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Optical constants of the nano-crystal and polymer composite thin film $PbTiO_3$/PEK-c

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Composite thin films of $PbTiO_3$ nano-crystals and high transparency PEK-c polymer were prepared by spin coating. The size of $PbTiO_3$ nanocrystals was evaluated to be 30–40 nm. The transparency spectra of PEK-c composite thin film in 360–800 nm were measured. The optical constants *n*, *k* of the film in the wavelength range 400–620 nm were investigated by the transmission spectrum. The dispersion of refractive index fits well to a three-term Sellmeier relation. At 633 nm wavelength the refractive index of $PbTiO_3$/PEK-c film was measured to be 1.6628 by a prism coupling method and showed a good agreement with the calculated value using the Sellmeier relation.

1. Introduction

In recent years, the rapid development of optical communication and optical computation has brought about the development of the materials and devices for both photonics and photoelectronics. Glassy polymers doped with the electro-optic active units have significant nonlinear optical effect after poling by an electric field. They have great potential for waveguide applications in integrated optics and photoelectronics [1].

Lead titanate ($PbTiO_3$) is a perovskite-type ferroeletric material. It has a high spontaneous polarization Ps (750 mC/m^2) and a small relative dielectric constant ε_r ($\sim$100). It also has high electro-optic coefficients. However, synthesis of large, perfect, and pure $PbTiO_3$ single crystals is very difficult [2]. In our research, $PbTiO_3$ nano-crystals were used as the nonlinear chromophores. The transparent polymer polyetherketone (PEK-c), which possesses a very high glass transition temperature and a low intrinsic dielectric coefficient, was selected as polymer host. By way of composition of the nano-crystals and polymer, it is hopeful to improve the stability of the electro-optic polymer materials and obtain materials with a high electro-optic figure of merit. A new high quality $PbTiO_3$/PEK-c thin film was prepared by spin coating technology.

Because the optical constants of a composite film and their dispersion are important design parameters in fabrication of an optical coating, we measured the refractive index of the $PbTiO_3$/PEK-c composite film at 632.8 nm using the Metricon 2010 prism coupler with rutile prism and the transmission spectrum of it using a UV-VIS-NIR spectrophotometer. In this article, the composite refractive index n_c of $PbTiO_3$/PEK-c polymer film has been studied in the wavelength range (400–620 nm) by measuring the transmittance of the film. A calculation based on the method described in [3] was performed for deducing optical constants at different wavelengths.

2. Experiments and results

2.1. Preparation of $PbTiO_3$ nano-crystals

Nanocrystalline $PbTiO_3$ has been synthesized by the chemical solution decomposition (CSD) technique. Firstly lead acetate trihydrate $[Pb(CH_3COO)_2 \cdot H_2O]$ was dissolved in 2-methoxyethanol. Then titanium

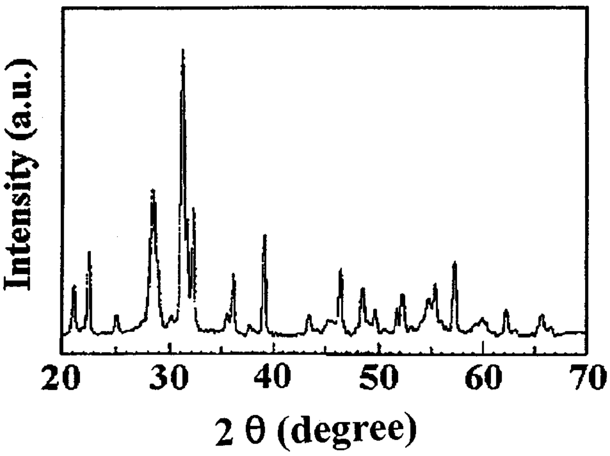

Figure 1 XRD pattern of $PbTiO_3$ nano-crystals.

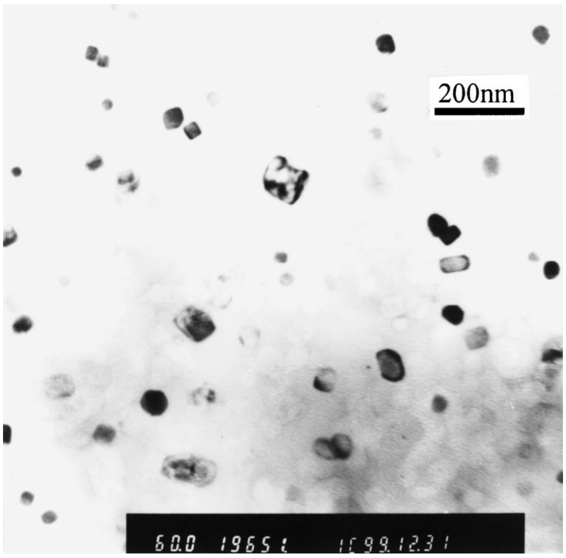

Figure 2 The TEM photograph of $PbTiO_3$ nano-crystals.

