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Non-linear optical properties of $(Pb_{1-x}Sr_x)TiO_3$ thin films

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Abstract Thin films of $(Pb_{1-x}Sr_x)TiO_3$, $x = 0, 0.5, 1.0$ have been prepared on glass substrates by the chemical-solution method using the spin-coating technique. The optical nonlinearity in the visible spectral region is investigated using short (5 ns) laser pulses at the off-resonant wavelength of 532 nm employing the open aperture z-scan technique. It is found that the third order nonlinear absorption is dependent on the lead content of the films, with the compositions $x = 0$, 0.5 exhibiting large values ($\beta \sim 10^{-7}$ m/W), thereby suggesting the possible use of these materials as optical limiters. No optical nonlinearity is observed for the composition with $x = 1.0$.

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1 Introduction

Lead titanate-based thin films are a very interesting class of materials, which possess unique physical characteristics, such as large spontaneous polarization, high dielectric constant, high optical transparency, high electro-optic effect and remarkable optical nonlinearity [1]. Previous reports on the nonlinear optical properties of ferroelectric oxide thin films have mainly concentrated on materials like lanthanum-doped lead titanate (PLT) [2], lead zirconium titanate (PZT) [3], lead magnesium niobate–lead titanate (PMN-PT) [4, 5], and lanthanum substituted lead zirconium titanate (PLZT) [1, 6]. Ferroelectric thin films of $(Pb_{1-x}Sr_x)TiO_3$ are of great interest for fabricating functional devices such as non-volatile memory, DRAM [7, 8] etc. However, their applications in photonics have been limited so far due to a lack of information on their nonlinear optical characteristics. The advantages of $(Pb_{1-x}Sr_x)TiO_3$ (PST) based systems are that (i) they can be processed at lower temperatures compared to their barium-based counterparts, leading to better device integration, and (ii) the Curie temperature of PST can be tailored by varying the Sr-content and thereby enhancing their scope for applications at different temperatures. Therefore, the aim of the present study is to determine the nonlinear absorption of ferroelectric thin films of $(Pb_{1-x}Sr_x)TiO_3$ as a function of Pb-content (with $x = 1$, 0.5, 0), hereafter referred to as ST, PST and PT respectively. We have employed the z-scan technique for this purpose, using nanosecond laser pulses. Basically this study offers experimental data for understanding the nonlinear optical mechanism in lead titanate-based thin films.

2 Experimental

The precursor solutions were prepared as per the procedure adapted from our earlier work [9]. Commercially available lead and strontium acetates were used as the starting materials. In the case of PT and PST systems, the solutions were batched with 10% excess lead to compensate for lead loss during thermal treatments and to prevent the formation of the undesirable pyrochlore phase [10, 11]. PST thin films were deposited on commercially available glass (Corning # 1737) by the spin-coating technique. The coated substrate was then dried at 110°C for half an hour

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Table 1 Linear transmission and nonlinear absorption coefficient of the thin films used for the z-scans at 532 nm

Values in parentheses are for thin films containing 15 atom percent excess lead

Composition	Thickness (nm)	Linear transmission	β (m/W) (±5%)
$SrTiO_3$	102	0.80	–
$Pb_{0.5}Sr_{0.5}TiO_3$	75	0.78	3.5×10^{-7} (3.1×10^{-8})
$PbTiO_3$	90	0.88	4.2×10^{-7} (8.3×10^{-8})

and then placed in a furnace and heated at 550–600°C for half an hour. This cycle was repeated several times to obtain films of the desired thickness. The crystalline phases were detected with an X-ray powder diffractometer (D5005, Bruker, Germany) with CuK_α radiation. The fundamental optical constants, which are required for analyzing the z-scan data, were obtained through optical transmittance measurements recorded using a UV–Visible spectrophotometer (JASCO 570 UV/VIS/NIR, Japan). The refractive index n_0 and film thickness t were determined from the transmittance curves using the envelope method [12]. The optical band gap E_g was determined by extrapolating the linear portion of the plot relating $(\alpha h\nu)^2$ and $h\nu$ to $(\alpha h\nu)^2 = 0$. Dielectric measurements were performed on films prepared on $Pt/Ti/SiO_2/Si$ substrates (Radiant Technologies, USA). Gold top electrodes (1 mm dia.) were deposited onto these thin films using RF sputtering. Capacitance and dielectric losses at room temperature were measured using an impedance analyzer (HP 4294A, Agilent, USA) at 1 kHz. The nonlinear absorption measurements were carried out by the open aperture (OA) z-scan technique developed by Sheik Bahae et al. [13]. The measurements were done at the wavelength of 532 nm using 5 ns (FWHM) laser pulses obtained from a frequency doubled Nd: YAG laser (Minilite, Continuum). The laser is set to the low pulse repetition rate of 1 Hz to prevent accumulative thermal effects in the samples. The laser pulse energy used in the experiments is 55 μJ. Films used for these measurements are thinner compared to those on which the transmittance measurements were recorded, and hence their linear transmissions are relatively higher at the excitation wavelength (Table 1).

