Journal of the European Ceramic Society 21 (2001) 1653–1656
www.elsevier.com/locate/jeurceramsoc

Microstructure and dielectric properties of barium–strontium titanate with a functionally graded structure

Jae-Ho Jeon *, Yoo-Dong Hahn, Hai-Doo Kim

Department of Materials Engineering, Korea Institute of Machinery and Materials, 66 Sangnam-Dong, Changwon, 641-010, South Korea

Received 4 September 2000; received in revised form 2 November 2000; accepted 15 November 2000

Abstract

A functionally graded perovskite material with varying Ba/Sr ratio was known to have a broad transition temperature and as a result it shows a low temperature coefficient and high dielectric constant in a wide temperature range. A multi-layered barium/strontium titanate functionally graded material was fabricated. Optical/scanning electron microscopy, energy dispersive spectrocsopy, and X-ray diffractometer were used for microstructural, chemical, and phase analysis, respectively. An impedance/gain-phase analyzer was used for dielectric constant measurement. The microstructure and dielectric property of $BaTiO_3$–$SrTiO_3$ system display various gradient distributions corresponding to constitutional change. The average grain size of $Ba_{1-x}Sr_xTiO_3$ phase was reduced as increasing the volume fraction of strontium. The dielectric properties of $BaTiO_3$–$SrTiO_3$ functionally graded materials were discussed in terms of microstructure and chemical composition. © 2001 Elsevier Science Ltd.

Keywords: $BaTiO_3$ and titanates; Dielectric properties; Functionally graded materials

1. Introduction

The concept of functionally graded materials (FGMs) was originated in the research field of thermal barrier materials.[1,2] Continuous changes in the composition, grain size, porosity, etc., of these materials result in gradients in such properties as mechanical strength and thermal conductivity. In recent years, the research area of FGMs has been expanding in the development of various functional materials, such as piezoelectric ceramics,[3] thermoelectric semiconductors[4] and biomaterials.[5]

$BaTiO_3$ has been widely used for high dielectric capacitors because of its very high dielectric constant at the Curie temperature ($T_c = 120°C$). Some corrective modifications are required for practical application.[6–8] In order to move the T_c to lower temperatures, $SrTiO_3$, $BaZrO_3$ and $SnTiO_3$ were usually added as shifters. A number of additives have been associated with the ability to flatten the dielectric constant versus temperature characteristic of $BaTiO_3$. A sharp peak of the dielectric constant at the T_c can be easily flattened, and, therefore, the temperature coefficient of the dielectric constant can be reduced, by adding the depressor material, such as $CaTiO_3$ and $MgTiO_3$. However, one of the most important characteristics of $BaTiO_3$, a very high dielectric constant at T_c, should be sacrificed.

If the Curie point can be changed as a function of position by grading its composition, the transition from the ferroelectric to the paraelectric phase would be broadened with respect to the temperature. Consequently, the temperature coefficient of the dielectric constant could be lowered. In the present investigation, multi-layered $BaTiO_3$–$SrTiO_3$ composites were fabricated by using the concept of FGMs in order to lower the temperature coefficient of the dielectric constant without depressors.

2. Experimental

Specimens were prepared from commercial $BaTiO_3$ and $SrTiO_3$ (Ferro Corp., Penn Yan, NY, USA) powders. According to the data provided by the producers, the purity and average size of BT were 99.8% and 1.5 μm, respectively, and those of ST were 99.8% and

* Corresponding author. Tel.: +82-55-280-3531; fax: +82-55-280-3399.

E-mail address: jjh@kmail.kimm.re.kr (J.-H. Jeon).

0955-2219/01/$ - see front matter © 2001 Elsevier Science Ltd.
PII: S0955-2219(01)00085-1

1.3 μm. Powder slurries were made by mixing $Ba_{1-x}Sr_xTiO_3$ (in units of mol%) powder mixtures (where $x=0.02$–0.4) for 24 h in a polyethylene bottle with ethyl alcohol and zirconia balls. The dried slurry was crushed in an agate bowl and sieved to 125 μm. The mixed powder for single layer compaction was slightly pressed into rectangular shapes of 10×10×1 mm. In the case of multi-layered compaction, the prepared powders were stacked sequentially with stepwise changes in mixing ratio and pressed into 10×10×10 mm. The compacts were isostatically pressed again under 150 MPa and then sintered at 1400°C for 1 h in air.

