Highly enhanced sinterability of fine-grained Ba_{0.6}Sr_{0.4}TiO₃—MgO bulk ceramics and in-situ nanocomposite thick films

Chan, Helen Lai-Wa; Zhang, Hongfang; Kong, Ling Bing; Mak, Chee-Leung; Kwok, Kin-Wing;
Wang, Yu

2014

Zhang, H., Kong, L. B., Mak, C.-L., Kwok, K.-W., Wang, Y., & Chan, H. L.-W. (2014). Highly enhanced sinterability of fine-grained Ba_{0.6}Sr_{0.4}TiO₃—MgO bulk ceramics and in-situ nanocomposite thick films. *Ceramics international*, 40(7), 10475-10481.

<https://hdl.handle.net/10356/101825>

<https://doi.org/10.1016/j.ceramint.2014.03.018>

© 2014 Elsevier Ltd and Techna Group S.r.l. This is the author created version of a work that has been peer reviewed and accepted for publication by *Ceramics International*, Elsevier Ltd. It incorporates referee's comments but changes resulting from the publishing process, such as copyediting, structural formatting, may not be reflected in this document. The published version is available at: [<http://dx.doi.org/10.1016/j.ceramint.2014.03.018>].

Downloaded on 26 Apr 2023 15:34:07 SGT

Highly enhanced sinterability of fine-grained $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ -MgO bulk ceramics and in-situ nanocomposite thick films

Hongfang Zhang^{a,*}, Ling Bing Kong^b, Chee-Leung Mak^c, Kin-Wing Kwok^c, Yu Wang^c,
Helen Lai-Wa Chan^c

^a*Department of Physics, Suzhou University of Science and Technology, Suzhou 215009, China*

^b*School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798*

^c*Department of Applied Physics, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong*

Abstract

Well-developed, fully dense and fine-grained $\text{MgO}-(\text{Ba}_{0.6}\text{Sr}_{0.4})\text{TiO}_3$ with 40 wt% MgO content (denoted as BST-MgO) bulk ceramics were fabricated by high-energy ball mechanochemical technique with a hybrid processing. Using this technique, the fabrication temperature was 1200°C i.e. 200°C lower than that required by conventional solid-state process. At the same time, dense, homogeneous and crack-free ceramic-ceramic 0-3 nanocomposite BST-MgO thick film was obtained at 700°C by using spin-coating. At 10 kHz and room temperature, the BST-MgO bulk ceramics exhibited a moderate dielectric constant of about 500 and low loss tangent of less than 0.005; while for the nanocomposite thick films, the dielectric constant and loss tangent were about 140 and less than 0.03 (at 100 kHz) respectively. In addition, both the bulk and thick film ceramics show a broad and diffused phase transition. The dielectric room-temperature tunabilities measured at 100 kHz were found as 4% at 1.5 kV/mm for the bulk ceramic, and 17 % at 10 kV/mm for nanocomposite thick film.

Keywords: A. Sintering; B. Nanocomposite; C. Dielectric properties; Hybrid processing

*Corresponding author. Tel.: +86-0512-6841 8463; fax: +86-0512-6841 8463.
E-mail address: zhf057@gmail.com

1. Introduction

Low temperature co-firing ceramic (LTCC) devices, consisting of ceramic materials as well as metals cofired at low sintering temperatures, are getting more and more important and popular [1, 2]. Ferroelectrics exhibiting an electric field dependent dielectric constant and relatively low loss are important candidate for the development of tunable microwave devices, such as voltage-controlled oscillators, tunable filters and phase shifters [3–5]. However, all applications require materials with low dielectric loss, high tunability and a moderate dielectric constant (<500). In general, high dielectric constant leads to high loss at microwave frequencies and does not satisfy the requirement of impedance matching and high power [6, 7]. Many studies have indicated that $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ (BST)-MgO composite materials (BST-MgO) exhibit a prominent feature of reduced permittivity and acceptable tunability, which are suitable for applications in microwave components [8–14]. However, using the conventional ceramic processing as the fabrication technique, the sintering temperature of these composite is still as high as 1350°C . This high fabrication temperature prevents these composites from adapting to the critical requirement of low temperature co-firing of thick film devices.

