In-situ Transmittance Measurement of Polarization and Dielectric Relaxation Behaviors of LiNbO3 Ferroelectric Nanocrystal in Polycarbonate Matrix

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ABSTRACT

LiNbO$_3$/polycarbonate (LNO/PC) composite films with different concentration of LiNbO$_3$ ferroelectric nanocrystals are prepared by spin coating method. The polarization and dielectric relaxation behaviors of LNO/PC composite films are characterized through in-situ transmission spectrum measurement. The LiNbO$_3$ ferroelectric nanocrystals are prepared by hydrothermal method with rhombohedral structure and the average crystal size is about 50 nm. It’s found that 15%LNO/PC composite film has the largest orientation change with the $\phi$ value of 62% and slow dielectric relaxation, almost no decay after 6 h. Based on the literatures, we can proposed that the preferential orientation of LiNbO$_3$ nanocrystals after poling is [001] direction. This suggests that in-situ transmittance measurement is a simple and effect way to evaluate the polarization and dielectric relaxation behaviors of ferroelectric nanocrystals/polymer systems.

INTRODUCTION

LiNbO$_3$ (LNO), one of the well known ferroelectric materials, has wide technological applications due to its outstanding physical properties, such as high piezoelectricity, pyroelectricity, acousto-optic and electro-optics coefficients [1]. Among these properties, the electro-optic effect of LNO is extremely eminent and has been used in optics like intense transient electric field sensor [2], waveguide [3] and electro-optic modulator [4]. LiNbO$_3$ crystals exhibits high stability and large electro-optic coefficients of $\gamma_{33} = 30.9\times10^{-12}$ m/v and $\gamma_{13} = 8.6\times10^{-12}$ m/v [5]. However, the synthesis of large, perfect LiNbO$_3$ crystals is very difficult and expensive. The research of preparation of nanocrystals and organic polymer
composites provides another choice, which combined both the merits of ferroelectric crystals and polymers.

Many ferroelectrics such as BaTiO$_3$ (BT), Pb(Zr,Ti)$_3$O$_3$ (PZT) and LiNbO$_3$ (LNO) have been investigated for the potential optical applications due to their high nonlinear optical (NLO) and electro-optic (EO) coefficients [6]. At the same time, optical organic polymers have been widely used due to their advantages like ease of processing, quick response, low dielectric constant and high transparency [7]. So many ferroelectric nanocrystal/polymer composite films based on EO effect emerge, including LiNbO$_3$ ferroelectric crystal/polymer systems. LiNbO$_3$ nanocrystal/polymer systems have been investigated for different applications such as LiNbO$_3$/poly(N-vinylcarbazole) [8,9], LiNbO$_3$/poly(vinylidene fluoride) [10] and LiNbO$_3$/poly(4-vinylpyridine) composites [11]. Whereas, there are fewer literatures focused on the dielectric relaxation behaviors and nanocrystal alignment of ferroelectric nanocrystals in polymer matrix.

Normally, the orientation of ferroelectric nanocrystals in polymer matrix is random before poling; an appropriate electric field is needed to induce the ferroelectric nanocrystals alignment in preferable directions so that exhibiting larger NLO and EO coefficients. Corona-onset poling at elevated temperature (COPET) is always used to pole the composite films with homogeneous electric field distribution [12]. In this paper, using polycarbonate (PC) as the host polymer material, different weight concentrations of LiNbO$_3$ ferroelectric crystals as fillers in composite films were fabricated. The polarization and dielectric relaxation behaviors of LiNbO$_3$ ferroelectric nanocrystal in polycarbonate matrix (LNO/PC) composite films were characterized through in-situ transmission spectra measurement. The preferential alignment orientation of LiNbO$_3$ ferroelectric nanocrystals after poling was proposed.

