Electric field-induced stress–birefringence in layered composites $PbZr_{1-x}Ti_xO_3$/Polycarbonate*

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Electro–optical composites based on the product of electro–strictive and elasto–optical effects are developed. Layered composites of $PbZr_{1-x}Ti_xO_3$ and polycarbonate are synthesised. Their electro–optical properties are studied. The nominal transverse electro–optical coefficient of the composite is observed to be about 3.6 times larger than that of $LiNbO_3$. Experiments and theoretical analyses show that the electro–optical effect of the composite has a strong 'size effect'. With the ratio of thickness/length decreasing or the width of elasto–optical phase increasing, the half-wave electric field intensity increases but the transverse electro–optical coefficient decreases for the layered composite.

Keywords: electro–optical effects, elastooptical effects, stress birefringence, multilayer composites

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1. Introduction

Electro–optical (E–O) materials have attracted continuous attention due to their wide applications in E–O devices, such as E–O modulators, deflectors and optical bistable devices.[1] Generally, there are two kinds of single-phase E–O materials, inorganic materials and polymers. Lithium niobate ($LiNbO_3$) is the most important inorganic E–O material[2] for its larger E–O coefficients, better optical homogeneity, and a transmissivity reaching 95% with wavelength ranging from 420 to 5200 nm. $LiTaO_3$ and $BaTiO_3$ belong to the same kinds of E–O mediums as $LiNbO_3$.[3] GaAs, ZnS and CdTe are E–O materials used in infrared waveband.[4] $Bi_{12}SiO_{20}$ and $Bi_{12}GeO_{20}$ are used in short waveband.[5,6] The realization of passive optical components in silicon in recent years[7,8] is big progress in the study of E–O materials due to the fact that electronic and optical functionalities can be integrated into monolithic components based on the versatile silicon platform. Furthermore, a significant linear electro–optic effect induced by breaking the crystal symmetry in the silicon through depositing a straining layer on the top of a silicon waveguide was recently discovered, making it possible to realize a silicon electro–optic modulator.[9] However, inorganic E–O materials are inconvenient and expensive to be used on a large scale because of their brittleness and poor machining properties.[10,11]

Although polymer materials display fast electronic response and good machining property, there is still a lot of work to do in reducing their optical loss and improving the stability of photochemistry and orientation polarization at high temperature.

There are reports on realizing the optical modulation of phase in the optical fibres coated with ferroelectric through electric field, suggesting a new type of E–O material composed of combining electro–strictive and elasto–optical materials.[12,13] Elasto–optical substances are those that are capable of displaying stress-birefringence effect. When the polarized light passes through these materials subjected to stress, the light separates into two light beams, i.e., ordinary beam and extraordinary beam, traveling at different velocities, which are each oriented parallel to the direction of principal stress, but perpendicular to each other, resulting in two different indices of refraction, which vary each as a function of the stress applied.[14,15] Since there are various types of electro–strictive and elasto–optical materials to choose, different kinds of E–O composites can be fabricated to satisfy various applications in E–O devices. Meanwhile, this kind of E–O composite is easy to prepare and cheap to obtain.

Different from the physical mechanism of single-phase E–O materials, the physical mechanism of the E–O composite originates from the product effect of electro–strain and elasto–optical effects. Under an applied electric field, the mechanical deformation of

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the electro–strain phase is coupled to the elasto–optical one through their interface, thereby changing the refractive index of elasto–optical phase. Evidently, the E–O properties of the composites rely on those of the elasto–optical and electrostrictive materials involved. Thus, electrostrictive and elasto–optical materials with excellent properties, respectively, should be needed to compose fine E–O composites. $Pb(Zr_xTi_{1-x})O_3$ (PZT), $BaTiO_3$ crystal or PVDF film with large electrostrictive coefficients can be used as the electro–strain phase.[16,17] Epoxy resin, polycarbonate, polyurethane and fused silica possessing higher optical sensitivities can be considered as the elasto–optical one.[18] In the present work, layered composites $Pb(Zr_xTi_{1-x})O_3$ / polycarbonate are synthesised and their E–O effects are studied.