The microstructures of the sintered specimens were observed after etching polished sections in a $50H_2O$–$45HNO_3$–5HF (vol.%) solution for 10–30 s. X-ray diffraction was performed to identify the phases present. The chemical compositions were measured by energy dispersive spectroscopy (EDS). In order to measure the dielectric properties of the multi-layered specimens, they were sliced with 0.8 mm in thickness perpendicular to the layer surface. The dielectric properties of the single- and multi-layered specimens with silver electrodes were measured by an impedance/gain-phase analyzer (HP 4194 A) at 1 kHz from −150° to 150°C.

3. Results and discussion

Fig. 1 shows XRD patterns of $Ba_{1-x}Sr_xTiO_3$ powder mixtures and the specimens sintered at 1400°C. The five patterns on the left-hand side and right-hand side of the figure come from powder mixtures and sintered samples, respectively. $BaTiO_3$ and $SrTiO_3$ peaks come out separately in the power mixtures. In the case of sintered specimens, all $BaTiO_3$ and $SrTiO_3$ peaks transformed to single BST peaks except $x=0$. This result indicates that single phase BST was formed due to a reaction between $BaTiO_3$ and $SrTiO_3$ during sintering because $BaTiO_3$ and $SrTiO_3$ produce a complete solid solution of BST at high temperatures.

Fig. 2 shows the dielectric constants of $Ba_{1-x}Sr_xTiO_3$ single layers sintered at 1400°C. The T_c moved to lower temperatures as x increased from 0 to 0.4. It has been commonly understood that T_c of BST decreases with increasing $SrTiO_3$. The maximum dielectric constant at T_c increases with increasing $SrTiO_3$ content. Fig. 3 shows the dielectric constant of a $Ba_{1-x}Sr_xTiO_3$ functionally graded material consisting of 5 layers ($x=0$, 0.1, 0.2, 0.3, 0.4), where each layer has the same thickness. Since the individual layers are arranged parallel to the applied field, the shape of the dielectric constant vs temperature peaks of the FGM looks like the summation of the dielectric constant vs temperature curves of the single layers, shown in Fig. 2.

Fig. 4 shows microstructures of the interface regions between adjacent layers of a 5-layer BST FGM sintered at 1400°C. There are noticeable boundaries in the interface regions due to a high porosity along the boundary and a large difference in grain size between

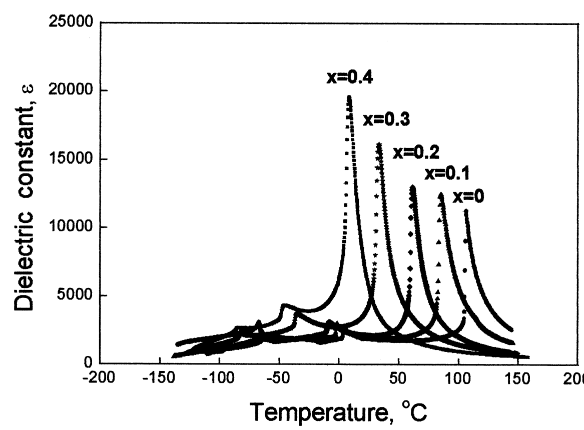

Fig. 2. Dielectric constants of $Ba_{1-x}Sr_xTiO_3$ single layers sintered at 1400°C for 1 h.

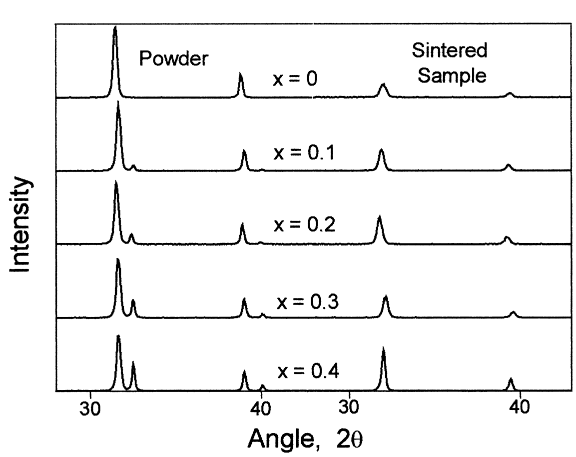

Fig. 1. XRD patterns of $Ba_{1-x}Sr_xTiO_3$ powder mixtures and specimens sintered at 1400°C for 1 h.

