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Bismuth(III) dialkyldithiophosphates: Facile single source precursors for the preparation of bismuth sulfide nanorods and bismuth phosphate thin films

Jasmine B. Biswal [a], Shivram S. Garje [a,*], Jitendra Nuwad [b], C.G.S. Pillai [b]

[a] Department of Chemistry, University of Mumbai, Vidyanagari, Santacruz (East), Mumbai 400098, India
[b] Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India

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ABSTRACT

Two different phase pure materials (Bi_2S_3 and $Bi_2P_4O_{13}$) have been prepared under different conditions using the same single source precursors. Solvothermal decomposition of the complexes, $Bi\{S_2P(OR)_2\}_3$ [where, R=Methyl (Me) (**1**), Ethyl (Et) (**2**), n-Propyl (Pr^n) (**3**) and iso-Propyl (Pr^i) (**4**)] in ethylene glycol gave orthorhombic bismuth sulfide nanorods, whereas aerosol assisted chemical vapor deposition (AACVD) of the same precursors deposited monoclinic bismuth tetraphosphate ($Bi_2P_4O_{13}$) thin films on glass substrates. Surface study of the thin films using SEM illustrated the formation of variety of nanoscale morphologies (spherical-, wire-, pendent-, doughnut- and flower-like) at different temperatures. AFM studies were carried out to evaluate quality of the films in terms of uniformity and roughness. Thin films of average roughness as low as 1.4 nm were deposited using these precursors. Photoluminescence studies of $Bi_2P_4O_{13}$ thin films were also carried out.

1. Introduction

Bismuth phosphate and bismuth sulfide have attracted considerable interest due to their applications in various fields. The former acts as a catalyst in many reactions [1–3] and is used to separate radioactive elements from different matrices [4]. Bismuth phosphates are also useful in ion-sensors [5] and in improving electrical properties of phosphate glasses which are of technological interest as electronic and ionic conductors [6,7]. Recently, the luminescent studies of bismuth phosphate nanostructures revealed their potential applications in optoelectronics [8].

Bi_2S_3 has narrow band gap of 1.1–1.5 eV [9,10]. Due its thermoelectric and photovoltaic properties, it is suitable for applications in thermoelectric [11,12] and photoelectrochemical devices [13,14]. A large number of methods such as solvothermal [15], solventless thermolysis [16], hydrothermal [17], single source precursor [18,19], etc. have been employed for the synthesis of Bi_2S_3 nanostructures like nano-rods [15–19], nanowires [16,17], nano-flowers [19], etc. However, the preparation of bismuth phosphate nanostructures has not been explored much. The synthesis of $BiPO_4$ nanostructures have been reported by single source precursor route [20], the solvothermal method [8,21], the polyol method [22], etc. To the best of authors' knowledge there is no report on the preparation of $Bi_2P_4O_{13}$ nanostructures or thin films. Herein we report the use of single source precursors, $Bi\{S_2P(OR)_2\}_3$, [where, R=Methyl (Me) (**1**), Ethyl (Et) (**2**), n-Propyl (Pr^n) (**3**) and iso-Propyl (Pr^i) (**4**)] for the preparation of orthorhombic Bi_2S_3 nanorods by solvothermal decomposition route and the deposition of uniform monoclinic $Bi_2P_4O_{13}$ thin films by aerosol assisted chemical vapor deposition (AACVD) technique. The use of single-source precursors for the preparation of two different materials have been demonstrated by O'Brien et al. [23] earlier. Just by changing decomposition temperature, they have successfully prepared nickel selenide and nickel phosphide thin films using imido-bis-(diisopropylthioselenophosphinate) nickel(II), $Ni[^iPr_2P(S)NP(Se)^iPr_2]_2$ as single source precursor. Similarly, Liu et al. [20], have used $[Bi\{Se_2P(OPr^i)_2\}_3]$ for the preparation of both $BiPO_4$ nanowires and Bi_2Se_3 nanoplates.

2. Experimental

2.1. Materials and methods

All the solvents used were of analytical grade and the reactions were carried out under oxygen free nitrogen atmosphere. The complexes, $Bi\{S_2P(OR)_2\}_3$ were synthesized by modification of literature methods (R=Me [24], Et [24,25], Pr^n [25], Pr^i [24,25]). Infrared spectra of the complexes were recorded on Perkin Elmer

* Corresponding author. Fax: +91 22 2652 85 47.
E-mail addresses: ssgarje@chem.mu.ac.in, ssgarje@gmail.com, ssgarje@yahoo.com (S.S. Garje).

