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Structural, optical and electrical characterization of Mn^{2+} and Cd^{2+} doped/co-doped PbS nanocrystals

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ABSTRACT

The strain and stress minimized nanoparticles of PbS, $Pb_{0.95}Mn_{0.05}S$, $Pb_{0.95}Cd_{0.05}S$ and $Pb_{0.90}Mn_{0.05}Cd_{0.05}S$ were successfully synthesized using solvothermal microwave irradiation (SMI) method. The quality/performance of the materials was found to be in the series $Pb_{0.90}Mn_{0.05}Cd_{0.05}S > Pb_{0.95}Cd_{0.05}S > Pb_{0.95}Mn_{0.05}S > PbS$. The average crystallite size in the best material $Pb_{0.90}Mn_{0.05}Cd_{0.05}S$ was found to be ~18 nm where the particles are distributed within the range 20–60 nm. Optical studies reveals the existence of direct band gap in the range of 2.025–2.235 eV (±0.012 eV). This is one of the widest E_g values reported for this system. Electrical measurements were performed on compacts of nanoparticles in the temperature range 313–433 K and frequency range 100 Hz–1 MHz. The conductivity profile exhibits two components; in which the activation energy (ΔE) values obtained for the temperature range 373–433 K is almost twice as compared to the ΔE value obtained for 313–373 K. Nonetheless, the conductivity at the higher temperatures was always higher than at the low temperatures and interestingly, the nanoparticles exhibits higher conductivity than their bulk counterpart. The feasible mechanism of conduction is discussed.

1. Introduction

Bulk PbS is a direct band gap IV–VI semiconductor (E_g = 0.41 eV) with the exciton Bohr radius value of 18 nm [1,2]. Recent reports suggest that the absorption edge of PbS exhibit large blue shift [3] while reducing the crystallite size from bulk to nano. It means, by suitable material tailoring techniques it could also be possible to achieve quantum confinement effects in this system. Depend upon the achieved E_g values, researchers have already demonstrated the potential applications of PbS system in a number of devices; as for example, electroluminescent devices [4], optical sensors [5], IR detectors [6] and solar absorbers [7], etc. For such applications, as per the known literature knowledge, PbS nanocrystals with sizes up to 50 nm may yield convincing results. However, since the intrinsic surface energy along the {1 1 1} facet of the nucleated PbS seed is higher, PbS crystals rapidly grow to bulk cubic structure. Several physical, chemical and thermal methods have been reported [8–17] for synthesizing semiconductor PbS nanoparticles, among these techniques, solvothermal microwave irradiation (SMI) [18] technique offers simple, cost effective and industrially scalable route for the production of high quality nanocrystals.

Recently, much attention has been paid for the synthesis of metal doped nano PbS. It was reported that the properties such as band gap, electrical conductivity, and thermoelectric power can be significantly modulated and fine-tuned by employing dopants through pertinent material processing approaches [19–21]. In the present work, we achieved the synthesis of highly stress and strain reduced nanoparticles of PbS, $Pb_{0.95}Mn_{0.05}S$, $Pb_{0.95}Cd_{0.05}S$ and $Pb_{0.90}Mn_{0.05}Cd_{0.05}S$. Synthesis was done using comparatively cheaper raw materials without the need of inert or vacuum conditions. The UV–Vis spectral analysis indicated that the optical band gap of the system was enhanced from 0.5 to 2.1–2.3 eV, which is a significant development. The electrical properties are rather curious, as the conduction activation energy above and below the temperature 373 K is entirely different at any range of frequencies.

2. Experimental details

2.1. Materials

Analytical reagent (AR) grade lead(II) acetate trihydrate ($Pb(CH_3COO)_2{\cdot}3H_2O$), manganese(II) acetate tetrahydrate ($Mn(CH_3COO)_2{\cdot}4H_2O$), cadmium acetate dihydrate ($Cd(CH_3COO)_2{\cdot}2H_2O$) and thiourea ($CS(NH_2)_2$) were purchased from Merch

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chemicals. Ethylene glycol ($C_2H_6O_2$) was purchased from Central Drug House (P) Ltd. These chemicals were used without further purification.

