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Material properties of bismuth layered ferroelectrics and lead zirconate titanate piezoelectric ceramics

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Abstract

The material properties of bismuth layer-structured ferroelectrics (BLSFs) and lead zirconate titanate (PZT) piezoelectric ceramics have been investigated. The fatigue strength of the PZT sample was higher than that of the BLSF. The electrical properties were altered as a result of cyclic loading. The piezoelectric constant (d_{33}) and electromechanical coupling coefficient (k_{33}) decreased with increasing applied load for both piezoelectric ceramics. However, the rate of reduction for the BLSF sample is smaller than that for the PZT ceramic. This different rate is attributed to the different material characteristics. During cyclic loading, the strain value increased with increasing cycle number for the PZT sample. Like the PZT ceramic, the strain value increases for the BLSF but the back strain occurred after the cyclic loading was conducted for certain period of times. This different strain behavior is influenced by the different domain switching characteristics and this was clarified from the respective strain–electric field relationships.

Keywords: Piezoelectric ceramic; Bismuth layered ferroelectrics; Lead zirconate titanate piezoelectric; Material property

1. Introduction

Many piezoelectric ceramics have been developed and used in various engineering applications, including buzzers, actuators and sensors. In particular, the lead zirconate titanate (PZT) piezoelectric ceramics have been employed widely, due to their excellent piezoelectric properties. However, with increasing limitations on the use of lead-based products because of environmental pollution issues caused by the PbO in PZT ceramics, ceramics containing less lead, or lead-free piezoelectrics, have received special attention [1]. There have been several types of lead-free piezoelectric ceramics, grouped into a number of families, e.g., barium and bismuth ceramics. Barium titanate piezoelectric ceramic has been utilized as a multilayer ceramic capacitor [2]. High piezoelectric constants of single crystal $BaTiO_3$ are produced by decreasing the ferroelectric domain size. Moreover, excellent material performance for high density BaTiO piezoelectric ceramics has been achieved by synthesizing 100 nm powders hydrothermally using a two-step sintering method [2].

The bismuth layered ferroelectrics (BLSFs) are very attractive from the viewpoint of their applications. The reason for this is that BLSF ceramics are characterized by a low dielectric constant, high Curie temperature (T_c) and large anisotropy in the electromechanical coupling factor. Indeed, lead-free BLSF ceramics are considered to be one of the candidates for a new piezoelectric material that can avoid environmental pollution issues. There are two main BLSF ceramics: (a) perovskite ferroelectric ceramics and (b) bi-layered structure ferroelectric thin films [3]. Simões et al. have investigated the effect of film orientation on the piezoelectric properties of bismuth layered compounds deposited on platinum coated silicon substrates. It appeared that the piezoelectric coefficient and the remnant polarization were larger for *a–b* axes orientated than for *c*-axis-oriented films [3]. To use lead-free BLSF piezoelectric ceramics in engineering applications instead of PZT ceramics, it is necessary to understand their mechanical properties and the material requirements for the application.

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However, information concerning piezoelectric performance and damage characteristics in BLSF ceramics is unsatisfactory. In addition, the fundamental work required to understand the mechanical properties of BLSF ceramics has not yet been carried out. This is an indispensable prerequisite for their use in engineering applications.

A recent report has described experimental investigations of the effects of material properties on the fatigue strength in PZT. In this instance, material failure during bipolar electric cycling occurred due to the coalescence of point defects [4]. The effect of plating silver electrodes on to the PZT ceramics on the fatigue properties was also reported [5]. It was shown that the fatigue strength decreases due to the change of material properties in the PZT ceramics caused by the penetration of the silver metal into the PZT. In fact, it is reported that lower mechanical properties were obtained for the PZT ceramics with Ag base electrodes compared to Ni [6]. A fundamental study of the failure characteristics has been carried out. This found that the major failure mechanisms were caused by domain switching and microcracks. In addition, a study of the experimental approach to fatigue for the PZT ceramics has been carried out, namely the *S–N* approach. This method includes an estimate of the number of cycles required to induce final failure. Despite several reported studies of the mechanical properties of piezoelectric ceramics, details of the influence of failure characteristics and domain switching mechanism on the mechanical properties have not been systematically investigated [7]. Moreover, previous work seems to have focused on the widely used PZT ceramic. In a search of the Scopus database, only nine academic papers were retrieved for a search on "bismuth layered ferroelectric ceramic", "mechanical property", "domain switching" and "failure characteristic".

