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Temperature dependence of electrical and electromechanical properties of $Pb(Mg_{1/3}Nb_{2/3})O_3$–$Pb(Ni_{1/3}Nb_{2/3})O_3$–$Pb(Zr,Ti)O_3$ thin films

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Abstract

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, PMN/PNN/PZT = 20/10/70) on $Pt/Ti/SiO_2/Si$ substrates by chemical solution deposition was 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 approximately 140–170 °C was observed. The field-induced displacement was measured by scanning probe microscopy, the bipolar displacement was not hysteretic, and the effective piezoelectric coefficient (d_{33}) was 66×10^{-12} m/V. The effective d_{33} decreased with temperature, but the value at 100 °C remained 45×10^{-12} m/V.

Keywords: A. Films; C. Ferroelectric properties; C. Piezoelectric properties; E. Actuators

1. Introduction

Recently, electric field-induced strains in thin films have attracted attention due to their potential applications in microelectromechanical systems (MEMS) [1,2]. Thus, research efforts have focused on $Pb(Zr,Ti)O_3$ (PZT) [1–4] due to reasonably good piezoelectric behavior and a relatively low annealing temperature, which is approximately 650 °C. However, the strong hysteretic behavior of the field-induced displacement in PZT is considered to be a problem in the analogue control of an actuator. Recently, 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 [5–7]. Compared with PZT [8], 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 approximately 800 °C was required, and high quality film preparation has been difficult to achieve [9–13]. Our aim is to modify PZT film properties regarding hysteretic behavior without raising the final annealing temperature. For film preparation, the chemical solution deposition was employed due to its ease of composition control and low temperature deposition, and the $Pb(Mg_{1/3}Nb_{2/3})O_3$–$Pb(Ni_{1/3}Nb_{2/3})O_3$ doped PZT films could be obtained by annealing at 650 °C.

In this paper, the properties of relaxor $Pb(Mg_{1/3}Nb_{2/3})O_3$–$Pb(Ni_{1/3}Nb_{2/3})O_3$ doped PZT films annealing at 650 °C were reported, including a description of their temperature dependence and a comparison with PZT films. In the case of relaxor-doped films, the temperature dependence of the properties is worrisome due to a lower transition temperature. Here, the electrical and electromechanical properties of the films in the temperature range between −250 and 200 °C and the electromechanical properties between −60 and 150 °C were reported and compared with the properties of PZT films.

2. Experimental procedure

PMN–PNN–PZT thin films are fabricated by a state-of-the-art chemical solution deposition from a precursor solution (Inostek Inc.) with PMN/PNN/PZT = 20/10/70. Zr to Ti ratio of PZT is 52/48 [14]. The total film thickness is 500 nm. The final annealing temperature is 650 °C. Thin-film Pt top electrodes were deposited. The polarization hysteresis loops and dielectric

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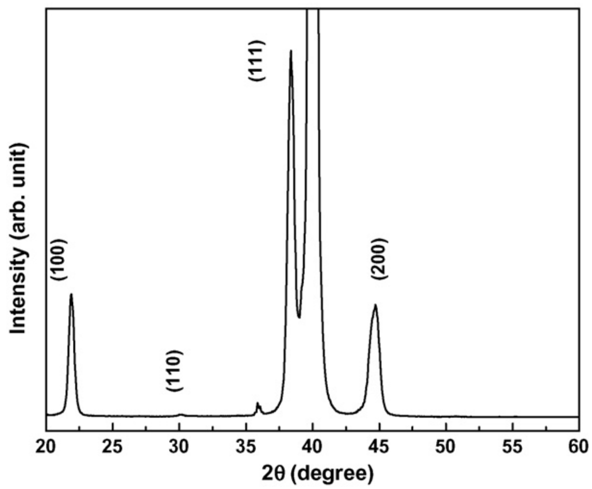

Fig. 1. X-ray diffraction pattern of 20PMN–10PNN–70PZT film.

constant were measured using, respectively, a TF2000 ferroelectric tester and an Agilent Technology impedance analyzer, 4192A. The field-induced strain of the films was measured using scanning probe microscopy. The details of the experimental setup are described elsewhere [4].

