Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 35 (2009) 2463–2467
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Rheology and physical properties of $Bi_{0.5}(Na_{0.82}K_{0.18})_{0.5}TiO_3$ piezoelectric thick films by aqueous gel-tape casting process

Ming Fu, Tiantian Xie *, Shenglin Jiang

Department of Electronic Science and Technology, Huazhong University of Science and Technology, Wuhan, 430074, China

Received 18 November 2008; received in revised form 30 November 2008; accepted 12 February 2009
Available online 11 March 2009

Abstract

Piezoelectric $Bi_{0.5}(Na_{0.82}K_{0.18})_{0.5}TiO_3$ thick films were prepared by aqueous gel-tape casting. $Bi_{0.5}(Na_{0.82}K_{0.18})_{0.5}TiO_3$ nano-powder with perovskite structure prepared by sol–gel process was obtained. The average particle size was 200 nm. A stable $Bi_{0.5}(Na_{0.82}K_{0.18})_{0.5}TiO_3$ suspension with 46 vol% solid loading and <1 Pa s viscosity was prepared when 0.8 wt% of ammonium polyacrylate was added with the pH value controlled in the range 7–9. The plasticizer glycerol had a positive effect on the fluidity of the suspensions. The tensile strength and strain to failure of the green tape were 0.42 MPa and 0.04 mm/mm when the addition of glycerol was 50 wt% of the premix solvent. The resulting about 100 μm thick films had relative permittivity of 910, dielectric loss of 4.9% at 10 kHz, remanent polarization of 24 $\mu C/cm^2$, coercive field of 56 kV/cm, and longitudinal effective piezoelectric coefficient d_{33}eff of 102 pC/N. The good performance illustrated that gel-tape casting was the effective way to prepare $Bi_{0.5}(Na_{0.82}K_{0.18})_{0.5}TiO_3$ thick film.

Keywords: A. Suspensions; A. Tape casting; C. Piezoelectric properties; C. Mechanical properties

1. Introduction

In recent years, with the growing demands for global environmental protection, lead-free materials have gained much attention on an increasing degree [1]. Sodium–bismuth titanate is one of the most important lead-free piezoelectric materials with perovskite structure discovered by Smolenskii et al. in 1960. The NBT composition exhibits a strong ferroelectricity and high Curie temperature $T_c = 320$ °C, it has been considered to be a good candidate to substitute lead-based materials (e.g., PZT), which have been widely used for various applications such as ultrasonic generators, actuators, filters and other electronic devices [2–6]. Piezoelectric thick films with thickness in the range of 10–100 μm are of increasing interests in miniaturized sensors and actuators because they offer many advantages including quick response, large displacement, high-induced stress, low energy consumption, and low cost. The thick films are difficult to produce using lapping and machining bulk ceramics due to the expense, waste, and difficulty in handling the ceramics. On the other hand, grain-oriented ceramics have attracted more interest because they may show a performance similar to significantly improve the piezoelectric properties of lead-free materials [7–9].

Tape casting is the most widely used technique for large-scale fabrication of grain-oriented piezoelectric thick film, but it has disadvantages such as health and environmental hazards and high cost. Aqueous solvents, which have the advantages of incombustibility, non-toxicity and low cost, are a substitute for non-aqueous solvents [10–12]. Aqueous gel-tape casting was derived from gel casting by Tshinghua University in 2001 [13–15]. Gel casting was brought forward by the researchers of the Oak Ridge National Laboratory [16]. In this process, ceramic slurries can be solidified by the polymerization of monomers to form green bodies. There are many advantages of this process such as high solid loading, instant solidification and uniform green microstructure.

In this paper, aqueous gel-tape casting was utilized to prepare $Bi_{0.5}(Na_{0.82}K_{0.18})_{0.5}TiO_3$ (BNKT) lead-free thick films. The rheological properties of the BNKT suspension were investigated. The mechanical properties of green tape were studied. The dielectric, piezoelectric and ferroelectric properties were also evaluated.

* Corresponding author. Tel.: +86 27 87542693; fax: +86 27 87542693.
E-mail address: dudu2413@163.com (T. Xie).

