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Large nonlinear optical response of a $Bi_{1.5}Zn_{1.0}Nb_{1.5}O_7$ thin film fabricated by pulsed laser deposition

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ABSTRACT

The $Bi_{1.5}Zn_{1.0}Nb_{1.5}O_7$ (BZN) thin film has been fabricated on MgO (001) substrate by pulsed laser deposition. The nonlinear optical properties of the BZN film were investigated using Z-scan technique at a wavelength of 532 nm with 25 ps pulse duration. The two-photon absorption coefficient and the nonlinear refractive index of the BZN film were obtained to be 4.2×10^{-6} cm/W and 1.6×10^{-10} cm^2/W respectively, which are comparable with those of some representative nonlinear optical materials. The large and fast response optical nonlinearities indicated that the BZN film is a promising candidate for future photonics devices.

1. Introduction

Bismuth-based oxide materials have recently attracted much attention due to their excellent electric–magnetic and optical properties for applications such as ferroelectric random access memory devices, high-frequency tunable devices, nonlinear optical devices and integrated photonics [1–5]. Over the past few years, many bismuth-based oxide materials have been widely studied. For example, $BiFeO_3$ and $BiMnO_3$ are extensively investigated as multiferroic materials [6] and large second- and third-order nonlinear optical properties were obtained [7–9]. $SrBi_2Ta_2O_9$ and $Bi_{3.25}La_{0.75}Ti_3O_{12}$ are well-known candidates for nonvolatile memory devices because of their fatigue-free properties [1,2]. The gigantic third-order optical nonlinearities were found in $SrBi_2Ta_2O_9$ and $Bi_{3.25}La_{0.75}Ti_3O_{12}$ films [10–13]. Large quadratic electro-optic coefficient and nonlinear refractive index in $Bi_4Ti_3O_{12}$ [14,15], $Bi_2Nd_2Ti_3O_{12}$ [5], $SrBi_2Nb_2O_9$ [16], $BaBi_4Ti_4O_{15}$ [17] films also were reported.

$Bi_{1.5}Zn_{1.0}Nb_{1.5}O_7$ (BZN) with cubic pyrochlore structure has attracted special interest as a dielectric material for microwave tunable applications due to its high permittivity and low loss [3,18]. The dielectric and some linear optical properties of BZN ceramics and films have been widely studied [19–21]. However, the nonlinear optical properties of BZN thin films have not been investigated thus far. In this paper, we report large third-order optical nonlinearity of BZN thin films using Z-scan method with pulse duration of 25 ps at 532 nm. The large third-order nonlinear optical response within picosecond time scale was obtained. The results show that the BZN film is a promising material for applications in nonlinear optical devices, especially the hybrid optical/electronic devices.

2. Experimental details

The BZN thin film was grown on MgO (001) substrate by pulsed laser deposition (PLD) technique. A stoichiometric $Bi_{1.5}Zn_{1.0}Nb_{1.5}O_7$ target sintered by conventional ceramic processing was used. A XeCl excimer laser (308 nm, 30 ns, 4 Hz) with the laser energy intensity of about 2 J/cm^2 was used to ablate the target. The distance of substrate to target was kept at 50 mm. The film was deposited at 700 °C under 30 Pa oxygen pressure, followed by annealing of 30 min at the 550 °C at pure oxygen. The thickness of the BZN film was measured to be $L = 0.45$ µm by a Dektak 8 surface stylus profiler (Veeco Company, USA).

The crystalline structure of the film was analyzed using a X-ray diffractometer (MAC-M18AHF, Japan) with Cu Kα radiation at 1.54 Å (40 kV × 50 mA), in θ–2θ scan mode with the scanning step 10°/min. The surface morphology of the BZN film was investigated by an atomic force microscopy (AFM, Digital Instruments Nanoscope IIIa, USA) in contact mode with a NPS-type Si_3N_4 tip. The optical transmittance spectra of the samples were measured from 300 to 850 nm using a SpectraPro-500i spectrophotometer (Acton Research Corporation, USA) at room temperature.

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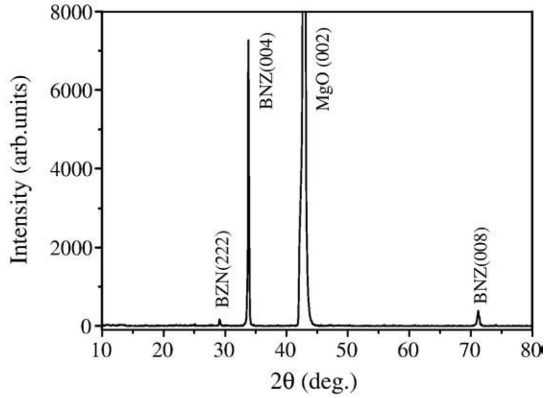

Fig. 1. XRD pattern of the BZN film on a MgO(001) substrate.

