

Tunability of third order nonlinear absorption in (Pb,La)(Zr,Ti)O₃ thin films

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This paper reports the demonstration of the tunability of the third order nonlinear optical absorption in (Pb_{1-3x/2}La_x)(Zr_{0.53}Ti_{0.47}) (PLZT) thin films. The optical nonlinearity is investigated employing the open aperture z-scan technique at the off-resonant wavelength of 532 nm. By altering the defect chemistry in PZT through A-site aliovalent lanthanum substitution, the nonlinear optical (NLO) absorption can be effectively tuned. The results of the influence of lanthanum concentration on leakage current and microstructure have also been combined to confirm the defect-mediated mechanism of NLO absorption in PLZT thin films. © 2011 American Institute of Physics.

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Pb(Zr,Ti)O₃ (PZT), known for its multifunctionality, is inherently a p-type material due to superoxidation.¹ In A-site lanthanum substituted PZT, the influence of La³⁺ concentration and the resulting charge compensation mechanisms have been well correlated with the dielectric and piezoelectric characteristics.² Recently, it has been shown³ that the third order nonlinear optical (NLO) absorption in lead titanate-based thin films is due to the defects associated with lead deficiency which have electronic levels within the energy band gap. Therefore, in principle, the addition of A-site donor dopants like La³⁺ could be effectively used in controlling the density of these defect states thereby tailoring the NLO properties. This has not yet been studied. Interestingly, previous studies in PLZT thin films report⁴⁻⁷ only nonlinear refraction. In the present study, we report nonlinear absorption phenomena and their relation to defect chemistry in PLZT thin films.

The PLZT solution was synthesized by chemical-solution method, as per the procedure adopted from our earlier work.³ Commercially available lead acetate trihydrate, lanthanum, and zirconium acetyl acetonates were used as the starting materials. The solution was batched with 10% excess lead to compensate for the lead loss during thermal treatments. The thin films were deposited on one side of the glass substrate (Corning No. 1737, NY, USA) by dip-coating method. Prior to the deposition of PLZT thin films, the substrate was coated with SrTiO₃ (ST) buffer layer (~50 nm thickness), as it does not have any nonlinear optical property³ and also acts as an effective barrier layer to prevent inter diffusion between the thin film and the substrate. The precursor solution for the ST layer was also prepared by chemical solution method. After coating each layer, the film was dried at 110 °C for 10 min and then subjected to an intermediate anneal at a temperature of 400 °C for 10 min before finally annealing at a temperature of 620 °C for 20 min. This process was repeated to obtain films of desired thickness. The x-ray diffraction (XRD) (Model D5005, Bruker, Germany) pattern recorded for the films (Fig. 1) showed high crystalline nature. The thickness of the film was

measured using a film thickness reflectometer (Model SR200, Angstrom Sun Technologies, USA) and is given in Table I. The optical band gap E_g was estimated from the transmittance spectra recorded using an UV-visible spectrophotometer (Model Lambda 35, Perkin Elmer, UK) using Tauc's relation,⁸ (αhν)²=const.×(hν-E_g). The observed values of E_g were in accordance with the reported⁷ value of 3.46 eV revealing that La³⁺ substitution does not significantly alter E_g. The absorption coefficient α was calculated from the transmittance spectra. The transmittance spectra revealed that the films were highly transparent [Fig. 2(A)]. The neat oscillations in the transmittance curves also indicated that the films have flat surface and uniform thickness which are necessary for optical applications.

The nonlinear optical absorption measurements were carried out using the open aperture z-scan technique developed by Sheik Bahae *et al.*⁹ The measurements were done at the wavelength of 532 nm, using 5 ns full width at half maximum (FWHM) laser pulses obtained from a frequency doubled Nd:Yttrium Aluminum Garnet (YAG) laser (Model Minilite 1, Continuum, USA) which was set to a low pulse

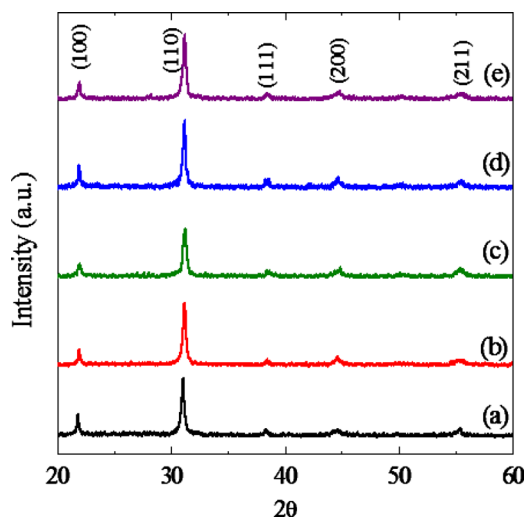


FIG. 1. (Color online) XRD pattern of (Pb_{1-3x/2}La_x)(Zr_{0.53}Ti_{0.47})O₃ thin films: (a) x=0.0, (b) x=0.001, (c) x=0.004, (d) x=0.008, and (e) x=0.010.

