

## Optical properties of $\text{Bi}_{2.25}\text{La}_{0.75}\text{TiNbO}_9$ thin films grown on fused silica substrates by PLD

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### ABSTRACT

Layered-perovskite ferroelectric  $\text{Bi}_{2.25}\text{La}_{0.75}\text{TiNbO}_9$  (LBTN-0.75) optical waveguiding thin films have been prepared on fused silica substrates by pulsed laser deposition (PLD). X-ray  $\theta$ - $2\theta$  scans revealed that the films are single-phase perovskite. The optical properties, such as the wavelength dependence of the transmittance and the refractive index, were determined. The average transmittance of the film is 75% in the wavelength range of 200–1100 nm and the band gap  $E_g = 3.46$  eV. The optical waveguiding properties of the films were characterized by using prism coupling method. The distinct  $m$ -lines of the guided transverse electric (TE) and transverse magnetic (TM) modes of the LBTN-0.75 films waveguide have been observed. The film homogeneity and the film–substrate interface were analyzed using the inverse Wentzel–Kramer–Brillouin (iWKB) method.

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## 1. Introduction

Bismuth layer-structured ferroelectrics (BLSFs) have attracted a lot of attention for their potential using in high-temperature piezoelectric devices [1,2] and ferroelectric random access memories [3,4]. On the other hand, most ferroelectric materials exhibit excellent optical properties and good nonlinear optical properties. Recently, much attention has been paid to the film of this material as optical waveguide [5,6], because it may extend the practical use of their properties in integrated optical systems. During these years, several techniques have been used to deposit waveguides in different materials. These films have been prepared by different deposition techniques, including pulsed laser deposition (PLD), sputter deposition, metal organic chemical vapor deposition, and molecular beam epitaxy. PLD have a lot of advantages to deposit waveguide, for example the short process time, the possibility to deposit with complex compositional, and the controlling of the film thickness by adjusting the laser parameters. It is well known that proper element doped (at the A site with  $\text{La}^{3+}$ ,  $\text{Nd}^{3+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Sm}^{3+}$ ,  $\text{Ca}^{2+}$  ions and/or B site with  $\text{Nb}^{5+}$ ,  $\text{Ta}^{5+}$ ,  $\text{W}^{6+}$ ,  $\text{V}^{5+}$  ions) in BLSFs

can effectively optimize their properties and the  $\text{Bi}_2\text{O}_2$  layers play a very important role in the properties of BLSFs: the  $\text{Bi}_2\text{O}_2$  layers act as the insulating layers [7]. Zhou et al. reported that  $\text{Bi}_{2.25}\text{La}_{0.75}\text{TiNbO}_9$  (LBTN-0.75) ceramics exhibit distinct ferroelectric properties [8]. LBTN-0.75 can be used in a high-temperature environment because of its relatively high Curie point ( $T_c > 350$  °C). However, the optical waveguiding properties of LBTN-0.75 thin films have not been reported up to now. In this paper, LBTN-0.75 waveguide thin films were fabricated on fused silica by a pulsed laser deposition (PLD) technique. The optical waveguiding properties of the films were characterized by using prism coupling method.

## 2. Experiment

LBTN-0.75 ceramics were prepared by conventional solid-state reaction technique. Firstly, mixtures of the  $\text{Bi}_2\text{O}_3$ ,  $\text{La}_2\text{O}_3$ ,  $\text{TiO}_2$ , and  $\text{Nb}_2\text{O}_5$  powders in stoichiometric ratios were ball milled for 12 h, then the dried mixture of powders were calcinated at 700 °C for 3 h. Excess 20 mol%  $\text{Bi}_2\text{O}_3$  was added to compensate for Bi evaporation during the sintering process. The screened uniform mixture of the powder was pressed into disks. Finally, the pellets were sintered at 1000 °C for 2 h in a conventional box furnace. Dense yellowish pellets we acquired through this procedure. The films

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were deposited on 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 5 Hz frequency). In our experiments, the average laser fluence, deposition temperature, and ambient pressure were 2.0 J/cm<sup>2</sup>, 700 °C, and 26 Pa, respectively. In order to get a uniform LBTN-0.75 thin film, the target and the substrate holder were rotated during deposition. After deposition, the films were in situ annealed in the chamber at 700 °C under 0.5 atm oxygen atmosphere for 30 min.