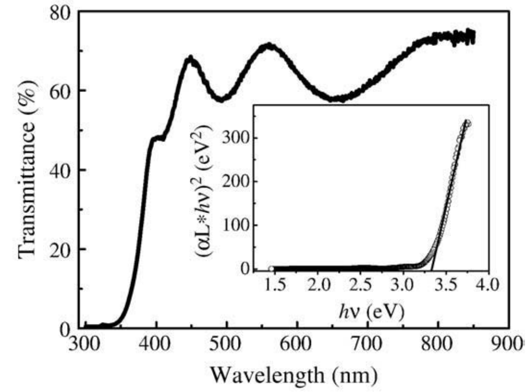

Fig. 3. Optical transmittance of the BZN film prepared on a MgO substrate. The relation $(\alpha L*h\nu)^2$ versus $h\nu$ is shown in the inset.

A single-beam Z-scan technique, which provided a sensitive method for the determination of the signs and values of the real and imaginary parts of third-order nonlinear optical susceptibility $\chi^{(3)}$, was employed for the optical nonlinearity measurements. The light source was a mode-locked Nd:YAG laser with a pulse duration of 25 ps and a wavelength of 532 nm. The p-polarized laser beam was a TEM_{00}-mode optical Gaussian spatial profile and was focused by a lens with a focal length of 150 mm. The radius of beam waist ω_0 was about 26 µm. The on-axis transmitted pulse energy, the reference pulse energy, and the ratios of them were simultaneously measured using an energy ratiometer (EPM 2000, Coherent Inc. USA). The laser repetition rate was set to 1 Hz to reduce the possible thermal accumulative effect. The measurement system was calibrated using CS_2 as standard. The absolute value of $\chi^{(3)}$ of CS_2 was obtained to be about 1.1×10^{-11} esu, which agrees well with the reported experimental result [22].

3. Results and discussion

Fig. 1 shows the X-ray diffraction (XRD) pattern of the BZN thin film. No other peaks except the peaks located at $2\theta = 29.13°$, 33.82°, and 71.21° were observed, which correspond to (222), (004), and (008) of BZN, indicating a pure phase [21] and *c*-axial preferred growth. The value of lattice constant was calculated to be 10.5865 Å from the above three peaks, which is slightly larger than that of the bulk material (10.553 Å) [21] because of the strain effect between the BZN film and the MgO substrate. Fig. 2 presents the AFM image of the sample. The root-mean-square (rms) surface roughness of the film in 2×2 µm^2 area is about 1.6 nm, suggesting a very smooth thin film.

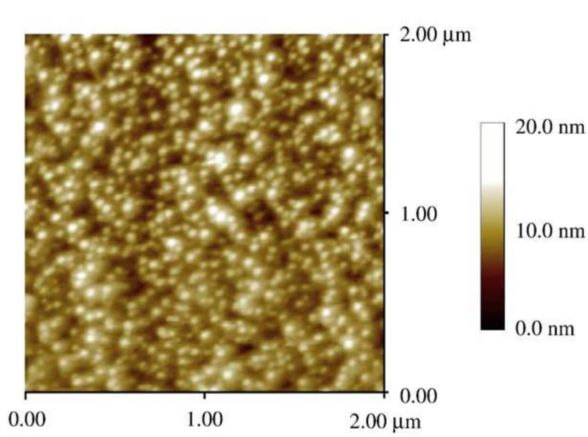

Fig. 2. Atomic force microscopy (AFM) image of the BZN thin film.

The optical transmittance spectra of the BZN film as the function of wavelength was shown in Fig. 3. The data were automatically corrected by the spectrophotometer accounting for the transmittance of the MgO substrate. The transmittance of the BZN film shows good transparency and decreases to zero at approximately 340 nm. The linear refractive index n_0 was determined from the transmittance curve using the envelope method [23]. The values of n_0 and absorption coefficient α of the film at 532 nm were calculated to be 2.42 and 7.8×10^3 cm^{-1}, respectively. The optical band gap (E_g) was determined using Tauc's formula assuming a direct transition between the bands. The relation $(\alpha L*h\nu)^2$ versus $h\nu$ is shown in the inset of Fig. 3, where $h\nu$ is the photon energy of incident light and L is the thickness of the film. The band gap of the BZN film was calculated be about 3.33 eV, which is somewhat larger than that of the bulk materials ($E_g = 2.87$ eV) [21]. The difference originated from the change of the lattice constant and Bi deficiency due to its relatively high volatility in the film deposition conditions [24,25].