3. Results and discussion

Fig. 1 shows the X-ray diffraction pattern of the 20PMN–10PNN–70PZT film annealed at 650 °C. The pattern indicates that the obtained film is pure perovskite and shows a mixed preferred orientation of (1 0 0) and (1 1 1).

The polarization hysteresis loop of the film at room temperature is shown in Fig. 2. The polarization hysteresis loop was slim and nonlinear and, compared with PZT, the hysteretic behavior was smaller. The small-signal dielectric constant (ε_r) and loss tangent of the films at room temperature (20 °C) were 2100 and 0.04, respectively. The polarization hysteresis loops at −200, 0, and 150 °C are shown in Fig. 3. The

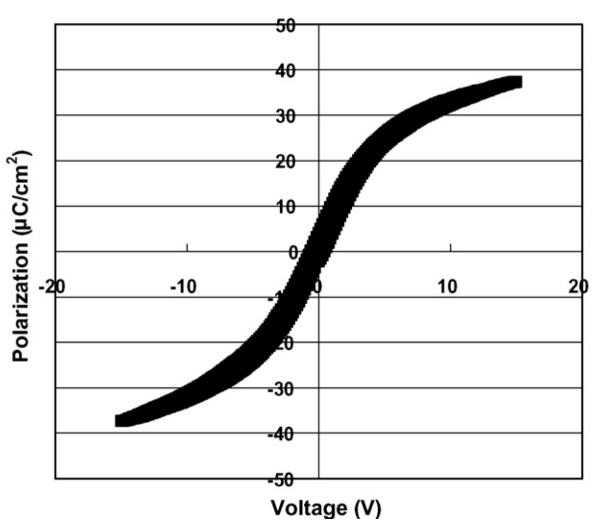

Fig. 2. Polarization hysteresis loop of 20PMN–10PNN–70PZT film at room temperature.

