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Study on the properties of a nanocrystal and polymer composite $PbTiO_3$/PEK-c film with optical anisotropy

D. XU
State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, People's Republic of China

Q. REN
Department of Optics, Shandong University, Jinan 250100, People's Republic of China

P. L. CHU, Y. T. CHOW, H. P. CHAN, S. Y. CHENG, B. CHOW
The Optoelectronics Research Centre, City University of Hong Kong, Kowloon, Hong Kong

S. Y. GUO
State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, People's Republic of China

H. L. YANG
Department of Optics, Shandong University, Jinan 250100, People's Republic of China

Composite thin films of $PbTiO_3$ nanocrystals and PEK-c polymer for applications in nonlinear optical devices were prepared by spin coating. The size of $PbTiO_3$ nanocrystals was estimated to be 30–40 nm. The microstructure of $PbTiO_3$/PEK-c composite polymer film before and after poling was analyzed by X-ray diffraction, which show that this film is *c* axis-orientated. The poled composite film displayed the refractive index anisotropy. In this sample the TE- and TM-indices differences are found to be 0.02945 for 633 nm and 0.03915 for 414 nm. The electro-optic coefficient γ_{33} of poled composite film was measured to be 12.89 pm V^{-1} at 633 nm by the transmission technique. The dielectric constant ε of it at 100 KHz under room temperature was determined to be 7.32. The figure of merit F_2 was estimated to be 492. In addition, a relaxation process was observed in the time range of 28 days and the relaxation time constant was calculated to be 2393 min.

1. Introduction

There is a great interest in nonlinear optical composite polymer materials suited to different types of photoelectronics devices for applications to optical communication and optical computation technologies. The compounding of active nonlinear optical (NLO) units in a polymer allows a high nonlinear optical effect to be added to traditional polymers while maintaining a low dielectric constant after poling in an electric field. In addition, the resulting composite materials can easily be processed into thin films for waveguide applications. They are potentially competitive materials for integrated optical devices such as electro-optic modulators and switches [1, 2].

Lead titanate ($PbTiO_3$) is a perovskite-type ferroeletric material. Its single domain crystal has a high spontaneous polarization P_s ($\sim$81 μC cm^{-2}), a dielectric constant ε ($\sim$107) and a pyroelectric coefficient p (6×10^{-8} C cm^{-2} K^{-1}). It also has a high electro-optic figure of merit F_2 ($\sim$574) [3]. However, the synthesis of large, perfect, and pure $PbTiO_3$ single crystals is very difficult. In our research, we used $PbTiO_3$ nanocrystals as active nonlinear units (guests) in the NLO polymer system. The transparent polymer polyetherketone (PEK-c) was chosen as the polymer host because of its high glass transition temperature T_g ($\sim$228°C) and intrinsic low dielectric coefficient ε ($\sim$3.2) [4]. PEK-c possesses high thermal stability for the resulting composite films. In face, the preliminary study on its optical and electro-optical properties shows promising result. We notice that the way of composting the nanocrystals and the polymer will also greatly affect the stability and electrooptic coefficients of the polymer materials.

The investigations into the optical behaviors of the poled composite polymer thin films, such as their optical and electro-optical properties, and determination of the poling condition for the composite polymer thin-film samples are of great interests. In the present work, a high quality composite film was prepared and the corona-onset poling at elevated temperature (COPET) was applied to the film to align the active nonlinear

units. Then the properties of the poled composite polymer film were investigated.