2.2. Sample preparation

In a typical synthesis procedure for the preparation of undoped PbS nanocrystals, 3.794 g of lead(II) acetate trihydrate was dissolved in 100 ml ethylene glycol and stirred for 1 h at room temperature. Also, 2.284 g of thiourea was dissolved in 100 ml of ethylene glycol. Then, the thiourea solution was slowly added to the above mentioned solution under magnetic stirring. The solution was kept in a domestic microwave oven (operated with frequency 2.45 GHz and power 800 W) and irradiated in air for 15 min with 40% of output power (about 40%: it means that the duty cycle was 24 s on, 36 s off). The colloidal precipitate obtained was cooled to room temperature naturally and washed with doubly distilled water and then with acetone to remove the impurities. Then the sample was centrifuged to get the precipitate out and dried in an oven at 80 °C for 6 h and collected as the yield. In order to prepare $Pb_{1-x}Mn_xS$, $Pb_{1-y}Cd_yS$ and $Pb_{1-x-y}Mn_xCd_yS$ (where $x = y = 0.05$), a 5 mol. % of the lead(II) acetate reactant was replaced by the Mn/Cd acetate precursor.

2.3. Reaction mechanism

The reaction mechanism of microwave assisted synthesis of pure PbS nanocrystal is summarized as below: Firstly, the strong complexation between lead(II) acetate and thiourea lead to the formation of lead–thiourea complex in the microwave synthesis, which prevents the production of a large number of free S^{2-} in the solution and will become favorable for the formation of the products. Secondly, the lead–thiourea complexes undergo thermal decomposition under microwave irradiation to produce lead sulfide (PbS). The reaction can be expressed as follows:

$$(CH_3COO)_2Pb \cdot 3H_2O + \underset{2H_2NCNH_2}{\overset{S}{\overset{\|}{}}} \xrightarrow[\text{Stirring}]{\text{Ethylene glycol}} [Pb(SCN_2H_4)_2](CH_3COO)_2$$

$$[Pb(SCN_2H_4)_2](CH_3COO)_2 \xrightarrow[\text{Microwave irradiation}]{\text{Decomposition under}} PbS\downarrow + 2CH_3COOH + N_2\uparrow + H_2S\uparrow + H_2O$$

2.4. Characterization

Structural characterization was performed using an automated PANalytical X-ray powder diffractometer with monochromated Cu Kα radiation ($\lambda = 1.541$ Å). The diffraction profiles have been refined and the structural details were analyzed by Rietveld refinement technique [22]. The crystallite size was calculated from the XRD profiles using Scherrer method [23], de Keijser's strain exclusion method [24] and Williamson–Hall (W–H) method [25]. The built-in average stress (S) developed in the material was determined by the relation [26]

$$S = \frac{\varepsilon Y}{2\sigma} \tag{1}$$

where ε (strain) was obtained from W–H plot, Y and σ are the Young's modulus and Poisson's ratio of the bulk sample, respectively. For PbS, the value of Y is 70.2 GPa and σ is 0.28 [27]. The strain present in the material was calculated by W–H method (more discussions are made in Section 3). The particle size analysis was performed by TEM facility – FEI Technai G^2 300 kV. Optical absorption measurements were done at room temperature using a SHIMADZU UV-1800 PC spectrometer with a medium scan speed sampling interval 1 nm in the wavelength range 300–1100 nm.

For electrical characterization, the synthesized powder materials were compacted into disk shaped pellets of dimensions 13 mm in diameter and 1 mm (±0.11 mm) in thickness by applying a uniaxial pressure of 0.49 GPa for 4 min using a hydraulic press and the pellets were then densified by sintering at 343 K for 1 h. The AC conductivity and dielectric properties were measured over 313–433 K temperature and 100 Hz–1 MHz frequency ranges. The capacitance (C) and dissipation factor ($\tan\delta$) measurements were carried out to an accuracy of ±1% with Agilant 4284A LCR meter. The observations were made while cooling the sample by using the conventional two-probe technique [28]. Temperature was controlled to an accuracy level of ±1 K. The air capacitance (C_{air}) in between the two electrodes was also measured. The dielectric constant (ε_r) of the nanocrystal was calculated using the relation,