**EXPERIMENTAL PROCEDURE**

LiNbO$_3$ ferroelectric nanocrystals were prepared by a hydrothermal method, which is widely used to synthesis nanomaterials with advantages such as low temperature, environmental friendliness and homogenous particle size distribution. Lithium hydroxide monohydrate (LiOH·H$_2$O) and niobium oxide (Nb$_2$O$_5$) were selected as raw materials. LiOH-H$_2$O was first dissolved in 40 mL deionized water with stirring, and then Nb$_2$O$_5$ were added into the solution. The precursors were transferred into a 50 mL capacity Teflon-lined autoclave and heated at 250 °C for 8h. After cooling naturally, the product was washed by diluted hydrochloric acid and deionized water several times. Finally, the powders were dried at 60 °C and sintered at 500 °C for 2h in furnace to obtained LiNbO$_3$ ferroelectric nanocrystals.

The LNO/PC composite films were prepared by a spin-coating method. 1 g PC polymer was dissolved in 20 mL chloroform first, then different weight ratios of LiNbO$_3$ ferroelectric nanocrystals were sonicated and dispersed into the PC solution. The weight ratios of LiNbO$_3$ to PC were 0, 5%, 10%, 15% and 20%, respectively. These suspension solutions were deposited on commercial ITO glass substrates by the spin-coating method at 2500 rpm for 20 s. After each coating, the films were baked on hot plat at 60 °C for 10 min to remove the excessive solvent. The procedure was repeated several times to obtain thick films and baked at 60 °C for 2 h in air at last.
X-ray diffraction (XRD) patterns of LiNbO₃ nanocrystals and LNO/PC composite films were recorded on Rigaku-D/Max 2000 with Cu Kα radiation. The transmission electron microscopy (TEM, Tecnai F20 S-Twin) was used to characterize the size and morphology of LiNbO₃ nanocrystals. In-situ transmission measurement was carried out on a Shimadzu UV-3600 spectrometer, to evaluate the dielectric relaxation behaviors and band-gap of LNO/PC composite films by introducing orientational order parameter (\( \phi \)). Modified corona-onset poling apparatus was used to pole the composite films, as seen in Fig. 1. The composite films were put into a quartz chamber with real time temperature control. This device can effectively suppress the loss of heat and ensure that the temperature distribution is homogeneous and stable during the poling process, compared with the traditional poling apparatus.

RESULTS AND DISCUSSION

The XRD patterns of LiNbO₃ powders and LNO/PC composite films are shown in Fig. 2. It’s clearly seen that the LiNbO₃ nanocrystals prepared by hydrothermal method exhibit almost pure rhombohedral structure (JCPDS card 20-0631) in R3c (161) space group. Several typical peaks at \( 2\theta = 23.7^\circ, 32.7^\circ, 34.8^\circ \) and \( 53.3^\circ \) can be assigned to (012), (104), (110) and (116) planes, respectively. In order to show the nanocrystals in PC matrix clearly, the XRD patterns of 20% LNO/PC composite film is displayed in Fig. 2. Compared with powders, the main diffraction peaks of LiNbO₃ nanocrystals in PC matrix can be indentified clearly though the peak intensity decreases. The size and morphology of LiNbO₃ nanocrystals are characterized by TEM and shown in the inset of Fig. 2. The average size is about 50 nm with spheroid shapes.

Figure 1. Modified corona-onset poling apparatus used to pole the composite films.
Figure 2. XRD patterns of LiNbO$_3$ powders and 25%LNO/PC composite film. The inset is the TEM imagine of LiNbO$_3$ powders prepared by hydrothermal method.

The orientational order parameter ($\phi$) is widely used in the design and characterization of poled EO polymers, especially the guest-host polymers with chromophore [13,14]. For the dipolar molecules, the rearrangement after poling results in that the absorption of the polymers is less than that of the films before poling [15]. To estimate the orientational change of chromophores before and after poling, the orientational order parameter ($\phi$) can be described as follows:

$$\phi = 1 - \frac{A_\perp}{A_0}$$

(1)

where $A_0$ and $A_\perp$ are the absorption peaks of the film before and after poling [14]. The larger $\phi$ value always means stronger second order NLO effect. For the ferroelectric nanocrystal/polymer composite, there are fewer literatures to characterize the polarization behaviors using transmission measurement. So we introduce the orientational order parameter to describe the polarization and dielectric relaxation behaviors of ferroelectric nanocrystal/polymer composites. Different with the dipolar molecules, the arrangement of ferroelectric nanocrystals in polymer matrix poled by electrical field always results in the decrease of transmission, which means the equation (1) can be modified as follows:

$$\phi = 1 - \frac{T_\perp}{T_0}$$

(2)

where $T_0$ and $T_\perp$ are the transmission valleys of the film before and after poling.

