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Effects of niobium doping on the piezoelectric properties of sol–gel-derived lead–zirconate–titanate films

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Sol–gel-derived lead–zirconate–titanate (PZT) films doped with various amounts of niobium (Nb) have been spin coated on silicone substrates, and their remanent polarization P_r, and effective longitudinal and transverse piezoelectric coefficients ($d_{33,c}$ and $e_{31,c}$) as well as the pyroelectric coefficient p, have been measured. The Zr/Ti ratio of the films is 53/47. Our results reveal that the Nb-dopant effects on the PZT films are very similar to the experimentally known effects on the corresponding bulk ceramics, i.e., enhancing both the longitudinal and transverse piezoelectric properties. However, because of the substrate clamping effect, the exact enhancement in the longitudinal piezoelectric properties cannot be evaluated by the $d_{33,c}$ measurement on the film samples. Accordingly, the observed $d_{33,c}$ value of the Nb-doped PZT films remains almost unchanged while the observed $-e_{31,c}$ (as well as P_r and p) increases with increasing Nb concentration, showing an optimum Nb concentration of 2 mol %. For the PZT film doped with 2% Nb, the observed values of P_r, $d_{33,c}$, $-e_{31,c}$, and p are about 30 μC/cm^2, 95 pm/V, 18 C/m^2, and 350 μC/m^2 K, respectively. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1635968]

I. INTRODUCTION

In recent years, ferroelectric lead–zirconate–titanate (PZT) films have been extensively studied for various applications, such as ultrasonic micromotors, micropumps, and cantilever actuators in microelectromechanical systems. Usually, PZT compositions near the morphotropic phase boundary (i.e., Zr/Ti~53/47) are chosen because large piezoelectric coefficients and electromechanical coupling factors have been obtained in bulk ceramics of similar compositions.[1] Besides the composition, it is also experimentally known that the piezoelectric properties of bulk ceramics can be optimized by the addition of dopants, and in particular, of donor-type dopants [e.g., lanthanum (La) and niobium (Nb)].[1–3] For example, by the doping of about 2 mol % Nb, the longitudinal and transverse piezoelectric coefficient (d_{33} and $-d_{31}$) of a PZT (52/48) ceramic are increased by about 60% and 80%, respectively.[1] In general, donor-type dopants also afford increments in the electrical resistance, dielectric constant as well as the elastic compliance of PZT bulk ceramics. The effects of donor-type dopants, particularly Nb, on the properties relative to ferroelectric memories have been discussed in a number of recent papers.[4,5] Similar to the effects on bulk ceramics, Nb increases the electrical resistance of PZT films and produces polarization hysteresis loops with low coercive fields and large remanent polarizations. However, their effects on the piezoelectric properties of PZT films have not been extensively and systematically studied, and, in particular, have not been correlated with the experimentally known effects on the corresponding bulk ceramics. Haccart *et al.*[6,7] and Remiens *et al.*[8] have studied the piezoelectric coefficients of Nb-doped PZT films prepared by magnetron sputtering. They reported that the optimum doping level of Nb is about 2 at. %, as in the case for the bulk ceramics. For the Nb-doped film, the observed d_{33} value is about 50% higher compared to the undoped PZT film (75 pm/V vs 50 pm/V), while the observed value of $-e_{31}$ (transverse piezoelectric charge coefficient) remains almost unchanged at a value of about 4 C/m^2. However, they have not compared the observed piezoelectric coefficients with those of the corresponding bulk ceramics.

To date, there are a number of methods established for the measurements of d_{33} and d_{31} of ferroelectric films. Among them, the noncontact optical interferometry method is the most widely used method for the d_{33} measurement,[9,10] whereas the wafer flexure[11] and cantilever deflection techniques[10,12] are the most common methods for measuring d_{31} and e_{31}, respectively. Since ferroelectric films are usually deposited on a rigid substrate, e.g., silicon, they are tightly clamped by the substrate and hence cannot deform freely. As a result, the observed piezoelectric coefficients (no matter which method is used) are different from those of bulk ceramics, and therefore usually called effective piezoelectric coefficients. For example, the effective d_{33} ($d_{33,c}$) determined by the laser interferometry method and the effective e_{31} ($e_{31,c}$) by the cantilever deflection technique are related to the (true) piezoelectric coefficients d_{33} and d_{31} as follows:[9,12]

$$d_{33,c} = d_{33} - \frac{2s_{13}^E d_{31}}{s_{11}^E + s_{12}^E}, \tag{1}$$

$$e_{31,c} = \frac{d_{31}}{s_{11}^E + s_{12}^E}, \tag{2}$$

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where s_{11}^E, s_{12}^E, and s_{13}^E are the elastic compliances of the films. It should be noted that because of Poisson effect d_{33} and d_{31}, hence, $d_{33,c}$ and $e_{31,c}$, have opposite signs.