The main purpose of this paper is therefore to investigate the mechanical properties and piezoelectric properties of the BLSF ceramics, and compare these with commercial PZT ceramics. In particular, the effects of the failure characteristics on the mechanical properties of the BLSF and PZT ceramics have been examined, following mechanical and electrical loadings.

2. Material and experimental procedures

2.1. Specimen preparation

The materials selected for the present investigation were commercial bulk BLSF and bulk PZT ceramics, produced by Fuji Ceramics Co. in Japan. Two different test specimens were prepared: (i) a rectangular block with dimensions 1 mm × 1 mm × 2 mm (l) and (ii) a thin round plate ϕ 9.0 mm × 0.12 mm (t). The thin round ceramic plate was attached to a thin brass plate ϕ 12.0 mm × 0.10 mm (t). The silver-based electrode plating was attached to the specimen surfaces by a firing process in atmosphere at 973 K for several hours. Following the attachment of the plating, the sample was polarized between the two electrodes. The densities (ρ) of PZT and BLSF ceramics were measured to be 7.65×10^3 kg/m^3 and 7.00×10^3 kg/m^3, respectively.

2.2. Mechanical properties

The mechanical properties of the samples were examined by static compressive loading and compressive–compressive cyclic loading at room temperature. For the measurements, an electro-servo-hydraulic system with 10 kN capacity (Instron 8871) was employed. In the mechanical testing, the stress and strain values were monitored by a data acquisition system in conjunction with a computer through a standard load cell and strain gauge. The loading speed for the static loading was 1 mm/min to failure. The fatigue properties were investigated from the relationship between the applied compressive stress and cycle number to failure, i.e. the *S–N* curve. The cyclic loading was performed with a sinusoidal waveform at a frequency of 30 Hz and load ratio of 0.1 up to 10^7 cycles, under load control. The maximum cyclic loads were determined based upon the compressive strength (σ_c) of the appropriate samples, e.g. 20–80% σ_c.

2.3. Piezoelectric properties

The piezoelectric properties of both rectangular samples were examined during cyclic loading, e.g. electromechanical coupling coefficient, k_{33}, and piezoelectric constant, d_{33}. In addition, the anti-resonance frequency f_a, resonance frequency f_r and electrostatic capacity C^T were measured in advance of the fatigue tests using an impedance analyzer. For these measurements, the parameters were examined as the applied load is removed to 0 N. With f_a and f_r values measured, k_{33} was obtained from the following formula [8]:

$$k_{33}=\sqrt{\frac{1}{a\left(f_r/f_a{-}f_r\right)+b}} \tag{1}$$

where a and b are coefficients that depend on the vibration mode. The piezoelectric constant, d_{33}, is expressed as

$$d_{33}=k_{33}\sqrt{\frac{\varepsilon_{33}}{C^E_{33}}} \tag{2}$$

where ε_{33} and C^E_{33} are the dielectric constant and elastic coefficient, respectively, estimated from the following equations:

$$\frac{\varepsilon_{33}=C^T t}{A} \tag{2a}$$

$$C^E_{33}=(2lf_r)^2\rho \tag{2b}$$

where t is the distance between the two electrodes and A is the area of electrode. l and ρ represent the length of the rectangular specimen and the density of the piezoelectric ceramic, respectively.

2.4. Strain versus electric field

To understand the strain behavior during cyclic loading, the electric field (E) vs. strain (S) relationships for the PZT and BLSF ceramics were investigated using the round plate specimens. A DC electric voltage was applied using a high-voltage power supply, ranging from ± 150 V for PZT to ± 900 V for BLSF, with the samples immersed in silicon oil. Note that due to different strain values, the electric voltages were altered. During the electrical loading, the strain in the specimen was measured using a strain gauge attached at the center of the round plate specimen.

