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Linear and nonlinear optical properties of rare earth doped of $Ba_{0.7}Sr_{0.3}TiO_3$ thin films

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Abstract $Ba_{0.7}Sr_{0.3}TiO_3$:Eu ferroelectric films were deposited on quartz substrates by pulsed laser deposition. The linear absorption coefficient and the linear refractive index calculated from the transmission spectrum at 532 nm were found to be 1.67×10^4 cm^{-1} and 1.82 respectively. The room temperature photoluminescence shows the characteristic emission of Eu^{3+} ions. The nonlinear optical properties of the film were investigated by a single beam Z-scan setup. The negative nonlinear refractive index and two photon absorption coefficient was found to be -1.508×10^{-6} m^2/GW and 240 m/GW respectively. The real and imaginary part of the third order susceptibility of the thin films is 2.58×10^{-17} m^2/V^2 and 1.16×10^{-16} m^2/V^2 respectively. The BST:Eu thin films show good optical limiting property.

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1 Introduction

Thin films of $Ba_{0.7}Sr_{0.3}TiO_3$ have been intensively studied for application in high density dynamic random access memories (DRAMs), monolithic microwave integrated circuit used for capacitors, tunable microwave filters and phased array antennas [1–3].

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Materials exhibiting nonlinear properties are of much interest, in particular those exhibiting strong nonlinear optical absorption as an optical limiting material. Optical limiting materials find potential application for the protection of eyes and optical sensors against damage on exposure to sudden intense light, since they provide a very fast response and generally show relatively high linear transmission. The mechanism producing nonlinear absorption is the reverse saturable absorption (RSA) or excited state absorption or two photon absorption [4].

$Ba_{(1-x)}Sr_xTiO_3$ (BST) thin films exhibit large microwave tunability up to 23.7 GHz [3]. This feature had motivated the study of nonlinear dielectric properties of these materials in the optical frequency region. The electro-optic (EO) characterizations of BST films reveal an EO coefficient with a very large saturation value of the field-induced birefringence at the wavelength of 632.8 nm [5]. Optical second-harmonic generation (SHG) has also been observed in the NIR (near infra-red) wavelength of 1.06 μm [6] using a Q-switched Nd-YAG laser and at 760 nm using mode-locked Ti:Sapphire laser [7, 8]. A thin film of BST shows nonlinear optical absorption and refraction and hence is a good candidate for nonlinear application. The nonlinear optical absorption and refraction of the polycrystalline $Ba_{0.7}Sr_{0.3}TiO_3$ film on quartz substrate have been reported as 1.2×10^{-6} m/W and 1.08×10^{-15} m^2/V^2, respectively [9]. But the nonlinear absorption and refraction coefficients of epitaxial $Ba_{0.6}Sr_{0.4}TiO_3$ thin films grown on MgO are much lower [10]. The large values of the nonlinear optical absorption and refraction observed for the BST polycrystalline film have been attributed to the small grain size and good homogeneity [9].

Rare earth (RE) ions exhibit a characteristic intra 4f shell luminescence which is almost insensitive to host material and temperature. This feature can be used to tune the emission color by the appropriate choice of rare earth dopant ions in the host material [11]. Barium strontium titanate is a dielectric material with excellent dielectric properties such as a high dielectric constant, small loss and with large breakdown strength. Hence it is a good material. BST:Eu ceramics has been reported to show excellent luminescent properties at room temperature for application in optoelectronic devices [12] but there is no report on the nonlinear optical properties of rare earth doped ferroelectric materials. In this paper we report the linear and nonlinear optical studies on pulsed laser deposited luminescent BST:Eu thin films.

2 Experimental

The target for pulsed laser deposition (PLD) was prepared by solid-state reaction of barium titanate ($BaTiO_3$), strontium titanate ($SrTiO_3$) and europium oxide (Eu_2O_3). The mixture was sintered at a temperature 1450°C in air for 5 hrs to obtain $Ba_{0.7}Sr_{0.3}TiO_3$:Eu (BST:Eu) target with Eu 3.5 wt%. The fourth harmonics of a Q-switched Nd: YAG laser (266 nm) was used for ablation. The repetition frequency was 10 Hz with a pulse width of 6–7 ns. The laser fluence was kept at 2 J/cm^2. The target to substrate distance was kept at 3.5 cm. The substrate temperature (T_s) was kept at 300°C. The oxygen partial pressure in the chamber was maintained at 0.1 mbar. The as deposited films were amorphous and were annealed in oxygen ambience at 600°C for 1 hr, which resulted in pervoskite phase.

