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PbS_xSe_{1-x} thin films from the thermal decomposition of lead(II) dodecylxanthate and bis(*N,N*-diethyl-*N'*-naphthoylselenoureato)lead(II) precursors

Selina Ama Saah,¹ Paul D. McNaughter,² M. Azad Malik,³ Johannes A. M. Awudza¹, Neerish Revaprasadu,⁴ and Paul O'Brien^{2,3*}

¹ *Department of Chemistry, Kwame Nkrumah University of Science and Technology, Kumasi, Ghana*

² *The School of Chemistry, The University of Manchester, Oxford Road, Manchester, M13 9PL, United Kingdom. Email: paul.obrien@manchester.ac.uk*

³ *The School of Materials, The University of Manchester, Oxford Road, Manchester, M13 9PL, United Kingdom*

⁴ *Department of Chemistry, University of Zululand, Private Bag X1001, KwaDlangezwa, 3886, South Africa.*

Abstract

Thin films of PbS_xSe_(1-x) ($0 \leq x \leq 1$) have been deposited by spin coating of bis(dodecylxanthato)lead(II) (**1**) and/or bis(*N,N*-diethyl-*N'*-naphthoylselenoureato)lead(II) (**2**) complexes onto glass substrates followed by heating. The mole fraction of the selenium precursor in the coating mixture was varied from 0 to 1 by mixing the S and Se precursors. The as-prepared thin films were then heated at temperatures ranging from 250 to 400 °C. Powder X-ray diffraction (p-XRD) showed all films were of the halite structure with preferred orientation along (200) plane. The PbS films showed a closely packed network of nanorods, each comprised of smaller nanoparticles. The nanorods were about 500 nm in length and 25 nm in width; the adhered particles had *ca.* 30 nm sides. The PbSe nanoparticles were also cubic. The alloys showed an intermediate morphology between the rods and cubes depending on the precursor ratio in the coating mixture. The band gaps estimated from Tauc plots for the films heated at 250 °C for 30 minutes were 1.03 and 0.79 eV for PbS and PbSe respectively. The alloyed PbS_xSe_(1-x) thin films exhibited band gaps between those of PbS and PbSe. The band gaps and lattice parameters of the alloys varied in a Vegardian manner and could be closely correlated to the composition of the precursor mixture.

Keywords: Lead xanthate; lead selenourea; band gap; lattice constant; spin coating.

Introduction

Spin coating of molecular precursors onto substrates followed by heating at modest temperatures is a potentially cost effective, scalable and technically straight-forward route to many important functional materials [1-2]. The dimensions and uniformity of the crystallites can be varied by controlling the thickness, processing temperature and composition of the films [3].

Lead chalcogenides, in the nanodispersed form share similar features, which include narrow bulk band gap ranging from 0.41 to 0.27 eV at 300 K and excitonic Bohr radius from *ca.* 20 to 50 nm from S to Se [4]. These properties offer unique opportunities for strong quantum confinement of charge carriers both individually and in excitonic modes [4, 5]. These materials are being actively explored for mid- and near- infrared applications such as infrared detectors, light emitting diodes and solar cells [6, 7].

Alloys of the type $\text{PbS}_x\text{Se}_{(1-x)}$ ($0 \leq x \leq 1$) are potentially useful materials that allow band gap engineering in thin films or a particulate form and also the exploitation of size-dependent quantum confinement effects [8]. PbS and PbSe are closely related in a structural sense; the anionic radii differ by only *ca.* 15% of each other and the lattice mismatch between the two halite phases is only *ca.* 2% [9]. Perhaps most importantly, $\text{PbS}_x\text{Se}_{(1-x)}$ can yield efficient photovoltaic devices (with power conversion efficiency of about 10%) through the combination of short circuit current (J_{SC}) and open circuit voltage (V_{OC}) unavailable in either of the parent PbS or PbSe materials [10, 11]. Such ternary materials can be prepared by mixing the parent semiconductors under appropriate solid solubility conditions [12]. We have been interested in investigating new routes to the syntheses of ternary $\text{PbS}_x\text{Se}_{(1-x)}$ thin films. Carefully designed precursors can match thermal decomposition profiles and lead to better compositional control.