2. Representation of elasto–optical natures of polycarbonate

Polycarbonate (PC) is a thermoplastic polymer. It has a high transparency, optical isotropy, no natural birefringence, and it is often used in the study of photoelasticity due to its very strong effect of stress-birefringence and very small optical and mechanical creeps at room temperature.[19−21] However, it is necessary to study its elasto–optical natures further before using it as the elasto–optical phase in an E–O composite.

The commercial PC plates with different thicknesses were used in this study and cut into strips of 10 mm in length (d_1), 1.8 mm in thickness (d_3) and different widths (d_2) corresponding to the thickness of the PC plates. For relieving the possible residual stress induced in the primary manufacturing process, all the PC samples were annealed by heating to 158 °C prior to use, and maintaining the temperature for 2 h, then cooling down to 140 °C at a rate of 5 °C/h, and finally the furnace cooled down to the ambient temperature.

Test of light absorption shows that the PC is almost transparent throughout the region of visible light but blocks all ultraviolet lights. Its absorbance (Abs) decreases slowly with the increase of wavelength λ, and it has a sharp peak of absorption appearing at about $\lambda = 676$ nm. For a PC sample of 4.5 mm in thickness, the Abs decreases from 0.084 at $\lambda = 440$ nm to about 0.050 at $\lambda = 780$ nm. The peak value of Abs is about 0.117.

Elasto–optical tests for the PC strips with different values of width d_2 were performed, where a compressive stress σ was supplied by a spring scale and perpendicular to the direction of the laser beam (He–Ne laser, $\lambda = 632.8$ nm), as shown in the inset of Fig. 1. For a birefringence material, the phase difference between the ordinary (o) and extraordinary (e) light beams is known as retardation δ, which is given as

$$\delta = 2\pi c d\sigma/\lambda, \tag{1}$$

where σ is the difference between principal stresses, $d = d_2$ is the distance that the beam passed through the PC, and c is the stress–optical constant, which can indicate the stress–optical sensitivity of an elasto–optical material.[19] The stress that induces a retardation of π is often called half-wave stress σ_π. The half-wave stress as a function of width d_2 is shown in Fig. 1. It is found that the half-wave stress continuously decreases with width increasing, and the data (the solid points) can be fitted to an inversely-proportional curve. This behaviour is in accordance with the prediction of Eq. (1). In fact, taking the retardation as π and the stress as σ_π can yield a simple relation $\sigma_\pi = \lambda/2cd_2$ from Eq. (1).

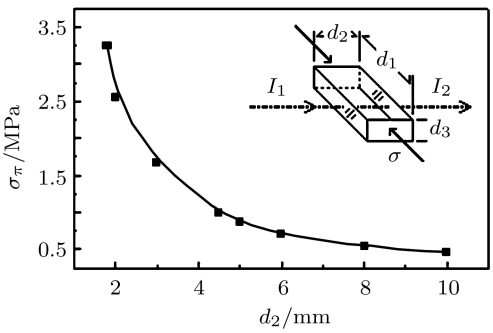


Fig. 1. Half-wave stress as a function of width (the distance that the beam passes) for the PC used.

3. Characterization of E–O composites

$Pb(Zr_xTi_{1-x})O_3$(PZT) as a piezoelectric ceramic of binary ferroelectric system is important due to its superior dielectric, piezoelectric, and electromechanical coupling coefficients and high performance in applications of actuators and transducers. Commercial PZT-5 ($PbZr_{0.5}Ti_{0.5}O_3$) plate with a thickness of 0.8 mm, a piezoelectric coefficient $d_{31} = 178$ pm/V and orientation in the direction of thickness was employed. The PZT plate was cut into strips each with

a length of 11 mm and width corresponding to the width of the PC strip used, then bonded to PC strips with super glue to form layered composite. The length of PZT was 1 mm longer than that of PC for making electrodes.