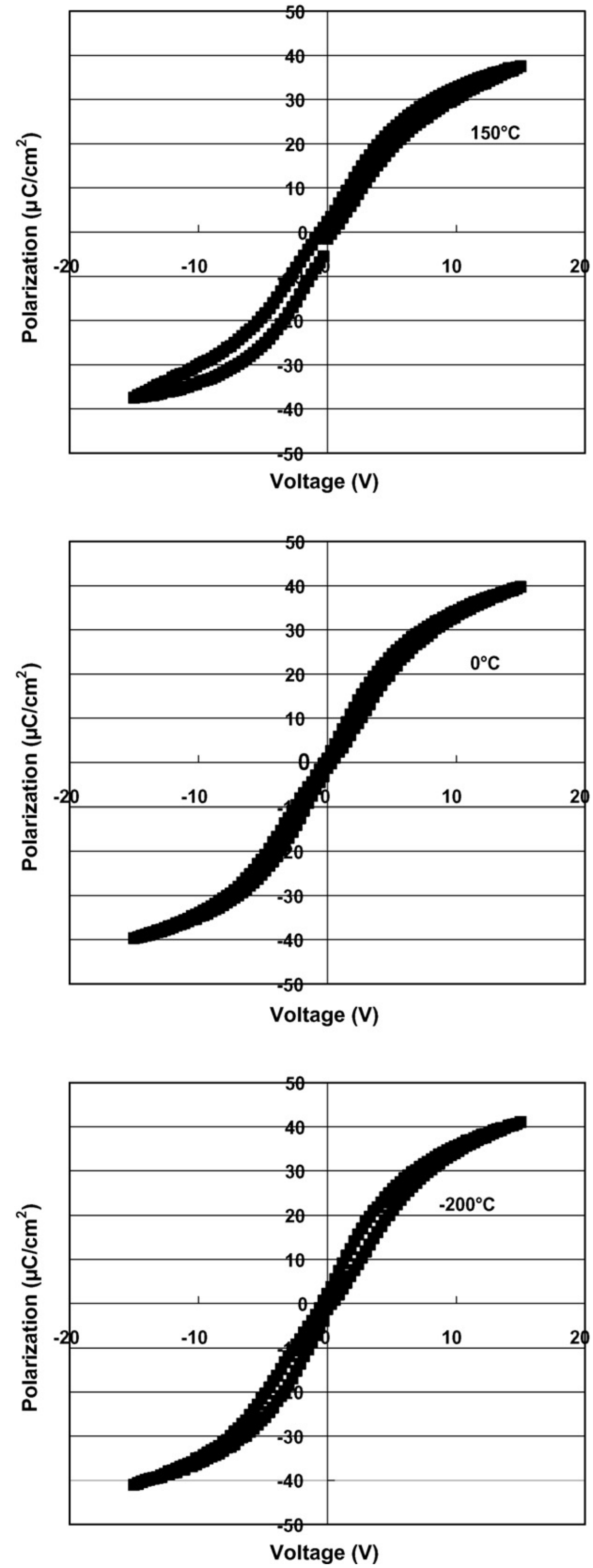

Fig. 3. Polarization hysteresis loops of 20PMN–10PNN–70PZT film at various temperatures.

polarization hysteresis loops were almost unchanged between temperatures in the range from −200 to 150 °C. The roundness of shape at 150 °C is probably due to increased leakage components in the films; a slight decrease in polarization is

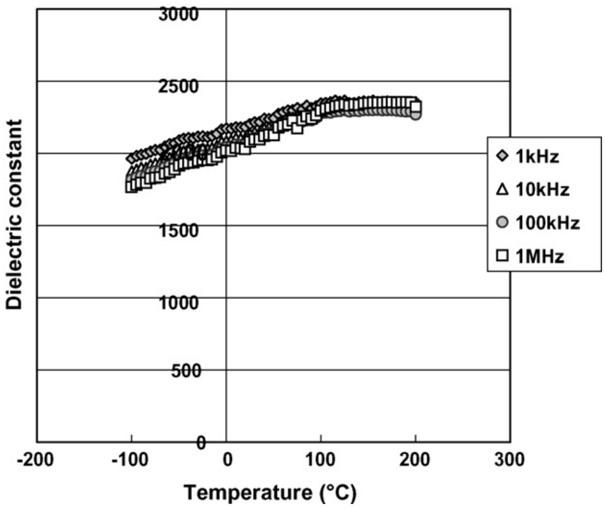

Fig. 4. Temperature dependence of the small-signal dielectric constant of the 20PMN–10PNN–70PZT film.

derived from a loss of spontaneous polarization. In the case of PZT, the coercive field (E_c) and the remanent polarization (P_r) increase with decreasing temperatures ranging from −100 to 150 °C [4], greatly different from that of the 20PMN–10PNN–70PZT film. The small-signal dielectric constant at zero bias increases with the temperature to a broad maximum at 140–170 °C and then slightly decreases, as shown in Fig. 4. The dielectric behavior is frequency dependent; the dielectric maximum increases with an increasing frequency. The composition of 20PMN–10PNN–70PZT is in the normal ferroelectrics region, however, its behaviors are considered to be influenced by the relaxor PMN–PNN characteristics. The dc bias dependence of the dielectric constant and loss tangent at −200, 0, and 150 °C are shown in Fig. 5. The dielectric constants of the films are less hysteretic with the dc bias voltage in this temperature range. Lower tangent delta values at 150 °C indicate a decrease in domain wall motion contribution due to the loss of spontaneous polarization.

Fig. 6 shows the field-induced displacement of the 20PMN–10PNN–70PZT films at various temperatures. From the slope

