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硫化铅纳米粒子的三阶非线性光学特性研究

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摘要:针对硫化铅(PbS)特殊的三阶非线性光学特性,本文在水溶液里合成了PbS纳米粒子。紫外-可见光谱显示,由于使用了封端剂,合成的样品更加稳定。用紫外-可见吸收光谱和X射线衍射斑研究了PbS纳米粒子的特性,结果表明,由于纳米粒子尺寸减小,其吸收光谱显示极大的蓝移。利用Scherre方程估计PbS粒子的平均粒径约为8.2 nm。最后,基于使用了632.8 nm He-Ne激光器的用单光束*Z*-扫描技术研究了所制备的纳米粒子的非线性光学特性。对3种具有不同摩尔数的样品的测试表明,计算所得的非线性折射率在-10^{-7}(cm^2/W)量级。

关 键 词:硫化铅;纳米粒子;*Z*-扫描;非线性光学特性

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Investigation of third-order nonlinear optical properties of lead sulfide nanoparticles

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Abstract: PbS is a direct bandgap IV-VI semiconductor with a bandgap of 0.41 eV and an exciton Bohr radius of 18 nm at room temperature. It has exceptional third-order nonlinear optical properties and applications for optical devices. In this paper, we synthesize PbS nanoparticles in aqueous solution using different capping agents. UV-Vis spectra show that the sample is much more stable. The nanoparticles are investigated by UV-Vis absorption spectrum and X-ray diffraction pattern. As a result of the nanoparticle size reduction, we observe a larger blue shift in absorption spectrum. Using the Scherre equation, the mean particle size is estimated about 8.2 nm. The *Z*-scan technique, which is a

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single beam method, is used to investigate the nonlinear optical properties of the as-prepared particles. We use a continues He-Ne laser with 632.8 nm wavelength in the set-up. The method is applied to three samples with different molarities and the nonlinear refractive index is calculated to be of the order of 10^{-7} (cm^2/W) with a negative sign.

Key words: PbS; nanoparticle; *Z*-scan; nonlinear optical property

1 Introduction

It is well established that in the nanometer region semiconductor materials show properties different from their bulk counterparts. So nanoparticles maybe useful in applications in optical limiting and optical switching devices, where high linear transmission and large nonlinearity and short response time are required[1].

Lead sulfide as an important semiconductor material has been studied at length in the past few decades. PbS is a direct band gap IV-VI semiconductor with a band gap of 0.41eV and an exciton Bohr radius of 18 nm at room temperature. It has exceptional third-order nonlinear optical properties and applications to optical devices[2]. PbS nanoparticles are synthesized by variety of techniques such as microwave-assisted[3], electron beam irradiation[4], sonochemical[5] and polymer-assisted reaction[6]. Among these methods, the new chemical capping agent method of synthesizing PbS quantum dots uses thioglycolic acid (TGA), because of its simplicity, very short synthesis time and excellent control over particles size. Previous aqueous-based synthesis of PbS nanoparticles used water-soluble polymer stabilizers which effects its optical properties. We examined the optical properties of the synthesized nanoparticles by UV-Vis absorption spectra and structural characterization by X-ray diffraction (XRD) patterns. The *Z*-scan technique, which is a single beam method, is used to investigate the nonlinear optical properties of the as-prepared particles. We utilize a continueou-wave He-Ne laser with 632.8 nm wavelength.

2 Experiment

We synthesized PbS nanoparticles in aqueous environment by following Zhao et al.[7], though we used a different capping agent which UV-Vis spectra show makes the sample much more stable.

To synthesize PbS nanoparticles, we used lead acetate dihydrate, sodium sulfide x-hydrate, thioglycolic acid (TGA) as capping agent and triethylamine to adjust the pH of the medium. Primary concentration of solution was 16.5 mM for lead. The procedure was performed at room temperature and the sample was stored in an ice bath in the dark for 1 h before its properties were tested.

For nanoparticle characterization, UV-Vis spectra of the particles were recorded at room temperature using a UNICO spectrophotometer. X-ray diffraction (XRD) analysis was carried out using a Philips X-ray diffractometer with Cu Kα (λ=0.154 184 nm) radiation.

To investigate nonlinear optical properties of the NCs, we used the *Z*-scan technique which is a single beam method. The setup of the *Z*-scan is shown in Fig. 1. By moving the sample in the z direction, self-focusing or self-defocusing of the sample which is caused by the intense light of the laser, leads to changes in the intensity received to the detector. As a result, we can see a peak-valley (valley-peak) pattern due to negative (positive) nonlinear refractive index changes in the sample. The difference in the peak-valley transmittance (ΔT_{P-V}) relates to the phase shift $|\Delta\Phi_0|$ in the following manner:

$$\Delta T_{P-V} = f|\Delta\Phi_0| ,$$

where $f=0.406(1-S)^{0.25}$ is an experimental constant and S is the linear transmittance of the aperture. The following expression indicates the relation between n_2 and $|\Delta\Phi_0|$:

$$\Delta\Phi_0=-(\frac{2\pi}{\lambda})n_2 I_0 L_{eff},$$

where the effective thickness (L_{eff}) of the sample is defined as $L_{eff}=\frac{1-e^{\alpha L}}{\alpha}$, where α is the linear absorption coefficient.

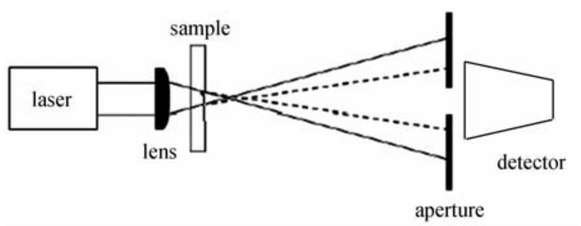

Fig. 1　Close aperture z-scan technique setup

3　Results and discussion

The nanoparticles properties were investigated by UV-Vis absorption spectrum and X-ray diffraction pattern.

