

Optical properties of epitaxial plzt thin films

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Abstract In the epitaxial $(\text{Pb}_{1-x}, \text{La}_x)(\text{Zr}_{1-y}, \text{Ti}_y)_{1-x/4}\text{O}_3$ [PLZT] films, the composition dependence of the refractive index and electric-optic (EO) coefficient near the morphotropic phase boundary (MPB) composition was investigated. A (100/001)-oriented PLZT 10/65/35 epitaxial film is found to have isotropic optical properties. Highly (100/001)-oriented epitaxial PLZT films with compositions near the MPB on Nb–SrTiO₃ substrates were fabricated using a sol–gel process. The value of birefringence from 4×10^{-3} to 5×10^{-4} in PLZT epitaxial film was smaller than that of lithium niobate single crystal. The refractive index decreases with increasing lanthanum content. The difference in the refractive index obtained depended upon the lanthanum content up to 2%. This value is adequate for fabrication of waveguide structures. The EO coefficient of

PLZT 9/65/35 thin films was 45 pm/V, which is larger than that of lithium niobate single crystal. A very small polarization dependence of the EO coefficient was also observed.

Keywords Electric-optic · Morphotropic phase boundary · Polarization dependence

1 Introduction

With the explosive increase in optical communication traffic, new high speed and high density optical devices are strongly required. Optical devices using electro-optic (EO) materials are one of the promising candidates for future optical communication systems because of its high frequency properties and optical transparency. Optical isotropy, which includes both small birefringence and small EO coefficient polarization dependence, is very important for optical systems, because optical anisotropy causes optical polarization dependent loss and polarization mode dispersion.

LiNbO₃ (LN) single crystals ($n_o=2.2872$, $n_e=2.2030$, $r_{33}=30.8$ pm/V, $r_{13}=8.6$ pm/V at $\lambda=633$ nm) with an ilmenite crystal structure is used as an EO material for optical devices. However, LN has a strong polarization dependence, because the crystal symmetry is low. Therefore, devices fabricated using LN have an inherent disadvantage for the smart optical devices, because they require a module to compensate for the polarization.

Lead lanthanum titanate zirconate ($(\text{Pb}_{1-3x/2}, \text{La}_x)(\text{Zr}_{1-y}, \text{Ti}_y)\text{O}_3$, hereafter designated as PLZT 100x/100-100y/100y) is well known as a ceramic with a high transparency and high EO coefficient $r_e=523$ pm/V [1]. Small and integrated optical devices have been prepared using PLZT

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thin films previously [2, 3]. r_c is defined by the equation as follows,

$$r_c = (n_3^3/n_1^3)r_{33} - r_{13} \quad (1)$$

where n_3 or n_1 are refractive index for the parallel or vertical direction of the applied field, and r_{33} or r_{13} are EO coefficients for the parallel or vertical direction of the applied field, respectively. The values of EO coefficient r_c of the PLZT thin films have already been reported [4–6]. The appearance of r_c indicates that these PLZT films have birefringence. The crystalline phase of PLZT changes with the composition. When the composition approaches to the morphotropic phase boundary (MPB), the crystal symmetry is enhanced. Therefore, it is expected that there is a high optical isotropy near the MPB composition. However, the composition dependence of the optical properties has not been investigated fully. In this work, the composition dependence near the MPB composition of refractive index and EO coefficient of the epitaxial PLZT films was investigated.

2 Experimental procedure

PLZT films were fabricated by a sol-gel or chemical solution deposition (CSD) process. The 0.6 mol/l precursor solutions were synthesized from lead acetate trihydrate (Pb(CH₃COO)₂·3H₂O), lanthanum isopropoxide (La(O-iC₃H₇)₃), zirconium n-propoxide (Zr(O-nC₃H₇)₄), and titanium isopropoxide (Ti(O-iC₃H₇)₄) in a dry nitrogen atmosphere. 2-methoxyethanol (CH₃OC₂H₄OH) was used as a solvent [7, 8]. 2, 4-pentanedione (CH₃COCH₂COCH₃) was used for a stabilizer. The prepared compositions were PLZT 0/52/48, 3/55/45, 6/60/40, 8/65/35, 9/65/35, 10/65/35, and 11/65/35. The compositions close to MPB were selected [3]. Excess lead oxide of 20 mol% was added to the precursors to compensate for lead loss during annealing.