It is well known that the properties of ferroelectrics are closely related to their crystallite grain size, which is determined by sintering temperature [15]. Additionally, many tunable microwave devices are fabricated by using thick film technology with conventional silver-palladium (Ag-Pd) electrodes. Therefore, the firing temperature should be lower than 1100°C . If silicon is used as the substrate, the firing temperature should be even lower to $700\sim 800^\circ\text{C}$, in order to avoid chemical reactions between the

films and the silicon substrate. Based on our previous studies [16–21], a hybrid processing route originated from the high-energy mechanochemical technique was proposed in this paper. Well-developed and fine-grained BST-MgO bulk ceramics with highly enhanced sinterability was achieved at 1200°C. In-situ ceramic-ceramic nanocomposite thick films with 0-3 connectivity were produced at 700°C. The microstructure and dielectric properties of these bulk ceramics and thick films were investigated.

2. Experimental procedure

2.1. Synthesis of nano-sized BST powders by using mechanochemical ball milling

Micron-sized BaTiO₃ (BT, Fenghua Advanced Technology Holding Co. LTD., China) and SrTiO₃ (ST, Fenghua Advanced Technology Holding Co. LTD., China) powders were used as the starting materials for the nano-sized BST powder. The composition ratio of Ba:Sr was fixed to be 60:40. The powders were milled together by using a Fritsch Pulverisette 5 planetary ball milling system operated at 200 rpm, with a 250-ml tungsten carbide vial and 5 balls of 20-mm diameter and 20 balls of 10-mm diameter. The ball-to-powder weight ratio was 20:1. The powders were milled for different milling times of 2, 10, 15 and 20 h. After different allotted milling times, a small amount of powder was taken out from the vial for analyses. These samples are referred as milled or mechanically activated mixtures. To ensure homogeneity of the mixture, all samples were thoroughly mixed by using a standard laboratory ball mill prior to the high-energy mechanical activation.

2.2. Preparation for composite slurry (or suspend) by a hybrid processing

To prepare the BST-MgO (with 40 wt% MgO) composite slurry, stoichiometric $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (International Lab, USA) was first dissolved in a mixture of deionized water and ethanol with a molar ratio of 1:3 to form a clear solution of 20 ml. Then, 4 g 20-h mechanically activated BST powders (as the filler) were dispersed into the $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution. Subsequently, homogeneous BST-MgO composite slurry was obtained by using the conventional ball milling for 2 h for further processes. In this experiment, the $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution was used as the matrix (noted as matrix-I) instead of using the mixture of BST sol precursor and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution as the matrix (noted as matrix-II). This is because of the stray phase occurred in the composite materials during the sintering procedure when matrix-II was employed. At the same time, the BST powders, fabricated by the conventional ceramic process and calcined at 1150°C for 2 h, were subjected to conventional ball milling for 24 h (denoted as BST-1150). These BST powders were used as the fillers dispersed into the $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution to form a slurry for comparison (noted as matrix-III).

2.3. Fabrication of BST-MgO bulk and ceramic-ceramic 0-3 thick film

2.3.1. BST-MgO composite ceramics

The two sets of BST-MgO composite slurries (i.e. matrix-I and matrix-III) were dried at 120°C for 24 h and then calcined at 800°C for 2 h. The calcined powders were subjected to granulation and then pressed into disk samples of 12 mm diameter and a 1 mm thickness. The green pellets were then sintered at 1200°C for 2 h in air. Silver

electrodes were fired on top and bottom surfaces of the disk samples for the electrical measurements.

