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Synthesis and physical properties of lead sulphide-polyvinyl alcohol-polyethylene glycol nanocomposite thick film

Moses. V. G. Isaiah* and G. Hamsavalli

Department of Physics, Velammal Engineering College, Chennai-600 066, Tamil Nadu, India.

***Corresponding author:** isaiahmoses758@gmail.com

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Abstract

The nanocomposite film of lead sulphide and poly(vinyl alcohol)/poly(ethylene glycol) has been prepared by solvent casting technique. Lead nitrate and sodium sulphide were used as lead (Pb^{2+}) and sulphur (S^{2-}) ion sources respectively. XRD pattern reveals that the formation of PbS nanocomposite film with cubic phase. SEM micrograph shows that the PbS nanoparticles are well monodispersed with spherical shape throughout polymer. Optical absorption spectrum results the strong quantum confinement effect due to the presence of small size of nanostructured PbS. Photoluminescence spectrum exhibits the two emission peaks corresponding to the blue-green and green emissions of PbS. The frequency dependent dielectric studies were analysed at different temperatures.

Keywords: *Nanocomposites, thick films, X-ray techniques, luminescence.*

1. Introduction

In recent years, semiconductor nanoparticles have been extensively studied due to their novel properties which are greatly different from those of their bulk materials. Nowadays, semiconductor/polymer nancomposites have attracted growing interest because these materials offer new performance by combining properties from both the semiconductor and the polymer matrix [1-4]. The nanoparticles exhibit unique properties, due to quantum size effects and the large number of unsaturated surface atoms. The polymeric matrix provides additional qualities, such as the processability, solubility and thermal stability of the systems. In this way, nanocomposite materials possessing novel catalytic, conductive, magnetic and optical properties can be obtained. The polymers are selected on the basis of their specific properties such as nonlinearity, electrical conduction, properties related to oxidation resistance of sulphide nanopaticles and they form a nanoreactor to restrict the growth of nanoparticle and prevent aggregation [5]. The main advantage of semiconductor nanoparticles dispersed in polymers is that good quality films of desired thickness can be prepared and stabilized for long periods of time [6].

Among the semiconducting nanoparticles, lead sulphide (PbS) is a IV–VI group of semiconductor having cubic crystal structure with a small band gap (0.41 eV, at 300 K) and a large exciton Bohr radius of 18 nm, which contribute to the strong quantum confinement effect over a large nanocrystalline size range. Therefore, nanoscaled PbS has shown some novel and excellent optical and electronic properties, such as IR photodetectors, photovoltaics, and mode-locked lasers [7-9]. Moreover, an exceptional third-order nonlinear optical property of PbS nanoparticles has been found, which makes PbS nanocrystals a promising candidate for photonic and optical switching device applications [10]. Even though a number of polymers have been used as hosts for PbS nanocomposites [11-16], there is no reported work on poly(vinyl alcohol)(PVA)/poly(ethylene glycol)(PEG) blends. PVA and PEG are highly water soluble hydrophilic polymers and have been wide range of applications in optical and electrical properties of nanoparticles. They have also been important advantages of good mechanical strength, long term temperature stability, acousto-optical, excellent film forming properties and surfactant materials of nanoparticles [16, 17]. Various methods have been developed to fabricate and characterize PbS/polymer nanocomposites [11-16]. In this report, we have synthesized the nanocomposite film of PbS nanoparticles and PVA/PEG by solvent casting technique. Structural, optical and dielectric properties of film have been studied in detail.

2. Experimental details

PbS nanocomposite film has been prepared by solvent casting technique. Lead nitrate and

sodium sulphide were mixed (molar ratio of 1:1) to form the colloidal solution. Then the mixture solution was stirred vigorously by magnetic stirrer. After 2 hours, colour of the whole solution turned into dark brown. This indicates that the formation of PbS nanoparticles. This reaction was continued upto 8 hours to form homogeneous solution. The resultant solution was washed with distilled water for several times and dried at 80°C to obtain PbS nanoparticles. Separately, a definite wt% ratio of PVA:PEG (65:35) was dissolved in distilled water and mixed together. This solution was stirred at 60°C until the transparent solution is formed. To this solution, a known quantity of PbS nanoparticles was added by same stirring rate and temperature. After ½ h, this solution was treated with high intensity ultrasound irradiation under ambient air to 30 min. Then this solution was poured in a clean glass petri-dish and the solvent was allowed to evaporate at room temperature for 2 days. Similarly, pure PVA/PEG film was prepared separately in distilled water. The structural properties of the nanocomposite film were studied with XRD using Shimadzu XRD-6000 diffractometer with CuKα radiation. The surface morphology of the film was examined by SEM using JEOL-JSM-6360 microscope. The optical absorption properties have been studied by PerkinElmer LAMBDA 35 UV-VIS-NIR spectrophotometer. Photoluminescence study has been carried out using the PerkinElmer LS55 spectrometer in region of 400-700 nm at room temperature. The dielectric measurements of sample in the frequency ranging from 1 kHz to 15 MHz over the temperature range of 303 K to 348 K were analyzed by N4L Phase Sensitive Millimeter interfaced with Impedance Analyzer.

