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# Enhancement of field-induced strain by La substitution in epitaxial Pb(Zr,Ti)O<sub>3</sub> films grown by metal organic chemical vapor deposition

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High-quality epitaxial La-substituted Pb(Zr<sub>0.65</sub>Ti<sub>0.35</sub>)O<sub>3</sub> films were grown on (100)<sub>c</sub>SrRuO<sub>3</sub>|| (100)<sub>c</sub>SrTiO<sub>3</sub> substrates at 600 °C using metal organic chemical vapor deposition. Single-phase perovskite was obtained for La/(Pb+La) ratios ranging from 0 to 33%; La ions were selectively substituted at the Pb sites when the La/(Pb+La) ratio was 6% or less and were substituted at both A and B sites when it was greater than 6%. Both the remanent polarization and coercive field monotonically decreased with the La/(Pb+La) ratio, and the maximum field-induced strain was around 6%. This means that La substitution enhances the field-induced strain. © 2007 American Institute of Physics. [DOI: 10.1063/1.2751580]

Lanthanum (La)-substituted Pb(Zr,Ti)O<sub>3</sub> has received a lot of attention for use as an electro-optical device. This is due to its high electro-optical coefficients and good transparency, even in a sintered body.<sup>1</sup> For sintered bodies, the largest field-induced strain and the largest electro-optical coefficient are found in La-substituted Pb(Zr,Ti)O<sub>3</sub>,<sup>2</sup> not in Pb(Zr,Ti)O<sub>3</sub>.

We grew high-quality epitaxial La-substituted Pb(Zr,Ti)O<sub>3</sub> films with various La/(Pb+La) ratios and investigated the effect of La substitution on the crystal structure, ferroelectricity, and elastic field-induced strain of the films. As a result, the increase in field-induced strain due to La substitution in Pb(Zr,Ti)O<sub>3</sub> films was ascertained.

We prepared (Pb,La)(Zr<sub>0.65</sub>Ti<sub>0.35</sub>)O<sub>3</sub>, PLZT, films on (100)<sub>c</sub>SrRuO<sub>3</sub>|| (100)<sub>c</sub>SrTiO<sub>3</sub> substrates.<sup>3,4</sup> The La/(Pb+La) ratio in the film was controlled between 0 and 33% at a fixed Zr/(Zr+Ti) ratio of 0.65.

The crystal structure and film orientation were determined using x-ray diffraction (XRD). Raman spectroscopy was used for the crystal symmetry analysis and to determine the site occupancy of La ions. The film composition was estimated using an x-ray fluorescence spectrometer calibrated using standard samples. The electric-field induced strain and ferroelectric properties of the films were measured simultaneously using a scanning probe microscope (SPM)

with the apparatus connected to a ferroelectric test system.

Transparent crack-free PLZT films having a thickness of 2.0–2.7 μm and a smooth surface (average roughness *R<sub>a</sub>* of 2.0–2.7 nm) were obtained irrespective of the La/(Pb+La) ratio.

Figure 1 shows the XRD patterns for the five La/(Pb+La) ratios used. Irrespective of the ratio, single-phase, epitaxially grown, perovskite films with (100) orientation were obtained: (100)PLZT|| (100)<sub>c</sub>SrRuO<sub>3</sub>|| (100)<sub>c</sub>SrTiO<sub>3</sub>. The full width at half maximum of the PLZT (200) peak was less than 0.4° for all films. The peak position of PLZT (200)

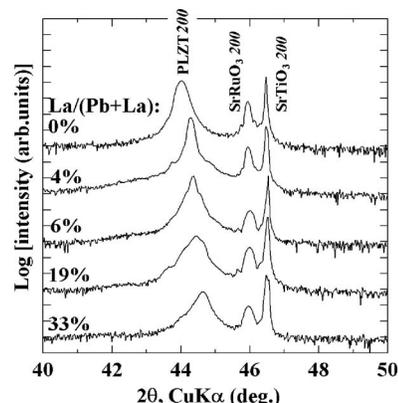


FIG. 1. XRD patterns for five La/(Pb+La) ratios.

