Enhanced femtosecond optical nonlinearity of Mn doped $Ba_{0.6}Sr_{0.4}TiO_3$ films

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We report the third-order optical nonlinearity of ferroelectric thin films of Mn doped $Ba_{0.6}Sr_{0.4}TiO_3$ using Z-scan measurement with femtosecond laser pulses at 800 nm. The nonlinear refraction index and two-photon absorption coefficient are measured to be 3.0×10^{-4} cm^2/GW and 1.7 cm/GW, respectively, which are about one order of magnitude larger than those of the undoped $Ba_{0.6}Sr_{0.4}TiO_3$ thin films. The enhancement is attributed to the acceptor behavior of Mn ions dopant. The figure of merit, T, defined by $T=\beta\lambda/n_2$, was calculated to be 0.44, less than 1. The results indicate that the thin films have great potential applications in nonlinear photonic devices. © *2011 American Institute of Physics*. [doi:10.1063/1.3527969]

I. INTRODUCTION

Ferroelectric materials are extensively studied for their numerous useful properties for applications such as ferroelectric random access memory devices, high-frequency tunable devices, integrated photonics, and nonlinear optical applications.[1–3] Ternary oxides barium strontium titanate $Ba_xSr_{1-x}TiO_3$ (BST) thin films represent an important class of ferroelectric materials, which possess excellent and tunable optical and electrical properties with their compositions and structures. BST thin films have been intensively investigated as an important material for applications in tunable microwave devices such as tunable phase shifters, filters, and antennas because of its high dielectric constant and relatively low dielectric loss.[4–6] BST thin films are also considered to be promising candidates for active waveguide applications since their high electro-optic coefficient and acceptable low optical losses.[7–9] The nonlinear optical properties, including second-optical and third-optical nonlinearity, were widely investigated at different wavelengths and time domains. The large nonlinear optical susceptibility indicates their good candidate materials for nonlinear photonics applications.[10,11] In recent years, BST thin films modified by the perovskite B-site acceptor were studied for microwave tunable device application given their low dielectric loss in the microwave frequency regime.[12–15] However, the influences of the B-site acceptor to the optical nonlinearity of the BST films have not been investigated to our knowledge. In this paper, we present our experimental investigations into the third-order nonlinear optical properties of the Mn doped $Ba_{0.6}Sr_{0.4}TiO_3$ ferroelectric thin films with femtosecond laser pulses.

II. EXPERIMENTS AND RESULTS

The Mn doped $Ba_{0.6}Sr_{0.4}TiO_3$ (Mn:BST) ferroelectric thin film was deposited on the (001) MgO substrate by pulsed laser deposition. The relevant 2% additional Mn doped $Ba_{0.6}Sr_{0.4}TiO_3$ ceramic target was prepared using conventional ceramic processing.[15] As for the deposition, a 308 nm XeCl excimer laser with laser energy about 2 J/cm^2 was used to ablate the ceramic targets. A 450 nm thick highly crystal Mn:BST film was grown on 0.5-mm-thick double-polished MgO substate at the temperature 750 °C with 10 Pa oxygen pressure. As for the comparison, an undoped $Ba_{0.6}Sr_{0.4}TiO_3$ (BST) film was also prepared under the same condition. The crystallization of the BST and Mn:BST films were characterized by x-ray diffraction (XRD), as shown in Fig. 1. Only BST and Mn:BST (00*l*)-type diffraction peaks together with the substrate MgO (002) peak were observed, indicating that the as-grown film is pure and c-axis orientation. The lattice parameter of updoped BST film is 3.9637 Å, which is smaller than Mn doped BST film, 3.9689 Å estimated from the (001) peak in the XRD spectra, as particularly shown in the inset of Fig. 1. The result indicated that Mn ions with larger radii induce the expansion of the lattice of BST thin film. The surface morphology of the Mn:BST film was measured by atomic force microscopy (AFM) (NANOSCOPE IIIA). The two dimensional image with the area 5×5 μm^2 was present in the inset of Fig. 1. The roughness of the film is about 5.5 nm.

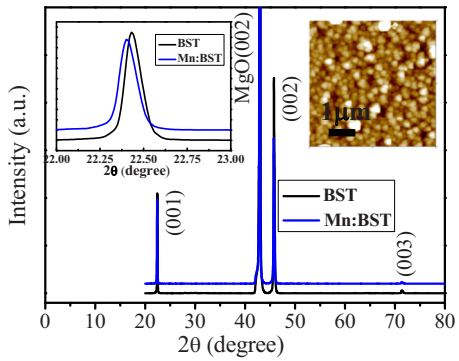

FIG. 1. (Color online) XRD patterns of undoped and Mn doped BST films. The left-up inset shows the detailed (001) peaks, and the right-up inset presents the AFM image of the Mn doped BST film.

