International Symposium of Research Students on Materials Science and Engineering
December 20-22, 2004, Chennai, India
Department of Metallurgical and Materials Engineering, Indian Institute of Technology Madras

SYNTHESIS, CHARACTERISATION AND NONLINEAR OPTICAL PROPERTIES OF STABLE PbS NANOCLUSTERS

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ABSTRACT

Quantum confinement effects in low-dimensional semiconductors influence the optical properties, rendering them excellent candidates for device applications in Photonics. This paper presents our recent results on the synthesis of stable optical quality films of PbS nanoclusters by a colloidal chemistry method in the size range of few nanometers using lead acetate and sodium sulphide as the precursors. Optical absorption spectra reveal large signature blue shift from the bulk absorption cutoff wavelength. Optical Nonlinearity induced in PbS nanoclusters at low power continuous wave laser excitation is studied by the z-scan method. The origin of the obtained nonlinearity is analysed in terms of thermal variation of refractive index.

Keywords: PbS nanoclusters, quantum confinement, nonlinear refractive index

1. INTRODUCTION

Bulk lead sulphide (PbS) is a direct bandgap material with a narrow bandgap of 0.41eV and bulk exciton Bohr radius of 9 nm. It has a variety of applications such as IR detectors, Pb^{2+} ion selective sensors etc .[1,2]. Nanoclusters of PbS widen the scope of these applications due to the possibility of band gap engineering all the way from the IR to the UV, apart from being candidate materials for new applications in nonlinear optics such as optical limiting and switching[3]. The major requirements for a good nonlinear optical (NLO) material are large nonlinear optical susceptibility, transparency, optical uniformity, optical stability and ease of preparation. Large nonlinear optical response is found to be exhibited in the regime of strong quantum confinement where the dimensions of the nanoclusters are less than the exciton Bohr diameter [4,5]. However, so far no comprehensive recipe has been arrived at on obtaining reasonably stable nanoclusters of desired size and size distribution, particularly in the case of PbS. The present work is on the synthesis of stable and strongly confined PbS nanocrystals by a chemical route. The samples are characterized by optical absorption and X-ray diffraction techniques. Optical nonlinearity is probed using a single beam closed z-scan technique with a low power continuous wave (cw) He-Ne laser.

2. EXPERIMENTAL TECHNIQUES

PbS nanoclusters are synthesized using methods of colloidal chemistry. Lead acetate and Sodium sulphide of analytic grade were used as precursors. Colloidal PbS nanoclusters are synthesized using a commercially available glue as the host matrix. This colloidal solution is air dried at room temperature to get optical quality films which is very stable unlike the colloidal solution. The concentrations of lead acetate used are 4mM, 5mM, 6mM and 8 mM

and the appropriate concentrations of sodium sulphide were used to obtain a 1:1 ratio of Pb^{2+}:S^{2-} in all cases. The corresponding sample codes are S1, S2, S3 and S4 respectively.

Optical Absorption (OA) spectra are recorded on a Hitachi UV-3400 recording spectrophotometer. The XRD patterns are recorded on a Shimadzu horizontal diffractometer (Cu-Kα radiation, λ=0.15418nm). The mean size of the nanoclusters is determined using the Scherrer's formula. Nonlinear optical studies are done using a single beam z-scan technique using a low power cw He-Ne laser (λ=632.8nm). From the actual beam profile measurements using the knife edge method, the spatial intensity profile of the laser is found to be nearly gaussian. We used an automated closed z-scan setup [6] as shown in Fig-1 to measure the changes in the intensity profile as the sample is moved along a focused gaussian laser beam. An aperture was placed in front of the detector kept in the far field so that only the central portion of the beam is detected. At each position along its path, the sample experiences a different laser fluence and the corresponding position-dependent transmission is measured by the detector. From this technique we get both the magnitude and sign of nonlinear refraction. An increase in transmittance followed by decrease in transmittance (peak-valley) in the plot of transmittance against distance moved denotes a negative nonlinear refraction, whereas a valley-peak configuration implies a positive nonlinearity.

3. RESULTS AND DISCUSSION

Fig. 2 shows the optical absorption spectra of t PbS nanoclusters. The large blue shift from the bulk PbS optical absorption cutoff of 3020 nm (corresponding to a bandgap of 0.41 eV can be clearly observed. The different curves are for the different samples prepared with varying concentration of PbS.

Fig. 3 shows the XRD pattern for sample S1. The pattern with diffused peak structure is typical of nanocrystalline materials. The diffraction peaks correspond to the cubic rock salt structure of PbS (JCPDS file No 5-592) with lattice parameter of 5.92A°. The mean cluster size for the samples used is estimated to be 11nm using Debye-Scherrer formula.