It can be seen that the effective piezoelectric coefficients are also dependent on the elastic properties of the films [Eqs. (1) and (2)]. Hence, the work in studying the donor-type dopant effects on PZT films and, in particular, in comparing the effects on films and bulk ceramics, become more complicated. In the present work, we will study the effects of the niobium dopant on the piezoelectric and pyroelectric properties of sol–gel-derived PZT films. Both $d_{33,c}$ and $e_{31,c}$ of the Nb-doped PZT films will be measured. The resulting effect of substrate clamping on the observed piezoelectric coefficients will be discussed. Since the sol–gel method offers good stoichiometry control of the film composition and chemical homogeneity, the observed effective piezoelectric coefficients will be compared with the theoretical values calculated using the material parameters of PZT bulk ceramics of similar compositions.

II. EXPERIMENT

The Nb-doped PZT (abbreviated as PNZT-x) films with Zr/Ti=53/47 and Nb concentration x varying from 0 to 3 mol % were prepared using a sol–gel method. A PNZT precursor solution was spin coated on a $Pt/Ti/SiO_2/Si$ substrate to give a film of thickness about 100 nm, which was then pyrolyzed at 450 °C for 10 min. After the deposition of three layers, the film was annealed in an oxygen atmosphere at 600 °C for 3 min in a rapid thermal processor. By repeating the process a few times, a PZT film of thickness 1.2 μm was obtained. The film was then annealed at 680 °C for 20 min in a furnace. A platinum top electrode of diameter 1 mm and thickness 150 nm was deposited on the film by dc sputtering in a pure argon atmosphere.

The crystallite structure of the PZT films was studied using an x-ray diffractometer (XRD) with nickel-filtered Cu $K\alpha$ radiation (X'pert System, Philips Electronic Instruments), and the microstructure was examined using a scanning electron microscope (Leica Stereoscan 440). A Sawyer–Tower circuit was used to measure the polarization hysteresis ($P-E$) loop of the films, from which the remanent polarization P_r was determined. Effective piezoelectric coefficients $d_{33,c}$ and $e_{31,c}$ of the films were measured using a single beam laser interferometry method and a cantilever deflection technique, respectively. The experimental details of the measurements have been reported in a previous publication.[10] To measure $d_{33,c}$, a small ac field (E) at 15 kHz was applied to the film sample in the thickness direction; and the surface displacement (Δt) induced in the sample was measured using a heterodyne single beam laser interferometer (SH-120, B.M. Industries). $d_{33,c}$ was then calculated as

$$d_{33,c}=\frac{\Delta t/t}{E}, \tag{3}$$

where t is the thickness of the PZT films. The substrate bending, which usually induces enormous error in the measurement using the single beam laser interferometry method, was effectively suppressed by gluing the substrate tightly to a large and rigid platform.[10] For the $e_{31,c}$ measurement, a rectangular sample (film/substrate) was bent dynamically at a frequency (f) of 10 Hz; and the current (I_0) induced on the film surface was measured using a lock-in amplifier (Fig. 1). $e_{31,c}$ was then given by

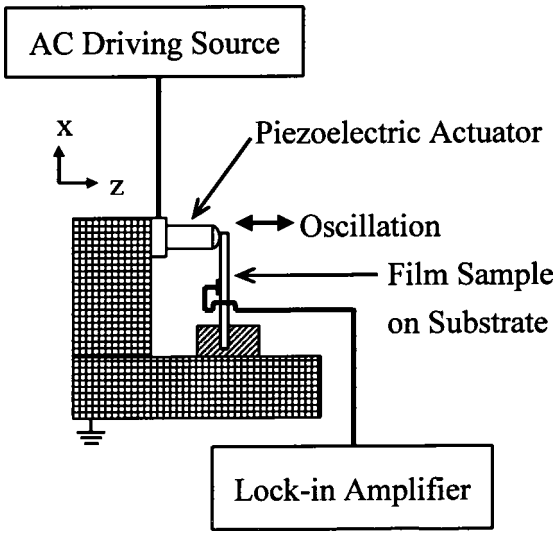

FIG. 1. Experimental setup for the measurement of the transverse piezoelectric charge coefficient e_{31}.