Fig. 4 shows typical curve of Z-scan measurements. The dots are measured data with each point corresponding to the average value of 10 pulses. The solid lines represent theoretical fits [22]. The open-aperture curve shows a normalized transmittance valley, indicating

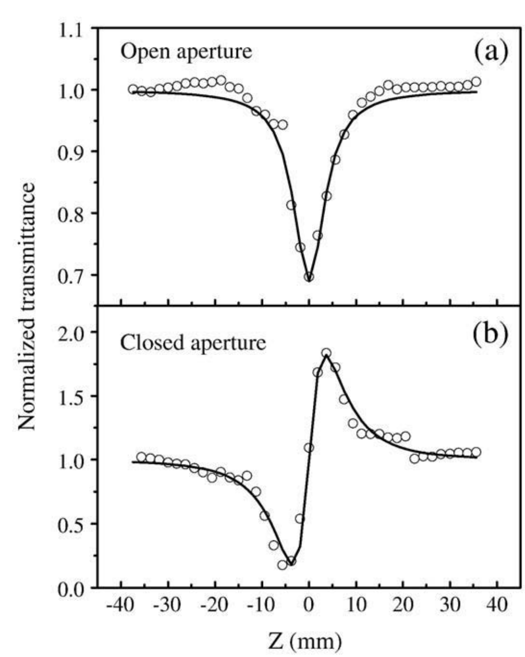

Fig. 4. Normalized (a) open-aperture and (b) closed-aperture Z-scan data of the BZN film. The solid lines indicate the theoretical fit.

the presence of nonlinear absorption in the BZN film. The closed-aperture profile, obtained after division of closed-aperture data with the open-aperture data to eliminate the contribution of nonlinear absorption, has a *valley-to-peak curve*, corresponding to a positive nonlinear refractive index.

The data were analyzed using the procedures described in Ref. [22]. The nonlinear absorption coefficient, β, and nonlinear refractive index, n_2, can be calculated from Fig. 4(a) and (b) by the relations,

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

$$\Delta T_{\mathrm{pv}}\approx 0.406(1-S)^{0.25}|\Delta\Phi_0|,\quad \text{for} |\Delta\Phi_0| \le \pi \tag{2}$$

$$\Delta\Phi_0=\frac{80\pi^2 n_2 I_0 L_{\mathrm{eff}}}{c n_0 \lambda} \tag{3}$$

where I_0 is the laser peak intensity, $L_{\mathrm{eff}}=[1-\exp(-\alpha L)]/\alpha$ is the effective thickness of the film (L is the sample thickness), α is the linear absorption coefficient of the sample, S, the linear transmittance of the aperture, is about 0.2, $\Delta T_{\mathrm{p-v}}$ is the difference between the normalized peak and valley transmittance. The calculated β and n_2 are 4.2×10^{-6} cm/W and 1.6×10^{-10} cm^2/W, respectively. The imaginary and real parts of $\chi^{(3)}$, Im $\chi^{(3)}$ and Re $\chi^{(3)}$, can be obtained to be 2.6×10^{-9}esu and 2.4×10^{-8} esu. The absolute value of $\chi^{(3)}$ of the BZN film was about 2.4×10^{-8} esu, which is comparable with the values of the other bismuth-based oxide thin films, such as Bi_2Nd_{2}-Ti_3O_{12} [5], $BiMnO_3$ [8], $Bi_{3.25}La_{0.75}Ti_3O_{12}$ [12,13], $SrBi_2Nb_2O_9$ [16] and among the best values of some other representative materials, such as V_2O_5 film [26], Au:TiO_2 film [27], PBTBQ copolymer [28] and so on.

Since the band gap E_g (3.33 eV) of the film is far from the one-photon energy of the Z-scan pump beam (532 nm, 2.33 eV), one-photon absorption can be ignored. Additionally, E_g is smaller than the two-photon energy (4.66 eV), so we believe that two-photon absorption (TPA) is the dominant mechanism of the nonlinear absorption. Because of the short pulse duration (25 ps), nonlocal contributions to the nonlinear refractive index, such as electrostriction and thermal effect, were insignificant because those effects have a response time much longer than 25 ps. The bound electronic Kerr effect and population redistribution associated with the two-photon absorption may be the main mechanism of nonlinear refraction. Further investigation would be required to determine the origin of optical nonlinearity of the BZN film precisely.

4. Conclusions

In conclusion, the BZN film with good surface morphology was grown on the MgO substrate by pulsed laser deposition technique. The nonlinear optical properties were determined using Z-scan method. The two-photon absorption coefficient and nonlinear refractive index were obtained to be 4.2×10^{-6} cm/W and 1.6×10^{-10} cm^2/W, respectively. The large optical nonlinearity and fast response time indicate that the BZN film is a promising candidate for applications in photonic devices, further for the hybrid optical/electronic devices due to its excellent dielectric properties.

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