We first study the E–O effect of bi-layer composite PZT/PC. It is found that the E–O effect obviously weakens with the increase of the distance between the incident point of the beam and the bonding interface. The smaller elastic modulus of PC may be responsible for the behaviour, suggesting a large stress gradient along the direction of the thickness when the PC is subjected to stress by PZT (see later). The stress gradient can be expected to decrease by reducing the thickness of PC and adopting a tri-layer structure PZT/PC/PZT. So the study focuses mainly on the E–O coupling of the tri-layer composite. The schematic diagram and geometric arrangement of measurement is shown in Fig. 2, where P_1 and P_2 are two polarizers, of which the polarizing axes are perpendicular to each other, I_1 and I_2 are the incident and excident light beams, respectively. Polarities of the two PZTs are parallel. The electric field on PZT is along the direction of thickness (h_3). Tri-layer composites with the same length (d_1) of 10 mm, and different values of width (d_2) and thickness (d_3) were prepared.

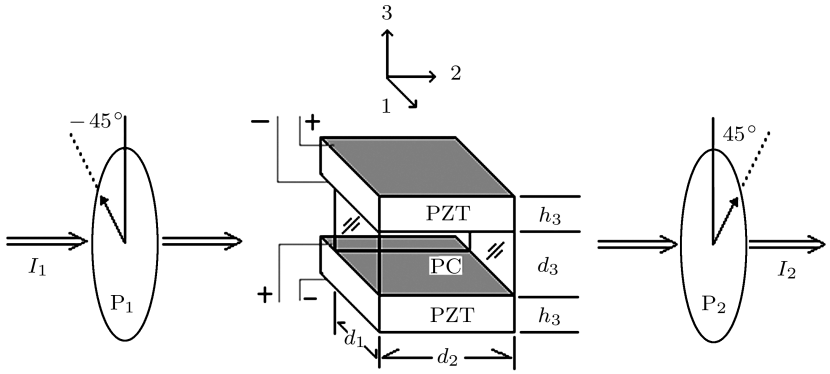


Fig. 2. Schematic diagrams of tri-layer composite and geometrical arrangement for E–O measurement.

4. Experimental results and discussion

Defining $I_2/I_{2\max}$ as normalized excident light intensity (NELI), where $I_{2\max}$ is the maximum value of the excident light. Figure 3 shows the NELIs each as a function of electric field for the tri-layer PZT/PC/PZT composites with different widths while the PC layer thickness is fixed at 1.8 mm. The measurement was performed in a static way, where the electric field was varied slowly.

Firstly, the electric field dependent NELI shows a characteristic very similar to that of electric hysteresis loop when the width of PC is 3 mm. This nature that is obviously related to the electric hysteresis of PZT leads to two values of NELI corresponding to one value of electric field. The practical value of NELI relies on the initial condition of PZT. Secondly, with the width of the tri-layer increasing, the E–O curves reveal a combined effect of the electric hysteresis of PZT and the stress-birefringence effect of PC. Defining the electric field intensity that induces a phase difference π between o and e light beams as half-wave-field intensity $E_\pi (= V/h_3$, V is the voltage applied on PZT), it follows from Fig. 3 that the E_π evidently decreases with d_2 increasing. This result is coincident with that observed in the elasto–optical test (Fig. 1).

Next, it is necessary to have an observation of the effect of the stress gradient along the thick direction. Figure 4 plots the E–O responses for the tri-layer PZT/PC/PZTs which each have a PC layer but their PC layer thicknesses are different from each other, where the tri-layers are all 6 mm in width. It can be seen, under the same electric field, the retardation increases with PC thickness d_3 decreasing. The present results can be explained only by the stress gradient along the direction of thickness. Thus, the layered composites display size effects not only along the direction of width but also along the direction of thickness.