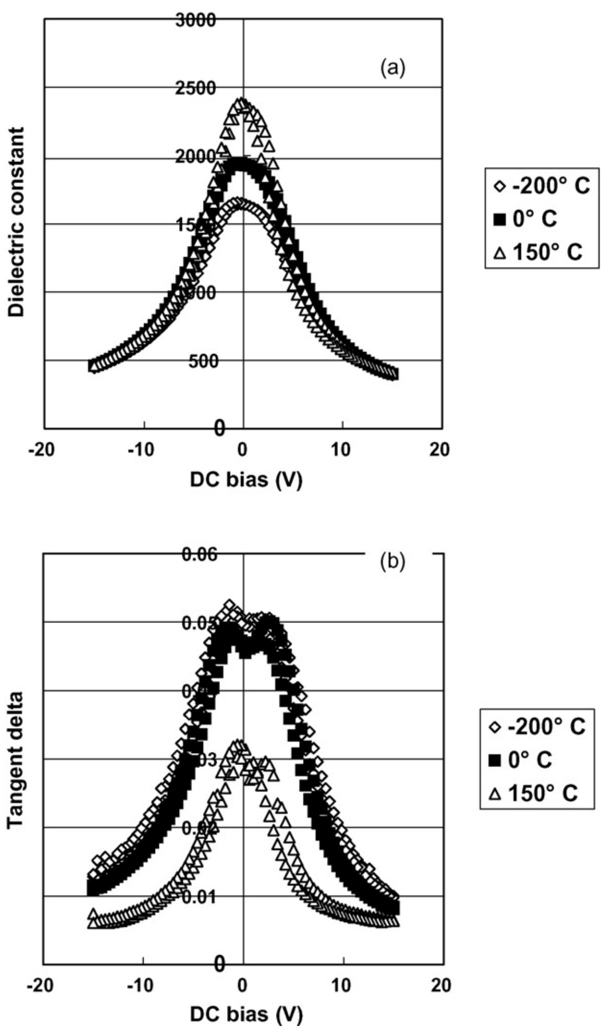

Fig. 5. Bias dependence of (a) small-signal dielectric constant and (b) loss tangent of 20PMN–10PNN–70PZT film at various temperatures.

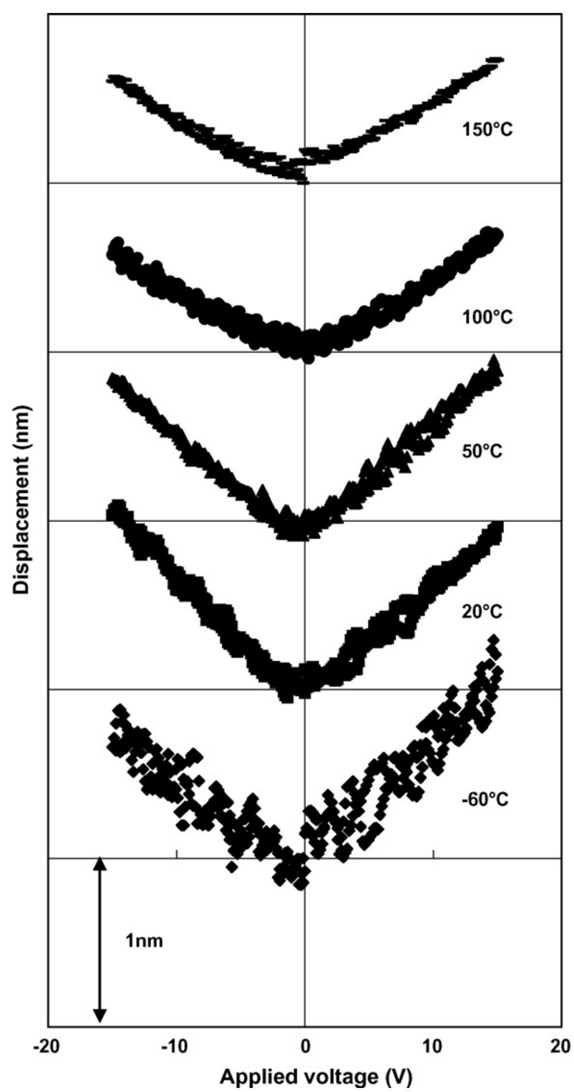

Fig. 6. Temperature dependence of field-induced displacements of 20PMN–10PNN–70PZT film.