Nonlinear refraction and absorption effects are likely to be excited in the samples on exposure to laser radiation, which are probed by the z scan technique. Nonlinear refraction is characterized by the intensity dependent refractive index change given by

$$\Delta n = n_2 I_o$$

where n_2 is the effective nonlinear index and I_o is the incident irradiance at the focal point

$$I_o = \frac{2P_{in}}{\Pi \omega_o^{\,2}}$$

P_{in} is the laser power and ω_o is the beam waist radius. In our system, ω_o=75μm and λ=632.8 nm, so the condition that the thickness of the sample $L << z_o = \frac{\Pi \omega_o^{\,2}}{\lambda}$ is satisfied. Here sample thickness L=1mm. The phase shift |ΔΦo| on the optical axis can be obtained by fitting the expression [6]

$$T(z, \Delta\phi_o) = 1 - \frac{4\Delta\phi_o x}{(x^2+9)(x^2+1)}$$

where $x = \frac{z}{z_o}$

to our normalized closed z-scan transmittance curve. |ΔΦo| is related to n_2 as [6]

$$|\Delta\phi_o| = -\left(\frac{2\pi}{\lambda}\right)\Delta n L_{eff}$$

$$= -\left(\frac{2\Pi}{\lambda}\right) n_2 I_o L_{eff}$$

where effective thickness of the sample is defined as $L_{eff} = \frac{1-\exp(-\alpha L)}{\alpha}$

where α is the linear absorption coefficient.

Figure 4 shows the normalised closed z-scan traces for sample S2. Since the peak precedes the valley indicating self defocusing effect, the sign of the nonlinear refractive index is negative. The symmetrical nature of the z scan trace indicates that there is no nonlinear absorption in the sample at the power levels used.

Table-1 shows the n_2 values for different concentrations. The predominant mechanism of nonlinearity is expected to be of thermooptic origin at the low laser powers used in the present work.

4. CONCLUSION

Stable PbS nanoclusters of mean size 11 nm are synthesized by a chemical route and characterized by XRD. The large blueshift on the optical absorption spectra and the nature of the XRD pattern are indicative of strong quantum confinement. Large optical nonlinearity, presumably of thermooptic origin is found to be exhibited by the samples, which renders these samples as ideal candidate materials for Photonics device applications.