$$e_{31,c}=\frac{\ell^3 I_0}{3\pi f A h(1-\nu)Z_0}\left[\ell-\frac{x_0+x_1}{2}\right]^{-1}, \tag{4}$$

where Z_0 is the deflection at the free end, A is the area of the top electrode, h is the thickness of the substrate, ν is Poisson ratio of the substrate, ℓ is the distance from the clamping edge to the free end of the sample, and x_0 and x_1 are the positions of the electrode extremities in the length direction. In the present work, a ν value of 0.172 for the substrate was used in the calculation.[11]

The pyroelectric coefficient p was measured using a dynamic method. Experimental details of the measurement have been reported in a previous publication.[13] The sample temperature was sinusoidally modulated at room temperature at a frequency (f) of 5 mHz and an amplitude (T_0) of 1 K using a Peltier element.; and the 90° out-of-phase component

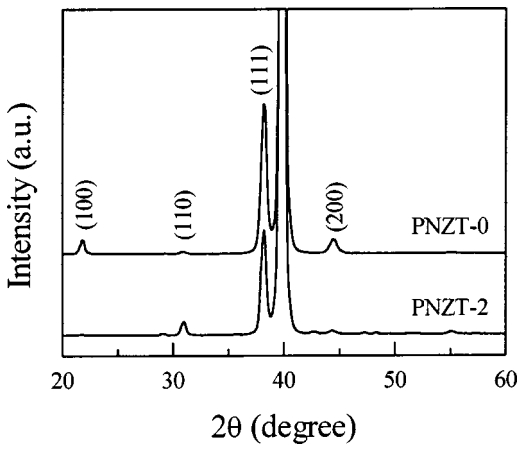

FIG. 2. XRD patterns of the PNZT-0 and PNZT-2 films.

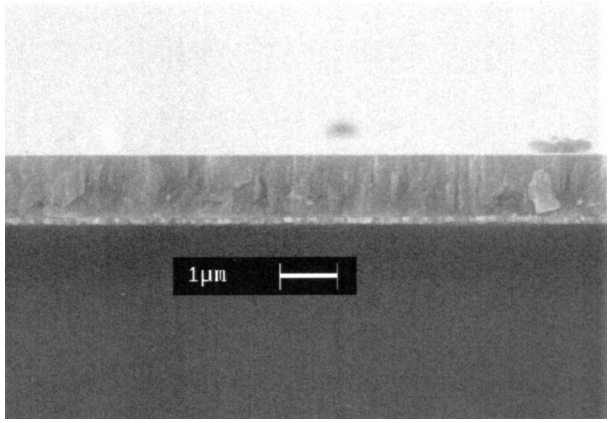

FIG. 3. SEM micrograph of the cross section of the PNZT-2 film of thickness 1.2 μm.

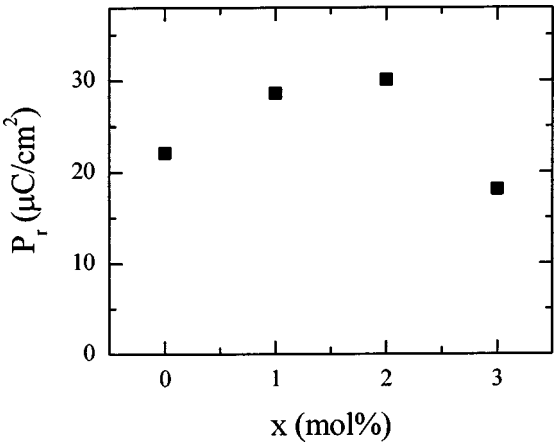

FIG. 5. Variations of the remanent polarization P_r with Nb concentration x.

of the resulting pyroelectric current (I_p) with respect to the temperature modulation was measured using a lock-in amplifier. p was then given by

$$p = \frac{I_p}{2\pi f A T_0}, \tag{5}$$

where A is the area of the top electrode.

III. RESULTS AND DISCUSSION

The XRD patterns of the PNZT-0 (i.e., PZT) and PNZT-2 (i.e., PZT doped with 2 mol % Nb) films are shown in Fig. 2. The films are well crystallized in the perovskite phase with (111)-preferred orientation. No pyrochlore phase formation is observed. Similar XRD patterns have also been observed for the other PNZT films. Figure 3 shows a typical example of a scanning electron microscopy (SEM) micrograph of the cross section of the PNZT-2 film. The film is dense and has a columnar grain structure.

