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Electrocaloric and pyroelectric properties of PZT and PMN–PNN–PZT thin films

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Abstract

The electrocaloric effects (EC) of PZT and PMN–PNN–PZT films were evaluated. PZT and PMN–PNN–PZT thin films with a thickness of 500 nm were fabricated by state-of-the-art chemical solution deposition from a precursor solution with PZT and (PMN − PNN)/PZT = 30/70. The polarization hysteresis loop was found to be slim and nonlinear, with smaller hysteretic behavior compared with PZT. The pyroelectric properties evaluated from polarization change and current measurement show that the properties of PMN–PNN–PZT films are superior to those of non-doped PZT films. The electrocaloric temperature changes ΔT due to applied ΔE were calculated. PZT and PMN–PNN–PZT films exhibited ΔT of 2.1 K and 3.6 K at 237.5 °C under a field of 500 kV/cm, respectively. Thermal-electrical energy converters based on pyroelectric effects were investigated for energy harvesting and possible use in ultralow-power sensor modules. The possibilities of pyroelectric energy harvesting using these PZT films were also investigated.

Keywords: Films; Ferroelectric properties and electrocaloric effect; PZT; Functional applications

1. Introduction

Conventional refrigerators that use a compressor have a variety of problems. They make a noticeable noise, down-scaling is difficult, and the commonly used refrigerants, freons, have been proven to be ozone-depleting compounds. Solid state electronic cooling devices using the thermoelectric effect (Peltier Effect) have been used; however, these devices require a large DC current, resulting in a waste of heat through Joule heating. Thus, the devices that make use thermoelectric cooling are not energy-efficient. A thin refrigerator using the electrocaloric effect (ECE) has recently attracted attention due to recent reports of the demonstration of a giant electrocaloric effect in thin films. ECE refrigerators are very attractive because they are compact, light and can be fabricated from inexpensive materials that are benign with respect to the environment.

The electrocaloric effect is a phenomenon in which a material shows a reversible temperature change under an applied electric field. [1] In order to create ECE cooling devices, materials with large ECEs are required. The electrocaloric temperature change ΔT due to applied ΔE is calculated from the following equation. Here, C and ρ are the specific heat and the density, respectively.

$$\Delta T = \frac{1}{C\rho}\int_{E_1}^{E_2} T\left(\frac{\partial P}{\partial T}\right)_E dE \quad (1)$$

Based on the equation, a large $(\partial P/\partial T)_E$, a large polarization change with temperature under high electric field, is desired. With respect to achieving large $(\partial P/\partial T)_E$, relaxor materials have recently attracted attention.

Thus far, relaxor-ferroelectric single crystals such as $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ (PMN–PT) have been of interest due to their excellent piezoelectric properties, which are superior to those of PZT ceramics. [2–8] Compared with PZT, the smaller field-induced strain hysteresis of these crystals is also attractive for actuator applications. Trial film preparations of these relaxor-ferroelectric crystals have been reported, but a higher annealing temperature of around 800 °C is required, and high quality film preparation has been found to be difficult [9]. Our aim

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was to modify PZT film properties regarding hysteretic behavior without raising the final annealing temperature. For film preparation, we employed a chemical solution deposition due to its ease of composition control and low temperature deposition, and we obtained $Pb(Mg_{1/3}Nb_{2/3})O_3$–$Pb(Ni_{1/3}Nb_{2/3})O_3$ doped PZT films by annealing at 650 °C. [10] The electrical and electromechanical properties of $Pb(Mg_{1/3}Nb_{2/3})O_3$–$Pb(Ni_{1/3}Nb_{2/3})O_3$–$Pb(Zr,Ti)O_3$ (PMN–PNN–PZT) thin films prepared on $Pt/Ti/SiO_2/Si$ substrates by chemical solution deposition were investigated. The PMN–PNN–PZT films annealed at 650 °C exhibited slim polarization hysteresis curves and a high dielectric constant of 2100 at room temperature. A broad dielectric maximum at around 140–170 °C was observed. The field-induced displacement was measured by scanning probe microscopy; it was found that the bipolar displacement was not hysteretic and the effective piezoelectric coefficient (d_{33}) was 66 pm/V. The effective d_{33} decreased with temperature, but the value at 100 °C remained 45 pm/V [10].