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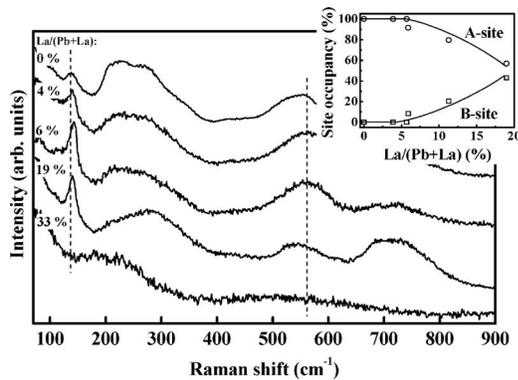


FIG. 2. Raman spectra of PLZT film for five La/(Pb+La) ratios. Inset shows calculated site occupancy of La ions in PLZT film.

shifted to a higher angle as the ratio was increased, indicating that the surface-normal lattice parameter decreased.

The Raman spectra of the films are shown in Fig. 2. The spectrum for the 0% ratio exhibited intense phonon modes at  $\sim 135$ ,  $200\text{--}275$ ,  $\sim 560$ , and  $680\text{--}725\text{ cm}^{-1}$ , which is typical for a rhombohedral system PLZT.<sup>5</sup> The crystal symmetry retained a rhombohedral system for the ratios up to 19%. The peaks were broader and weaker at the 33% ratio, indicating the crystal symmetry change from rhombohedral to cubic.

The peak at  $\sim 135\text{ cm}^{-1}$  corresponds to the Pb-site (A site in a perovskite structure,  $ABO_3$ )-based lattice mode,<sup>6</sup> while that at  $\sim 560\text{ cm}^{-1}$  corresponds to the Zr/Ti-O (B site-O) stretching mode.<sup>7</sup> The site occupancy of La ions at the A and B sites are shown in the insert in Fig. 2. The La ions were selectively substituted at A sites below 6% and were substituted at both A and B sites over 6%. This shows that the solid solubility limit of La ion substitution at A sites was 6% in the present study.

Figure 3 shows typical polarization ( $P$ )-electric field ( $E$ ) hysteresis loops measured up to 100 kV/cm and 5 Hz. Well-saturated hysteresis loops were observed for all compositions and became slim as the ratio was increased. The remanent polarization ( $P_r$ ) and the coercive field ( $E_c$ ) monotonically decreased from 56 to 0  $\mu\text{C}/\text{cm}^2$  and 35 to 0 kV/cm, respectively, as the ratio was increased.

The field-induced strain measured at 5 Hz in bipolar (a) and unipolar (b) electric fields is shown in Fig. 4. Both increased with the ratio up to about 6%, and then decreased. This La/(Pb+La) ratio of 6% agrees with the solid solubility limit of La ion substitution at A sites. This result shows that PLZT with a La/(Pb+La) ratio of about 6% has a larger field-induced strain than nondoped  $\text{Pb}(\text{Zr}_{0.65}\text{Ti}_{0.35})\text{O}_3$  and suggests the possibility of a close correlation between the

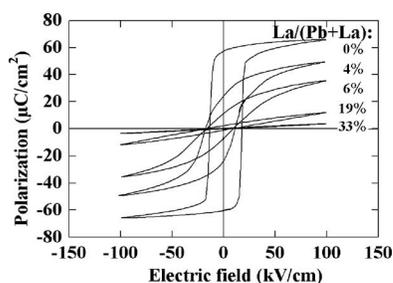


FIG. 3. Hysteresis loops for five La/(Pb+La) ratios for  $\text{Zr}/(\text{Zr}+\text{Ti})=65\%$  at 5 Hz.

