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Large optical nonlinearities in BiMnO₃ thin films

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Large third-order optical nonlinearities were observed in epitaxial thin films of BiMnO₃ grown on SrTiO₃ substrates. Using 140 fs laser pulses at 900 nm, a negative nonlinear refractive index ($n_I \sim -0.53 \text{ cm}^2/\text{GW}$) and a nonlinear absorption coefficient ($\alpha_I \sim -0.08 \text{ cm/kW}$) for BiMnO₃ are measured at room temperature. Large electric-field-induced enhancement of three to four orders of magnitude in the second-harmonic response at 450 nm is observed with effective nonlinear coefficients of $d_{\text{eff}} \sim 40(115) \text{ pm/V}$ at 300 (473) K under applied fields of ~ 707 (177) V/mm, respectively, from a 110 nm multivariant thin film. © 2003 American Institute of Physics.
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Bismuth manganite is of interest since it is predicted to be a multiferroic, possessing ferroelectricity below ~ 750 K, and both ferroelectricity and ferromagnetism below 105 K.¹⁻⁴ The optical properties of BiMnO₃ (BMO) have not been reported thus far. In this letter, we report large third-order optical nonlinearities and giant field-induced second-order nonlinearities in thin films of BMO grown on SrTiO₃ (STO) substrates by the pulsed-laser deposition (PLD) technique. With these levels of optical nonlinearities, this material is a candidate for optical modulation.⁵⁻⁸

Epitaxial and *phase-pure* BMO thin films were synthesized by PLD on STO substrate using a bismuth-rich target.⁹ The films studied here are of BMO (111̄)/STO (111), with in-plane orientations of [1̄10] BMO/[101] STO (exact relation) and [112] BMO/[1̄12̄] STO (approximate relation). Typical film stoichiometry, as determined by Rutherford backscattering spectrometry (RBS), was slightly Bi deficient (Bi \sim 0.96–0.98). There were no amorphous or secondary phases as confirmed by transmission electron microscopy.¹⁰ Using a rotating-compensator spectroscopic ellipsometer, the (linear) refractive index n (in the film plane) and the extinction coefficient k for the film, with thickness of 93 nm, were determined over the wavelength range of 200 to 790 nm. We used the three-medium model of air/film/substrate (air/BMO/STO) to analyze the ellipsometric data. A function described by using two Lorentz oscillators was found to best fit to the data (Fig. 1), given by

$$\tilde{N} = (n + ik)^2 = \tilde{n}_\infty^2 + \sum_{i=1}^2 \frac{F_i^2}{E_{0i}^2 - E^2 - i\Gamma_i E}, \quad (1)$$

where \tilde{n} is the complex refractive index, $\tilde{n}_\infty^2 = 1.07 \pm 0.22$ and the other constants (in the units of eV) are given as $F_1 = 2.13 \pm 0.37$, $E_{o1} = 3.27 \pm 0.05$ and $\Gamma_1 = 1.69 \pm 0.30$ for oscillator 1 and $F_2 = 15.04 \pm 7.66$, $E_{o2} = 7.09 \pm 3.49$ and $\Gamma_2 = 26.31 \pm 25.94$ for oscillator 2. The large error bars in the parameters of oscillator 2 are due to the fact that its resonance frequency lies well outside the measured spectral range. There are no data over ~ 7 eV due to weak reflection

of the sample. Specifically, we obtain the linear complex indices to be $\tilde{N}_f^\omega = 2.217 + 0.56i$ and $\tilde{N}_f^{2\omega} = 1.88 + 0.8i$ for corresponding wavelengths of 900 and 450 nm, respectively.

A single-beam Z-scan technique⁹ was employed for nonlinear refraction, (index change, $\Delta n = n_I I_o$) and nonlinear absorption (absorption change, $\Delta \alpha = \beta I_o$) measurements at room temperature, where I_o is the incident intensity on the film. The light source was a mode-locked Ti:sapphire laser with a repetition rate of 82 MHz, a pulse width of 140 fs at the sample, and a wavelength of 900 nm. The light beam was a TEM₀₀-mode optical Gaussian spatial profile and was focused by a lens with a focal length of 100 mm. The radius w_o at the beam waist was 16 μm . The transmittance of the sample was simultaneously measured with and without an aperture at the far-field of the lens. The signal was acquired by lock-in detection mode with a chopper placed before the focusing lens and used for reference.

