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Third-order optical nonlinear absorption in $Bi_{1.95}La_{1.05}TiNbO_9$ thin films

Hengzhi Chen [a], Bin Yang [a,*], Mingfu Zhang [b], Feiyan Wang [c], Kokwai Cheah [c], Wenwu Cao [a,d]

[a] Center for Condensed Matter Science and Technology, Department of Physics, Harbin Institute of Technology, Harbin 150001, China
[b] Center for Composite Materials, Harbin Institute of Technology, Harbin 150001, China
[c] Department of Physics, Hong Kong Baptist University, Hong Kong SAR, China
[d] Materials Research Institute, The Pennsylvania State University, University Park, Pennsylvania 16802, USA

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ABSTRACT

Single phase $Bi_{1.95}La_{1.05}TiNbO_9$ (LBTN-1.05) thin films with a layered aurivillius structure have been fabricated on fused silica substrates by pulsed laser deposition at 700 °C. The X-ray diffraction pattern revealed that the films are single-phase aurivillius. The band gap, linear refractive index and linear absorption coefficient were obtained by optical transmittance measurements. The film exhibits a high transmittance (>70%) in visible-infrared region and the dispersion relation of the refractive index vs. wavelength follows the single electronic oscillator model. The nonlinear optical absorption property of the film was determined by the single beam Z-scan method using 800 nm with a duration of 100 fs. A large positive nonlinear absorption coefficient $\beta = 5.95 \times 10^{-8}$ m/W was determined experimentally. The results showed that the LBTN-1.05 is a promising material for applications in absorbing-type optical devices.

1. Introduction

Bismuth-layered aurivillius structured ferroelectric thin films with high fatigue resistance, fast switching speed, and good polarization retention [1], have attracted a lot of attention due to their potential applications in nonvolatile random access memory devices. Among such ferroelectrics, Bi_3TiNbO_9 (BTN) thin film is one of the most attractive candidates for nonvolatile memory applications. Interestingly, most ferroelectric materials also exhibit excellent optical and nonlinear optical properties. Thin films of ferroelectric oxides such as $Bi_{3.75}Nd_{0.25}Ti_3O_{12}$, $SrBi_2Nb_2O_9$, $Bi_{3.25}La_{0.75}Ti_3O_{12}$, $Bi_2Nd_2Ti_3O_{12}$, and $(Na_{0.9}K_{0.1})Bi_{0.5}TiO_3$ showed a large nonlinear refractive index n_2 and a large nonlinear absorption coefficient β [2–6]. BTN thin films also have good optical waveguiding properties [7]. It has been reported that partial substitution of Bi by lanthanide ions, which has a smaller ionic radii than Bi, leads to improved oxygen ion stability in the lattice and hence improves fatigue resistance and produces better ferroelectric properties [8,9]. Zhou et al. reported that LBTN-x ceramics exhibit distinct ferroelectric properties [10].

$Bi_{1.95}La_{1.05}TiNbO_9$ (LBTN-1.05) is a promising material for application in spacecrafts because of its relatively high Curie point (Tc>400 °C). A good understanding of the optical properties of LBTN-1.05 films can help evaluate its potential as an active electro-optical material. In this work, we have grown LBTN-1.05 thin films on silica substrates by a pulse laser deposition (PLD) technique and investigated their optical transmittance and third-order optical nonlinearities by using the transmittance measurement and the *Z*-scan technique with femtosecond laser pulses.

2. Experiment

LBTN-1.05 ceramics were prepared by conventional sintering method. First, mixtures of La_2O_3, Bi_2O_3, TiO_2, and Nb_2O_5 powders were ball milled for 12 h in an agate tank. The dried mixtures were calcined at 700 °C for 3 h. Excess 20 mol% Bi_2O_3 was added to compensate for Bi evaporation during the sintering process. Then, the screened uniform mixture of the powder was pressed into 2 cm diameter disks. Finally, the pellets were sintered at 1000 °C for 2 h in a conventional box furnace. Dense yellowish pellets were obtained through this procedure.