2.3.2. Ceramic-ceramic 0-3 nanocomposite BST-MgO thick films

To prepare the BST-MgO thick films, appropriate amount of poly-vinylpyrrolidone (PVP(K30), International Lab, USA) was added in the sol matrix to improve its adhere ability with the substrate. Four layers of slurry were spin-coated onto Pt/Ti/SiO₂/Si substrates. Each layer was heat-treated at 550°C for 5 min before another layer was deposited on to the substrate. After then, the films were annealed at 700°C for 2 h. In order to reduce the surface roughness, a capping layer formed by the pure BST precursor solution (Ba/Sr: 60/40) [19] was spin-coated on the 4-layer thick films subsequently. Finally, the films (4-layer thick films including a capping layer) were annealed at 700°C for another 2 h. A series of gold/chromium top electrodes of dimensions 1 mm × 1 mm were deposited on the film by using dc sputtering method.

2.4. Characterization

Phase compositions of the powders were examined by using room temperature X-ray diffraction (XRD, Philips X'Pert-Pro MPD) with CuK_α radiation (1.5406 Å, 40 kV, 100 mA) at a scan step of 0.02°. Scanning electron microscope (FE-SEM, JSM-6335F, JEOL, Tokyo, Japan) and transmission electron microscopy (TEM, HITACHI H-800) were employed to record and analyze the morphologies of the ball-milled powders, bulk ceramics and thick films. Element analysis was conducted by using energy dispersive X-ray spectroscopy (EDS, Oxford/Inca, Energy 250) during the SEM measurements. In addition, TEM specimens were prepared by dispersing the powders onto a TEM copper

grid coated with lacey carbon. Then, ethanol solution was sprayed on the deposited powders, which were dried in air. Densities of the bulk samples were evaluated by using Archimedes' method. Temperature-dependent dielectric constant and loss tangent were measured by using an impedance meter (Keithley, 6517A) and a low temperature control system (Cryostat, Oxford). The dielectric tunability, determined as $C(0)-C(E)/C(0)$ where $C(0)$ and $C(E)$ are the film capacitances measured at zero-field or under an applied dc electric field E respectively, was measured by using an impedance analyzer (Agilent 4294A).

3. Results and Discussion

3.1. Nano-sized BST powders triggered by mechanochemical milling

Figure 1 shows XRD patterns of the mixture of BT and ST powders with mechanochemically milled for different time durations. As expected, prior to mechanical activation, the powder mixture exhibited sharp distinctive peaks of tetragonal BT and cubic ST phases, indicating the good crystallinity and relatively large particle size of the BT and ST powders. This also specified that no reaction was triggered before the mechanochemically milling. Upon milling for 2 h, no BST peak was observed, but the ST and BT diffraction peaks were broadened and reduced in intensity, indicating great refinement in particle/grain size. After milling for 10 h, almost all the peaks of ST and BT vanished except for the strongest (110) peak at 32.08° (the unreacted residual indicated by the blue arrow in Fig. 1(e)). At the same time, a new peak centered at 31.518° was observed. This peak was identified as the diffraction peak arisen from the perovskite BST phase, indicating that perovskite BST was triggered in the mechanically

activated mixture. The significant broadening in the diffraction peaks upon 10 h mechanical activation suggested that a significant refinement in crystallite and particle sizes of the constituent oxides, together with a degree of possible amorphization, were turned on by the mechanical activation [22]. Increasing mechanical activation time led to a progressive formation of perovskite BST. However, 20-h mechanical activation could not facilitate the complete conversion of BST, because a small trace of ST was still observed in the XRD pattern. As shown in Fig. 1(a), one unidentified phase peak (at 34.22° indicated by a circle) introduced by the starting materials was disappeared after milling for 10 h, owing to mechanochemical reaction during the high energy ball milling process.