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Spectrum One FTIR spectrometer in the range of 400–4000 cm^{-1}. ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra of the complexes were recorded in $CDCl_3$ on Bruker Avance II 300 MHz NMR spectrometer operating at 300, 75.47 and 121.50 MHz, respectively. The chemical shifts were referred to tetramethyl silane (TMS) as an internal standard. Triphenyl phosphine was used as a standard for $^{31}P\{^1H\}$ NMR. The thermogravimetric analysis (TGA) of these precursors were performed on Perkin Elmer instrument, Pyris Diamond TG/DTA model with heating rate of 10 °C min^{-1} under nitrogen atmosphere. X-ray diffraction patterns of the materials were recorded using Cu*K*α radiation on a Philips X'pert PRO PANalytical X-ray diffractometer with an accelerating voltage of 45 kV at a scanning rate of 0.05°/s. Scanning electron microscopy (SEM) images were recorded on ULTRA 55 FESEM of Zeiss and Seron Inc. AIS2100 instruments. Energy dispersive X-ray analysis (EDAX) measurements were carried out on Oxford Inca instrument. The surface morphology and roughness of thin films were studied using Scanning probe microscope (SPM-Solver P47, NT-MDT, Russia). The measurements were carried out in contact mode. Silicon nitride cantilevers having force constant of 3 N/m were employed for measurement. The transmission electron microscopy (TEM) images were taken on a PHILIPS, CM 200 microscope with an operating voltage of 200 kV. The absorption spectra of the materials were recorded on a UV-2450 Shimadzu spectrophotometer. The photoluminescence spectra were taken on a Perkin Elmer LS 55 Fluorescence spectrometer. Raman spectra were recorded on RENISHAW inVia Raman Microscope using 514 nm Argon ion laser in the range of 100–1200 cm^{-1}.

2.2. Synthesis of precursors

2.2.1. $Bi\{S_2P(OMe)_2\}_3$ (**1**)

To a tetrahydrofuran (THF) solution of $BiCl_3$ (0.63 g, 2.00 mmol), 1.56 g (3.00 mmol) of $Pb\{S_2P(OMe)_2\}_2$ dissolved in 20 ml THF was added with constant stirring and the reaction mixture was stirred at room temperature for 10 h. The precipitated lead chloride was filtered through a G-4 sintered funnel. The filtrate was evaporated under vacuum to yield a bright yellow crystalline solid (yield: 1.34 g, 98.5%), mp 56 °C. Anal. Calcd. for $C_6H_{18}BiO_6P_3S_6$: C, 10.59; H, 2.66; Bi, 30.71; S, 28.27%. Found: C, 10.64; H, 2.58; Bi, 31.16; S, 27.97%. IR (in Nujol) cm^{-1}: 1177 (ν_{C-O}), 1029 (ν_{P-OR}), 640 (ν_{asym} PS_2), 517 (ν_{sym} PS_2). ^1H NMR ($CDCl_3$) δ: 3.83 (d, $^3J(^{31}P–O–C–^1H)$=15.62 Hz, $–OCH_3$), $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 54.24 (d, $^2J(^{31}P–O–^{13}C)$=5.51 Hz, $–OCH_3$), $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 101.6 ppm.

Similarly, precursors **2**–**4** were synthesized. Their details are given below.

2.2.2. $Bi\{S_2P(OEt)_2\}_3$ (**2**)

Recrystallized from dichloromethane–hexane as bright yellow crystalline solid (yield: 0.98 g, 91.5%), mp 55 °C. Anal. Calcd. for $C_{12}H_{30}BiO_6P_3S_6$: C, 18.85; H, 3.95; Bi, 27.33; S, 25.16%. Found: C, 18.53; H, 3.84; Bi, 27.65; S, 24.98%. IR (in Nujol) cm^{-1}: 1161 (ν_{C-O}), 1008 (ν_{P-OR}), 612 (ν_{asym} PS_2), 517 (ν_{sym} PS_2). ^1H NMR ($CDCl_3$) δ: 1.38–1.43 (t, $^3J(^1H–C–C–^1H)$=7.20 Hz, $–CH_3$), 4.18–4.28 (dq, $^3J(^{31}P–O–C–^1H)$=9.90 Hz; $^3J(^1H–C–C–^1H)$=7.20 Hz, $–OCH_2$), $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 15.93 (d, $^3J(^{31}P–O–C–^{13}C)$=8.68 Hz, $–CH_3$), 64.23 (d, $^2J(^{31}P–O–^{13}C)$=5.51 Hz,–O–CH_2–), $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 96.3 ppm.