3. Results and discussion

3.1. Electrical properties

Fig. 1 shows the variation of the material properties (d_{33}, k_{33} and C^E_{33}) as a function of the cycle number for the both piezoelectric ceramics. Note that the percentage in the legend indicates the rate of the applied maximum compressive stress to the compressive strength (σ_c), as obtained in this work. For the PZT ceramics, high values for the piezoelectric constant (d_{33}) and electromechanical coupling coefficient (k_{33}) are obtained during the cyclic loading at the low applied stress σ_{max} 45 MPa ($=5\%\ \sigma_c$), as shown in Fig. 1(a). However, the d_{33} and k_{33} values decrease suddenly when the high stress σ_{max} 135 MPa ($=15\%\ \sigma_c$) is applied. The rate of reduction of the material properties (d_{33} and k_{33}) in the PZT ceramics is more than 30%. The d_{33} and k_{33} values for PZT are, however, reduced intermittently with increasing cycle number for the 90 MPa sample ($=10\%\ \sigma_c$), and its value settles after 20 cycles to a similar level to that found for the samples tested at σ_{max} 135 MPa. This reduction in the piezoelectric properties would be affected by any material damage in the PZT ceramics, e.g. domain switching. An opposite trend was obtained for the elastic constant C^E_{33} for PZT. As seen in Fig. 1(a), the C^E_{33} value increases with increasing applied stress, e.g. the 90 MPa sample, and its value settles at around 80 GPa after 20 cycles. Note that the increment for C^E_{33} is about 41%. Such an increment of elastic constant may be due to high internal stress arising from the domain switching [9].

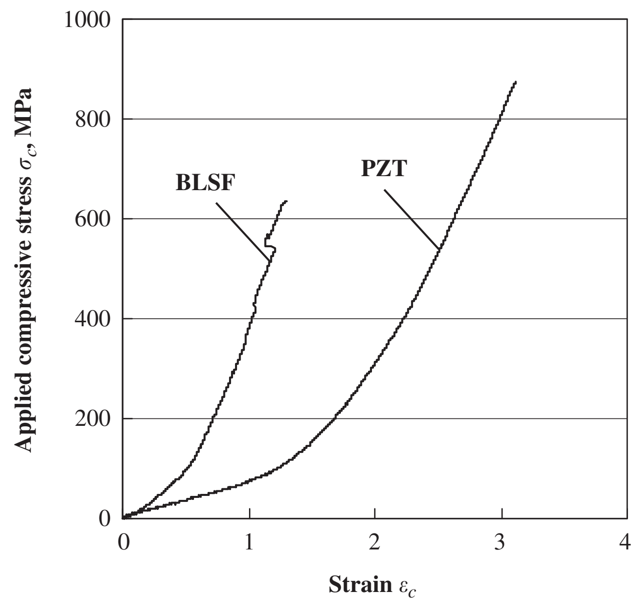

Fig. 2. Relationship between the compressive stress (σ_c) and strain (ε_c) for the PZT and BLSF ceramics.