Metal xanthates in particular decompose cleanly at relatively low temperatures by Chugaev elimination to yield the corresponding metal sulfides [1, 2]. Most reports on the syntheses of nanoparticulate $\text{PbS}_x\text{Se}_{(1-x)}$ concern hot injection methods [9-11, 13-16], flash evaporation [17], thermal evaporation [18] or vacuum evaporation [12] techniques, which all

require moderately harsh conditions including high vacuum, expensive apparatus and very toxic starting materials.

In this paper, we report the syntheses of $\text{PbS}_x\text{Se}_{(1-x)}$ ($0 \leq x \leq 1$) thin films by spin coating *bis*(dodecylxanthato) lead (II) (**1**) and *bis*(*N,N*-diethyl-*N'*-naphthoylselenoureate)lead(II) (**2**) followed by heating at moderate temperatures. This pathway opens research window to the traditional colloidal approach to nanomaterial syntheses.

Experimental

Materials and methods

1-Dodecanol (98%), potassium hydroxide ($\geq 85\%$), 2-naphthoyl chloride (99.8%), potassium selenocynate (95%), sodium ethoxide (95%), lead(II) acetate trihydrate ($\geq 99.9\%$), carbon disulphide ($\geq 99\%$), diethylamine ($\geq 99.5\%$), petroleum ether 40-60 °C ($\geq 90\%$), toluene (99.8), hexane (95%), acetone ($\geq 99.9\%$), ethanol (≥ 99.8), chloroform ($\geq 99\%$) and diethyl ether ($\geq 99.9\%$) were purchased from Sigma-Aldrich and used without any further purification.

Syntheses and characterization of *Bis*(dodecylxanthato)lead(II) (**1**)

Complex (**1**) was synthesized following the method reported in the literature [19]. Briefly, 1-dodecanol (9.3 g, 50 mmol) in a three necked flask was heated to 50 °C, then KOH (2.8 g, 50 mmol) was added and the mixture stirred until complete dissolution. The mixture was cooled to room temperature and CS_2 (7.6 g, 50 mmol) added drop-wise until the formation of a pale yellow precipitate. Petroleum ether (100 ml) was added with continued stirring for 30 minutes. Finally, the precipitate was filtered, rinsed several times with water (30 ml) and petroleum ether (30 ml) to yield the dodecyl xanthate ligand. Lead acetate trihydrate (3.2 g, 8.3 mmol) was dissolved in water (20 ml) and added drop-wise to the dodecyl xanthate ligand (5.0 g, 16.7 mmol) in methanol (50 ml). The mixture was stirred for 1 hour and the resulting precipitate filtered, washed with excess water and dried. The crude product was recrystallized from toluene to yield the *bis*(dodecylxanthato)lead(II) complex (82.3%). Elemental analysis; % calc. (found): C, 42.8 (43.3); H, 6.9 (7.0); S, 17.6 (17.4); and Pb 28.4 (27.6). m.p 87 °C. MS (ESI^+), $m/z = [\text{M}+\text{Na}]^+$ 754. $\nu_{(\text{C-O})}$ 1099 cm^{-1} , $\nu_{(\text{C-S})}$ 1015 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz) δ/ppm : 0.80 (t, $J = 6.9$ Hz, 6H; CH_3), 4.55 (t, $J = 6.7$ Hz, 4H; CH_2).

