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Pyroelectric and Sensor Properties of Ferroelectric Thin Films for Energy Conversion

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Abstract

High pyroelectric coefficients and improved conversion effects were successfully demonstrated in highly (111)-oriented ferroelectric PZT 90/10 films on Pt/Si substrates. The strong preferred orientation exhibited by these films was obtained through controlled heat-treatment using a specially developed MOD process on $Pt/Ti/SiO_2/Si$ substrates. Within the FE_{LT}–FE_{HT} phase transition range of 80∼100°C, the films exhibited significant changes in spontaneous polarization, by roughly a factor of 2 (∼ 7 μC cm^{-2}). A pyroelectric current, correlated to a pyroelectric coefficient of 30 ± 10 nC cm^2 K, was obtained around room temperature without poling treatment. A prototype pyroelectric transformer based on these films gave a voltage output of 0·8 volt from a 1 mm^2 area on a 1·0 μm thick film. Compared to bulk ceramics and thick films, these thin films also exhibited at least one order of magnitude higher working frequency. © *1999 Elsevier Science Limited. All rights reserved*

Keywords: films, ferroelectric properties, pyroelectric properties, PZT, sensors.

1 Introduction

Ferroelectric thin films have been investigated for use in non-volatile memories, as well as for piezoelectric, pyroelectric, and optoelectronic devices.[1–4] Recently, advances in processing technique have resulted in depositing preferentially oriented ferroelectric films (e.g. $PbTiO_3$, PZT, PLZT), which exhibit strong pyroelectric response even without being poled.[5,6] Takayama and Tomita reported scarcely a change in pyroelectric coefficient when the highly *c*- or *a*-axis oriented PZT films were poled under a field of 100 kV cm^{-1} for 30 min at 200°C.[5]

As pyroelectric materials, the Zr-rich $Pb(Zr_{1-x}Ti_x)O_3$ ceramics are particularly interesting due to their relatively low permittivity and significantly large pyroelectric coefficients. For pyroelectric applications, PZT materials with the composition $x \approx 0{\cdot}1$ have been widely studied, because of the large spontaneous polarization change associated with the phase transition between the lower temperature rhombohedral (FE_{LT}) and higher temperature rhombohedral ferroelectric phase (FE_{HT}) at ∼90°C.[7,8] This transition results in a large change in pyroelectric coefficient, with a small dielectric constant change, which makes these materials especially attractive for energy detection and conversion applications.

In this work, highly oriented ferroelectric Zr-rich PZT (90/10) thin films were obtained on Pt/Si substrates through controlled heat-treatment using a specially developed metallo-organic deposition (MOD) process. Dielectric, ferroelectric, and pyroelectric properties for the films are reported, as are prototype device characteristics for sensing applications.

2 Experimental

The metallo-organic deposition (MOD) process employed for preparing the PZT films is based on use of the precursor compounds zirconyl trimethylacetate, lead acetate, and titanium butoxide. These precursors were dissolved in a mixed solvent system consisting of propionic acid and amylamine. The resultant solution was filtered through a Teflon filter with a pore size of 0·2 μm, and subsequently spin-coated onto (111)-Pt/Ti/SiO_2/Si substrates at 3000 RPM for 30 s. The wet films were then dried and calcined on a hot plate at 250–400°C for 5 min in air. This process was repeated several times until the desired thickness (0·6–1·0 μm) was achieved.

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Finally the films were densified at 500–700°C under slightly oxidizing conditions for ~30 min.