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TABLE I. Linear transmission and effective two-photon absorption coefficient of the thin films used for z-scan at 532 nm.

Composition (Pb _{1-3x/2} La _x)(Zr _{0.53} Ti _{0.47})O ₃	Linear transmission (%)	Film thickness (nm)	Band gap E _g (eV)	β _{eff} (1 × 10 ⁻⁸ m/W)
x=0.00	64	900	3.39	7.0
x=0.001	80	900	3.33	1.02
x=0.004	72	910	3.35	0.28
x=0.008	76	870	3.37	6.3
x=0.01	80	900	3.36	7.2

repetition rate of 1 Hz to prevent accumulative thermal effects in the samples. The laser pulse energy used in the experiments is 55 μJ.

Results of the open aperture z-scan are shown in Fig. 3(A). The experimental data are found to fit well numerically to a two-photon absorption (TPA) type process given by the equation¹⁰

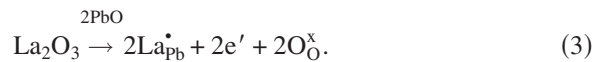
$$T = [(1-R)^2 \exp(-\alpha_0 L) / \sqrt{\pi q_0}] \int_{-\infty}^{+\infty} \ln[1 + q_0 \times \exp(-t^2)] dt, \quad (1)$$

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 Eq. (1) is given by $\beta_{\text{eff}}(1-R)I_0L_{\text{eff}}$, where I_0 is the on-axis peak intensity, L_{eff} is given by $[1 - \exp(-\alpha_0 L)] / \alpha_0$, and β_{eff} is the effective two-photon absorption coefficient. The values of β_{eff} obtained for the films are given in Table I. This observed two-photon type nonlinearity $[(1/2)E_g < \hbar\omega < E_g]$ can originate from genuine two-photon as well as two-step (excited state) absorptions. We attribute the effective TPA presently obtained in PLZT mostly to excited state absorption, caused by the presence of electronic levels within the energy band gap due to lattice defects, V''_{Pb} . The formation of these defect states could be explained on the basis of the following mechanisms using the Kröger–Vink notation:

- (i) The undoped PZT is intrinsically p-type due to the presence of holes,

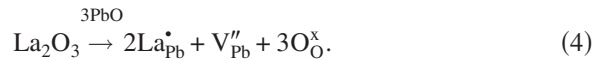


- (ii) On addition of low levels of lanthanum, $0 \leq x \leq 0.004$, the number of vacancies will be partly compensated by the A-site donor dopant,



The decrease of the two-photon absorption in this La-concentration regime [Fig. 3(A)(a) to Fig. 3(A)(c); Table I] is therefore attributed to the decrease in the density of intermediate energy states. In the case of undoped PZT thin films the optical absorption spectra [Fig. 2(B)] reveal the presence of intermediate energy levels in the region 2.2–2.3 eV within the band-gap. As the La-concentration reaches $x=0.004$, this absorption peak disappears [Fig. 2(B)(c)] which is consistent with the NLO behavior.

- (iii) For higher La dopant concentrations ($x > 0.004$), charge compensation takes place through the formation of A-site vacancies,



This causes increase in the density of intermediate energy states leading to increase in NLO absorption [Fig. 3(A)(d) and Fig. 3(A)(e); Table I].

In PZT, La-doping has been reported to significantly influence the leakage currents.^{11–14} Leakage current measurements were recorded on PLZT thin film capacitors on Pt/Ti/SiO₂/Si substrates (Inostek, Korea) coated with SrTiO₃ layer (~50 nm thickness) using the piezoevaluation system (TF analyzer 2000, aixACCT, Germany). During the measurements, the voltage was increased in steps of 2 V with

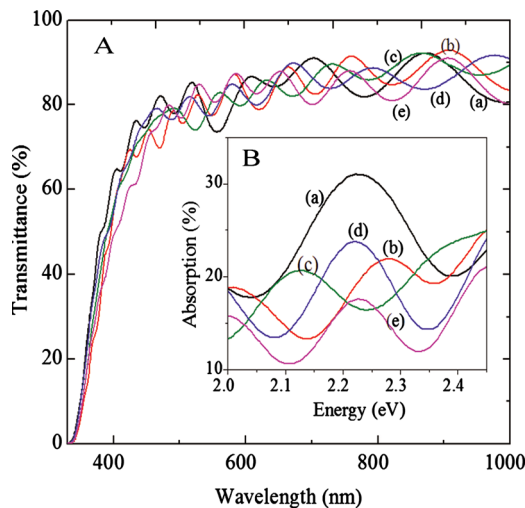


FIG. 2. (Color online) (A) Transmittance and (B) absorption spectra of (Pb_{1-3x/2}La_x)(Zr_{0.53}Ti_{0.47})O₃ thin films: (a) $x=0.0$, (b) $x=0.001$, (c) $x=0.004$, (d) $x=0.008$, and (e) $x=0.010$.