butoxide [$Ti(OC_4H_9)_4$] was added into the solution to form the $PbTiO_3$ precursor solution under stirring. The mole ratio of Pb and Ti was selected to be 110 : 100. The solution was baked to vaporize the solvent, leaving $PbTiO_3$ ultrafine precursor powder. Finally the dried powder was processed by rapid thermal annealing (RTA) at 700°C for 60 s and transformed into nanocrystalline $PbTiO_3$.

The crystal structure of the microcrystals was identified by XRD with Cu $K_{\alpha 1}$ ($\lambda = 0.15406$ nm) radiation operated at 40 kV and 20 mA. Fig. 1 shows the XRD pattern of $PbTiO_3$ powder. It conforms to the standard XRD pattern of $PbTiO_3$. The size of $PbTiO_3$ microcrystals was evaluated by transmission electron microscopy (TEM: H-800 Hitachi). Fig. 2 is the TEM photograph of $PbTiO_3$ microcrystals. The size of the $PbTiO_3$ microcrystals is about 30–40 nm.

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

The $PbTiO_3$/PEK-c composite films were prepared by spin coating. The weight ratio of $PbTiO_3$ microcrystals to the polymer PEK-c is 20%. After the polymer was dissolved into chloroform, $PbTiO_3$ was put into the solution, and the mixture was blended quite well using ultrasonic vibration. After the $PbTiO_3$ was dispersed, the solution was directly deposited on a 1.06-mm-thick K18 glass substrate by spin coating at 2000 rpm for 40 s. Finally the film was put in a baking oven at 80°C for 30 min to remove residual solvent.

2.3. Measurement and calculation of optical constants

The optical properties of a material may be represented by the refractive index n and the extinction coefficient k which are the real and imaginary parts of the complex refractive index $n_c = n - ik$ respectively. The refractive index n at 632.8 nm was measured firstly using a Metricon 2010 prism coupler with rutile prism. The measured value of the refractive index was 1.6628. The thickness value was obtained simultaneously, as 1.22 μm. Although the method possesses fine precision, only the refractive index of the film at 632.8 nm was measured. The measurement of the transmission spectrum of light through a thin absorbing film on a transparent substrate is sufficient to determine the real and imaginary parts of the complex refractive index, as well as the absorption coefficient α of the film. The method is used to determine $n(\lambda)$ and $\alpha(\lambda)$ from the interference fringes of the transmission spectrum alone, provided the film sample is homogeneous and parallel-faced, the thickness d of the film is about a few microns. The effective bandwidth of the spectrophotometer is kept smaller than the half-width of the interference maximum. So an interference fringe pattern appears on the transmission spectrum of the thin film. The accuracy of the method is of the order of 1% [3].

A UV-VIS-NIR spectrophotometer (Lambda 19) was used for measuring the transmission spectrum of the film. The variation in transmittance T of $PbTiO_3$/PEK-c film with wavelength is shown in Fig. 3.

We consider the extreme values of the transmission spectrum as the continuous functions of wavelength λ, corresponding to the envelopes of the maxima and the minima in the transmission spectrum. For a fixed wavelength, functions $T_{max}(\lambda)$ and $T_{min}(\lambda)$ give us the values of T_{max} and T_{min}. Then the refractive index of a film can be calculated by

$$n = \left[N + \left(N^2 - n_0^2 n_1^2\right)^{1/2}\right]^{1/2} \qquad (1)$$

where

$$N = \frac{n_0^2 + n_1^2}{2} + 2n_0 n_1 \frac{T_{max} - T_{min}}{T_{max} T_{min}}$$

where n_0 denotes the refractive index of air and n_1 denotes the refractive index of the transparent substrate at a given wavelength respectively. The variation in the refractive index n_1 with wavelength for the transparent substrate is shown in Fig. 4.

Equation 1 shows that n at a given wavelength is explicitly determined from T_{max}, T_{min}, n_0 and n_1 at the same wavelength.