Phase evolution and orientation in the films were controlled by heating rate and were characterized by X-ray diffractometry and SEM. Pt electrodes with a diameter of 1–2 mm were deposited onto the films for electrical measurements. Ferroelectric hysteresis characteristics were measured using a modified Sawyer–Tower circuit at a frequency of 60 Hz. Relative permittivity (ε) and dissipation factor (D) were measured at different frequencies and temperatures, using a Hewlett Packard 4194 impedance/gain phase analyzer. Leakage current measurements were carried out using a Keithley 2000 electrometer at 1·0 V measurement intervals. Pyroelectric currents were measured using a Keithley 617 electrometer interfaced with a HP 386 computer, at a constant heating rate of 2°C min^{-1} in the steady state mode. To measure the voltage and current response of the PZT films, a dynamic pyroelectric circuit was constructed. For these measurements, the films were irradiated with an incident chopped He-Ne laser. The laser, of power 1 mV cm^{-1} was used to directly irradiate the top sensing Pt electrode. The current and voltage responses were measured using a DSP lock-in amplifier.

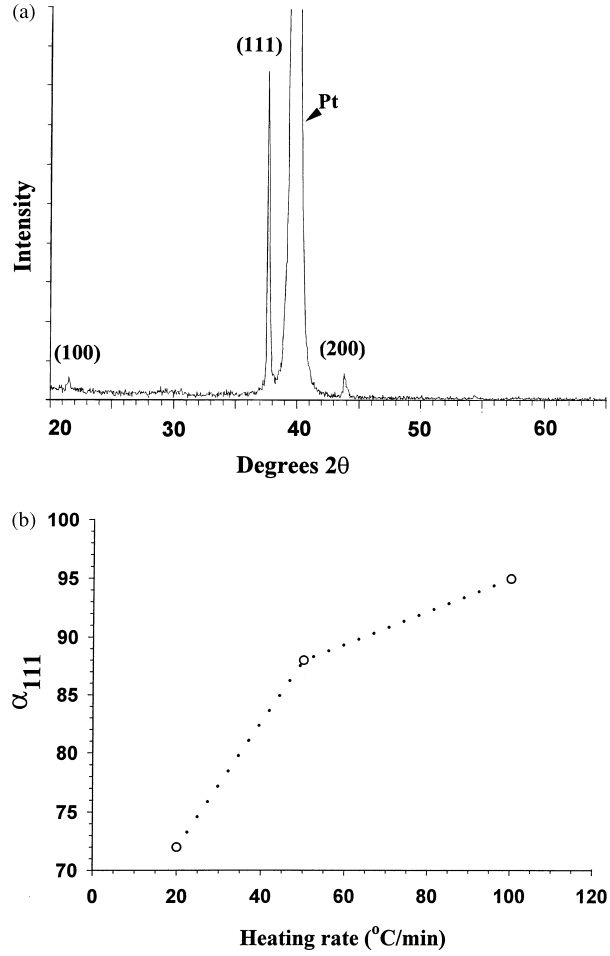

Fig. 1. (a) X-ray pattern of (111)-oriented PZT 90/10 films; (b) dependence of film orientation on heating rate.

3 Results and Discussion

In this study, film microstructure and orientation were both found to be very sensitive to heat treatment conditions. Figure 1 shows that only at a rapid heating rate (~100°C min^{-1}) was the dominant (111) texture of the PZT (90/10) film developed on the (111) Pt/Ti/SiO_2/Si substrates. Also, oriented PZT films were only developed on substrates with a near perfect (111)-oriented Pt buffer layer. For the high Zr-content PZT films, the presence of the non-ferroelectric pyrochlore phase is in general detrimental to the attainment of required electrical properties. In order to minimize the pyrochlore phase content, a PbO surface coating was deposited onto the films, before the final high temperature annealing. By employing this sacrificial top coating, Zr-rich films with a pure perovskite phase were successfully fabricated.

The measured temperature dependence of the dielectric constant (Fig. 2) shows the Curie temperature of the films to be ~210°C, similar to bulk ceramic, except for the broad peak, attributable to the small grain size and to stresses developed in the films during heat treatment. Room temperature dielectric constants for the films were in the range of 300–400, with dielectric loss less than 3% at 1 kHz. Frequency dependence showed a slight decrease in both the dielectric constant and loss in the frequency range of 100–500 kHz. These measurements were carried out on highly oriented as-processed PZT 90/10 films. Similar measurements conducted on poled films for comparison, showed only negligible differences. The as-processed films were, therefore, used for all subsequent pyroelectric and device measurements.