Figure 2 shows the Z-scan data at wavelengths of 900 nm, for a BMO film of 122 nm thickness. The incident light was linearly polarized and parallel to the STO [1̄12̄] sub-

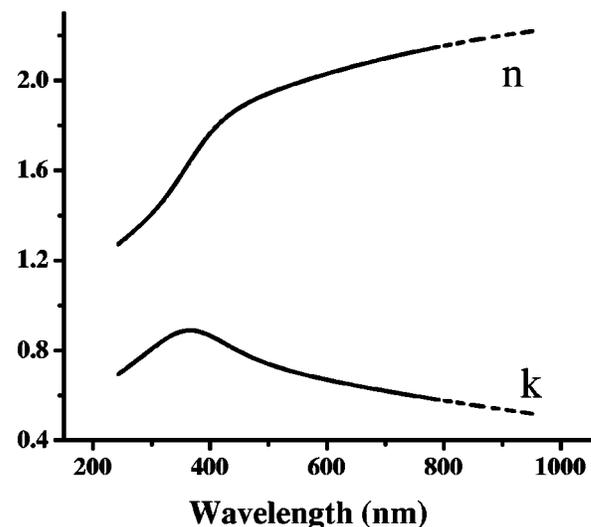


FIG. 1. Dispersion curves of BiMnO₃(111̄) film as obtained from the spectroscopic ellipsometry. Data from 200 to 790 nm are fit to the experimental transmission curves and the data shown as dashed lines from 790 to 950 nm wavelength ranges are extrapolated using the fitted function.

^{a)}Deceased.

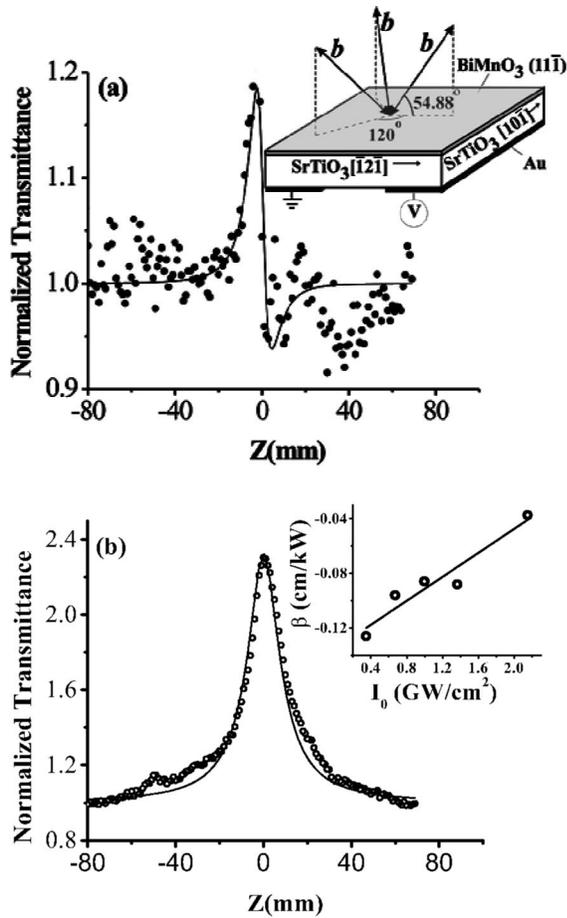


FIG. 2. Z-scan traces for a BMO thin film deposited on a STO substrate. (a) Ratio of closed aperture data to open aperture data and (b) open aperture data. The peak intensity was 1.3 GW/cm^2 at the focus of the laser beam at 900 nm and 140 fs pulse width. Inset in (a) shows the schematic of the crystallographic orientation of the film deposited on the STO substrate. The arrows projecting out of the (111) plane at an angle of 58.44° show the possible orientations of ferroelectric polarization in the film, with threefold symmetry between them in the growth plane. Au electrodes were deposited on the substrate side such that the electric field applied is parallel to the $[\bar{1}21]$ substrate edge and hence along the projection of one set of probable ferroelectric polarization in the growth plane. Incident light is linearly polarized and parallel to the $[\bar{1}21]$ edge of the substrate. Inset in (b) shows the β dependence on the peak incident intensity I_0 .