The microstructures of the films were characterized by X-ray diffraction (XRD). The morphologies of the films were observed by scanning electron microscope (SEM, FEI SIRISON 200, Philips). The transmittance spectra were measured by a Hitachi U-3410 UV/vis spectrophotometer and the optical waveguiding properties of the films were investigated by the prism-coupler method using a 632.8 nm wavelength laser beam coupled into the film.

### 3. Results and discussion

Fig. 1 shows the  $\theta$ - $2\theta$  patterns of the LBTN-0.75 thin films deposited on fused silica substrates. The peaks are indexed according to the standard powder diffraction data (JCPDF No. 73-2180). It indicates that all deposited films studied in this work are of single phase. Although there are excess Bi<sub>2</sub>O<sub>3</sub> in the targets, no Bi<sub>2</sub>O<sub>3</sub> peaks were observed. It means that the excess 20% mol bismuth ions in starting materials compensate for the Bi evaporation during the preparation of LBTN-0.75 targets and the thin films.

Fig. 2 shows the cross-section SEM image of the LBTN-0.75 films. The interface of substrate and the LBTN-0.75 films is quite sharp and we can find that thickness of this film is about 1600 nm.

Fig. 3 shows the measured optical transmittance of the LBTN-0.75 thin films in the wavelength range of 200–1100 nm. The film is highly transparent in the visible-near infrared region with a transmittance between 60% and 90%. 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 transparency of the films drops rapidly at 400 nm and decreases to zero at approximately 350 nm. The optical bandgap energy  $E_g$  of the LBTN thin films is estimated to be 3.46 eV from the graph of  $(h\nu\alpha)^2$  vs.  $h\nu$  based on the relation between the linear absorption coefficient  $\alpha$  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 [9].

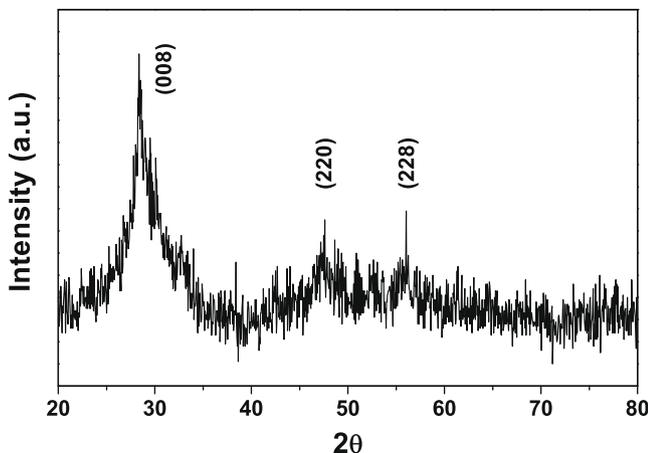


Fig. 1. X-ray diffraction pattern of LBTN-0.75 thin films deposited on fused silica substrates.

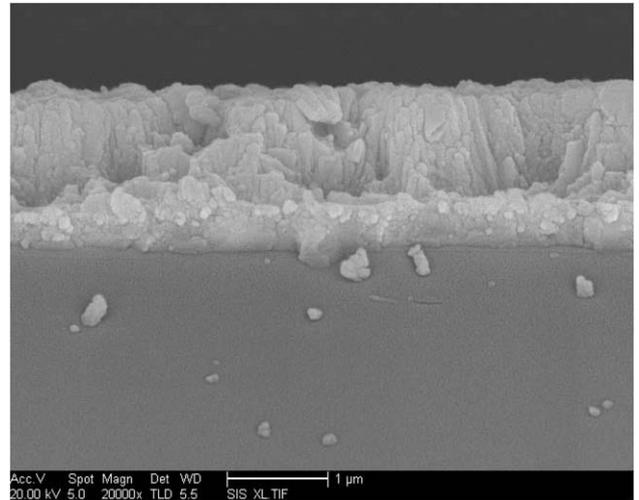


Fig. 2. Cross section of LBTN-0.75 thin films on fused silica substrates.