0272-8842/$34.00
doi:10.1016/j.ceramint.2009.02.014

2. Experimental procedure

2.1. Powder preparation

The BNKT powder was synthesized by sol–gel method. Tetrabutyl titanate, sodium acetate, potassium acetate and bismuth nitrate were used as raw materials. Glacial acetic acid and glycol ether were used as solvent. Triethanolamine was used as catalyst. Acetylacetone was used as complexing agent to stabilize tetrabutyl titanate. Detailed information about the synthesis of BNKT powder was similar to reference [17].

2.2. Thick film preparation by aqueous gel-tape casting

The process of the gel-tape casting process used in this work was similar to reference [13]. In the first step, acrylamide (AM) as the monomer and methylene-bisacrylamide (MBAM) as the cross-linker were mixed in water to yield the premix solution whose concentration was 15 wt% and the ratio of AM: MBAM was 48:1. In the next step, ammonium polyacrylate (PAA) was chosen as the dispersant and BNKT powder was suspended in the premix solution. Glycerol was selected as Plasticizer. Before tape casting, the initiator ammonium persulfate solution (APS) and catalyst (*N*,*N*,*N*′*N*′-tetramethyl-ethylenediamine, TEMED) were added to the supension. The device to perform gel-tape casting is the conventional tape casting equipment except for adding a nitrogen protector to prevent oxygen antipolymerization. A gap of 180 μm under the blade was selected for all the casting tests. After drying, the thickness of the tapes was about 130 μm. The dried thick film was then debinded and burial sintered at 1120 °C for 1 h.

2.3. Characterization

The pH value was adjusted by dilute HAc and NH_4OH. The pH value was measured by a pH Meter, The ξ potential of the BNKT powder was determined by Zetaplus, The viscosity of the BNKT suspension was determined using a rotary rheometer. The apparent density was measured using the Archimedes method. The mechanical properties of the green tape were evaluated by tensile properties. The tensile testing of green tapes was accomplished using an Instron universal testing machine with a 100 N load cell. Tensile measurements were done at room temperature (24 °C) and humidity of 50 ± 5%. Dog bone shape tensile specimens with 9 mm tensile width and 32 mm gauge length were cut parallely to the casting direction with a razor blade. The cell sensibility was 0.1 N and the traverse speed was set to 1 mm min^{-1}. The stress and strain values obtained correspond to the average of at least 10 measurements.

The BNKT thick films were poled at 100 °C for 10 min in silicon oil. The piezoelectric constant (d_{33}) was measured using a quasistatic piezoelectric d_{33} meter (Model ZJ-3A, Institute of Acoustics Academic Sinica, China). Ferroelectric properties were tested by a modified Sawyer–Tower circuit for ferroelectric hysteresis measurements. The dielectric constant and the dissipation loss factor ($t_g\delta$) were determined using the impedance analyzer (Model HP4192A, Hewlett-packard). Microstructure morphology was observed using a scanning electron microscope (SEM; Model Hittachi S-570, Japan). The XRD diffraction was carried out by XRD (Model D/Max-IIIC, Japan, using CuKα radiation).

3. Results and discussions

3.1. Powder characterization

Fig. 1 shows the XRD diffraction of BNKT powder heat treated in different temperature for 2 h. As the heat treating temperature is 500 °C, though the perovskite structure has been formed, the impurity $Bi_2Ti_2O_7$ peaks still exists. As the temperature reaches 650 °C, $Bi_2Ti_2O_7$ peaks vanished and the pure perovskite structure formed. Fig. 2 shows the SEM photograph of BNKT powder heat treated at 650 °C for 2 h. It was shown that the particle size distribution was homogeneous and the powder was well dispersed. The average particle size was about 0.2 μm.

3.2. Rheology of gel-tape casting suspensions

A stable and flowable ceramic suspension requires low viscosity and a high Zeta (ξ) potential. The pH value significantly affects the ξ potential in the ceramic suspension, The ξ potential of the BNKT suspension as a function of the pH value is shown in Fig. 3. The experimental results are based on the following conditions (1) The system without PAA: the isoelectric point is at pH 3, indicating that particles under this condition tend to flocculate; (2) The system with dispersant PAA: the ξ potentials show negative values in the entire pH range. It may be inferred that an alkaline environment contributes to the dispersion of particles in the ceramic suspension because the ξ potential becomes more negative with increasing pH value, adding only 0.5 wt% PAA, a ξ potential value of −60 mV at a pH value of around 8 can lead to a stable colloid. Fig. 4 illustrates the effects of dispersant content and solid loading on the viscosity of the BNKT suspension. It suggests that the addition of 0.8 wt% PAA dispersant results in