3. Results and discussion

3.1. X-ray diffraction studies

Fig. 1(a) shows the XRD pattern of PbS nanocomposite film. The diffraction peaks corresponding to (111), (200), (220) and (311) planes confirmed that the PbS nanocrystallites are in cubic phase. The calculated lattice constants are found to be a = b = c = 5.890 Å, which are in good agreement with the JCPDS Card File No. 5-592. For comparison, the obtained interplanar spacing (d) values of PbS film along with the JCPDS data are given in Table. 1. The average nanocrystallite size of PbS, which was determined from the half-width of diffraction using Debye Scherrer's formula [18], is found to be 19.4 nm. The peaks are observed at 20.1° and 23.7° due to the PVA and PEG polymers. The surface morphology of PbS nanoparticles and nanocomposite film is shown in Fig 1(b) and 1(c). It can be observed (Fig. 1b) that the PbS nanoparticles are dispersed as globular shape with aggregation due to the absence of polymer. But, as shown in Fig. 1(c), the spherical shape of PbS nanoparticles are well monodispersed in the film due to the presence of polymer. The grain size is found to be varying from 23 nm to 54 nm. The minimal aggregation of crystallites causes the variation of grain size. However, the size measured by SEM is almost similar to the size calculated from the XRD.

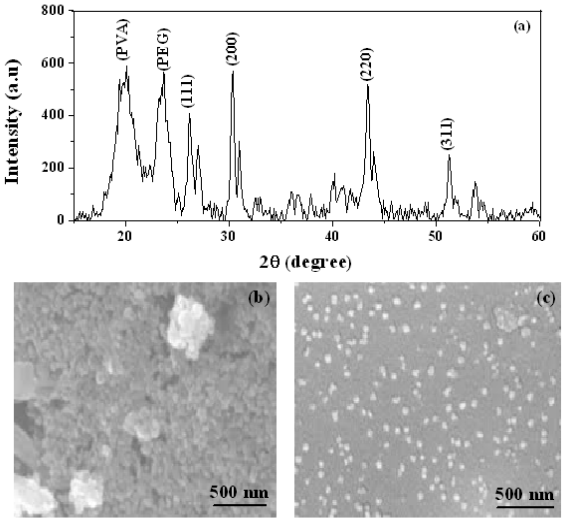

Fig. 1 *(a)XRD spectrum of PbS nanocomposite film, SEM micrograph of (b) PbS nanocomposite film and (c) PbS nanoparticles only*

Table. 1 Comparison of interplanar spacing (d, Å) values from JCPDS and XRD

hkl	JCPDS	XRD
(111)	3.424	3.395
(200)	2.965	2.945
(220)	2.096	2.087
(311)	1.788	1.782

3.2. Optical studies

Fig. 2(a) shows optical absorption spectrum of title film. As the size of the semiconductor particle decreases to the nanoscale the band gap of the semiconductor increases causing a blue shift in the UV-Vis absorption spectrum. While compared with bulk PbS (3020 nm), the absorption edge of PbS film (250 nm) is shifted towards to shorter wavelength. It exhibits the large blue shift in the film due to the strong quantum confinement effect. The well defined absorption edge at 250 nm is attributed to the optical transition of the first excitonic state. A typical $(\alpha h\nu)^2$ versus energy plot for nanocomposite film is shown as inset of Fig. 2(a). By extrapolating the straight line portion of the curve to intercept the

energy axis, the band gap energy of PbS film has been calculated from Tauc relation [11] and is found to be 4.7 eV. It is greater than the band gap of bulk PbS (0.41 eV). This indicates the formation of small size of PbS nanoparticles. The particle size of PbS nanoparticles using hyperbolic band model equation [19] is found to be 1.1 nm. When the size of the particle is reduced in nanometer scale, the energy states separation is too high. So that it shows that the optical band gap was highly enhanced.