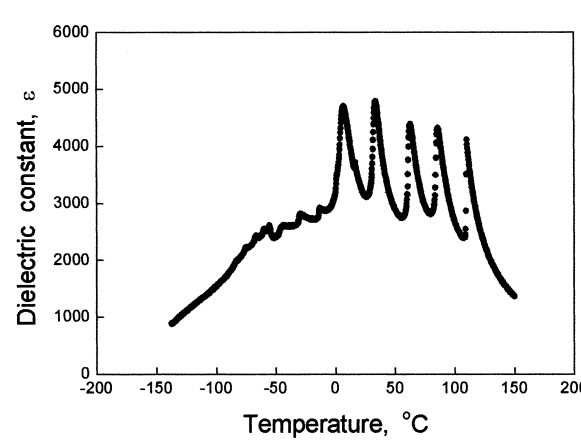

Fig. 3. Dielectric constant of a $Ba_{1-x}Sr_xTiO_3$ functionally graded material with 5 layers of same thickness sintered at 1400°C for 1 h.

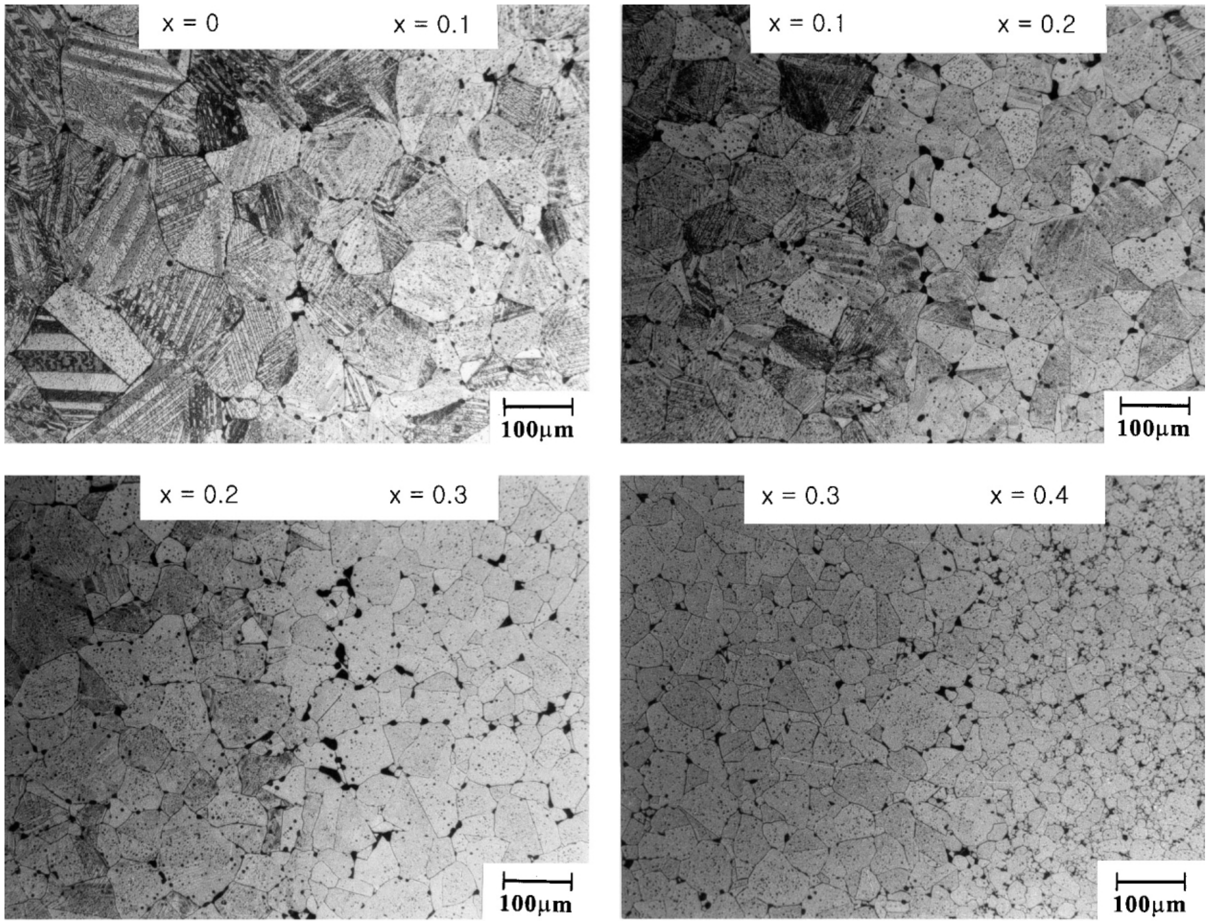

Fig. 4. Optical micrographs of the interface regions between adjacent layers of a $Ba_{1-x}Sr_xTiO_3$ FGM with five layers sintered at 1400°C.

adjacent layers. The average grain size decreased with increasing $SrTiO_3$ content.

