Low-Temperature Sintering of Barium Calcium Zirconium Titanate Lead-Free Piezoelectric Ceramics

John G. Fisher[†], Dae-Gi Lee, Jeong-Hyeon Oh, Ha-Nul Kim, Dieu Nguyen, Jee-Hoon Kim, Jong-Sook Lee, and Ho-Yong Lee*

School of Materials Science and Engineering, Chonnam National University, Gwangju 500-757, Republic of Korea

**Department of Advanced Materials Engineering, Sun Moon University, Chungnam 336-708, Republic of Korea*

(Received November 1, 2012; Revised January 30, 2013; Accepted February 1, 2013)

ABSTRACT

The need for lead-free piezoceramics has caused a renewal of interest in BaTiO₃-based systems. Recently, it was found that ceramics in the (Ba,Ca)(Zr,Ti)O₃ system have properties comparable to those of Pb(Zr,Ti)O₃. However, these ceramics require rather high sintering temperatures of 1450-1550°C. In this work, the effect of TiO₂ and CuO addition on the sintering behavior, microstructure, dielectric and piezoelectric properties of (Ba_{0.85}Ca_{0.15})(Zr_{0.1}Ti_{0.9})O₃ (BCTZ) ceramics will be discussed. BCTZ ceramics were prepared by the mixed oxide route and 1 mol % of TiO₂ or CuO was added. Undoped and doped ceramics were sintered at 1350°C for 1-5 h. CuO was found to be a very effective sintering aid, with samples sintered for 1 h at 1350°C having a bulk density of 95% theoretical density; however the piezoelectric properties were greatly reduced, probably due to the small grain size.

Key words : Lead-free Piezoceramics, BaTiO₃, Sintering, Dielectric Properties, Piezoelectric Properties

1. Introduction

BaTiO₃ was used for acoustic and ultrasonic generation and detection but its low Curie point of ~ 120°C meant that it was quickly superseded by Pb(Zr,Ti)O₃ (PZT).¹⁾ In recent years, the need for lead-free replacements for PZT has caused a renewal of interest in BaTiO₃-based ceramics. Recently, Liu and Ren found that ceramics in the (Ba, Ca)(Zr,Ti)O₃ system have piezoelectric properties comparable to those of Pb(Zr,Ti)O₃, although the Curie point is even lower than that of BaTiO₃.²⁾ The high piezoelectric properties were obtained from compositions close to a triple point between rhombohedral, tetragonal and cubic phases. Unfortunately, these ceramics require rather high sintering temperatures of 1450-1550°C.^{3,4)} Lowering the sintering temperature would not only reduce production costs, but also raise the possibility of preparing thick film or multilayer co-fired actuators. As of yet, little work has been done on the addition of sintering aids to this system. Chen *et al.* found that addition of CuO could lower the sintering temperature to 1400°C while retaining good piezoelectric properties.⁵⁾ In the present work, the effect of TiO₂ and CuO addition on the sintering behavior, microstructure, dielectric and piezoelectric properties of (Ba_{0.85}Ca_{0.15})(Zr_{0.1}Ti_{0.9})O₃ (BCTZ) ceramics will be discussed.

2. Experimental Procedure

Powders of composition (Ba_{0.85}Ca_{0.15})(Zr_{0.1}Ti_{0.9})O₃ were prepared using the mixed oxide method. Appropriate amounts of BaCO₃ (99.8%, Alfa Aesar), CaCO₃ (99.5%, Alfa Aesar), ZrO₂ (99.5%, Alfa Aesar) and TiO₂ (99.8%, Alfa Aesar) were mixed by ball milling for 24 h in ethanol using a polypropylene jar and ZrO₂ milling media. After ball-milling, the ethanol was evaporated off, the powder crushed in an agate mortar and pestle and sieved to pass a 180 μm sieve. Powders were calcined in air in a closed high purity alumina crucible. Calcination temperatures of 1250°C, 1350°C and 1450°C were used. Calcination time was 5 or 10 h. Heating and cooling rates were 5°C.min⁻¹. Calcined powders were examined using X-ray diffraction (XRD, X'Pert PRO, PANalytical, Almelo, the Netherlands). Additions of 1 mol % of TiO₂ or CuO (99.7%, Alfa Aesar) were made to the powder that had been calcined at 1450°C for 10 h and the doped powders were ball-milled, crushed and sieved as before. An undoped powder was also ball-milled.

