Poling and properties of nano-composite thin film PT/PEK-C

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The composite thin films of PT nanometer particles and high transparent polymer PEK-C were prepared. The poling conditions that PT particles in composites are aligned under external electric field was optimized through the dielectric properties of PT and PEK-C polymer and effective field intensity theory. Through the X-ray diffraction of poled composite thin film, it was obtained that the c axis orientation ratio η of nano-crystal $PbTiO_3$ was calculated to be 68%. The transparency spectra in the range 380–900 nm was measured. The optical band-gaps of poled and unpoled composite thin films were estimated to be 3.14 and 3.06 eV, respectively. © *1999 Kluwer Academic Publishers*

1. Introduction

Composite materials have a wide range of applications because of their improved properties over individual constituents. Ceramic/polymer composites, for example, PT and PZT ceramic composites with organic polymer have been improved to have advanced pyroelectric and piezoelectric properties [1–3]. In recent years, considerable interest has been shown in the preparation and properties of nano-particles with high electro-optic properties and their composites with organic polymer [4–13]. But the orientations of nanometer particles as active particles in composites are arbitrary before poling. So the composites are isotropic and possess a center of symmetry now. In order to has pyroelectric, piezoelectric and electro-optic properties, composites must consist of active particles oriented in such a way that the total systems are noncentrosymmetry. So poling process that makes active particles to be aligned is necessary for this kind of composites. After poling the symmetry of the composite thin films can be regarded as ∞ mm [14]. Because the dielectric constants of inorganic nano-particles are much larger than that of organic polymer, the poling that makes inorganic nano-particles to be aligned always difficult. In this literature, the poling condition of PT/PEK-C nano-composite thin films that we prepared was optimized through the dielectric properties of PT and PEK-C polymer and effective field theory by using COPET (corona-onset poling at elevated temperature). Then the c axis orientation ratio of PT particles in composites was calculated by measuring XRD of composite thin films. The optical band-gap energy of poled and unpoled nano-composite thin films was estimated.

2. Experiments and results
2.1. Preparation of PT nano-particles

PT ultrafine powder were prepared by Sol-Gel method [15]. Firstly, the precursor solution for PT nano-particles was prepared. Hydrate lead acetate $(Pb(OAc)_2 \cdot 3H_2O)$ was dissolved in ethoxyethanol at about 80 °C under stirring. The water associated with lead acetate was eliminated by heating to about 130 °C, and then sloichiometric titanium n-butoxside $(Ti(OC_4H_9)_4)$ was added to the solution. After refluxing the solution for 0.5 h, the resultant butoxylacetate was eliminated and PT precursor solution was obtained. Then water dissolved in ethoxyethnol was added to the solution under stirring. With increasing turbidity, the precipitation was washed with water and acetone three times, filtered and then dried at 80 °C for 24 h. The dried powders were fired at 600 °C. Ultrafine particles of PT in pure pervoskite structure were obtained, for the XRD pattern (Fig. 1a) is same as that given in the Powder Diffraction File 6-0452. Fig. 2 is the TEM photographs of PT ultrafine particles that the size of PT particles is 40–80 nm, and the shapes of most PT particles are spheroid or ellipsoid.

2.2. Preparation of PT/PEK-C thin films

The PT/PEK-C composite thin films were prepared by spin coating method, chloroform was used as solvent. The volume ratio of PT in PT/PEK-C composites is about 0.018. The concentration of the fluid used to spin coating is 10 wt %. The rate of spin coating is about 2000 r/m. Thickness of prepared thin film was measured to be 2.33 μm by quasi-waveguide method [16].

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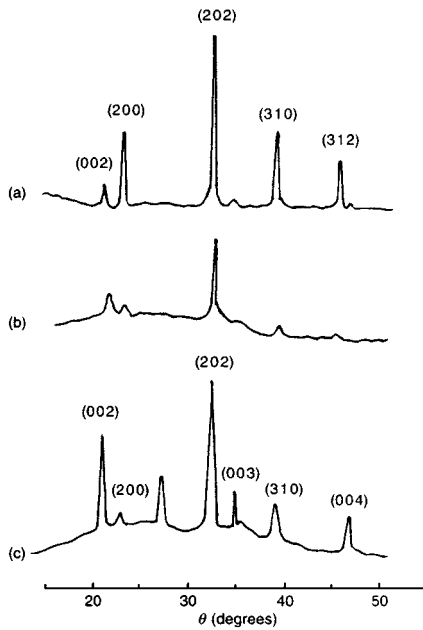
Figure 1 XRD patterns. (a) PT ultrafine particles. (b) unpoled PT/PEK-C thin film: (c) poled PT/PEK-C thin film.
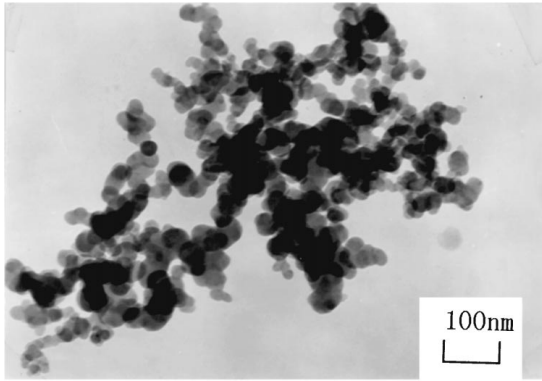

Figure 2 The TEM of PT nano-particles.

