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Z-scan measurement for the nonlinear absorption of $Bi_{2.55}La_{0.45}TiNbO_9$ thin films

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ABSTRACT

$Bi_{2.55}La_{0.45}TiNbO_9$ (BLTN-0.45) thin films with layered aurivillius structure were fabricated on fused silica substrates by pulsed laser deposition technique. Their structure, fundamental optical constants, and nonlinear absorption characteristics have been studied. The film exhibits a high transmittance (>60%) in visible-infrared region. The optical band gap energy was found to be 3.44 eV. The optical constant and thickness of the films were characterized using spectroscopic ellipsometric (SE) method. The nonlinear optical absorption properties of the films were investigated by the single-beam Z-scan method at a wavelength of 800 nm laser with a duration of 80 fs. We obtained the nonlinear absorption coefficient $\beta = 4.64 \times 10^{-8}$ m/W. The results show that the BLTN-0.45 thin film is a promising material for applications in absorbing-type optical device.

1. Introduction

In recent years, bismuth layer-structured ferroelectrics (BLSFs) have attracted a lot of attention for their potential use in high-temperature piezoelectric devices [1,2] and ferroelectric random access memories [3,4], because of their relatively high Curie point (T_c) and excellent fatigue endurance property, respectively. As one of BLSFs, Bi_3TiNbO_9 (BTN) has good ferroelectric properties and excellent fatigue free properties [5]. It has been reported that substitution by lanthanide ions having a smaller ionic radii than Bi led to improved oxygen ion stability in the lattice and hence improved fatigue resistance, and maintained a more significant structural distortion and improved ferroelectric properties[6,7]. Zhou et al. reported that BLTN-*x* ceramics exhibit distinct ferroelectric properties [8]. On the other hand, most ferroelectric materials exhibit excellent optical and nonlinear optical properties. Thin films of ferroelectric oxides have shown a large nonlinear refractive index n_2 and a nonlinear absorption coefficient β [9–12]. Optical properties of $Bi_{2.55}La_{0.45}TiNbO_9$ (BLTN-0.45) thin films have been less investigated until now. These thin films can be potentially used in spacecrafts because of their relatively high Curie point (T_c>800 °C). In this work, we have employed Z-scan technique with femtosecond laser pulses to investigate the third-order optical nonlinear absorption of BLTN-0.45 thin films. The fundamental optical constants of the films were obtained through spectroscopic ellipsometric measurement.

2. Experiment

BLTN-0.45 pellets used as PLD targets were prepared by a conventional solid-state reaction technique with starting materials Bi_2O_3, TiO_2, Nb_2O_5, and La_2O_3. The powders of Bi_2O_3, La_2O_3, TiO_2, and Nb_2O_5 with a molar ratio of Bi:La:Ti:Nb = 2.55:0.45:1:1 were mixed by ball milling in ethanol for 12 h. The dried mixtures were calcined at 700 °C for 3 h. The screened uniform mixture of the powder was finally pressed into disks of 2 cm diameter and sintered at 1000 °C for 2 h in a conventional box furnace. Dense yellowish pellets were acquired through this procedure.

The films were deposited on double-sided polished fused silica substrates using a KrF excimer pulsed laser with 248 nm wavelength, 30 ns pulse width and 4 Hz frequency. In our experiments, the average laser fluence, deposition temperature, and ambient pressure were 2.0 J/cm^2, 700 °C, and 100 mTorr, respectively. After deposition, the films were in-situ annealed in the chamber at 700 °C under 0.5 atm oxygen atmosphere for 30 min.

The microstructure of the as grown films was characterized by X-ray diffract ion (XRD). The spectroscopic ellipsometric data were

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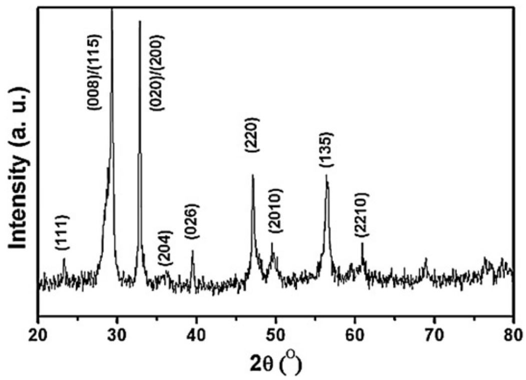