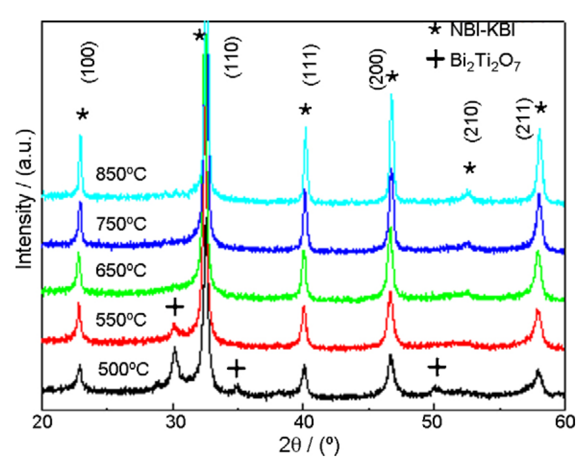

Fig. 1. XRD diffraction of BNKT powder heat treated in different temperature for 2 h.

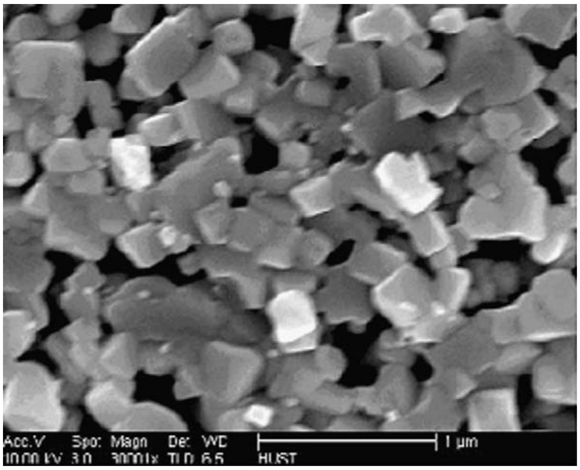

Fig. 2. SEM photograph of BNKT powder heat treated at 650 °C for 2 h.

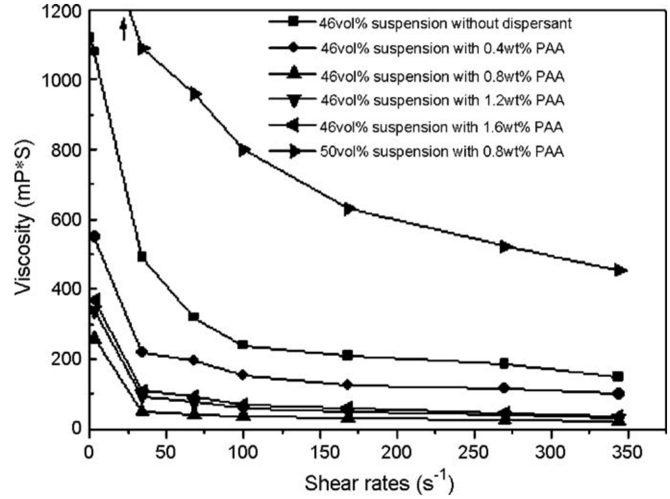

Fig. 4. Dispersant and Solid loading dependence of viscosity of the BNKT suspension.

the lowest viscosity of the slurry with a solid loading of 46 vol%. Slurries with 50 vol % BNKT solids loading exhibit an extremely higher viscosity as compared to the 46 vol % that decrease the fluidity of the suspension, inducing gas porosity in suspension and shape flaws in tape casting. Thus in this paper, 46 vol% solids loading was adopted.

Fig. 5 shows the effect of plasticizer on the viscosity of suspension. The suspension viscosity was decreased with the addition of glycerol. The low M_w of glycerol is preferred to fabricate the flexible green tapes and it makes easy for it to access and penetrate to the cross-linked network structure of PAM chains and act just like solvent to increase the distance of the polymer chain. It is found that glycerol has a positive effect on the fluidity of the BNKT suspension.