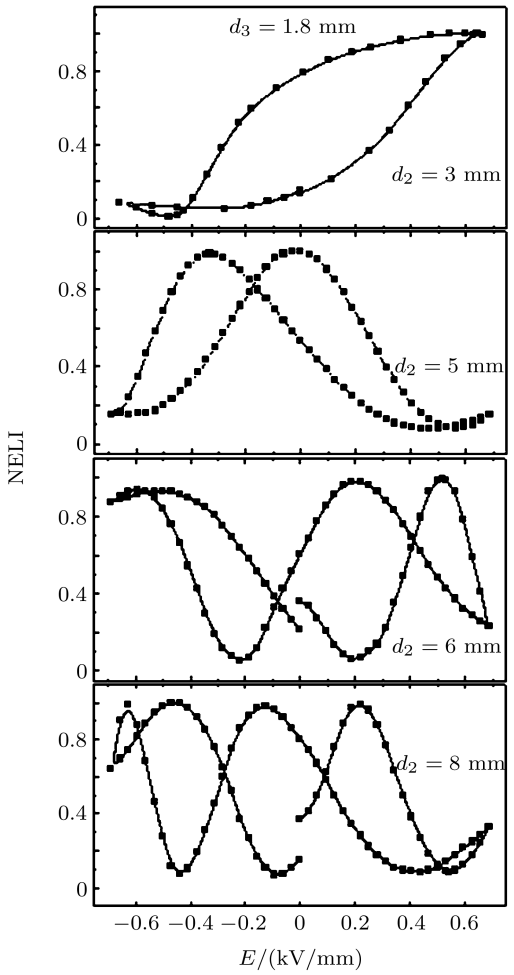


Fig. 3. Electric field dependences of the NELI for the layered composites with a thickness of 1.8 mm and different widths of PC.

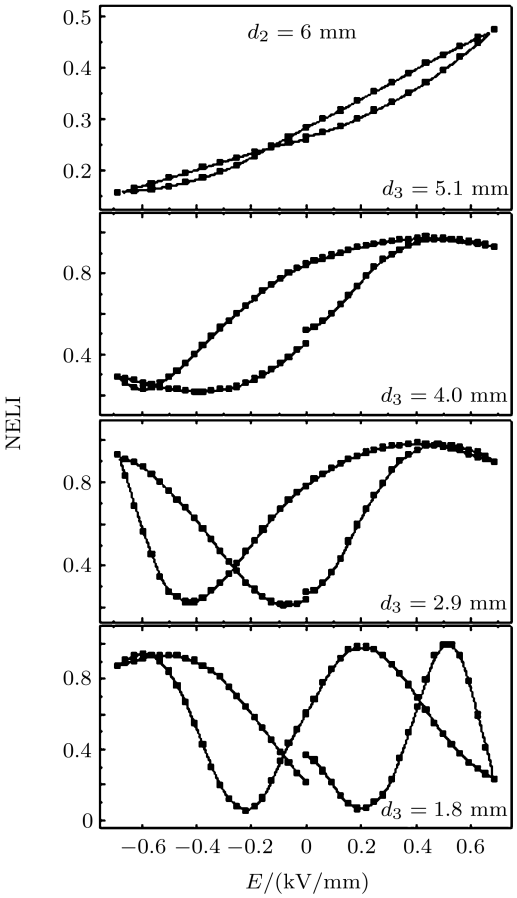


Fig. 4. Electric field dependences of the NELI for the layered composites with a width of 6 mm and different thicknesses of PC.

For a freebody bilayer structure, assuming that elastic coupling in the interface is ideal, any flexural deformation of the layer can be ignored, and the stress is uniform throughout the thickness, from the constitutive equation for the ferroelectric phase and the stress–strain equation for the elasto–optical phase, one can derive the stress near and parallel to the interface as follows:

$$\sigma_0 = \frac{1}{\dfrac{1-\mu}{\mathrm{Y}} - 2\mathrm{s}\dfrac{1-\nu}{\nu}} d_{31}E \approx \frac{Y}{1-\mu} d_{31}E, \qquad (2)$$

where Y and μ are the Young modulus and Poisson's ratio of stress–optical phase, respectively, s is the strain parallel to the interface in the PC, ν and d_{31} are the volume fraction and the piezoelectric coefficient of the ferroelectric phase, respectively. The symbol '$\approx$' on the right-hand side of Eq. (2) is obtained by considering $2s(1-\nu)/\nu << (1-\mu)/Y$, in general.