Figure 2 shows the SEM images of (a) the commercially available BT powder, (b) ST powder, and (c) the 20-h milled powder. Figure 2(d) shows the TEM image of the 20-h milled powders. In Figs. 2(a) and (b), the commercial BT and ST powders were spherical shapes of about 200 nm in diameter. After ball milling for 20 h, the sample was significantly refined (in Fig. 2(c)). After 20 h mechanical activation, the powder consisted of well-dispersed nanoparticles at about 20 nm in size in Fig. 2(d). Nevertheless, some degree of aggregation of the powder was observed. On the other hand, the BST-1150 powders formed by the 24-h conventional ball milling were made up of irregular shaped particles of tens of micrometers in size (not shown here) [21].

3.2. Highly enhanced sintering behavior

Figure 3 shows the XRD patterns of (a) BST-MgO composite slurry dried at 120°C , (b) the dried BST-MgO composite slurry calcined at 800°C for 2 h, and (c) BST-MgO

bulk ceramic composites sintered at 1200°C for 2 h using powders triggered by the high energy ball milling. The XRD pattern of the dried BST-MgO slurry in Fig. 3(a) only displayed the peaks of the BST powder and no MgO peaks were observed, indicating that the MgO was still amorphous. In Figs. 3(b) and (c), BST and MgO phases coexisted in the sample, and no intermediate and interfacial phases were observed. This implied that the formation of a single phase BST was completed after calcination at 800°C. Although only two peaks (200) and (220) of MgO phase were observed in Fig. 3(c), the existence of MgO in the composite ceramic was further confirmed by using the EDS analysis.

Figures 4(a) and 4(b) illustrate the SEM images of the BST-MgO ceramics sintered at 1200°C for 2 h by using mechanically activated powders and conventional ball milled powders as precursors respectively. Inset of Fig. 4(a) shows the results of the EDS element analysis of the marked district. In Fig. 4(a), it is noticed that by using the nano-sized BST triggered by the high energy ball milling the ceramics were densely packed at a sintering temperature of 1200°C with an average grain size of about 300 nm. In contrast, in Fig. 4(b), by using the powders prepared by conventional ball milling, the sample consisted of loosely packed and porous microstructure under the same sintering temperature condition. From the inset of Fig. 4(a), the EDS analysis indicated that the composition of the marked area composited of Ba, Ti, Sr and Mg element only. This further confirmed that both BST and MgO phases were co-existed in the composite sample.

It has been reported that the sintering temperature of MgO should be over 1450°C [23]. Therefore, sintering temperature range between 1350~1600°C is indispensable to fabricate BST-MgO ceramics by using the conventional solid-state process. However,

high sintering temperature easily leads to voids, exaggerated grain growth and diffusion between different phases, thus the resultant ceramics usually possess deteriorated properties. In this respect, the proposed hybrid processing using nano-sized powders triggered by high energy ball milling is a very advantageous method in fabricating BST-MgO composite ceramics at low temperatures. Indeed, sintering temperature as low as 1200°C (about 200°C lower than that required by the conventional solid-state process) is sufficient to fabricate BST-MgO ceramic composite with a reasonably high density of 4.50 g/cm³. During the high-energy ball milling, mechanical energy is provided to the milled powders by high strength collision and high-pressure impact between the milling media and the milled powder. This additional mechanical energy improves the size reduction of BT and ST grains as well as reaction between the two phases. Additionally, the high-energy ball milling also induces structural defects and disorder in the BST powders, which makes them even more reactive. All these factors would favor diffusion and atomic rearrangements of the milled BST at very low temperatures [24]. Also, the characteristic of the hybrid processing route ensures the homogeneous and fine-grained microstructure of the final composite because the sol solution facilitates uniform distribution.