The $P-E$ loops of the PNZT-0 and PNZT-2 films measured at room temperature are shown in Fig. 4, while the variation of P_r with x (Nb concentration) is shown in Fig. 5. It is seen that P_r increases and then decreases with increasing x, reaching a maximum value of about 30 μC/cm^2 at $x = 2$ mol % (Fig. 5). This clearly shows that, as in the case for bulk ceramics, the Nb dopant affords increment in the remanent polarization of the PZT films. Accordingly, the resulting piezoelectric and pyroelectric properties of the PNZT films should also be enhanced.

To evaluate the piezoelectric properties, the PNZT films were poled under various dc fields at room temperature for 3 min. Our results reveal that for all the film samples, the observed $d_{33,c}$ and $-e_{31,c}$ values first increase with increasing poling field and then become saturated at a dc field of about 20 MV/m. Figure 6 shows, as an example, the dependences of $d_{33,c}$ and $e_{31,c}$ on the poling field for the PNZT-2 film. In the following discussion, only the saturated piezoelectric coefficients, i.e., the piezoelectric coefficients of a fully polarized PNZT film, will be reported.

Figure 7 shows the variations of $d_{33,c}$ and $e_{31,c}$ with x. It is seen that $d_{33,c}$ remains almost unchanged at a value of about 96 pm/V as x increases from 0 to 2 mol %, and then decreases by about 20% as x increases to 3 mol %. On the other hand, $-e_{31,c}$ first increases almost linearly with increasing x and then decreases, reaching a maximum value at $x = 2$ mol %. This is similar to the trend of increasing P_r with x, as shown in Fig. 5. As compared to the undoped PZT film (PNZT-0), the observed $-e_{31,c}$ value of the PNZT-2 film

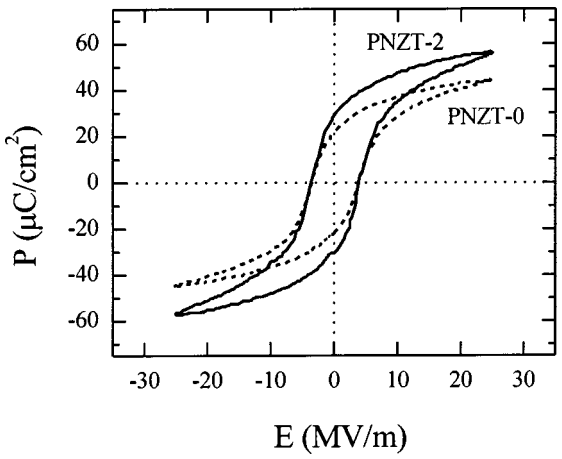

FIG. 4. Polarization hysteresis ($P-E$) loops for the PNZT-0 and PNZT-2 films.

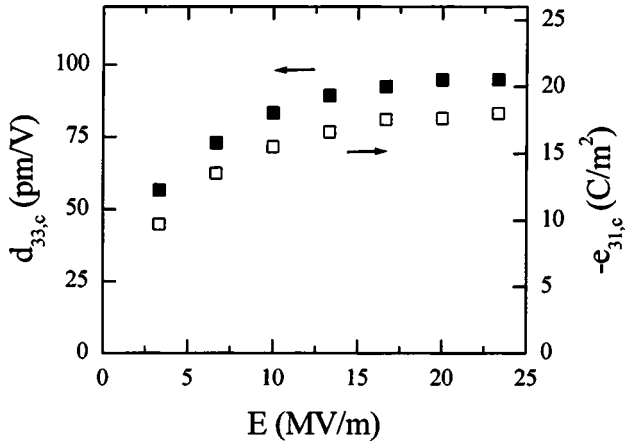

FIG. 6. Variations of the effective longitudinal and transverse piezoelectric coefficients ($d_{33,c}$ and $e_{31,c}$) of the PNZT-2 films with dc poling field E.