The precursor was spin-coated at 3,000 rpm onto (100)-oriented niobium-doped strontium titanate (hereafter designated as Nb-STO) substrates. Each sample was heated to

evaporate the solvent at 320 °C for 1 min. Then, the samples were heated to crystallize the film with a rapid thermal annealing method. The annealing temperature was optimized for each PLZT composition in a temperature range of 625 to 750 °C under an oxygen atmosphere. The above process was repeated until the thickness of the PLZT film was over 2 μm on a Nb-STO substrate.

The phase and orientation of the PLZT films were determined by X-ray diffraction (XRD). The lattice constant was calculated from the peak position of the XRD patterns in the 2theta-theta profile. The prism coupling method was used for optical measurements [3]. The polarization mode is defined as follows. TM- and TE-modes for a light wave are parallel and vertical to the direction of electric field, respectively. Laser light with a wavelength of 1,550 nm was coupled to the PLZT film through a silicon prism. The reflection intensity and the incident angle were then measured. To measure the change of the index under the applied dc electric fields, a tungsten layer with a thickness of 10 nm was deposited by sputtering methods on the surface of the PLZT film as the upper electrode. Nb-STO substrate was used as the lower electrode. The EO coefficient was calculated using the following equation,

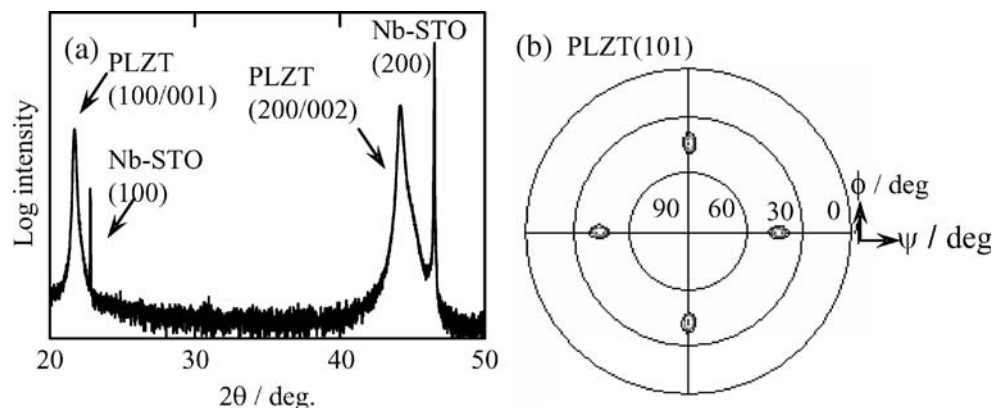
$$\Delta n = -\frac{1}{2}n^3rE = -\frac{1}{2}n^3r\frac{V}{t} \quad (2)$$

where n is the refractive index, r is the EO coefficient, E is the applied dc electric field, V is the applied voltage, and t is the thickness of PLZT films.

3 Results and discussion

Figure 1 shows the XRD pattern of the PLZT 10/65/35 film with a thickness of 2.7 μm. The (00L) peaks of PLZT and Nb-STO were only observed in 2theta-theta measurement profile [Fig. 1(a)]. The four-fold symmetry of the pole of (101) plane from the (100/001) PLZT orientation was also observed in the pole figure [Fig. 1(b)]. These results

Fig. 1 XRD patterns of the PLZT 10/65/35 film grown on Nb-STO substrate, (a) 2θ - θ scan profile and (b) pole figure of the PLZT(101) plane from the (a) PLZT(100/001) orientation



indicate that the PLZT film was epitaxially grown on the Nb–STO substrate. All PLZT films with other compositions were also confirmed to be grown epitaxially by same analysis.