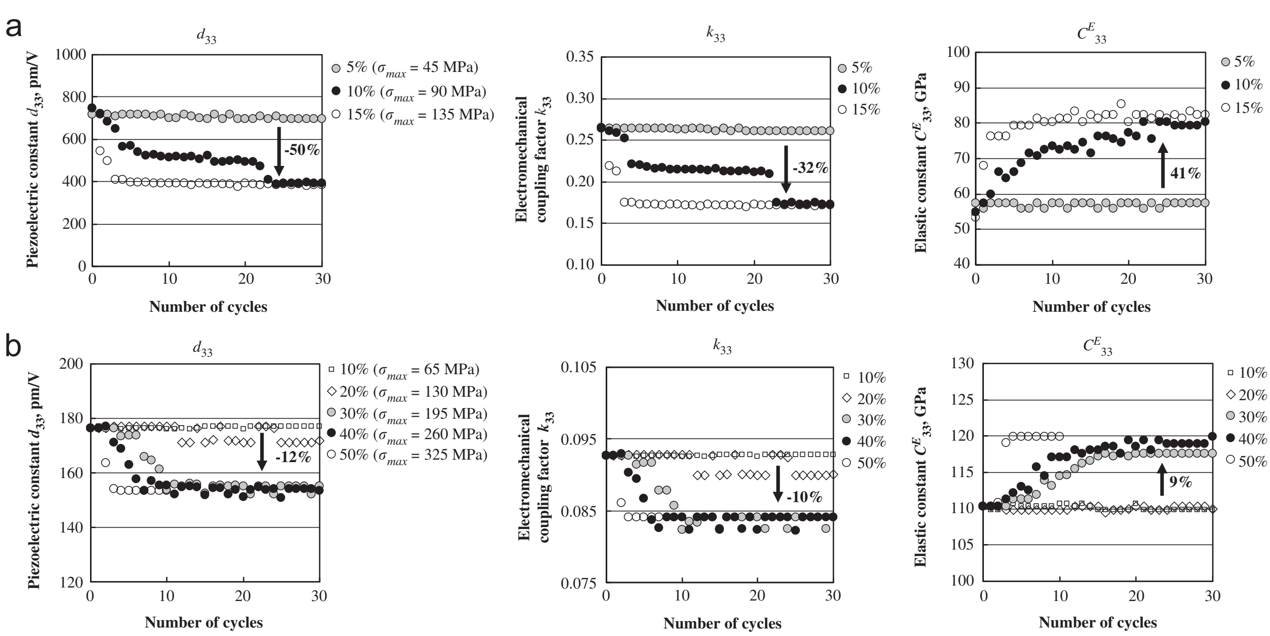

Fig. 1. Variation of the material properties (d_{33}, k_{33} and C^E_{33}) as a function of the cycle number for (a) PZT and (b) BLSF ceramics.

Similar trends to these material properties were seen in the BLSF samples, as shown in Fig. 1(b), but the increment and reduction rates are different to those of the PZT samples. The reduction for d_{33} and k_{33} and increment for C^E_{33} are as low as about 10% for the BLSF samples, which is more than three times smaller than those for the PZT samples. Moreover, the loading level at which the material properties start to change is different for the BLSF and PZT ceramics. A high applied load, more than 30% σ_c, is required to alter the material properties of BLSF, while only 10% σ_c is needed for PZT. Such different material properties are affected by the different failure characteristics.

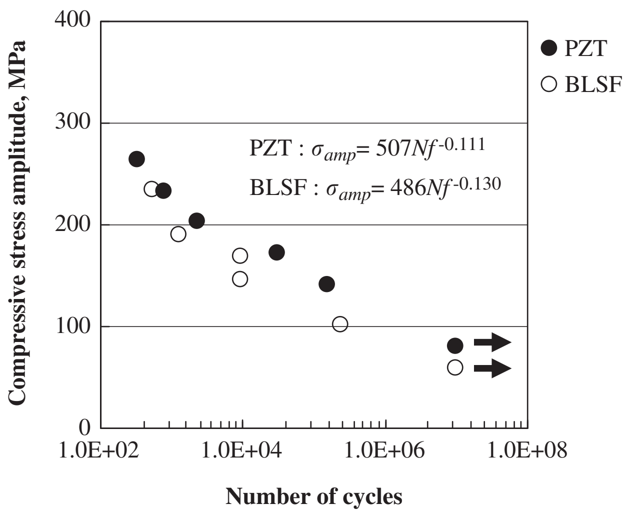

Fig. 3. Relationship between the stress amplitude and fatigue life (*S–N*) for the PZT and BLSF ceramics.

3.2. Mechanical properties

Fig. 2 shows the relationship between the compressive stress (σ_c) and strain (ε_c) for both the BLSF and PZT samples. As can be seen, different mechanical properties are obtained, e.g. higher strain value and higher compressive strength are obtained for the PZT ceramics compared to the BLSF samples. In addition, the PZT sample was greatly deformed during the compressive loading, which may be attributed to the more severe domain switching [10].