Figure 3 shows the typical hysteresis loop obtained for the PZT 90/10 films. The remnant

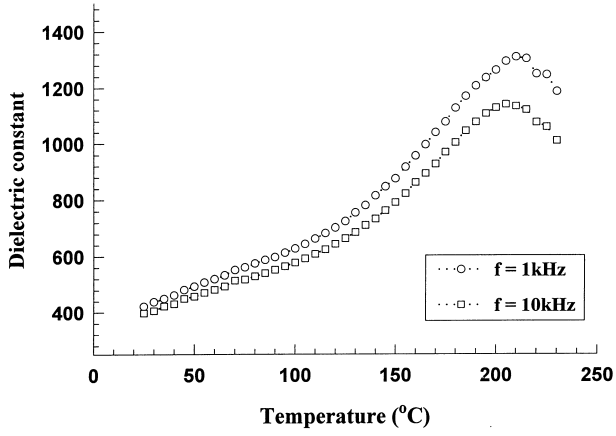

Fig. 2. Temperature dependence of dielectric constant. For PZT 90/10 film.

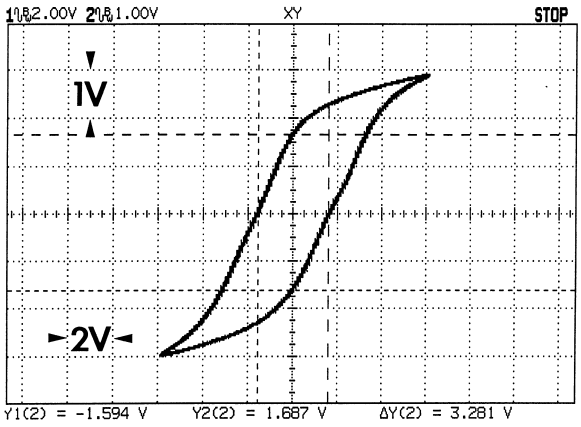

Fig. 3. P–E hysteresis loop of PZT 90/10 films.

polarization for the films, determined from hysteresis loop measurements, were in the range of 15–20 μC cm^{-2} with coercive fields of 20–30 kV cm^{-1}. Hysteresis loop measurements were also performed as a function of temperature in order to determine the polarization behavior in the temperature range 25–230°C. Figure 4 shows the change in remnant polarization P_r as a function of temperature. Two transition regions are clearly evident, around 90°C and 210°C, respectively. The 210°C anomalous change corresponds to the Curie temperature (T_c) while the change at ~90°C can be related to the phase transition between the rhombohedral FE_{LT} phase and rhombohedral FE_{HT} phase. Corresponding to this phase change, the remnant polarization over the transition range of 80–100°C decreases sharply by roughly a factor of 2 (from ~15 to ~8 μC cm^{-2} in Fig. 4), in going from the FE_{LT} to the FE_{HT} phase. The magnitude of this change is higher than that reported for bulk ceramics (< 4 μC cm^{-2}) of like composition or for the single crystal (~5 μC cm^{-2}) material.[7,8] Both the magnitude and sharp change in the polarization of the PZT 90/10 films can be attributed to the high degree of orientation as well as to the highly stressed state of the films.

The pyroelectric coefficient p is defined as dP/dT, and it can, therefore, be estimated from the slope of the polarization curve as a function of temperature. Figure 4 shows three distinct regions for the films, where: p~60 nC cm^{-2} (30°–80°C); p~400 nC cm^{-2} (80–100°C); and p~5 nC cm^{-2} (100–150°C), respectively.

