Optical interband transitions in relaxor-based ferroelectric 0.93Pb(Zn_{1/3}Nb_{2/3})O₃–0.07PbTiO₃ single crystal

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The optical transmission spectrum of $[111]_c$ poled relaxor-based ferroelectric single crystal 0.93Pb(Zn_{1/3}Nb_{2/3})O₃–0.07PbTiO₃ (PZN–0.07PT) was measured in the range of ultraviolet to near infrared. The optical absorption edge has been determined and the wavelength dependence of the absorption coefficient was calculated. The direct energy gap $E_{gd}=3.144$ eV, indirect energy gap $E_{gi}=2.915$ eV, and phonon energy $E_p=0.097$ eV (or 782 cm^{−1}) were determined based on the theory of band to band transitions. It was also confirmed by Raman spectra that the indirect transition for the $[111]_c$ poled PZN–0.07PT single crystal is mainly due to the contribution of 780 cm^{−1} phonon corresponding to the Nb–O–Zn bond stretching mode. © 2010 American Institute of Physics. [doi:10.1063/1.3446293]

I. INTRODUCTION

Relaxor-based ferroelectric single crystal $(1-x)\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$ (PZN– x PT) is a solid solution of relaxor ferroelectric $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PZN) and normal ferroelectric PbTiO_3 (PT).¹ The PZN– x PT single crystals near the rhombohedral-tetragonal morphotropic phase boundary (MPB, $x \approx 0.09$) possess superior dielectric and piezoelectric constants, very high electromechanical coupling factor,^{2,3} and large linear electro-optic coefficients.^{4,5} Recently, PZN–(6–7)%PT single crystals, which is slightly away from MPB have been found to exhibit the best compositional uniformity⁶ and a stable single domain state can be achieved when being poled along the $[111]_c$ direction.⁷ This $[111]_c$ poled single domain PZN–0.07PT single crystal is transparent and could be used for a variety of linear and nonlinear optical applications.

The electronic transitions during the optical absorption process are of great interest, not only for their possible applications in optic devices but also to answer some basic physics questions on the energy levels of ferroelectrics. In this work, we have carried out a systematic study on the optical interband transitions of $[111]_c$ poled PZN–0.07PT single domain single crystal. The band gaps were determined for both direct and indirect transitions by optical transmittance and Raman spectra.

II. EXPERIMENTAL PROCEDURE

High-quality PZN–0.07PT single crystal sample used in this work for the optical transmittance and Raman spectra measurements was purchased from Microfine Materials Technologies P/L (Singapore). The crystal was grown by high temperature flux technique, then oriented and cut along the three main crystallographic directions $[1\bar{1}0]^T \times [11\bar{2}]^L \times [111]^W$ by the Laue back reflection method.^{6–8} The dimen-

sions of the sample are $1.0^T \times 5.0^L \times 2.0^W$ mm³. The sample was sputter-coated with Ni/Cr–Pd/Au electrodes on the $[111]_c$ and $[\bar{1}\bar{1}\bar{1}]_c$ surfaces and was poled in silicone oil at room temperature with an electric field of 4 kV/cm. The $[1\bar{1}0]$ faces of the sample were polished to optical quality in order to conduct optical measurements.

Optical transmission spectrum of the $[111]_c$ poled PZN–0.07PT single crystal was recorded at room temperature using an unpolarized light propagating along $[1\bar{1}0]$ and a UV-VIS-NIR spectrophotometer (SP-752PC). The transmission curve can be seen in Fig. 1. The wavelength range is from 200 to 1000 nm with 1 nm interval in order to accurately find out the optical absorption edge in near UV.

Raman spectroscopy has been proven a convenient method to study the phonon vibration characteristics of ferroelectrics.^{9,10} The polarized Raman spectra of the $[111]_c$ poled PZN–0.07PT single crystal in the wavenumber range of 70–1000 cm^{−1} were taken by a Jobin Yvon HR800 micro-Raman spectrometer using the 514.5 nm excitation line from an Ar ion laser (Spectra Physics Stabilite 2017), and the results are shown in Fig. 2. The beam spot size on the sample surface is about 1 μm using a long working-

FIG. 1. Transmission spectra of $[111]_c$ poled PZN–0.07PT single crystal at room temperature. The thickness of the sample is 1.0 mm.

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FIG. 2. (Color online) Polarized Raman spectra of $[111]_c$ poled PZN-0.07PT single crystal in VV and VH geometries at room temperature.

distance $\times 100$ objective lens. The Raman spectra were recorded in the backscattering geometry in both parallel (VV) and cross (VH) polarizations. In the parallel scattering geometry, polarizations of the incident and scattered light are all in the $[11\bar{2}]_c$ direction. In the cross scattering geometry, the polarization of the incident light is along $[11\bar{2}]_c$ while the scattered light is along $[111]_c$.