To prepare samples for sintering, 0.5 g of powder was pressed by hand in a 10 mm diameter steel die. The samples were then cold isostatically pressed at 1500 kg/cm² (147 MPa). Samples were placed on a bed of BaZrO₃ powder in a double alumina crucible with lids and sintered at 1350°C for periods of 1-5 h. Heating and cooling rates were 5°C.min⁻¹. Sample density was measured by the bulk method (sample weights and dimensions). The structure of samples sintered for 5 h was examined using powder XRD. A scan range of 10-80 degrees 2θ, a step size of 0.013° and a scan speed of 3.5°.min⁻¹ was used. Samples sintered for 5 h were sectioned

[†]Corresponding author : John G. Fisher
E-mail : johnfisher@jnu.ac.kr
Tel : +82-62-530-1702 Fax : +82-62-530-1699

vertically using a low speed diamond wheel saw, polished to a 1 mm finished and thermally etched at 1250°C for 1 h. Samples were Pt coated and the microstructure examined by scanning electron microscopy (SEM, JEOL JSM-7500F, Tokyo, Japan).

For measurement of Polarization – Electric Field hysteresis loops, silver paste was applied and fired onto both sides of the samples. P-E loops were measured at room temperature using a Sawyer Tower circuit (RT66B combined with 4KV HVI, Radiant Technologies Inc. USA). For measurement of dielectric and piezoelectric properties, Au electrodes were sputtered on both sides of the samples. The samples were poled in silicone oil at 25°C under a dc field of 3 kV/mm. The dielectric and piezoelectric properties were measured using an impedance analyzer (Agilent 4294A Precision Impedance Analyzer, USA). d_{33} was measured by a d_{33} meter (APC YE2730A d_{33} Meter, APC International Ltd., USA).

3. Results

X-ray diffraction traces of the calcined powders are shown in Fig. 1. All of the patterns can be indexed using JCPDS card # 01-086-1570 for rhombohedral BaTiO_3 , space group $R3m$. The powder calcined at 1250°C for 5 h contains several secondary phases. Peaks belonging to monoclinic ZrO_2 (JCPDS card # 882390), cubic ZrO_2 (JCPDS card # 98-010-5553) and Ti_2O_3 (JCPDS card # 894746) are present. Repeated ball milling and calcination at 1250°C was not effective in removing secondary phases. Increasing the calcination temperature and time leads to a reduction in the amount of secondary phases. However, even after calcination at 1450°C for 10 h, a small amount of cubic ZrO_2 , not easily visible in Fig. 1, remained. Accordingly the powder calcined at 1450°C for 10 h was used for subsequent experiments. Previous workers have also noted the difficulty in preparing single-phase BCTZ powders by the mixed-oxide method.⁴⁾

The bulk density of BCTZ samples sintered at 1350°C for 1-5 h is shown in Fig. 2. For the theoretical density, the cal-

culated density of 5.687 g/cm³ for the tetragonal phase was used.⁴⁾ The density of the undoped samples sintered for 1 h is very low, only 62% theoretical density. Increasing the sintering time causes a small increase in density to 66% theoretical density. For the samples doped with 1 mol% TiO_2 , the density after 1 h of sintering is the same as for the undoped sample. Further sintering leads to an increase in density to 75% theoretical density. Addition of 1 mol% of CuO leads to a dramatic increase in density to 95% theoretical density after only 1 h of sintering. Further sintering leads to a decrease in density.

XRD traces of the samples sintered at 1350°C for 5 h are shown in Fig. 3(a). A magnified view of the region between 55–80° 2 θ is shown in Fig. 3(b). No secondary phases are visible in any of the samples. The undoped sample consists of a rhombohedral phase which can be indexed using JCPDS card # 01-086-1570 for rhombohedral BaTiO_3 . Split or broad peaks due to the rhombohedral peak splitting are visible at 66° and 75°. Addition of 1 mol% TiO_2 appears to cause a reduction in the rhombohedral peak splitting at 66°. The 1 mol % CuO doped sample can be indexed using JCPDS card # 89-2475 for cubic BaTiO_3 . The satellite peaks to the right of the main peaks are due to $K\alpha_2$ splitting. Unit cell parameters were calculated by the least-squares method⁶⁾ using the computer program MDI Jade 6.5 (Materials Data Inc., California, USA) and are given in Table 1. Addition of TiO_2 causes a reduction in the rhombohedral distortion and addition of CuO causes the structure to change to cubic.