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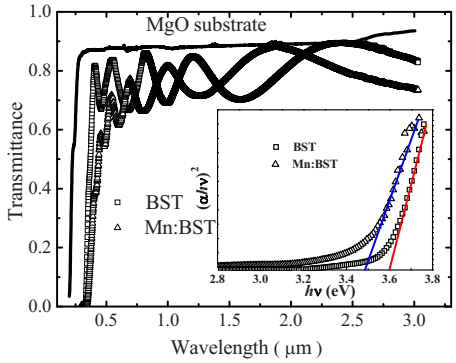

FIG. 2. (Color online) Optical transmittance spectra of the undoped and Mn doped BST thin film on MgO substrate. The inset shows the extrapolation of the relation of $(\alpha_0 h\nu)^2$ vs $h\nu$. The optical bandgaps E_g were estimated to be 3.6 eV and 3.48 eV for undoped and Mn doped BST films, respectively.

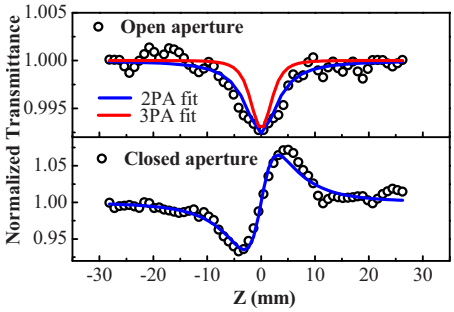

FIG. 4. (Color online) Z-scan curves measured at $I_0=354$ GW/cm^2 for the 450-nm-thick Mn doped BST film deposited on the 0.5-mm-thick MgO substrate. Open circles are the OA and CA Z-scan experimental data, and the solid lines are the best-fit curves. The OA data were fitted using two-photon (2PA) and three-photon (3PA), respectively.

The linear optical transmittance spectra of the Mn:BST and undoped BST thin films on the MgO substrate was recorded in the wavelength range of 0.3–3.0 μm at room temperature, as shown in Fig. 2. It is clear that the Mn:BST thin film is highly transparent in the visible and infrared wavelength region. Furthermore, the pronounced oscillation in the transmittance spectrum indicates that the Mn:BST thin film has a flat surface and good homogeneity. Figure 3 presents the linear refractive index n_0 of the Mn:BST and undoped BST film, which was determined from the transmittance curve using the envelope method. The solid lines show the Sellmeier-type dispersion fitting.[16] The value of n_0 and linear absorption coefficient α_0 of Mn:BST film were determined to be about 2.25×10^3 cm^{-1} and 8.5×10^3 cm^{-1} at 800 nm, respectively. The optical band gap (E_g) of the films can be estimated using the formulae $(\alpha_0 h\nu)^2=\text{Const}\ (h\nu-E_g)$ assuming a direct transition between valence and conduction band, where $h\nu$ is the photon energy of incident light. We obtained the $E_g=3.48$ eV and 3.6 eV for Mn:BST and undoped BST films, respectively, by the extrapolation of the relation of $(\alpha_0 h\nu)^2$ versus $h\nu$, shown in the inset of Fig. 2.

The nonlinear-optical measurements were performed by using single beam Z-scan technique.[17] The femtosecond laser pulses were obtained from a conventional chirped pulse amplification system comprising of an Ti:sapphire oscillator (Tsunami, Spectra-Physic Inc.) that delivered laser pulses

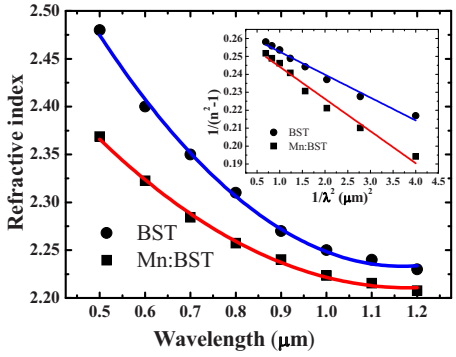

FIG. 3. (Color online) Wavelength dependence of the linear refractive index of the undoped and Mn doped BST thin film. The dots and squares are the calculated data and the solid lines are the theoretical fittings by the Sellmeier-type formulae.

with pulse duration 120 fs, 82 MHz at 800 nm and a regenerative Ti:sapphire amplifier (TSA-10, Spectra-Physic Inc.), from which we obtained 10 Hz amplified pulses of about 200 fs. The spatial distribution of the pulses, measured with a laser beam diagnostics system (Spiricon Inc. USA), was nearly Gaussian after passing through a spatial filter. Furthermore, the temporal profile of the pulses was also nearly Gaussian as confirmed by autocorrelation measurements. The data are not shown here.

The laser pulses were focused onto the sample with a minimum beam waist (ω_0) of 30 μm. The Rayleigh length z_0 was calculated to be 3.5 mm, which was much longer than the film plus substrate thickness. The transmitted-beam energy, the reference beam energy, and the ratios of them were simultaneously recorded using an energy ratiometer (EPM 2000, Coherent Inc.) to remove the laser fluctuations. The closed-aperture (CA) and open-aperture (OA) Z-scan curves were obtained, respectively, with and without an aperture placed in front of the detector. For the CA Z-scans, the linear transmittance of the far-field aperture was fixed at 20% by adjusting the aperture radius. The Z-scan measurement system was calibrated with ZnSe single crystal.