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TABLES

Table-1

	S_1	S_2	S_3	S_4
n_2 (m^2/W) 10^{-11}	-4.2	-5.6	-9.7	-12.7

FIGURES

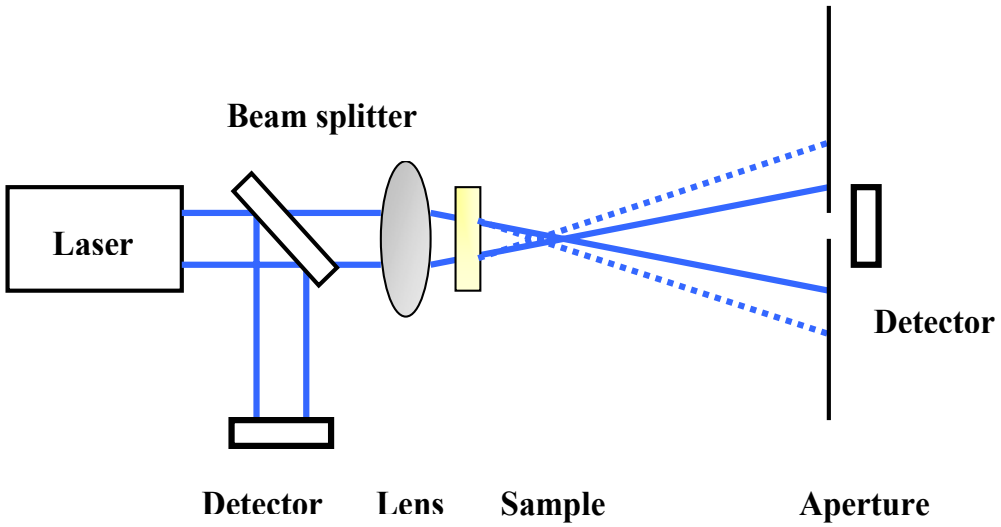

Fig- 1 Closed z-scan setup

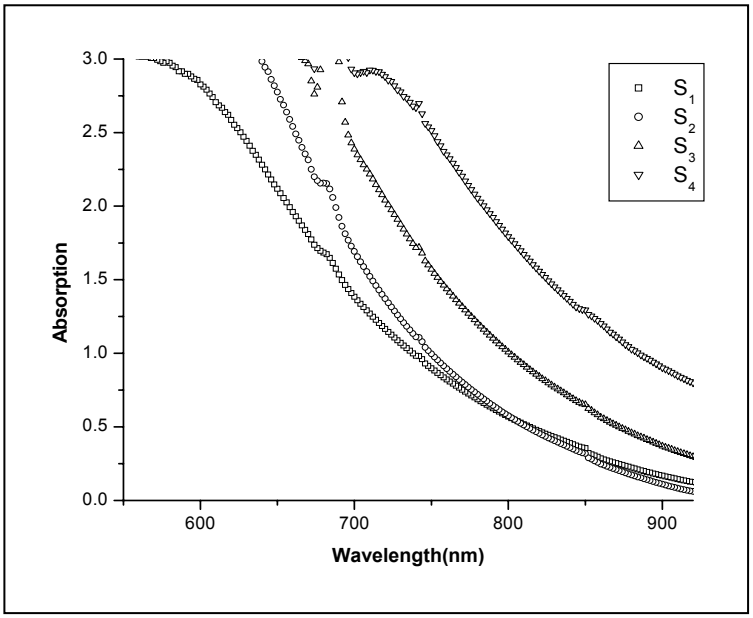

Fig-2 Optical absorption spectra of samples S_1 to S_4

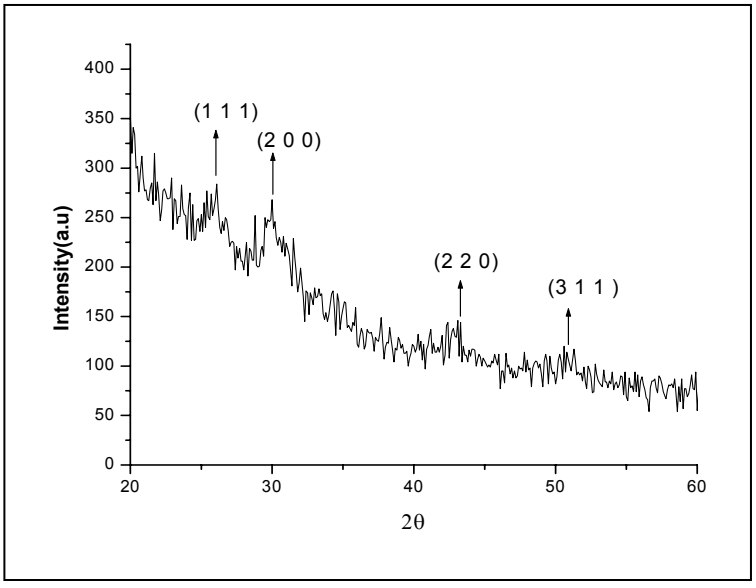

Fig-3 XRD pattern of sample S_1

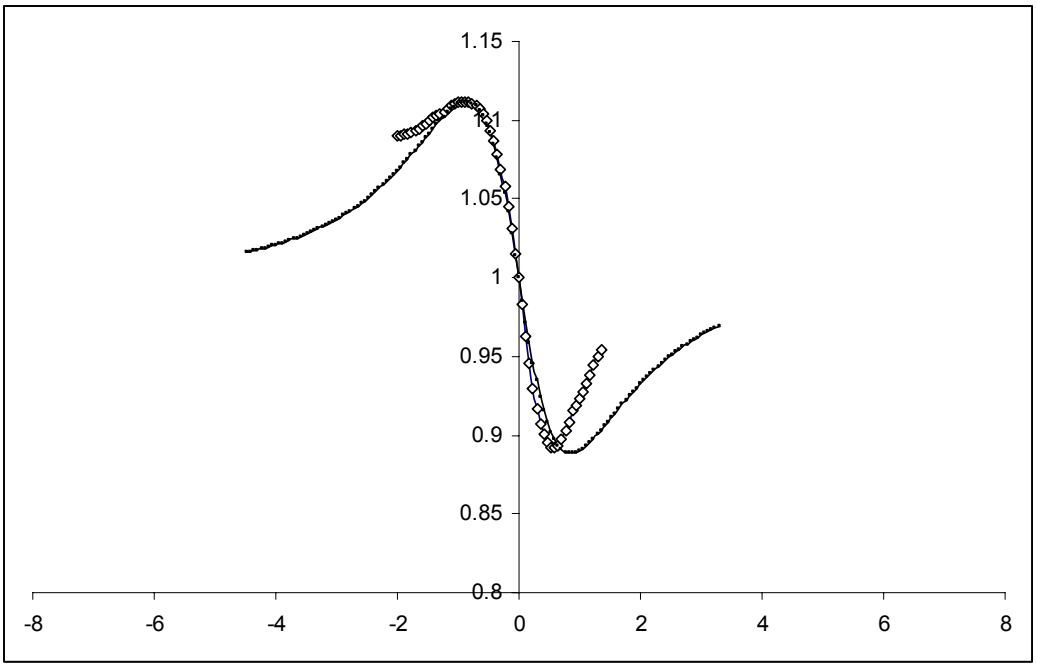

Fig-4 Closed z-scan trace. Solid line represents a theoretical fit.