By using static measurements, in which a 2°C min^{-1} heating rate (dT/dt) was employed, the pyroelectric current i was directly obtained from the following expression:

$$i = \frac{dQ}{dt} = A\frac{dP}{dt} = A\frac{dP}{dT}\frac{dT}{dt} = Ap\frac{dT}{dt} \qquad (1)$$

where P is the polarization, A is the area of the top electrode, and Q is the released charge on the electrodes. Figure 5 shows the pyroelectric coefficient obtained by this method over the temperature range 25–120°C. The average room temperature pyroelectric coefficient was 30 ± 10 nC cm^{-2} K, with the $FE_{LT} \rightarrow FE_{HT}$ transition occurring at ~90°C, in agreement with the data shown in Fig. 4. When the films were poled under an electric field of 100 kV cm^{-1}, the pyroelectric coefficient was also in the range of 30 ± 10 nC cm^{-2} K. This demonstrates that in the (111)-oriented PZT 90/10 films, not only are the grains fully aligned along [111] direction, but the ferroelectric domains are also self-aligned in this direction.

Figure 6 shows the dependence of the voltage responsivity (R_v) for the PZT films with chopping frequency. The voltage responsivity is given as:

$$R_v = \left|\frac{v}{w}\right| = \frac{\eta p R A \omega}{G\left(1+\omega^2\tau_T^2\right)^{1/2}\left(1+\omega^2\tau_E^2\right)^{1/2}} \qquad (2)$$

where η is the emissivity, τ_T the thermal time constant, τ_E the electric time constant, G the thermal conductance, and R the resistance. Between the

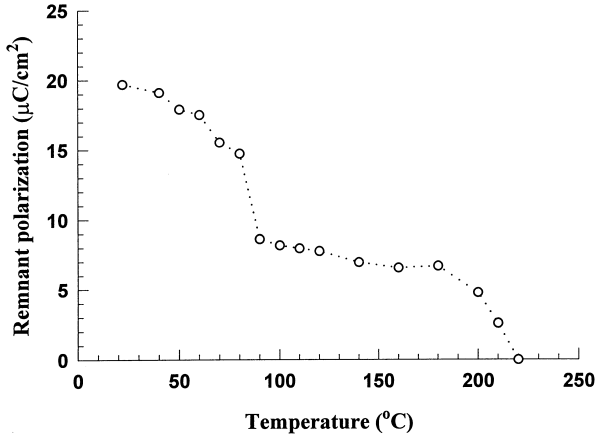

Fig. 4. Temperature dependence of the remnant polarization in PZT 90/10 films.

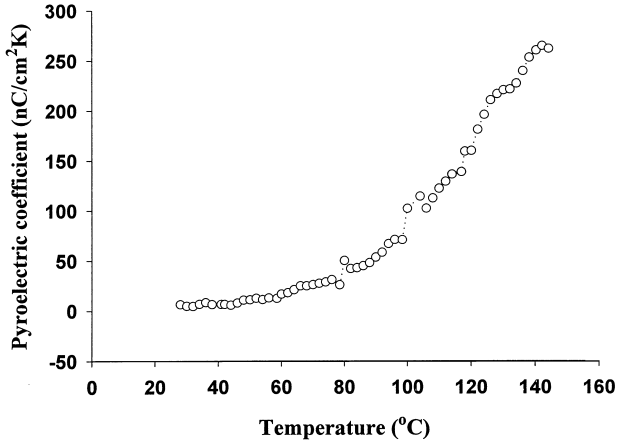

Fig. 5. Pyroelectric coefficient of PZT films under different temperatures.