It is well established that the maximum dielectric constant at Tc of $BaTiO_3$ decreases as the average grain size decreases.[9,10] Under the condition of same grain size, based on the results of this research, BST solid solutions have higher dielectric constant at T_c than pure $BaTiO_3$, and the height of the dielectric constant at T_c increases with increasing $SrTiO_3$ content.

Sharp peaks of the dielectric constant vs temperature, as shown in Fig. 3 suggest that a 5-layer system is not enough to exhibit a low temperature coefficient in a wide temperature range. In order to increase the linearity of the dielectric constant with temperature change, the number of layers was increased to 21 in $Ba_{1-x}Sr_xTiO_3$ (x = 0–0.4, step of 0.02) with the same thickness for each layer. The result of dielectric constant measurement was shown in Fig. 5. The linearity of the dielectric constant was remarkably improved in the range between 20° and 120°C. Fig. 6 shows a microstructure of the central area of a 21-layer BST FGM sintered at 1400°C. It is difficult to observe any microstructural boundaries between individual layers. Fig. 7 shows the results of chemical composition analysis across layers of 5- and 21-layer BST FGMs. Discontinuous jumps of Sr concentration were found at the interfaces in 5-layer FGM, but they were released in 21-layer FGM.

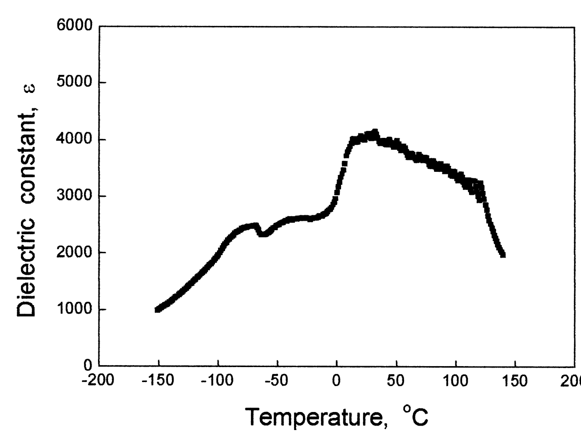

Fig. 5. Dielectric constant of a $Ba_{1-x}Sr_xTiO_3$ functionally graded material with 21 layers of same thickness sintered at 1400°C for 1 h.

Even though the 21-layer BST FGM displays a complete linear characteristic of the dielectric constant between 20° and 120°C, there is a slope due to a difference of the dielectric constant between individual layers. In order to reduce this slope, the thickness of individual layer was changed in inverse proportion to the height of the dielectric constant at the T_c of the individual layer as shown in Fig. 2. Fig. 8 shows the dielectric constant variation of a 21-layer BST FGM with controlled thickness. The slope of the dielectric constant between 20° and 120°C decreased by this control.

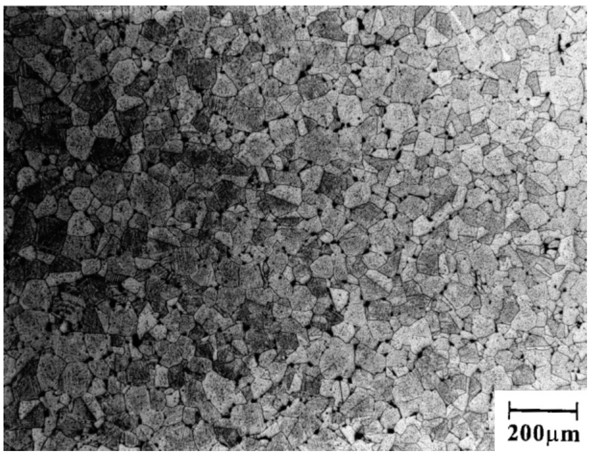

Fig. 6. An optical micrograph of the central region of a $Ba_{1-x}Sr_xTiO_3$ FGM consisting of 21 layers with the same thickness sintered at 1400°C.