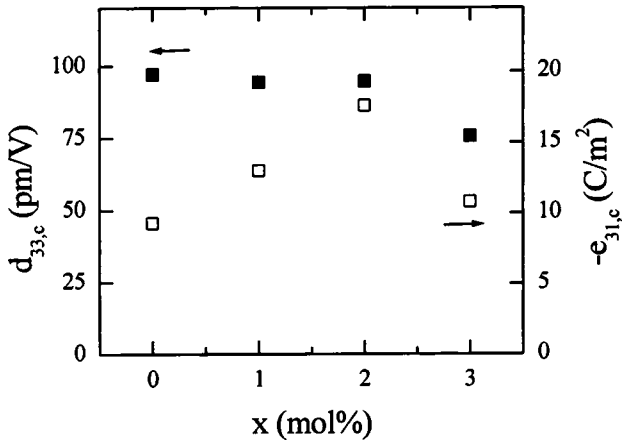

FIG. 7. Variations of the effective longitudinal and transverse piezoelectric coefficients ($d_{33,c}$ and $e_{31,c}$) with Nb concentration x.

is increased by about 100%, greatly from a value of 9.3 to 18 C/cm^2. In view of these results, it seems that the Nb-dopant effects on the sol–gel-derived PZT films are quite different from the experimentally known effects on bulk ceramics. For PZT bulk ceramics, not only the transverse piezoelectric coefficients ($-d_{31}$), but also the longitudinal piezoelectric coefficients (d_{33}), are increased considerably after the doping of 2 mol % Nb.[1]

To provide additional evidence of the Nb-dopant effect, the pyroelectric coefficient p of the films has also been measured as a function of x (Nb concentration), giving the results shown in Fig. 8. It can be seen that p shows a very similar dependence on x as P_r and $e_{31,c}$. As x increases from 0 to 2 mol %, the observed p value increases greatly from 200 to 350 μC/m^2 K. Although p is defined as the change of the net polarization with increasing temperature, it can still provide vital evidence of the magnitude of the net polarization of a PZT film. Kohli and Muralt have shown that p is linearly proportional to the net polarization of a PZT film.[14] Accordingly, the large increase in p ($\sim$75%), which is consistent with that observed in $-e_{31,c}$($\sim$100%), clearly indicates that the net polarization of the PZT film is increased significantly after the doping of 2 mol % Nb.

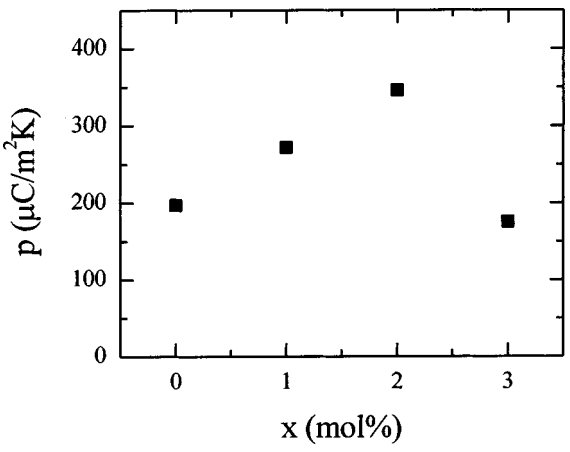

FIG. 8. Variation of the pyroelectric coefficient p with Nb concentration x.

TABLE I. Material parameters of PZT and Nb-doped PZT bulk ceramics.[a]

	$Pb(Zr_{0.52}Ti_{0.48})O_3$	$Pb_{0.988}(Zr_{0.52}Ti_{0.48})_{0.976}Nb_{0.024}O_3$
d_{33} (pm/V)	223	374
$-d_{31}$ (pm/V)	93.5	171
s_{11}^E (10^{-12} m^2/N)	13.8	16.4
$-s_{12}^E$ (10^{-12} m^2/N)	4.07	5.74
$-s_{13}^E$ (10^{-12} m^2/N)	5.80	7.22

[a]See Ref. 1.

It is suggested that the apparent discrepancy in the observed $d_{33,c}$ (i.e., remaining almost unchanged with x) is most likely caused by the substrate clamping effect. As mentioned in Sec. I, due to the tight clamping by rigid substrates, only the effective piezoelectric coefficients ($d_{33,c}$ and $e_{31,c}$) of the films are measured, and they are dependent not only on the (true) piezoelectric coefficients, but also on the elastic compliances of the films [see Eqs. (1) and (2)].