Syntheses and characterization of *Bis*(*N,N*-diethyl-*N'* naphthoylselenoureate)lead (II) (**2**)

Bis(N,N-diethyl-*N'*-naphthoylselenourea)lead(II) (**2**) was synthesized as reported in the literature with slight modification [20]. Typically, the *N,N*-diethyl-*N'*-naphthoylselenourea ligand (4.0 g, 12 mmol) was dissolved in ethanol (100 ml) and stirred until complete dissolution. Sodium ethoxide (0.8 g, 12 mmol) was then added. Lead acetate trihydrate (2.3 g, 6 mmol) which had been dissolved in water (20 ml) was then added drop-wise to the mixture. The resulting precipitate was filtered and recrystallized from toluene and hexane to yield the *bis*(*N,N*-diethyl-*N'*-naphthoylselenourea)lead(II) complex (80%) Elemental analysis; % calc. (found): C, 44.1 (44.2); H, 3.9 (3.8); N, 6.4 (6.3); and Pb 23.8 (23.9). m.p 152 °C. MS (ESI⁺), m/z = [M+H]⁺ 873. $\nu_{(C-O)}$ 1507 cm⁻¹, $\nu_{(C-N)}$ 1352 cm⁻¹, $\nu_{(C-Se)}$ 888 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz) δ /ppm: 1.08 (t, J = 7.2 Hz, 6H; CH₃), 8.21 (m, J = 8.6 Hz, 6H; Ar). ⁷⁷Se NMR δ /ppm: 291 (s, CSe₂).

Deposition of PbS_xSe_(1-x) thin films by spin coating and heating

In a typical deposition of PbS or PbSe thin films, 0.27 mmol of (**1**) or (**2**) was dissolved in chloroform (1.5 ml) and spin coated onto a glass slide at a spin speed of 1500 rpm for 20 seconds using an Ossila spin coater. For ternary PbS_xSe_(1-x) thin films, different mole ratios of (**1**) and (**2**) were mixed to an overall concentration of 0.27 mmol, dissolved in chloroform and spin coated as above. The coated slides were then heated under argon gas for 30 minutes at temperatures ranging from 250 to 400 °C in 50 °C increments.

Analyses

Elemental (EA) and thermogravimetric (TGA) analyses were carried out by the Microelemental Analysis service at University of Manchester. EA was performed using a Flash 2000 Thermo Scientific elemental analyzer and TGA data obtained with Mettler Toledo TGA/DSC1 stare system between the ranges of 30–600 °C at a heating rate of 10 °C min⁻¹ under nitrogen flow. Mass spectrometry was performed by The University of Manchester Mass Spectrometry Suite. Powder X-ray diffraction (p-XRD) analyses were done using a Bruker AXS D8 diffractometer employing Cu-K α radiation (λ =1.5418 Å) at 40 kV and 40 mA at room temperature. The thin films were scanned between 20 to 90° with a step size of 0.02° and dwell time of 3 s. Scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) spectroscopy were carried out using a Philips XL 30 FEG scanning electron microscope equipped with a DX4 EDX detector and was used to determine surface morphology and elemental composition of the thin films. All samples were carbon coated

using Edwards coating system E306A prior to SEM and EDX analyses. Absorption measurements were performed on Perkin Elmer UV-VIS-NIR lambda 1050 spectrometer.

Results and discussion

The chemical structures of the molecular complexes used as single source precursors for PbS, PbSe and $\text{PbS}_x\text{Se}_{1-x}$ thin films in this study are shown in Fig. 1. The experimental elemental analyses (%) for both complexes were found to be within 0.5% of the calculated values, and the correct exact masses were observed by electrospray mass spectrometry which confirmed that the synthesized complexes were pure and agreed with the proposed stoichiometric formulae. ^1H and ^{77}Se NMR spectra confirmed the requisite number of proton and selenium environments in all cases and the expected J couplings were also observed in the ^1H NMR spectra.

Fig. 1 Structures of the single source precursors used in this study. (a) *bis*(dodecylxanthato)lead(II) (**1**) and (b) *bis*(*N,N*-diethyl-*N'* naphthoylselenoureato)lead (II) (**2**).