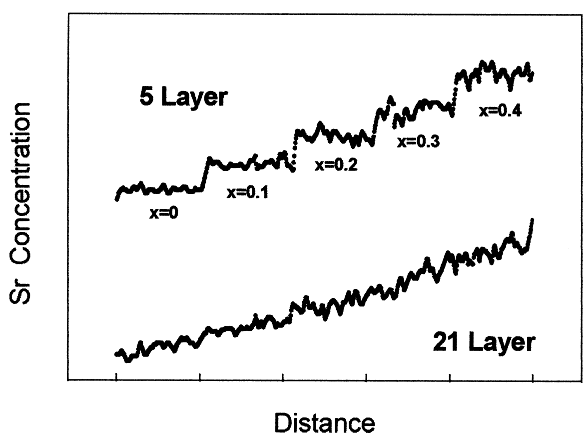

Fig. 7. Results of chemical composition analysis across layers of $Ba_{1-x}Sr_xTiO_3$ FGMs sintered at 1400°C.

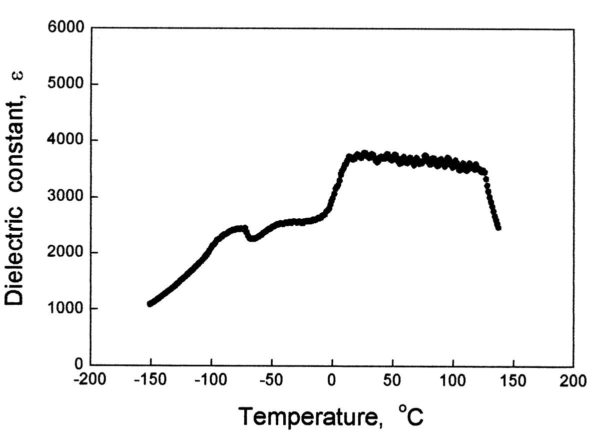

Fig. 8. Dielectric constant of a $Ba_{1-x}Sr_xTiO_3$ functionally graded material with 21 layers of controlled thickness sintered at 1400°C.

4. Conclusions

Functionally graded $Ba_{1-x}Sr_xTiO_3$ materials were fabricated by a conventional powder processing. The average grain size and the T_c of $Ba_{1-x}Sr_xTiO_3$ materials decreased with the rise of $SrTiO_3$ content. Microstructural and chemical discontinuity at the interfaces of 5-layer FGM display sharp peaks of the dielectric constant at the T_c of the individual layer. A 21-layer $Ba_{1-x}Sr_xTiO_3$ FGM with controlled thickness shows a flat characteristic of the dielectric constant in a wide temperature range.

Acknowledgements

The authors would like to thank Dr. S.-Y. Jeong, Mr. S.-Y. Koo and Mrs. B.-J. Koo for their effort to measure the dielectric constant of BST materials.

References

1. Mortensen, A. and Suresh, S., Functionally graded metals and metal–ceramic composites: part 1. Processing. *Int. Mater. Rev.*, 1995, **40**(6), 239–265.
2. Neubrand, A. and Rödel, J., Gradient materials: an overview of a novel concept. *Z. Metallkd.*, 1997, **88**(5), 358–371.
3. Wu, C. C. M., Kahn, M. and Moy, W., Piezoelectric ceramics with functional gradient: a new application in material design. *J. Am. Ceram. Soc.*, 1996, **97**(3), 809–812.
4. Koizumi, M., Recent progress in FGMs research in Japan. *Int. J. SHS*, 1997, **6**(3), 295–306.
5. Chu, C., Zhu, J., Yin, Z. and Wang, S., Hydroxyapatite-Ti functionally graded biomaterial fabricated by powder metallurgy. *Mater. Sci. Eng.*, 1999, **A271**, 95–100.
6. Herbert, J. H., *Ceramic Dielectrics and Capacitors.* Gordon and Breach Science Publishers, New York, 1985 pp. 128–187.
7. Goodman, G., Ceramic capacitor materials. In *Ceramic Materials for Electronics*, ed. R. C. Buchanan. Marcel Dekker, New York, 1986, pp. 79–138.
8. Kahn, M., Burks, D. P., Burn, I. and Schulze, W. A., Ceramic capacitor technology. In *Electronic Ceramics*, ed. L. M. Levinson. Marcel Dekker, New York, 1988, pp. 191–274.
9. Yamaji, A., Enomoto, Y., Kinoshita, K. and Murakami, T., Preparation, characterization, and properties of Dy-doped small-grained $BaTiO_3$ ceramics. *J. Am. Ceram. Soc.*, 1977, **60**(3–4), 97–101.
10. Arlt, G., Hennings, D. and de With, G., Dielectric properties of fine-grained barium titanate ceramics. *J. Appl. Phys.*, 1985, **58**(4), 1619–1625.