Fig. 4(a) and (b) shows SEM micrographs of undoped and 1 mol % TiO_2 doped samples sintered at 1350°C for 5 h. The undoped sample has equiaxed rounded grains about 0.5–2 μm in diameter. Considerable porosity is visible. The sample

Fig. 1. X-ray diffraction traces of calcined $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ powders.

Fig. 2. Bulk density of $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ ceramics sintered at 1350°C.

Table 1. Unit Cell Parameters of $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ Ceramics Sintered at 1350°C for 5 h

Sample	a (Å)	β (°)
Undoped	4.00356 (0.000245)	89.8638 (0.0064)
1 mol% TiO_2 doped	3.99893 (0.000254)	89.9238 (0.0055)
1 mol% CuO doped	4.0061 (0.000139)	90

Fig. 3. (a) X-ray diffraction traces of $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ ceramics sintered at 1350°C for 5 h. (b) Magnified view of the region between 55-80° 2θ.

doped with 1 mol% TiO₂ has smaller grains and smaller pores. Fig. 4(c)-(e) shows micrographs of the 1 mol% CuO doped samples sintered at 1350°C for 1, 3 and 5 h. The

1 mol% CuO doped samples have very little porosity. The sample sintered for 1 h has grains 1-2 μm in diameter. The grain size has increased to 2-3 μm in diameter for the sample sintered for 3 h, with further sintering causing no further grain growth. The grain shape becomes progressively more cubic as sintering time increases (Fig. 4(e)). Backscattered electron imaging shows that the CuO doped sample sintered for 5 h is single phase (Fig. 4(f)).

Due to their low density, the electrical properties of the undoped and 1 mol% TiO₂ doped samples were not measured. The *P-E* hysteresis loops for the 1 mol% CuO doped BCTZ ceramic sintered at 1350°C for 1 h are shown in Fig. 5. The legend indicates the maximum electric field for each loop. The loops are narrow and have very shallow slopes, with low values of P_m , P_r and E_c . The slope and value of P_m for the loop with a maximum electric field of 2500 V/mm are much higher than that of the other loops. The specimen broke into pieces at electric field of 3000 V/mm. All of the loops have a pinched appearance; this is more clearly seen in Fig. 5(b), where the 2500 V/mm curve has been removed.

The variation of relative permittivity and loss tangent with temperature for the 1 mol% CuO doped BCTZ ceramic sintered at 1350°C for 1 h is shown in Fig. 6. The black arrows show the direction of increasing measurement frequency in the range 0.1-10 kHz. The sample shows a broad peak in relative permittivity with a maximum at 53°C (Fig. 6(a)). There is no change in the peak temperature with measurement frequency. The value of relative permittivity decreases slightly in the frequency range 0.1-10 kHz and then increases again. The sample had almost identical values of ϵ_r at 1 kHz and 100 kHz. The sample shows a broad peak in loss tangent at 40°C, again with no dispersion (Fig. 6(b)). The variation of loss tangent with frequency is identical to that of ϵ_r . Dielectric, ferroelectric and piezoelectric properties of the sample are given in Table 2. Also shown are the values of Chen *et al.* for a BCTZ sample doped with 1 mol% CuO and sintered at 1400°C for 2 h.

Fig. 4. SEM micrographs of: (a) undoped; (b) 1 mol % TiO₂ doped $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ ceramics sintered at 1350°C for 1 h and 1 mol% CuO doped $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ ceramics sintered at 1350°C for: (c) 1 h, (d) 3 h, and (e) 5 h. Fig. 4(f) is a backscattered electron image of the sample in Fig. 4(e).

Fig. 5. (a) P - E hysteresis loops of for 1 mol% CuO doped $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ ceramic sintered at 1350°C for 1 h. (b) hysteresis loops in electric field range 500-2000 V/mm.

Fig. 6. Variation of (a) relative permittivity and (b) loss tangent with temperature for 1 mol% CuO doped $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ ceramic sintered at 1350°C for 1 h.