Thermogravimetric analysis (TGA) of the complexes, under nitrogen at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ from $30\text{--}600\text{ }^{\circ}\text{C}$, was performed to determine their thermal decomposition profiles. The *bis*(dodecylxanthato) lead (II) complex (**1**) decomposed in two steps to a plateau which is indicative of the formation of a residue with a constant weight. The first step begins at $91.4\text{ }^{\circ}\text{C}$ and completed at $193.9\text{ }^{\circ}\text{C}$ with a 23.7% weight loss corresponding to the loss of one

dodecyl alkyl chain (23.2%). The second step starts at 198.7 °C and is completed at 326.9 °C with a maximum weight loss of 46.9%, resulting in a residue amounting to 29.4% of the initial weight. This value is lower than 32.8% calculated for 100% conversion to PbS in the complex (1). The high stability of higher alkyl chain metal xanthates may have caused some evaporation of the precursor or sublimation of sulfur from the product [1, 21]. The lead selenoureato complex (2) decomposed in four steps to give a residual weight of 37.8%, which is higher than the expected value of 32.8% for PbSe. This could be due to some carbon contamination because of its relative bulkiness [22].

Fig. 2 Thermogravimetric analysis (TGA) profile of complexes (1) and (2) at a heating rate of 10 °C min⁻¹ under nitrogen at 100 ml min⁻¹

The p-XRD patterns of the as-deposited PbS and PbSe thin films after heating at temperatures ranging from 250–400 °C were consistent with the face-centred cubic (halite) structure of PbS (ICDD 00-005-0592) and PbSe (ICDD 01-077-0245) showing no oxide contamination (Fig. 3). Preferred growth along (200) plane was observed in all cases of the thin films as report in literature [1, 6, 21].

The crystallite sizes were calculated using the Scherrer equation.

$$D = \frac{k\lambda}{\beta \cos \theta} \quad \text{Equation 1}$$

where; D is the crystallite size, k is a dimensionless shape factor, λ is the wavelength of the radiation, B is the line broadening at half the maximum intensity (FWHM) after subtracting the instrumental broadening and θ is the Bragg angle.

The crystallite sizes obtained by Scherrer analysis for the particles along the (200) plane of the as-prepared PbS thin films were 17.4, 21.6, 22.4 and 22.8 nm for 250, 300, 350 and 400 °C respectively. Increasing the temperature led to larger crystallites in the thin films [23]. There was a similar variation in the PbSe growth with critical dimensions ranging from 33.7 to 35.5 nm. The calculated lattice constant (a) ranged from 5.936 ± 0.005 Å for PbS and 6.126 ± 0.005 Å for PbSe. These values compare closely with the literature values of 5.936 Å and 6.127 Å for PbS and PbSe respectively Table S1 (Supporting Information) [8].

Fig. 3 Powder XRD patterns of (a) PbS and (b) PbSe thin films deposited by spin coating of complex (1) and (2) respectively following heating for 30 minutes at various temperatures as indicated.

The p-XRD patterns of the as-prepared $\text{PbS}_x\text{Se}_{(1-x)}$ thin films grown on glass substrates varied with the composition of the precursor mixture (Fig. 4). The p-XRD pattern of $\text{PbS}_x\text{Se}_{(1-x)}$ thin films exhibit the same general pattern of cubic reflections as observed for the parent PbS and PbSe compounds. This indicates that the $\text{PbS}_x\text{Se}_{(1-x)}$ thin film alloys retained the halite structure. The $\text{PbS}_x\text{Se}_{(1-x)}$ alloys also exhibit linearity in the incorporation of the selenium in the thin films as compared to the mole fraction present in the original precursor solution [10]. Generally, increasing the mole fraction of selenium in the feed precursor caused a gradual

shift of the diffraction angle of the p-XRD pattern to lower 2θ values. To illustrate this, the (200) reflection of PbS was at 30.1° which moves to 29.5° for $\text{PbS}_{0.5}\text{Se}_{0.5}$ and settles at 29.1° for PbSe. This provides some evidence for the formation of a single ternary $\text{PbS}_x\text{Se}_{(1-x)}$ alloy rather than mixed phases of PbS and PbSe. At a selenium mole fraction of 0.3 in the feed precursor mixture, all the selenium was incorporated into the $\text{PbS}_x\text{Se}_{(1-x)}$ thin film resulting in the formation of a $\text{PbS}_{0.5}\text{Se}_{0.5}$ ternary alloy. At this feed precursor ratio, the p-XRD peaks were intermediate between the standard matching lines of PbS and PbSe.

