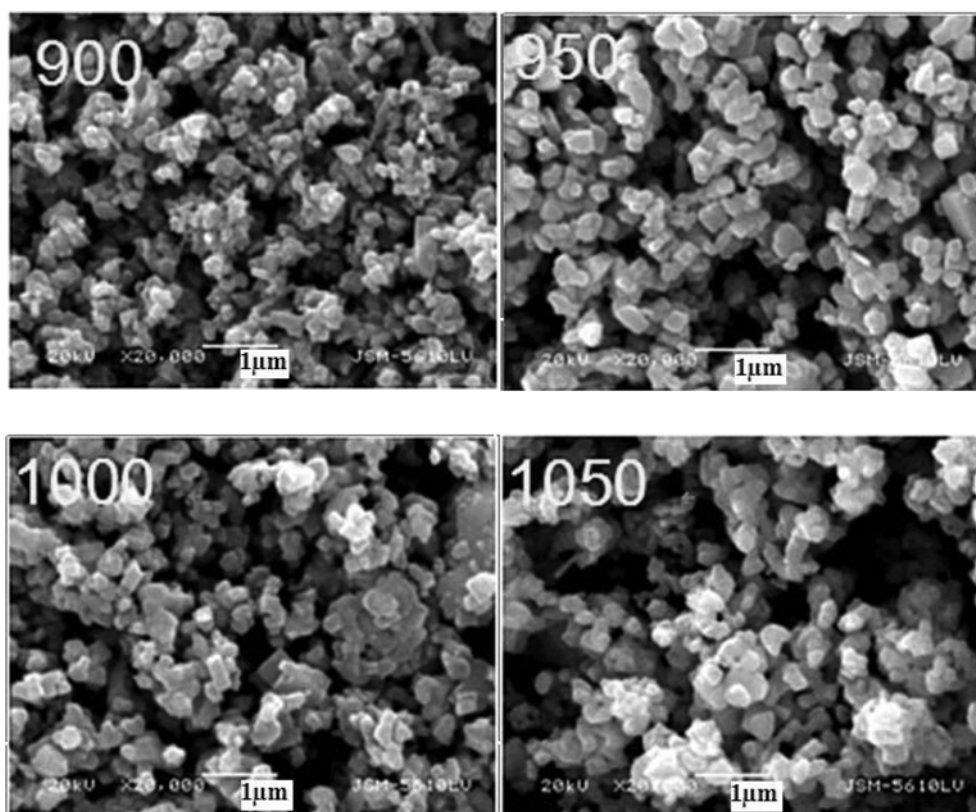


Fig. 2. SEM micrographs of BST powders calcined at 900-1050 °C for 2 h.

values are in the range of 86.8%-99.6%. It is found that the distributions of the density values obey a commonly applied rule: by increasing the sintering temperature, the density increases and then decreases above a threshold value. A higher sintering temperature is required for the BST samples calcined at 900 °C in order to obtain a better densification. On the whole, for a calcining temperature of 950 °C, the BST specimens approximately have a better densification with the various sintering conditions with the highest relative density of 99.6%.

SEM images of the BST samples for the different calcination temperatures sintered at 1300 °C for 2 h are shown in Fig. 4(a), (b), (c), and d. From Fig. 4, the average grain size of the BST ceramics calcined at 950 °C is the smallest, 250 nm, and the average grain size in samples calcined at 900, 1000 and 1050 °C are 400 nm, 1 µm, and 2 µm, respectively. These results show that the growth rate of the BST ceramic samples calcined at 950 °C is the smallest, which is due to a more uniform primary particle distribution and less agglomeration compared with the other calcined powders (see Fig. 2).

The BaTiO₃ system is well known to grow by an abnormal grain growth mode during sintering [10-12]. In the case of BST calcined at 1050 °C, sintering 1300 °C for 2 h is enough to complete the abnormal grain growth and

the microstructure consists of abnormally growing grains and fine matrix grains. However, the resulting microstructure is detrimental to electrical properties.

Fig. 5(a) shows the dielectric-temperature characteristics of BST ceramics prepared from BST powders with different calcination temperatures and sintered at 1300 °C for 2 h. Fig. 5(b) shows the P-E characteristics of BST ceramics sintered at 1250-1350 °C for 2 h, at the same calcination temperature of 950 °C. In Fig. 5(a), the T-C phase transition temperature of the dielectric constant increases slightly and then decreases with an increase in the calcination temperature. In addition, it is obvious that the samples calcined at 950 and 1000 °C with an average grain size of about 250 nm and 1 µm (from Fig. 4.) show higher dielectric constant maximum and the former shows a lower dielectric loss than the latter. However, the sample calcined at 900 °C with an average grain size of about 400 nm shows the lowest dielectric constant maximum.