Table 2. Piezoelectric Properties of 1 mol% CuO Doped $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ Ceramic Sintered at 1350°C for 1 h

ϵ_r at 1 kHz and 25°C	$\tan \delta$ at 1 kHz and 25°C	T max ϵ_r	P_m ($\mu\text{C}/\text{cm}^2$)	P_r ($\mu\text{C}/\text{cm}^2$)	E_c (V/mm)	d_{33} (pC/N)	k_t	k_p	ref.
4450	0.007	53°C	9.88	0.64	111	72	0.112	0.113	This work
~ 2850	~ 0.008	$\sim 88^\circ\text{C}$	~ 15	6	~ 230	350	-	~ 0.4	5

4. Discussion

The undoped BCTZ samples showed very poor densification, as expected at the relatively low sintering temperature of 1350°C . According to the BaO-TiO₂ phase diagram, the solid solubility of TiO₂ in BaTiO₃ is very limited at the sintering temperature.^{7,8)} The excess titanium reacts with BaTiO₃ to form a liquid phase at temperatures $> 1332^\circ\text{C}$, which may promote sintering. However, substitution of Ca and Zr into BaTiO₃ may increase the solidus temperature, preventing formation of a liquid phase.^{9,10)} Hence the effect of TiO₂ addition on the densification behavior is limited. If TiO₂ forms a limited solid solution with BCTZ, then A-site and oxygen vacancies will be required to maintain site and charge balance. These vacancies will increase bulk diffusion rates, which could account for the increased density.¹¹⁾

CuO melts at 1326°C and forms low melting point eutec-

tics with BaO,¹²⁾ TiO₂,¹³⁾ and ZrO₂.¹⁴⁾ CuO-based melts are known to be highly wetting of BaZrO₃ ceramics.^{15,16)} Therefore, it is expected that the CuO will react with BCTZ to form a liquid phase which then wets the particle surfaces and promotes sintering by either contact flattening or pore filling.¹¹⁾ It was previously found that CuO addition could lower the sintering temperature of BCTZ to 1400°C ⁵⁾; the present work shows that the sintering temperature can be lowered further to 1350°C while still maintaining high density.

If TiO₂ forms a limited solid solution with BCTZ, then A-site and oxygen vacancies will be required to maintain site and charge balance. This could cause the decrease in the unit cell parameter and the rhombohedral distortion seen in the XRD results (Fig. 3(b) and Table 1). For a coordination number of 6, Cu²⁺ has an ionic radius of 0.073 nm. Ti⁴⁺ and Zr⁴⁺ have ionic radii of 0.061 and 0.072 nm respectively.¹⁷⁾

Therefore Cu^{2+} is likely to substitute for Ti^{4+} or Zr^{4+} ions in the perovskite lattice. This could cause the slight increase in the unit cell parameter and the change in phase from rhombohedral to cubic, as seen in the XRD results in Fig. 3 and Table 1.

The ϵ_r vs. T curve of the CuO doped BCTZ sample shows a single broad peak with a temperature of maximum permittivity of 53°C (Fig. 6). No peak corresponding to a rhombohedral - tetragonal phase change is present, which agrees well with the XRD results (Fig. 3). In the work of Chen *et al.*, CuO doping appears to change the phase from tetragonal to rhombohedral or cubic, reduces the temperature of maximum permittivity and broadens the ϵ_r vs. T peak.⁵⁾ Hao *et al.* found that samples with small grain size exhibited more relaxor-like behaviour, with broad ϵ_r vs. T peaks.¹⁸⁾ Similar to the work of Hao *et al.*, our CuO doped BCTZ sample with a small grain size of $\sim 1\text{-}2\ \mu\text{m}$ shows a broad ϵ_r vs. T peak; however there is little dispersion with measurement frequency in our sample. The narrow P - E hysteresis loops indicate that the sample is a relaxor.¹⁹⁾ The pinching of the P - E hysteresis loops is likely caused by the interaction of a non-polar phase at temperatures close to the temperature of maximum permittivity.²⁰⁾ The hysteresis loop at $2500\ \text{V/mm}$ is less pinched and exhibits abruptly higher polarization, which may be interpreted as reversal of the spontaneous polarization of the material.¹⁾ The mechanical fracture at the higher field of $3000\ \text{V/mm}$ also supports the large electrostriction or reverse piezoelectric effect with increased polarization. The dielectric and ferroelectric properties of the sample are somewhat inconsistent. The narrow, pinched P - E loops, the small values of P_r and E_c , and the broad ϵ_r vs. T peak suggest relaxor behavior, but the ϵ_r vs. T peak shows no dispersion with measuring frequency. The reason for this behavior is not yet clear. The relaxor-like behavior of our sample is likely due to a combination of small grain size and the effect of CuO doping.^{5, 18)} Although the XRD results show a cubic unit cell, the existence of a narrow P - E loop indicates that the unit cell is pseudo-cubic.