2. Experimental

2.1. Preparation of $PbTiO_3$ nanocrystals

Nanocrystalline $PbTiO_3$ has been synthesized by the chemical solution decomposition (CSD) technique. First, lead acetate trihydrate [$Pb(CH_3COO)_2 \cdot H_2O$] was dissolved in 2-methoxyethanol. Then titanium butoxide [$Ti(OC_4H_9)_4$] was added to the solution to form a $PbTiO_3$ precursor solution under stirring. The mole ratio of Pb to Ti was chosen to be 110:100. The solution was heated to vaporize the solvent yielding an ultrafine $PbTiO_3$ precursor powder. Finally, the dried powder was processed by rapid thermal annealing (RTA) at 700°C for 60 s and transformed into nano-crystalline $PbTiO_3$. The size of the $PbTiO_3$ nanocrystal was estimated under a transmission electron microscopy (TEM: H-800 Hitachi). Fig. 1 shows the TEM photograph of the $PbTiO_3$ nanocrystals which have an average size of about 30–40 nm.

2.2. Preparation of $PbTiO_3$/PEK-c composite thin film

The $PbTiO_3$/PEK-c composite thin films were prepared using the spin coating technique. The weight ratio of $PbTiO_3$ microcrystals to polymer PEK-c was 15%. After the polymer was thoroughly dissolved in chloroform, the $PbTiO_3$ nanocrystals were placed in the solution, and the mixture was blended ultrasonically. After dispersing the $PbTiO_3$ nanocrystals, the solution was then deposited on a 1.06-mm-thick ITO K18 glass substrate by spin coating at 2000 rpm for 40 s.

The resulting film was baked with rising tardily temperature to remove the residual solvent, and was poled using the corona poling technique at the same time, as indicated schematically in Fig. 2, in order to introduce a noncentresymmetric structure into the film. In this technique, the temporary dipole of $PbTiO_3$ nanocrystals were induced because of its pyroelectricity, an electric field was applied to the film heated near to its glass transition temperature T_g (∼190°C). As a consequence,

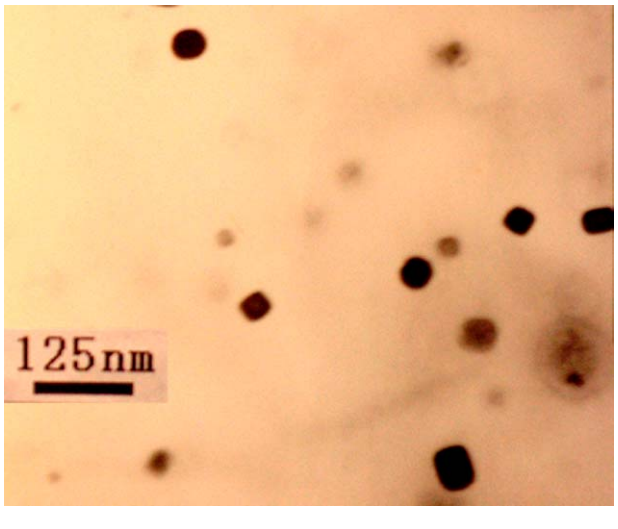

Figure 1 TEM photograph of $PbTiO_3$ nanocrystals.

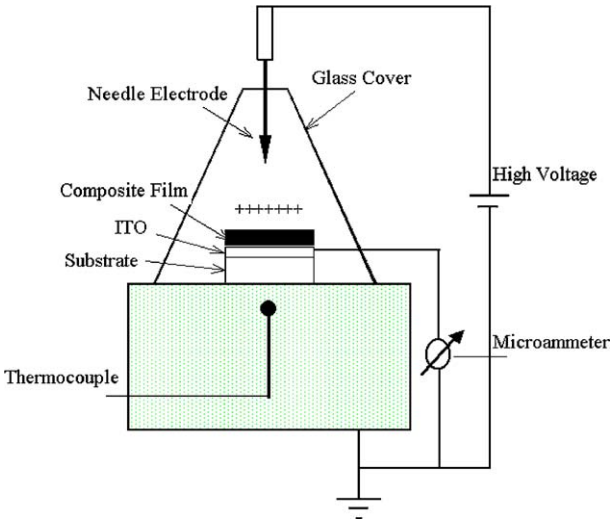

Figure 2 Experimental setup of the corona poling technique.

the nanocrystal units become aligned, resulting in an increase of the nonlinear optical effects in the film. In our case, the temperature was monitored by a fine temperature control. The voltage applied to the tungsten needle electrode was 2 kV. The sample is poled for 2 h in whole periods, and then it was allowed to cool down to room temperature.