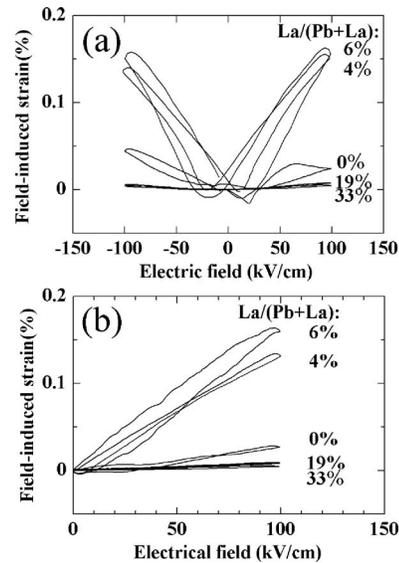


FIG. 4. La/(Pb+La) ratio dependency of field-induced strain in bipolar (a) and unipolar (b) electric fields measured at 5 Hz.

substitution sites of La ions and the amount of field-induced strain in the PLZT film.

The improvement in the piezoelectricity by La substitution was also reported in the sintered body<sup>1</sup> and it was not limited to the film form. These are consisted of two factors, the intrinsic and the extrinsic ones.<sup>8,9</sup> Since the largest non-linear  $C$ - $V$  characteristic was obtained at La content of 6% (not shown here), the extrinsic factor is considered to be the major in this study.<sup>10</sup> We are under measure *in situ* XRD in order to reveal the origin of large piezoelectric property.

The strain in ferroelectric materials is given by  $x=QP^2$ , and the field-induced strain observed by SPM in a unipolar electric field from zero to the maximum electric field is given by  $\Delta x_{\text{SPM}}=Q_{\text{SPM}}(P_{\text{max}}^2-P_r^2)$ , where  $Q_{\text{SPM}}$  is the electrostatic constant and  $P_r$  and  $P_{\text{max}}$  are the polarization for an electrical field of zero and the maximum value.

Figure 5 shows the field-induced strain and  $[P_{\text{max}}^2-P_r^2]$  as a function of the La/(Pb+La) ratio. The strain took a

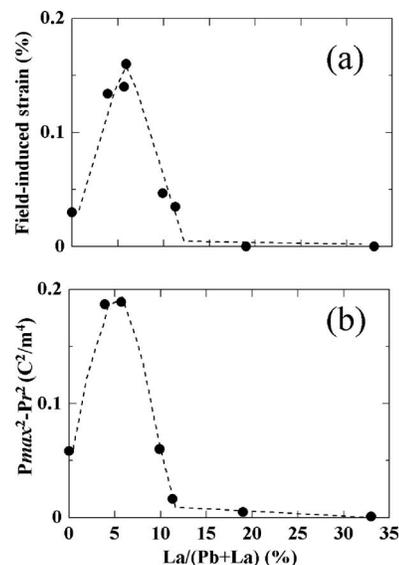


FIG. 5. La/(Pb+La) ratio dependency of field-induced strain and  $[P_{\text{max}}^2-P_r^2]$ .

maximum at a ratio of 6% and was in good agreement with the estimation from the polarization property. This result clearly indicates that PLZT film, which has a large field-induced strain, is a suitable candidate for microelectromechanical system applications.

In summary, high-quality epitaxial (Pb,La)(Zr<sub>0.65</sub>Ti<sub>0.35</sub>)O<sub>3</sub> films were grown on (100)<sub>c</sub>SrRuO<sub>3</sub>|| (100)<sub>c</sub>SrTiO<sub>3</sub> substrates at 600 °C using metal organic chemical vapor deposition. Both  $P_r$  and  $E_c$  monotonically decreased with the La/(Pb+La) ratio. The field-induced strain showed a maximum at around 6%, where La ions were selectively substituted at the A sites of PLZT film. This indicates that PLZT is a candidate piezoelectric material with a large field-induced strain.

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