Linear electro-optic properties of relaxor-based ferroelectric $0.24\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3-(0.76-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$ single crystals

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Linear electro-optic properties of $0.24\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3-(0.76-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$ single crystals, with compositions in the rhombohedral, morphotropic phase boundary (MPB) and tetragonal phases, have been investigated. Very large effective electro-optic coefficient γ_c (204 pm/V) was observed in a crystal with the MPB composition when it is poled along [001]. The rhombohedral phase ($x=0.27$ and 0.30) single crystals poled along [111] direction and tetragonal phase ($x=0.39$) single crystal poled along [001] direction are in single domain, and their electro-optic coefficients ($\gamma_c=76$, 94 , and 43 pm/V for the crystals with $x=0.27$, 0.30 , and 0.39 , respectively) were found to be much higher than that of traditional electro-optic single crystal LiNbO_3 ($\gamma_c=19.9$ pm/V). The electro-optic coefficients of the single crystal in the rhombohedral phase have excellent temperature stability in the experimental temperature range of $10\text{--}40^\circ\text{C}$. The half-wave voltage V_π was calculated to be much lower (less than 1000 V) than that of LiNbO_3 single crystal (2800 V). These superior properties make the ternary relaxor-PT single crystals very promising for electro-optic modulation applications. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4811811>]

I. INTRODUCTION

LiNbO_3 single crystals are commonly used as optical functional materials for their excellent electro-optic (EO), photorefractive, and nonlinear optical properties. Higher EO coefficient materials can make smaller size devices with lower operating voltage. Relaxor-PT ferroelectric single crystals, such as $(1-x)\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$ (PZN- x PT) and $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$ (PMN- x PT), were found to possess very high piezoelectric constants and very large linear electro-optic coefficients.^{1,2} Ternary relaxor-based ferroelectric single crystals $(1-x-y)\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3-y\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$ (PIN-PMN-PT) have attracted much attention in recent years for their excellent piezoelectric properties and applications in ultrasonic transducers and actuators.^{3–8} It has been reported that the ternary PIN-PMN-PT single crystal system has about 30°C higher Curie temperature and higher coercive field than that of PMN-PT single crystals with as excellent piezoelectric properties as that of PMN-PT single crystals.^{6,8} Recently, the optical transmission spectra of PIN-PMN-PT single crystals have been characterized and the results showed that the single domain single crystals have high optical transmittance and can be used for optical application.⁹ In this work, the linear EO properties of single domain and multidomain $0.24\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3-(0.76-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$ single crystals have been studied. Composition, temperature, and crystal orientation dependence of EO coefficients are measured, compared, and discussed.

II. EXPERIMENTAL

High-quality $0.24\text{PIN}-(0.76-x)\text{PMN}-x\text{PT}$ single crystals used in this work for EO coefficients measurements were grown by the modified Bridgman method. The PIN content is insensitive to composition segregation, but the composition of the PT along the growth direction varies due to the segregation of titanium in the crystal. Samples of desired geometries were cut from the same slice of a crystal boule, the PIN content is 0.24 and the PT contents of 0.27 , 0.30 , 0.33 , and 0.39 were selected for our study. All samples were oriented by using the Laue x-ray machine^{10–12} with an accuracy of $\pm 0.5^\circ$. $0.24\text{PIN}-0.43\text{PMN}-0.33\text{PT}$ single crystal is in the morphotropic phase boundary (MPB) composition. The spontaneous polarization direction is $\langle 111 \rangle$ for crystals on the rhombohedral side of the MPB, and $\langle 001 \rangle$ for crystals on the tetragonal side of the MPB. In this work, all directions are labeled using pseudo-cubic coordinates. For PT contents of 0.27 and 0.30 , the single crystals were cut along crystallographic directions $[1\bar{1}0]^L \times [11\bar{2}]^T \times [111]^W$ in pseudo-cubic coordinates and poled along [111] direction. For PT contents of 0.33 and 0.39 , the single crystals were cut along crystallographic directions $[100]^L \times [010]^T \times [001]^W$ and poled along [001] direction. The samples were sputtered with gold electrodes and poled in silicone oil with a field of 10 kV/cm at room temperature. The surfaces of the samples were polished to optical quality.

The refractive indices n_o and n_e of $0.24\text{PIN}-(0.76-x)\text{PMN}-x\text{PT}$ single crystals were measured by the Brewster's angle method and the values measured at 632.8 nm are listed in Table I.

