Structural and Third Order Nonlinear Optical Properties of PbS:La Thin Films

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ABSTRACT

The present study examines the third order NLO and electrochemical properties of spray deposited lanthanum doped PbS (PbS:La) thin films. FCC crystallization was confirmed by XRD patterns along the plane (2 0 0). The crystallite size of PbS increases with La doping concentration and ranges from 25 to 34 nm.PbS:La thin films demonstrate self-defocusing due to temperature effects caused by absorption of single photons or free carriers. As a result of the low cationic field strength and high polarizability of La^{3+} ions, PbS exhibits a higher nonlinear refractive index. The nonlinear susceptibility and refractive index were found to be in the range 3.12 x 10^{-6} to 5.23 x 10^{-6}esu and 2.65 x 10^{-9} to 3.52 x 10^{-9} cm^2/W, respectively. The PbS:La thin films improve the structural properties and therefore, it becomes suitable candidature for the applications in nonlinear optical devices.

Keywords: Films; PbS, Impurity; Impedance; z-scan

1. Introduction

Recently, lead chalcogenides (PbSe, PbTe, and PbS) have dominated research due to their technological significance. They are used in a wide range of electro-optical devices due to their unique physicochemical properties. Bulk lead sulfide (PbS) is an IV-VI semiconductor with a narrow band gap, robust quantum confinement, and relatively large exciton Bohr radius. PbS in thin film form are widely used in infrared detection, photography, solar absorption, photoresistors and diode lasers [1]. Furthermore, its low temperature deposition and flexibility on chemical precursors allow it to grow on a wide variety of substrates for photodetectors. Since PbS is optically active and its band gap can be adjusted, it can efficiently absorb the full solar spectrum. PbS thin films can be controlled in their surface and structural shape as well as their particle size by changing preparation conditions. This allows the optical bandgap to be tuned as well as the electrical resistivity to be reduced. It will facilitate the application of PbS thin films to solar cells [2]. It has been shown that substitutional doping as well as doping at Pb-vacancy sites can reduce the optical band gap, carrier density, and resistivity of PbS, thus improving its optoelectronic and nonlinear optical properties. In addition, doping can improve the separation efficiency of photogenerated electrons and holes in PbS. An exceptional p-type appealing coater, PbS thin film is characterized by its high absorption coefficient (10^5 cm^{-1}), strong mobility, and broad excitation spectrum. The multiple exciton generation (MEG) caused by single photon absorption makes PbS thin film photoanodes and solar cells more efficient. For utilizing thin films in nonlinear photonics, photovoltaics, photoconductivity, fast optical switching and information processing applications, nonlinear optical (NLO) properties play a vital role [3]. The physical process of nonlinear absorption is the absorption of free carriers and multiphotons. Optoelectronic properties of PbS has been improved through Ag doping by Trabelsi et al. [4]. Improved optoelectronic properties have been realized for PbS through Pt doping [5]. Besides these, trivalent rare-earth ions have

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been found to effectively adjust sulfide thin films in terms of their physical properties. Especially, La^{3+} effectively improved the nonlinear optical properties of CdS [6]. Outside of these works, reports discussing the nonlinear properties of La-doped PbS thin filmsare extremely scarce in the scientific literature. No published work has addressed the third order nonlinear optical features of La-doped PbS thin films. In the present study, lanthanum (La^{3+}) is doped with PbS to improve its third order NLO properties. Spray pyrolysis was used to deposit PbS thin films containing 0, 2, 4 and 6 wt.% La doping concentrations.

2. Experimental details

Lead nitrate, thiourea andlanthanum chloride are the chemicals used to deposit PbS:La thin films. The substrates are tiny glass slides and the solvent is deionized water. In 50 mL of water, 0.1M lead nitrate and thiourea were dissolved to make a liquid. The aforementioned mixture was then spiked with lanthanum chloride at concentrations of 0, 2, 4, and 6 weight percent relative to lead nitrate and sprayed (spray rate 6 mL/min) onto cleaned micro glass slides maintained at 400ºC to obtain PbS:La thin films which were indexed as L0, L2, L4 and L6 for 0, 2, 4 and 6 wt.% La doping concentrations.

