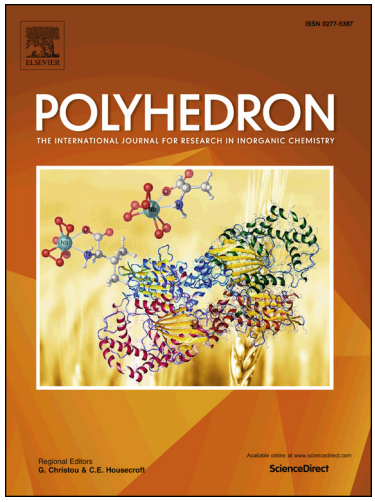

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Deposition of Bi_2S_3 thin films from heterocyclic bismuth(III) dithiocarbamato complexes

Walter N. Kun[a,b], Sixberth Mlowe[a], Linda D. Nyamen[b], Matthew P. Akerman[c], Paul O'Brien[d], Peter T. Ndifon[b*] and Neerish Revaprasadu[a*]

[a]*Department of Chemistry University of Zululand Private Bag X1001, Kwa-Dlangezwa, 3886 (South Africa) E-mail : RevaprasaduN@unizulu.ac.za*
[b]*Department of Inorganic Chemistry University of Yaoundé I, P.O. Box 812, Yaoundé (Cameroon) e-mail : pndifon@yahoo.com*
[c]*Department of Chemistry University of KwaZulu-Natal Private Bag X01, Scottsville, Pietermaritzburg, 3209 (South Africa)*
[d]*Schools of Chemistry and Materials University of Manchester Oxford Road, Manchester, M13 9PL (UK*

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ABSTRACT

Two heterocyclic dithiocarbamate complexes, tris-(piperidinedithiocarbamato)bismuth(III) (**1**) and tris-(tetrahydroquinolinedithiocarbamato) bismuth(III) (**2**) were synthesized and characterized by elemental analysis and thermogravimetric analysis. The structure of complex (**1**) was confirmed by single-crystal X-ray analysis. Both complexes were used as single source precursors for the deposition of bismuth sulfide thin films by aerosol assisted chemical vapour deposition (AACVD) at 350, 400, 450 °C and spin coating followed by thermal treatment at 350 °C, 400 °C and 450 °C. Both deposition methods, gave sulfur deficient polycrystalline films of bismuthinite. Scanning electron microscopy (SEM) images of the films showed morphology was dependent on the solvent mixture, temperature, precursor type and method of deposition. AACVD gave films with hexagonal nanoplatelets, leaf-like platelet, ribbon-like fibre, needle-like fibre morphologies. Films in the form of rods and interwoven nanowires were obtained from spin coating.

1. Introduction

Binary V-VI metal chalcogenides have drawn considerable attention as they are an important class of semiconductors which have properties important for: photoconducting targets, electronic and optoelectronic devices, thermoelectric devices, hydrogen storage materials and sensors [1-4]. Amongst these materials, Bi_2S_3 is an interesting material with a direct band gap of 1.7 eV close to optimal for terrestrial PV solar cells. The band gap can be tuned by varying the size of the crystallite with a high optical absorption coefficient ($\geq 10^5$ cm^{-1}) [5,6]. The structure of bismuthinite (Fig. 1) is quite complex involving two different bismuth centres with differing coordination number. It is orthorhombic (*Pnma*), in which Bi_2S_3 units form infinite chains parallel to the *c* axis connected via weaker van der Waals interactions between the unit cells [7]. Conventionally these structures of bismuth have been described in terms of a stereochemically active lone pair based on a VSREPR approach. Pyykkö [8] suggested many years ago that relativistic effects on the energy of the p-orbital provide a more plausible picture of the electron density. Bismuthinite is an n-type crystalline semiconductor with coordinated polyhedral composition of Bi-S bond length increasing with increasing Bi concentration (ESI Table S1) [9].

Due to its size-dependent band Bi_2S_3 has exhaustively been investigated for possible applications in photodiode arrays, photovoltaic converters and potential applications in thermoelectric cooling devices based on the Peltier effect [10,11]. Photoeletrochemical devices based on Bi_2S_3 have demonstrated potential in rechargeable electrical septum storage cells and redox couple storage devices [12,13]. Recently a new application of Bi_2S_3 as an imaging agent in X-ray computed tomography application has led to renewed interest in Bi_2S_3 nanomaterials and thin films [2]. Crystallinity and electrical resistivity are both important properties of thin films in their use in electronic applications [14]. Highly crystalline and low electrical resistant films have been obtained by vapour disposal based techniques such as chemical vapour deposition (CVD), spray pyrolysis, electrodeposition [13-18]. However, these methods employ the use of specialized equipment which are expensive. Conventional CVD relies on volatile precursors to form the thin film [19]. The nature of precursors, toxicity and sustainability are issues to consider. Therefore, alternative thin film deposition techniques have been developed to find routes with higher sustainability [19,20]. Aerosol-assisted chemical vapour deposition (AACVD) offers improved versatility and flexibility as compared to conventional CVD processes. AACVD involves solution based precursor delivery using solvents from which an aerosol can be

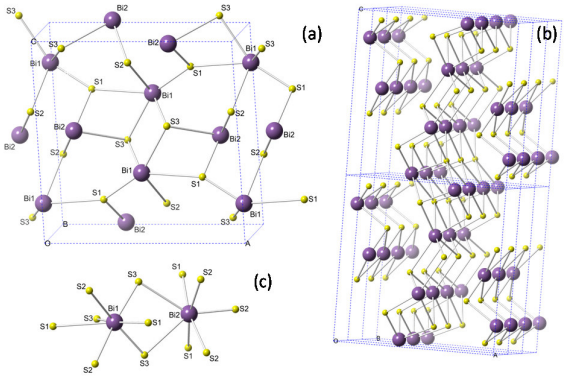

Fig. 1. (a) Bismuthinite unit cell with Bi-S separations up to 4 Å, (b) with shorter Bi-S contacts to emphasise layers and (c) coordination sphere at Bi(1) and Bi(2).