The composite polymer film, of the order of a few microns, is spin-coated onto a 1.06-mm-thick glass substrate, which is sputtered with an approximately 250-Å-thick layer of transparent conducting material, indium tin oxide (ITO). During the poling process, this ITO layer serves as one of the electrodes, while the other electrode is a conducting needle located about 1 cm above the surface of the polymer film.

2.3. Characterization of $PbTiO_3$/PEK-c composite thin film

The microstructure of the film before and after poling was analyzed by X-ray diffraction (XRD), using Cu $K_{\alpha 1}$ ($\lambda = 0.15406$ nm) radiation, operated at 40 kV and 20 mA. An Impendence analyzer 4192A was used to measure the temperature dependence of dielectric constants of film at 100 KHz. Differential scanning calorimetry (DSC) was carried out on a Perkin-Elmer DSC-2C with a heating rate of 20°C/min. The refractive indices of it at 633 and 414 nm by means of a Metricon 2010 prism coupler with rutile prism. The electro-optic coefficient, γ_{33}, of poled $PbTiO_3$/PEK-c composite polymer film is measured using the simple transmission technique. In the measurement, the composite polymer film is sandwiched between two tightly contacted layers of ITO. A He-Ne laser beam (633 nm) is incident through this composite layer (the glass substrate, the ITO, the composite polymer film, the ITO, the glass substrate) at an angle θ. The polarization of the input beam is set 45° to the plane of incidence so that the parallel (p wave) and perpendicular (s wave) components of the optical field are equal in amplitude. He transmitted beam propagates through a $\lambda/4$ wave plate, an analyzer and into a detector. Intensity of optical beam is measured by a lock-in amplifier.

3. Results and discussion

3.1. Poling of the composite polymer films

The glass transition temperature T_g of the $PbTiO_3$/PEK-c composite polymer system is about 190°C as indicated in Fig. 3a, which displays their dielectric constants ε as a function of temperature. This value is confirmed using a differential scanning calorimeter (DSC) plots shown in Fig. 3b. The corona-onset poling at elevated temperature is a favored technique for producing noncentrosymmetric nonlinear optical materials. The $PbTiO_3$/PEK-c composite polymer thin films were poled at about 180°C just below the glass transition temperature T_g to increase the mobility of the nanocrystals. As a result, the poled composite polymer thin films can exhibit relatively good nonlinear optical properties. At the same time, it is can be seen from Fig. 3a, the dielectric constant ε of the composite polymer thin film was found to be 7.32 at room temperature and 100 KHz. We also observed that the dielectric constants of $PbTiO_3$/PEK-c composite polymer thin films increased with the concentration of doped $PbTiO_3$ nanocrystals.