In the present work, the piezoelectric properties of the CuO doped BCTZ samples were found to be poor. The poor properties may be due to the small grain size of $\sim 1\text{-}2\ \mu\text{m}$ (Fig. 4(c)). Grain boundaries pin domain walls, making it harder to pole the ceramics. A large fraction of the piezoelectric response comes from domain wall contributions i.e. motion of domain walls.²¹⁾ The contribution of domain wall motion to piezoelectric properties is reduced in fine-grained ceramics, reducing their piezoelectric properties.^{22, 23)} Hao *et al.* recently studied the effect of grain size on the electrical properties of BCTZ ceramics and found a marked decrease in piezoelectric properties as the grain size decreased below $10\ \mu\text{m}$.¹⁸⁾ The CuO doped samples of Chen *et al.* also had a grain size between $5\text{-}10\ \mu\text{m}$, even when sintered at 1350°C .⁵⁾ The smaller grain size in the present work is probably due to the larger content of liquid phase sintering aid, $1\ \text{mol}\ \%$ CuO as opposed to $0.5\ \text{mol}\ \%$ CuO in the work of Chen *et al.*. The increased volume of liquid phase at the solid/liquid inter-

faces increases diffusion distances between grains, reducing grain growth rates.²⁴⁾ As a consequence, the samples of Chen *et al.* had superior piezoelectric properties to the samples in the present work.

5. Conclusion

The effect of $1\ \text{mol}\ \%$ TiO_2 or CuO addition on the sintering behavior, microstructure and electrical properties of $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ lead-free piezoelectric ceramics has been studied. Addition of TiO_2 caused only a small improvement in the density of samples sintered at 1350°C . Addition of $1\ \text{mol}\ \%$ CuO greatly improved densification, with samples reaching 95% theoretical density after sintering for 1 h at 1350°C . TiO_2 addition caused a decrease in the rhombohedral distortion of the unit cell, whereas addition of CuO caused the structure of $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ to change from rhombohedral to pseudo-cubic. All of the sintered samples have grain sizes $1\text{-}3\ \mu\text{m}$. The combination of CuO doping and small grain size caused the material to show relaxor-like behavior, with a broad ϵ_r vs. T peak and narrow, pinched P - E hysteresis loops. The piezoelectric properties of the CuO doped samples were poor, probably due to the small grain size.

Acknowledgment

This work was funded by Chonnam National University, 2012 and by the Fusion Research Program for Green Technologies through the National Research Foundation of Korea (NRF), funded by the Ministry of Education, Science and Technology (Project No. 2011-0019304). The authors would like to thank Cheol Kim and Seong-Cheon Byeon for operating the XRD and SEM respectively.

REFERENCES

1. A. J. Moulson and J. M. Herbert, "Chapter 6: Piezoelectric Ceramics," p. 339-410, *Electroceramics*, 2nd Edition, Chichester, Wiley, 2003.
2. W. Liu and X. Ren, "Large Piezoelectric Effect in Pb-Free Ceramics," *Phys. Rev. Lett.*, **103** 257602 1-4 (2009).
3. W. Li, Z. Xu, R. Chu, P. Fu, and G. Zang, "Piezoelectric and Dielectric Properties of $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Ti}_{0.95}\text{Zr}_{0.05})\text{O}_3$ Lead-Free Ceramics," *J. Am. Ceram. Soc.*, **93** 2942-44 (2010).
4. P. Wang P, Y. Li, and Y. Lu, "Enhanced Piezoelectric Properties of $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Ti}_{0.9}\text{Zr}_{0.1})\text{O}_3$ Lead-free Ceramics by Optimizing Calcination and Sintering Temperature," *J. Eur. Ceram. Soc.*, **31**, 2005-12 (2011).
5. T. Chen, T. Zhang, G. Wang, J. Zhou, J. Zhang, and Y. Liu, "Effect of CuO on the Microstructure and Electrical Properties of $\text{Ba}_{0.85}\text{Ca}_{0.15}\text{Ti}_{0.90}\text{Zr}_{0.10}\text{O}_3$ Piezoceramics," *J. Mater. Sci.*, **47** 4612-19 (2012).
6. B. D. Cullity and S. R. Stock, "Chapter 13: Precise Parameter Measurements," p. 363-84, *Elements of X-Ray Diffraction*, Third Edition, Prentice-Hall, New Jersey, 2001.
7. D. E. Rase and R. Roy, "Phase Equilibria in the System