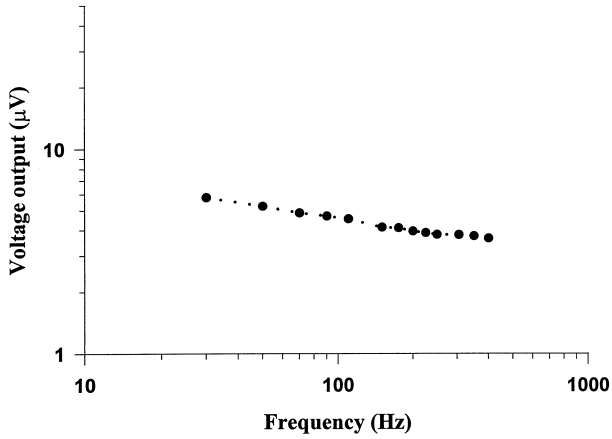

Fig. 6. Voltage response of PZT films under different chopping frequencies.

frequency range of 30–400 kHz, the voltage responsivity decreased linearly with increase in chopping frequency. This indicates that the reciprocal electric time constant ($1/\tau_E$) for the PZT 90/10 films lies below 30 Hz. Figure 7 shows the current response of the PZT 90/10 films, for the frequency range 5–700 Hz. As seen, the current response linearly increases up to 700 Hz, indicating that the reciprocal thermal time constant ($1/\tau_T$) is above 700 Hz. The lower frequency observed in the films for the reciprocal of the electric time constant, compared to the reciprocal thermal time constant $1/\tau_T$, is the reverse order to that typically observed in PZT bulk ceramics and thick films. This can be attributed to the small heat capacitance of the PZT film coupled with the large thermal conduction in the Pt layer. Similar results have been reported for PLT films studied by Takayama *et al.*,[9] and BIT films by Tran *et al.*[10]

The large spontaneous polarization change in the FE_{LT}–FE_{HT} transition range, combined with the low thermal conductance and quick response, make these PZT 90/10 films potential candidates for energy conversion applications. As shown in Fig. 8, an electric circuit was constructed to measure the thermal-electric conversion. In the circuit, the PZT thin films were heated in a pulse mode of approximate 0·2 s interval, which caused the generation of a large pyroelectric signal on thermal cycling, as shown in Fig. 9.

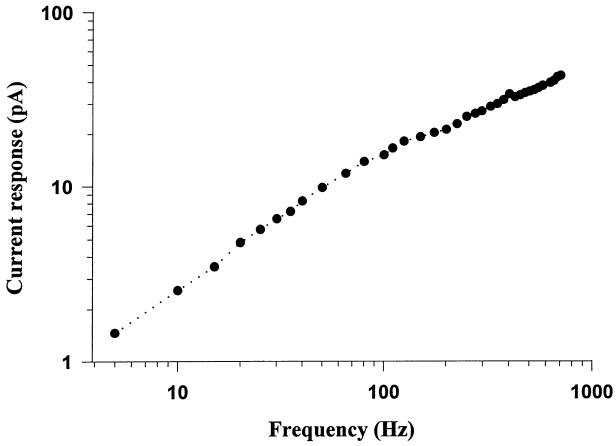

Fig. 7. Current response of PZT films under different chopping frequencies.

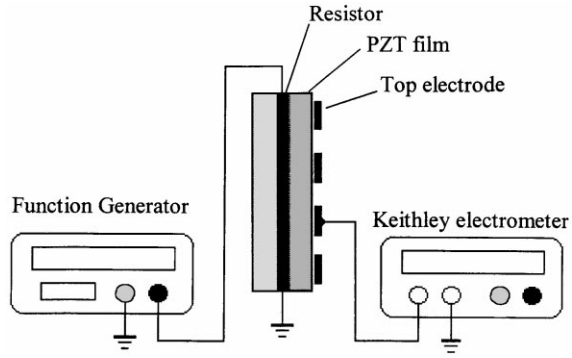

Fig. 8. Circuit for prototype pyroelectric transformer.

Within the temperature range of 40–80°C, the films also showed a quick response at the same working frequency of 5 Hz. Again, this value is an order of magnitude faster than that reported for bulk ceramics and thick films (0·01–0·05 Hz).[11] Across the phase transition range (80–110°C), a signal of ~0·8 volts was generated from a 1 mm^2 area on a 1 μm thick film. This is about 3 times the value obtained outside the transition temperature range.

