International Journal of Materials Engineering and Technology
Volume 6, Number 1, 2011, Pages 1-10
Published Online: September 2011
This paper is available online at http://pphmj.com/journals/ijmet.htm

PIEZOELECTRIC PROPERTIES OF LEAD-FREE PIEZOELECTRIC CERAMICS UNDER CYCLIC LOADING

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Abstract

To better understand the material properties of bismuth layer structured ferroelectrics (BLSF) ceramics, the piezoelectric properties of BLSF ceramics have been investigated as a function of mechanical loading. Piezoelectric properties, such as the piezoelectric constant (d_{33}) and electrostatic capacity (C^T), decrease non-lineally with increasing cycle number and applied stress. Such a change of material degradation is influenced by the severity of the material damage in the BLSF ceramic. The value of the critical damage at the sample final fracture point due to cyclic and static compressive loading can be determined by proposed exponential and polynomial expressions. It appears that the failure of BLSF ceramics occurs even with a low damage variable below 0.10.

Keywords and phrases: lead-free piezoelectric ceramic, bithmuth, piezoelectric property, fatigue property, mechanical property.

Received June 7, 2011

1. Introduction

Piezoelectric ceramics possess the unique property of a spontaneous polarization that is reversible in an applied electric field. A number of piezoelectric ceramics have been employed in various engineering applications, including buzzers, actuators, acceleration sensors, ultrasonic sensors, knocking sensors and gas sensors. In particular, lead zirconate titanate piezoelectric (PZT) ceramics have been widely used because of their excellent electromechanical response. However, with the increasing limitations of lead-based products due to environmental pollution caused by the PbO in PZT ceramics, lead-free piezoelectric ceramics have received special attention [1]. There exist several types of lead-free piezoelectric ceramics, grouped into several families, e.g., Barium and Bismuth. Barium titanate has been the first piezoelectric ceramic to be used in practice, forming the basic material for multilayer ceramic capacitors [2]. The piezoelectric constants of single crystal BaTiO3 increases with the decrease of ferroelectric domain size. To produce excellent material performance for these piezoelectric ceramics, high-density BaTiO piezoelectric ceramics were produced by synthesising 100-nm powders hydrothermally followed by a two step sintering method [2].

The family of bismuth layered ferroelectrics (BLSF) is very attractive from the viewpoint of their applications. This is because BLSF ceramics are characterized by their low dielectric constant, high Curie temperature (T_c) and large anisotropy in the electromechanical coupling factor. In fact, bismuth layer structured ferroelectrics are considered to be a candidate as a new piezoelectric material. The effect of film orientation on the piezoelectric properties of bismuth layered compounds deposited on platinum coated silicon substrates has been investigated, showing that the piezoelectric coefficient and the remnant polarization were larger for *a-b* axes orientated than for c-axis-oriented films [3].

In order to employ lead-free BLSF piezoelectric ceramics in engineering application for a long period of time, it is necessary to understand the material response to the application due to any change of material properties with time. The efficiency of the piezoelectric property in the ceramic can be altered by cyclic loading [4], where material failure can occur, caused by microcrack and domain switching [5]. Information concerning piezoelectric performance and damage characteristics in lead-free BLSF ceramics are indispensable for their design for engineering applications. The main purpose of this paper is, therefore, to investigate the piezoelectric properties of BLSF ceramics and any subsequent damage during static and cyclic loading processes.

2. Experimental Procedures

2.1. Materials

The piezoceramic selected for this work was a commercial bismuth layered ferroelectric (BLSF) of nominal composition $Bi_4Ti_3O_x$ (B600), produced by Fuji Ceramics Co. The specimen was a round rod (length 2.0 mm and diameter 4.0 mm) with a density of $6.94 \mathrm{g/cm^3}$. The Curie point of the BLSF ceramic is 660°C. An electroplated layer was applied to two sides of the specimens by a firing process in atmosphere, before the electrical poling process was carried out. The BLSF ceramics adopt an orthorhombic structure, e.g., $a = 0.545\,\mathrm{nm}$, $b = 0.541\,\mathrm{nm}$ and $c = 3.28\,\mathrm{nm}$. The piezoelectric properties of the BLSF ceramics after polarization, measured by an impedance analyzer (Agilent Technologies, 4294A) were: (i) effective elastic constant (c_{33}^E) 92.6 GPa, (ii) electromechanical coupling coefficient (k_{33}) 0.28, (iii) piezoelectric constant (d_{33}) 151.7 pm/v and (iv) permittivity (ε_{33}) 26.5 nF/m (or dielectric constant $(\varepsilon_{33}/\varepsilon_0)$ 2996). To estimate the piezoelectric properties, the anti resonance frequency f_a, resonance frequency f_r and electrostatic capacity C^T were measured by the impedance analyzer. With f_a and f_r values, k_{33} can be obtained from:

$$k_{33} = \sqrt{\frac{1}{a\dfrac{f_r}{f_a - f_r} + b}}, \tag{1}$$

where a and b are coefficients depending on the vibration mode. The piezoelectric constant, d_{33}, is obtained from

$$d_{33} = k_{33}\sqrt{\frac{\varepsilon_{33}}{c_{33}^E}}, \tag{2}$$

where ε_{33} and c_{33}^E are the dielectric constant and elastic coefficient, respectively, determined from the following equations:

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

$$c_{33}^E = (2lf_r)^2 \rho, \tag{2b}$$

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

2.2. Experiments

The static compressive strength was examined for the BLSF ceramics using a screw driven type universal testing machine with 10 kN capacity (Shimadzu EZGraph). The resolutions of load and displacement in this testing machine are 0.01 N and 1 μm, respectively. The loading speed for the compression tests was 1 mm/min to final fracture. This fatigue test was also conducted with compression-compression mechanical cyclic loads using an electro-servo-hydraulic system with 100 kN capacity (Shimadzu EHF-EB100kN-20L) under a load control mode. The cyclic loading was executed with a sinusoidal waveform at a frequency of 20 Hz and load ratio of $R(P_{\min}/P_{\max}) = 0.1$. The maximum cyclic stress, $\sigma_{\max}$, was determined on the basis of the compressive strength, σ_c, where $\sigma_{\max}$ is designed to be less than 90% of σ_c.

The static and cyclic loadings were applied along the direction normal to the entire surface of the electrodes. The piezoelectric properties of the BLSF ceramic were measured during the loading processes, where the piezoelectric constant, d_{33} and electrostatic capacity C^T were investigated.

3. Results and Discussion

Figure 1 shows the stress-deflection curve for the BLSF ceramic. It is clear that there is a nonlinear stress-deflection curve, with the compression strength $\sigma_c \approx 500\text{MPa}$. The compressive strength of BLSF is about 33% lower than that of a commercial PZT ceramic [5]. Figure 2 shows the relationship between the maximum stress and number of cycles to final failure (*S*-*N* relations) for the BLSF ceramics and PZT ceramics [4]. In a similar way to a conventional *S*-*N* diagram, the number of cycles to final fracture increased with decrease of the stress level. The endurance limit (σ_l) at 10^7 cycles is approximately 170 MPa. The line in Figure 2 is the approximate expression of the data plots obtained from a power law dependence of cyclic stresses, σ_a, and cycles to failure, N_f :

$$\sigma_a = \sigma_f N_f^{-z}, \tag{3}$$

where σ_f is the fatigue strength coefficient and z is the fatigue exponent. The σ_f (MPa) and z values for the BLSF ceramics, obtained by least squares analysis, are 644.27 MPa and 0.092, respectively. In this case, high fatigue life is related to a high values of the fatigue strength coefficient σ_f and low values of the fatigue strength exponent z. Similar to the compressive strength mentioned above, the fatigue properties of the BLSF ceramics were lower than those of the PZT ceramic, for which $\sigma_f = 884.18\text{MPa}$ and $z = 0.052$ [4].