$$\varepsilon_r = \frac{C}{C_{air}}. \tag{2}$$

The AC electrical conductivity (σ_{ac}) was calculated using the relation

$$\sigma_{ac} = \varepsilon_o \varepsilon_r\ \omega\ \tan\ \delta, \tag{3}$$

where ε_o is the permittivity of free space (8.854×10^{-12} F/m) and ω is the angular frequency ($\omega = 2\pi f$; $f = 100$, 1, 10, 100 and 1000 kHz in the present study). From the AC electrical conductivity the activation energy has been calculated following the relation

$$\ln\sigma_{ac} = \ln\sigma_o - \frac{\Delta E}{kT} \tag{4}$$

ΔE-activation energy, T-absolute temperature, k-Boltzmann constant and σ_o is a constant.

3. Results and discussions

The PbS system reported in the literature exhibits diverse band gap values which ranges between 0.4 and 1.2 eV [26,29–33]. The upper value suggests that PbS system can be a close contender to the expensive nano Si for energy conversion applications. However, considering the losses incurred during the conversion process, the E_g value of PbS needs to be enhanced. Apparently there are many attempts for the synthesis of nano PbS but only thin film approaches results better value [34–36]. The powder synthesis methods either offer bulk crystals or unstable nanoparticles [12,37–39], mainly due to the high surface energy and stress/strain inducted on the particles by the material tailoring constraints. Hence our main focus was to synthesize the smallest possible PbS particles (doped/undoped) with the least possible stress and strain in the material.

3.1. Structural studies

In the present investigation, we have succeeded on the synthesis of good quality – highly stress/strain controlled nano PbS samples through a cost effective method called solvothermal microwave irradiation (SMI) method. Fig. 1 shows the refined powder X-ray diffraction (PXRD) profiles of the as-prepared samples. The qualitative XRD peak analysis reveals that only PbS crystals got formed and no phases of oxides, impurities or separate nucleation of Pb/S has occurred. The comparison of the calculated structural parameters with the standard JCPDS data (JCPDS file No. 05-0592) of PbS system reveals that all the synthesized materials possess cubic structure. The lattice parameter of the undoped PbS nanoparticles closely matches with the standard values known for the bulk PbS system (see Table 1). In all the cases of dopant incorporated samples, the lattice parameter values decrease without affecting the cubic structure. This effect, witnessed as a shift in the peak position, is due to the fact that the ionic radii of the Cd and Mn dopants are smaller than the ionic radii of Pb. All the structural details of the as-prepared samples are given in Table 1.

Careful observation on the (2 0 0) peak indicates that there is not only shifting in the peaks as a result of incorporation of dopants, but also a broadening of peaks due to the influence of dopants on the size of the crystallites (see Fig. S1 in the supporting information). From the profile broadening of diffraction peaks, the average crystallite size was calculated by three different methods (Scherrer method, de Keijser's strain subtraction method and W–H methods) [23–25] and the stress/strain minimization was illustrated with the support of the Williamson–Hall plots (W–H plot). In W–H method, the relation between the crystallite size (D) and the strain (ε) can be expressed as [33],

$$\frac{\beta\cos\theta}{k\lambda} = \frac{1}{D} + \frac{4\varepsilon\sin\theta}{k\lambda} \tag{5}$$

where β is the full width at half maximum (FWHM) intensity, ε is the average strain in the material, k is the shape factor (0.9) and λ is the wavelength of the X-ray. The reciprocal of y intercept straight away gives us the crystallite size value and the strain can be obtained from the slope of the straight line (generally, higher slope represents the presence of higher strain). In our case, as seen in Fig. 2, the nearly flat W–H straight lines suggests that all the PbS materials possess very less strain. The crystal size, strain and stress related information is summarized in Table 2. Interestingly, the strain is very much reduced in the smaller particles; a trend which is difficult to get when we process nanoparticles. The size vs strain curve is demonstrated in the supporting information Fig. S2. Moreover, in