Fig. 3 shows the relationship between the stress amplitude and fatigue life, i.e. *S–N* relationship. The arrows in the *S–N* curves indicate test specimens which did not fail within 10^7 cycles, reaching the endurance limit (σ_{end}). It can be seen that the overall *S–N* relationship for the PZT sample is at slightly high values compared to that for the BLSF sample. The endurance limits for the PZT and BLSF samples are about 180 MPa and 130 MPa, respectively. The *S–N* relations for both samples are expressed with a power law dependence of the stress amplitude and

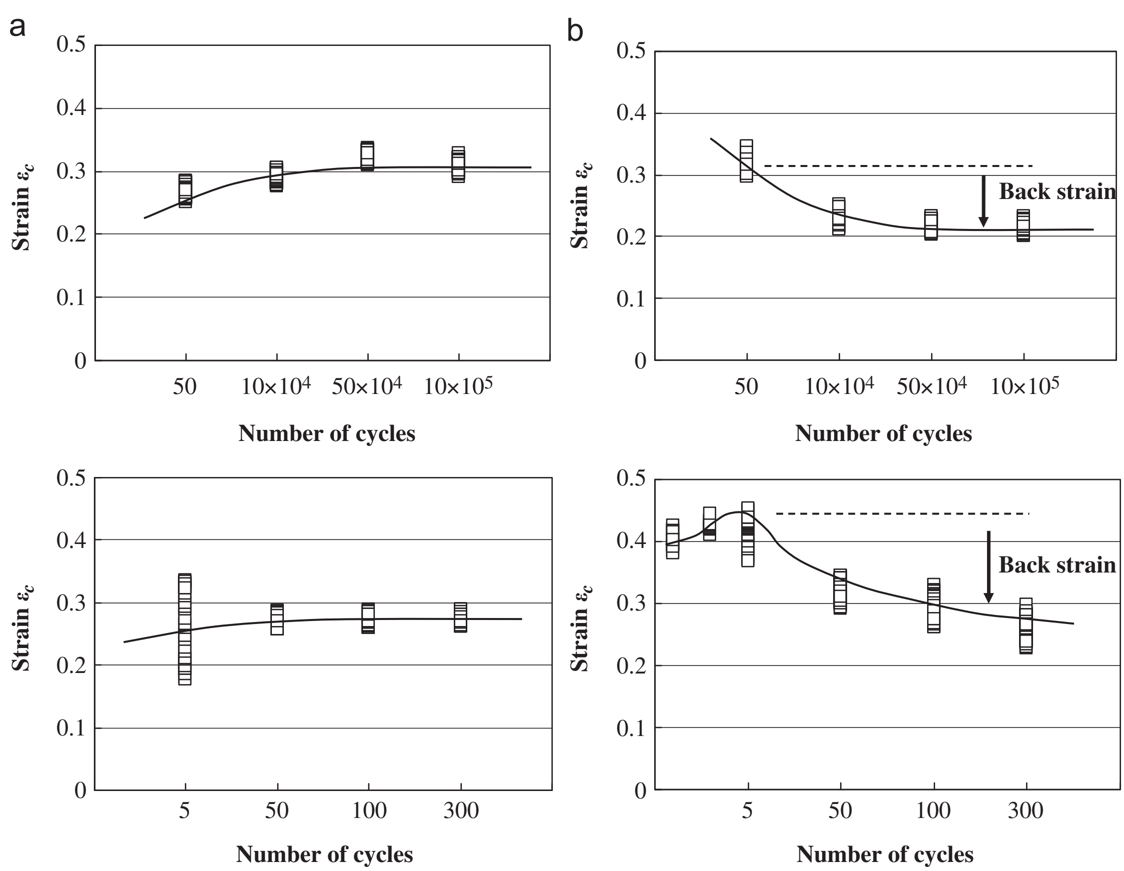

Fig. 4. Variation of the compressive strain as a function of cycle number for (a) PZT and (b) BLSF ceramics.

cycle number to final failure, $\sigma_{amp}=\sigma_f N_f^b$, where σ_{amp} is the stress amplitude in MPa, σ_f is the fatigue strength coefficient, N_f is the cycle number to failure and b is the fatigue exponent. In this case, a high fatigue life is expected for a high fatigue strength coefficient σ_f. The values of σ_f for both samples, obtained by least squares analysis, are $\sigma_f=486$ MPa for BLSF and $\sigma_f=507$ MPa for PZT. Such different fatigue properties for the PZT and BLSF samples are related to the different compressive strength, as mentioned above.