Figure 3(a)(b) shows the variation of the reduction rate of piezoelectric constant $(d_{33,\,cycle})$ and electrostatic capacity (C^T_{cycle}) as a function of the cycle number. It should be noted that the percent scale indicates the ratio of the applied maximum cyclic stress $(\sigma_{\max})$ to the static compressive strength (σ_c). As seen in Figure 3(a), the reduction rate of the piezoelectric constant $(\Delta d_{33,\,cyclic})$ increases continuously with increasing cycle number. A high increment rate for $\Delta d_{33,\,cyclic}$ is obtained in the sample during cyclic loading at the high applied stress $\sigma_{\max}/\sigma_c$: 70%, whereas a low reduction rate is seen for low applied stress $(\sigma_{\max}/\sigma_c$: 30%). An interesting result in Figure 3(a) is that the high value of $\Delta d_{33,\,cycle}$ obtained just before the sample fracture is as low as 0.03, as indicated by the dashed line in Figure 3(a), and similar values are seen for all loading conditions. A related trend is also observed in the results for the electrostatic capacity (C^T_{cycle}) (Figure 3(b)). The reduction rate just before fracture for the electrostatic capacity (ΔC^T_{cycle}) is about 0.10, which is more than 3 times higher than that for $\Delta d_{33,\,cycle}$. To estimate the reduction rate of the piezoelectric properties $(\Delta d_{33,\,cycle}$ and $\Delta C^T_{cycle})$ for the BLSF ceramic, numerical approaches were carried out on the basis of the experimental data (Figure

3(a) and (b)). In this case, $\Delta d_{33,\,cycle}$ and ΔC^{T}_{cycle} were approximated with exponential laws:

$$\Delta d_{33,\,cyclic} = 0.0019 N^{-0.0011\sigma_{\mathrm{MAX}}} \tag{4}$$

$$\Delta C^{T}_{cyclic} = 0.0045 N^{-0.0012\sigma_{\mathrm{MAX}}}, \tag{5}$$

where N is the number of cycles and $\sigma_{\max}$ (MPa) is the applied maximum stress. Because the reduction rates just before the fracture for $\Delta d_{33,\,cycle}$ and ΔC^{T}_{cycle} are 0.03 and 0.1, respectively (Figure 3), equations (4) and (5) can be modified to determine the critical cyclic number (N_f):

$$N_f = 15.79^{909.1/\alpha_{\mathrm{MAX}}} \text{ for the piezoelectric constant} \tag{4a}$$

$$N_f = 20.00^{833.3/\sigma_{\mathrm{MAX}}} \text{ for the electrostatic capacity.} \tag{5a}$$

To further understand the variation of the piezoelectric properties due to mechanical loading, the $d_{33,\,static}$ and C^{T}_{static} values were investigated during static compressive loading. Figure 4(a) (b) displays the variation of the reduction rates for both piezoelectric constant $(\Delta d_{33,\,static})$ and electrostatic capacity (ΔC^{T}_{static}), respectively, as a function of applied compression stress. As in Figure 4, the values of $\Delta d_{33,\,static}$ and ΔC^{T}_{static} increase non-lineally with increase of the static applied load although the data is slightly scattered. The critical $d_{33,\,static}$ and C^{T}_{static} values are found to be about 0.05 and 0.10, respectively, which are relatively close to the values obtained in the fatigue tests. Based upon the experimental data shown in Figure 4(a) (b), the reduction 7 rates for $\Delta d_{33,\,static}$ and ΔC^{T}_{static} are expressed as follows:

$$\Delta d_{33,\,static} = 3.0 \times 10^{-7} \sigma^2 \tag{6}$$

$$\Delta C^{T}_{static} = 3.6 \times 10^{-7} \sigma^2. \tag{7}$$

From the above experimental results, it can be briefly concluded that the piezoelectric properties and the critical cycle number of the BLSF ceramic are approximated. In this case, the change of material properties must be caused by the material damage, e.g., micro-crack and domain switching, which will be discussed in a separate paper.

4. Conclusions

The material properties of bismuth layer structured ferroelectrics (BLSF) ceramics have been examined under the static and cyclic compression stress. Based upon the experimental results and discussion, the following conclusions can be drawn.

(1) The compressive strength and fatigue properties of BLSF were clarified. The compressive strength of the BLSF ceramic appeared to be 67% of that for conventional PZT ceramics.