It is experimentally known that the donor-type dopant can increase not only the piezoelectric properties, but also the elastic compliances of PZT bulk ceramics. Table I shows the material parameters of $Pb(Zr_{0.52}Ti_{0.48})O_3$ and $Pb_{0.988}(Zr_{0.52}Ti_{0.48})_{0.976}Nb_{0.024}O_3$ bulk ceramics.[1] It is noted that the material parameters are increased by different amounts after the doping of Nb. Using Eqs. (1) and (2) and the material parameters listed in Table I, $d_{33,c}$ and $e_{31,c}$ of the ceramics in thin-film form (deposited on rigid substrates) are calculated, giving the results listed in Table II. It can be seen that, after the doping of 2 mol % Nb, the increment in $d_{33,c}$ is greatly suppressed to 25% as compared to that in d_{33} (60%), while the change in $e_{31,c}$ is still large (67%). This is in agreement with our experimental results showing that there is only a large increase in $-e_{31,c}$, but almost no change in $d_{33,c}$ (Fig. 7). In view of these, it is suggested to use the transverse piezoelectric coefficient $e_{31,c}$ as a measure for evaluating the Nb-dopant effects on PZT films.

Since the PZT and Nb-doped PZT bulk ceramics (listed in Table I) have similar compositions and Nb concentrations as our PNZT films, the observed $d_{33,c}$ and $e_{31,c}$ values of the PNZT-0 and PNZT-2 films are also listed in Table II for comparison. It is seen that the observed $d_{33,c}$ values of the films are smaller than the calculated values of the corresponding ceramics, while there is good agreement between the observed and calculated $e_{31,c}$ values for both undoped and doped PZT. The discrepancy in $d_{33,c}$ is partly due to the experimental error of the measurement (approximately 7%) and partly due to the additional clamping by the film itself [which has not been taken into account in the derivation of Eq. (1)]. In the $d_{33,c}$ measurement, only the film region under

TABLE II. Effective piezoelectric coefficients $d_{33,c}$ and $e_{31,c}$ of PZT and Nb-doped PZT bulk ceramics and PNZT-x films.

	$d_{33,c}$ (pm/V)	$-e_{31,c}$ (pC/N)
$Pb(Zr_{0.52}Ti_{0.48})O_3$ ceramic	112	9.6
$Pb_{0.988}(Zr_{0.52}Ti_{0.48})_{0.976}Nb_{0.024}O_3$ ceramic	142	16
PNZT-0 film	97	9.3
PNZT-2 film	95	18

the top electrode is polarized and excited to deform upon the application of an ac field. The surrounding film region is unpolarized and will impose resistance to the deformation, thus causing a decrease in the observed displacement of the polarized film region.[15] Since the whole film (including polarized and unpolarized regions) is deformed (by bending) in the $e_{31,c}$ measurement, there is no similar kind of error in the observed $e_{31,c}$ value. In addition, the relatively large uncertainty in the reported value of s_{13}^E may also be the cause for the discrepancy in $d_{33,c}$. Practically, s_{13}^E is calculated from the observed values of four material parameters, including s_{11}^E and s_{12}^E, which are determined by a number of tests based on the resonance methods using bulk samples in various shapes.[16] A calculation has shown that if the s_{13}^E value of the Nb-doped PZT ceramic is changed from -7.22×10^{-12} to $-7.94\times10^{-12}\,\mathrm{m^2/N}$ (10%, a reasonable experimental error for this parameter), the calculated $d_{33,c}$ value of the ceramic is decreased by about 16%, from 142 to 119 pm/V, while $e_{31,c}$ remains unchanged.

IV. CONCLUSION

The Nb effects on the piezoelectric and pyroelectric properties of sol–gel-derived PZT films have been studied. The optimum Nb concentration for improving the piezoelectric and pyroelectric properties is about 2 mol %. For the PNZT-2 film, the observed P_r, $d_{33,c}$, $-e_{31,c}$, and p values are about 30 $\mu\mathrm{C/cm^2}$, 95 pm/V, 18 $\mathrm{C/m^2}$ and 350 $\mu\mathrm{C/m^2\,K}$, respectively. The observed $d_{33,c}$ and $e_{31,c}$ values agree well with the theoretical values calculated using the material parameters of PZT bulk ceramics with similar compositions and Nb concentrations. This reveals that the Nb dopant has similar effects on the sol–gel-derived films and bulk ceramics, i.e., enhancing both the longitudinal and transverse piezoelectric properties. However, since $d_{33,c}$ (as well as $e_{31,c}$) is also dependent on the elastic properties of the films as a result of the substrate bending effect, the exact enhancement in the longitudinal piezoelectric properties cannot be evaluated by the $d_{33,c}$ measurement. Accordingly, the observed $d_{33,c}$ value of the PNZT films remains almost unchanged while the observed value of $-e_{31,c}$ increases with increasing Nb concentration.

ACKNOWLEDGMENT

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