Large nonlinear optical response of polycrystalline $Bi_{3.25}La_{0.75}Ti_3O_{12}$ ferroelectric thin films on quartz substrates

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We measure the nonlinear susceptibility of $Bi_{3.25}La_{0.75}Ti_3O_{12}$ (BLT) thin films grown on quartz substrates using the Z-scan technique with picosecond laser pulses at a wavelength of 532 nm. The third-order nonlinear refractive index coefficient γ and absorption coefficient β of the BLT thin film are 3.1×10^{-10} cm^2/W and 3×10^{-5} cm/W, respectively, which are much larger than those of most ferroelectric films. The results show that the BLT thin films on quartz substrates are good candidate materials for applications in nonlinear optical devices. © 2007 Optical Society of America

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The use of ferroelectric films with large nonlinear optical properties has been of tremendous interest in the semiconductor and optics communities due to the films' numerous useful properties for applications such as ferroelectric random access memory devices, high-frequency tunable devices, integrated photonics, and nonlinear optical applications [1–4]. Over the past few years, the optical properties of ferroelectric thin films such as $Bi_2Nd_2Ti_3O_{12}$ (BNT), $Pb_{0.7}La_{0.3}TiO_3$, and $SrBi_2Ta_2O_9$ (SBT) have been widely studied [5–7]. In addition, large quadratic electro-optic coefficients in $Bi_4Ti_3O_{12}$ thin films on MgO and $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_{3-x}PbTiO_3$ superlattices were reported [8,9].

Several measurements using the Z-scan technique show that ferroelectric thin films have large nonlinear optical properties. Li *et al.* estimated the nonlinear refractive index n_2 of $LiNbO_3$:MgO as 2×10^{-15} cm^2/W [10]. Nonlinear response and optical limiting in SBT thin films were investigated [11]. Leng *et al.* reported that lanthanum-modified lead zirconate titanate thin films have a negative nonlinear refractive index n_2 of 2.3×10^{-19} cm^2/W [12]. Gu *et al.* measured the optical nonlinearities of BNT thin films having a two-photon absorption coefficient of 3.1×10^{-5} cm/W and a nonlinear refraction coefficient of 0.7×10^{-9} cm^2/W [5]. In addition, large nonlinear optical properties of $Ba_{0.7}Sr_{0.3}TiO_3$ were measured [13].

Another attractive ferroelectric thin film is $Bi_{3.25}La_{0.75}Ti_3O_{12}$ (BLT), which has excellent fatigue-free properties on metal electrodes [14], and its linear optical properties have been well investigated [15]. Shi *et al.* also reported a large third-order nonlinear susceptibility of BLT thin films measured at 800 nm with a femtosecond laser and stated that the third-order nonlinear absorption is caused by the saturated absorption [16].

In this Letter, the authors measure the nonlinear optical properties of BLT thin films on quartz substrates using the Z-scan technique with picosecond laser pulses at a wavelength of 532 nm. Although this material has been studied previously by Shi *et al.* [16], we obtain somewhat different results. According to [16], the pulse energy was 1.2 μJ, and its peak intensity was about 720 GW/cm^2, which could damage the material. In addition, the symmetric bell-shaped transmittance can be interpreted as not only saturated absorption but also material damage. However, our experiment is conducted under conditions especially chosen to avoid the results of laser damage, and our results show that the BLT thin films exhibit giant nonlinear properties. The large nonlinear coefficients show the possibility of using BLT thin films for various applications.

The thin films of $Bi_{3.25}La_{0.75}Ti_3O_{12}$ were grown using a solgel method on quartz substrates. Coating of the solution onto the substrate was performed by spin coating at 3000 rpm for 30 s. The coated layers were preheated on a hot plate at 400°C for 10 min to remove the solvent in air. After coating and preheating processes, the films were annealed at 800°C for 20 min in a furnace. These steps were repeated five times to obtain thick enough films. The x-ray diffraction pattern of the BLT thin film is shown in Fig. 1(a), and it shows that the as-grown BLT thin film has bismuth-layered perovskite structure. In addition, the pattern shows the (00*l*) reflection peaks as well as a (117) peak, indicating the phase of the film is well-formed and polycrystalline. As shown in Fig. 1(b), the surface was measured with an atomic force microscope, exhibiting that the roughness is about 17 nm and the grain size is about 200 nm.