The crystallinity of the thin films was determined by X ray diffraction (XRD) using CuK$_\alpha$ radiation ($\lambda = 1.5418$ Å). The thickness of the samples was measured using Dektak 6M surface profiler. Room temperature photoluminescence (PL) and photoluminescence excitation (PLE) studies were carried out using fluorimeter (Horiba Jobin Yuon Floromax-3). The optical transmittance spectra of the samples were recorded in the range 190–1800 nm using (Jasco V-570) UV-vis-NIR spectrophotometer. A single beam Z-scan technique was employed for nonlinear absorption and nonlinear refraction measurements at room temperature.

A single Gaussian laser beam in tight focus geometry as depicted in Fig. 1 was used to measure the absorption and refraction of a medium in the far field as a function of the sample position z measured with respect to the focal plane. A beam splitter was used to get the transmitted and the reference beam simultaneously. The light intensity transmitted across the nonlinear material is measured through an aperture in front of the detector (closed Z-scan) to measure the magnitude and sign of the nonlinear refractive index. The transmitted beam detected without the aperture (open aperture Z-scan) gives the nonlinear absorption [13].

In the present study the second harmonics of a Q-switched Nd:YAG laser at 532 nm having a repetition rate of

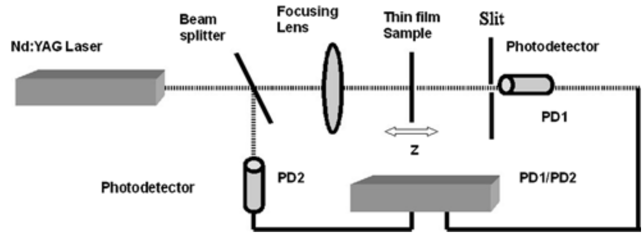

Fig. 1 Single beam Z-scan setup

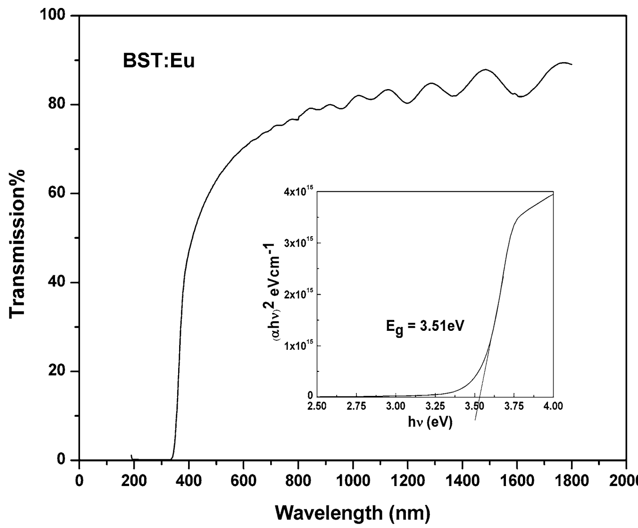

Fig. 2 Transmission spectra of BST:Eu thin film. The *inset* shows the $(\alpha h\nu)^2$ versus hν plot

10 Hz was used as the light source. The focal length of the lens used was 25 cm. Using a translation stage the sample was moved in a spatially varying intensity region on either side of the focus of the laser beam. The transmitted and reference energies can be measured using probe heads PD_1 and PD_2 of the energy ratio-meter. The entire setup is automated using LabVIEW.

3 Results and discussion

The xrd pattern (not shown) of BST:Eu thin films deposited on fused quartz substrate showed to be of a polycrystalline nature with pervoskite structure. The grain sizes of the films were calculated using Scherrer's formula from (1),

$$d = \frac{0.9\lambda}{\beta \cos\theta}, \tag{1}$$

where d is the grain size, λ is the wavelength of the X ray used, β is the FWHM in radians of the peak at the diffraction angle θ. The grain size was found to be about 29.5 nm. The thickness of the sample measured using a stylus profiler was 500 nm.