The films were deposited on double-sided polished fused silica substrates of 1 cm × 0.5 cm dimension by pulsed laser ablation using a KrF excimer pulsed laser (LPX205i, Lambda Physik, 248 nm wavelength, 30 ns pulse width and a 4 Hz frequency). In our experiments, the average laser fluence, deposition temperature, and ambient pressure were 2.0 J/cm^2, 700 °C, and 13 Pa, respectively.

After deposition, the films were in-situ annealed in the chamber at 700 °C under 0.5 atm oxygen atmosphere for 30 min. In order to get a uniform thin film of LBTN-1.05, the target and the substrate holder were rotated during deposition.

The microstructure of the as grown films was characterized by a Siemems D5000 X-ray diffraction (XRD) in Cu K_α. The transmittance spectra were measured by a Hitachi U-3410 UV/VIS spectrophotometer.

* Corresponding author. Tel./fax: +86 451 86402771.
E-mail address: binyang@hit.edu.cn (B. Yang).

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The nonlinear absorption coefficients of the LBTN-1.05 films were determined by single beam *Z*-scan technique. In our experiments, a regenerative amplifier (1 kHz, Spectra-Physics, Spitfire) produces 100 fs pulses at 800 nm. Typical peak power density used was 1 GW/cm^2. The focal length of the lens is 200 mm and the sample transmission was monitored by an energy ratiometer.

3. Results and discussion

In order to investigate the structural properties of the LBTN-1.05 thin films, we used a Siemens D5000 powder X-ray diffractometer (XRD) in Cu K_α radiation. Fig. 1 shows the θ–2θ patterns of the LBTN-1.05 thin films deposited on fused silica substrates. The peaks are indexed according to the standard powder diffraction data (JCPDF No. 73-2180). All X-ray peaks can be indexed by the LBTN-1.05 tetragonal phase. Although there are excess Bi_2O_3 in the target, no Bi_2O_3 peaks were observed. This means that the excess 20% mol bismuth ions in starting materials were all being used to compensate for the Bi evaporation during the preparation of LBTN-1.05 targets and the thin films.

The optical transmittance spectra of the LBTN-1.05 thin films were measured by a Lambda-2 S UV/VIS spectrophotometer. Fig. 2 shows the wavelength dependence of optical transmittance of the LBTN-1.05 thin films in the wavelength range of 200–1200 nm. 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 70% and 97% and the transmittance decreases drastically to zero at about 344 nm. Assuming a direct transition between the valence and conduction bands, the optical bandgap energy E_g of the LBTN-1.05 thin films is estimated to be 3.53 eV from the graph of $(h\nu\alpha)^2$ vs $h\nu$ based on the relation between the linear absorption coefficient α and bandgap energy E_g: $(h\nu\alpha)^2 = C(h\nu - E_g)$, where C is a constant and $h\nu$ is the incident light energy[11].

For a single layer weakly absorbing film on a transparent substrate, the linear refractive indices as a function of wavelength and film thickness can be obtained from the transmission spectra by using the envelope method [12,13]. A dispersion curve of the LBTN-1.05 thin film is shown in Fig. 3. Open circles represent data obtained by transmittance measurements. The dispersion data in the interband-transition region are modeled based on a single electronic oscillator. This theory assumes that the material is composed of a series of independent oscillators which are set into forced vibrations by incident radiation. According to the single electronic oscillator model proposed by Didomenico and Wemple [14], the dispersion of the refraction index is given by the well-known Sellmeier relation:

$$n^2 = 1 + \frac{S_0\lambda_0^2}{1-(\lambda_0/\lambda)^2}, \tag{1}$$

where λ_0 is the average oscillator position and S_0 is the average oscillator strength. By fitting the refractive index data to Eq. (1), the values of λ_0 and S_0 were found to be 333 ± 0.6 nm and $2.52 \pm 0.09 \times 10^{13}$ m^{-2}, respectively. The energy of the oscillator given by $\varepsilon_0 = (hc)/(e\lambda_0)$ (c is the speed of light, h is Plank's constant, and e is the electronic charge) is calculated to be 3.72 eV. The linear refractive index n_0 of the films is calculated to be 2.016 at 800 nm through Sellmeier-type dispersion fitting. The linear absorption coefficient α and the thickness of the film calculated by this method are about 3.04×10^4 m^{-1} and 1372 nm, respectively.

