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# La Content Dependence of Piezoelectric Properties of Polycrystalline (Pb, La)($Zr_{0.65}$, $Ti_{0.35}$)$O_3$ Films

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The systematic investigation on the piezoelectric properties of lanthanum-substituted lead zirconate titanate (PLZT) films was carried out. Polycrystalline PLZT films with La-contents of 0, 3, 6, 9 and 12 mol% were formed on $Pt/Ti/SiO_2/Si$ substrates at 700°C by chemical solution deposition (CSD). 111 preferred oriented PLZT films were directly grown on the substrates, and PZT seeding layers were introduced onto substrates for randomly oriented PLZT films. The longitudinal displacement curves were measured with *D-E* hysteresis loops simultaneously at ±300 kV/cm by AFM probing system. The maximum longitudinal displacements were attained at La content of 6 mol% in both orientations. The change in optical length induced by the longitudinal displacement was estimated to be from 0.2 to 0.4%. On the other hand, the shift in resonant wavelength induced by applying DC bias voltage is typically to be 0.5 to 1.0% in PLZT films. Therefore, we concluded that the influence of piezoelectric displacements on electrooptic effect is not small.
Key words: piezoelectric, PLZT, polycrystalline, La content

## 1. INTRODUCTION

Ferroelectric materials have unique optical properties such as an electrooptic effect, nonlinear optic property and photorefractive effect, and have been applied to stand-alone optical devices, such as an optical shutter[1], a second harmonic generator[2] and an optical associative memory[3]. These devices are already realized, and not new. However, if ferroelectric materials were embedded with semiconductor integrated circuits, novel optical devices such as an integrated optical waveguide switch[4,5] and tunable photonic crystals[6] would be realized. Especially, a spatial light modulator (SLM) using a ferroelectric film has attracted a great deal of attention as a novel optical display[7]. In a reflection-type SLM, the interference of lights is utilized to modulate light intensity. An optical length of a ferroelectric film is changed by applying bias voltage to the film due to electrooptic effect. At the same time, variation in film thickness caused by piezoelectric behavior also has an influence on the interference. However, no one has reported the contribution of piezoelectric displacement on the optical length change.

Therefore, the systematic investigation of the piezoelectric properties of polycrystalline PLZT films is required. In this paper, we report the piezoelectric properties of CSD-derived PLZT films which are promising candidates of optoelectrical materials with various La content and different orientation measured by AFM and investigate their influence on optical properties.

## 2. EXPERIMENTAL

(Pb,La)($Zr_{0.65}$,$Ti_{0.35}$)$O_3$ films were grown on (111)$Pt/Ti/SiO_2$/(100)Si substrates by CSD. The chemical solutions provided by Kojundo Chemical Laboratory were used as precursor solutions. The five PLZT(*X*/*Y*/65/35) precursor solutions with different La and Pb contents shown in Table I were prepared for this study. In our process, the Pb content ratio of 125% relative to stoichiometric values was optimum for the fabrication of PLZT films with well-filled structure[8]. In this study, we prepared PLZT films with different orientations. The PLZT films with (111) preferred orientation were directly grown on substrates, hereafter process (a). On the other hand, the PLZT films with random orientation were grown on PZT seeding layer introduced onto substrate, hereafter process (b). Other procedures were the same in both PLZT films. The PLZT precursor solutions were deposited at 3000 rpm for 50 s. The spin-coated films were dried at 100-120℃ for 5 min and calcined at 350℃ for 5 min. After spin-

Table I. Compositions of PLZT(*X*/*Y*/65/35) precursor solutions used in this study.

| La content (Y) | Pb content (X)<br>Pb content ratio relative to stoichiometric value 125% |
|---|---|
| 0 | 125 |
| 3 | 121 |
| 6 | 118 |
| 9 | 114 |
| 12 | 110 |

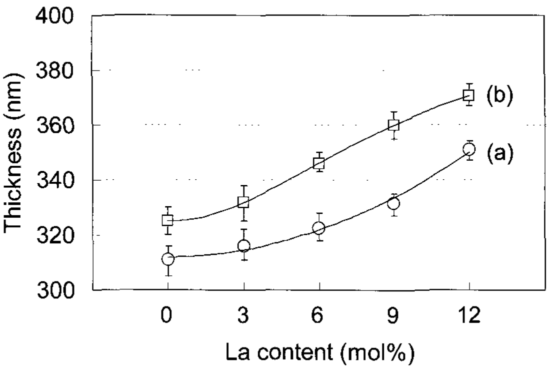


Fig. 1. Final film thickness of PLZT(*X*/*Y*/65/35) films prepared by process (a) and (b) as a function of La content.