Figure 5(a) shows the temperature dependent dielectric constant and loss tangent of the sample sintered at 1200°C using the nano-sized powder triggered by the high energy ball milling in the temperature range of -60°C to 80°C at three frequencies (1 kHz, 10 kHz and 100 kHz). A noticeable diffused dielectric behavior was observed in the figure, reflecting a strong frequency dispersion feature of the sample. The relatively broad and diffused phase transition was clearly identified at about -20°C, which could be attributed

to the presence of the non-ferroelectric MgO in the BST ferroelectric matrix. The fine structure of the sample was also responsible for its low dielectric constant and phase diffusion [10]. Reduced temperature variation of dielectric behavior is desirable for applications in electrically tunable microwave devices, in terms of maintaining high temperature and frequency stabilities [14]. A moderate dielectric constant (about 500) and loss tangent (less than 0.005) at 10 kHz were obtained in the composite at room temperature. Figure 5(b) shows the room-temperature dielectric constant as a function of dc electric field at 100 kHz. The room temperature dielectric tunability was found to be 4% at 1.5 kV/mm at 100 kHz, due to the presence of the non-ferroelectric MgO as well as the fine structure of the sample.

3.3. Microstructure and properties of the ceramic-ceramic 0-3 BST-MgO nanocomposite thick film

Figure 6 shows the XRD pattern of the thick film deposited on the Pt/Ti/SiO₂/Si substrate at annealing temperature of 700°C for 2 h. Except for the substrate peak, diffraction peaks of BST and MgO coexisted without any observation of other stray phases. This result was in a good agreement with the bulk ceramic samples as shown in Figs. 3(b) and (c). Figure 7 shows surface morphology of the thick films (a) without and (b) with the one-layer BST thin film as a capping layer. The inset in Fig. 7(b) shows the cross-sectional SEM image of the thick film with a capping layer. In Fig. 7(a), the crack-free film was very dense and uniform with a rough surface. However, the surface smoothness was improved greatly by using the capping layer as shown in Fig. 7(b). The film was about 3 μm in thickness with an estimated thickness of each layer to be about

0.8 μm . Although occasionally pinholes were observed in the film, they were not interconnected and thus had no adverse effect on the dielectric properties. On the basis of these results, we demonstrated that a final capping sol-gel layer can reduce the porosity and enhance the surface density of the film.

Figure 8(a) shows the temperature dependent dielectric constant and loss tangent of the thick film with a capping layer in the temperature range of -150°C to 150°C at three selected frequencies (1 kHz, 10 kHz and 100 kHz). The thick film exhibited a broad and diffused phase transition identified at about -50°C , which is similar to its ceramic counterpart. This might be ascribed to the nano-scale grain size of the film. Also, another diffusion phase occurred at about 50°C cannot be explained currently. It is perhaps caused by the pure BST capping layer, whose Curie transition is smeared due to the small grain size annealing at 700°C . As shown in the figure, the dielectric constant was about 140 at 10 kHz and room temperature. Figure 8(b) shows the room-temperature dielectric constant as a function of dc electric field at 100 kHz. It is noticed that dielectric constant decreased almost linearly with the bias voltage, showing a tunability of about 17% at 10 kV/cm with a low loss tangent less than 0.03.

4. Conclusions

Dense and fine-grained BST-MgO composite ceramics have been obtained at a sintering temperature as low as 1200°C , which is about 200°C lower than that required by the conventional solid-state process. The result can be attributed to the synergistic characteristics of nano-sized BST powders triggered by the high energy ball milling and the hybrid process. At the same time, in situ dense, uniform and crack-free ceramic-

ceramic 0-3 nanocomposite BST-MgO thick films were fabricated at an annealing temperature of 700°C by using spin-coating method. At 10 kHz and room temperature, dielectric constant and loss tangent of the BST-MgO bulk ceramic were about 500 and 0.005, while those of the thick film were about 140 (at 10 kHz) and less than 0.03 (at 100 kHz), respectively. The room-temperature tunabilities of the bulk and thick films ceramic were 4 % at 1.5 kV/mm and 17% at 10 kV/cm at 100 kHz respectively. It is believed that this simple, effective and reproducible process should be applicable to many other electroceramic composite materials at relatively low firing temperatures.