strate edge. The closed aperture Z-scan spectrum with $S = 0.09$ (where S is ratio of the linear transmittance of the closed aperture to that of open aperture) was strongly modulated by the nonlinear absorption. As seen in Fig. 2(a), the ratio of closed to open aperture signals was still dominated by the nonlinear absorption. The signature of negative optical nonlinearity is seen with the typical peak preceding the valley. The scans are corrected for the background. Open aperture data in Fig. 2(b) shows strong nonlinear absorption with a negative absorption coefficient. The increase in transmittance with incident power shows a typical *saturable absorption* type of optical nonlinearity. The β and n_1 were determined from open aperture data and closed to open aperture ratio, respectively. The nonlinear refractive index $n_1 \sim -0.53 \text{ cm}^2/\text{GW}$, and the nonlinear absorption $\beta \sim -0.08 \text{ cm/kW}$ were determined using the theoretical fits. These fits in Fig. 2 are based on Ref. 11 and the notations used therein. For $\beta \sim -0.08 \text{ cm/kW}$, $I_0 \sim 2.16 \text{ GW/cm}^2$ and $L_{\text{eff}} \sim 0.085 \mu\text{m}$, we have $|\beta I_0 L_{\text{eff}}| > 1$ in our case. Therefore,

we used the analytical expression for the normalized transmission (Eqs. 29 and A2 in Ref. 11) rather than the truncated series of binomial expression. The effective $\chi^{(3)}$ ($-\omega; \omega, \omega, -\omega$) is $-(6.6 + 7.13i) \times 10^{-8} \text{ esu}$.

The maximum decrease in absorption coefficient ($\Delta\alpha$) with peak intensity of 1.3 GW/cm^2 at focus is $\sim 8 \times 10^4 \text{ cm}^{-1}$. The maximum decrease in nonlinear index (Δn) with peak intensity of 1.3 GW/cm^2 is 0.689 . The inset in Fig. 2(b) shows the linear dependence of β with incident peak intensity as obtained from open aperture Z-scan for this film. It hints at higher order contributions to the third order nonlinear optical signal, with $d\beta/dI_0 \sim 43.89 \times 10^{-9} \text{ cm}^3/\text{W}^2$. Earlier both open and closed aperture Z-scan was performed on a blank substrate of STO. Blank substrates which are subject to the same conditions as during bismuth manganite film deposition (heated for 42 min at 755°C in 150 mTorr O_2 followed by quenching to room temperature), but without actually growing the film, do show a third-order response, with values of $n_1 \sim 0.63 \times 10^{-4} \text{ cm}^2/\text{GW}$ and $\beta \sim -1.3 \times 10^{-5} \text{ cm/kW}$. The substrate contribution to the nonlinearity and hence the transmittance was subtracted from that of film-plus-substrate sample response in order to deduce the just-reported estimates for the BMO film.

Z-scan studies of the film were performed at various chopper frequencies such as 3.24 kHz , 1.44 kHz , and 97 Hz . No change in the signal was observed even at the slowest of frequencies (97 Hz), indicating that the signal is essentially due to the material response and not thermal in origin. No nonlinear scattering was observed as the BMO film was traversed along the propagation direction. X-ray diffraction of the BMO film was done at the spots where Z-scan was carried out and it did not result in any changes in the spectrum before and after the scan, suggesting that there has not been any change in the structural phases of the film due to laser heating. There was no visible damage to the optical quality of the film, or any change in the linear transmittance after the Z-scan study was done.

To further probe the optical nonlinearity, we probed the film response under external electric fields and measured the Z-scan signal. The BMO film shows dielectric loss ($\tan \delta \sim 150$) at room temperature. Therefore we deposited gold electrodes pads separated by 2 mm on the substrate side, allowing for the clearance of the beam for the Z-scan experiment. The substrate was about 0.90 mm thick. The electrode orientation was such that the applied field was parallel to the $[\bar{1}21]$ edge of STO [see Fig. 2(a) inset]. The Z-scan signal was monitored with the field applied. We observed a decrease in the peak transmittance by about 10% when a field of $\pm 1.5 \text{ kV}/2 \text{ mm}$ was applied for the open aperture case. The estimated field at the film is about 523 V/mm obtained at the interface by ignoring the presence of the film. This decrease in peak transmittance was independent of the polarity of the field applied. This could be partly explained if we assume that the large nonlinearities are due to highly polarizable electronic species (such as bismuth) in the material. With a bias field on, the medium gets partially polarized, thereby suppressing additional polarizability due to the light field and reducing $\chi^{(3)}$ nonlinearity.