Other single source precursors that have been used for the synthesis of $\text{PbS}_x\text{Se}_{(1-x)}$ nanowires using solution-liquid-solution growth technique include lead(II)diethyldithiocarbamate and lead(II)imido *bis*(selenodiisopropylphosphinate) [15]. A similar shift from the PbS to PbSe phase was observed as the ratio of the lead(II)imido *bis*(selenodiisopropylphosphinate) complex was increased in the feed precursor from 0 to 1.

Fig. 4 (a) p-XRD patterns of $\text{PbS}_x\text{Se}_{(1-x)}$ obtained by spin coating mixtures of precursors following annealing for 30 minutes at 250°C and (b) expanded form of (a) along the (220) plain with corresponding (triangle) PbSe and (circle) PbS.

A plot of lattice constant against mole fraction of selenium in the feed precursor increased linearly and monotonically, only reaching a plateau when the mole fraction of selenium in the feed precursor is above 0.5 (Fig. 5). The linear behaviour observed as a result of all the selenium in the feed precursor being incorporated into the $\text{PbS}_x\text{Se}_{(1-x)}$ thin films (at selenium feed ratio ≤ 0.5) confirms that unit cell parameters vary linearly with composition for a

continuous substitutional solid [10, 24]. This is consistent with the p-XRD pattern which shows a gradual shift from the PbS standard pattern to a PbSe at these feed ratios.

Fig. 5 (a) Relation between the cubic lattice constant “ a ” and (b) % Se from EDX spectroscopy to the ratio of $[\text{Se}]/[\text{S}+\text{Se}]$ in the precursor concentration used for spin coating.

The morphologies of the as-prepared nanoparticles deposited on glass substrates were investigated using secondary electron SEM. The PbS thin films showed a closely packed network of nanorods, each covered with cubic particles. The nanorods were *ca.* 500 nm in length and 25 nm in width. The side lengths of the particles were 34 ± 4 , 44 ± 3 , 47 ± 5 and 50 ± 4 nm, which increased with increasing deposition temperature from 250, 300, 350 and 400 °C respectively (Fig. 6). The crystallite sizes from p-XRD calculated using the Scherrer equation were between 17.4–22.4 nm. These were multiples of the particle sizes obtained from the SEM implying that the particles and elongated features were polycrystalline [23]. Although PbS is known to have anisotropic growth with common morphologies such as cubes, spheres,

stars, rods and wires [1, 15, 21]. The growth of PbS nanorods with a cube at the tip have been reported by the O'Brien group [1, 21]. However, there is no report on such unique elongated structure with cubes at equal lengths along the entire length for PbS nanocrystals.

Fig. 6 SEM images of PbS nanoparticles deposited on glass substrate obtained from decomposition of complex at (a) 250, (b) 300, (c) 350, (d) 400 °C and (e, f) high magnification SEM images of (a) and (b).

PbSe thin films showed cubes which apparently agglomerated at higher processing temperatures (Fig. 7). Several researchers have reported cubic morphology for PbSe nanomaterials [20, 25]. The estimated particle sizes from the SEM were 322 ± 19 , 403 ± 10 , 437 ± 16 and 441 ± 17 nm at temperatures of 250, 300, 350 and 400 °C respectively. The increasing size with increasing temperature is consistent with the increase in the intensity of the peaks observed in the p-XRD pattern (Fig. 3 (b)). EDX showed approximately 1:1 ratio of Pb and S or Se.