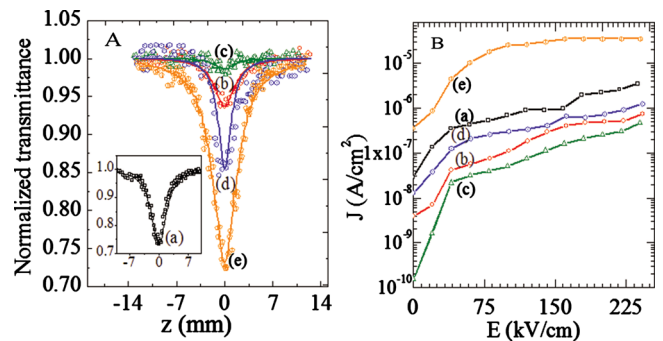


FIG. 3. (Color online) (A) Open aperture z-scan and (B) leakage current plots of (Pb_{1-3x/2}La_x)(Zr_{0.53}Ti_{0.47})O₃ thin films: (a) $x=0.0$, (b) $x=0.001$, (c) $x=0.004$, (d) $x=0.008$, and (e) $x=0.010$.

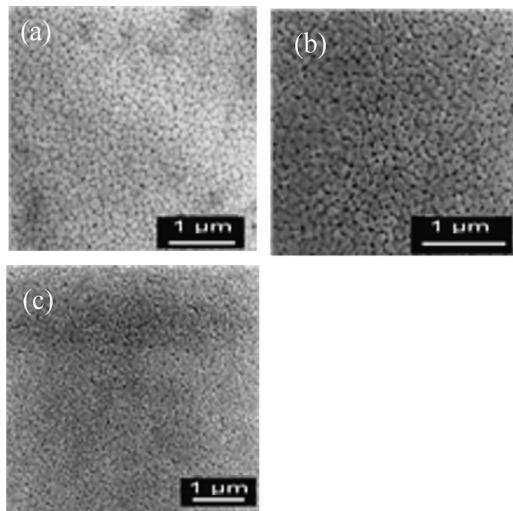


FIG. 4. HR-SEM of $(\text{Pb}_{1-3x/2}\text{La}_x)(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ thin films: (a) $x=0.0$, (b) $x=0.004$, and (c) $x=0.010$.

a hold time of 2 s at each measurement voltage to confirm that the current values were at steady state.^{11,15} For undoped PZT, the leakage current is due to the conductivity of holes [Eq. (2); Fig. 3(B)(a)]. Upon addition of low concentrations of La^{3+} , $0 < x \leq 0.004$, the resistivity increases [Fig. 3(B)(b) and Fig. 3(B)(c)]. This is consistent with the electron-hole compensation mechanism [Eq. (3)]. The composition with $x=0.004$ showed the lowest leakage current density which further establishes low concentration of defect states. However, on further increase in La^{3+} concentration, leakage current increases [Fig. 3(B)(d) and Fig. 3(B)(e)] due to increase in $[\text{V}_{\text{Pb}}'']$ defect states [Eq. (4)].

In PLZT, the change in vacancy concentration leads to a different densification behavior for undoped and doped samples.^{2,16} Microstructural characteristics of PLZT thin films were carried out using high resolution scanning electron microscope (HR-SEM) (Model Quanta 200 FEG, FEI, USA). The microstructures of the PLZT thin films are shown in Fig. 4. In undoped PZT, the presence of lead vacancies [Eq. (2)] cause high volume diffusion leading to high densification [Fig. 4(a)]. For low levels of La^{3+} additions, $x \leq 0.004$, grain growth is observed [Fig. 4(b)]. This is attributed to a relatively high ratio of grain growth to densification rate due to reduced volume diffusion as a result of decrease in the concentration of lead vacancies [Eq. (3)]. On further increasing the La^{3+} concentration, increase in $[\text{V}_{\text{Pb}}'']$ defect states [Eq. (4)] causes enhanced volume diffusion resulting in relatively higher densification rate leading to reduction in average grain size^{2,16,17} [Fig. 4(c)].

In conclusion, we have shown that nonlinear optical absorption in PLZT thin films is directly related to the density of defect states in the energy band gap. By appropriate A-site donor doping, it is possible to tune the NLO absorption in these thin films. The influence of lattice defects and their concentration on the NLO absorption is further supported by the observed leakage current and microstructural characteristics of the films. Because of the high nonlinearity, these films have the potential to be used in the fabrication of miniature photonic devices for optical limiting, modulation, and switching, which can be of application in areas such as sensor protection and telecommunications. Such devices usually depend on the ability of an optical medium to change its absorption or refraction upon light irradiation. These results indicate that PLZT thin films are potential media for such photonics applications.

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