Fig. 1. X-ray diffraction pattern of BLTN-0.45 thin film deposited on fused silica substrate.

collected using a GESP-5 (Sopra) spectroscopic ellipsometer in the wavelength range of 300–800 nm at the incidence angle of 75°. The nonlinear absorption coefficients of the BLTN-0.45 films were determined by single-beam Z-scan technique. In our experiments, a Ti sapphire laser with a wavelength of 800 nm, a repetition rate of 1 kHz, and a pulse width of 80 fs was employed as the light source. The focal length of the lens is 200 mm. A typical peak power density was 1 GW/cm^2. The sample transmission was monitored by an energy ratiometer.

3. Results and discussion

The XRD pattern of BLTN-0.45 thin films indicates that the samples studied in this work are of single phase as shown in Fig. 1. The peaks are indexed according to the standard powder diffraction data (JCPDF No. 73-2180).

The optical transmittance spectra corrected for the attenuation of the fused silica substrate were performed by a Lambda-2S UV/VIS spectrophotometer. The measured results in the wavelength range of 200–1400 nm are shown in Fig. 2. The oscillations in transmittance come from the interference due to reflection from the top surface of the film and the interface between the film and substrate. The well-oscillating transmittance indicates that the films have a flat surface and a uniform thickness. The films are highly transparent in the visible-near infrared region with a transmittance between 60% and 96%. The transparency of the films drops rapidly in the UV region and the absorption edge is located at 350 nm. The optical band gaps (E_g) of BLTN-0.45 thin film is estimated to be 3.44 eV.

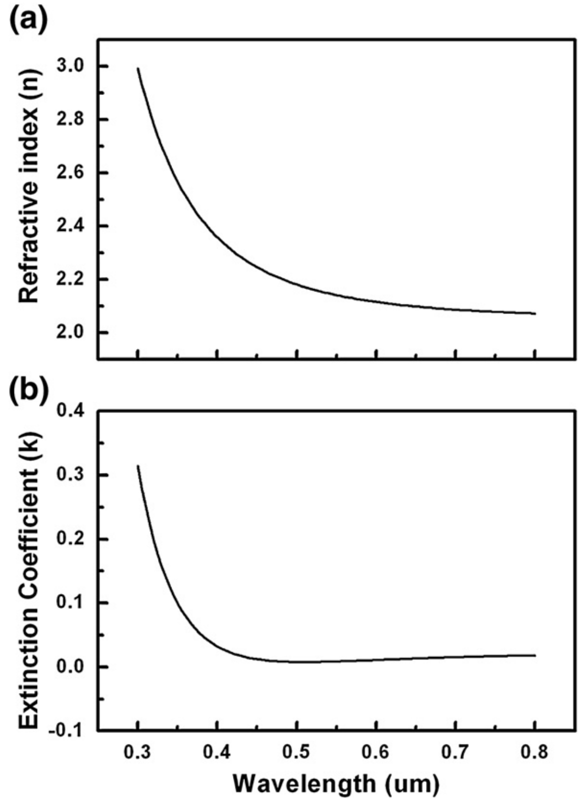

Fig. 3. Dispersion of the refractive index (a) and extinction coefficient (b) of BLTN-0.45 film obtained by ellipsometry.

The linear refractive index, extinction coefficient and thickness of the BLTN-0.45 film deposited on fused silica substrates were characterized using spectroscopic ellipsometric (SE) method at an incidence angle of 75° in the spectral range of 300–800 nm. Fig. 3(a) and (b) shows the wavelength dependence of the averages of refractive index and extinction coefficient of BLTN-0.45 film, respectively. The linear refractive index, extinction coefficient and the thickness of the BLTN-0.45 film at 800 nm were determined to be 2.072, 0.018 and 1.20 μm, respectively.

The nonlinear optical absorption properties of the BLTN-0.45 thin films were measured using a single-beam Z-scan technique. Fig. 4 shows a typical open-aperture Z-scan experimental curve for BLTN-0.45 thin films grown on silica substrates. The curve is symmetric with respect to the focus point ($z = 0$). The solid line is theoretical fitting.