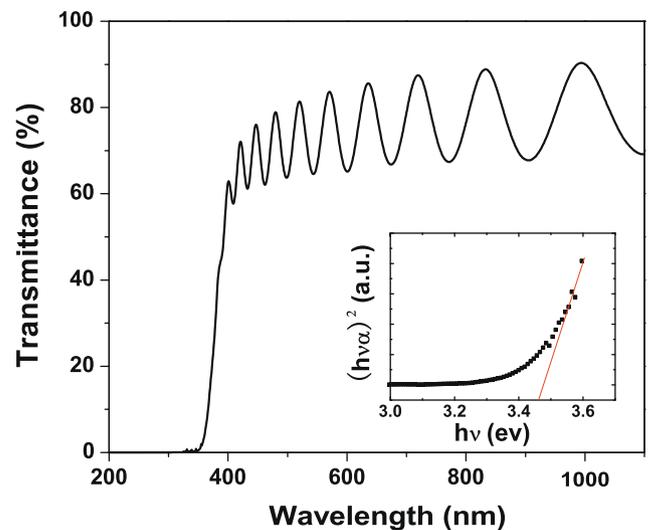


Fig. 3. Optical transmittance of LBTN-0.75 thin films on fused silica substrates. The inset is a plot of  $(h\nu\alpha)^2$  vs.  $h\nu$ .

The linear refractive indices as a function of wavelength and film thickness can be obtained from the transmission spectra by using the envelope method [10,11]. The linear refractive index  $n_0$  at 632.8 nm and thickness of the films calculated by this method are about 2.18 and 1.123  $\mu\text{m}$ , respectively. A dispersion curve of the LBTN-0.75 thin film is shown in Fig. 4. Open circles represent data obtained by transmittance measurements. According to the single electronic oscillator model proposed by Didomenico and Wemple [12], the dispersion of the refraction index is given by the well-known Sellmeier relation:

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

where  $S_0$  is an average oscillator strength and  $\lambda_0$  is the average oscillator position. By fitting the refractive-index data to Eq. (1), the values of  $S_0$  and  $\lambda_0$  were found to be  $6.96 \times 10^{13} \text{ m}^{-2}$  and 218 nm, respectively. The energy of the oscillator given by  $\epsilon_0 = hc/e\lambda_0$  ( $c$  is the speed of light,  $h$  is the Planck's constant, and  $e$  is the electron charge) is calculated to be 5.69 eV.

The prism-coupling technique is a proven technique to rapidly and accurately measure the thickness and refractive index of thin

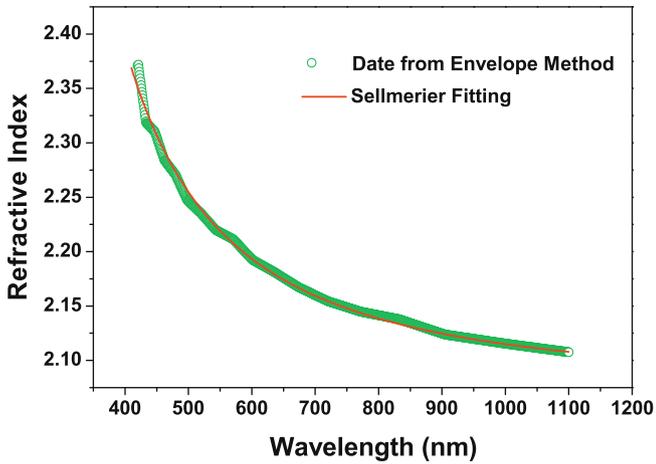


Fig. 4. Refractive index as a function of wavelength and the dispersion curve of LBTN-0.75 thin films on fused silica substrates. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

films [13,14]. Coupling curves for a LBTN-0.75 thin film fabricated on fused silica substrate are shown in Fig. 5. At certain angle of incidence  $\theta$ , sharp reflectivity dips which appear in the recorded

