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Formation of Nanoparticle Ternary Group 11 (Cu, Ag) Bismuth Sulfides and Au(0) utilizing Bismuth Dithioates under Mild Conditions

Dimuthu C. Senevirathna,^[a] Melissa V. Werrett,^[a] Narendra Pai,^[a] Victoria. L. Blair,^[a] Leone Spiccia,^[a] and Philip C. Andrews^{*[a]}

Abstract: The formation of mixed metal sulfides of AgBiS₂ and Cu₃BiS₂ via a simple two-step process utilizing bismuth dithioates as single source Bi and S precursors is described. Sono-chemical reaction of Bi₂O₃ with six different aryldithioc acids (benzodithioic, BDT-H; 4-methoxybenzodithioic, 4-MBDT-H; 3-methylbenzodithioic, 3-MBDT-H; 2-mesitylenedithioic, 2-MDT-H; 4-fluorobenzodithioic, 4-FBDT-H; and 2-thiophenedithioic, 2-TDT-H) resulted in the following complexes; [Bi(BDT)₃] 1, [Bi(4-MBDT)₃] 2, [{Bi(3-MBDT)₃}₂·C₇H₈] (3_2 ·C₇H₈), [Bi(2-MDT)₃] 4, [Bi(4-FBDT)₃] 5 and [Bi(2-TDT)₃] 6. Microwave irradiation of these bismuth(III)aryldithioate complexes with AgNO₃ or CuCl under mild reaction conditions (140 °C) resulted in the respective mixed metal sulfides. Attempt to synthesize AuBiS₂ using similar reaction protocols were unsuccessful and resulting only in the formation of elemental Au(0), S₈ and BiOCI.

Implementation of semiconductor metal chalcogenides in forefront technologies such as opto-electronics, thermo-electrics, optical recording, and catalysis, as well as for the creation of advanced coatings, pigments and lubricants is rapidly expanding.^[1-3] From the perspective of opto-electronic applications, cadmium and lead chalcogenides are arguably among the most intensively studied compounds^[3,4] from which highly useful tunable properties are successfully exploited in industry.^[5] However, the pernicious toxicity of both Cd and Pb stimulates the search for new materials with similar properties that can be formed from abundant and non-toxic elements. Currently, this is difficult to achieve with binary systems, but ternary chalcogenides offer an interesting alternative with potentially higher flexibility for the band level engineering, which is critical for photoabsorption and photoconductive applications.

Multinary chalcogenides have been increasingly investigated and in particular,^[6,7] nano size particles offer extended possibilities to control the composition and internal structure of the materials prior to processing, compared to the bulk. For example, copper indium selenide has off-stoichiometric structures in the bulk (*e.g.* Culn₃Se₅, Culn₅Se₈, Cu₂In₄Se₇) which leads to less deep trap states resulting in compromising its optoelectronic properties.^[8] Among metal chalcogenides with environmentally benign elements, bismuth sulfide (Bi₂S₃) is of

[a] Mr. D. C. Senevirathna, Dr. M. V. Werrett, Mr. N.Pai, Dr. V. L. Blair, Prof L. Spiccia, Prof. P. C. Andrews. School of Chemistry Monash University Clayton, Melbourne, VIC 3800 Australia phil.andrews@monash.edu

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particular interest as a semiconductor with a comparatively narrow direct bandgap and absorption edge at *ca* 950 nm^[9] that can be modified *via* incorporation of another metal.^[10,11]

Ternary first group metal bismuth chalcogenides are solvent processable and with a tunable bandgap,^[11] intrinsically low lattice thermal conductivity,^[3] and photoconductivity.^[12] AgBiS₂ and Cu₃BiS₃ are known to exhibit even broader absorption than Bi₂S₃ and provide improved charge mobility. AgBiS₂, a highly stable, non-toxic material with its photoconductivity, absorption coefficient $(10^5 \text{ to } 10^3 \text{ cm}^{-1})$ and beneficial thermoelectric properties, has been used as a sensitizer, counter electrode and charge transfer material in solar cells.^[12,13] Of the two crystalline phases of AgBiS₂; the room temperature β hexagonal phase and the α cubic rock salt phase (formed at *ca* 473 K),^[3,14] it is the cubic phase which has shown appreciable photovoltaic performance.^[12] Likewise, Cu_3BiS_3 with its orthorhombic crystal structure and direct band gap, as well as high absorption coefficient of ~105 cm⁻¹ and possibility of being a p-type material, shape it as a prospective material for photovoltaic and optoelectronic applications.^[11]