(2) The piezoelectric properties of the BLSF ceramics decrease with increase of the applied stress and cycle number. The reduction rates for C^T and d_{33} during static and cyclic loadings were numerically estimated using an exponential law and polynomial law. From the estimation, the critical cycle number of the BLSF ceramics can be determined.

Acknowledgements

The authors would also like to express the appreciation to Daiki Iizuka at Akita Prefectural University for technical supports.

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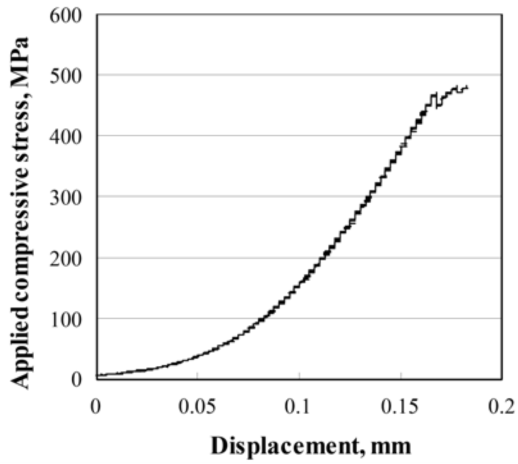

Figure 1. Compressive stress versus displacement for the BLSF ceramic.

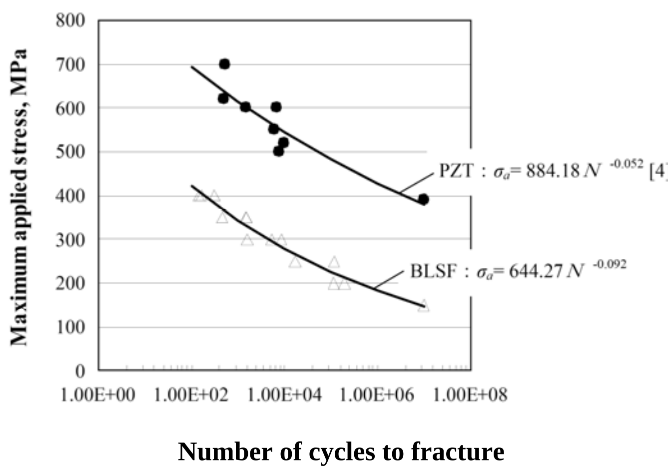

Figure 2. Maximum stress vs. number of cycles to fracture for the BLSF and PZT ceramics.