2.1 Characterization

X-ray diffraction patterns were recorded by X´ pert PRO Analytical diffractometer. It can be used to analyze many features of the microstructure of tha material, including lattice parameter, imperfections, crystallographic orientation and degree of crystallinity. For NLO studies, a CW laser operating at 532 nm with an output power of 100 mW, a focal length of 103 mm, and a beam diameter of 7 mm was used. The z-scan technique is a simple and popular experimental technique to measure intensity dependent nonlinear susceptibilities of materials.

3. Results and analysis

3.1 XRD

Diffraction peaks along the (1 1 1), (2 0 0), (3 1 1), (2 2 2) and (4 0 0) planes observed in the XRD patterns (Fig. 1) matched with the patterns of fcc structure of PbS (JCPDS card No. 65-0692). Based on the dominance of the (2 0 0) peak, it seems all the films are strongly oriented in that direction [7]. The absence of impurity peaks from La-element/Lanthanum oxide supports the formation of PbS:La compound instead of perceptions of individual elements. A lower electro-negativity of La^{3+} ions can arise from various mechanisms, such as S^{2-} vacancies or Pb^{2+} ions migrating into the interstitial sites in the PbS lattice. Due to La^{3+} occupying cation vacancies that deteriorate secondary phase development, La^{3+} incorporation into the PbS lattice ensured good crystal structure [8].

