

## Refractive indices and linear electro-optic properties of $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$ single crystals

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The refractive indices and linear electro-optic (EO) properties of  $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$  single crystals were investigated over a broad composition range. The orientation and temperature effect on the EO coefficients were also examined. Large EO coefficients  $r_c$  were observed near the morphotropic phase boundary (MPB). More importantly,  $r_c$  of the single crystals on the tetragonal side of the MPB were nearly invariant in the experimental temperature range of 20–80°C. The calculated half-wave voltage  $V_\pi$  was much lower than that of widely used EO single crystal  $\text{LiNbO}_3$ . These excellent EO properties as well as being able to produce large-size and high-quality single crystals make this kind of single crystal very promising for EO modulation applications. The observed EO properties were also analyzed with the spontaneous polarization and dielectric constants. © 2004 American Institute of Physics.

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Optical materials with high electro-optic (EO) response are highly desirable for uses in optical communications, optical signal processing, and other commercial applications. As high EO coefficients will allow for smaller size devices and lower operating voltages, a growing number of investigations have been focusing on different materials to achieve high optical responses. Most oxygen-octahedra ferroelectrics, which exhibit excellent electromechanical properties, also have outstanding optical properties.<sup>1,2</sup> Relaxor ferroelectric  $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$  (PMN- $x$ PT) have come into prominence due to their extra-high electromechanical coupling factor, piezoelectric, and dielectric coefficients, and field induced strain response.<sup>3,4</sup> However, in spite of these extensive utilizations, the values of their optical properties are not perfectly known. The lack of high quality single crystal with large size restricts the further investigation and optical applications. Recently, we have grown large-size and high optical quality PMN- $x$ PT single crystals by a modified Bridgman technique, and their performance has been characterized.<sup>5</sup> The results show that the PMN- $x$ PT single crystals have high optical transmittance and can be used as optical material in a wide range of wavelengths (0.45–5.5  $\mu\text{m}$ ).<sup>5,6</sup> In this letter, a systematical study of the refractive indices and linear EO properties of PMN- $x$ PT single crystals was carried out. Composition, temperature, and crystal orientation dependence of EO coefficients are also presented and discussed.

The ferroelectric PMN- $x$ PT single crystals were grown by a modified Bridgman technique.<sup>5,7,8</sup> The single crystal

samples were oriented and cut as confirmed by x-ray diffractometer. Typical specimen dimensions were  $3 \times 3 \times 1 \text{ mm}^3$  and silver paste was painted on the sample surfaces ( $3 \times 1 \text{ mm}^2$ ). Then, the samples were poled along the spontaneous polarization direction under an electric field of 1 kV/mm for 15 min near  $T_m$  in silicone oil, and then slowly cooled to room temperature while maintaining half of the applied electric field. PMN- $x$ PT crystals have a tetragonal-rhombohedral morphotropic phase boundary (MPB). The spontaneous polarization direction is  $\langle 111 \rangle$  for crystals on the rhombohedral side of the MPB ( $x \leq 0.33$ ), and  $\langle 001 \rangle$  for crystals on the tetragonal side ( $x \geq 0.33$ ), respectively. To study the crystal orientation effect, PMN-0.33PT was investigated in both directions. The poled samples were carefully polished to an optical grade, without affecting the crystal polarization.

The refractive index is one of the most important factors determining the use of a new-style material for optical applications; moreover, it is required for calculating EO coefficients. But few studies have been reported on the refractive indices of PMN- $x$ PT single crystals except for PMN-0.38PT.<sup>9,10</sup> The lack of experimental data are mainly due to the difficulties of applying traditional Brewster's angle or the minimum deviation method to crystals with poor quality. Hence, the first step is to measure these indices. A prism coupler (Metricon Model 2010) which can measure refractive index and its anisotropy for bulk sample with high accuracy (the worst case index accuracy is  $\pm 0.001$  and resolution is  $\pm 0.0001$ ) was used in our measurement. Only TE-mode (electric field vibrating transverse to the plane of incidence) measurement can be used for PMN- $x$ PT single

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TABLE I. Values of the refractive indices, EO coefficients, and the half-wave voltage  $V_\pi$  for PMN- $x$ PT single crystals at room temperature.