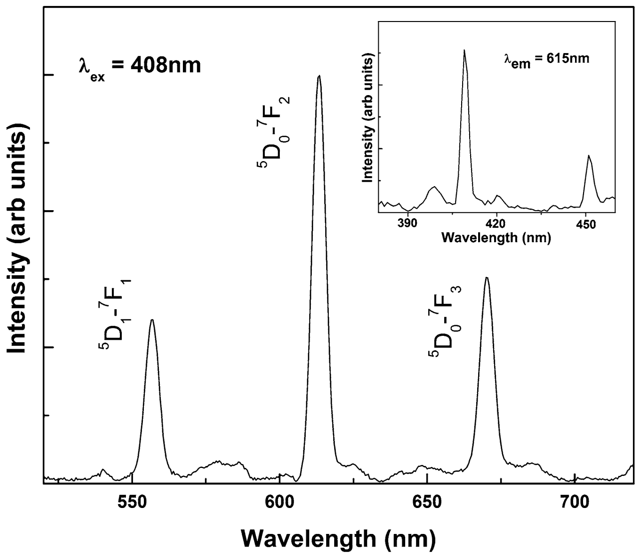

Fig. 3 Room temperature photoluminescence emission spectra of thin film BST:Eu with $\lambda_{ex} = 408$ nm. The *inset* shows the PLE spectra of BST:Eu thin films (emission wavelength $\lambda_{em} = 615$ nm)

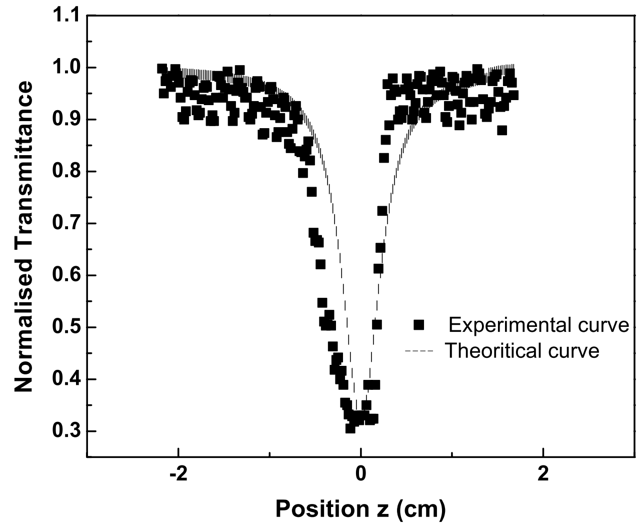

Fig. 4 The open aperture Z-scan curve of BST:Eu thin films. The *dotted line* is the theoretical fit

Figure 2 shows the transmission spectra in the range 190–1800 nm. The films show excellent transparency with an absorption edge at 357 nm. The absorption edge of BST:Eu thin films were examined using a Tauc plot [14].

The absorption coefficient α is related to the photon energy hν as given by (2):

$$(\alpha h\nu) = A(h\nu - E_g)^n, \tag{2}$$

where E_g is the energy band gap and $n = 1/2$ for direct allowed transitions between the valence and the conduction band. Inset of Fig. 2 shows the plot of $(\alpha h\nu)^2$ versus hν. The bandgap of BST:Eu thin films is found to be 3.51 eV.

The linear refractive index of thin films is calculated from the transmittance spectrum using the envelope method [15]. At 532 nm the linear refractive index is found to be 1.82.

The linear absorption coefficient α at 532 nm was estimated to be 1.67×10^4 cm^{-1} from the transmittance spectrum using the relation $\alpha(\lambda) = 1/d \ln(1/T(\lambda))$ where T is transmittance of the thin film and d the thickness of the film.

The photoluminescence spectra of the thin films were recorded at an excitation wavelength (λ_{ex}) of 408 nm (Fig. 3). The emission band clearly shows the presence of Eu^{3+} in the host lattice. The emission in the region 550–700 nm is in good agreement with radiative transitions of various energy levels of Eu^{3+} [16, 17]. The PL emission peaks at 615 nm and 669 nm are the characteristic $^5D_0$–$^7F_2$ and $^5D_0$–$^7F_3$ transitions respectively of Eu^{3+} ions [18, 19]. The emission at 550 nm is due to the transition of $^5D_1$ ^{7}–F_1 [17]. The most prominent emission related to Eu^{3+} in the red spectral region is due to the $^5D_0$ ^{7}–F_2 transition.

The PLE spectrum of the thin films is shown in the inset of Fig. 3. The excitation peaks at 408 nm and 458 nm correspond to the $^7F_0$–$^5D_3$ and $^7F_0$–$^5D_2$ transitions of Eu^{3+} ions corresponding to the energies 2.99 eV and 2.66 eV. The broad band at 398 nm corresponds to the $^7F_0$–$^5L_6$ transition (3.147 eV) [19].