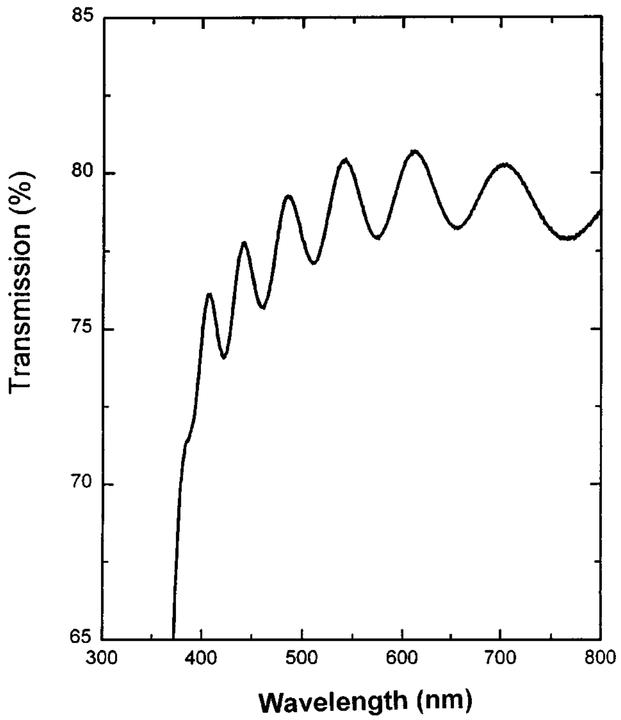

Figure 3 Variation in transmission with wavelength for $PbTiO_3$/PEK-c film.

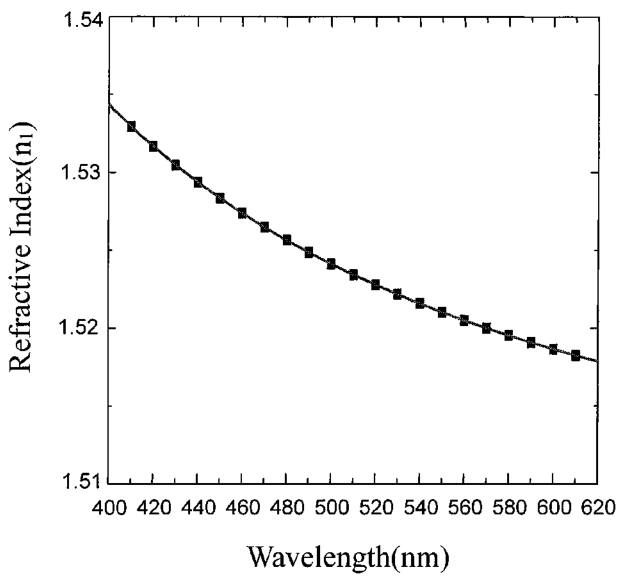

Figure 4 Variation in refractive index n_1 with wavelength for substrate.

The thickness d of a thin film can be calculated using the following equation:

$$d = \frac{M\lambda_1\lambda_2}{2[n(\lambda_1)\lambda_2 - n(\lambda_2)\lambda_1]} \tag{2}$$

where M is the number of oscillations between the two extrema; λ_1, $n(\lambda_1)$ and λ_2, $n(\lambda_2)$ are the corresponding wavelengths and indices of refraction. Knowing n and d, the absorption coefficient α of a thin film is calculated by the formula

$$\alpha = -\frac{1}{d}\, InK \tag{3}$$

where

$$K = \frac{(n+1)(n_1+n)\left[1-(T_{\max}/T_{\min})^{1/2}\right]}{(n-1)(n_1-n)\left[1+(T_{\max}/T_{\min})^{1/2}\right]}$$

The extinction coefficient k of a thin film is given by

$$k = \frac{\lambda}{4\pi}\alpha \tag{4}$$

Knowing n and k, we are able to calculate the real and imaginary parts of the complex dielectric constant, ε_r and ε'', using the equations:

$$\varepsilon_r = n^2 - k^2 \tag{5}$$

$$\varepsilon'' = 2nk \tag{6}$$

The loss factor $\tan\delta$ is given by

$$\tan\delta = \frac{\varepsilon''}{\varepsilon_r} \tag{7}$$

We have calculated the refractive index n of the film at different wavelengths using Equation 1. The spectral dependence of the refractive index n for $PbTiO_3$/PEK-c film is shown in Fig. 5. The value of the refractive index n decreases with increasing wavelength. The dispersion of the refractive index for the $PbTiO_3$/PEK-c film was fitted to the three-term Sellmeier dispersion formula [4]

$$n = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} \tag{8}$$

where λ is in microns, A, B and C are the Sellmeier's coefficients, and A is 1.68438, B is -0.01678, C is 0.003. At 633 nm wavelength the refractive index of $PbTiO_3$/PEK-c film was calculated to be 1.6612 using the Sellmeier relation. The thickness d of the thin film is calculated using Equation 2.

