Enhanced piezoelectric properties of $(\text{Ba}_{0.3}\text{Bi}_{0.7})(\text{Mg}_{0.05}\text{Fe}_{0.6}\text{Ti}_{0.35})\text{O}_3$ piezoelectric ceramics with high Curie temperature

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$(\text{Ba}_{0.3}\text{Bi}_{0.7})(\text{Mg}_{0.05}\text{Fe}_{0.6}\text{Ti}_{0.35})\text{O}_3$ ceramics were either doped with vanadium or sintered in calcined powder with the same composition. Compared to an undoped ceramic sintered without the calcined powder, both ceramics showed reduced leakage current densities (lower than $1 \times 10^{-7} \text{ A/cm}^2$) and absence of dielectric relaxation behaviors observed in frequency- and temperature-dependent dielectric measurements. The Curie temperatures of both samples were higher than 460°C . The maximum field-induced strain over the applied field, $S_{\text{max}}/E_{\text{max}}$, of 366 pm/V of the undoped ceramic sintered without the calcined powder increased to 455 and 799 pm/V for the V-doped ceramics and the ceramics sintered with the calcined powder, respectively. The increase was related to a reduced concentration of bismuth vacancy–oxygen vacancy defect dipoles.

Keywords: Piezoelectrics; domain structure; lead-free; high Curie temperature; dopant.

1. Introduction

$\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT) has been used for electromechanical applications owing to the large piezoelectric properties over a wide temperature range.¹ Lead is, however, a toxic element, and therefore lead-free piezoelectrics have extensively been studied.^{2–12} To date, no piezoelectric material with the piezoelectric response and Curie temperature simultaneously comparable to those of PZT was found.¹³ The large piezoelectric responses of PZT are attributed to the morphotropic phase boundary (MPB), which separates tetragonal and rhombohedral phases. There are several reported studies to understand the origin of the large response at MPB. A theoretical study explained that the increased response was attributed to increased numbers of polarizable directions as a result of coexistence of the two phases.¹⁴ Recent transmission electron microscopy studies showed nanosized, fine domains at MPB.¹⁵ The motion of the fine domains by the electric field was observed, which was suggested to lead the large piezoelectric properties.¹⁶ Since nanosized domains are also reported for solid-solutions of relaxors $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ and $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ and ferroelectric PbTiO_3 with large piezoelectric properties,^{17,18} they may be associated with the increased piezoelectric response of PZT at MPB.

Microstructure and electric properties have been studied for lead-free piezoelectric solid-solutions of relaxor-like $(1-x)\text{BaTiO}_3-x\text{Bi}(\text{Mg}_{1/2}\text{Ti}_{1/2})\text{O}_3$ (BT–BMT) with the dielectric maximum temperature maximized to 360°C at $x = 0.5$ ^{19,20} and ferroelectric BiFeO_3 (BF) with the Curie temperature of $\sim 830^\circ\text{C}$.²¹ An early work showed nanodomains within the BTBMT–BF system.^{22,23} The domain structure of the $0.3\text{BT}–0.1\text{BMT}–0.6\text{BF}$ ($= (\text{Ba}_{0.3}\text{Bi}_{0.7})(\text{Mg}_{0.05}\text{Fe}_{0.6}\text{Ti}_{0.35})\text{O}_3$)

ceramics mainly consisted of nanodomains with a small amount of large, ferroelectric domains (macrodomains).²² The dielectric displacement–electric field loop was ferroelectric, but the loop appeared round and leaky. When the sample was doped with an acceptor of Mn, the lossy response was suppressed, although the piezoelectric and dielectric properties were reduced.²⁴

The aim of this study is to develop $(\text{Ba}_{0.3}\text{Bi}_{0.7})(\text{Mg}_{0.05}\text{Fe}_{0.6}\text{Ti}_{0.35})\text{O}_3$ ceramics with reduced leakage current and without sacrificing the properties. To this end, effect of a donor doping and a sintering condition was investigated. Donor doping is known to increase the resistivity of Bi-based ferroelectrics of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$,^{25,26} and vanadium²⁷ was selected in this study. Sintering a Bi-based sample in a bismuth-rich atmosphere would suppress the Bi_2O_3 evaporation, as reported for a lead-based system.²⁸ To determine if this is true for the $(\text{Ba}_{0.3}\text{Bi}_{0.7})(\text{Mg}_{0.05}\text{Fe}_{0.6}\text{Ti}_{0.35})\text{O}_3$ ceramics, the compacts were sintered either in a closed crucible fully filled with the calcined powder with the same composition or in a closed, empty crucible.