The open aperture Z-scan curve comprises a normalised transmittance as a result of nonlinear absorption as shown in Fig. 4. The experimental data are fitted with the theoretical values (dash lines). The theoretical equation for the normalised transmittance T, for two photon absorption at a given position of the sample z, is given by (3) [13]. We have

$$T(z, S = 1) = \left(1/\sqrt{\pi}\right) q_0(z, 0) \times \int \left[\ln\left(1 + q_0(z, 0)\right) e^{-\tau^2}\right] d\tau, \tag{3}$$

where $q_0(z, t)$ is the fitting parameter given by (4), $S = 1$ for open aperture,

$$q_0(z, t) = \frac{\beta I_0(t) L_{\text{eff}}}{(1 + z^2/z_0^2)}; \tag{4}$$

β is the nonlinear absorption coefficient, z_0 is the Rayleigh parameter, I_0(t) is the on axis irradiance at the focus and L_{eff} is the effective focal length, given by (5):

$$L_{\text{eff}} = \frac{(1 - e^{-L\alpha})}{\alpha}, \tag{5}$$

where L is the sample length and α is the linear absorption coefficient. The experimental curve is theoretically fitted by (3) and the nonlinear absorption coefficient β is calculated. The two photon absorption (TPA) coefficient or the nonlinear absorption coefficient of the BST:Eu thin film is about 242 m/GW. Since quartz substrates have a very low nonlinear absorption at 532 nm, the observed nonlinear absorption

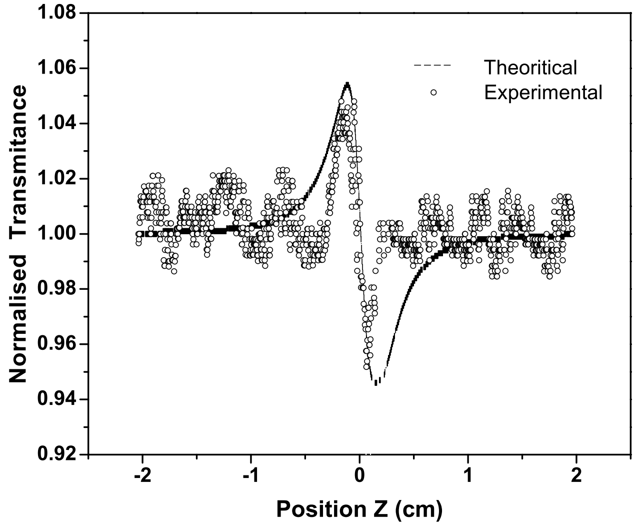

Fig. 5 Closed aperture Z-scan curve of BST:Eu thin film ($S = 0.1$). The *dotted line* is the theoretical fit

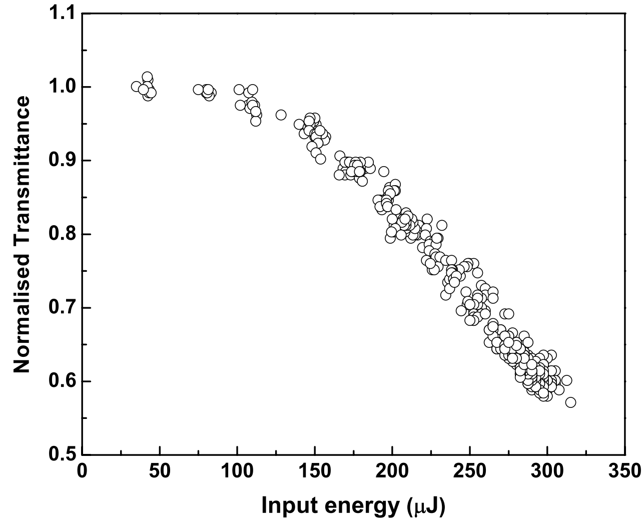

Fig. 6 Optical limiting in BST:Eu thin film

is from BST:Eu thin films. The imaginary part of the third order nonlinear susceptibility $\mathrm{Im}\,\chi^{(3)}$ is calculated using (6) [13]:

$$\beta = \frac{3k\,\mathrm{Im}\,\chi^{(3)}}{2\epsilon_0 c n_0}, \tag{6}$$

where $k = 2\pi/\lambda$ ($\lambda = 532$ nm), ϵ_0 is free space dielectric constant, n_0 is linear refractive index and c the velocity of light. The imaginary part of the third order susceptibility of BST:Eu thin films was found to be 1.16×10^{-16} m^2/V^2. The optical nonlinearity has been enhanced [20, 21] by the dielectric and local field effect as well as the homogeneity in diameter, distribution and orientation in the films. Here the third order nonlinearity is high compared to that of reported epitaxial undoped BST thin films on MgO substrates [10]. This high value of the nonlinear absorption in Eu doped BST thin films may be attributed to the small grain size for films deposited by laser ablation. The large nonlinear optical effects in rare earth doped BST thin films show that these have great potential application in nonlinear optical devices.

The typical closed aperture Z-scan curve for the BST:Eu film is shown in Fig. 5. The measured data show a negative nonlinear refractive index n_2 with peak-to-valley curve. The curve was obtained by dividing the closed aperture data with the corresponding open aperture data, after normalizing each scan.

The data were analysed using the procedure described by Sheik-Bahae [13]. The on axis phase shift at the focus, $\Delta\phi_0$, can be obtained through the best theoretical fit from the normalised closed aperture transmittance $T(z, \Delta\phi_0)$ at the sample position z, by (7) [13]. We have

$$T(z, \Delta\phi_0) \approx \left[1 + \frac{4\Delta\phi_0 x}{(x^2+9)(x^2+1)}\right], \tag{7}$$

where $x = z/z_0$. The nonlinear refractive index γ and the real part of third order optical nonlinear susceptibility $\mathrm{Re}\,\chi^{(3)}$ is given by (8) and (9) [13]:

$$\gamma = \frac{\lambda\Delta\phi_0}{2L_{\mathrm{eff}} I_0}, \tag{8}$$

$$\mathrm{Re}\chi^{(3)} = 2(n_0)^2 \varepsilon_0 c\gamma, \tag{9}$$

where $\lambda = 532$ nm is the wavelength of the laser used, ϵ_0 is the free space dielectric constant, n_0 is the linear refractive index and c the velocity of light. The nonlinear refractive index for the BST:Eu thin films is -1.508×10^{-6} m^2/GW and the real part of the third order optical susceptibility, $\mathrm{Re}\,\chi^{(3)}$, is 2.58×10^{-17} m^2/V^2. The negative nonlinear refractive index indicates the self-defocussing optical nonlinearity. The third order nonlinear susceptibility can be expressed as $\chi^{(3)} = \mathrm{Re}\,\chi^{(3)} + \mathrm{i}\,\mathrm{Im}\,\chi^{(3)}$.

The property of two photon absorption makes BST:Eu useful for novel application as an optical limiter. An ideal optical limiter has a linear transmission only up to threshold input fluence I_{th}, which can vary in different materials. If the input fluence is increased above the I_{th}, the output fluence remains constant. So the transmittance T of the sample falls down with increasing input fluence. The optical limiting characteristic of the samples is the plot of input energy and normalized transmittance T of the sample (Fig. 6). The I_{th} of the 500 nm thick BST:Eu thin film sample is 125 μJ.

4 Conclusion

Rare earth doped BST thin films were deposited on quartz substrates by pulsed laser deposition. The films were polycrystalline with pervoskite phase. The linear absorption coefficient and linear refractive index of the samples calculated from the transmittance spectra is $1.67 \times 10^4\ cm^{-1}$ and 1.82, respectively. The PL spectra show the characteristic emission of Eu^{3+}. The nonlinear optical properties were investigated by a single beam Z-scan setup. The films show an excellent nonlinear optical property. The nonlinear absorption coefficient and nonlinear refractive index are found to be 242 m/GW and $-1.508 \times 10^{-6}\ m^2/GW$ at 532 nm. The real and imaginary part of the third order susceptibility is $2.58 \times 10^{-17}\ m^2/V^2$ and $1.16 \times 10^{-16}\ m^2/V^2$, respectively. The large nonlinear optical absorption in BST:Eu thin films was attributed to the local field and small grain size. The thin film shows a good optical limiting property with a threshold input fluence of 125 μJ. This indicated that the BST:Eu thin films can be used both for luminescence application as well as for nonlinear optical device application. The rare earth doped ferroelectric BST thin film is a potential candidate for optoelectronic device application.

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