The optical transmittance spectrum of the BLT thin film was measured at the wavelength of 320–1550 nm using a Perkin-Elmer UV/VIS Spec-

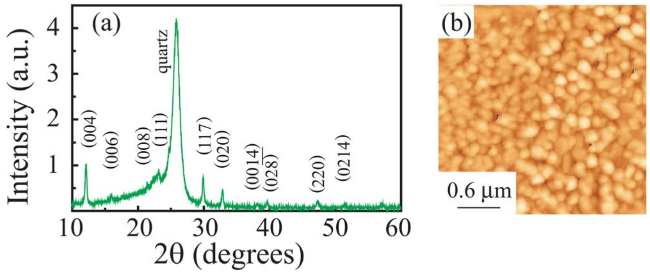

Fig. 1. (Color online) (a) X-ray diffraction pattern of the BLT thin film on a quartz substrate. (b) Atomic force microscope image of the BLT thin film pattern.

trometer Lambda 900, and the film thickness, the linear refractive index, and the absorption coefficient of the BLT thin film at 532 nm were measured to be $L = 0.495\ \mu$m, $n = 2.487$, and $\alpha = 2.46 \times 10^3$ 1/cm, respectively, using the envelope method proposed by Manifacier *et al.* [17]. Furthermore, assuming a direct transition between the valence and conduction bands, the optical bandgap energy of the BLT film was determined by [18]

$$(\alpha h\nu)^2 = C(h\nu - E_g), \tag{1}$$

where C is a constant and E_g is the optical bandgap energy. As shown in Fig. 2, the estimated value of the bandgap energy of the BLT thin film is 3.79 eV, corresponding to photon energy of 328 nm wavelength.

The nonlinear optical properties of the BLT thin films on quartz substrates were measured using a single-beam Z-scan technique. The light source was a mode-locked frequency-doubled Nd:YAG laser at 532 nm with a pulse duration of 35 ps and a repetition rate of 10 Hz. The laser beam was focused on the film by a lens of 30 cm focal length, and the incident intensity at the focal point is 0.19 GW/cm^2. The experimental system was calibrated using a reference sample CS_2.

The typical Z-scan result of the BLT thin film with the s-polarization for an open aperture is shown in Fig. 3, and the data are fitted using the equation for a thin sample of thickness L [19]:

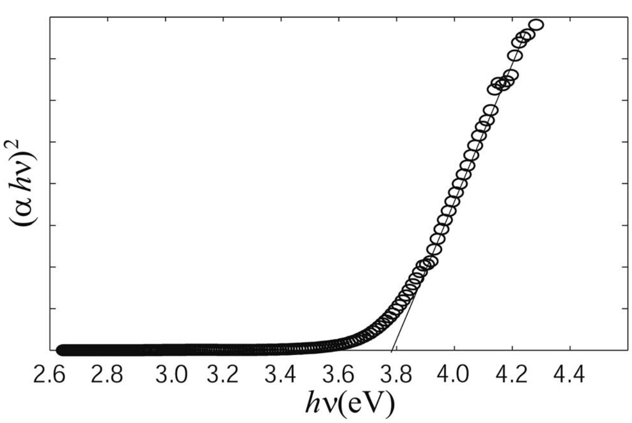

Fig. 2. Plot of $(\alpha h\nu)^2$ versus photoenergy for the BLT thin films.

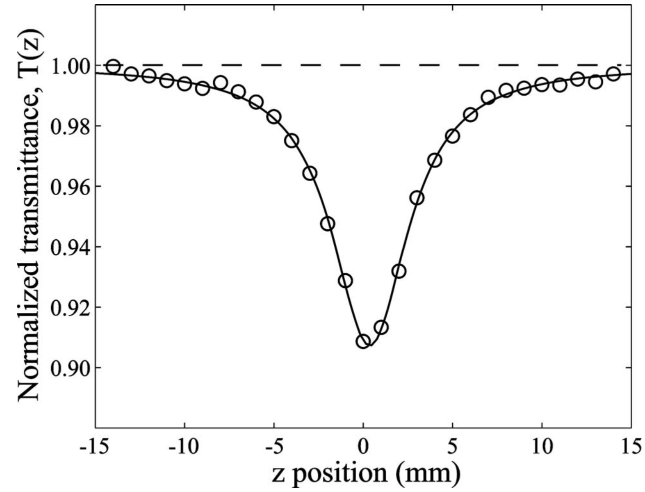

Fig. 3. Experimentally measured (symbols) and theoretically fitted [using Eq. (2), indicated by the lines] open aperture transmittance of the BLT thin film on a quartz substrate versus scan position. The transmittance is normalized, so the dashed horizontal line at the transmission of 1 represents the transmittance where sample is located far from the focal point.

$$T(z) = 1 - \frac{1}{2^{3/2}} \frac{\beta I_0 L_{\mathrm{eff}}}{(1 + z^2/z_0^2)}, \tag{2}$$

where β represents the third-order nonlinear absorption coefficient at 532 nm, I_0 is the incident intensity at the focal point, $L_{\mathrm{eff}} = [1 - \exp(-\alpha L)]/\alpha$, and z_0 is the Rayleigh range, and its value was about 2.5 mm. The measured third-order nonlinear absorption coefficient is $\beta = 3 \times 10^{-5}$ cm/W, and the sign of β is opposite with the results of Shi *et al.* for a BLT film at 800 nm with a femtosecond laser [16].