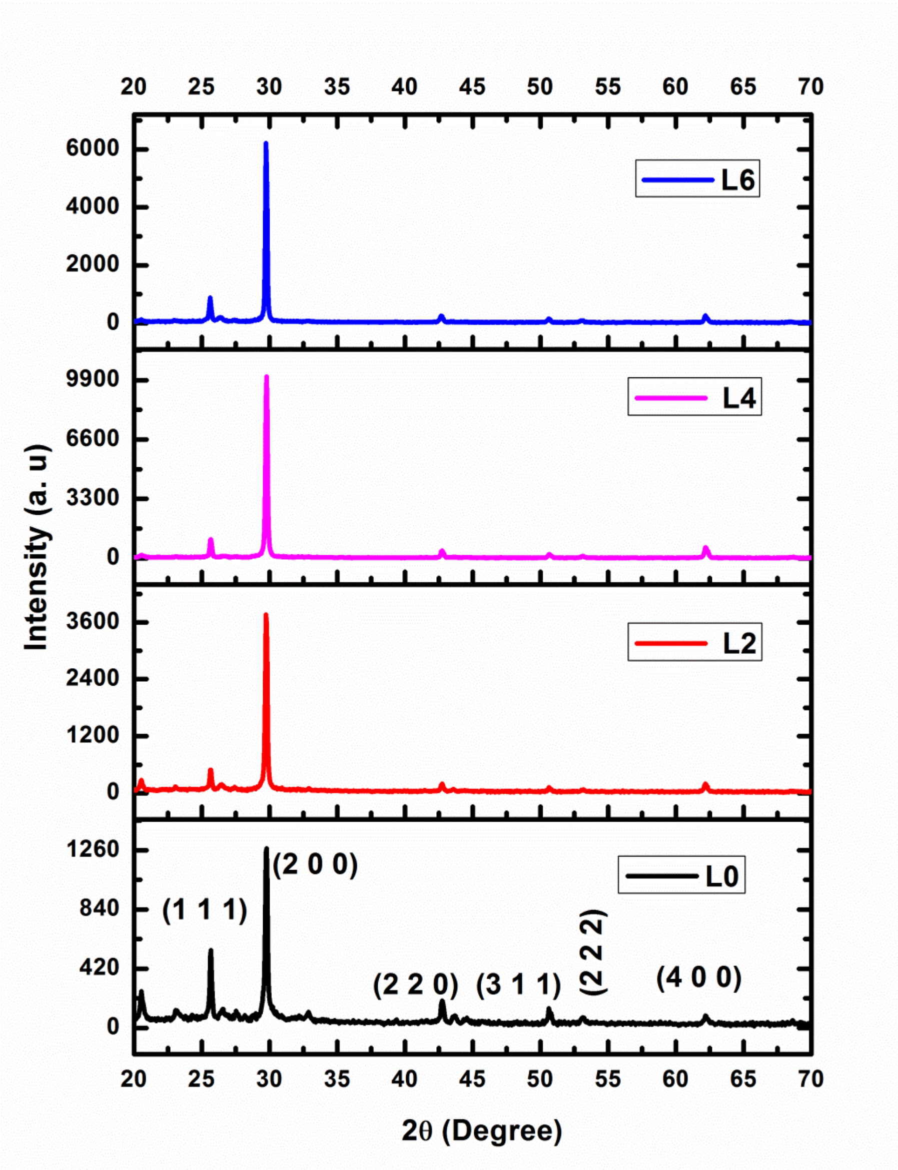

Fig. 1 X- ray diffraction patterns of PbS:La thin films

As La doping increased up to 4 wt.% in pure PbS, the intensity of the (2 0 0) peak increased and decreased for further doping concentration. Enhanced intensity up to 4 wt.% La doping concentration is related to the variation in microstructural parameters. PbS lattices doped with 0 to 4 wt.% La experience unit cell compression. With further doping the unit cell suddenly expands. In PbS, the compression or expansion is determined by the ionic radius of the Pb^{2+} (1.33 Å) and La^{3+} (1.16 Å) ions. A majority of La^{3+} ions may be occupied at vacancies, substitutional, or interstitial sites of Pb^{2+} in PbS lattice, or at interstitial sites in crystal structure, up to 4 weight percent. The stability of the PbS lattice depends on La^{3+} occupying more and more Pb^{2+} sites. In general, the intensity of XRD patterns depends on the concentration of lattice strain in the crystal structure, which is influenced by structural deformation, disorder, and inhomogeneity. The intensity of the diffraction peaks at 4 wt.% La doping concentration was thus enhanced, and their narrow broadening with crystallite size was observed [9]. The D and ε values were compiled in Table 1.

Table 1: Structural parameters of PbS:La thin films

Sample	D (nm)	ε x10^{-3}
L0	25	4.64
L2	30	4.21
L4	34	3.18
L6	31	3.40

Crystallite size and strain are well known to be correlated. The reduced micro strain observed up to 4 wt.% La-doping (Table 1) might have increased the crystallite size; whereas for the L6 film increased strain might have obstructed crystallization.

3.2 NLO

Several photonic devices rely on light-matter interaction, such as optical switches, limiting devices, and laser-controlled machines. EM waves consist of oscillating electric and magnetic fields, in which the electric field plays a key role in separating the charges. Consequently, the material's body develops an electric field. As light intensity vary the nonlinearity of the electric field inside materials changes from linear to nonlinear [10]. In materials exposed to strong electric fields, nonlinearity is defined by their geometry and nonlinear polarization. PbS:La thin films closed aperture curves are shown in Fig. 2