To investigate the influence of LiNbO$_3$ nanocrystals concentration, the LNO/PC composite films with LiNbO$_3$ to PC weight ratios of 0, 5%, 10%, 15% and 20% are prepared and the orientational order parameters are calculate based on equation (2), as shown in Fig. 3. Different LNO/PC composite films have better transparency in the range of 300-800 nm, while the transmittance reduced after poling due to the rearrangement of LiNbO$_3$ nanocrystals, especially for the 15%LNO/PC composite films, with the transmission valley dropping from 87% to 33%. In Fig. 3, the $\phi$ firstly increases with the increase of LiNbO$_3$ nanocrystals concentration and
reaches to 62% in 15%LNO/PC composite film, then decreases with the further increase of LiNbO$_3$ nanocrystals concentration due to the aggregation of nanocrystals, which results in the difficulty to align the nanocrystals under external electric field. The 15%LNO/PC composite film has the largest orientation change after poling, which means the best second order NLO properties.

![Transmittance spectra of LNO/PC composite films before and after poling; and the dependence of LNO concentration on orientational order parameter ($\phi$), calculated based on equation (2).](image)

**Figure 3.** Transmittance spectra of LNO/PC composite films before and after poling; and the dependence of LNO concentration on orientational order parameter ($\phi$), calculated based on equation (2).

To evaluate the stability of LiNbO$_3$ nanocrystals in PC matrix after poling, the dielectric relaxation behaviors of 15% LNO/PC composite film are investigated via in-situ transmittance measurement. Fig. 4 displays the temporal dependence of orientational order parameter of 15%LNO/PC composite film at room temperature. It can be clearly seen that the $\phi$ value of 15%LNO/PC films has no obvious change by the time. That is to say, the LiNbO$_3$ nanocrystals align after poling and the orientation has no much change with time. Compared with the dipolar molecules doped in polymers, the poled ferroelectric nanocrystals in polymer matrix are stable after rearrangement and have slower dielectric relaxation [16]. So LNO/PC composite films are promising candidate for the applications in optics.
Figure 4. The temporal dependence of transmittance spectra and orientational order parameter (inset) of 15%LNO/PC composite film after poling at room temperature.

Through the transmittance measurement, we know that the LiNbO$_3$ ferroelectric nanocrystals align after poling, while the preferential orientation of LiNbO$_3$ nanocrystals is not very clear. For ferroelectric nanocrystals/polymer system, the nanocrystals will be aligned to the most stable state with lowest energy under external electric field [17]. For LiNbO$_3$ nanocrystals, the spontaneous polarization pointing is along [001] direction, which means it’s the most susceptible direction under external electric field [18]. Based on the literatures, we can proposed that the preferential orientation of LiNbO$_3$ nanocrystals under electric field is [001] direction [19, 20]. More convincing results should be obtained in further research studies to illustrate the orientation of LiNbO$_3$ ferroelectric nanocrystals after poling.

CONCLUSIONS

LiNbO$_3$/polycarbonate (LNO/PC) composite films with different concentration of LiNbO$_3$ ferroelectric nanocrystals are prepared by spin coating method. The polarization and dielectric relaxation behaviors of LNO/PC composite films are characterized through in-situ transmission spectrum measurement. The LiNbO$_3$ ferroelectric nanocrystals are prepared by hydrothermal method with rhombohedral structure and the average crystal size is about 50 nm. It’s found that 15%LNO/PC composite film has the largest orientation change with the $\phi$ value of 62% and slow dielectric relaxation, almost no decay after 6 h. Based on the literatures, we can proposed that the preferential orientation of LiNbO$_3$ nanocrystals after poling is [001] direction. This suggests that in-situ transmittance measurement is a simple and effect way to evaluate the polarization and dielectric relaxation behaviors of ferroelectric nanocrystals/polymer systems.

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