Fig. 7 SEM images of PbSe nanoparticles deposited on glass substrate obtained from decomposition of complex at (a) 250, (b) 300, (c) 350 and (d) 400 °C.

The ternary $\text{PbS}_x\text{Se}_{(1-x)}$ thin films at $0.33 \leq x \leq 0.80$ at Se ratios ranging from 0.1 to 0.5 in the precursor mixture showed predominantly cubic morphologies with varying sizes. However, at $\text{PbS}_{0.5}\text{Se}_{0.5}$ a close packed mixed morphology of cubes and few rods were observed (Fig. 8). The rods could have been formed from the breaking of the fibrous structures of the PbS. Increasing the content of complex (1) in the precursor mixture increased the amount of the 1-dimensional morphology of the $\text{PbS}_x\text{Se}_{(1-x)}$ thin films.

Fig. 8 SEM images of $\text{PbS}_x\text{Se}_{(1-x)}$ thin films obtained from mixing (1):(2) at (a) 1:1, (b) 1.5:1, (c) 2.3:1, (d) 4:1 and (e) 9:1.

EDX analyses showed only peaks characteristic of Pb, S or Se Fig S1 (Supporting Information). All thin films were lead rich, but the relative sulfur content increased linearly as the ratio of (2) in the feed precursor was decreased (Fig 5). At a selenium mole fraction of 0.3 in the feed precursor, the %S content increased sharply and the formation of the alloy, $\text{PbS}_{0.5}\text{Se}_{0.5}$ was observed. The p-XRD pattern also confirmed the formation of a ternary alloy with the peaks shifting between those of pure PbS and PbSe.

Absorption spectra of the thin films are shown in supplementary information (Fig S2). We have estimated band gaps for our films using Tauc plots with the criterion that the correlation coefficient for the linear part of the plot used should be greater than 0.999, presented in supplementary information (Fig S3). The values for such films range from 0.7 to 2.3 eV work is summarised in more detail in the supplementary information table S1. Figure 9 shows the plot of mole fraction of precursor used against band gaps determined.

Fig. 9 Band gap against χ_S , i.e. $[S]/[S+Se]$, in precursor feed mixture

There are many reports on the measurements and calculation of band gaps for lead chalcogenides [27-40], with the bulk band gaps for pure PbS and PbSe at 0.41 and 0.27 eV respectively [4]. In line with other work this study leads to values in the range of 0.90 to 1.03 eV which are much larger than expected. Wider band gap energies have been reported for particles with sizes greater than their Bohr exciton radii which may be as a result of transitions other than the first excitonic absorption peak [26, 28-33]. Afonicheva and Matyushkin [26] plotted observed optical band gap against deposition time which was equated with crystallite size band gaps were on a plot asymptotically rising to a limit about 2.5 eV for the shortest times and levelling to a limit around 0.8 eV for the films with longest deposition times. Both theoretical and experimental determination of the dependence of band gap values on composition of $PbS_xSe_{(1-x)}$ have been reported to show a linear relationship between the band gap energy of thin film and the composition (Fig. 9) [10, 14, 40].

Conclusion

PbS, PbSe and $PbS_xSe_{(1-x)}$ thin films have been prepared by a spin coating method using single source precursors. It was found that all of the selenium in the precursor mixture was incorporated into the alloy. Analyses by p-XRD and SEM revealed that PbS and $PbS_xSe_{(1-x)}$ thin films consist of grains with critical dimensions of 30-50 nm; the size of which increases at higher heating temperatures. The estimated band gaps from the Tauc plots of films heated

at 250 °C for 30 minutes were 1.03 and 0.79 eV for PbS and PbSe respectively which is somewhat blue shifted from the bulk values of 0.41 and 0.27 eV due to observation of higher order transitions. The alloys formed have band gaps in between these values.

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Conflict of Interest The authors declare that they have no conflict of interest.

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