The poling efficiency η [5],

$$\eta = \frac{\mu E_P}{KT} \tag{1}$$

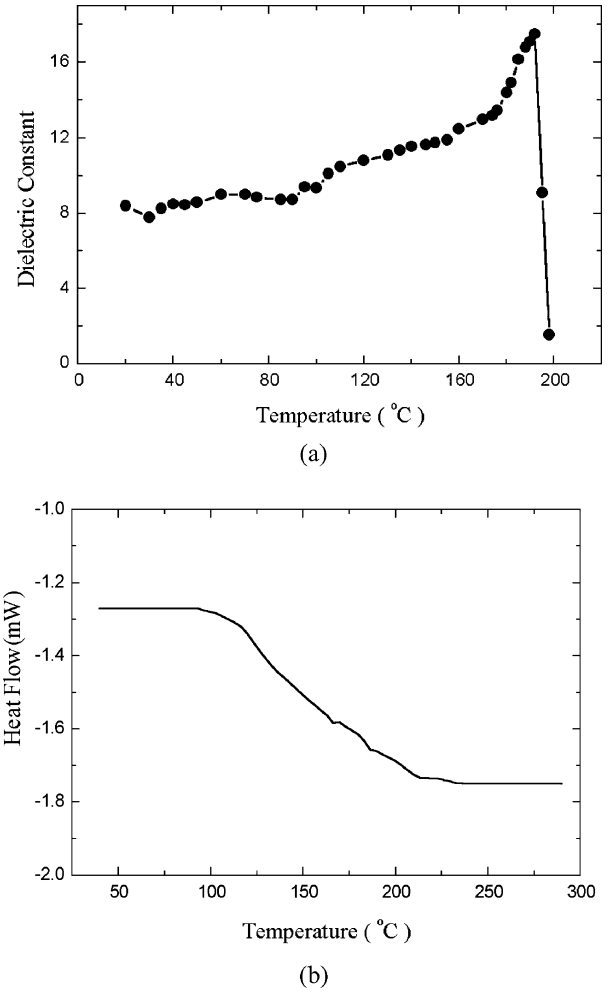

Figure 3 (a) Temperature dependence of the dielectric constant (at 100 KHz) of the $PbTiO_3$/PEK-c composite polymer thin film. (b) Thermal analysis plots of the $PbTiO_3$/PEK-c composite polymer system (scan rate: 20.00°C/min, onset: 94.67°C).

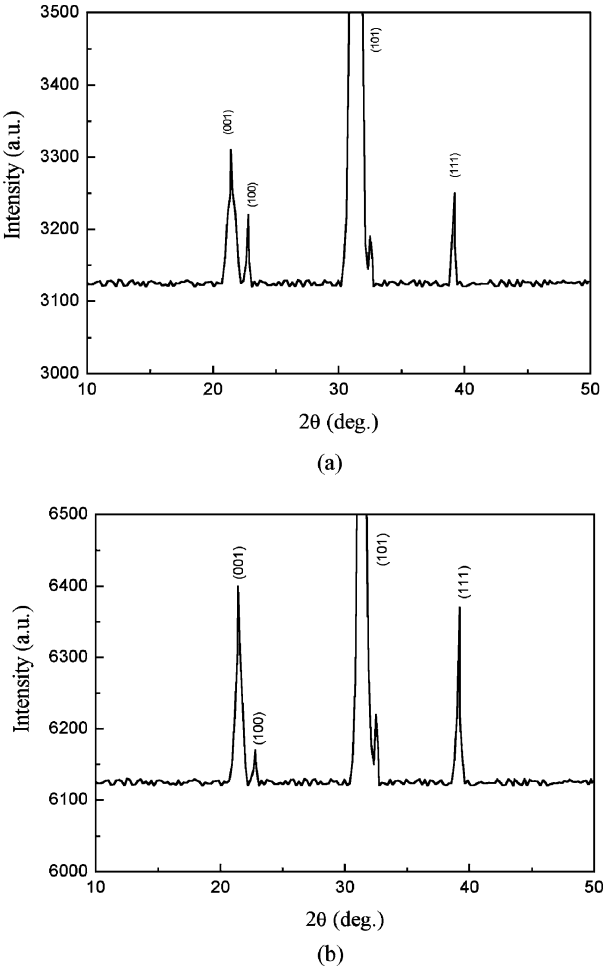

Figure 4 X-ray diffraction patterns of the un-polarized (a) and polarized (b) $PbTiO_3$/PEK-c composite film of thickness 2.33 μm.