Acknowledgments

This work was supported by the Natural Science Foundation of Jiangsu Province (BK20131153). LBK would like to acknowledge the financial support of SUG (M4080845, 2012) by Nanyang Technological University and AcRF Tier 1 (RG 44/12 (M4011056.070), 2013) by MOE, Singapore.

References:

- [1] A. J. Bell, Ferroelectrics: The role of ceramic science and engineering, *Journal of the European Ceramic Society* 28 (2008) 1307–1317.
- [2] N. Setter and R. Waser, Electroceramic materials, *Acta Materialia* 48(2000) 151–178.
- [3] C. H. Mueller, R. R. Romanofsky and F. A. Miranda, Ferroelectric thin film and broadband satellite systems Potentials, *IEEE* 20 (2001) 36–39.
- [4] S. S. Gevorgian and E. L. Kollberg, Do we really need ferroelectrics in paraelectric phase only in electrically controlled microwave devices? *Microwave Theory and Techniques*, *IEEE Transactions* 49 (2001) 2117–2124.
- [5] D. S. Korn and H. D. Wu, A comprehensive review of microwave system requirements on thin-film ferroelectrics, *Integrated Ferroelectrics* 24 (1999) 215–237.
- [6] M. W. Cole, P. C. Joshi, and M. H. Ervin, La doped $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ thin films for tunable device applications, *Journal of Applied Physics* 89 (2001) 6336–40.
- [7] R. A. York, Tunable Dielectrics for RF Circuits, In: M. Steer and W.D. Palmer (Eds.), *Multifunctional Adaptive Microwave Circuits and Systems*, Scitech Publishing Inc, NC, 2009, pp. 1–54.
- [8] M. W. Zhang, J. W. Zhai, B. Shen and X. Yao, MgO Doping Effects on Dielectric Properties of $\text{Ba}_{0.55}\text{Sr}_{0.45}\text{TiO}_3$ Ceramics, *Journal of the American Ceramic Society* 94 (2011) 3883–3888.
- [9] J. Q. Qi, H. Y. Tian, Y. Wang, G. K. H. Pang, L. T. Li, and Helen L. W. Chan, Analyzing core-shell structured zinc doped MgO wrapped $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ nanoparticles, *Journal of Physical Chemistry B*. 109 (2005) 14006–14010.

- [10] W. Chang, L. Sengupta, MgO-mixed Ba_{0.6}Sr_{0.4}TiO₃ bulk ceramics and thin films for tunable microwave applications, *Journal of Applied Physics* 92 (2002) 3941–46.
- [11] I. S. Kim, J. S. Song, S. J. Jeong, S. H. Jeon, J. K. Chung and W. J. Kim, Tunable Properties of Ferroelectric Thick Films With MgO Added on (BaSr)TiO₃, *Journal of Electrical Engineering & Technology* 391(2007) 391–395.
- [12] U. C. Chung, C. Elissalde, M. Maglione, C. Estournes, M. Pate, and J. P. Ganne, Low-Losses, Highly Tunable Ba_{0.6}Sr_{0.4}TiO₃/MgO Composite,” *Applied Physics Letter* 92 (2008) 042902–5.
- [13] X. H. Wang, W. Z. Lu, J. Liu, Y. L. Zhou, and D. X. Zhou, Effects of La₂O₃ Additions on Properties of Ba_{0.6}Sr_{0.4}TiO₃–MgO Ceramics for Phase Shifter Applications, *Journal of the European Ceramic Society* 26 (2006) 1981–5.
- [14] S. Louise, Ng. Eric, S. Steven et. al. Ceramic Ferroelectric Composite Material – BSTO-MGO, U.S. Patent 5427988 (1995).
- [15] K. Keizer and A. J. Burggra, Grain Size Effects on the Ferroelectric-Paraelectric Transition, the Dielectric Constant, and the Lattice Parameters in Lanthana-Substituted Lead Titanate, *Physica status solidi (a)* 26 (1974) 561–569.
- [16] H. F. Zhang, C. L. Mak, Preparation and characteristics of fine-grained ferroelectric glass-ceramic composites via a modified hybrid route at low temperature sintering. *Journal of Electroceramics* 27 (2011) 126–133.
- [17] H. F. Zhang, S.W. Or, and Helen W. L. Chan, F. Yang, Formation and characterization of three-ply structured multiferroic Sm_{0.88}Nd_{0.12}Fe_{1.93}-Pb(Zr_{0.53}Ti_{0.47})O₃ ceramic composites via a solid solution process, *Journal of the European Ceramic Society* 31 (2011) 1753–1761.