3.3. Mechanical properties of green body

The mechanical behaviour of the green BNKT tape which was made by gel-tape casting using the above slip composition was measured using tensile testing. Fig. 6 shows the tensile strength-elongation curves of BNKT green tape with different addition of glycerol. The green tape without plasticizer exhibits the typical brittle behaviour. In general, the physical properties of polymer products are strongly dependent on the interaction between polymer chains. In case of PAM macromolecule network, which is made up by polymerization and cross-link of AM, used as binder, interaction between polymer chains can be formed during gelation due to the strong C–N and C–C bonding. It is very brittle in room temperature because of the high vitrification point (T_g is higher than 160 °C). It was recognized that green tapes prepared with glycerol showed lower tensile strength and larger elongation than that without plasticizer, indicating that glycerol affected flexibility of the green tape. As the glycerol increasing, the tensile strength declined and the elongation increased monotonically. But the relative green density was decreased correspondingly as shown in Fig. 7. The low green density will affect the sintering ability of the materials. In this work, 50 wt% glycerol was selected. The ultimate tensile strength of the tape was 0.42 MPa with a standard deviation of 0.05 MPa and the strain to failure of

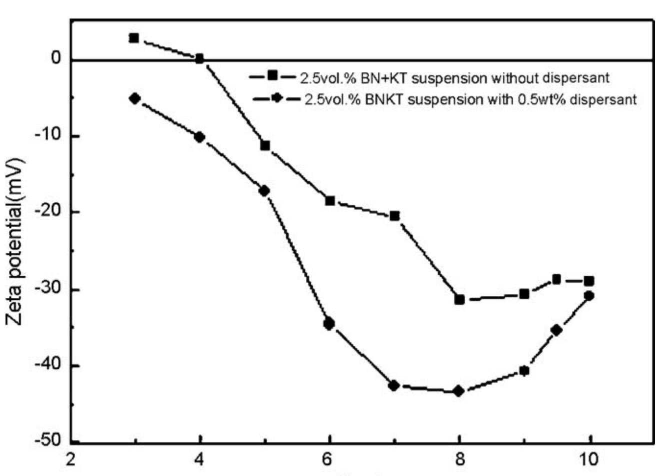

Fig. 3. Influences of the dispersant and pH value on ξ potential of the BNKT suspension.

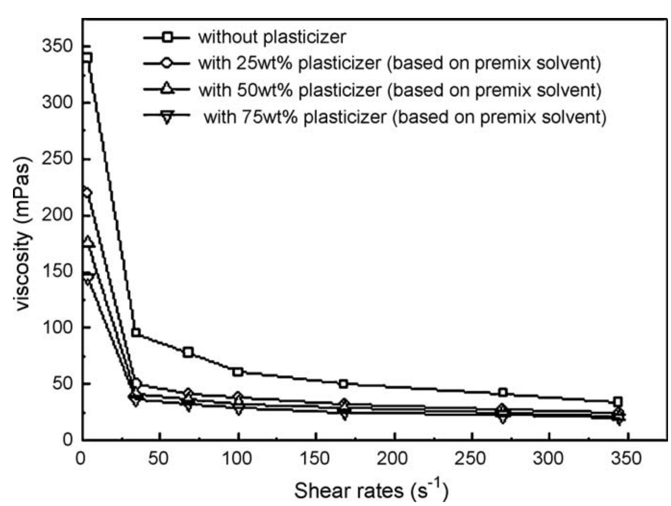

Fig. 5. Viscosity curves of BNKT suspensions prepared with different amount of glycerol.

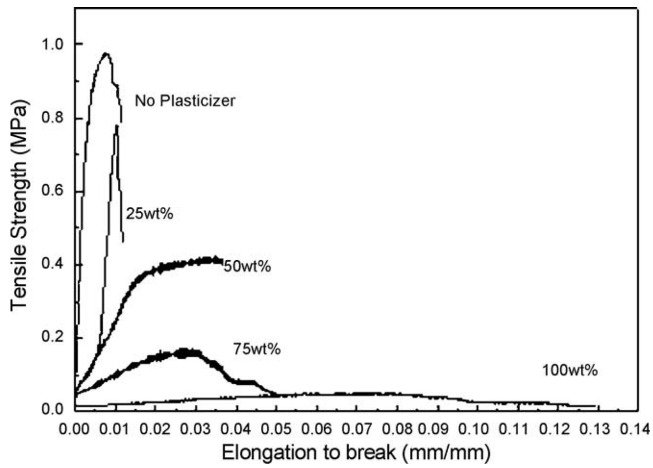

Fig. 6. Tensile strength-elongation curves of BNKT green tape with different addition of glycerol.