Figure 10 shows typical current versus time curves, obtained on applying various dc voltages to the PZT (90/10) films. Following an instantaneous rise the current stabilized at a level at least two orders of magnitude less than the initial value, except for dc voltages larger than 6 V. As expected, the true leakage current increased with applied dc voltage. At 1 V dc, the leakage current density of the PZT (90/10) films was $\sim 10^{-9}$ A cm^{-2}, while at 4 volts the current was $\sim 10^{-8}$ A cm^{-2}. When the dc field exceeded 100 kV cm^{-1}, a saturated current could not be obtained. Figure 11 shows that under these latter conditions the J–V curve has a strong varistor-like behavior, where $J \sim V^{\alpha}$. At low field, the factor $\alpha = 1$, which indicates ohmic conduction but highly insulating films. For the high dc field, $\alpha \sim 24$, consistent with the typical behavior exhibited by such varistor materials as ZnO.[12]

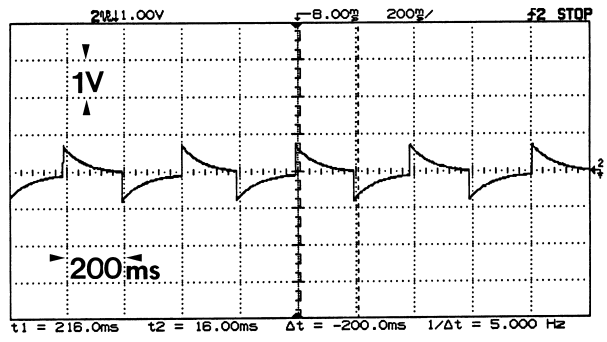

Fig. 9. Voltage output of PZT films under thermal pulse mode.

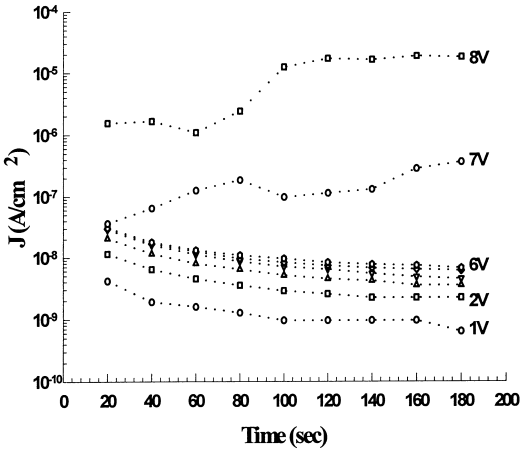

Fig. 10. Current versus time curves of PZT films at different d.c. voltages.

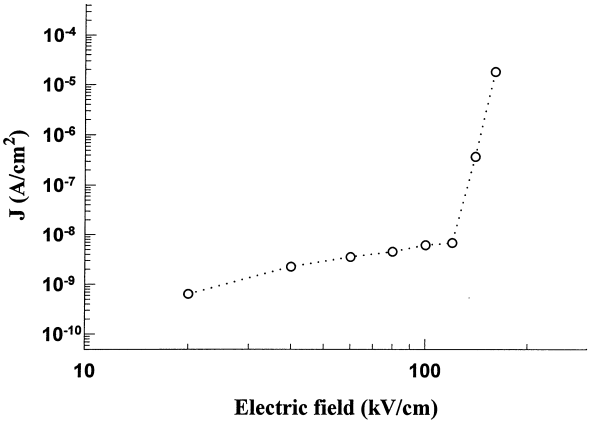

Fig. 11. *J–E* curve of PZT films.