where μ is the intrinsic dipole moment of nonlinear optical units, E_P is the poling electric-field intensity, K is the Boltzman constant, and T is the poling absolute temperature. In order to raise the poling efficiency of composite materials, the nonlinear optical units with a strong intrinsic dipole moment should be selected. The microstructure of the film before and after poling was analyzed by XRD. Fig. 4 shows the XRD patterns of the $PbTiO_3$/PEK-c composite film of thickness 2.33 μm before and after poling separately. From the equation of diffraction, we obtained the microscopic net plane distance d corresponding to all angles θ of the X-ray peaks. The net plane indices corresponding to the distances d were then found using the American Society for Testing and Materials (ASTM) data card. It is can be seen from Fig. 4, there are many peaks on the X-ray diffraction pattern of the un-polarized $PbTiO_3$/PEK-c composite film. Some of these peaks also appear in the pattern of the polarized $PbTiO_3$/PEK-c composite film. However, in the pattern of the polarized $PbTiO_3$/PEK-c composite film, the peak of (001) is stronger and the peak of (100) is weaker, showing that this film is c axis-oriented. And c axis orientation ratio β is defined as [6]

$$\beta = I\,(001) / [I\,(001) + I\,(100)] \tag{2}$$

where I (001) and I (100) are the XRD intensities of the (001) and (100) net planes, respectively. The ratio β of the film was calculated to be 68%.

3.2. Optical properties

The refractive indices of $PbTiO_3$/PEK-c composite polymer thin film at 633 and 414 nm before and after poling were separately measured by means of a Metricon 2010 prism coupler. A He-Ne laser (633 nm) and a semiconductor laser (414 nm) were used as the light sources, which were respectively coupled into the thin-film by a right-angle retile coupling prism through a focused lens. In order to ensure a good coupling, the measured thin-film waveguide must be kept in close contact with the prism base. This prism and the measured sample were mounted on a well-controlled rotation stage that was used to orient the transverse electric (TE) and the transverse magnetic (TM) modes of 633 and 414 nm laser beams waveguided into the film to excite the particular propagation modes in the film. By turning the rotation stage at certain incidence angles, optical energy can be fed into one of the waveguide modes of the film. Due to the in-homogeneities of the film, the excited mode will rapidly scatter into the other modes of the film, which will then coupled back to the outside medium through the same prism. In our prepared sample, two of such bright lines can be observed using our setup. Each of these m-lines represents a mode of a fixed order. The coupling of the laser beam by the prism into the planar waveguide is governed by the angle θ of incidence of the light onto the prism base. This angle θ determines the phase velocity, $v = c/n_p \sin\theta$ (c is the speed of light in free space), of the incident wave in the prism. Strong coupling of the light into the waveguide film occurs only when we choose θ so that v equals the phase velocity v_m of one of the characteristic modes of propagation in the waveguide ($m = 0$, 1). The waveguide properties of the un-poled and poled composite polymer $PbTiO_3$/PEK-c film were measured by the mode spectrum given by the reflected intensity versus the angle θ of incidence. The results were shown in Table I. From Table I, the refractive index difference between TE-polarized and TM-polarized, Δn, which is resulted by poling, is found to be 0.02945 for 633 nm and 0.03915 for 414 nm, showing very good optical anisotropy properties. The thickness of the thin-film can be determined to be 2.33 μm simultaneously.

3.3. Electro-optical properties

The investigations on the electro-optical properties and photo-stability of the poled composite polymer thin films are of great interests for the design of integrated optical devices. The simple reflection technique for measuring the electro-optic coefficient of poled polymer films was reported [7]. In this method, a second (top) layer of gold or aluminum acting as reflector and electrode is directly evaporated onto the surface of the composite polymer film under a high temperature. In this way the sample may be destroyed. A simple method, transmission technique [8], for the measurement of electro-optic coefficients of the poled composite polymer film is developed by us. Sample preparation is extremely simple and nowaveguide or electrode patterning is required. This technique is based on the polarization rotation of a laser beam due to the electro-optic effect. A He-Ne laser beam (633 nm) is incident through this composite layer of sample (the glass substrate, the ITO, the composite polymer film layer, the ITO, the glass substrate) at an angle θ. The polarization of the input beam is set 45° to the plane of incidence so that the parallel (p wave) and perpendicular (s wave) components of the optical field are equal in amplitude. The transmitted beam propagates through a λ/4 wave plate, an analyzer, and into a detector. The intensity of the beam is measured by a lock-in amplifier equipped detector. In our measurement configuration, if the phase difference between the s and p waves is ψ_{sp}, the output laser intensity I_0 at the detector can be described by