Strain behaviors in the BLSF and PZT ceramics were investigated during cyclic loading at $\sigma_{max}=100$ MPa. For this experiment, bulk specimens are used, and the strain values are measured using a small strain gauge. Fig. 4 displays the strain variation as a function of cycle number. The strain value increases with increasing cyclic loading, and settles after 50×10^4 cycles for the PZT ceramics. An interesting strain behavior is observed for the BLSF samples, as shown in Fig. 4(b). As with the PZT ceramic, the strain value increases for BLSF in the early part of the fatigue test, but back strain occurred after the cyclic loading was carried for a certain period of time (about 5 cycles). Such different strain characteristics between BLSF and PZT may be related to the different material properties, e.g. domain switching. To understand the influence of domain switching on the strain characteristics for both samples, the relationship between strain value and electric field was investigated.

3.3. Strain characteristic during electric loading

Fig. 5 presents the strain–electric field curves for the PZT and BLSF ceramics (R-ratio $=-1$) using the round plate specimens, as mentioned previously. As in Fig. 5(a) and (b), butterfly and hysteresis loops of strain vs. electric field (S–E) are obtained for the PZT and BLSF ceramics, respectively. A similar butterfly shape is observed in several related piezoelectric ceramics [11–13], and is due to domain reorientation [13]. In spite of the higher electric field used for BLSF, the overall strain level of BLSF is low compared to PZT. Basically, different strain modes occur in the two samples, lattice and switching strains. When a negative electric field is applied to the PZT ceramic, lattice strain may occur (to point A in Fig. 5). After that, it seems that 180° domain switching occurs between points A and B, and reverse-switching can be observed from points B to O. Similar strain behaviors are observed with positive voltage. In the BLSF ceramics, different S–E relations are obtained. Compressive strain is seen between points O and A as the first step, where 90° domain switching might occur because of the higher stain. As can be seen, slightly extended compressive strain is observed from points A to B, in which lattice strain might occur. When the electric loading is carried out using positive voltage, opposite strain behavior, caused by domain switching and lattice strain, is obtained between points B and D.