III. RESULTS AND DISCUSSIONS

Based on the optical transmission spectrum in Fig. 1, the crystal is nearly transparent in visible to near infrared region but becomes completely opaque at 390 nm, which is the optical absorption edge at near UV. Our results as well as some published results for other compositions demonstrated that the optical absorption edges of PZN- x PT have redshift with increasing PT contents, i.e., it is 380 nm, 390 nm, 400 nm, and slightly more than 400 nm for $x=0.45$,¹¹ 0.07 (this work), 0.09,¹² and 0.10,¹³ respectively. Similar phenomena have been found in the relaxor-based ferroelectric PMN- x PT single crystals¹⁴ and thin films.¹⁵ For the $A(B_1B_2)O_3$ -type perovskite compounds, the common $(B_1B_2)O_6$ oxygen-octahedral structure determines the basic energy levels in the crystal. Hence, PZN- x PT and PMN- x PT single crystals with different compositions should have similar optical absorption edges with slight differences due to the different B-site (including B_1 and B_2) cations.¹¹

The optical absorption coefficient α can be calculated from¹⁶

$$\alpha = -\frac{1}{L} \ln \frac{1 - (1 - R)^2 + \sqrt{(1 - R)^4 + 4R^2T^2}}{2R^2T}, \quad (1)$$

where T is the transmittance, R is the surface reflectivity, and L is the thickness of the sample.

For optical interband transitions, the absorption coefficient α is deemed to be zero in the near infrared range where T becomes a constant because of the very low photon energy. In this case, Eq. (1) reduces to $T = (1 - R)/(1 + R)$, and this offered a means to derive the value of R .

It is known that the optical interband transitions include the direct and indirect transitions. The optical band gaps can be estimated by the predominant mechanism of the band to

FIG. 3. (Color online) Variations in $(\alpha h\nu)^2$ and $(\alpha h\nu)^{1/2}$ vs photon energy $h\nu$ for $[111]_c$ poled PZN-0.07PT single crystal.

band transitions. In the allowed direct transition, the electrons in the valence band transit vertically to the conduction band only under the action of photons. The absorption coefficient as a function of photon energy in the allowed direct transition can be expressed as¹⁷

$$\alpha = \frac{A}{h\nu} (h\nu - E_{gd})^{1/2}, \quad (2)$$

where A is a constant, ν is the frequency, h is the Planck constant and E_{gd} is the allowed direct energy gap.

In the indirect transition, the electrons transit from the top of the valence band to the bottom of the conduction band with coparticipation of photons and suitable phonons. In this case, the absorption coefficient can be fitted to the following formula:¹⁸

$$\alpha = \frac{B}{h\nu} (h\nu - E_{gi} \pm E_p)^2, \quad (3)$$

where B is another constant, E_{gi} is the indirect energy gap, and E_p is the energy of the absorbed (+) or emitted (−) phonons.

The plot of the $(\alpha h\nu)^2$ versus $h\nu$ for the $[111]_c$ poled PZN-0.07PT single crystal in the photon energy range from 2.9 to 3.2 eV is shown in Fig. 3. The direct band gap energy was determined as $E_{gd} = 3.144$ eV by extrapolating the linear portion of the curve to zero. The dependence of $(\alpha h\nu)^{1/2}$ on $h\nu$, as shown in Fig. 3, exhibits three distinct linear segments. This is similar to the characteristics of the absorption edges of PMN- x PT single crystals and other perovskite ferroelectrics.¹⁹ The values of $E_{g1} = E_{gi} + E_p$ and $E_{g2} = E_{gi} - E_p$ were obtained to be $E_{g1} = 3.012$ eV and $E_{g2} = 2.817$ eV by extrapolating $(\alpha h\nu)^{1/2}$ versus $h\nu$ curves to zero. Therefore, the indirect energy gap and the phonon energy can also be determined as $E_{gi} = 1/2(E_{g1} + E_{g2}) = 2.915$ eV and $E_p = 1/2(E_{g1} - E_{g2}) = 0.097$ eV (or 782 cm^{-1}), respectively.

From the Raman spectra shown in Fig. 2, we observed that all Raman bands are broad, which is typical for perovskite relaxor ferroelectrics. The VV and VH Raman spectra show large difference. The Raman modes near 136, 270, 522, 600, and 780 cm^{-1} appear in the VV geometry but 96, 164, 270, 505, and 780 cm^{-1} Raman modes appear in the VH

geometry, which reflects the Raman selection rules. In addition, it can be seen that the intensity of phonon at 780 cm^{-1} in the VV geometry is very strong and its frequency is also the highest among all active phonons. More importantly, the phonon energy calculated from the transmittance spectra agrees perfectly with the value of the 780 cm^{-1} phonon in the Raman spectra. Thus, it is reasonable to believe that the indirect transition is mainly due to the contribution of the 780 cm^{-1} phonon, corresponding to the Nb–O–Zn bond stretching mode.^{10,20}

IV. CONCLUSIONS

The optical transmission spectra have been measured for the relaxor-based ferroelectric single crystal PZN–0.07PT polarized along $[111]_c$. The direct energy gap, indirect energy gap, and the photon energy have been determined based on the predominant mechanism of the band to band transitions. Based on the measured Raman spectra, the 780 cm^{-1} phonon, corresponding to the Nb–O–Zn bond stretching mode, plays the dominant role in the indirect transition in the PZN–0.07PT single crystal.

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