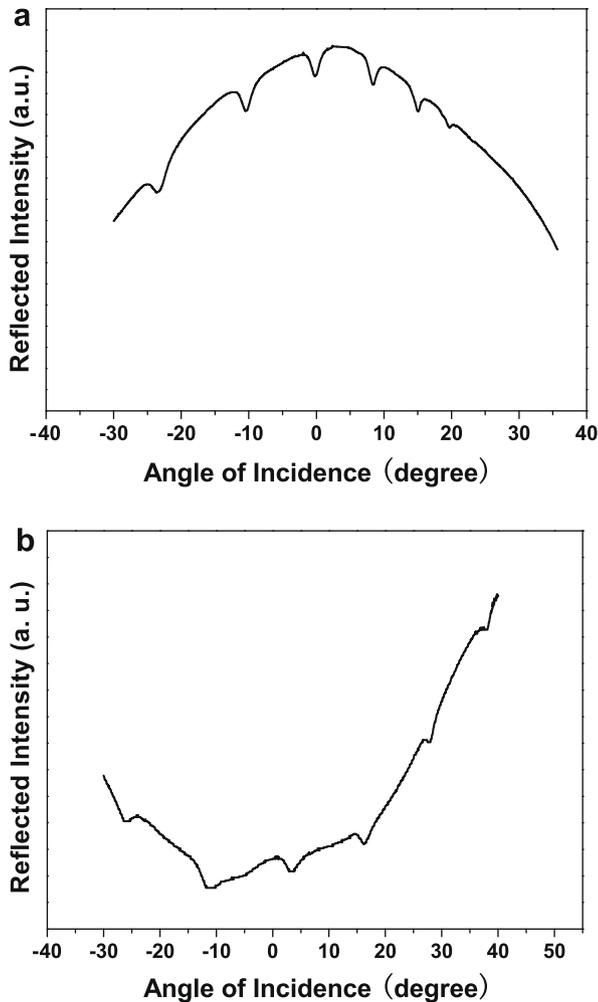


Fig. 5. (a) TE and (b) TM guiding modes spectra for a LBTN-0.75 thin film deposited by PLD on fused silica substrate.

Table 1

Experimental and theoretical effective indices reported for TE and TM guided modes.

Polarization	Mode $M$	$N_m$ (exp.)	$N_m$ (theor.)
TE	0	2.2240	2.2161
	1	2.1741	2.1647
	2	2.0967	2.0906
	3	1.9930	1.9945
	4	1.8626	1.8812
TM	5	1.6878	1.7029
	0	2.3900	2.3825
	1	2.3048	2.2945
	2	2.1873	2.1758
	3	2.0380	2.0268
4	1.8529	1.8445	
5	1.6580	1.6341	

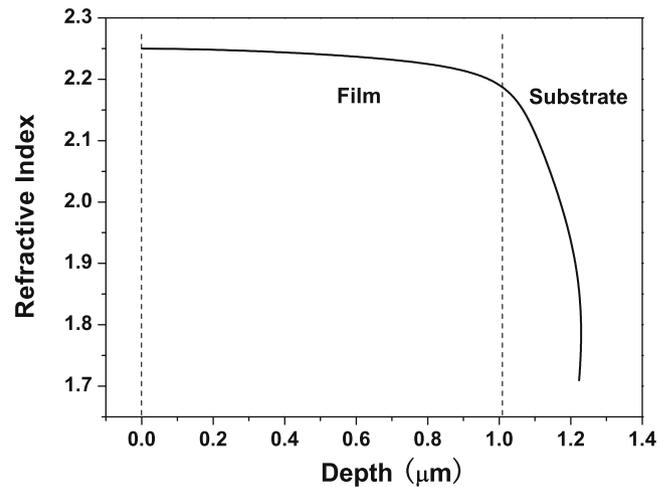


Fig. 6. Ordinary refractive index profile (TE) of LBTN-0.75 thin films reconstructed using the iWKB method.

TE and TM spectra correspond to the excitation of guided modes. The ordinary and the extraordinary refractive indices are determined by using light of transverse electric (TE) and transverse magnetic (TM) polarization, respectively. From the angular position of TE or TM guided modes, we deduced the corresponding effective indices as shown in Table 1. These values are used to compute the thin film parameters, such as refractive index and thickness [15]. We found that  $n_{TE} = 2.2341$ ,  $n_{TM} = 2.4129$  and the film thickness  $d = 1.009 \mu\text{m}$ . These results are in rather good agreement with the values obtained from the optical transmittance measurement.