BNKT green tapes was 0.04 mm/mm with a standard deviation of 0.0082 mm/mm. These mechanical properties produced sufficient handing of the green tapes for further process and subsequent binder burnout and sintering stages. Green tapes produced a maximum relative green density of 56.5%.

3.4. Microstructure and electrical properties

The morphology of the thick film prepared by gel-tape casting was shown in Fig. 8. It shows obviously that the specimen exhibits a narrow and dense grain distribution. The electrical properties of the BNKT samples prepared by gel-tape casting were listed in Table 1. The thick film prepared by gel-tape casting has a relative density of 96.5%. Also, it shows a good piezoelectric property. The high dielectric constant and low dielectric loss were also obtained by the gel-tape casting. The electric properties of the BNKT thick film we close to bulk ceramics [18]. It demonstrates that gel-tape casting is the effective way to prepare BNKT thick film. Further research on the textured BNKT piezoelectric thick film could be expanded based on it.

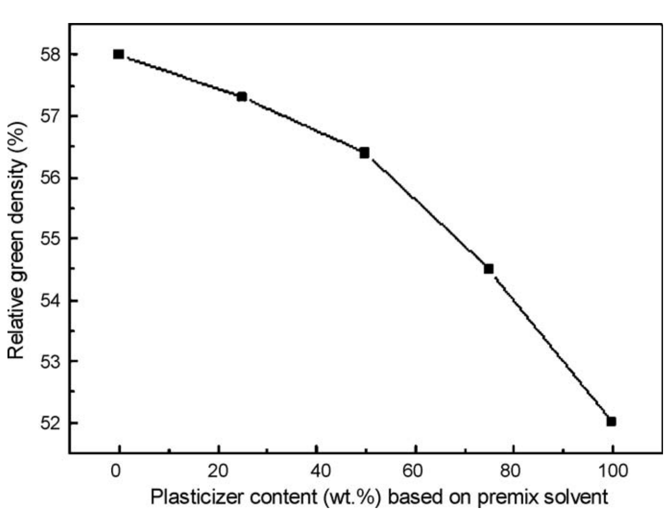

Fig. 7. Relative green density with different amount of glycerol.

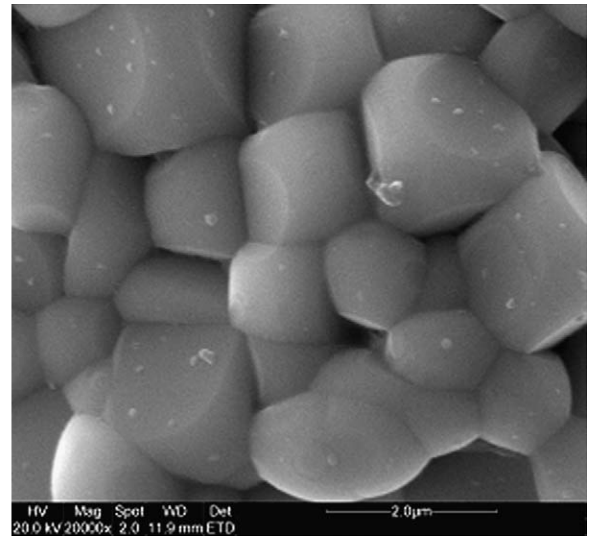

Fig. 8. SEM photograph of the surface of BNKT thick film prepared by gel-tape-casting.

Table 1
Electric properties of BNKT sample prepared by gel-tape casting.

Sample	d_{33}(pC/N)	k_t	ε_r	$t_g\delta$	Pr(μC/cm^2)	Ec (kV/cm)
BNKT	102	20%	910	0.049	24	56

4. Conclusions

Piezoelectric BNKT thick films were prepared by aqueous gel-tape casting process. The BNKT nano-powder prepared by sol–gel process with the pure perovskite structure was obtained and the average particle size was about 0.2 μm. A stable BNKT suspension with 46 vol% of solid loading and <1 Pa s of viscosity was successfully prepared when 0.8 wt% of PAA was added with the pH valur controlled in the range 7–9. The plasticizer glycerol had a positive effect on the fluidity of the suspensions. The tensile strength and the strain to failure of the green tape were 0.42 MPa and 0.04 mm/mm when the addition of glycerol was 50 wt% of the premix solvent, which produced sufficient handing of the green tapes for further process. The relative green density reaches 56.5%. The resulting about 100 μm thick films sintered at 1120 °C for 1 h have maximum relative permittivity of 910, dielectric loss of 4.9% at 10 kHz, remanent polarization of 24 μC/cm^2, coercive field of 56 kV/cm, and longitudinal effective piezoelectric coefficient d_{33}eff of 102 pC/N.