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TABLE I. Values of the refractive indices, electro-optic coefficients, and the half-wave voltage for single- and multi-domain 0.24PIN-(0.76 - x)PMN- x PT, (1 - x)PMN- x PT (Ref. 18), and LiNbO₃ (Refs. 15 and 17) single crystals at room temperature.

Composition	Poling direction	n_o	n_e	$-d_{31}$ (pC/N)	γ_{33} (pm/V)	γ_{13} (pm/V)	γ_c (pm/V)	V_π (V)
0.24PIN-0.49PMN-0.27PT	[111]	2.509	2.577	21	76	~ 0	76	487
0.24PIN-0.46PMN-0.30PT	[111]	2.515	2.580	30	95	1	94	392
0.24PIN-0.37PMN-0.39PT	[001]	2.540	2.582	89	56	14	43	855
0.74PMN-0.26PT	[111]	2.584	2.595	...	...	...	91	411
0.70PMN-0.30PT	[111]	2.590	2.598	...	...	...	107	347
0.62PMN-0.38PT	[001]	2.616	2.600	...	...	...	41	878
0.24PIN-0.43PMN-0.33PT	[001]	2.524	2.544	...	...	...	204	188
0.67PMN-0.33PT	[001]	2.599	2.562	...	...	...	182	202
LiNbO ₃	[001]	2.200	2.286	...	...	...	19.9	2800

III. RESULTS AND DISCUSSION

The electro-optic effect describes the change in the refractive index (Δn_{ij}) due to an applied electric field (E_k), which is given by¹³

$$\Delta n_{ij} = -\frac{1}{2} n_{ij}^3 \sum_{k=1}^3 \gamma_{ijk} E_k, \quad (1)$$

where γ_{ijk} and n_{ij} are the linear electro-optic coefficients and refractive index, respectively. The linear electro-optic coefficients γ_{13} ($=\gamma_{113}$) and γ_{33} ($=\gamma_{333}$) were measured at low frequency by the modified Mach-Zehnder interferometric method. The light source is a He-Ne laser with the wavelength of 632.8 nm.

For the electro-optic coefficient measurements, the applied electric field along the spontaneous polarization direction will cause a change in the crystal dimension along the optical path direction (ΔL) due to the converse piezoelectric effect

$$\Delta L = d_{31} E_3 L = d_{31} L \frac{V}{d}, \quad (2)$$

where L is the length along the optical path, d is the electrode spacing perpendicular to the optical path, d_{31} is the transverse piezoelectric constant measured by a k_{31} piezoelectric vibrator, and V is the applied voltage. In order to determine the true values of the electro-optic coefficients γ_{13} and γ_{33} , the contribution of the piezoelectric effect to the apparent electro-optic coefficients γ_{13}^* and γ_{33}^* was measured. Correction was made using the following relations:¹³

$$\gamma_{13}^* = \gamma_{13} - 2 \frac{(n_o - 1)}{n_o^3} d_{31}, \quad (3a)$$

$$\gamma_{33}^* = \gamma_{33} - 2 \frac{(n_e - 1)}{n_e^3} d_{31}. \quad (3b)$$

During electro-optic coefficient measurements, the polarization direction of the laser beam is perpendicular to the electric field direction for measuring γ_{13}^* and parallel to the electric field direction for measuring γ_{33}^* . The electro-optic measurement system was calibrated by testing a LiNbO₃ crystal for which the electro-optic properties are well documented in the literature.

The effective electro-optic coefficient γ_c was obtained, which can be calculated from the measured values of n_o , n_e , γ_{13} , and γ_{33} by the following formula:^{14,15}

$$\gamma_c = \gamma_{33} - \left(\frac{n_o}{n_e} \right)^3 \gamma_{13}. \quad (4)$$

Domain structures of poled 0.24PIN-(0.76 - x)PMN- x PT single crystals are shown in Fig. 1. For the single crystals with $x=0.27$ and 0.30, the crystal symmetry is rhombohedral and the spontaneous polarization is along the [111] direction. After poling along the [111] direction, the crystals become single domain as shown in Figs. 2(a) and 2(b), which appear extinction under a polarized optical microscope. The single crystal with $x=0.39$ has tetragonal symmetry and its spontaneous polarization is along the [001] direction. It becomes single domain after poling along [001]

FIG. 1. Domain structures of 0.24PIN-(0.76 - x)PMN- x PT single crystals with (a) $x=0.27$, (b) $x=0.30$ and (c) $x=0.33$ poled along [111] direction, and (d) $x=0.33$ and (e) $x=0.39$ poled along [001] direction.