Equation (2) may hold only in the case where the stress is uniform throughout the thickness. However, the stress-gradient exists as mentioned above when the stress is exerted along the surface(s) of PC. According to the Saint–Venant's principle in solid mechanics,[22] for a tri-layer structure in the present case, assume that the stresses along the upper and lower surfaces of PC are both the same (σ_0), $d_3 \leq 3d_1$, and $d_3 - 1.5d_1 \leq z \leq 1.5d_1$, then the stress of each point in PC (σ_z) and the distance z from the point on which a stress σ_0 is exerted will satisfy the following relation:

$$\sigma_z = \sigma_0 \cos^2\left(\pi \frac{z}{3d_1}\right) + \sigma_0 \cos^2\left[\frac{(d_3 - z)\pi}{3d_1}\right]. \qquad (3)$$

For convenience, assuming the beam to pass through the point $z = d_3/2$, and considering Eq. (2), Eq. (3) may be rewritten as

$$\sigma = \frac{2Y d_{31}E}{1-\mu} \cos^2\left(\frac{\pi}{6}\frac{d_3}{d_1}\right). \qquad (4)$$

If o and e light beams direct to coordinate axes 1 and

3, respectively, the retardation should be

$$\delta = \frac{4cd_2\pi}{\lambda}\frac{Yd_{31}E}{1-\mu}\cos^2\left(\frac{\pi}{6}\frac{d_3}{d_1}\right), \quad (5)$$

which may be called E–O retardation here. The Half-wave field intensity is an important parameter for representing single-phase E–O materials and is given as $E_\pi = \lambda/(2n_0^3\gamma d)$, where n_0 is the refractive index of an E–O material at zero field, $d = d_2$ in the present case, and γ is the transverse E–O coefficient, that is, the sensitivity of the E–O response under an applied electric field perpendicular to the beam. Taking $\delta = \pi$, one can also obtain a half-wave field intensity for the composite from Eq. (5) as

$$E_\pi = \frac{\lambda(1-\mu)}{4cd_2Yd_{31}\cos^2(\pi d_3/6d_1)}. \quad (6)$$

Comparing Eq. (6) with the relation $E_\pi = \lambda/2n_0^3\gamma d_2$, a nominal transverse E–O coefficient can be achieved for the composite as follows:

$$\gamma = \frac{2cYd_{31}\cos^2(\pi d_3/6d_1)}{(1-\mu)n_0^3}. \quad (7)$$

Taking $\lambda = 632.8$ nm, and $d_{31} = 175\times10^{-12}$ m/V for PZT,[23] $n_0 = 1.584$, $Y = 2430\times10^6$ N/m^2, $\mu = 0.38$, $d_3/d_1 = 0.2$ and $c \approx 78.34.\times10^{-12}$ Pa^{-1} (corresponding to $d_2 = 6$ mm) for PC,[19] where $c(\approx 78.34\times10^{-12}\pm5\%)$ Pa^{-1} is obtained from Fig. 1 by using the experimental data. Equation (7) gives the nominal transverse E–O coefficient $\gamma \approx 24.35\pm10\%$ (10^{-12} mV^{-1}) in accordance with preparation technology for the composites. This value is about 3.6 times that of $LiNbO_3$ (in static electric field $\gamma_{22} = 6.8\times10^{-12}$ mV^{-1}).[24] Equation (7) indicates that the sensitivity of the E–O response depends not only on the distance that the beam passes, d_2, but also on the ratio of thickness to length of the PC, d_3/d_1, showing a 'size effect' as mentioned before. Simultaneously, the nominal transverse E–O coefficient also relies on the wavelength of the light and the parameters of materials involved besides the size effect.