Composition	Poling direction	$n_o$	$n_e$	$r_c$ (pm/V)	$V_\pi$ (V)
PMN-0.26PT	$\langle 111 \rangle$	2.584	2.595	91	411
PMN-0.30PT	$\langle 111 \rangle$	2.590	2.598	107	347
PMN-0.33PT	$\langle 111 \rangle$	2.598	2.602	109	337
PMN-0.33PT	$\langle 001 \rangle$	2.599	2.562	182	202
PMN-0.35PT	$\langle 001 \rangle$	2.602	2.588	81	452
PMN-0.38PT	$\langle 001 \rangle$	2.616	2.600	41	878
PMN-0.42PT	$\langle 001 \rangle$	2.622	2.603	21	1708

crystals because their refractive indices are out of the measurement range of TM-mode (magnetic field transverse to, and electric field parallel to the plane of incidence) but we still can obtain both the values of  $n_o$  and  $n_e$  by using different incidence plane, respectively, perpendicular to the optic axis for  $n_o$ , and parallel to the optic axis for  $n_e$ . The values measured at 633 nm are listed in Table I. We can see that as the PT content increases, the refractive indices  $n_o$  of PMN- $x$ PT single crystals increase. The results correspond with the suggestion made by Bing *et al.* and have been observed in  $(1-x)\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$  (PZN- $x$ PT) single crystals.<sup>11</sup> It may be due to the higher refractive index of pure PT as compared to that of pure PMN. By the way, the values of PMN-0.38PT single crystal obtained here ( $n_o=2.616$  and  $n_e=2.600$ ) are slightly lower than those of reported by the minimum deviation method ( $n_o=2.620$  and  $n_e=2.601$ ).<sup>9,10</sup> It may be caused by the roughness of the surface and the segregation behavior existed in PMN- $x$ PT single crystals.<sup>12</sup>

The EO effect describes the change in the refractive index ( $\Delta n_{ij}$ ) due to an applied electric field ( $E_k$ ). For poled ferroelectric crystals, we have<sup>13</sup>

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

where  $r_{ijk}$  is the linear EO coefficient. EO measurements were performed with an original and very sensitive method<sup>14,15</sup> which is based on the Sénarmont compensating setup. Figure 1 shows the arrangement of the optical and the electronic components in the system. In this work, the polarization direction of the polarizer was set at  $\pi/4$  with respect to the birefringence axis of the sample, and the electric field was applied along the optic axis of the sample. The effective

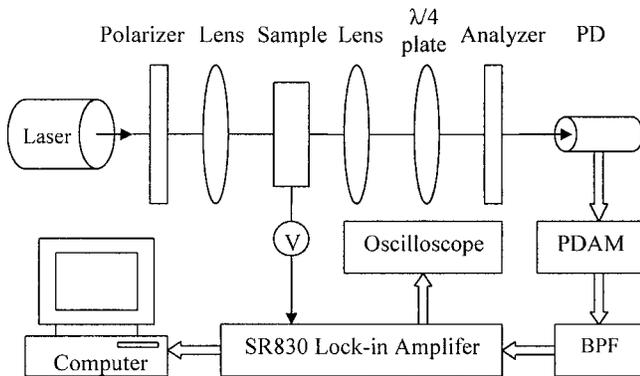


FIG. 1. Schematic arrangement of the optical and the electronic components in the frequency-doubling electro-optic modulation (FDEOM) method. A photodiode (PD) connected to a high-gain photodiode amplifier (PDAM) and a band-pass filter (BPF) is set at the output of the optical setup.

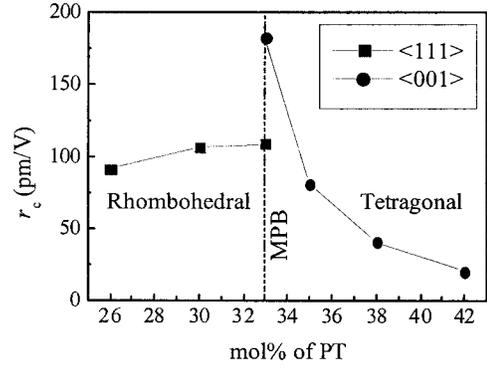


FIG. 2. Composition dependence of the EO coefficients of PMN- $x$ PT single crystals at room temperature.