In this study, the ECE of the PMN–PNN–PZT as well as the pyroelectric properties are reported. One reason to study pyroelectric properties is in that the pyroelectric effects are physical inverse effects of ECE. In addition, the possibilities for thermal-electrical energy converters based on pyroelectric effect were investigated for energy harvesting and possible use in ultralow-power sensor modules. Thus far, different elements based on ceramics and thin films of lead zirconate titanate (PZT) were characterized. The charge extracted was stored in a capacitor comparing performances offered by different rectifying circuits. Results show that the harvested energy can be compatible with use in autonomous sensors working in low-duty-cycle switched-supply mode.

2. Experimental

PMN–PNN–PZT thin films were fabricated by a state-of-the-art chemical solution deposition from a precursor solution (Inostek Inc.) with (PMN − PNN)/PZT = 30/70. [6] The total film thickness was 500 nm, and the final annealing temperature was 650 °C. Thin-film Pt top electrodes were deposited. The polarization hysteresis loops and dielectric constant were measured using, respectively, a TF2000 ferroelectric tester and an Agilent Technology impedance analyzer, 4192A. To characterize the fabricated devices, the experimental set-up included a Peltier cell, a temperature sensor to drive and monitor temperature profiles, as shown in Fig. 1. The cooling was carried out by forced running water inside the copper heater plate. The output currents were measured using TOA DC microvolt ammeter, DC-18R, the converted DC output voltages were collected into data logger.

3. Results and discussion

3.1. Electrocaloric properties

The polarization hysteresis loop is slim and nonlinear, and compared with PZT, the hysteretic behavior is smaller.

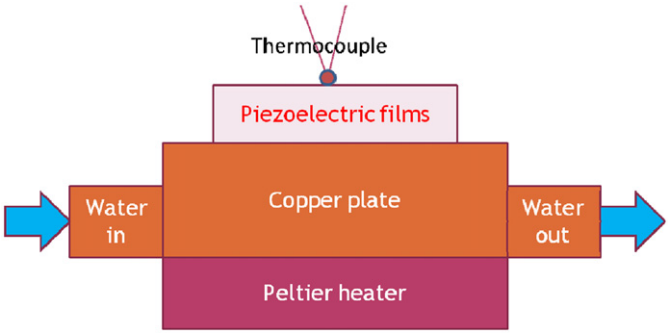

Fig. 1. Experimental set-up for measuring the thermal response of PZT and PMN–PNN–PZT films.

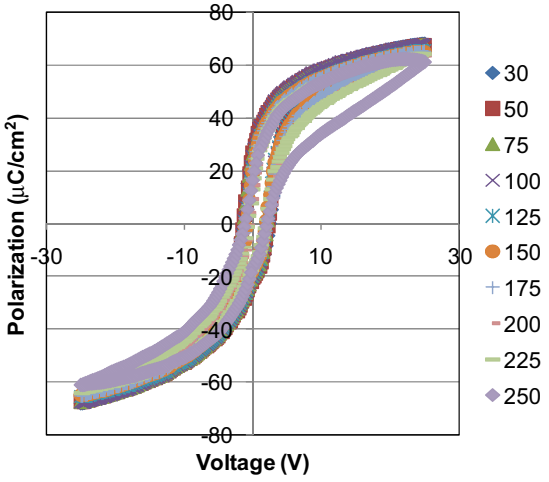

Fig. 2. Temperature dependence of polarization hysteresis loops of PZT films.

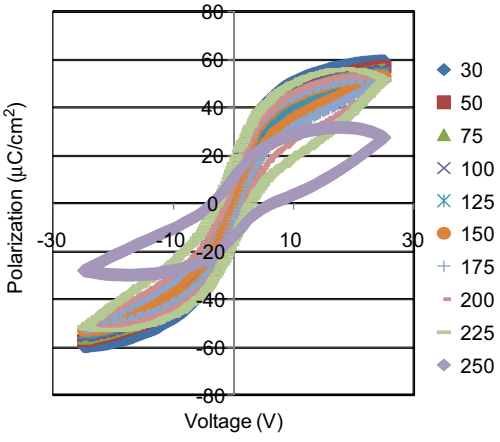

Fig. 3. Temperature dependence of polarization hysteresis loops of PMN–PNN–PZT films.

The temperature dependencies of the PZT and PMN–PNN–PZT films are shown in Figs. 2 and 3, respectively. The polarizations under 500 kV at various temperatures are shown in Fig. 4. It should be noted that the polarizations of the PMN–PNN–PZT films decreased rapidly, compared with those of the PZT films, likely due to either the lower Curie temperature, the relaxor behavior, or both.