4 Conclusions

In this investigation, (111)-oriented rhombohedral ferroelectric PZT 90/10 thin films were successfully fabricated on (111)Pt/Si substrates, through controlled heat-treatment using a specially developed MOD process. The results showed that rapid thermal treatment enhanced development of the film texture, in which domains were self aligned in the [111] direction. The films exhibited pyroelectric coefficients of $30 \pm 10\,\text{nC cm}^{-2}\,\text{K}$ at room temperature, increasing to $\sim 400\,\text{nC cm}^2\,\text{K}$ in the transition range (80–100°C). Transformer-like behavior was demonstrated for these films, taking advantage of the high pyroelectric coefficient and sharp polarization change in the FE_{LT}–FE_{HT} range. A voltage output of $\sim 0{\cdot}8\,\text{V}$ for $1\,\text{mm}^2$ area on $1{\cdot}0\,\mu\text{m}$ thick films was obtained. The working frequency of 5 Hz obtained for the films is significantly faster than for bulk ceramics and thick films.

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References

1. Li, K. K., Wang, F. and Haertling, G. H., Antiferroelectric lead zirconate thin films derived from acetate precursors. *J. Mat. Sci.*, 1995, **30**, 1386–1390.
2. Tani, T., Li, J.-F., Viehland, D. and Payne, D. A., Antiferroelectric switching and induced strains for sol–gel derived lead zirconate thin layers. *J. Appl. Phys.*, 1994, **75**(6), 3017–3023.
3. Guanghua, Y., Zheng, W. and Sayer, M., Preparation of $Pb(Zr,Ti)O_3$ thin films by sol gel processing. *J. Appl. Phys.*, 1988, **64**(5), 2717–2724.
4. Paz de Araujo, C. A. and Taylor, G. W., Integrated ferroelectrics. *Ferroelectrics*, 1991, **116**(1–2), 215–228.
5. Takayama, R. and Tomita, Y., Preparation of epitaxial $Pb(Zr_xTi_{1-x})O_3$ thin films and their crystallographic, pyroelectric and ferroelectric properties. *J. Appl. Phys.*, 1989, **65**(4), 1666–1670.
6. Iijima, K., Tomita, Y., Takayama, R. and Ueda, I., Preparation of c-axis oriented $PbTiO_3$ thin films and their crystallographic, dielectric and pyroelectric properties. *J. Appl. Phys.*, 1986, **60**(1), 361–367.
7. Clarke, R., Glazer, A. M., Ainger, F. W., Appleby, D., Poole, N. J. and Porter, S. G., Phase transitions in lead zirconate-titanate and their applications in thermal detectors. *Ferroelectrics*, 1976, **11**(1–2), 359–364.
8. Zeyfang, R. R., Sehr, W. H. and Kiehl, K. V., Enhanced pyroelectric properties at a F.E.—F.E. phase transition. *Ferroelectrics*, 1976, **11**(1–2), 355–358.
9. Takayama, R., Tomita, Y., Iijima, K. and Ueda, I., Preparation and characteristics of pyroelectric infrared sensors made of c-axis oriented La-modified $PbTiO_3$ thin films. *J. Appl. Phys.*, 1987, **61**(1), 411–415.
10. Tran, K. D. and Buchanan, R. C., Orientation effects on pyroelectric properties of solution derived bismuth titanate films. In *Ferroelectric Thin Films VI*, MRS Symposium Proc., vol. 493, Materials Research Society, Warrendale, PA, 1998, p. 509–515.
11. Wang, Y. L., Buchanan, R. C. and Roseman, R. D., The study of composite effects of functional ceramics and its potential applications. In *Proceedings of the Tenth IEEE International Symposium on Applications of Ferroelectrics, IEE*, ed. B. M. Kulwicki, A. Amin and A. Safari, IEEE Service Center, Piscataway, NJ, 1996, pp. 739–742.
12. Levinson, L. M. and Phillipp, H. R., Applications and characterization of ZnO varistors. In *Ceramic Materials for Electronics: Processing, Properties, and Applications* (2nd edn), ed. R. C. Buchanan. Marcel Dekker, New York, 1991, pp. 369–372.