- BaO-TiO₂,” *J. Am. Ceram. Soc.*, **38** 102-13 (1955).
8. K. W. Kirby and B. A. Wechsler, “Phase Relations in the Barium Titanate-Titanium Oxide System,” *J. Am. Ceram. Soc.*, **74** 1841-47 (1991).
 9. G. H. Jonker and W. Kwestroo, “The Ternary Systems BaO-TiO₂-SnO₂ and BaO-TiO₂-ZrO₂,” *J. Am. Ceram. Soc.*, **41** 390-94 (1958).
 10. W. Kwestroo and H. A. M. Paping, “The Systems BaO-SrO-TiO₂, BaO-CaO-TiO₂, and SrO-CaO-TiO₂,” *J. Am. Ceram. Soc.*, **42** 292-99 (1959).
 11. S. J. L. Kang, “Chapter 16: Densification Models and Theories,” p. 227-47, *Sintering: Densification, Grain Growth & Microstructure*, Elsevier, Oxford, 2005.
 12. I. Horsak, J. Sestak, and B. Stepanek, “Simple Computer Program Used for the Calculation of Stable and Metastable Phase Boundary Lines for the Pseudobinary Edges in the BaO-CuO_x-YO_{1.5} System,” *Thermochim. Acta*, **234** 233-43 (1994).
 13. F. H. Lu, F. X. Fang, and Y. S. Chen, “Eutectic Reaction Between Copper Oxide and Titanium Dioxide,” *J. Eur. Ceram. Soc.*, **21** 1093-99 (2001).
 14. A. M. M. Gadalla and J. White, “Equilibrium Relationship in the System CuO-Cu₂O-ZrO₂,” *Trans. Br. Ceram. Soc.*, **65** 383-90 (1966).
 15. J. C. Schmidt, A. Tigges, and G. J. Schmitz, “Synthesis of Polycrystalline BaZrO₃ Coatings,” *Mater. Sci. Eng. B*, **53** 115-18 (1998).
 16. A. L. Vinokurov, O. A. Shiyakhtin, Y. J. Oh, A. V. Orlov, and Y. D. Tretyakov, “Comparative Analysis of Barrier Properties of BaCeO₃ Ceramics,” *Supercond. Sci. Technol.*, **16** 416-21 (2003).
 17. R. D. Shannon, “Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides,” *Acta Cryst.*, **A32** 751-67 (1976).
 18. J. Hao, W. Bai, W. Li, and J. Zhai, “Correlation Between the Microstructure and Electrical Properties in High-Performance (Ba_{0.85}Ca_{0.15})(Zr_{0.1}Ti_{0.9})O₃ Lead-Free Piezoelectric Ceramics,” *J. Am. Ceram. Soc.*, **95** 1998-2006 (2012).
 19. Y. Guo, K. Kakimoto, and H. Ohsato, “Ferroelectric-Relaxor Behavior of (Na_{0.5}K_{0.5})NbO₃-Based Ceramics,” *J. Phys. Chem. Solids*, **65** 1831-35 (2004).
 20. W. Jo, T. Granzow, E. Aulbach, J. Rodel, and D. Damjanovic, “Origin of the Large Strain Response in (K_{0.5}Na_{0.5})NbO₃-modified (Bi_{0.5}Na_{0.5})TiO₃-BaTiO₃ Lead-free Piezoceramics,” *J. Appl. Phys.*, **105** 094102 1-5 (2009).
 21. Q. M. Zhang, H. Wang, N. Kim, and L. E. Cross, “Direct Evaluation of Domain-Wall and Intrinsic Contributions to the Dielectric and Piezoelectric Response and their Temperature Dependence on Lead Zirconate-titanate Ceramics,” *J. Appl. Phys.*, **75** 454-59 (1994).
 22. M. Demartin and D. Damjanovic, “Dependence of the Direct Piezoelectric Effect in Coarse and Fine Grain Barium Titanate Ceramics on Dynamic and Static Pressure,” *Appl. Phys. Lett.*, **68** 3046-48 (1996).
 23. C. A. Randall, N. Kim, J. P. Kucera, W. Cao, and T. R. Shrout, “Intrinsic and Extrinsic Size Effects in Fine-Grained Morphotropic-Phase-Boundary Lead Zirconate Titanate Ceramics,” *J. Am. Ceram. Soc.*, **81** 677-88 (1998).
 24. J. D. Powers and A. M. Glaeser, “Grain Boundary Migration in Ceramics,” *Interface Sci.*, **6** 23-39 (1998).