Additionally, as an electro–optical modulator, it is necessary to have an observation of its response time to ac signals. For a tri-layer composite of 10 mm × 6 mm × 2 mm in size, the initial test, which was performed by using a function generator with a maximum frequency of 2 MHz, shows that the response frequency of the layered composites is no less than 25 kHz. So the response time is not greater than 40 μs. The lower limit of the response time now is unknown.

5. Conclusion

Combining electro–strain material with elastooptical medium can form an electrooptical composite with electro–birefringence effect. The tri-later structure of PZT/PC/PZT may be a better structure for exhibiting fine E–O effect. This composite displays a strong 'size effect'. For a composite with an appropriate size of PC layer and the preparation technology, a greater transverse electro–optical coefficient γ, which is about 3.6 times that of $LiNbO_3$, can be obtained. The value of γ can be expected to be enhanced when the PC layer has a size of film, i.e., its length and width are sufficiently large and thickness is as thin as that of the film, which should be limited only by the diameter of the beam, for an ideal layered composite of PZT/PC/PZT.

References

[1] Li C S, Cui X and Yoshino Toshihiko 2001 *IEEE Trans. Instrumentation and Measurement* **50** 1375

[2] Zhang B, Wu B Y and Zhou W Q 2001 *J. Optoelectronics Laser* **12** 1199 (in Chinese)

[3] Hammer J M and Phillips W 1974 *Appl. Phys. Lett.* **24** 545

[4] Boyd G D and Livescu G 1992 *Opt. Quantum Electron.* **24** S147

[5] Kargin Yu F, Egorysheva A V, Volkov V V, Frolova M N, Borodin M V, Shandarov S M and Shandarov V M 2005 *J. Crystal Growth* **275** e2403

[6] Frolova M N, Borodin M V, Shandarov S M, Shandarov V M, Kargin Yu F, Egorysheva A V and Kip D 2003 *Trends Opt. Photonics* **87** 403

[7] Trinh P D, Yegnanarayanan S, Coppinger F and Jalali B 1997 *IEEE Photon. Technol. Lett.* **9** 940

[8] Pavesi L and Lockwood D J 2004 *Silicon Photonics* (Berlin: Springer)

[9] Jacobsen Rune S, Andersen Karin N, Borel Peter I, Fage-Pedersen Jacob, Frandsen Lars H, Hansen Ole, Kristensen Martin, Lavrinenko Andrei V, Moulin Gaid, Ou Haiyan, Peucheret Christophe, Zsigri Beata and Bjarklev Anders 2006 *Nature* **441** 199

[10] Wang X D, Basséras P, Dwayne Miller R J and Vanherzeele Herman 1991 *Appl. Phys. Lett.* **59** 519

[11] Taira Takunori and Kobayashi Takao 1995 *Appl. Opt.* **34** 4298

[12] Barrow D A, Lisboa O and Jen C K 1996 *J. Appl. Phys.* **79** 3323

[13] Bhatti A, Alraweshidy H S and Murtaza G 1999 *Photon. Technol. Lett.* **11** 812
[14] Ning Y N, Liu T Y and Jackson D A 1992 *Rev. Sci. Instrum.* **63** 5771
[15] Koo K P and Sigel G H 1982 *IEEE J. Quantum Electronics* **18** 670
[16] Cao H and Evans A G 1993 *J. Am. Ceram. Soc.* **76** 890
[17] Schaufele A B and Hardtl K H 1996 *J. Am. Ceram. Soc.* **79** 2637
[18] Yupapin P V P and Kusamran S 1993 *Smart. Mater. Struct.* **2** f57
[19] Pappalettre C and Galietti U 2008 *Strain* **31** 69
[20] Baldi A, Bertolino F and Ginesu F 2007 *Optics and Lasers in Engineering* **45** 612
[21] Blakemore R H and Marsden B 2008 *Strain* **16** 124
[22] Horgan C O1996 *Appl. Mech. Rev.* **49** S101
[23] Bichurin M I, Petrov V M and Srinivasan G 2003 *Phys. Rev.* B **68** 054402
[24] Bammer F and Holzinger B 2007 *Optics and Laser Technology* **39** 1002