2. Experimental Procedure

Three different samples were studied: undoped $(\text{Ba}_{0.3}\text{Bi}_{0.7})(\text{Mg}_{0.05}\text{Fe}_{0.6}\text{Ti}_{0.35})\text{O}_3$ ceramics sintered in a closed crucible without a cover calcined powder with the same composition (undoped sample), undoped $(\text{Ba}_{0.3}\text{Bi}_{0.7})(\text{Mg}_{0.05}\text{Fe}_{0.6}\text{Ti}_{0.35})\text{O}_3$ ceramics sintered in a closed crucible fully filled with the cover calcined powder (embedded sample), and V-doped ceramics with the composition of $(\text{Ba}_{0.3}\text{Bi}_{0.6+0.1(1-y/6)})(\text{Mg}_{0.05}\text{Fe}_{0.6}\text{Ti}_{0.3+0.05(1-y)/2\text{V}y/2})\text{O}_3$ with $y = 0.02$ sintered in

the closed crucible without the cover calcined powder (V-doped sample). The crucible is made of Al_2O_3 (99%) with a size of $\varphi 36 \text{ mm} \times 30 \text{ mm}$. A lid made of the same alumina was placed on the crucible. The samples were prepared by a solid-state synthesis. Powders of BaTiO_3 (Sakai Chemical, BT01), Bi_2O_3 (99.999%, Rare Metallic), MgO (99.9%, Rare Metallic), TiO_2 (Ishihara Sangyo, MPT-851), $\alpha\text{-Fe}_2\text{O}_3$ (99.99%, Rare Metallic), and V_2O_5 (99.0%, Kanto Chemical) were weighed and ball-milled with zirconia balls and ethanol for 16 h. After drying at 80°C , the powders were ground and calcined at 800°C for 6 h in a closed crucible. The calcined powders were again ground, and then the crystal structures were examined by X-ray diffraction (XRD; Rigaku, RINT2000) with Cu K α radiation. They were again ball-milled for 16 h, followed by drying. After adding a binder, the powders were uniaxially pressed at 250 MPa to disc compacts. The binder was removed at 600°C . The compacts were sintered at 1000°C for 2 h at a heating rate of 300°C/h in the crucible with or without the calcined powder. The densities of the samples were measured by an Archimedes method. For crystal structure characterization, polished surfaces of the sintered samples were examined by the XRD analysis.

For electric characterizations, the samples were polished down to 0.4 mm in thickness. Gold electrodes were formed on both surfaces by sputtering, and the samples were heated at 300°C for 10 min to improve the adhesion. The samples were sawed into a size of $4 \times 1.5 \times 0.4 \text{ mm}^3$. The room temperature dielectric constant and loss were measured at frequencies from 40 Hz to 1 MHz using an impedance analyzer (HP4294A, Agilent). Temperature dependence of the dielectric properties was measured at 10 kHz, 100 kHz, and 1 MHz using a LCR meter (6440B, Wayne Kerr Electronics), with increasing temperature from room temperature to $500\text{--}550^\circ\text{C}$ at a heating rate of 3°C/min . The dielectric displacement–electric field loops were measured by a ferroelectric characteristics evaluation system (FCE-3, Toyo Corporation). The strain–electric field curves were measured using a strain measuring system (Model JP005-SE, Kitamoto Denshi) with a displacement meter (Millitron 1202 IC, Mahr).

3. Results and Discussion

3.1. Physical and structural properties

Figure 1 shows the XRD patterns of the sintered samples. Only the perovskite phase was observed. The crystal structures of all the samples were a pseudo-cubic, and this is consistent with previous studies.^{22,24} The pseudo-cubic lattice parameter was calculated by a least-square fit of selected XRD peaks. The pseudo-cubic lattice parameter for the samples was $0.3997(8) \pm 0.0000(3) \text{ nm}$ and did not change among the samples. Here, the lattice constant of the V-doped sample was the same as that of the undoped and embedded samples,

Fig. 1. The XRD patterns of the undoped, V-doped, and embedded samples.

probably because the amount of the V dopant was small, which was consistent with previous study.²⁷ The densities of the samples were 95–96% of the theoretical values.