Figure 2 shows the changes in the ratio of the lattice constant and birefringence of the epitaxial PLZT film as a function of the lanthanum content. Although the MPB composition was selected in the range below 9 atom% of lanthanum content, the PLZT films have a tetragonal phase. This may be due to the fact that the PLZT crystal is distorted by stress from the Nb–STO substrate. The tetragonality of PLZT films decreased as the lanthanum content increased and it seems to be pseudocubic with over 10 atom% lanthanum content. This behavior of lattice constant was similar to that observed in bulk ceramics. Birefringence of refractive index also decreases from 4×10^{-3} to 1×10^{-3} as lanthanum content increased. Birefringence of all compositions in this work is smaller than that of LN single crystal (8.4×10^{-2}). The small birefringence of the epitaxial PLZT films is due to their pseudocubic crystal structure. Birefringence is well correlated to the crystal tetragonality.

Figure 3 shows the change of refractive index and EO coefficient of the PLZT films as a function of lanthanum content. The refractive index decreased from 2.45 to 2.39 as the lanthanum content increased from 0 to 11 atom%. The refractive index can be controlled by lanthanum content up to 2%. This change is enough to fabricate a waveguide structure by controlling the PLZT composition. The difference of EO coefficient with TM- and TE-mode is also small. No data of EO coefficient without r_c has been reported in this PLZT system. This indicates that the EO properties of the (100/001)-oriented epitaxial PLZT film change isotropically. The EO coefficient increased from 25 to 45 pm/V as the lanthanum content increased from 0 to 9 atom%. The value of the PLZT 9/65/35 EO coefficient

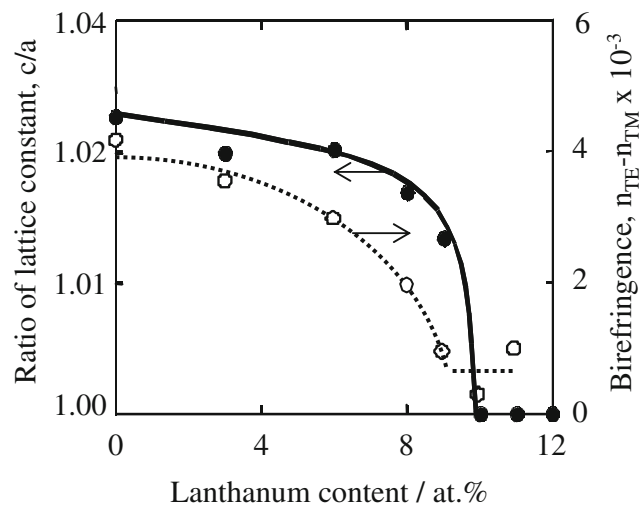


Fig. 2 Change of the ratio of the lattice constant and birefringence of the PLZT epitaxial films as a function of lanthanum content

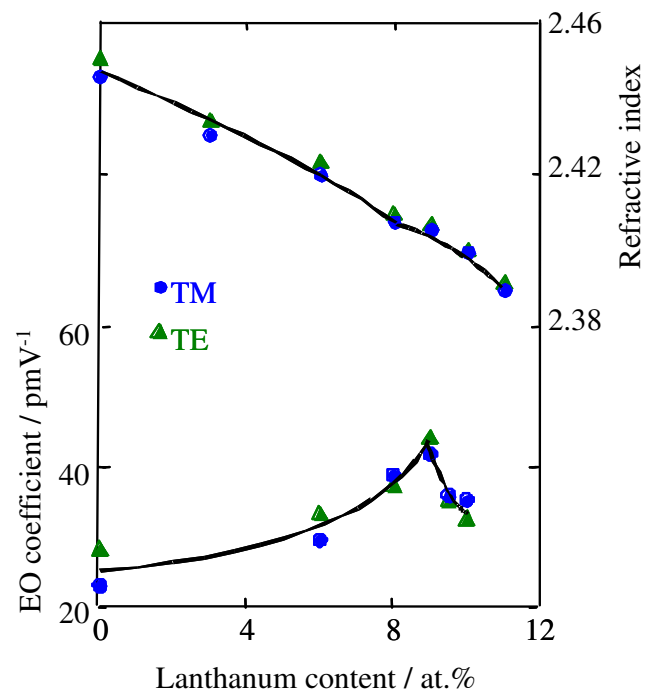


Fig. 3 Change of refractive index and EO coefficient of the PLZT epitaxial films as a function of lanthanum content