A wide range of synthesis methods exist to produce cubic phase AgBiS₂ nanomaterials. Those include vacuum fusing^[3] microwave synthesis,^[14] flux technique,^[15,16] solvothermal^[17,18] and ligand assisted methods.^[12] A common feature of the reported synthetic approaches is the use of an isolated individual precursor for each element in the ternary system. High temperature flux methods use Bi and Ag metals with sulfur powder as the starting materials,^[3,19] whereas bismuth and silver nitrates or acetates with a variety of chalcogen precursors like thiourea^[14] thiosemicarbazide,^[18] L-cysteine,[17] hexamethyldislathiane^[12] or Na₂S^[13] have been employed for the low temperature synthesis, e.g. by using hydrothermal or microwave irradiation. Similarly, a broad arsenal of methods to synthesize Cu₃BiS₃, using individual precursors for each component in the system, have been reported. These methods include spray pyrolysis,^[20] sputtering,^[11,21,22] co-evaporation,^[23,24] solid-state synthesis, [25,26] solvothermal [27,28] and microwave methods.[29]

Controlling the stoichiometry, size and impurity in chalcogenides is an important factor, since this directly affects the photo absorption and intrinsic defects in the material. However, many methods used for isolating ternary chalcogenides require high temperature or vacuum^[2,13] as well as individual precursors for *each* component in the system. Reducing the number of precursors is advantageous to improve purity, reduce defects and avoid the chance of pre-reaction forming binary counter products.^[30] Here, lies the relevance of mitigating a modified synthesis strategy with novel dual source precursors for producing ternary chalcogenides.

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As we have recently reported, aryldithioic acids (ArCS₂H) react efficiently with crude bismuthinite (Bi₂S₃) to form bismuth(III) aryldithioates, [Bi(S₂CAr)₃] in high yield and high purity.^[31] We have since discovered that crude bismite (Bi₂O₃) can be substituted for bismuthinite in this process reducing the reaction time from 4 h to 1 h. Crystalline Bi₂S₃ nanorods can then be easily generated from [Bi(S₂CAr)₃], upon mild solution decomposition.^[31,32]

Building on this process we can now report the highly efficient synthesis of nanoparticles of $AgBiS_2$ and Cu_3BiS_3 from the reaction/decomposition of $[Bi(S_2CAr)_3]$, formed from a range of aryldithioc acids (Figure 1), in the presence of $AgNO_3$ or CuCl respectively. However, an analogous reaction with HAuCl₄ did not generate AuBiS₂, but resulted in deposition of elemental gold via the gold(I) dithioate complex [Au(S_2CAr)]. This is summarized in Scheme 1.



Figure 1. Structures and abbreviations of the aryldithioic acids used in the synthesis of bismuth(III) dithioate complexes 1 - 6.



Scheme 1. Synthesis pathway for mixed metal sulfide nanoparticles, as well as gold. The bismuth dithioate ($[Bi(S_2CAr)_3]$) is formed from the reaction of Bi_2O_3/Bi_2S_3 with an aryldithioic acid. The mixed metal sulfide is subsequently produced from the reaction/decomposition of $[Bi(S_2CAr)_3]$ with a group eleven salt. In the case where HAuCl₄ is used, the mixed metal sulfide AuBiS₂, is not isolated and instead gold is finally recovered.

The method described herein uses microwave irradiation to produce finely dispersed nano-sized mixed metal sulfides (and Au). Full synthetic details are provided in the Supporting As a representative Information (SI). example, the heterogeneous sono-chemical reaction of bismite (Bi2O3) with 3methylbenzenedithioic acid (3-MBDT-H) in toluene gave the corresponding bismuth(III) arenedithioate, crystallized as [{Bi(3- $MBDT_{3}_{2} \cdot C_{7}H_{8}$] ($3_{2} \cdot C_{7}H_{8}$), as a red-orange solid after one hour. Complete conversion could be observed visually through full consumption of the crude yellow Bi₂O₃. The resulting solid is easily isolated by filtration and subsequently purified by recrystallization from hot toluene. Each complex ([Bi(BDT)₃] 1, [Bi(4-MBDT)₃] 2, [{Bi(3-MBDT)₃}₂·C₇H₈] (3₂·C₇H₈), [Bi(2-MDT)₃] 4, [Bi(4-FBDT)₃] 5, [Bi(2-TDT)₃] 6) was therefore isolated as an air-stable red (1-3, 5-6) or yellow (4) crystalline solid (yield 75-85%). Elemental analysis, FTIR, ¹H and ¹³C NMR and mass spectrometry confirmed the composition of the crystalline solids. This data is provided in further detail in the Supporting Information.

The solid state structures of $[Bi(4-MBDT)_3]$ **2**, $[{Bi(3-MBDT)_3}_2 \cdot C_7H_8]$ (**3**₂·C₇H₈) and $[Bi(2-MDT)_3]$ **4**, were determined by single crystal X-ray diffraction from crystals grown in either toluene (**3**) or DMSO (**2** and **4**). As an illustrative example, the crystal structure of $[{Bi(3-MBDT)_3}_2 \cdot C_7H_8]$ (**3**₂·C₇H₈) is shown in Figure 2, with **2** and **4** given in the SI along with a summary of all the crystallographic data.