$$I_0 = 2I_c \sin^2 \frac{\psi_{sp}}{2} \tag{3}$$

where I_c is half the maximum intensity, as shown in Fig. 5. Let n_e and n_o be the main indices of refraction, respectively, in the perpendicular and parallel direction to the plane of the composite polymer film. The index of refraction n_p for the p wave is given by

$$n_p = \frac{n_o n_e}{\left(n_o^2 \sin^2 \alpha_p + n_e^2 \cos^2 \alpha_p\right)^{1/2}} \tag{4}$$

and for the s wave, $n_s = n_o$, where α_p is the refraction angle of the p wave inside the film and is related to the

TABLE I The values of the refractive indices for $PbTiO_3$/PEK-c composite polymer thin film

			Δn	
λ (nm)	n (Un-polarized film)	n (Polarized film)	TE	TM
633	1.55165	1.57160	1.54215	0.02945
414	1.65352	1.72659	1.68744	0.03915

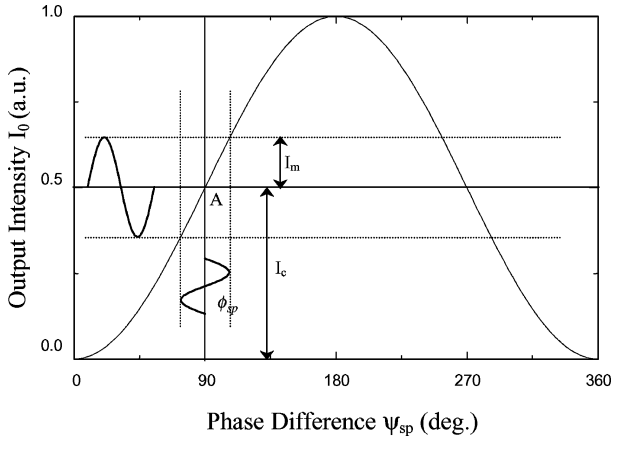

Figure 5 Output laser intensity as a function of phase retardation between the s and p wave.

incident angle θ by

$$\sin\theta = n_{\mathrm{p}} \sin\alpha_{\mathrm{p}} \tag{5}$$

If a modulating voltage $V = V_{\mathrm{m}} \sin\omega_{\mathrm{m}} t$ is applied across the electrodes, where V_{m} is the peak value of the modulating voltage, ω_m is the modulation frequency, a change in the phase angle $\delta\psi$ in both the s and p waves is induced by the change in refractive index δn due to the electro-optic effect. There is also a change in path length δl due to the change in the refraction angle α. Hence

$$\delta\psi = \frac{2\pi}{\lambda}(l\delta n + n\delta l) \tag{6}$$

The change in path length is derived from $l = 2d/\cos\alpha$, where λ is the optical wavelength and d is the thickness of the composite polymer film. With the use of the approximations $n_{\mathrm{o}} \approx n_{\mathrm{e}} \approx n$, and, due to the symmetry considerations in [9], $\gamma_{33} = 3\gamma_{13}$, the following equations can be derived:

$$\delta\psi_{\mathrm{sp}} = \delta\psi_{\mathrm{p}} - \delta\psi_{\mathrm{s}} = -\frac{2\pi\sin^2\alpha}{3\lambda\cos\alpha} n^3 \gamma_{33} V_{\mathrm{m}} \sin\omega t \tag{7}$$