It is known that the dielectric properties of BaTiO₃ are strongly dependent on its grain size. Coarse-grained ceramics of pure BaTiO₃ (20-50 µm) show a lower dielectric constant maximum [13] than fine grained BaTiO₃ (0.7-1 µm) [14-15]. At even smaller grain sizes, a strong decrease of " ϵ_r " was observed. Many authors considered

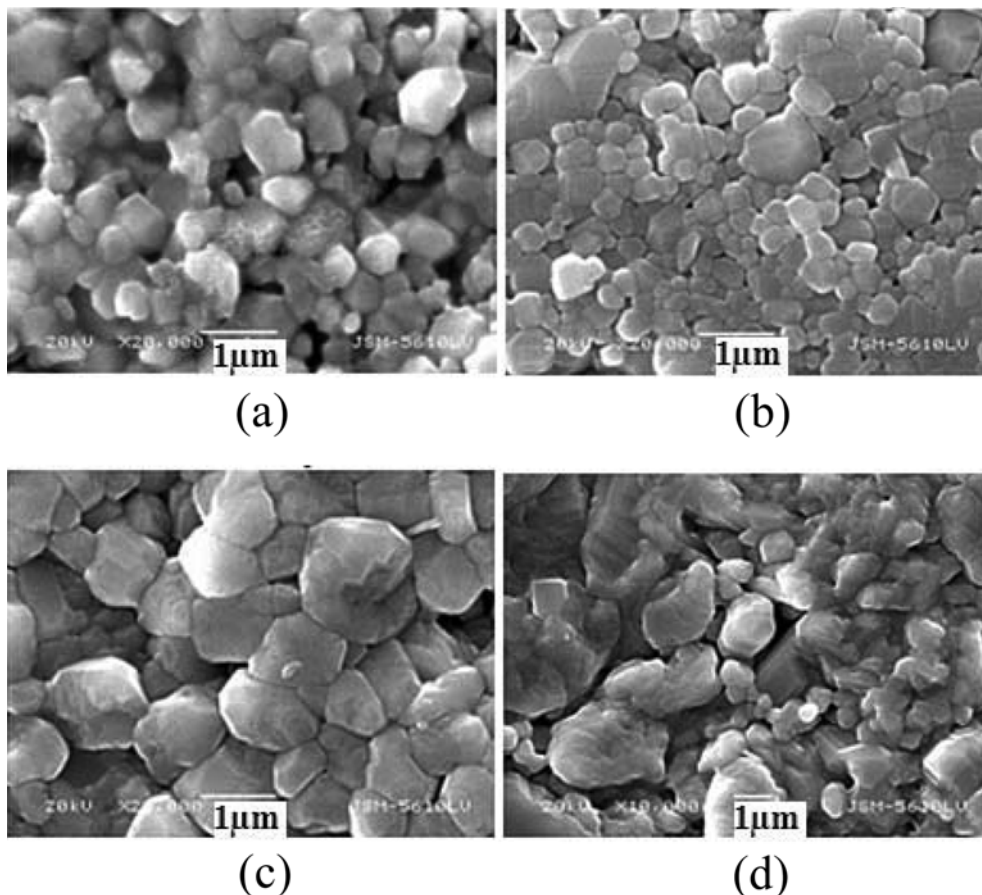


Fig. 4. SEM micrographs(thermal etching) of 1300 °C sintered BST ceramics with different calcination temperatures (a) 900 °C (b) 950 °C (c) 1000 °C (d)1050 °C.

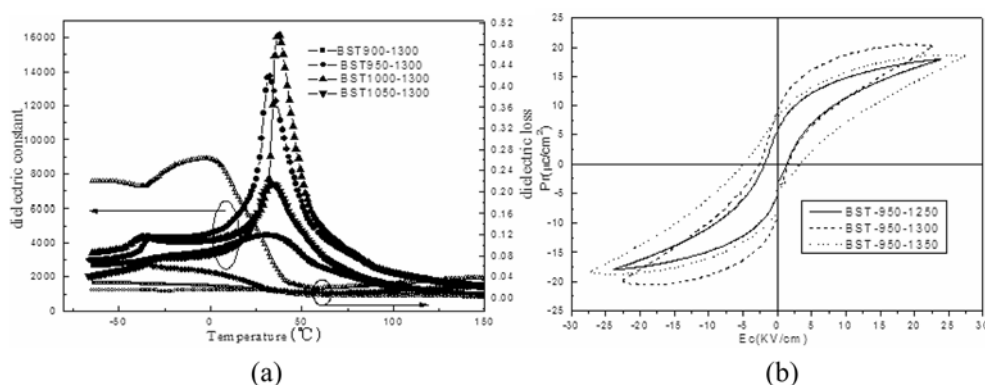


Fig. 5. (a) The temperature dependence of the dielectric constant at 100 kHz for BST ceramics derived from powder prepared at various calcination temperatures and then sintered at 1300 °C. (b) P-E hysteresis loops of 950 °C calcined BST ceramics sintered at 1250-1350 °C.