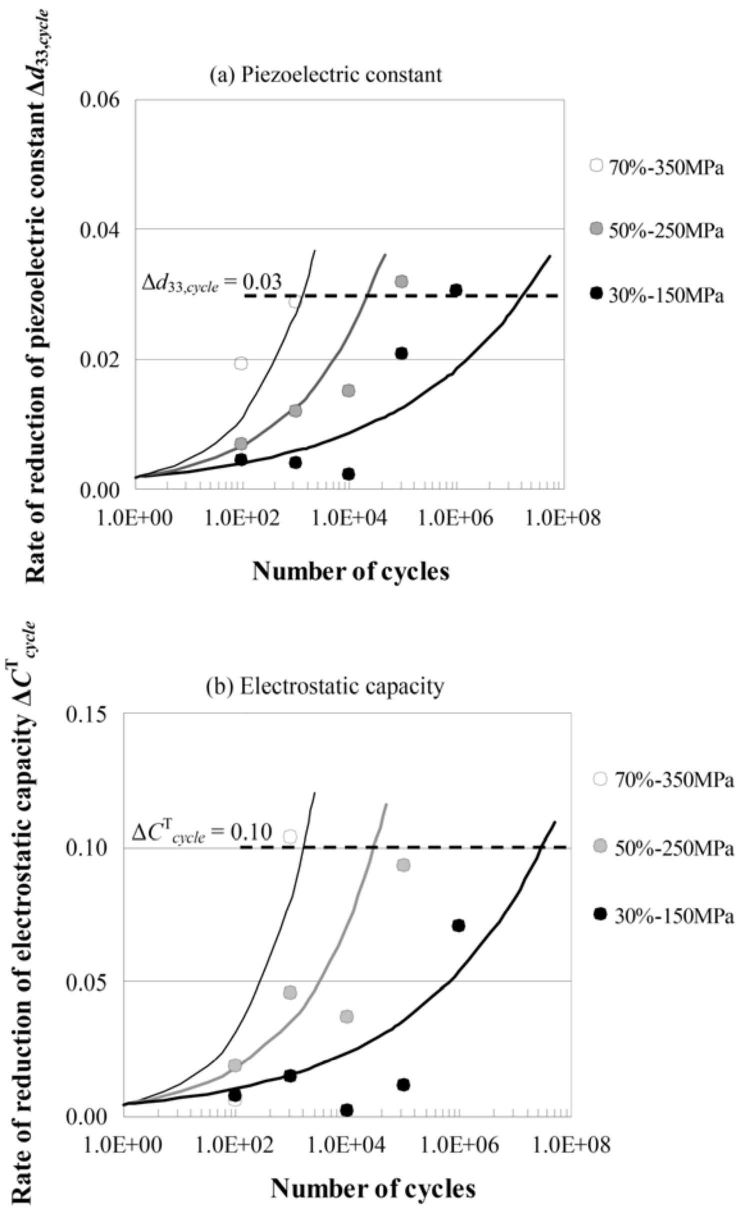

Figure 3(a)(b). Variation of the rate of reduction of electrical properties as a function of the cycle number: (a) piezoelectric constant $(\Delta d_{33,\,cycle})$ and (b) electrostatic capacity (ΔC^{T}_{cycle}).

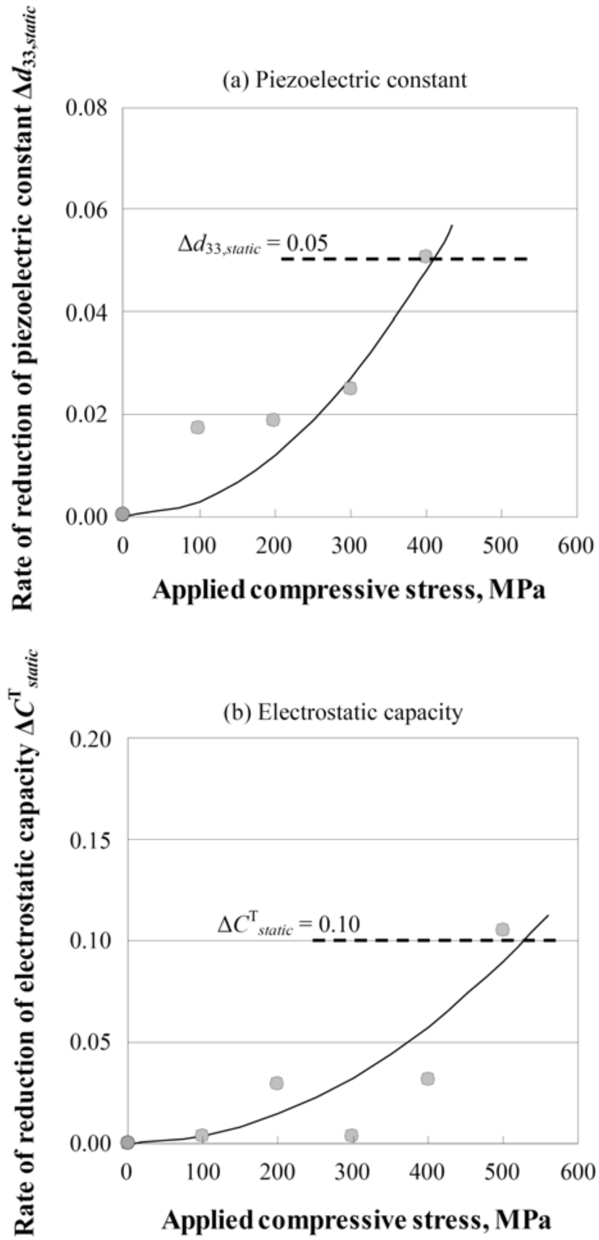

Figure 4(a)(b). Variation of the rate of reduction of the electrical properties as a function of applied compression stress: (a) piezoelectric constant $(\Delta d_{33,\, static})$ and (b) electrostatic capacity (ΔC^{T}_{static}).