Furthermore, the change in the normalized transmittance of the closed aperture Z-scan is shown in Fig. 4. The valley-to-peak curve indicates a positive optical nonlinearity (self-focusing), and the plot is fitted using the equation [20]

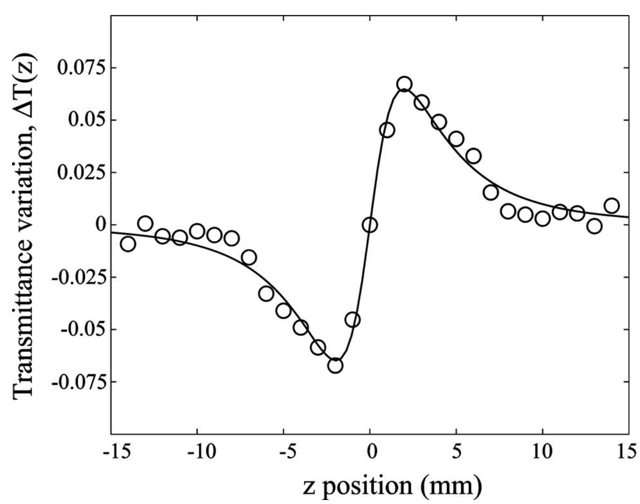

Fig. 4. Experimentally measured (symbols) and theoretically fitted [using Eq. (3), as indicated by the lines] transmittance variation of the BLT thin fim versus scan position for the closed aperture Z-scan.

$$\Delta T(z) = \frac{T(z) - T(-z)}{2} = \frac{4\Delta\phi z/z_0}{(1+z^2/z_0^2)(9+z^2/z_0^2)}, \quad (3)$$

where $\Delta\phi$ is related to the nonlinear refractive index coefficient as $\gamma=\lambda\Delta\phi/(2\pi I_0 L_{\mathrm{eff}})=3.1\times10^{-10}\ \mathrm{cm}^2/\mathrm{W}$ [13]. The measured values of β and γ are much bigger than those of other ferroelectric thin films, with a few exceptions [5,13]. Furthermore, γ is about 100 times bigger than that of the BLT thin film at 800 nm with a fs laser ($\beta=1.9\times10^{-12}\ \mathrm{cm}^2/\mathrm{W}$) [16].

Using the measured values of γ and β, we estimate the real and imaginary parts of the third-order nonlinear susceptibility ($Re(\chi^{(3)})=1\times10^{-11}\ \mathrm{cm}^2/\mathrm{V}^2$ and $Im(\chi^{(3)})=0.42\times10^{-11}\ \mathrm{cm}^2/\mathrm{V}^2$) and can conclude that both the real and imaginary parts of the third-order nonlinear susceptibility contribute to the large nonlinear optical effects.

As shown in Fig. 3, the transmittance exhibits a dip, so we can ignore the nonlinear absorption by one-photon saturable absorption. Since the photon energy of the Z-scan pump beam, 2.33 eV, is far from the bandgap energy of 3.78 eV, one-photon absorption is very small, and we believe that two-photon absorption is the dominant mechanism of the nonlinear absorption. In addition, the short picosecond pulse can eliminate the contribution to the nonlinear refractive index from photorefractive, electrostriction, and thermal effects since those effects have a response time much longer than 35 ps [21]. We believe that bound electronic Kerr effect and population distribution associated with the two-photon absorption are the main mechanisms of the third-order nonlinear refractive index. However, there are other possible mechanisms contributing to the refractive index, such as saturated absorption, the cascaded second-order effect, and free-carrier absorption. Additional investigation would be required to determine the precise origin of the observed nonlinear absorption of BLT.

In summary, the third-order nonlinear optical susceptibility of BLT ferroelectric thin films with the layered perovskite structure was investigated using the Z-scan technique at a wavelength of 532 nm with a pulse duration of 35 ps. A large nonlinear absorption and refractive index were observed, and the nonlinear refractive index coefficient γ was determined as $3.1\times10^{-10}\ \mathrm{cm}^2/\mathrm{W}$. These results show that BLT ferroelectric thin films are a good candidate for nonlinear optical devices.

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