FIG. 2. Temperature dependence of the electro-optic coefficients of 0.24PIN-0.46PMN-0.30PT single crystal.

as shown in Fig. 2(e). These single crystals have high optical transmittance and remarkable optical properties, and also have stable electro-optic properties. The single crystal with $x=0.33$ (MPB composition) has multi-domain structure after poling along either [111] or [001] directions as shown in Figs. 2(c) and 2(d). The multi-domain structure can lead to the instability of electro-optic properties when measured in different areas of the single crystal or under different electric fields. Thus, the single crystal with MPB composition has no advantage as optical functional material, although it has very high electro-optic coefficients. In this work, we measured the effective electro-optic coefficients of MPB composition 0.24PIN-0.43PMN-0.33PT single crystal poled along [001] direction with $\gamma_c = 204$ pm/V. The result is higher than that of 0.67PMN-0.33PT single crystal poled along [001] direction ($\gamma_c = 182$ pm/V).¹⁸ The large γ_c may be attributed to the coexistence of the tetragonal and rhombohedral phases. The measured electro-optic coefficients of single domain 0.24PIN-(0.76 - x)PMN- x PT single crystals are listed in Table I. From the measured results, we can see that large values of γ_c are obtained for the 0.24PIN-(0.76 - x)PMN- x PT single crystals in both the rhombohedral and tetragonal phases. They are all higher than that of traditional electro-optic single crystal LiNbO₃ (19.9 pm/V).¹⁵ Table I lists the comparison of electro-optic coefficients between 0.24PIN-(0.76 - x)PMN- x PT and (1 - x)PMN- x PT single crystals. The electro-optic coefficients of the two kind crystals with similar PT contents have no obvious difference. But the ternary 0.24PIN-(0.76 - x)PMN- x PT single crystals have better domain stability than (1 - x)PMN- x PT single crystals, so that 0.24PIN-(0.76 - x)PMN- x PT single crystal can be used under higher electric field.

The temperature stability of the electro-optic coefficients is very important for electro-optic devices. Fig. 2 shows the temperature dependence of γ_{33} and γ_{13} for 0.24PIN-0.46PMN-0.30PT single crystals. One can see that the electro-optic coefficients γ_{33} and γ_{13} exhibit a weak increase from 10 °C to 40 °C. This excellent temperature stability of the electro-optic coefficients is very attractive for electro-optic device applications.

Half-wave voltage V_π is another important parameter for electro-optic modulators, which is given by¹⁶

$$V_\pi = \lambda / (n_e^3 \cdot \gamma_c). \quad (5)$$

Here, V_π is the voltage needed to obtain a phase retardation of π , which is independent of its dimensions. In order to obtain higher efficiency for electro-optic modulation applications, V_π should be as small as possible. The 0.24PIN-(0.76 - x)PMN- x PT single crystals have much lower V_π compared with LiNbO₃ single crystal¹⁷ as shown in Table I. Higher electro-optic coefficients, excellent temperature stability and lower half-wave voltage make the 0.24PIN-(0.76 - x)PMN- x PT single crystals much better materials for EO applications than traditional LiNbO₃ single crystal.

IV. CONCLUSION

In summary, a large effective electro-optic coefficient γ_c (204 pm/V) was observed when the 0.24PIN-0.43PMN-0.33PT (MPB composition) single crystal is poled along [001] direction. The electro-optic coefficients of single domain 0.24PIN-(0.76 - x)PMN- x PT single crystals were found to be much higher than that of traditional electro-optic single crystal LiNbO₃ when poled along their spontaneous polarization direction. In addition, it was found that the electro-optic coefficients of the single crystal have very high temperature stability in the temperature range of 10–40 °C, in the vicinity of room temperature. The half-wave voltage V_π (<1000 V) of 0.24PIN-(0.76 - x)PMN- x PT was calculated to be much lower than that of LiNbO₃ single crystal (2800 V), which allows the device to be made much smaller. In fact, the smallest V_π found in MPB composition is only 188 V. These excellent electro-optic properties make the ternary PIN-PMN-PT single crystals excellent candidates for electro-optic modulation applications.

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