3.2. Leakage and dielectric properties

The leakage current density–electric field response is shown in Fig. 2. The leakage current density of the undoped sample reached to 10^{-6} A/cm^2 at 40 kV/cm . Beyond the electric field, the sample was broken down. A large leakage current density has been reported for Bi-based materials.^{27,29,30} When the undoped sample was embedded or V-doped, the leakage current density was reduced to $10^{-9}\text{--}10^{-8} \text{ A/cm}^2$. The reduction in the leakage current density of the embedded sample was attributed to the suppression of a bismuth oxide evaporation. The bismuth oxide evaporation as BiO^+ or BiO_2^- in the undoped sample might lose a local electrical neutrality,³¹ which resulted in a change in oxidation state of Fe ions between Fe^{3+} and Fe^{2+} .

The change in the oxidation state are known to lead a hopping conduction between the Fe ions and increased the leakage current density.^{29,30} For the V-doped sample, bismuth vacancies were generated, that is, $\text{Bi}_{1-x/6}(\text{Mg}_{1/2}\text{Ti}_{(1-x)/2}\text{V}_{x/2})\text{O}_3$. This could inhibit a further generation of

Fig. 2. The room temperature leakage current density–electric field (J – E) response of the undoped, V-doped, and embedded samples.

Fig. 3. The frequency dependence of the room temperature dielectric constant, ϵ' , and dielectric loss, $\tan \delta$, of (1) undoped, (2) V-doped, and (3) embedded samples.

bismuth vacancies as well as oxygen vacancies, which reduced the leakage current density, as proposed for V-doped $\text{Bi}_4\text{Ti}_3\text{O}_{12}$.²⁷

The frequency dependence of the dielectric properties is shown in Fig. 3. A clear increase in the dielectric loss at low frequencies was observed for the undoped sample. This increase can be ascribed to an electric conduction and/or a dielectric relaxation which is either a migration of space charges or a reorientation of defect dipoles.³² In the undoped sample, a concentration of the oxygen vacancies can be high due to the Bi_2O_3 evaporation. As reported for other perovskite oxides,^{33,34} these oxygen vacancies can migrate as space charges or move around bismuth vacancies, resulting in bismuth vacancy–oxygen vacancy defect dipoles. When the sample was sintered with the calcined powder or doped with V, the increase in the dielectric loss was suppressed.

The temperature dependence of the dielectric properties is shown in Fig. 4. For the dielectric constant profile of the undoped sample, there are two peaks observed. One is the peak at 480°C, which is associated with the Curie temperature.²² The peak dielectric constant decreased with increasing frequency. This was related to an electric conduction, as evidenced by the large increase in the dielectric loss at high temperatures. The other is the peak with a strong frequency dependence near 230°C, accompanied with the dielectric loss peak. Such a peak is related to the dielectric relaxation,^{33,34} and thus this supports that the dielectric loss increase observed in Fig. 3 was, at least, associated with the dielectric relaxation. For the sample doped with V or sintered in the calcined powder, the peak near 230°C was suppressed. Thus, in the undoped sample, the peak near 230°C (Fig. 4) and low frequency dielectric loss (Fig. 3) could be related to a large concentration of the defect dipoles such as $\text{V}_{\text{Bi}}-\text{V}_{\text{O}}$, while the higher leakage (Fig. 2) might be related to a large concentration of different defect dipoles such as $\text{Fe}^{2+}-\text{V}_{\text{O}}$. These defects might connect to form leakage paths, and thus result in the large leakage current density. For the V-doped and embedded samples, the defect concentration was reduced. The defects were isolated and did not form the leakage paths, leading to the reduced leakage.

Fig. 4. The temperature dependence of the dielectric constant, ϵ' , and dielectric loss, $\tan \delta$, measured at the frequencies of 10 kHz, 100 kHz, and 1 MHz. The arrows indicate the direction of increasing frequency.