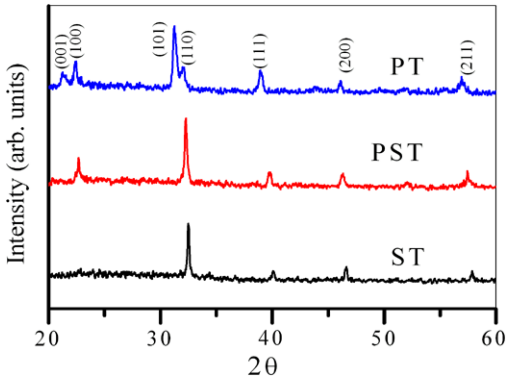

Fig. 1 XRD of ST, PST, and PT thin films

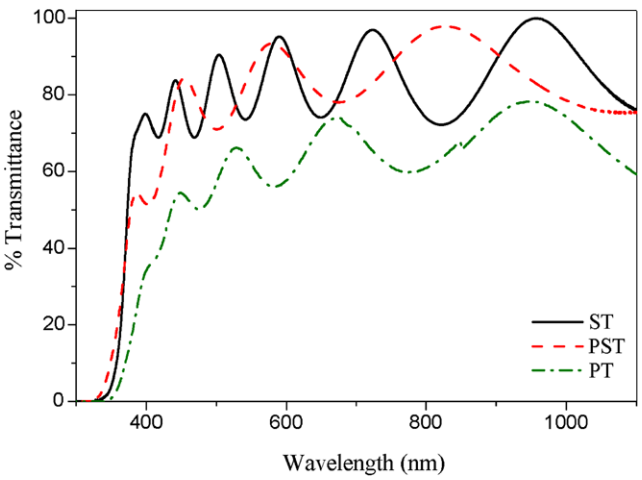

Fig. 2 Optical transmittance spectra of the ST, PST, and PT films of thickness 620 nm, 385 nm and 450 nm respectively

3 Results and discussion

XRD patterns (Fig. 1) reveal the high crystallinity and monophasic nature of the ST, PST, and PT thin films. The neat oscillations in the transmittance curves (Fig. 2) indicate that the films have a flat surface, uniform thickness and also sufficient optical transparency in the visible region, which is necessary for optical applications. The refractive index of 2.41 obtained for ST thin films at $\lambda = 532$ nm is in accordance with the reported value of 2.41 [14], and higher than the values in the range of 1.95–2.25 reported [15–17] in thin films. Refractive indices of 2.34 and 2.27 obtained for PT and PST respectively are lower than the reported values in the range of 2.6–2.7 in PT-based thin films [3, 18]. For lead-based perovskite films, lower values of the refractive index are attributed to lattice defects due to Pb-deficiency [19] and the probable presence of a pyrochlore layer with lower refractive index ($n = 1.65$ at 632 nm) at the interface between the film and the substrate. The optical band gap (E_g) of the PT, PST and ST thin films shown in Fig. 3 are 3.5, 3.55 and 3.51 eV respectively, which agree well with those reported for these thin films [3, 16, 18].

The thin films exhibited good electrical characteristics. The dielectric permittivity (ε_r) and loss ($\tan\delta$) for the thin