We also probed the film using the second-harmonic gen-

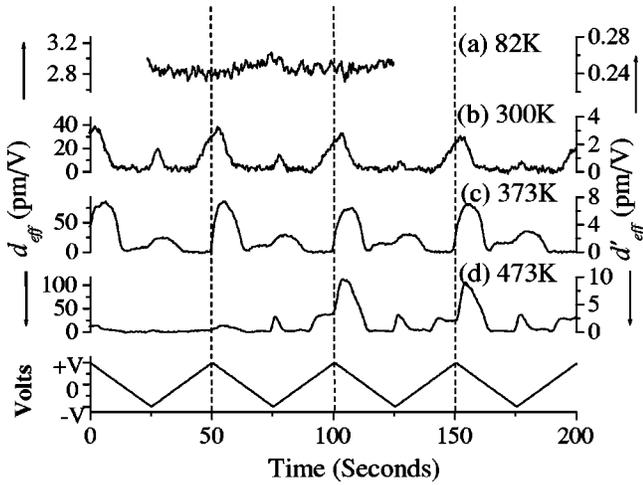


FIG. 3. SHG signal as a function of triangular voltage wave form applied at specific temperatures indicated. Maximum applied voltages across the 2 mm electrodes gap are $V = \pm 2$ kV at 82 K (a), 300 K (b), and 373 K (c), and ± 500 V at 473 K (d). At room temperature (300 K) without any field applied, d'_{eff} was found to be 0.11 pm/V.

erated (SHG) signal, as these are also noncentrosymmetric with proven ferromagnetism below 105 K⁹ and likely ferroelectricity¹ below 770 K. When a triangular ramp voltage with ± 2 kV across the 2-mm-gap electrodes was applied to the film from the substrate side (approximate field at the film ~ 707 V/mm), an asymmetric enhancement of the SHG signal with the polarity of electric field is seen. This asymmetry also changes with repeated voltage cycles, indicating a changing microstructural bias in the film consistent with domain reversal in a ferroelectric microstructure. (No SHG signals were observed for blank substrates at any of the temperatures studied.) In addition, we find that the enhancement of the SHG signal under field increases with temperature. Measurements at four different temperatures of 82, 300, 373, and 473 K were carried out (Fig. 3). We quantify the enhanced SHG signal in terms of d'_{eff} by comparing the maximum signal with that for a z -cut LiTaO₃ using the $d_{22} = 1.672$ pm/V coefficient of the latter in the following equation:^{12,13}

$$d_{\text{eff}}^2 = d_r^2 \left(\frac{P_f^{2\omega}}{P_r^{2\omega}} \right) \left(\frac{P_r^\omega T_r^\omega}{P_f^\omega T_f^\omega} \right)^2 \frac{A_f}{A_r} \left(\frac{n_f^\omega}{n_r^\omega} \right)^2 \frac{n_f^{2\omega}}{n_r^{2\omega}} \left(\frac{l_{c,r}}{l_{c,f}} \right)^2 \frac{e^{-\alpha_r^{2\omega} l_{c,r}}}{e^{-\alpha_f^{2\omega} l_{c,f}}}, \quad (2)$$

where subscripts r and f refer to the reference and the film, respectively, $P^{2\omega}$ (P^ω) are the second-harmonic (fundamental) signal powers measured, T is the transmission coefficient of the fundamental, A is the area of the probed beam, n are the indices of refraction, l_c the coherence lengths, and α the absorption coefficient of the film at 2ω . The SHG signal detected gets averaged over various contributions of different domains probed by the beam as it propagates through it. The beam diameter is 126 μm . The ferroelectric domain size is currently not known, but is typically of the order of 100 nm in ferroelectric thin films.^{12,14}