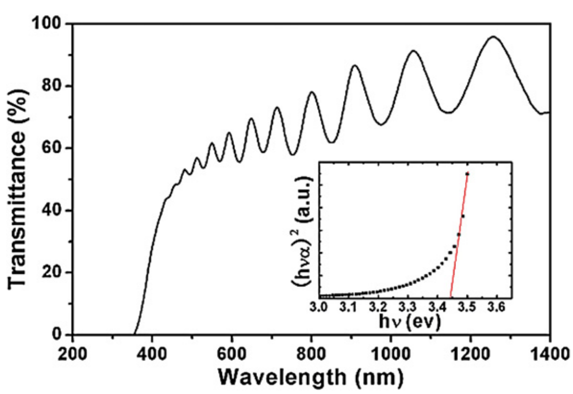

Fig. 2. Optical transmittance of BLTN-0.45 thin film on fused silica substrate. The inset is a plot of $(h\nu\alpha)^2$ vs. $h\nu$ for the BLTN-0.45 thin film.

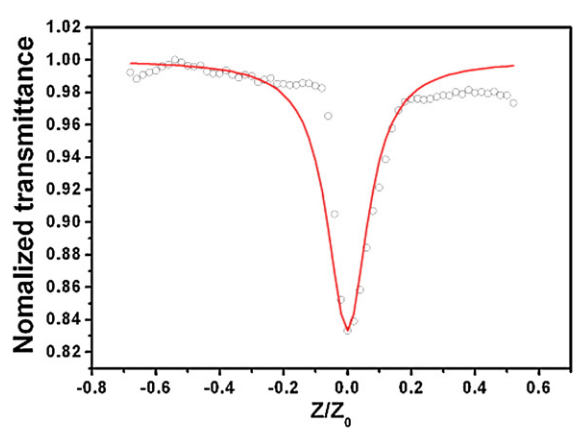

Fig. 4. Open-aperture Z-scan data of BLTN-0.45 thin film using 80 fs pulses at 800 nm. The symbols are the measured data and the solid line is the theoretical fitting.

When direct absorption is negligible, one can deduce the nonlinear absorption coefficient β from the open-aperture Z-scan data [13].

$$T = \sum_{m=0}^{\infty} \frac{(-\beta I_0 L_{eff})^m}{(1 + z^2/z_0^2)^m (m+1)^{3/2}}, \quad \text{for} \left| \frac{\beta I_0 L_{eff}}{1 + z^2/z_0^2} \right| < 1 \qquad (1)$$

where $L_{\mathrm{eff}} = [1 - \exp(-\alpha L)]/\alpha$ is the effective film thickness, L is the film thickness, α is the linear absorption coefficient, I_0 is the laser intensity at the focal point, and $z_0 = 2\pi\omega_0^2/\lambda$ is the Rayleigh range of the beam. The obtained β value for BLTN-0.45 film is 4.64×10^{-8} m/W. Because the silica substrate shows very weak nonlinear optical property, the large nonlinear absorption observed here results from the BLTN-0.45 film.

The nonlinear absorption coefficient of $SrBi_2Nb_2O_9$, $Bi_{3.25}La_{0.75}Ti_3O_{12}$, $Bi_2Nd_2Ti_3O_{12}$, and $(Na_{0.9}K_{0.1})Bi_{0.5}TiO_3$ thin films are 1.1×10^{-7}, -6.76×10^{-8}, 3.1×10^{-7}, and 6.59×10^{-9} m/W, respectively [9–12]. The high nonlinear absorption of BLTN-0.45 film compares favorably with the nonlinearities of these materials. These results suggest that the new BLTN-0.45 films have potential applications in nonlinear optics devices.

4. Conclusion

BLTN-0.45 thin films with good optical transparency and well-crystallized layered perovskite structure were prepared on fused silica substrates by the pulsed laser deposition method. The optical constant and thickness of the BLTN-0.45 film were characterized using spectroscopic ellipsometric (SE) method. The linear refractive index, extinction coefficient and the thickness of the BLTN-0.45 film at 800 nm were determined to be 2.072, 0.018 and 1.20 μm, respectively. Its nonlinear optical properties were obtained using a Z-scan technique at a wavelength of 800 nm with a laser duration of 80 fs. The nonlinear absorption coefficient of BLTN-0.45 thin films is determined to be 4.64×10^{-8} m/W. All these results show that BLTN-0.45 thin film is a promising material in nonlinear optical applications.

Acknowledgment

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