Fig. 5 shows a plot of the output beam intensity I_0 as a function of the phase retardation ψ_{sp} between the s and p waves as described by Equation 3. When this intensity is biased at the half-intensity I_{c}, at points A, the curve is at its linear region, and for small modulations, the ratio between the modulated beam intensity measured I and the midpoint intensity I_{c} can be approximated by $I/I_{\mathrm{c}} \approx \psi_{\mathrm{sp}}$. And hence

$$\gamma_{33} = \frac{3\lambda I_{\mathrm{m}}}{2\pi I_{\mathrm{c}} V_{\mathrm{m}}} \cdot \frac{(n^2 - \sin^2\theta)^{\frac{1}{2}}}{n^2 \sin^2\theta} \tag{8}$$

where I_{m} is the amplitude of the modulation. In the experiment the point A was selected as working point. In reality, we used a $\lambda/4$ wave plate instead of the compensator to make the measurement work at the point A.

In the electro-optic coefficient measurement of the poled $PbTiO_3$/PEK-c composite polymer film sample, a modulating voltage was applied across the ITO electrodes at 1 KHz, and the incident angle θ of 633 nm laser light was set at 30°. Under this condition the half-intensity I_{c} was determined as 407 mV. The refractive indices for the poled $PbTiO_3$/PEK-c composite polymer film at 633 nm were accurately measured with a prism coupler where the TE- and TM-polarized laser light was coupled in and out of the films. The thickness was determined simultaneously to be 2.33 μm. From Equation 8, we find the value $\gamma_{33} = 12.89$ pm V^{-1} at room temperature and for a 633 nm wavelength. The dielectric constant ε of the composite polymer film at 100 kHz under room temperature was determined to be 7.32. The figure of merit $F_2 = n^7\gamma^2/\varepsilon$ was estimated to be 492.

We obtained the information of the active nonlinear units orientation relaxation in polymer hosts by tracking the attenuation of linear electro-optic coefficient with time. In common, the orientation of units doped in polymer will relax quickly and then tend to stabilize by degrees after poling. The experimental results were showed in Fig. 6.

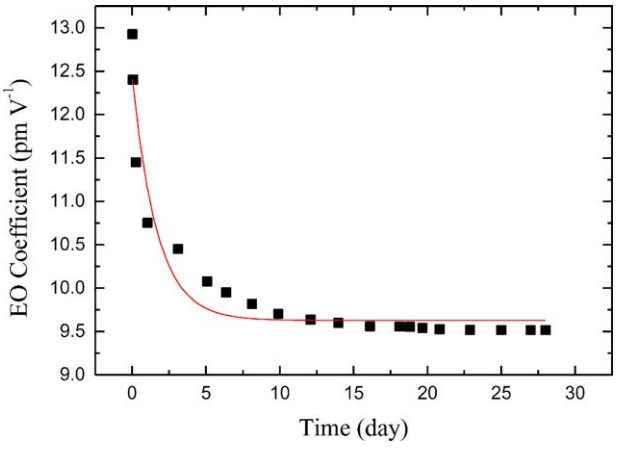

Figure 6 Decay of linear EO coefficient with time.

Fitting our experimental results according to the equation,

$$y(t) = y_0 + A\exp(-t/\tau) \tag{9}$$

the relaxation time constant τ was obtained to be 2393 min. The fitting result indicated that the sample's electro-optic coefficient attenuate quickly in the starting days. The polymer film is metastable after the active nonlinear units were aligned in the condition of added electrical field because it exists that the polymer carcass's position resistance effect, in-stress between the active nonlinear unites resulting from poling and unbalance electrostatic attraction between the nonlinear units with dipole. When the nonlinear unit's tumbling potential barrier is small, the polarized active nonlinear units will turn back because of the polymer carcass' vibration. With the time going on, the nonlinear unit's orientation becomes stable and the variation of EO coefficient also turns to be smooth. In order to effectively solve the question of poled sample's quick relaxation, we choose $PbTiO_3$ nanocrystals, with pyroelectricity, as nonlinear units. These nanocrystal units, which are ball or ellipse shape and have no perpetual dipole, are used to substitute organic conjugated nonlinear molecular units which are branches and tendrils shape and have permanent dipole commonly; and choose PEK-c, which has weak molecular chain vibration and high glass-transition temperature, as host to add the tumbling potential barrier of nonlinear $PbTiO_3$ nanocrystals. The stability of poled polymer composite film's EO performance was greatly improved. The relaxation curve indicates that the film material tends to be stable after about 5 days and maintain approving EO coefficient value, as shown in Fig. 6. The experimental phenomenon confirmed our idea about the design of composite film materials.