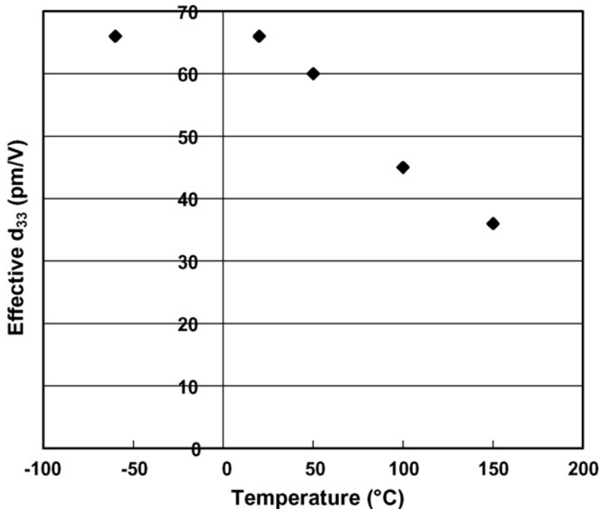

Fig. 7. Plots of effective d_{33} of the 20PMN–10PNN–70PZT film with temperatures.

of the loops, the effective piezoelectric coefficient at room temperature was calculated to be 66×10^{-12} m/V. The loops were linear in shape, and the butterfly-shaped hysteretic behavior is negligible in the measured temperature range. These behaviors correspond well to non-hysteretic polarization hysteresis loops and bias-dependent dielectric constant curves. These bipolar displacement loops have better linearity than those of the PZTs and are considered to be better in practical actuator applications that require analogue control of the actuation. The temperature dependent effective d_{33} computing from the slope of the loop is shown in Fig. 7. The decrease in the field-induced displacement is mainly due to the loss of spontaneous polarization. Considering that the transition temperature of the film lies around 140–170 °C, the decrease in field-induced displacement is natural. Even at 150 °C, the film exhibits a displacement roughly half as much as at room temperature. It can be said that the film displacement is more than that would be expected from normal ferroelectrics. In normal ferroelectrics, the field-induced displacement diminishes at the transition temperature. The observed relatively mild temperature dependence of the 20PMN–10PNN–70PZT films is partly due to the contribution of electrostriction. In ferroelectrics, piezoelectric displacements are regarded as electrostriction biased by spontaneous polarization. The intrinsic piezoelectric coefficient, d_{int}, and strain, x, are expressed as

$$x = Q(P_s + \Delta P_s)^2 = QP_s{}^2 + 2Q\varepsilon_0\varepsilon P_s E + Q\varepsilon_0^2\varepsilon^2 E^2,$$
$$d_{int} = 2Q\varepsilon_0\varepsilon P_s, \qquad \Delta P_s = \varepsilon_0\varepsilon E$$

here, Q, ε_0, ε, P_s and E are the electrostrictive coefficient, dielectric constant of vacuum, relative dielectric constant, spontaneous polarization and electric field, respectively. The coefficient of electrostriction, $M = Q\varepsilon_0^2\varepsilon^2$, is independent of spontaneous polarization, and therefore the electrostriction displacement occurs without spontaneous polarization.

4. Conclusions

The electrical and electromechanical properties of the $Pb(Mg_{1/3}Nb_{2/3})O_3$–$Pb(Ni_{1/3}Nb_{2/3})O_3$–$(PbTi,Zr)O_3$ (PMN–PNN–PZT, PMN/PNN/PZT = 20/10/70) thin films were investigated. The films exhibited smaller hysteretic polarization hysteresis loops and dc bias voltage dependence of dielectric constant curves. The transition temperature estimated from the temperature dependence of the small-signal dielectric constant is around 140–170 °C. The field-induced vertical displacement of the film was measured using scanning probe microscopy. A bipolar displacement with negligible hysteresis was obtained, and the effective piezoelectric coefficient (d_{33}) of the film was 66×10^{-12} m/V at room temperature. These properties reflect those of relaxor ferroelectrics. The temperature dependence of the longitudinal displacement could be measured using scanning force microscopy with a vacuum chamber, heater and liquid nitrogen flowing system. The effective d_{33} decreased with temperature, but the value at 100 °C remained at 45×10^{-12} m/V. The temperature dependence is worse than PZTs, but it can be said this behavior is not a fatally bad characteristic and that the film could be used in the temperature range from −60 to 100 °C as microactuators. By making a comparison with the PZT films, our work suggests that 20PMN–10PNN–70PZT film is a potential candidate to replace PZT films for ferroelectric MEMS applications due to their non-hysteretic dielectric and electromechanical behaviors and that it is especially suitable for an actuator requiring analogue position control such as an actuator in a micro-mirror equipped in display devices.

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