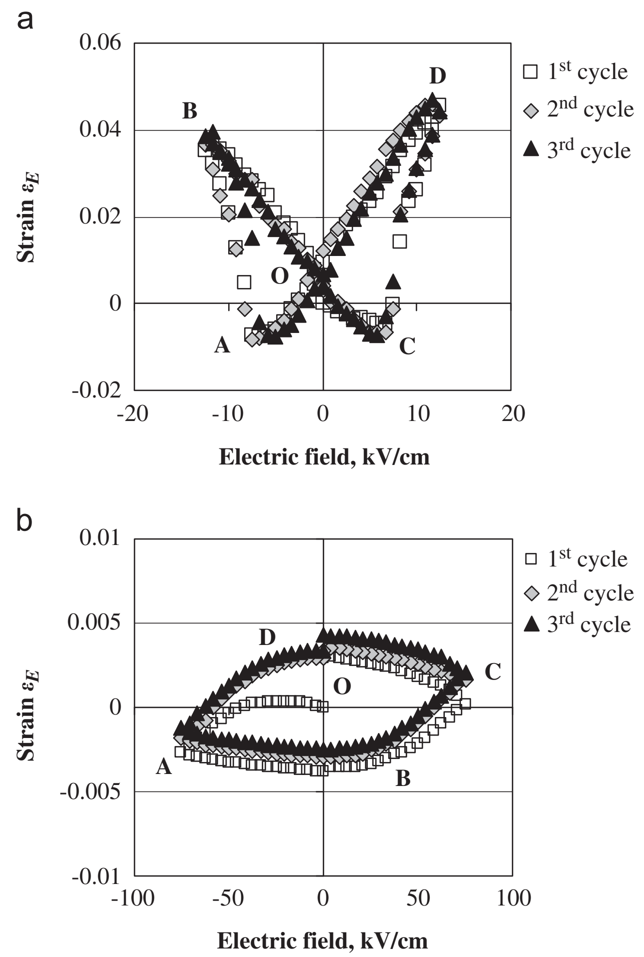

Fig. 5. Strain vs. electric field (S–E) for the PZT and BLSF ceramics (R-ratio $=-1$).

The strain characteristics obtained in both ceramics were further examined under electrical loading with only negative voltage (R-ratio $=-\infty$). This approach was executed using the same procedure as the mechanical cyclic loading tests, as shown in Figs. 3 and 4, i.e. compression–compression stress. Fig. 6 displays the strain vs. electric field (S–E) for both ceramics. Compared to the results of strain vs. electric field in Fig. 5, only half of the S–E relationship is observed. However, the half profile is only applicable in the first cycle in both samples. After the 2nd cycle, the strain occurs repeatedly, so the lattice strain would be affected in both samples. The reason for this may be that for negative applied loads only, reverse-switching does not occur so the domain switching occurs only in the 1st cycle. It is interesting to mention that, after the 2nd cycle, the lattice strain for BLSF cannot be zero, even after removing the load to 0 V, while the strain value becomes zero at 0 V for the PZT ceramics. In addition, the strain occurs in the positive and negative directions in the PZT and BLSF samples, respectively. Such different strain characteristics between PZT and BLSF may cause different strain characteristics during the mechanical cyclic loading, as shown in Fig. 4. However, the details are not completely clear, so further study will be required.

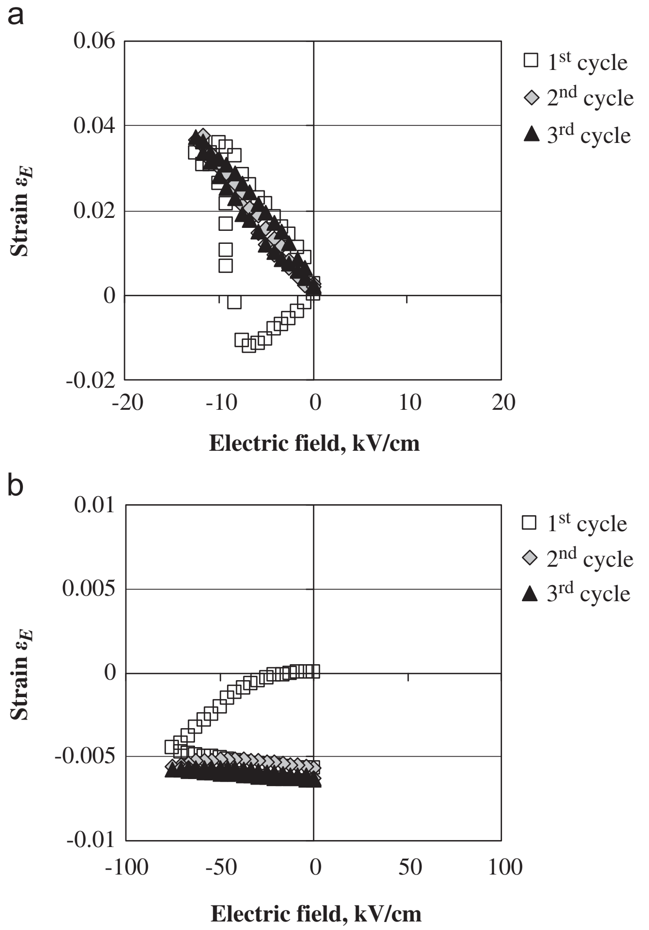

Fig. 6. Strain vs. electric field (*S*–*E*) for the PZT and BLSF ceramics (*R*-ratio $=-\infty$).