We redefine Eq. (2) as $d_{\text{eff}}^2 = d_{\text{eff}}'^2 \exp(\alpha_f^{2\omega} l_{c,f} - \alpha_r^{2\omega} l_{c,r})$. For an as-deposited film, the $d_{\text{eff}}' \sim 0.11$ pm/V for the temperature range of 300 to 473 K under zero electric field. With a ± 2 kV/2 mm field applied, an enhancement of the SHG signal was observed, with maximum $d_{\text{eff}}' \sim 0.26$, 3.32, and 7.19

pm/V (enhancement factors of 3.5, 1420, and 6714 times, respectively, over the no-field signal) at temperatures of 82, 300, and 373 K, respectively (Fig. 3). At 473 K, we were only able to apply ± 0.5 kV/2 (approximate field at film ~ 177 V/mm) because of the large dielectric losses at higher temperatures. A maximum $d_{\text{eff}}' \sim 9.64$ pm/V (enhancement of 13 000 times) was obtained at 473 K. With the absorption of the SHG signal taken into account, the maximum coefficients were, $d_{\text{eff}} \sim 3.04$ pm/V (82 K), 39.63 pm/V (300 K), 85.83 pm/V (373 K), and 115.08 pm/V (473 K). These coefficients were obtained from the maximum-enhanced SHG signal during any cycle when it was subjected to a periodic triangular voltage wave form. We notice that the SHG signal strength shows time dependence when subject to a periodic wave form, resulting in different amounts of enhancement. To look at the buildup of the SHG signal under steady state conditions, we applied a step voltage of -2 kV at room temperature for ~ 30 min (not shown). There was an immediate enhancement of the SHG signal by 3000 times over a time scale of 22 s, followed by a slow saturation to a steady-state value, which was equivalent to an enhancement of ~ 35 000 times over the no-field signal, and an effective $d_{\text{eff}}' \sim 16.5$ pm/V and a $d_{\text{eff}} \sim 193$ pm/V. The observed field-induced changes in second harmonic response can arise from a rearrangement of ferroelectric domains as well as from third-order nonlinear optical response, $\chi^{(3)}(-2\omega; \omega, \omega, 0)$. The separation of these effects will require a less complex domain microstructure in the film.

To conclude we have observed large second- and third-order optical nonlinearities in BiMnO₃ thin films that can be affected by applying external electric fields potentially leading to interesting device applications based on its optical nonlinearity.

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- ¹A. Moreira dos Santos, S. Parashar, A. R. Raju, Y. S. Zhao, A. K. Cheetham, and C. N. R. Rao, *Solid State Commun.* **122**, 49 (2002).
- ²E. Ohshima, Y. Saya, M. Nantoh, and M. Kawai, *Solid State Commun.* **116**, 73 (2000).
- ³H. Faqir, H. Chiba, M. Kikuchi, Y. Syono, M. Mansori, P. Satre, and A. Sebaoun, *J. Solid State Chem.* **142**, 113 (1999).
- ⁴H. Chiba, T. Atou, and Y. Syono, *J. Solid State Chem.* **132**, 139 (1997).
- ⁵D. R. Liu, K. S. Wu, M. F. Shih, and M. Y. Chern, *Opt. Lett.* **27**, 1549 (2002).
- ⁶I. C. Khoo, P. H. Chen, M. Y. Shih, A. Shishido, S. Slussarenko, and M. V. Wood, *Mol. Cryst. Liq. Cryst.* **358**, 1 (2001).
- ⁷G. Yang, H. G. Tan, A. Jiang, Y. Zhou, and Z. Chen, *Appl. Opt.* **41**, 1729 (2002).
- ⁸Y. Z. Gu, W. F. Zhang, D. H. Gu, and F. Y. Gu, *Opt. Lett.* **26**, 1788 (2001).
- ⁹A. Moreira dos Santos, A. K. Cheetham, W. Tian, X. Pan, Y. Jia, N. J. Murphy, J. Lettieri, and D. G. Schlom, *Appl. Phys. Lett.* (submitted).
- ¹⁰A. Sharan, J. Lettieri, W. Tian, X. Pan, D. G. Schlom, and V. Gopalan, *Phys. Rev. B* (submitted).
- ¹¹M. Sheik Bahae, A. A. Said, T. H. Wei, D. J. Hagan, and E. W. Stryland, *IEEE J. Quantum Electron.* **26**, 760 (1990).
- ¹²Y. Barad, J. Lettieri, C. D. Theis, D. G. Schlom, V. Gopalan, J. C. Jiang, and X. Q. Pan, *J. Appl. Phys.* **89**, 1387 (2001); **89**, 5230 (2001).
- ¹³We note that the equivalent Eq. 11 in Ref. 12 has an error in the terms involving the order of coherence lengths $l_{c,r}$ and $l_{c,f}$.
- ¹⁴V. Gopalan and R. Raj, *J. Appl. Phys.* **81**, 865 (1997).