(45 pm/V) was higher than that for the single crystal of LN. When the La content is in the range 9–11%, the birefringence is smallest as shown in Fig. 2, because the lattice constant of c -axis is consisted with that of axis. However, the behavior of EO coefficient is reversed for that of birefringence. Although this reason is unclear at present, we guess it as follows. Curie temperature of PLZT is close to around room temperature in the range of 9–11% of La content. The relative permittivity is largest in this La

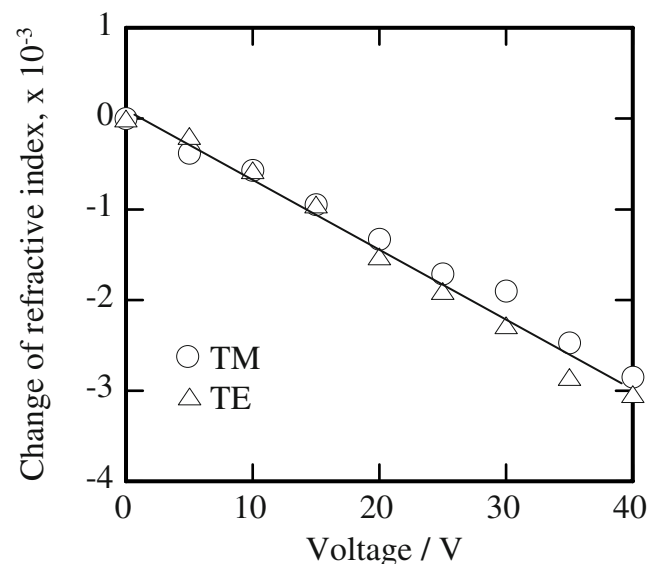


Fig. 4 Change of refractive index of the PLZT10/65/35 epitaxial film as a function of applied voltage

content range. We believe that this increase of EO coefficient may be attributed to the increase of relative permittivity. The EO coefficient decreases with the increase of over 9 mol% of lanthanum content. It is considered that the composition of PLZT 10/65/35 approaches close to the cubic phase. It has been reported that PLZT bulk ceramics or thin films have polarization dependence [1, 3–6]. However, the (100/001)-oriented epitaxial PLZT films indicate less polarization dependence of the EO coefficient.

Figure 4 shows the change of refractive index of the epitaxial PLZT 10/65/35 film by applying voltage. The slope indicates the EO coefficient. The change of EO coefficients with TM (r_{33}) and TE (r_{13}) mode is almost the same. From equation 1 and the results in Fig. 4, this behavior indicates that the EO coefficient r_c of this epitaxial PLZT 10/65/35 film is nearly equal to zero. This value is quite different from that of PLZT 8/65/35 bulk ceramic, $r_c=523$ pm/V. We consider that the large EO coefficient r_c in the bulk PLZT ceramics is impacted by grains with random orientations, because the PLZT ceramic bulk is polycrystalline with no preferred orientation.

4 Conclusions

A (100/001)-oriented PLZT 10/65/35 epitaxial film was found to have isotropic optical properties. Highly (100/001)-oriented epitaxial PLZT films with compositions near MPB on Nb–STO substrate were fabricated using a sol–gel

method. The refractive index depending on lanthanum content decreases up to 2%. This value is adequate for fabrications of waveguide structures. Birefringence also decreased from 4×10^{-3} to 5×10^{-4} as lanthanum content increased. The EO coefficient of PLZT 9/65/35 thin films was 45 pm/V, which is higher than that of single crystal LN. Very little polarization dependence of the EO coefficient was also observed.

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