Acknowledgments

This work has been supported the National High Technology Research and Development Program of China (No. 2007AA032120), and the National Natural Science Foundation of China (No. 60777043). The authors also wish to thank the Analytical and Testing Center of Huazhong University of Science and Technology.

References

[1] Y. Saito, H. Takao, T. Tani, T. Nonoyama, K. Takatori, T. Homma, T. Nagaya, M. Nakamura, Lead-free piezoceramics, Nature (London) 432 (2002) 84–87.

[2] S.P. Beeby, N. Ross, N.M. White, Thick film PZT/micromachined silicon accelerometer, Electron. Lett. 35 (1999) 2060–2062.

[3] T. Morita, M. Kurosawa, T. Higuchi, Cylindrical Micro Ultrasonic Motor Utilizing Bulk Lead Zirconate Titanate (PZT), Jpn. J. Appl. Phys. 38 (1999) 3347–3350.

[4] T. Yan, B.E. Jones, R.T. Rakowski, M.J. Tudor, S.P. Beeby, N.M. White, Design and fabrication of thick-film PZT-metallic triple beam resonators, Sens. Actuators A 115 (2004) 401–407.

[5] N.R. Harris, M. Hill, N.M. White, S.P. Beeby, Acoustic power output measurements for thick-film PZT transducers, Electron Lett. 40 (2004) 636–637.

[6] S. Wang, K.H. Lam, C.L. Sun, K.W. Kwok, H.L.W. Chan, M.S. Guo, X.Z. Zhao, Energy harvesting with piezoelectric drum transducer, Appl. Phys. Lett. 90 (2007) 113506.

[7] T. Kimura, Application of texture engineering to piezoelctric ceramics, J. Ceram. Soc. Jpn. 114 (2006) 15–25.

[8] E.M. Sabolsky, G.L. Messing, S. Trolier-McKinstry, Kinetics of Templated grain growth of $0.65Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.35PbTiO_3$, J. Am. Ceram. Soc. 84 (2001) 2507–2513.

[9] E. Fukuchi, T. Kimura, Effect of potassium concentration on the grain orientation in bismuth sodium potassium titanate, J. Am. Ceram. Soc. 85 (2002) 1461–1466.

[10] D. Hotza, P. Greil, Review: aqueous tape casting of ceramic powders., Mater. Sci. Eng. A202 (1995) 206–217.

[11] N. Ushifusa, M.J. Cima, Aqueous processing of mullite-containing green sheets, J. Am. Ceram. Soc. Z74 (1991) 2443–2447.

[12] C. Pagnoux, T. Chartier, M.F. Granja, F. Doreau, J.M.F. Ferreira, J.F. Baumard, Aqueous suspensions for tape-casting based acrylic binders, J. Eur. Ceram. Soc. 18 (1998) 241–247.

[13] J.H. Xiang, Y. Huang, Z.P. Xie, Study of gel-tape-casting process of ceramic materials, Mater. Sci. Eng. A 323 (2002) 336–341.

[14] Z.P. Xie, C.L. Ma, Y. Huang, Effects of additives on alumina sheets forming by a novel gel-tape-casting, Mater. Des. 24 (2003) 287–291.

[15] Q.Q. Tan, G. Min, Z.T. Zhang, et al., Polymerizing mechanism and technical factors optimization of nanometer tetragonal polycrystalline zirconia slurries for the aqueous-gel-tape-casting process, Mater. Sc. Eng. A 382 (2004) 1–7.

[16] O.O. Omatete, A. Bleier, C.G. Westmoreland, A.C. Young, Gelcast zirconia–alumina composites, Ceram. Eng. Sci. Proc. 12 (1991) 2084–2094.

[17] V. Somani, S.J. Kalita, Synthesis and characterization of nanocrystalline Barium Strontium Titanate powder via sol–gel processing, J. Electroceram. 18 (2007) 57–65.

[18] D.X. Zhou, H. Li, S.P. Gong, K. Han, Y.X. Hu, Preparation of lead-free piezoelectric ceramics by aueous gelcating, J. Am. Ceram. Soc. 91 (2008) 2792–2796.