The Curie temperature was reduced by 20°C for the V-doped sample. A reduction in the Curie temperature by V-doping was reported for $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics, although the reduction was smaller.²⁷ On the other hand, the Curie temperature was raised by 15°C for the embedded sample. A possible reason for this is a reduced oxygen vacancy concentration, as reported for BaTiO_3 .³⁵

At temperatures between room temperature and 200°C, a frequency dispersion in the dielectric constant and loss was observed for the V-doped sample and the embedded sample. A similar dispersion was found in BT-BF and BT-BiScO₃ solid solutions,^{36,37} and therefore this could be a characteristic of BaTiO_3 –Bi-based perovskite systems. The origin was suggested to be reentrant, which meant that the material could be treated as dipolar glass.³⁶

3.3. Ferroelectric and piezoelectric properties

The dielectric displacement–electric field loops of the samples are shown in Fig. 5. A leaky, round loop was observed for the undoped sample. This was at least associated with the increased leakage current density presented in Fig. 2. The space charges, as suggested in the frequency and

Fig. 5. The dielectric displacement–electric field (D – E) loops of the undoped, V-doped, and embedded samples, measured at 10 Hz.

temperature studies, could contribute to this as well. The hysteresis loop was slightly pinched. Pinched hysteresis loops were reported for ferroelectrics including BF₃,^{38–41} and were attributed to defect dipoles. For the embedded sample and the V-doped sample, such a lossy response was suppressed. No large difference was observed for the loops. Note that the hysteresis loops were also slightly pinched, suggesting a small amount of the defect dipoles that was not detected by the $\tan \delta$ –frequency response.

The bipolar strain–electric field curves of the samples are shown in Fig. 6(a). It was found that the field-induced strain was increased for the embedded and V-doped samples, compared to the undoped sample. This was attributed to a reduced concentration of the defect dipoles that pinned the domain wall motion. The asymmetric curve was observed for the V-doped sample. Such a curve was reported for a BiFeO₃ ceramic.⁴² Note that the coercive field was smaller than those of the dielectric displacement–electric field loops because of the lower measuring frequencies. With increasing frequency, a coercive field of a ferroelectric increases due to a delayed response of domain walls with respect to the applied electric field,⁴³ and the frequency dependence was mainly attributed to a slow response of a non-180° domain wall motion.^{42,44} Recent studies showed the strong frequency dependence of the coercive field in 0.7Pb(Mg_{1/3}Nb_{2/3})O₃–0.3PbTiO₃ and 0.955Pb(Mg_{1/3}Nb_{2/3})O₃–0.045PbTiO₃ systems with compositions having nanodomains.^{45,46} These might suggest that the strong frequency dependence of the coercive field of the samples in this study was associated with an increased concentration of non-180° domain walls due to their nanodomains. The unipolar strain–electric field curves of the samples are shown in Fig. 6(b). Note that the samples were not poled. As expected, increased responses were observed for the embedded sample and the V-doped sample. The strain maximum/applied electric field amplitude, $S_{\max}/E_{\max}$, at $E_{\max} = 50$ kV/cm, 0.1 Hz, was 366, 799, and 455 pm/V for the undoped sample, the embedded sample, and the V-doped sample, respectively. These results indicate that the sintering

(a)

(b)

Fig. 6. (a) The bipolar and (b) unipolar strain–electric field curves of (1) undoped, (2) V-doped, and (3) embedded samples, measured at 0.1 Hz. The samples were not poled.

with the calcined powder and the V-doping (especially the embedded case) are effective in reducing defect dipole population and increasing large-field piezoelectric response. The origin of the smaller strain response of the V-doped sample compared to that of the embedded sample is unclear and needs further study.

4. Conclusion

The leakage, dielectric, and piezoelectric properties of the undoped, embedded, and V-doped (Ba_{0.3}Bi_{0.7})(Mg_{0.05}Fe_{0.6}Ti_{0.35})O₃ ceramics were studied. The large current densities and the dielectric relaxation of the undoped sample were suppressed for the embedded sample and the V-doped sample. The electric-field-induced strain was increased for the embedded and V-doped samples. This was associated with reduced concentration of the defect dipoles.