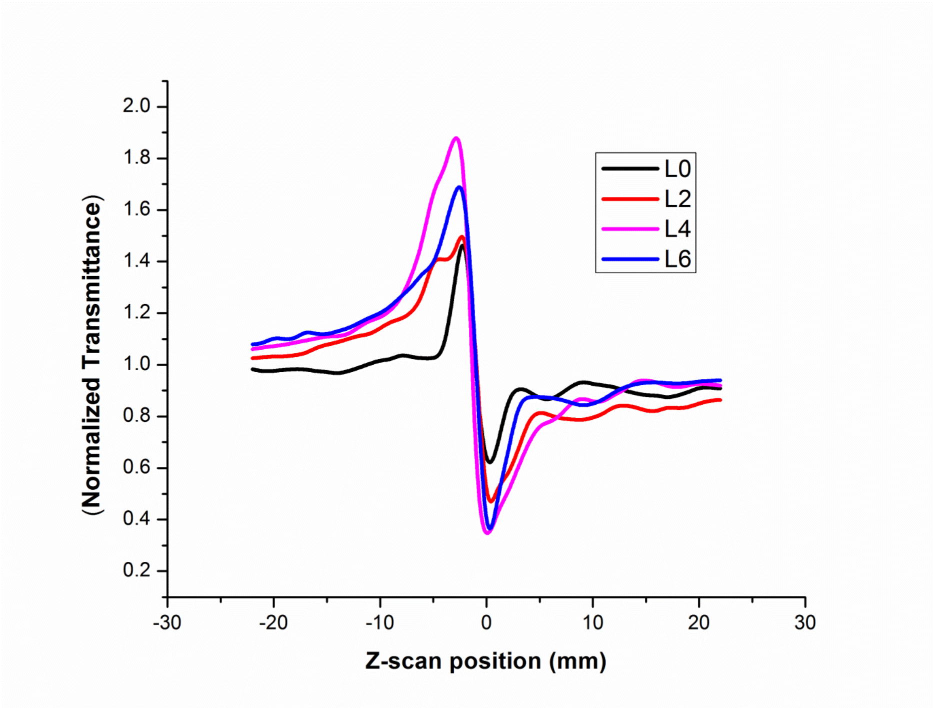

Fig. 2: Closed aperture curves of PbS:La thin films

The peak-valley arrangement observed for all the films indicates negative nonlinearity with self defocusing nature. The self-defocusing effect in PbS:La thin films is a result of temperature-induced absorption of single photons or free carriers, as Neo et al. [11] have stated. Molaei et al. [12] reported atomic saturation absorption mechanism is involved in the closed aperture scan of PbS/CdS QDs rather than thermal effects. PbS:La thin films can diverge a high-intensity beamdue to negative nonlinearity [13].

In order to determine a device's nonlinear optical properties, nonlinear refractive index, and susceptibility are used. Refractive index (n_2) is about 10^{-9} cm^2/W (Table 2). The nonlinear refractive index value depends on the film quality, preparation route, solvent, annealing temperature, growth environment and metal ion doping. As the lanthanum concentration increased in the PbS matrix, the nonlinear refractive index increased, possibly due to La^{3+} ions' low cationic field strength and high polarizability. Bairy et al. [14] obtained similar findings for Zn doped CdS thin films. Fig. 3 shows the open aperture curves which displayed a valley behavior and the deepest range of valley of PbS increases with La doping and the L4 film has the deepest valley confirming its stronger nonlinear absorption performance [15].