2.2.3. $Bi\{S_2P(OPr^n)_2\}_3$ (**3**)

Recrystallized from dichloromethane–hexane as bright yellow crystalline and low melting solid (yield: 2.87 g, 96.7%). Anal. Calcd. for $C_{18}H_{42}BiO_6P_3S_6$: C, 25.47; H, 4.98; Bi, 24.62; S, 22.66%. Found: C, 25.66; H, 5.05; Bi, 25.05; S, 22.14%. IR (in Nujol) cm^{-1}: 1150 (ν_{C-O}), 988 (ν_{P-OR}), 622 (ν_{asym} PS_2), 531 (ν_{sym} PS_2). ^1H NMR($CDCl_3$) δ: 0.94–1.00 (t, 7.50 Hz, $–CH_3$), 1.74–1.81 (sextet, $–CH_2$), 4.08–4.16 (dt, $^3J(^{31}P–O–C–^1H)$=9.30 Hz; $^3J(^1H–C–C–^1H)$=6.60 Hz, $–OCH_2$), $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 10.16 (s, $–CH_3$), 23.34 (d, $^3J(^{31}P–O–C–^{13}C)$=8.53 Hz, $–CH_2–$), 69.63 (d, $^2J(^{31}P–O–^{13}C)$=6.11 Hz, $–OCH_2$), $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 96.9 ppm.

2.2.4. $Bi\{S_2P(OPr^i)_2\}_3$ (**4**)

Recrystallized from dichloromethane–hexane as bright yellow crystalline solid (yield: 2.82 g (94.9%)), mp 68 °C. Anal. Calcd. for $C_{18}H_{42}BiO_6P_3S_6$: C, 25.47; H, 4.98; Bi, 24.62; S, 22.66%. Found: C, 25.48; H, 4.96; Bi, 24.85; S, 22.70%. IR (in Nujol) cm^{-1}: 1179 (ν_{C-O}), 985 (ν_{P-OR}), 635 (ν_{asym} PS_2), 526 (ν_{sym} PS_2). ^1H NMR ($CDCl_3$) δ: 1.37–1.39 (d, 6.30 Hz, $–CH_3$), 4.83–4.95 (septet, $^3J(^1H–C–C–^1H)$=6.30 Hz, –OCH), $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 23.74 (d, $^3J(^{31}P–O–C–^{13}C)$=4.75 Hz, $–CH_3$), 73.59 (d, $^2J(^{31}P–O–^{13}C)$=5.51 Hz, –OCH), $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 92.9 ppm.

2.3. Preparation of Bi_2S_3 nanorods by solvothermal decomposition of precursors

In a typical experiment, 300 mg of precursor and 15 ml of ethylene glycol were taken in a round bottom flask. The reaction mixture was refluxed for 2 h at 197 °C under nitrogen atmosphere with continuous stirring. The color of the solution changed to black. After 2 h, the reaction was cooled to room temperature. The grayish black material was isolated by centrifuging followed by thorough washings with methanol. It was then dried under vacuum.

The materials thus obtained were characterized by XRD, EDAX, SEM, TEM and Raman spectroscopy.

2.4. Deposition of $Bi_2P_4O_{13}$ thin films

Bismuth phosphate thin films were deposited by the aerosol assisted chemical vapor deposition (AACVD) technique. The films were grown on microscopic glass slides under a nitrogen atmosphere, using a horizontal hollow reactor. In a typical deposition, 200 mg of precursor was dissolved in toluene (15 ml) in a two necked round bottom flask. The glass slides were cleaned prior to use by washing successively with dilute nitric acid and distilled water. About 5–6 substrates of 1×2 cm^2 dimensions were placed inside a quartz tube in an AACVD reactor and were heated at the desired temperature under nitrogen atmosphere for 10 min. The precursor solution was then placed on an ultrasonic humidifier in order to generate aerosol droplets. The aerosol was carried into the hot wall zone of the reactor with the help of nitrogen as a carrier gas with a flow rate of 1.5 l/h. The deposition was carried out for 1 h at different temperatures ranging from 250 to 375 °C. Decomposition of precursors took place to give uniform deposition of $Bi_2P_4O_{13}$ thin films on glass substrates. After deposition, the reactor was cooled to room temperature under nitrogen atmosphere to avoid in situ oxidation. Then the films were taken out.

3. Results and discussion

3.1. Synthesis and spectroscopy of precursors

Treatment of $BiCl_3$ with $Pb\{S_2P(OR)_2\}_2$ (R=Me, Et, Pr^n and Pr^i) in THF gave complexes of the type, $Bi\{S_2P(OR)_2\}_3$ (R=Me (**1**), Et (**2**), Pr^n (**3**) and Pr^i (**4**)) (Eq. (1)) in high yields (91.5–98.5%) which on recrystallization from dichloromethane–hexane mixture resulted in bright yellow crystalline solids.

$$2\,BiCl_3 + 3\,Pb\{S_2P(OR)_2\}_2 \xrightarrow{THF} 2\,Bi\{S_2P(OR)_2\}_3 + 3\,PbCl_2 \quad (1)$$