The obtained value of d is 1.28 μm. The value of the refractive index n at 632.8 nm and the thickness d are

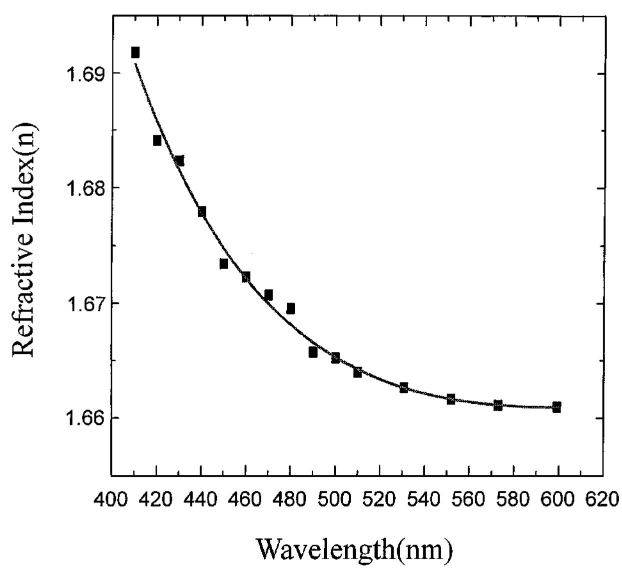

Figure 5 Variation in refractive index n with wavelength for $PbTiO_3$/PEK-c film.

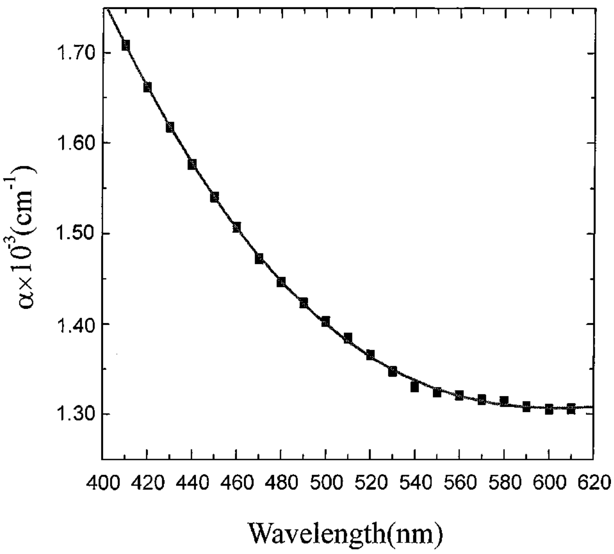

Figure 6 Absorption coefficient α against wavelength for $PbTiO_3$/PEK-c film.

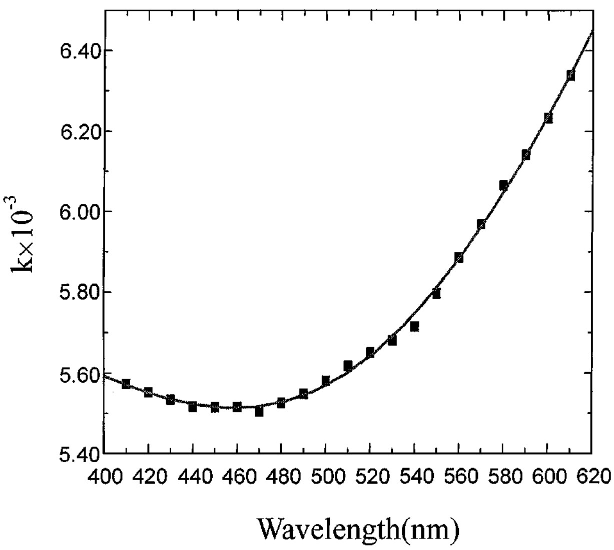

Figure 7 Variation in extinction coefficient k with wavelength for $PbTiO_3$/PEK-c film.

consistent with the result of measuring by the Metricon 2010 prism coupler.

The absorption coefficient α and the extinction coefficient k of the film are calculated using Equations 3 and 4 respectively. Figs 6 and 7 show the plots of α and k against wavelength for PT/PEK-c film. It is clear from Fig. 6 that the values of the absorption coefficient α for PT/PEK-c film are of the order of 10^3 cm^{-1}, that is the film is weakly absorbing.

The calculation of the real part ε_r and imaginary part ε'' of the complex relative dielectric constant of the thin film has also been made using (5) and (6). The variations in these two parameters with wavelength are shown in Figs 8 and 9.

From these figures, we can see that the real part ε_r of the dielectric constant decreases with increasing wavelength. The loss factor $\tan\delta$ of $PbTiO_3$/PEK-c film has been calculated using Equation 7 from the values of ε_r and ε'' obtained above. The variation in the loss factor $\tan\delta$ with wavelength is shown in Fig. 10.