OA and CA Z-scan measurements were performed first on a 0.5 mm MgO to exclude the optical nonlinearity from the substrate at the peak intensity $I_0=354$ GW/cm^2. There were no obvious peaks or valleys for the typical Z-scan curves, indicating the optical nonlinearity of the MgO substrate was too small to be detected under the condition. The reasons may be the extremely large optical bandgap of MgO crystal (7.7 eV, about five times as the incident photonic engery 1.55 eV) and low high order process under the incident laser intensity (about one-tenth of the value of peak irradiance in Ref. 11). Figure 4 shows the typical OA and CA Z-scan curves of the Mn:BST film on MgO substrate at the above peak intensity. The optical loss due to Fresnel reflection on the air/film and film/MgO interface has been taken into account. Each point corresponded to the average value of 50 pulses, and the solid lines represent theoretical fits. It has to be emphasized that the bandgap (E_g) of the films is 3.48 eV, which satisfies $2\hbar\nu<E_g<3\hbar\nu$ ($\hbar\nu=1.55$ eV, the photon energy corresponding to 800 nm wavelength), suggesting the probable three photon engaged nonlinear absorption process.[18] The OA data were fitted by using two-photon

and three-photon absorption, $T_{OA(2PA)}=1/(1+\alpha_2 L_{eff}(I_0/(1+(z/z_0)^2))$ and $T_{OA(3PA)}=1/[1+2\alpha_3 L'_{eff}(I_0/(1+(z/z_0)^2))^2]^{1/2}$, where $L_{eff}=1-e^{-\alpha_0 L}/\alpha_0$ and $L^{\varphi}_{eff}=1-e^{-2\alpha_0 L}/2\alpha_0$ are the effective thickness of the film for two-photon and three-photon absorption, respectively.[19] Obviously, the two-photon absorption fits the experimental data well, indicating the presence of some trap or defect states between the conduction and valence bands, as reported.[20] The optical nonlinearity of Mn:BST film mainly contributes to the curves because of the undetected weak nonlinear optical response from MgO substrate. The valley-shaped OA and valley-peak shaped CA curves indicated positive nonlinear absorption and refractive index for the Mn:BST film. The nonlinear optical absorption coefficient can be obtained by the related formulas.[17,21] The calculated β and n_2 were 1.7 cm/GW and 3.0×10^{-4} cm^2/GW, which are among the best values of some representative nonlinear optical materials measured at the same conditions.[22–24] The relations of normalized transmittance T for OA and ΔT_{p-v} for CA as a function of incident intensity were obtained when I_0 varied from 180 to 530 GW/cm^2. The linear relation with no significant deviation from the intensity dependence indicated the cubic nonlinearity.

We estimate the real and imaginary parts of the third-order nonlinear susceptibility $Re\chi^{(3)}=5.5\times10^{-15}$ cm^2/V^2 and $Im\chi^{(3)}=2.0\times10^{-16}$ cm^2/V^2 from the value of n_2 and β. The figure of merit (FOM), T, defined by $T=\beta\lambda/n_2$, was calculated to be 0.44, which meets the essential requirement of all-optical switching devices.[25,26] The results suggests that the Mn:BST thin film with such large optical nonlinearities and predominant FOM should have a great potential for nonlinear photonic devices.

The optical nonlinearity of pure $Ba_{0.6}Sr_{0.4}TiO_3$ thin film was also studied in our platform. The almost same values of nonlinear absorption and refraction of pure BST, as measured in Ref. 11, were obtained. It is worth noting that the values of β and n_2 of the Mn doped BST films were about twenty and five times larger than the values of the pure BST film measured at 790 nm, respectively.[11] The enhanced optical nonlinearity could be ascribed to the acceptor behavior of Mn ions dopant, which prevented reduction in Ti^{4+} to Ti^{3+} by neutralizing the donor action of oxygen vacancies (Vö).[13–15] According to the bond-orbit theory for transition-metal oxides, the high nonlinear refraction of BST is ascribed to the hyperpolarizability of the Ti–O pairs, which is attributed to the large number of low-lying, empty 3*d* electronic states of Ti^{4+} ions, providing conduction-band states derived from both their outer *d* and *s* shells.[27,28] Generally, decrease in Ti^{4+} in pure BST films causes decrease in unoccupied *d* electronic states, leading to reduction in the nonlinear refraction index.

We believe that the Mn ions and other ions dopant as the acceptor in $Ba_xSr_{1-x}TiO_3$ films for $0<x<1$ should play the same role in the prevention of Ti^{4+} to Ti^{3+}, which could reduce the dielectric loss and enhance the third-order optical nonlinearity in the films. The optimization of optical nonlinearity and FOM in ions doped $Ba_xSr_{1-x}TiO_3$ $(0<x<1)$ films will be studied further.

III. CONCLUSIONS

We have investigated the third-order optical nonlinearity of Mn doped BST thin film using Z-scan measurement with femtosecond laser pulses. The enhanced optical nonlinearity of the films, compared with that of the pure BST films, is attributed to the acceptor behavior of Mn ions dopants. The large third-order optical nonlinearity and prominent FOM show that the Mn doped BST thin films have great potential applications in nonlinear photonic devices.

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