EO coefficient  $r_c$  was obtained, which was a combined coefficient expressed as<sup>9,16</sup>

$$r_c = r_{jjk} - (n_i/n_j)^3 r_{iik}. \quad (2)$$

A summary of the effective EO coefficients measured at room temperature is presented in Table I. The results reveal several interesting features. First, large values of  $r_c$  are observed for the PMN- $x$ PT single crystals in both the rhombohedral and tetragonal phases. They are all higher than that of widely used electro-optic single crystal  $\text{LiNbO}_3$  (19.9 pm/V).<sup>16</sup> These excellent EO properties, as well as being able to obtain high quality single crystals with large size, make the PMN- $x$ PT single crystals a promising candidate for EO material. Second, large  $r_c$  is obtained for the compositions near the MPB, as shown in Fig. 2. This optical property may be attributed to the phase transition between the tetragonal and rhombohedral phases. The phase transition due to the electric field and stress is associated with large changes in the crystal lattice constants and the refractive index. Third, for the same composition near the MPB (e.g., PMN-0.33PT), the  $r_c$  value of the crystal poled in the  $\langle 001 \rangle$  direction is much higher than that of the crystal poled in the  $\langle 111 \rangle$  direction, as shown in Table I and Fig. 2. The result is similar with that of the PZN- $x$ PT single crystals,<sup>13</sup> and is caused by their spontaneous polarization and dielectric constants as discussed below.

The qualitative aging experiments were also performed on the EO coefficients and it was found that even the poled samples were used for various other measurements at room temperature, the EO coefficients were nearly the same when measurement after several months. Therefore, the optical coefficients reported here are the stable material properties of PMN- $x$ PT single crystals.

The half-wave voltage  $V_\pi$  is an important figure of merit for EO modulator. It is often used for selecting bulk EO materials, and is defined by<sup>15</sup>

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

$V_\pi$  corresponds to the voltage needed to obtain a phase retardation of  $\pi$  from a bulk sample which is independent of its dimensions. In order to obtain a large efficiency for EO modulation applications,  $V_\pi$  should be as small as possible. As shown in Table I, PMN- $x$ PT single crystals also have much lower  $V_\pi$  compared with  $\text{LiNbO}_3$  single crystal (2800 V).<sup>17</sup> Higher EO coefficients and lower  $V_\pi$  enable operation at lower voltages and smaller device dimensions.

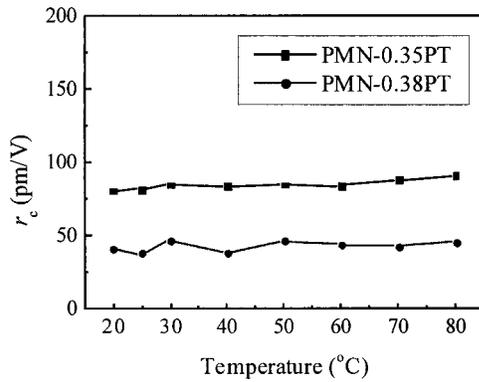


FIG. 3. Temperature dependence of the EO coefficients of (001)-oriented PMN- $x$ PT single crystals.

Thus, PMN- $x$ PT single crystals are of interest for the development of EO devices instead of LiNbO<sub>3</sub>.

We now discuss the temperature dependence of these EO coefficients, which is also important for optical devices. A precise feedback controlled heater was used, and the temperature was monitored with an infrared radiation thermometer (Keyence IT 2–50) with  $\pm 0.2^\circ\text{C}$  accuracy and  $\pm 0.1^\circ\text{C}$  resolution. As shown in Fig. 3, the EO coefficients exhibit a weak increase for PMN-0.35PT single crystal with temperature increases from 20–80°C, and are nearly invariant for PMN-0.38PT. The negligible temperature dependent property is also very attractive for device applications and may be related with their dielectric constant and spontaneous polarization. For ferroelectric single crystals in tetragonal phase, the measured linear EO coefficients can be related to the polarization-related quadratic EO coefficients  $g_{11}$  and  $g_{12}$  as follows:<sup>1,2,18</sup>

$$r_{33} = 2K_{33}\epsilon_0 P_S g_{11} \text{ and } r_{13} = 2K_{33}\epsilon_0 P_S g_{12}, \quad (4)$$

where  $P_S$  and  $K_{33}$  are the spontaneous polarization and dielectric constant, respectively, and  $\epsilon_0 = 8.85 \text{ pF/m}$  is the vacuum permittivity. From Eqs. (2) and (4), we obtain

$$r_c = 2K_{33}\epsilon_0 P_S \left[ g_{11} - \left( \frac{n_o}{n_e} \right)^3 g_{12} \right]. \quad (5)$$