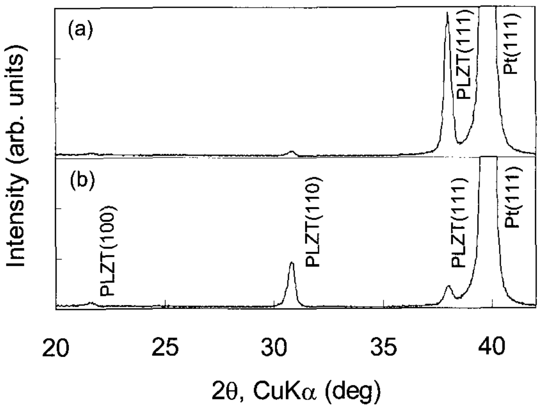


Fig. 2. XRD profiles of the PLZT(121/3/65/35) films prepared by process (a) and (b), respectively.

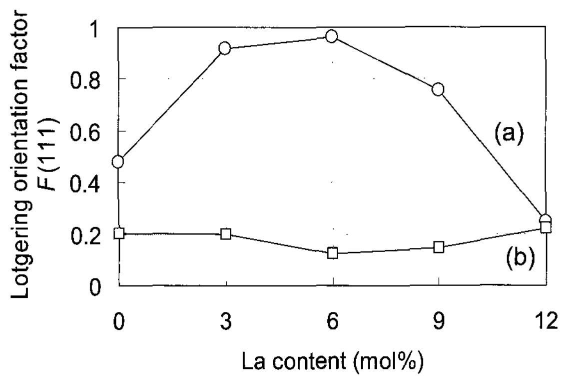


Fig. 3. Lotgering orientation factor *F*(111) of the PLZT(*X*/*Y*/65/35) films prepared by process (a) and (b) as a function of La content.

coating and calcination had been repeated four times, the films were sintered at 700℃ for 10 min in a gas mixture of $O_2$ and Ar at an Ar : $O_2$ flow ratio of 95 : 5 ml/min by rapid thermal annealing (RTA).

The crystal structure and orientation of the films were determined by X-ray diffraction analysis (XRD; PANalytical X'Pert MRD) with CuKα radiation. For the evaluation of electrical and piezoelectric properties, top electrodes (0.1 mm diameter) made of indium tin oxide (ITO) were deposited on the film surface by rf magnetron sputtering. To measure the *D-E* hysteresis loops and the longitudinal displacement-field curves simultaneously, an AFM probing system with a conductive cantilever (Nano-R, Toyo Corporation) was connected with a ferroelectric test system (FCE-PZ, Toyo Corporation). Bipolar drive voltages were applied to the PLZT films, and the longitudinal displacement was evaluated using a PID controlled *Z*-feedback signal of the AFM cantilever. The samples were measured with drive frequencies of approximately 5 Hz and maximum electric field amplitude of ±300 kV/cm. Details of the measurement method are described elsewhere[9].

## 3. RESULTS AND DISCUSSION

### 3.1 Crystal orientation

Final film thickness varied from 310 to 370 nm depending on La content and process as shown in Fig.1. Precursor solutions with higher La contents caused thicker films because of higher viscosity. The films prepared by process (b) were thicker than the films by process (a) because the PZT seeding layer had a thickness of approximately 20 nm.

All the PLZT films were crystallized into a single perovskite phase. Figure 2(a) and 2(b) show the XRD profiles of the PLZT(3/65/35) films prepared by processes (a) and (b), respectively. The PLZT film of process (a) mostly had a 111 preferred orientation while the PLZT film of process (b) had a random orientation. Figure 3 shows Lotgering orientation factor[10] *F*(111) of the PLZT films as a function of La content. A completely 111 orientated sample will have the Lotgering orientation factor *F*(111) of unity and a fully random oriented sample an *F*(111) of zero. In the case of process (a), *F*(111) increased with increasing La content from 0 to 6 mol%, and then decreased. On the other hand, *F*(111) had almost the same values in the case of process (b). The PLZT(12/65/35) films had a random orientation in both process (a) and (b).

Summary of this section is as follows: Film thickness increased with increasing La content and with the PZT seeding layer. PLZT films with 111 preferred orientations were obtained at La content ranging from 0 to 9 mol% by process (a) although the Lotgering orientation factor was relatively low at La content of zero. On the other hand, PLZT films with mostly random orientation were obtained at any La contents by process (b).

### 3.2 Electrical and piezoelectric properties

Figure 4 shows the longitudinal displacement curves measured with *D-E* hysteresis loops simultaneously at the maximum applied field of ±300 kV/cm, and a frequency of approximately 5 Hz. The maximum polarization ($P_{max}$) decreased and the squareness of the hysteresis loops monotonically deteriorated with increasing La content, and finally, ferroelectricity almost disappeared in the PLZT(12/65/35) films in both crystal orientations. At the same La content, the films with random orientation showed slightly larger $P_{max}$ value than the films with 111 preferred orientations. The shape of longitudinal displacement curves also varied depending on La content and crystal orientation.