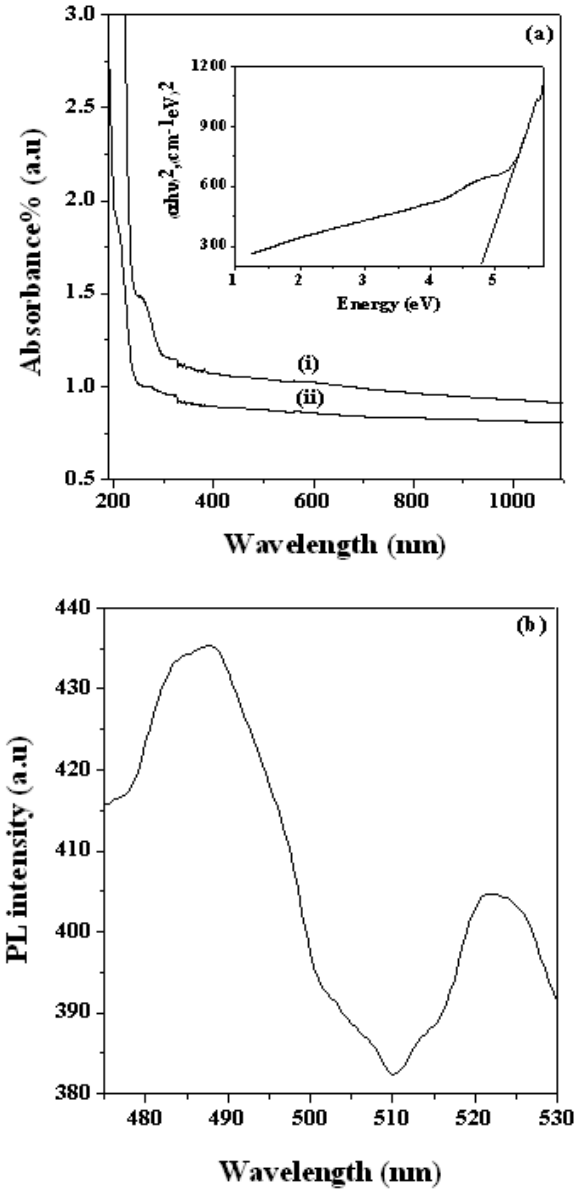

Fig. 2 *(a) Absorption spectrum of (i) PbS nanocomposite film and (ii) pure PVA/PEG film. Inset shows plot of $(\alpha h\upsilon)^2$ vs energy and (b) Photoluminescence spectrum of PbS nanocomposite film*

Photoluminescence spectrum with an excitation wavelength 305 nm is shown in Fig. 2(b). It exhibits a broadened peak due to the small dimension of the nanoparticles. It can be observed that the two emission peaks centered on 487 nm and 521 nm. The band present at 487 nm is, known as blue-green emission peak, ascribed to removal of sulfur anion vacancies. The second emission of PbS at about 521 nm is known as green band, which is observed from the recombination of electrons in singly occupied oxygen vacancies with photoexcited holes. Similar emission peaks have been reported by earlier workers [15, 20].

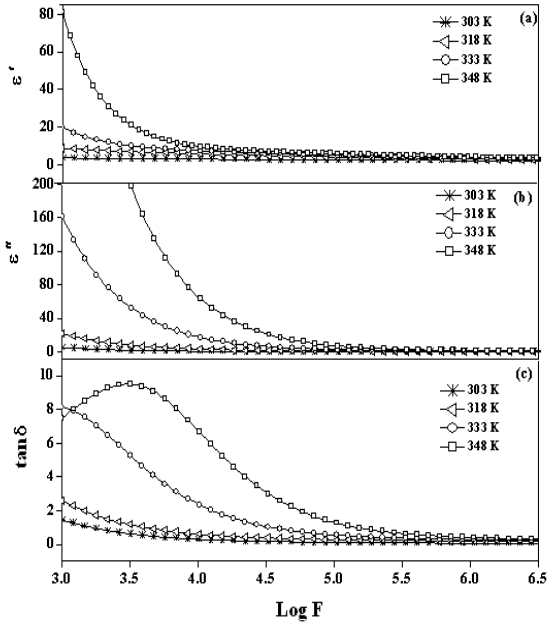

Fig. 3 *Temperature and frequency dependent of (a) ε′ and (b) ε″ parts of dielectric constant and (c) tanδ of PbS nanocomposite film*

3.3 Dielectric studies

Fig. 3 shows the frequency dependence of (a) real (ε') and (b) imaginary (ε") parts of dielectric constant and (c) loss tangent (tanδ) of title nanocomposite film at different temperatures. The high values of ε', ε" and tanδ at low frequency with increasing temperature, which might be due to the electrode and interfacial effects of the films. They show a linear decrease with increase of frequency and are saturated at higher frequencies. This may be attributed to the tendency of dipoles in film to orient themselves in the direction of the applied field. One can be observed from Fig. 3, essential increase of ε" value, compared with ε' which is due to electronic conductivity between the PbS nanoparticles and

polymer matrix [21]. Fig. 3(c) shows a peak and it shifted towards the higher frequency on increase in temperature. It indicates the presence of relaxing dipoles of PbS nanoparticles which is due to the number of charge carriers increased by thermal activation.

4. Conclusion

We have successfully prepared PbS nanocomposite film using solvent casting technique. The crystal structure and particle size were determined by XRD. SEM showed the spherical shape of nanoparticles is well monodispersed in the film. Optical absorption spectrum revealed a strong blue shift indicating the presence of quantum confinement effect. Photoluminescence spectrum exhibited blue-green and green bands of nanostructured PbS. The dielectric permittivity increased at lower frequency with increasing temperature favours the conductivity of the film which is directly related to an increase in mobility of localized charge carriers.

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