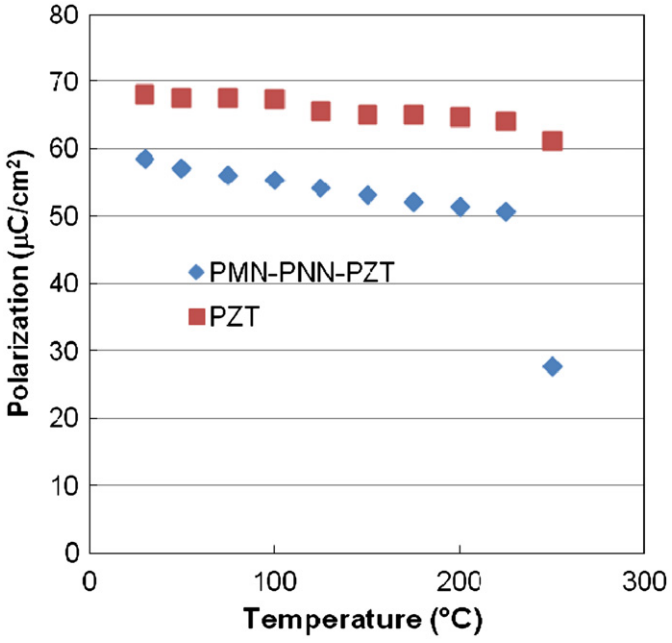

Fig. 4. Polarizations of the PZT and PMN–PNN–PZT films at various temperatures under a field of 500 kV/cm.

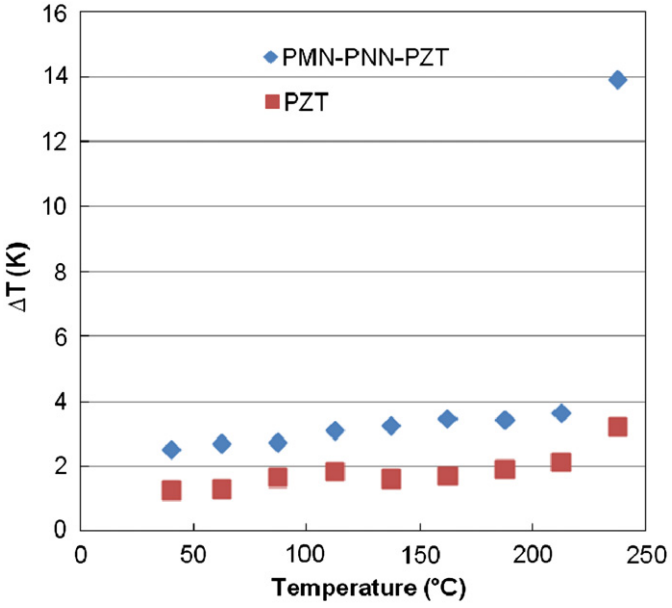

Fig. 5. Electrocaloric temperature change ΔT due to applied ΔE.

The electrocaloric temperature change ΔT due to applied ΔE is calculated from the Eq. (1), as shown in Fig. 5. Here, the curve fitting was applied to average polarization change. A C value of 330 J/kg K and ρ of 8.0 g/cm^3 are used for the calculation, respectively. Very large value is apparently calculated for PMN–PNN–PZT films for the abrupt polarization drop between 225 and 250 °C; however, the round shape in hysteresis loop indicates contribution of leakage components activated at high temperature in the films. Since the computation of the $(\partial P/\partial T)_E$ in the Eq. (1) includes uncertainty, it is not safe that the ΔT is

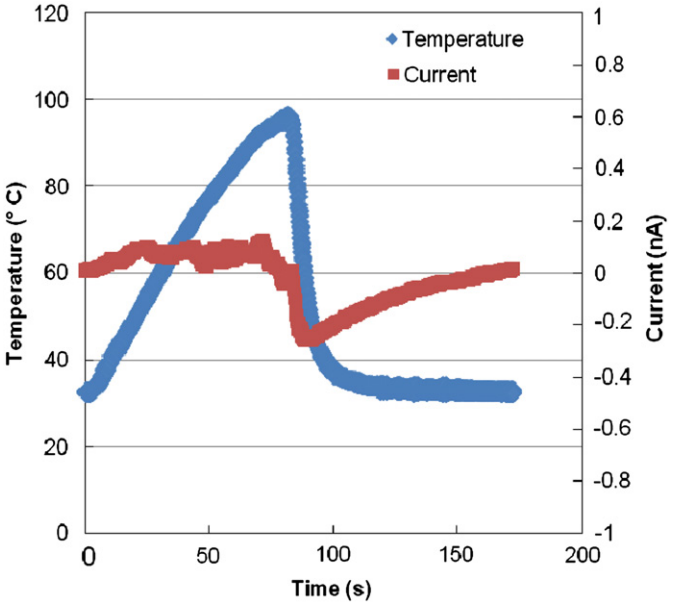

Fig. 6. Output currents from PZT thin films.