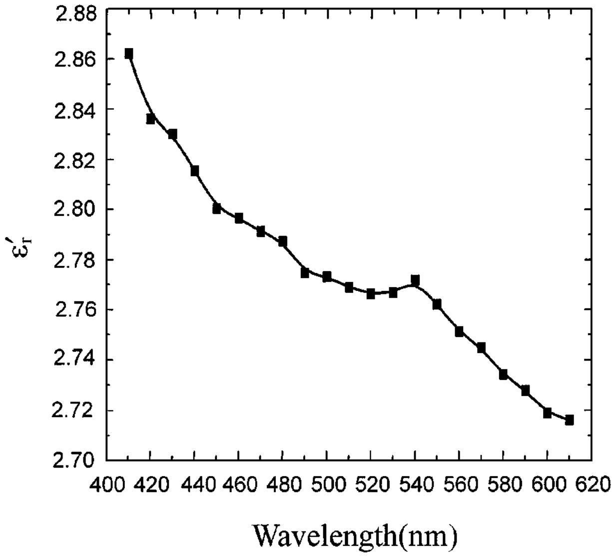

Figure 8 Real part ε_r' of the dielectric constant as a function of wavelength for $PbTiO_3$/PEK-c film.

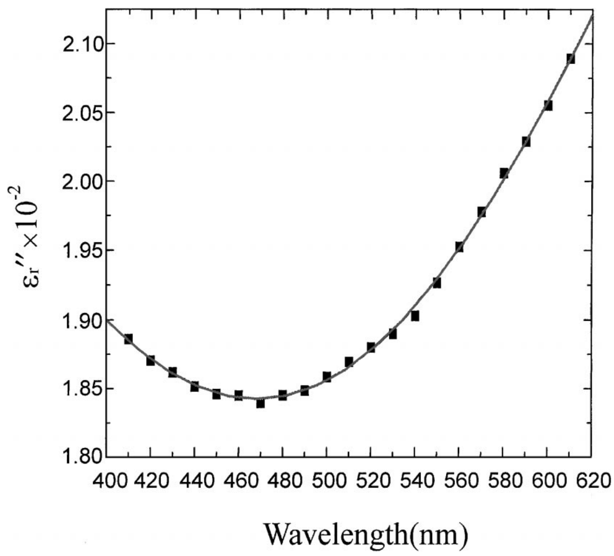

Figure 9 Imaginary part ε'' of the dielectric constant as a function of wavelength for $PbTiO_3$/PEK-c film.

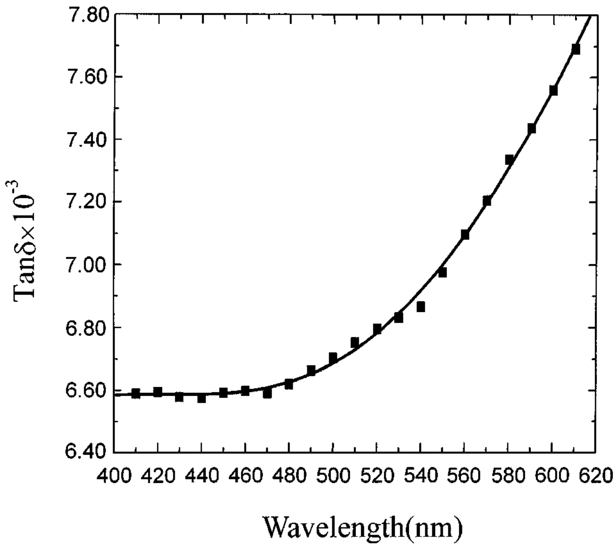

Figure 10 Variation in loss factor $\tan\delta$ with wavelength for $PbTiO_3$/PEK-c film.

3. Conclusions

In conclusion, the composite thin films of $PbTiO_3$ nanocrystals and high transparency polymer PEK-c were prepared. The size of $PbTiO_3$ microcrystals was evaluated to be 30–40 nm by transmission electron microscopy. The new $PbTiO_3$/PEK-c polymer thin film is homogeneous and parallel-faced and shows good transparency. The transparency spectra in the range from 360 nm to 800 nm were measured. The greatest transmittance in this range is 80.7%. Because the value of T can be acquired to three significant figures, so the values of n, k, α, ε_r, ε'' and $\tan\delta$ are expressed to three significant figures also. It is demonstrated in our work that the very simple way of calculating the optical constants and their dispersion, is valid in the case of a weakly absorbing film surrounded by non-absorbing media.

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