The *Z*-scan data without a collecting aperture for LBTN-1.05 thin films grown on silica substrates are shown in Fig. 4. The normalized transmittance data comprises a deep valley, indicating the presence of nonlinear absorption in the film. The solid line is the theoretical fitting. Usually, the nonlinear absorption can be explained by two well-known mechanisms: multi-photon absorption and free carrier absorption [6]. In semiconductors, the contribution to nonlinear absorption from the N-photon (N≥3) absorption is much smaller than two-photon absorption (TPA) [15]. Thus the nonlinear optical absorption in

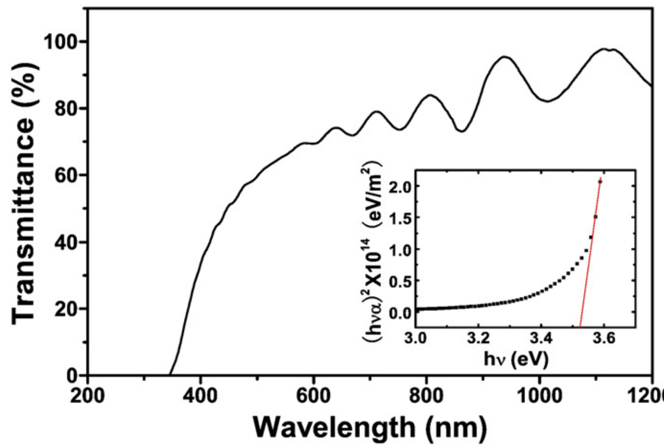

Fig. 2. Optical transmittance of LBTN-1.05 thin film on fused silica substrate. The inset is a plot of $(h\nu\alpha)^2$ vs. $h\nu$ for the LBTN-1.05 thin film.

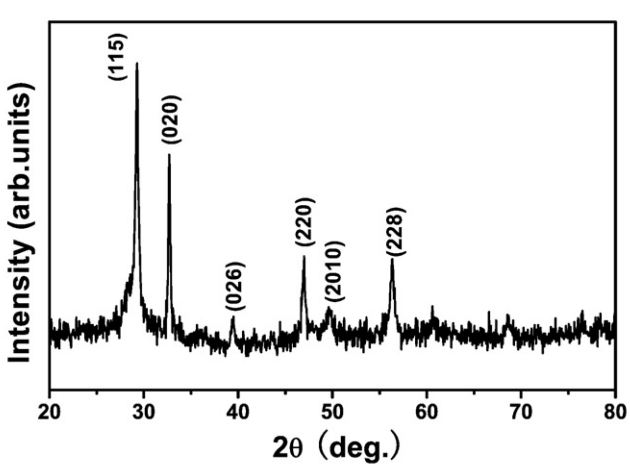

Fig. 1. X-ray diffraction pattern of LBTN-1.05 thin film deposited on fused silica substrate.

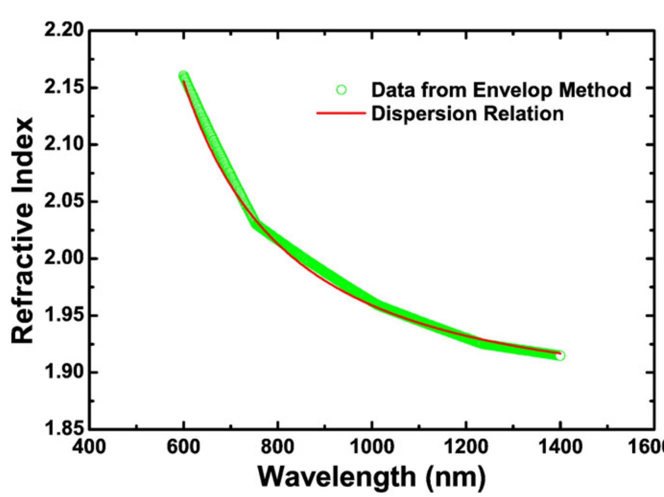

Fig. 3. Refractive index as a function of wavelength and the dispersion curve of LBTN-1.05 thin film on fused silica substrate.