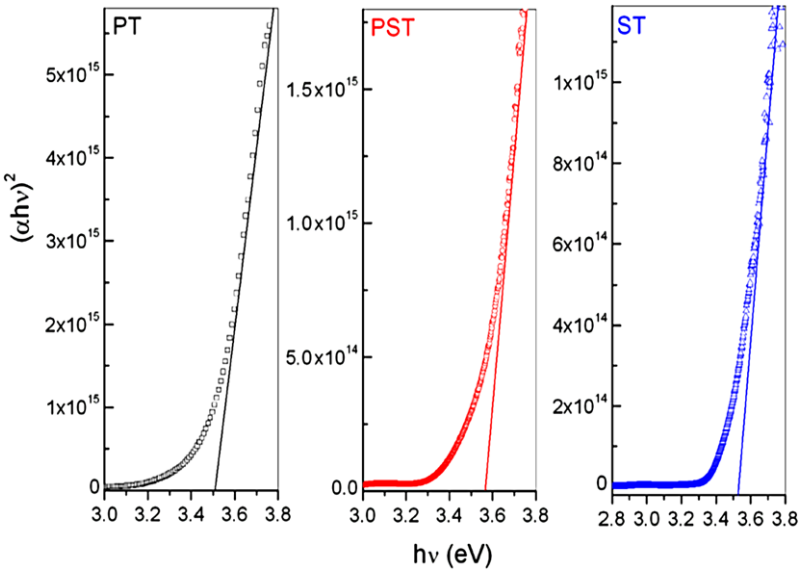

Fig. 3 Optical band gap of the PT, PST and ST films

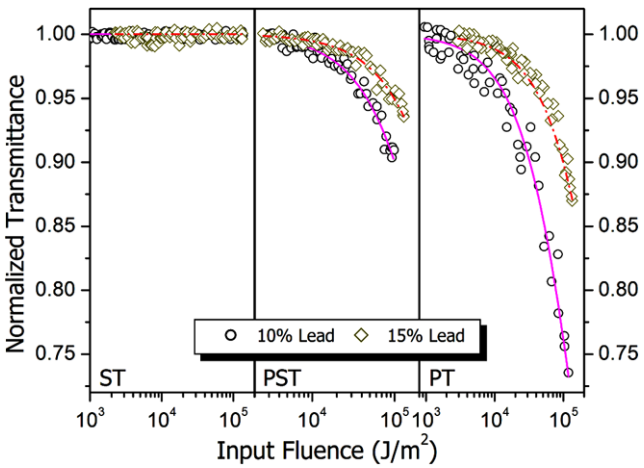

Fig. 4 Nonlinear transmittance of the $Pb_{1-x}Sr_xTiO_3$ films. *Circles* and *squares* are data points extracted from the open aperture z-scan measurements, and *solid curves* are numerical simulations obtained from (1)

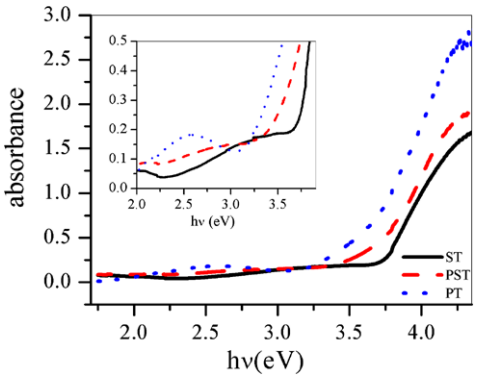

Fig. 5 Absorption spectra of the ST, PT and PST thin films used for the z-scan measurements

films are 350 and 0.01, 580 and 0.01, and 218 and 0.02, for PT, PST and ST, respectively.

Results of the open aperture z-scan experiments are shown in Fig. 4. The normalized transmittance of the samples (transmission normalized to the linear transmission of the sample) is plotted as a function of the incident laser fluence. These data are calculated from the z-scan data considering the fact that for a Gaussian beam, each z position corresponds to an input fluence of $4\sqrt{\ln 2}E_{\text{in}}/\pi^{3/2}\omega(z)^2$, where E_{in} is the input laser pulse energy and $\omega(z)$ is the beam radius. It is found that the nonlinearity is critically dependent on the Pb-content of the films with PT showing the highest effect and ST the least. Therefore, the optical nonlinearity in these films can be directly controlled by altering the Pb-content in the films.

The experimental data are found to fit well to a two-photon type absorption (TPA) given by the equation [20]

$$T = \left((1-R)^2 \exp(-\alpha_0 L)/\sqrt{\pi} q_0\right) \times \int_{-\infty}^{+\infty} \ln\left[1 + q_0 \exp\left(-t^2\right)\right] dt \quad (1)$$

where T is the net transmission of the samples, L and R are the sample length and surface reflectivity respectively, and α_0 is the linear absorption coefficient. q_0 in (1) is given by $\beta(1-R)I_0 L_{\text{eff}}$, where I_0 is the on-axis peak intensity, L_{eff} is given by $[1-\exp(-\alpha_0 L)]/\alpha_0$, and β is the effective nonlinear absorption coefficient. This two-photon type nonlinearity ($\frac{1}{2}E_g < \hbar\omega < E_g$) originates from genuine two-photon as well as two-step (excited state) absorptions. The TPA obtained in PT and PST is attributed to the introduction of electronic levels within the energy band gap due to the defects associated with Pb-deficiency [21]. The optical absorbance spectrum of the films used for the z-scans (Fig. 5) in fact reveals the presence of intermediate energy levels within the

band gap around 2.3 eV, in resonance with the excitation wavelength of 532 nm. Moreover, the absorbance at the two-photon energy of 4.6 eV also seems to be larger for PT and PST, from the trend seen in the absorption spectrum. Enhancement of the TPA with increasing Pb-content can thus be attributed to an increase in the density of intermediate energy states and the two-photon terminal state. In ST, the absence of these interband energy levels accounts for the absence of the TPA process.

The obtained β values are fairly high, and are in the range of 10^{-7} m/W, comparable to those obtained in Nd-doped bismuth titanate [22]. As expected, the β values are relatively higher for the PT samples (Table 1). In the case of films batched with 15 percent excess lead there is a reduction in β by one order (10^{-8} m/W) (Fig. 4 and Table 1), clearly indicating the reduction in defects associated with Pb-deficiency.

4 Conclusion

Thin films of $Pb_{1-x}Sr_xTiO_3$ have been characterized in the linear and nonlinear optical regimes. The optical nonlinearity at 532 nm is rather high, and it is critically dependent on the Pb-content. Because of the high nonlinearity, these films have the potential to be used in the fabrication of miniature photonic devices for optical power limiting, modulation and switching, which can be of application in areas like sensor protection and telecommunications. Such devices usually depend on the ability of an optical medium to change its absorption or refraction upon light irradiation. Since two-photon absorption is a fast quantum process the devices designed from these films will be able to act quite fast. It is an added advantage that the magnitude of the nonlinearity can be easily controlled through the film composition.

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