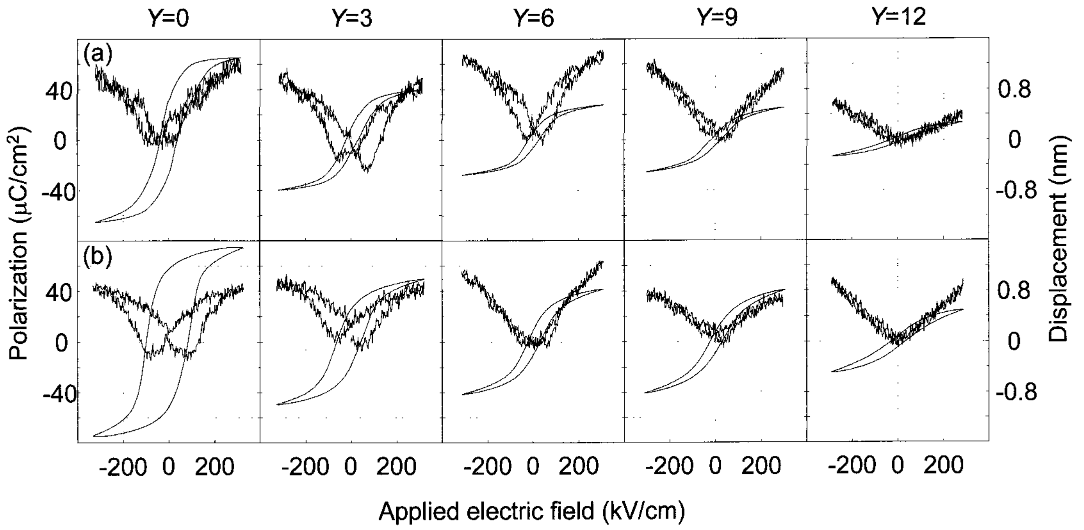


Fig. 4. The longitudinal displacement curves measured with D-E hysteresis loops simultaneously of PLZT(*X*/*Y*/65/35) films. (a) 111 preferred oriented films (b) randomly oriented films

The maximum displacement value was evaluated by percentage for film thickness because film thickness was not constant for various La content and crystal orientations. Figure 5 shows the percentage of the maximum displacement for a film thickness as a function of La content. The maximum displacement was defined as the difference between the displacements at zero bias and 300 kV/cm. In the films with 111 preferred orientation, the percentage slightly increased with increasing the La content from 0 to 6 mol%, and then decreased with increasing La content from 6 to 12 mol%. In the films with random orientation, the percentage were almost the same at La content of 0, 3, 9, 12 mol% although the maximum value of 0.35% was attained at La content of 6 mol%. At the same La content, 111 preferred oriented film showed larger displacement than randomly oriented one except the La content of 12 mol% at which both films had random orientation. The correlation between the maximum polarization and the maximum displacement was not clear in our results. Any way, the change in optical length induced by piezoelectric displacement was estimated to be from 0.2 to 0.4% for film thickness. On the other hand, the shift in resonant wavelength induced by applying DC bias voltage was typically to be 0.5 to 1.0% in PLZT films[11]. Therefore, we concluded that the influence of piezoelectric displacements on electrooptic effect is not small.

## 4. CONCLUSIONS

Polycrystalline PLZT(*X*/*Y*/65/35) films with different crystal orientations were fabricated on Pt/Ti/$SiO_2$/Si substrates from five precursor solutions with La content of 0, 3, 6, 9 and 12 mol% by CSD. The electrical and piezoelectric properties of these PLZT films were evaluated. 111 preferred oriented PLZT films were obtained at the La content ranging from 0 to 9 mol% by process (a) and randomly oriented films were obtained at any La contents by process (b). The maximum polarization monotonically decreased with increasing La content while the percentage of longitudinal displacement for a film thickness was maximum at a La content of 6 mol% in both films with 111 preferred and random orientations. In the same La content, 111 preferred oriented films showed larger displacement than randomly oriented ones. The change in optical length induced by piezoelectric displacement was estimated to be from 0.2 to 0.4% for film thickness. Finally, we concluded that the influence of piezoelectric displacements on electrooptic effect is not small because the shift in resonant wavelength induced by applying DC bias voltage was typically to be 0.5 to 1.0% in optical PLZT films. Therefore, for large optical length, not only the refractive index change but also the piezoelectric property is important.

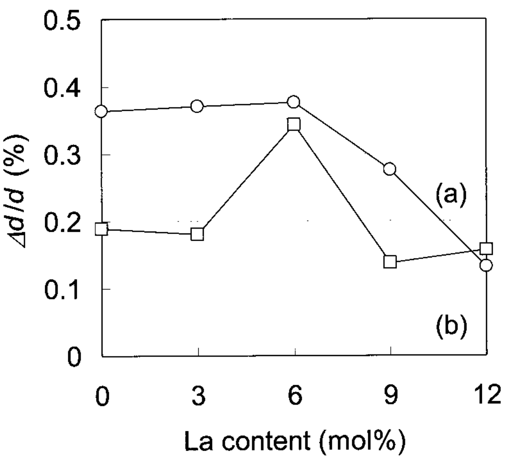


Fig. 5. The percentage values of the maximum displacement for a film thickness as a function of La content. (a) 111 preferred oriented films (b) randomly oriented films

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