4. Conclusions

In summary, the novel composite thin films of $PbTiO_3$ nanocrystals and PEK-c polymer were prepared. The

size of $PbTiO_3$ nanocrystals was estimated to be 30–40 nm using a transmission electron microscopy. The $PbTiO_3$/PEK-c composite polymer thin film was prepared by spin-coating technique. The films are then electrically poled to induce asymmetry in the material by heating the film to a temperature close to its glass transition and applying an electric field. The nanocrystals are oriented because of their strong electric dipole moment, yielding a non-centrosymmetric arrangement. The glass transition temperature T_g of the $PbTiO_3$/PEK-c composite polymer system is about 190°C which is measured from their dielectric constants ε versus temperature curve and confirmed with their differential scanning calorimeter plots (DSC). The optimal poling temperature is lower than the glass transmission temperature of the investigated composite polymer system. In order to achieve more efficient poling, determination of the glass transition temperature T_g of the $PbTiO_3$/PEK-c composite polymer system is very crucial. The microstructures of the film before and after poling were analyzed by XRD. The XRD results show that this film is c axis-orientated. And c axis orientation ratio β was calculated to be 68%. By using the Metricon prism coupling system, the refractive indices of the un-poled and poled composite polymer film were measured respectively. The poled composite thin film displayed the refractive index anisotropy. In this sample the TE- and TM-indices differences are found to be 0.02945 for 633 nm and 0.03915 for 414 nm, showing very good optical anisotropy properties. The thickness of the $PbTiO_3$/PEK-c composite polymer thin film was determined to be 2.33 μm simultaneously. In addition, The electro-optic coefficient γ_{33} of poled composite film was measured to be 12.89 pm V^{-1} at 633 nm by the transmission technique. The dielectric constant ε of it at 100 kHz under room temperature was determined to be 7.32. The figure of merit $F_2 = n^7\gamma^2/\varepsilon$ was estimated to be 492. In addition, a relaxation process was observed in the time range of 28 days and the relaxation time constant was calculated to be 2393 min.

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References

1. S. R. MARDER, B. KIPPELEN, A. K. Y. JEN and N. PEYGHAMBARIAN, *Nature* **388** (1997) 845.
2. A. CHEN, V. CHUYANOV, S. GARNER, H. ZHANG, W. H. STEIER, J. CHEN, J. ZHU, F. WANG, M. HE, S. S. H. MAO and L. R. DALTON, *Opt. Lett.* **23** (1998) 478.
3. M. D. FONTANA, F. ABDI and K. WOJCIK, *J. Appl. Phys.* **77** (1995) 2102.
4. T. L. CHEN, Y. G. YUAN and J. P. XU, *Chinese J. Appl. Chem.* **5** (1988) 52.
5. F. KAJZAR and J. D. SWALENS, "Organic Thin Films for Waveguiding Nonlinear Optics" (Gordon and Breach Science Publishers, Amsterdam, Netherlands, 1996).
6. K. IIJIMA, Y. TOMITA, R. TAKAYAMA and I. UEDA, *J. Appl. Phys.* **60** (1986) 361.
7. C. C. TENG and H. T. MAN, *Appl. Phys. Lett.* **56** (1990) 1734.
8. Q. REN, D. XU, Y. T. CHOW, Z. H. LV, C. B. MA, G. H. ZHANG, H. P. CHAN and P. L. CHU, *Appl. Phys.* A **76** (2003) 183.
9. Y. SHUTO and M. AMANO, *J. Appl. Phys.* **77** (1995) 4632.

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