that when the grain size is lower than 700 nm, the lattice structure of BaTiO_3 ceramic changes from tetragonal to pseudocubic, and the dielectric constant value is very low [16]. In BST, this effect is more complex, because it is necessary to consider also the influence of the Sr ion solution. According to the measured results of our BST ceramics, it seems that the size effect on the dielectric constant is not similar to that of BaTiO_3 ceramics. BST with a smaller grain size calcined at 950 °C has a higher dielectric constant than BST calcined at 900 °C with a heavy diffuseness. This phenomenon can not be only explained by the grain size effect and the origin is still unclear and needs to be further studied.

From Fig. 5(b), it is obvious that the remanent polarization (Pr) firstly increases and then decreases when the sintering temperature increases. The coercive electric field (E_c) increases with an increase in the temperature. With a sintering temperature of 1300 °C, the Pr of BST ceramics has a maximum $\text{Pr} = 9.2 \mu\text{C}/\text{cm}^2$, and the E_c is lower than 1.58 kV/cm.

Conclusions

BST powders were prepared by a solid-state reaction process at various calcining temperatures. The powders calcined at 950 °C show a single perovskite phase structure and the least aggregation with an average particle size about 110 nm. The BST ceramics calcined at 950 °C give the highest densification at all the chosen sintering temperatures. The dielectric property measurement confirmed that the dielectric properties are not dependent on the grain size and the 950 °C calcined BST ceramic sintered at 1300 °C for 2 h shows better dielectric and ferroelectric properties with permittivity $\epsilon_r = 7676$, the low loss factor $\tan\delta = 0.01$ and $\text{Pr} = 9.2 \mu\text{C}/\text{cm}^2$, $E_c = 1.58 \text{ kV}/\text{cm}$ at room temperature.

Acknowledgement

The authors would like to thank for the support of Natural Science Foundation of China (No.:50872102), the Key Grant Project of Chinese Ministry of Education (No.:309022), the program for New Century Excellent Talents in University (No.:NCET-08-0808) and the Chenguang Science Plan of Wuhan (No.:200750731268).

References

1. E. Andrich, *Electron. Appl.*, 26 (1965) 123-144.
2. Z.H. Yao, H.X. Liu and Y. Liu, *et al.*, *Mater. Chem. Phys.*, 109 (2008) 475-481.
3. Hari Singh Nalwa M.Sc, New York: Academic Press, 2 (1999) 533-539.
4. H.X. Liu, Z.J. Liu and S.X. Ouyang, *Aata Chim. Sinica.*, 57 (1999) 472-477.
5. H.X. Liu, X.Q. Sun and Q.L. Zhao, *et al.*, *SolidState Electron.*, 47 (2003) 2295-2298.
6. W.S. Clabaugh, E.M. Swiggard and R. Gilchrist, *J. Res. Nat. Bur. Std.*, 56 (1956) 289-291.
7. G. Hennings, D. Rosenstein and H. Schreinemacher, *J. Eur. Ceram. Soc.*, 8 (1991) 107-115.
8. H. Ikawa, N. Munekata, T. Ozeki, M. Takemoto and T. Shirakami, *Trans. Mater. Res. Soc. Jpn.*, 27 (2002) 707-710.
9. K. Tokita and S. Sato, *Key Eng. Mater.*, 301 (2005) 219-222.
10. L.A. Xue and R.J. Brook, *J. Am. Ceram. Soc.*, 72 (1989) 341-344.
11. M. Drofenik, *J. Am. Ceram. Soc.*, 76 (1993) 123-128.
12. G. Kästner, R. Wagner, and V. Hilarius, *Philos. Mag. A*, 69 (1994) 1051-1071.
13. N.C. Sharma, E.R. McCartney, *J. Aus. Ceram. Soc.*, 10 (1974) 16-20.
14. G. Arlt, H. Peusens, *Ferro*, 48 (1983) 213-224.
15. G. Arlt, D. Hennings and G. With, *J. Appl. Phys.* 58 (1985) 1619-1625.
16. A.S. Shaikh, R.W. Vest and G.M. Vest, *IEEE Trans. Ultra. Ferro. and Freq. Contrl.* 36 (1989) 407-412.