As  $g$  coefficients are nearly invariant with temperature and frequency,<sup>1</sup> the change of the linear EO coefficient  $r_c$  should be determined by the dielectric constant times the spontaneous polarization ( $K_{33}P_S$ ). Indeed, the reported directly measured values of  $K_{33}$  and  $P_S$  for PMN-0.35PT and PMN-0.38PT single crystals with temperature confirm this

effect.<sup>10,19</sup> Moreover, the large values of  $r_c$  appear in the compositions near the MPB and the orientation effect also result from the values of  $K_{33}P_S$ .

In summary, large EO coefficients  $r_c$  were observed for PMN- $x$ PT single crystals near the MPB. In addition, the coefficients are nearly invariant in the experimental temperature range for the tetragonal phase single crystals. The calculated half-wave voltage  $V_\pi$  is much lower than that of widely used EO single crystal LiNbO<sub>3</sub>. These excellent EO properties make PMN- $x$ PT single crystals very promising for EO modulation applications. Detailed analysis indicates that the observed EO properties including their composition and temperature dependence are related with their spontaneous polarization and dielectric constants.

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- <sup>1</sup>M. DiDomenico, Jr. and S. H. Wemple, *J. Appl. Phys.* **40**, 720 (1969).
- <sup>2</sup>S. H. Wemple and M. DiDomenico, Jr., *J. Appl. Phys.* **40**, 735 (1969).
- <sup>3</sup>R. F. Service, *Science* **275**, 1878 (1997).
- <sup>4</sup>S.-E. Park and T. R. Shrout, *J. Appl. Phys.* **82**, 1804 (1997).
- <sup>5</sup>X. Wan, J. Wang, H. L. W. Chan, C. Choy, H. Luo, and Z. Yin, *J. Cryst. Growth* **263**, 251 (2004).
- <sup>6</sup>X. Wan, H. Luo, J. Wang, H. L. W. Chan, and C. Choy, *Solid State Commun.* **129**, 401 (2004).
- <sup>7</sup>H. Luo, G. Xu, P. Wang, and Z. Yin, *Ferroelectrics* **231**, 97 (1999).
- <sup>8</sup>X. Wan, X. Tang, J. Wang, H. L. W. Chan, C. Choy, and H. Luo, *Appl. Phys. Lett.* **84**, 4711 (2004).
- <sup>9</sup>X. Wan, H. Xu, T. He, D. Lin, and H. Luo, *J. Appl. Phys.* **93**, 4766 (2003).
- <sup>10</sup>X. Wan, T. He, D. Lin, H. Xu, and H. Luo, *Acta Phys. Sin.* **52**, 2319 (2003).
- <sup>11</sup>Y. H. Bing, R. Guo, and A. S. Bhalla, *Ferroelectrics* **242**, 1 (2000).
- <sup>12</sup>H. Luo, G. Xu, P. Wang, H. Xu, and Z. Yin, *Jpn. J. Appl. Phys., Part 1* **39**, 5581 (2000).
- <sup>13</sup>Y. Barad, Y. Lu, Z.-Y. Cheng, S.-E. Park, and Q. M. Zhang, *Appl. Phys. Lett.* **77**, 1247 (2000).
- <sup>14</sup>K. Cheng, Ph.D. thesis, The Hong Kong Polytechnic University, 2004.
- <sup>15</sup>M. Aillerie, N. Théofanous, and M. D. Fontana, *Appl. Phys. B: Lasers Opt.* **70**, 317 (2000).
- <sup>16</sup>M. Aillerie, M. D. Fontana, F. Abdi, C. C.-Nedelec, N. Théofanous, and G. Alexakis, *J. Appl. Phys.* **65**, 2406 (1989).
- <sup>17</sup>J. P. Salvestrini, M. D. Fontana, M. Aillerie, and Z. Czapla, *Appl. Phys. Lett.* **64**, 1920 (1994).
- <sup>18</sup>S. H. Wemple, M. DiDomenico, Jr., and I. Camlibeel, *Appl. Phys. Lett.* **12**, 209 (1968).
- <sup>19</sup>X. Zhao, J. Wang, K.-H. Chew, H. L. W. Chan, C. Choy, Z. Yin, and H. Luo, *Mater. Lett.* **58**, 2053 (2004).

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