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References

- ¹B. Jaffe, W. R. Cook and H. L. Jaffe, *Piezoelectric Ceramics* (Academic Press, New York, 1971).
- ²Y. Saito, H. Takao, T. Tani, T. Nonoyama, K. Takatori, T. Homma, T. Nagaya and M. Nakamura, Lead-free piezoceramics, *Nature* **432**, 84 (2004).
- ³K. Kakimoto, T. Imura, Y. Fukui, M. Kuno, K. Yamagiwa, T. Mitsuoka and K. Ohbayashi, Processing of piezoelectric (Li,Na,K)NbO₃ porous ceramics and (Li,Na,K)NbO₃/KNbO₃ composite, *Jpn. J. Appl. Phys.* **46**, 7089 (2008).
- ⁴E. Z. Li, H. Kakimoto, T. Hoshina and T. Tsurumi, A shear-mode ultrasonic motor using potassium sodium niobate-based ceramics with high mechanical quality factor, *Jpn. J. Appl. Phys.* **47**, 7702 (2008).
- ⁵Y. Hiruma, T. Watanabe, H. Nagata and T. Takenaka, Piezoelectric properties of (Bi_{1/2}Na_{1/2})TiO₃-based solid solution for lead-free high-power applications, *Jpn. J. Appl. Phys.* **47**, 7659 (2008).
- ⁶Y. Isikawa, Y. Akiyama and T. Hayashi, Piezoelectric and dielectric properties of (Bi,Na,K,Ag)TiO₃-BaTiO₃ lead-free piezoelectric ceramics, *Jpn. J. Appl. Phys.* **48**, 09KD03 (2009).
- ⁷S. Yasui, O. Sakata, M. Nakajima, S. Utsugi, K. Yazawa, T. Yamada and H. Funakubo, Piezoelectric properties of {100}-oriented epitaxial BiCoO₃-BiFeO₃ films measured using synchrotron X-ray diffraction, *Jpn. J. Appl. Phys.* **48**, 09KD06 (2009).
- ⁸M. Suzuki, A. Morishita, Y. Kitanaka, Y. Noguchi and M. Miyayama, Polarization and piezoelectric properties of high performance bismuth sodium titanate single crystals grown by high-oxygen-pressure flux method, *Jpn. J. Appl. Phys.* **49**, 09MD09 (2010).
- ⁹H. Nagata, M. Saitoh, Y. Hiruma and T. Takenaka, Fabrication and piezoelectric properties of textured (Bi_{1/2}K_{1/2})TiO₃ ferroelectric ceramics, *Jpn. J. Appl. Phys.* **49**, 09MD08 (2010).
- ¹⁰Y. Doshida, H. Shimizu, Y. Mizuno, K. Itoh, S. Hirose and H. Tamura, Nonlinear behavior and high-power properties of (Bi,Na,Ba)TiO₃ and (Sr,Ca)₂NaNb₅O₁₅ piezoelectric ceramics, *Jpn. J. Appl. Phys.* **50**, 09ND06 (2011).
- ¹¹M. Kobune, K. Teraoka, H. Nishioka, H. Yamaguchi and K. Honda, Fabrication and characterization of binary piezoelectric (Bi_{1/2}Na_{1/2})TiO₃-Ba(Cu_{1/3}Nb_{2/3})O₃ solid solutions, *Jpn. J. Appl. Phys.* **50**, 09ND08 (2011).
- ¹²T. Watanabe, M. Shimada, T. Aiba, H. Yabuta, K. Miura, K. Oka, M. Azuma, S. Wada and N. Kumada, Structural transformation of hexagonal (0001)BaTiO₃ ceramics to tetragonal (111)BaTiO₃ ceramics, *Jpn. J. Appl. Phys.* **50**, 09ND01 (2011).
- ¹³T. R. Shrout and S. J. Zhang, Lead-free piezoelectric ceramics: Alternatives for PZT? *J. Electroceram.* **19**, 113 (2007).
- ¹⁴W. W. Cao and L. E. Cross, Theoretical model for the morphotropic phase boundary in lead zirconate-lead titanate solid solution, *Phys. Rev. B* **47**, 4825 (1993).
- ¹⁵K. A. Schönau, L. A. Schmitt, M. Knapp, H. Fuess, R. d.-A. Eichel, H. Kungl and M. J. Hoffmann, Nanodomain structure of Pb[Zr_{1-x}Ti_x]O₃ at its morphotropic phase boundary — Investigations from local to average structure, *Phys. Rev. B* **75**, 184117 (2007).
- ¹⁶R. Theissmann, L. A. Schmitt, J. Kling, R. Schierholz, K. A. Schonau, H. Fuess, M. Knapp, H. Kungl and M. J. Hoffmann, Nanodomains in morphotropic lead zirconate titanate ceramics: On the origin of the strong piezoelectric effect, *J. Appl. Phys.* **102**, 024111 (2007).