2.3. Poling

COPET can produce high voltage on the surfaces of the thin films, then results in high electric field intensity in thin films [17]. But the difference of dielectric constants between PT and PEK-C polymer is very large. It's necessary that make the effective electric field inten-

sity high that acts on the PT particles in the composite thin films. Fig. 3 shows the temperature dependence of dielectric constants of compacted sample of PT ultrafine particles (Fig. 3a) and PEK-C polymer (Fig. 3b). Impendence analyser 4192A was used to measure dielectric constants ($f = 10$ KHz). It's obvious that in the temperature range of 0–250 °C, the ranges of dielectric constants of PT and PEK-C are about 90–120 and 4–10, respectively. The relative increasing of dielectric constants of PT in the temperature range is smaller than that of PEK-C. Particularly, dielectric constants of PEK-C increase very fast near glass-transition temperature T_g. The concentration of PT ultrafine particles in composite thin films is low, and the shapes of PT nano-particles are spheroid or ellipsoid (see Fig. 2). By Fura Kara effective field theory [18], under external electric poling field E_p, the effective electric field intensity E that acts on isolated spherical particles in composite materials can be written as:

$$\frac{E}{E_p} = \frac{2\varepsilon_1}{[2\varepsilon_1 + \varepsilon_2 + \phi(\varepsilon_1 - \varepsilon_2)]} \quad (1)$$

Where ε_1 and ε_2 are dielectric constant of PEK-C and PT, respectively. ϕ is the volume ratio of PT. By the value range of ε_1 and ε_2 in the temperature range of 0–250 °C and formula (1), the 3D figure that shows the relationships of E/E_p vs ε_1 and ε_2 can be obtained as Fig. 4. We can see that E/E_p decreases when ε_2 increases. For the increasing of ε_2 is slow in the temperature range, the effect of ε_2 on E/E_p is small. Conversely, E/E_p increases when ε_1 increases. Furthermore, ε_1 increases fast near T_g, and E/E_p increases fast also near T_g. So the temperature of COPET should be near T_g according effective field theory. From Fig. 3b, T_g of PT/PEK-C composite thin film is about 200 °C, because of plasticization. Plasticization should be considered when to determine the poling temperature of the nano-composite thin films. Besides the viscosity of polymer descends, and the alignment of PT ultrafine particles is easy at high temperature. But the conductivity of PT/PEK-C composite thin films increases fast when temperature increases at high temperature, i.e. the thin films are broken down easily at high temperature. In a word, so as to optimize the poling temperature,
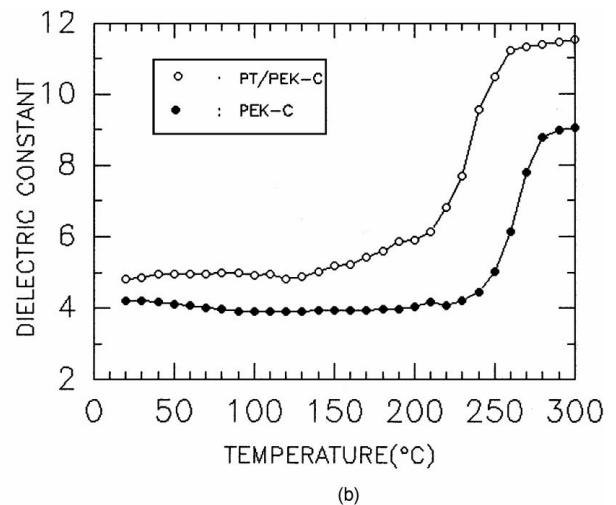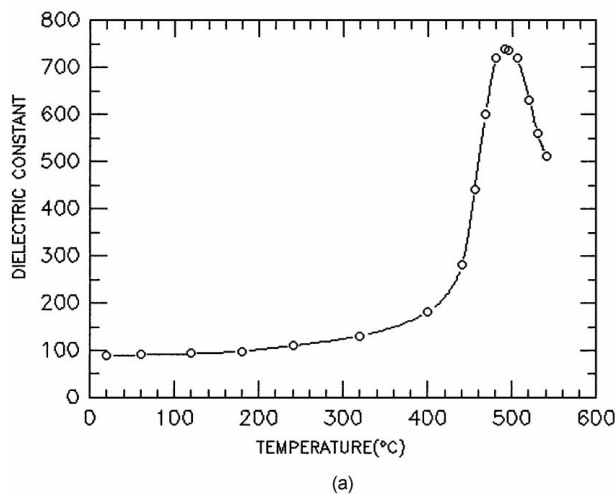