To analyze the film homogeneity and the interface film–substrate, we have reconstructed the index profile directly from the optical waveguiding information using an improved version of the inverse Wentzel–Kramer–Brillouin (iWKB) method [16]. This method only depends on the refractive index distributions within the waveguiding layer. Using the polynomial interpolation of the measured effective indices, we calculated the refractive index profiles as a smooth function of the thickness. As shown in Fig. 6, the index is maximum at the surface and remains fairly constant throughout the thickness and decreases rapidly near the film/substrate interface. This index characteristic indicates uniformity of the index with depth with a perfect step change in index at the interface [17].

#### 4. Conclusion

In summary, LBTN-0.75 thin films with layered perovskite structure were prepared on fused silica by pulsed laser deposition

method. The optical constants were determined from the transmittance spectra using the envelope method. The optical bandgap energy was found to be 3.46 eV. The dispersion curve in the refractive index was fitted by the Sellmeier dispersion relation and described by an electronic oscillator model. The average position  $\lambda_0$ , average strength  $S_0$ , and energy  $\varepsilon_0$  of the oscillator are 218 nm,  $6.96 \times 10^{13} \text{ m}^{-2}$ , and 5.69 eV, respectively. From the linear refractive index curve, the refractive index of LBTN-0.75 films at 632.8 nm is 2.18, which is the same as those obtained from the prism-coupling technique. The refractive indices were determined to be  $n_o = 2.2341$  and  $n_e = 2.4129$  at 632.8 nm. The index of the LBTN-0.75 films was found to be homogeneous within the films. The favorable optical waveguiding performance achieved in the LBTN-0.75 film deposited on fused silica implies the possibility of using the waveguiding film for integrated optics and optically active devices.

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#### References

- [1] L. Pardo, A. Castro, P. Millan, C. Alemany, R. Jimenez, B. Jimenez, *Acta Mater.* 48 (2000) 2421.
- [2] S.H. Hong, S. Trolier-Mckinstry, G.L. Messing, *J. Am. Ceram. Soc.* 83 (2000) 113.
- [3] B.H. Park, B.S. Kang, S.D. Bu, T.W. Noh, J. Lee, W. Jo, *Nature (London)* 401 (1999) 682.
- [4] C.A. Paz de Araujo, J.D. Cuchiaro, L.D. McMillan, M.C. Scott, J.F. Scott, *Nature* 374 (1995) 627.
- [5] B. Yang, Y.P. Wang, F. Wang, Y.F. Chen, S.N. Zhu, Z.G. Liu, W.W. Cao, *Appl. Phys. A* 81 (2005) 183.
- [6] J. Yin, Z.C. Wu, Z.L. Wang, Y.Y. Zhu, Z.G. Liu, *J. Phys. D: Appl. Phys.* 31 (1998) 3185.
- [7] S.K. Kim, M. Miyayama, H. Yanagida, *Mater. Res. Bull.* 31 (1996) 121.
- [8] Z.Y. Zhou, X.L. Dong, H.X. Yan, *Scripta Mater.* 55 (2006) 791.
- [9] U. Pal, D. Samanta, S. Ghoral, A.K. Chaudhuri, *J. Appl. Phys.* 74 (1993) 6368.
- [10] J.C. Manificier, J. Gasiot, J.P. Fillard, *J. Phys. E* 9 (1976) 1002.
- [11] R. Swanepoel, *J. Phys. E: Sci. Instrum.* 16 (1983) 1214.
- [12] M. Didomenico, S.H. Wemple, *J. Appl. Phys.* 40 (1969) 720.
- [13] P.K. Tien, R. Ulrich, J.R. Martin, *Appl. Phys. Lett.* 14 (1969) 291.
- [14] E. Dogheche, D. Remiens, A. Boudrioua, J.C. Loulergue, *Appl. Phys. Lett.* 74 (1999) 1209.
- [15] R. Ulrich, R. Torge, *Appl. Opt.* 12 (1973) 2910.
- [16] K.S. Chiang, *J. Lightwave Technol.* 3 (1985) 85.
- [17] E. Dogheche, B. Belgacem, D. Remiens, P. Ruterana, F. Omnes, *Appl. Phys. Lett.* 75 (1999) 3324.