4. Conclusions

This work reports the mechanical properties and piezoelectric properties of the BLSF and PZT piezoelectric ceramics. In particular, the effects of domain switching on their fatigue and failure characteristics were examined. Based on our results, the following conclusions can be made:

1) The fatigue strength of the PZT sample is apparently higher than that of the BLSF sample. The endurance limit for PZT is about 180 MPa, which is about 1.4 times higher than for BLSF.
2) High values are obtained for d_{33} and k_{33} in both samples during cyclic loading at low applied stress, whereas low values are found for high applied stress. In contrast, the C_{33}^{E} value increases with increasing applied stress. Such a change of material properties is due to material failure arising from the domain switching.
3) The strain value increases with increasing cyclic loading for the PZT sample. However, a contrasting trend of strain behavior can be seen for the BLSF sample, where back strain occurred after cyclic loading for a few times. Such strain characteristics could be affected by the different domain switching behavior, and this occurrence could also be related to the strain–electric field relationships, where butterfly and hysteresis loops are obtained for the PZT and BLSF samples, respectively.

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References

[1] W. Zhao, J. Ya, Y. Xin, Z. Liu, L. E, D. Zhao, Fabrication of lead-free piezoelectric ceramics by (reactive) templated grain growth, Recent Patents on Materials Science 1 (2008) 241–248.
[2] T. Karaki, K. Yan, T. Miyamoto, M. Adachi, Lead-free piezoelectric ceramics with large dielectric and piezoelectric constants manufactured from $BaTiO_3$ nano-powder, Japanese Journal of Applied Physics 46 (2007) L97–L98.
[3] Japan AEM Association, Lead-free piezoelectric ceramic and device, 1st ed., Yokendo, Inc., Tokyo, 2008, pp. 44–45.
[4] J. Nuffer, D.C. Lupascu, J. Rödel, Damage evolution in ferroelectric PZT induced by dipolar electric cycling, Acta Materialia 48 (2000) 3783–3794.
[5] M. Okayasu, S. Aoki, M. Mizuno, Effects of silver-based metal electroplate on fatigue properties of PZT ceramics, International Journal of Fatigue 30 (2008) 1115–1124.
[6] M. Okayasu, G. Ozeki, M. Mizuno, Fatigue failure characteristics of lead zirconate titanate piezoelectric ceramics, Journal of the European Ceramic Society 30 (2010) 713–725.
[7] A.Z. Simões, C.S. Riccardi, A. Ries, M.A. Ramirez, E. Longo, J.A. Varela, Ferrroelectric and piezoelectric properties of bismuth layered thin films grown on (100) Pt electrodes, Journal of Materials Processing Technology 196 (2008) 10–14.
[8] Fuji Ceramics Co.: Piezoelectric Ceramics: Technical Handbook (Fuji Ceramics Co.).
[9] M. Okayasu, N. Odagiri, M. Mizuno, Damage characteristics of lead zirconate titanate piezoelectric ceramic during cyclic loading, International Journal of Fatigue 31 (2009) 1434–1441.
[10] J.M. Calderon-Moreno, M. Popa, Stress dependence of reversible and irreversible domain switching in PZT during cyclic loading, Materials Science Engineering A 336 (2002) 124–128.
[11] H. Kungl, R. Theissmann, M. Knapp, C. Baehtz, H. Fuess, S. Wagner, T. Fett, M.J. Hoffmann, Estimation of strain from piezoelectric effect and domain switching in morphotropic PZT by combined analysis of macroscopic strain measurements and synchrotron X-ray data, Acta Materialia 55 (2007) 1849–1861.
[12] N. Uchida, T. Ikeda, Electrostriction in perovskite-type ferroelectric ceramics, Japanese Journal of Applied Physics 6 (1967) 1079–1088.
[13] T. Tsurumi, Y. Kumano, N. Ohashi, T. Takenaka, O. Fukunaga, 90° domain reorientation and electric-field-induced strain of tetragonal lead zirconate titanate ceramics, Japanese Journal of Applied Physics 36 (1997) 5970–5975.