- [18] H. F. Zhang, S. W. Or, and Helen W. L. Chan, Multiferroic properties of $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4\text{-Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{TiO}_3$ ceramic composites, *Journal of Applied Physics* 104 (2008) 104109.
- [19] H. F. Zhang, X. Yao, and L.Y. Zhang, Microstructure and dielectric properties of barium strontium titanate thick films and ceramics with a concrete-like structure, *Journal of the American Ceramic Society* 90 (2007) 2333–2340.
- [20] H. F. Zhang, S. W. Or, and Helen W. L. Chan, Synthesis of fine-crystalline $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3\text{-MgO}$ ceramics by novel hybrid processing route, *Journal of Physics and Chemistry of Solids* 70 (2009) 1218–1222.
- [21] H. F. Zhang, L.Y. Zhang, X. Yao, Fabrication and electrical properties of barium strontium titanate thick films by modified Sol–Gel method, *Journal of Electroceramics* 21(2008) 503–507.
- [22] J. Wang, J. M. Xue, D. M. Wan, W. Ng, Mechanochemical fabrication of single phase PMN of perovskite structure, *Solid State Ionics*, 124 (1999) 271–279.
- [23] Y. Fang, D. Agrawal, G. Skandan nd M. Jain, Fabrication of translucent MgO ceramics using nanopowders, *Material Letters*, 58 (2004) 551– 554.
- [24] L. B. Kong, J. Ma, W. Zhu and O.K. Tan, Highly enhanced sinterability of commercial PZT powders by high-energy ball milling, *Material Letters* 46 (2000) 274–280.

Figure captions

Fig. 1. XRD patterns of the mixture mechanochemically activated for different time durations.

Fig. 2. SEM images of (a) the commercially available BT powder, (b) ST powder and (c) the 20-h milled mixture, together with (d) TEM image of the 20-h milled powder.

Fig. 3. XRD patterns of (a) the BST-MgO composite slurry dried at 120°C, (b) the dried BST-MgO slurry calcined at 800°C for 2 h, (c) BST-MgO ceramics sintered at 1200°C for 2 h using powders triggered by the high-energy ball milling.

Fig. 4. Surface morphologies of the BST composite ceramics sintered at 1200°C for 2 h: (a) using mechanically activated BST powders, (b) using conventional ball milled BST powders, together with the EDS analysis of marked district in the inset of (a).

Fig. 5. (a) Temperature dependent of dielectric constant and loss tangent of the BST-MgO ceramics sintered at 1200°C using the nano-sized powder triggered by the high energy ball milling, and (b) room-temperature dielectric constant as a function of dc electric field at 100 kHz.

Fig. 6. XRD pattern of the BST thick films deposited on Pt/Ti/SiO₂/Si at 700°C for 2 h.

Fig. 7. SEM images of the BST-MgO thick films annealed at 700°C for 2 h: (a) without a capping layer, (b) with a capping layer spin-coated on film, together with the cross-sectional SEM image with a capping layer as the inset of (b).

Fig. 8. (a) Variations of dielectric constant and loss tangent of the BST-MgO thick film with a capping layer, and (b) room-temperature dielectric constant as a function of dc electric field at 100 kHz.

Fig.1

Fig.2

Fig.3

Fig.4

Fig.5

Fig.6

Fig.7

Fig.8