- ¹⁷I. K. Bdikin, V. V. Shvartsman and A. L. Kholkin, Nanoscale domains and local piezoelectric hysteresis in Pb (Zn_{1/3}Nb_{2/3})O₃-4.5% PbTiO₃ single crystals, *Appl. Phys. Lett.* **83**, 4232 (2003).
- ¹⁸D. Viehland, M. C. Kim, Z. Xu and J. F. Li, Long-time present tweedlike precursors and paraelectric clusters in ferroelectrics containing strong quenched randomness, *Appl. Phys. Lett.* **67**, 2471 (1995).
- ¹⁹S. Wada, K. Yamato, P. Pulpan, N. Kumada, B. Y. Lee, T. Iijima, C. Moriyoshi and Y. Kuroiwa, Piezoelectric properties of high Curie temperature barium titanate-bismuth perovskite-type oxide system ceramics, *J. Appl. Phys.* **108**, 094114 (2010).
- ²⁰I. Fujii, K. Yamato, M. Shimada, J. Hayashi, H. Yabuta, M. Kubota, K. Nakashima, N. Kumada and S. Wada, Relaxor characteristics of BaTiO₃-Bi(Mg_{1/2}Ti_{1/2})O₃ ceramics, *Key Eng. Mater.* **485**, 31 (2011).
- ²¹M. M. Kumar, V. R. Palkar, K. Srinivas and S. V. Suryanarayana, Ferroelectricity in a pure BiFeO₃ ceramic, *Appl. Phys. Lett.* **76**, 2764 (2000).
- ²²R. Mitsui, I. Fujii, K. Nakashima, N. Kumada, Y. Kuroiwa and S. Wada, Enhancement in the piezoelectric properties of BaTiO₃-Bi(Mg_{1/2}Ti_{1/2})O₃-BiFeO₃ system ceramics by nanodomain, *Ceram. Int.* **39**, S695 (2013).
- ²³H. Yabuta, M. Shimada, T. Watanabe, J. Hayashi, M. Kubota, K. Miura, T. Fukui, I. Fujii and S. Wada, Microstructure of BaTiO₃-Bi(Mg_{1/2}Ti_{1/2})O₃-BiFeO₃ piezoelectric ceramics, *Jpn. J. Appl. Phys.* **51**, 09LD04 (2012).
- ²⁴I. Fujii, R. Mitsui, K. Nakashima, N. Kumada, M. Shimada, T. Watanabe, J. Hayashi, H. Yabuta, M. Kubota, T. Fukui and S. Wada, Structural, dielectric and piezoelectric properties of Mn-doped BaTiO₃-Bi(Mg_{1/2}Ti_{1/2})O₃-BiFeO₃ ceramics, *Jpn. J. Appl. Phys.* **50**, 09ND07 (2011).
- ²⁵H. S. Shulman, M. Testorf, D. Damjanovic and N. Setter, Microstructure, electrical conductivity, and piezoelectric properties of bismuth titanate, *J. Am. Ceram. Soc.* **79**, 3124 (1996).
- ²⁶S. H. Hong, S. Trolier-McKinstry and G. L. Messing, Dielectric and electromechanical properties of textured niobium-doped bismuth titanate ceramics, *J. Am. Ceram. Soc.* **83**, 113 (2000).
- ²⁷Y. Noguchi and M. Miyayama, Large remanent polarization of vanadium-doped Bi₄Ti₃O₁₂, *Appl. Phys. Lett.* **78**, 1903 (2001).
- ²⁸G. S. Snow, Fabrication of transparent electrooptic PLZT ceramics by atmosphere sintering, *J. Am. Ceram. Soc.* **56**, 91 (1973).
- ²⁹Y. P. Wang, L. Zhou, M. F. Zhang, X. Y. Chen, J. M. Liu and Z. G. Liu, Room-temperature saturated ferroelectric polarization in BiFeO₃ ceramics synthesized by rapid liquid phase sintering, *Appl. Phys. Lett.* **84**, 1731 (2004).
- ³⁰S. Hunpratub, P. Thongbai, T. Yamwong, R. Yimnirun and S. Maensiri, Dielectric relaxations and dielectric response in multiferroic BiFeO₃ ceramics, *Appl. Phys. Lett.* **94**, 062904 (2009).
- ³¹M. Maglione and M. A. Subramanian, Dielectric and polarization experiments in high loss dielectrics: A word of caution, *Appl. Phys. Lett.* **93**, 032902 (2008).
- ³²A. J. Moulson and J. M. Herbert, *Electroceramics: Materials, Properties, Applications* (Wiley, Chichester, 2003).
- ³³O. Bidault, P. Goux, M. Kchikech, M. Belkaoui and M. Maglione, Space-charge relaxation in perovskites, *Phys. Rev. B* **49**, 7868 (1994).
- ³⁴C. Ang, Z. Yu and L. E. Cross, Oxygen-vacancy-related low-frequency dielectric relaxation and electrical conduction in Bi: SrTiO₃, *Phys. Rev. B* **62**, 228 (2000).