(a)

(b)

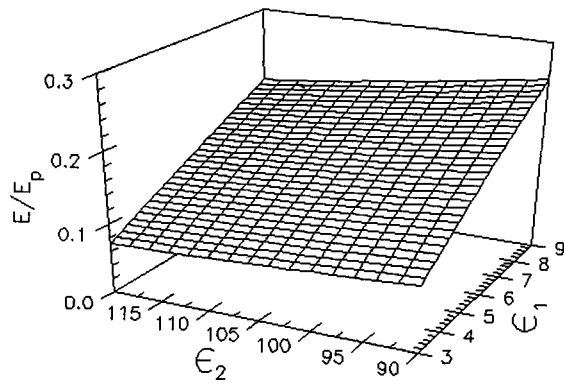*Figure 3* Temperature dependence of dielectric constant. (a) PbTiO$_3$, (b) PEK-C and PT/PEK-C.

Figure 4 The dependence of E/E_p on dielectric constant ε_1 and ε_2.

Figure 5 Transmission spectra of PT/PEK-C thin film. (a) unpoled; (b) poled.

all above factors should be considered. Our optimum poling conditions according to above factors are that poling temperature, poling voltage and poling current are about 200 °C, 6 kV and 5 μA, respectively.

2.4. XRD spectra of composite thin films
The microstructure of composite thin films before and after poling was analyzed by XRD spectra, using $CuK_{\alpha 1}$ ($\lambda = 0.15406$ nm) radiation operated at 40 kV and 20 mA. Fig. 1b, c shows the XRD patterns of unpoled and poled PT/PEK-C composite thin films. In Fig. 1c, not only is the peak of (0 0 2) stronger and sharper, but peaks of (0 0 3) and (0 0 4) also appeared, showing that poled composite thin film is c axis-orientated. The c axis orientation ratio η of PT particles can be written as [10]:

$$\eta = \frac{I(0\,0\,2)}{[I(0\,0\,2) + I(2\,0\,0)]} \quad (2)$$

Where $I(0\,0\,2)$ and $I(2\,0\,0)$ are the XRD intensities of the $I(0\,0\,2)$ and $I(2\,0\,0)$ net planes, respectively. The ratio η of the poled thin film was calculated to be 68%.

2.5. Transmission spectra
The transmittances of the unpoled and poled films were measured by means of a recording spectrometer (Shimadu UV-3000) (Fig. 5). The poled film shows high transparency in the range 380–900 nm, and the greatest transmittance in this range is 91.6%. The absorption edge of the poled film shifts to longer wavelength. The absorption coefficient α of poled and unpoled film near the absorption edge can be calculated directly from the pots of transmittance T against wavelength using the following relation [19]:

$$\alpha = \frac{1}{d} \ln\left(\frac{1}{T}\right) \quad (3)$$

Where $d = 2.33$ μm. Then using the relationship between the optical band-gap E_g, the absorption coefficient α and the energy of the incident photon $h\nu$ [20]:

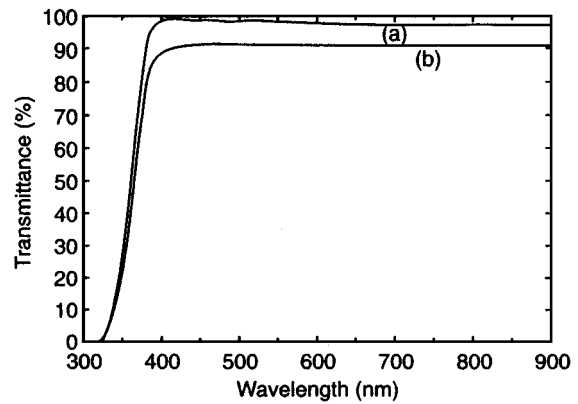$$(\alpha h\nu)^{\frac{1}{2}} \propto (h\nu - E_g) \quad (4)$$

By using intercept method, optical band-gaps of unpoled and poled films can be obtained to be 3.14 and 3.06 eV, respectively. It shows that the optical band-gap E_g depends mainly on the states of the orientations of PT particles in the composite thin films. The alignment makes the optical band-gap E_g decrease by 0.08 eV.

3. Conclusions
Using PT ultrafine particles and high transparent polymer PEK-C, nano-composite thin films were prepared. By the dielectric properties of PT compacted sample and PEK-C polymer, the COPET condition was optimized through using Fura Kara effective field theory. The c axis orientation ratio of PT particles in poled nano-composite thin films is 68%. The optical band-gap E_g decreases by 0.08 eV after poling.

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