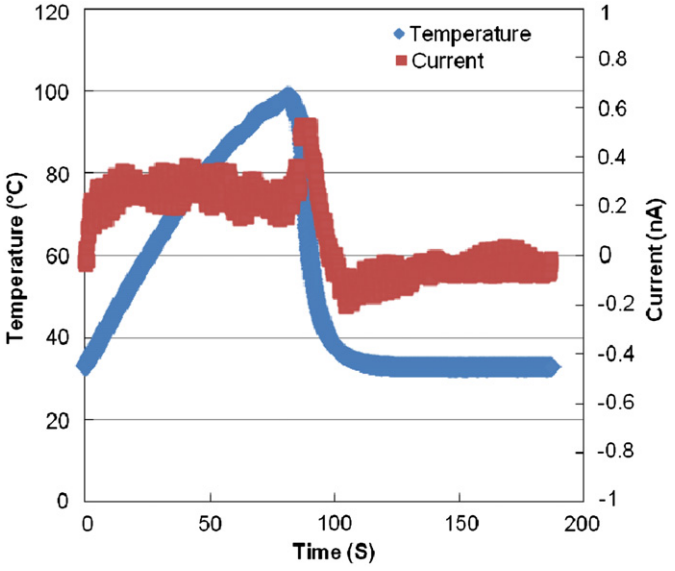

Fig. 7. Output currents from PMN–PNN–PZT thin films.

realized. [11] The certain expected adiabatic change in temperature ΔT of the PZT–PMN–PNN films was 3.6 K under 500 kV/cm at 237.5 °C. At present, the value is smaller than the reported giant electrocaloric effect (0.48 K/V) in 350-nm $PbZr_{0.95}Ti_{0.05}O_3$ films near the ferroelectric Curie temperature of 222 °C. However, the results of this study indicate that the even 30 mol% amount of relaxor addition to PZT films significantly improves ECE, suggesting the validity of a new approach to materials selections for ECE.

3.2. Pyroelectric properties

The temperature response from PZT and PMN–PNN–PZT films are shown in Figs. 6 and 7, respectively. Output

Table 1
Experimental pyroelectric coefficients of PZT and PMN–PNN–PZT films. ($C\,cm^{-2}\,K^{-1}$).

Measuring method	PMN–PNN–PZT	PZT
Electrocaloric (250–50 kV/cm at 30 °C)	9.7×10^{-8}	5.3×10^{-8}
$\Delta Pr/\Delta T$	6.5×10^{-8}	2.7×10^{-8}
Current measurement	5.3×10^{-8}	3.4×10^{-8}

currents switch their direction and maximum currents flow when the temperature changes drastically. Experimental pyroelectric coefficients of the PZT and PMN–PNN–PZT are summarized in Table 1. The value calculated from the ECE shows the largest values in both films. In the case of ECE measurements, films are polarized by the high-field application; therefore, experimental pyroelectric coefficients are enhanced. In the case of current measurement, only the change in the remanent polarization produce pyroelectric current, the measured pyroelectric coefficients appear to be smaller than those from dynamic measurement. The values from the PMN–PNN–PZT are larger than the one from PZT, showing that the pyroelectric properties are raised by the addition of the relaxor PMN–PNN element to PZT. Concerning thermal energy harvesting, the output current from the films are nano-ampere levels, and promising results have not been obtained.

Conclusions

The temperature dependence of electric, electrocaloric, and pyroelectric properties of PZT–PMN–PNN thin films were evaluated. PZT–PMN–PNN thin films exhibited larger electrocaloric and pyroelectric properties compared with PZT thin films. The expected adiabatic change in temperature of PZT–PMN–PNN films was 3.6 K under 500 kV/cm at 237.5 °C. The experimental pyroelectric coefficient of PZT–PMN–PNN films was 5.3×10^{-8} ($C\,cm^{-2}\,K^{-1}$).

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