Room temperature UV-Vis spectra were taken of the as-prepared NCs instantly and 50 days after synthesizing are shown in Fig. 2.

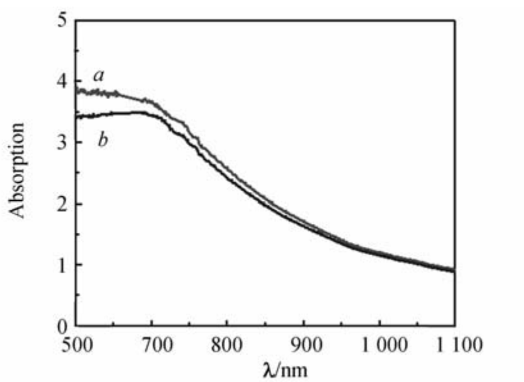

Fig. 2　UV-Vis spectra of the as-prepared sample (a) right after synthesis, (b) 50 days after synthesis.

As a result of nanoparticles size reduction, we observed a large blue shift in the absorption spectrum compared with bulk PbS (band gap energy for bulk-phase PbS is 0.41 eV; =3 020 nm[7] and the band-bap of the as-prepared particles estimated about 1.3 eV). Comparing the two spectra, it is concluded that the sample was almost stable in the period, so we can claim that TGA is a good candidate for synthesizing PbS nanoparticles.

Fig. 3 shows the XRD pattern of the sample. Five major peaks can be recognized which are indexed to the PbS face-centre cubic (fcc) phase (JCPDS 05-0592). The broadness of the diffraction peaks can be ascribed to the small particles size[8]. Using the Scherre equation, the mean particles size was estimated to be about 8.2 nm which supports our previous claim.

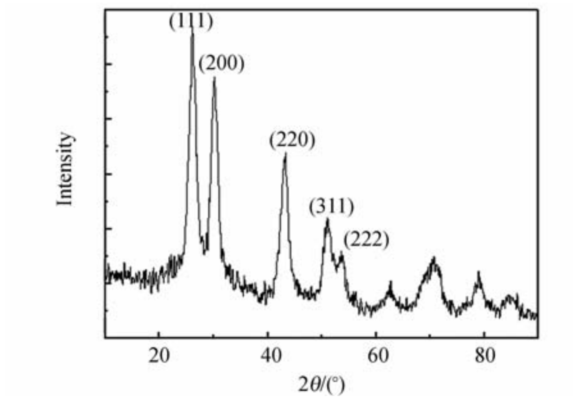

Fig. 3　X-ray pattern of PbS nanoparticles

Then we apply Z-scan technique to investigate the nonlinear refractive index of the sample. By changing the molarity of the sample, the influence of this parameter was examined. First, we tried to obtain linear absorption for each molarity by use of the following relation:

$$\alpha=-\frac{1}{L}\ln\left(\frac{P}{P_0}\right)$$

The results are shown in Tab. 1.

The close-aperture Z-scan experiment was used to obtain the sign and the magnitude of the nonlinear refractive index simultaneously. The results of the experiment are shown in Fig. 4.

The justification in using peak-to-valley is

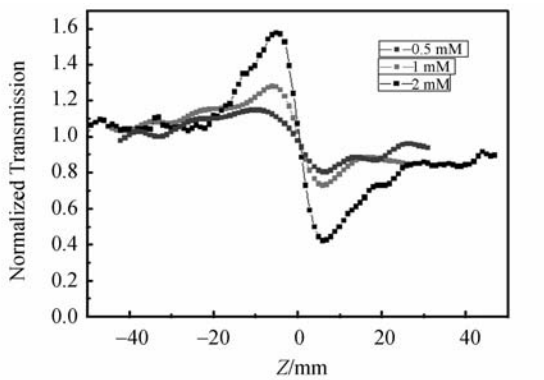

Fig. 4 Close-aperture Z-scan experimental curves of PbS nanoparticles for three different molarities

that the sign of the refractive indices of the samples are negative and the magnitudes are calculated and written in Tab. 1.

The difference in peak-to-valley transmission for different molarities can be justified as follows: for lower molarities, we have fewer numbers of particles per unit volume, so the response of medium to the applied field is weak and there is not a good peak-valley pattern in the output diagram. Results of calculations confirm the expression: the highest refractive index belongs to the sample with the highest molarity.

Tab. 1 Calculated values of linear absorption coefficient and non-linear refractive index for three molarities

ΔT	n_2 (cm^2/W)	$\Delta\varphi_0$	α (cm^{-1})	P_0 (mW)	Molrity
0.39	1.00×10^{-7}	0.96	1.30	15	0.5
0.57	1.52×10^{-7}	1.43	1.79	15	1
1.14	3.13×10^{-7}	2.86	2.36	15	2

4 Conclusions

In this paper, we synthesised stable, water-soluble PbS nanoparticles which leads to stable colloid. Using common methods of characterization of nanoparticles, we concluded that TGA is a suitable capping agent to synthesis lead sulfide nanoparticles. Nonlinear optical properties of the sample were investigated by the Z-scan technique in which a continues-wave He-Ne laser beam was used. We concluded that this material is a self-defocusing medium whose nonlinear refractive index is increasing with the increase in molarity.

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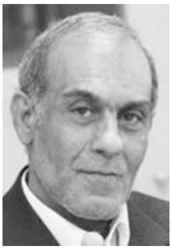

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