- ³⁵S. Lee, Z. K. Liu, M. H. Kim and C. A. Randall, Influence of nonstoichiometry on ferroelectric phase transition in BaTiO₃, *J. Appl. Phys.* **101**, 054119 (2007).
- ³⁶H. Y. Guo, C. Lei and Z.-G. Ye, Re-entrant type relaxor behavior in (1-x)BaTiO₃-xBiScO₃ solid solution, *Appl. Phys. Lett.* **92**, 172901 (2008).
- ³⁷S. O. Leontsev and R. E. Eitel, Dielectric and piezoelectric properties in Mn-modified (1-x)BiFeO₃-xBaTiO₃ ceramics, *J. Am. Ceram. Soc.* **92**, 2957 (2009).
- ³⁸H. J. Hagemann, Loss mechanisms and domain wall stabilization in doped BaTiO₃, *J. Phys. C: Solid State Phys.* **11**, 3333 (1978).
- ³⁹K. Carl and K. H. Hardtl, Electrical after-effects in Pb(Ti, Zr)O₃ ceramics, *Ferroelectrics* **17**, 473 (1977).
- ⁴⁰G. L. Yuan, Y. Yang and S. W. Or, Aging-induced double ferroelectric hysteresis loops in BiFeO₃ multiferroic ceramic, *Appl. Phys. Lett.* **91**, 122907 (2007).
- ⁴¹A. Y. Kim, Y. J. Lee, J. S. Kim, S. H. Han, H. W. Kang, H. G. Lee and C. I. Cheon, Ferroelectric properties of BiFeO₃ ceramics sintered under low oxygen partial pressure, *J. Korean Phys. Soc.* **60**, 83 (2012).
- ⁴²T. Rojac, M. Kosec and D. Damjanovic, Large electric-field induced strain in BiFeO₃ ceramics, *J. Am. Ceram. Soc.* **94**, 4108 (2011).
- ⁴³F. Jona and G. Shirane, *Ferroelectric Crystals* (Macmillan, New York, 1962).
- ⁴⁴J. E. Daniels, T. R. Finlayson, M. Davis, D. Damjanovic, A. J. Studer, M. Hoffman and J. L. Jones, Neutron diffraction study of the polarization reversal mechanism in [111]_c-oriented Pb (Zn_{1/3}Nb_{2/3})O₃-xPbTiO₃, *J. Appl. Phys.* **101**, 104108 (2007).
- ⁴⁵D. Viehland and Y. H. Chen, Random-field model for ferroelectric domain dynamics and polarization reversal, *J. Appl. Phys.* **88**, 6696 (2000).
- ⁴⁶J. H. Yin and W. W. Cao, Coercive field of 0.955Pb (Zn_{1/3}Nb_{2/3})O₃-0.045PbTiO₃ single crystal and its frequency dependence, *Appl. Phys. Lett.* **80**, 1043 (2002).