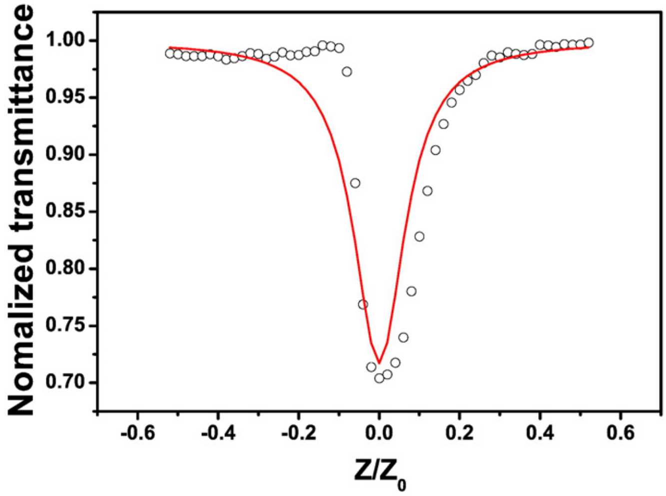

Fig. 4. Open-aperture Z-scan data of LBTN-1.05 thin film using 100 fs pulses at 800 nm. The symbols are the measured data and the solid line is the theoretical fitting.

LBTN-1.05 thin film is mainly attributed to TPA. The bandgap of LBTN-1.05 (3.53 eV) thin film is larger than the excitation energy of the laser ($2h\nu = 3.1$ eV), so that TPA is not attributed to a direct transition process. However, the TPA can occur at 800 nm in LBTN-1.05 thin films resulting from the interaction of the strong laser pulse with intermediate levels in the forbidden gap induced by impurities [16].

The nonlinear absorption coefficient β for the LBTN-1.05 thin films can be calculated from the normalized transmittance T by the following relation [17]

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

where L_{eff} is the effective film thickness, 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 fitting gives the nonlinear absorption coefficient $\beta = 5.95 \times 10^{-8}$ m/W. Because the silica substrate has a very small optical nonlinearity, the large nonlinear absorption observed here results from the LBTN-1.05 film.

The nonlinear absorption coefficient of $Bi_{3.75}Nd_{0.25}Ti_3O_{12}$, $SrBi_2Nb_2O_9$, $Bi_{3.25}La_{0.75}Ti_3O_{12}$, $Bi_2Nd_2Ti_3O_{12}$, and $(Na_{0.9}\,K_{0.1})Bi_{0.5}TiO_3$ thin films are 5.24×10^{-7}, 1.1×10^{-7}, -6.76×10^{-8}, 3.1×10^{-7}, and 6.59×10^{-9} m/W, respectively [2–6]. The high nonlinear absorption of LBTN-1.05 film compares favorably with the nonlinearities of those materials. Therefore, the LBTN-1.05 films have potential applications in nonlinear optics devices. Most importantly, this thin film may be applicable in spacecrafts because of its relatively high Curie temperature.

4. Conclusions

LBTN-1.05 thin films with bismuth-layered aurivillius structure have been deposited on fused silica substrates by PLD method. The optical constants were determined from the transmittance spectra using the envelope method. The film exhibits a high transmittance (>70%) in visible-infrared region. The optical bandgap energy was found to be 3.53 eV. The dispersion in the refractive index was fitted by the Sellmeier dispersion relation and described by an electronic oscillator model. The linear refractive index n_0 of the films is calculated to be 2.016 at 800 nm through Sellmeier-type dispersion fitting. The nonlinear absorption coefficient of LBTN-1.05 thin films is determined to be 5.95×10^{-8} m/W. These good optical properties show that LBTN-1.05 thin film is a promising material for nonlinear optical applications.

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