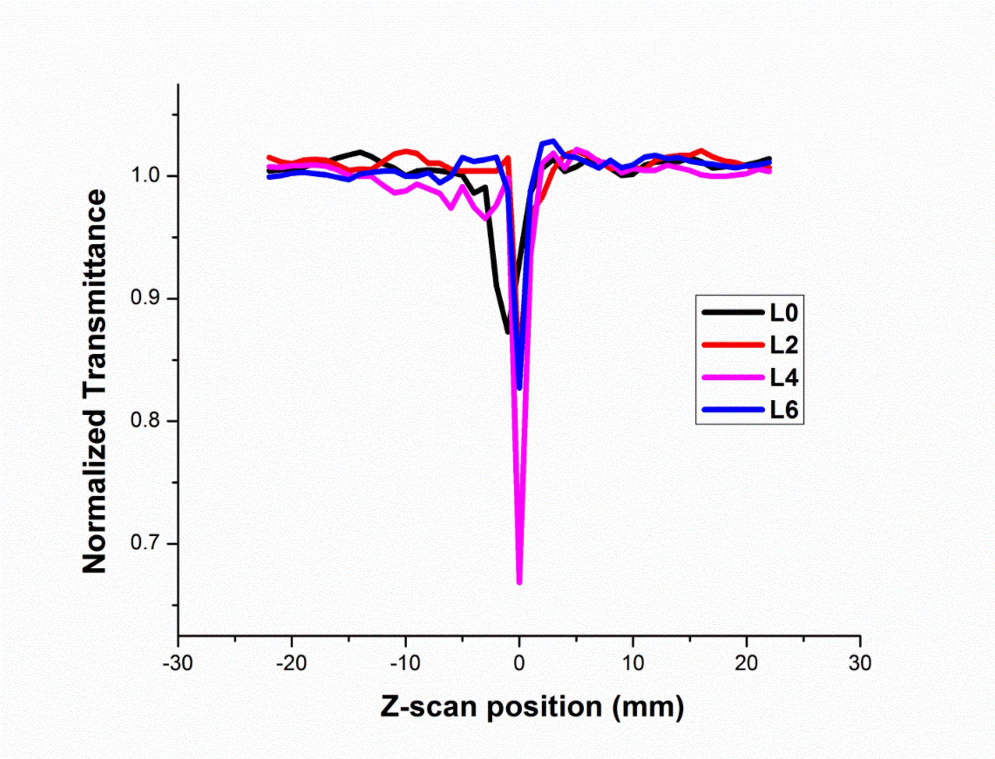

Fig. 3: Open aperture curves of PbS:La thin films

Due to the RSA effect, the transmittance drops at Z = 0 because the excited state has an increased cross sectional area, which permits considerable photon absorption. Third order nonlinear absorption is mostly caused by flaws associated with electron levels in the energy band gap and the La-deficiency. Default positions and voids affect PbS:La thin films NLO characteristics. The nonlinear absorption coefficient (β) increased with La doping (Table 2) due to oxygen deficiencies on the surface of PbS. The strong nonlinear absorption observed with La doping might be due to modification in the energy states and band gap of PbS.

The cubic susceptibility (χ^3) [Real (R_e), Imaginary (I_m) and absolute] of PbS:La thin films were determined using the equations (1), (2) and (3).

$$R_e\chi^{(3)} = \frac{\varepsilon_0 c^2 n_0^2 n_2}{\pi} \qquad (1)$$

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$$I_m\chi^{(3)} = \frac{\varepsilon_0 c^2 n_0^2 \lambda\beta}{4\pi^2} \quad (2)$$

$$\chi^{(3)} = \sqrt{(R_e\chi^{(3)})^2 + (I_m\chi^{(3)})^2} \quad (3)$$

Table 2: NLO parameters of PbS:La thin films

Sample	n_2 (cm^2/W)	β (cm/W)	$R_e\ \chi^3$(cm^2/W)	$I_m\ \chi^3$ (cm^2/W)	χ^3 (esu)
L0	$2.65x10^{-9}$	$1.07x10^{-4}$	$3.12x10^{-6}$	$1.03x10^{-7}$	$3.12x10^{-6}$
L2	$2.73x10^{-9}$	$1.71x10^{-4}$	$4.31x10^{-6}$	$1.04x10^{-7}$	$4.31x10^{-6}$
L4	$3.52x10^{-9}$	$2.70x10^{-4}$	$5.23x10^{-6}$	$1.09x10^{-7}$	$5.23x10^{-6}$
L6	$3.12x10^{-9}$	$2.02x10^{-4}$	$4.91x10^{-6}$	$1.05x10^{-7}$	$4.91x10^{-6}$

Table 2 provides a summary of these susceptibility measurements. The symmetry of a material's structure has a significant impact on its nonlinear susceptibility. In PbS:La thin films, $\chi^{(3)}$ depends on the induced lattice strain. Due to the non-homogeneous lattice strain, the centrosymmetric property of PbS is broken. As a result of La doping, PbS NLO properties improved, potentially due to a reduction in strains (Table 1). More excited electrons can be trapped due to increased thickness because defect states in the sub band range are denser. Compared to previous work on PbS films doped with Nd [16] and PbS quantum dots [17], the NLO properties of PbS:La thin films showed remarkable improvements with La incorporation. In NLO measurements, it is evident that dispersion medium, external electron donor and acceptor, laser parameters, and particle size have a significant impact on refractive index and absorption coefficient.

4. Conclusion

Using spray pyrolysis, La-doped PbS thin films were effectively deposited. Various levels of La doping have influenced the properties of PbS thin films. The films polycrystalline composition was confirmed by XRD analyses, with the main peak being the (2 0 0) plane. Crystallite size value increased from 25 to 34 nm with Lanthanum doping concentration up to 4 wt. % and then decreased to 31 nm for 6 wt.% Lanthanum doping concentration. L4 thin film exhibited better nonlinear optical parameters at third order. The nonlinear refractive index and susceptibility values of the L4 thin film were 3.52 x 10^{-9} cm^2/W and 5.23 x 10^{-6}esu, respectively. As a result of these results, PbS:La thin films, in particular those coated with 4% Lanthanum concentration (L4), offer excellent NLO applications.

5. Declarations

5.1 Acknowledgement

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5.2 Competing Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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