Figure 2. Molecular structure of $[{Bi(3-MBDT)_3}_2-C_7H_8]$ ($3_2-C_7H_8$). Thermal ellipsoids are given at 50% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Bi(1)-S(1), 2.7319(8); Bi(1)-S(2), 2.8496(8); Bi(1)-S(3), 2.7544(8); Bi(1)-S(4), 2.9134(8); Bi(1)-S(5), 2.5731(7); Bi(1)-S(6), 2.9209(8); S(1)-Bi(1)-S(2); 63.34(2); S(3)-Bi(1)-S(4), 62.50(2); S(5)-Bi(1)-S(6), 64.29(2).

Susequent formation of AgBiS₂ and Cu₃BiS₃ nanoparticles was achieved in two simple steps. Firstly, the crystalline $[Bi(S_2CAr)_3]$ complexes **1** - **6** were isolated and dissolved in DMSO with oleic acid or 1-dodecanethiol as the surfactant. Next, a stoichiometric amount of AgNO₃ or CuCl was added and the solution exposed to microwave iradiation at 140 °C for 40

minutes. The solution darkened and a black precipitate formed. The resultant black precipitate was washed several times with ethanol, collected by centrifugation and prepared for analysis.

When this method was repeated with HAuCl₄, as a gold source, a different outcome was observed. After combining $[Bi(S_2CAr)_3]$ and oleic acid in DMSO, HAuCl₄ was added and a suspension of a red-brick color precipitate immediately formed. Upon microwave irradiation (140 °C, 40 min) this transformed into a pale yellow solution with concomitant deposition of Au(0) metal (as confirmed by energy dispersive X-ray spectroscopy (EDX), Figure S12). The pale yellow solution was kept, and upon slow evaporation, yielded crystals of elemental sulfur alongside bismuth(III) oxychloride (BiOCl) as confirmed by scanning electron microscopy (SEM), EDX and single crystal X-ray diffraction (Figures S13 and S14). This unusual result suggests Au(III) is reduced to Au(0) while S²⁻ present from the decomposition of either or both $[Bi(S_2CAr)_3]$ and $[Au(S_2CAr)]$, oxidizes to S(0).

This redox process was further investigated. First, the redbrick precipitate formed from the combination of HAuCl₄ with [Bi(S₂CAr)₃] (in DMSO) was identified as [Au(3-MBDT)] (7), in which gold has reduced to the Au(I) oxidation state. A similar result occurs when using Au(I) directly, as AuCl. Compound 7 is insoluble in all NMR solvents so elemental analysis and FTIR was used to confirm the composition. However, compound 7 was soluble in acetone in the presence of PPh₃ and upon slow evaporation, crystals of [Au(3-MBDT)(PPh₃)₂] (8) were obtained, as determined by single crystal X-ray diffraction. The solid-state structure is shown in Figure 3 and a summary of crystallographic details provided in the SI.



Figure 3. Molecular structure of $[Au(3-MBDT)(PPh_3)_2]$ (8). Thermal ellipsoids are given at 50% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Au(1)-S(1), 2.8347(6); Au(1)-S(2), 2.5712(6); Au(1)-P(1), 2.3402(6); Au(1)-P(2), 2.3024(6); S(1)-Au(1)-S(2); 65.453(17).

The complex contains one Au(I) atom which is coordinated by two sulfur atoms from the 3-MBTD ligand in a bidentate fashion, and PPh₃ ligands giving an overall distorted tetrahedron geometry around the Au(I) center. It is isostructural with $[Au(BDT)(PPh_3)_2]^{[33]}$ and $[Au(S_2C-p-tolyI)(PPh_3)_2]^{[33]}$

Heating a DMSO suspension of the red-brick precipitate of [Au(3-MBDT)] (7) to 140 °C for 40 minutes under microwave irradiation produced a single piece of Au(0) (0.191 g, yield 97%) confirming our earlier observation that Au(III) from HAuCl₄ can be easily reduced to Au(0) in two simple steps.

The formation and isolation of $AgBiS_2$ and Cu_3BiS_3 nanoparticles was confirmed using transmission electron microscopy (TEM), selective area electron diffraction (SAED) and EDX. EDX microanalysis was used to confirm the presence and relative ratios of each element in $AgBiS_2$ and Cu_3BiS_3 nanoparticles (Figures S15 and S16) which proved to be consistent with $AgBiS_2$ and Cu_3BiS_3 . As shown in Figure 4 (top) the Cu_3BiS_3 particles appear rounded (possibly spherical) with diameters ranging from 60-80 nm. The $AgBiS_2$ particles (Figure 4, bottom) are generally larger (80-90 nm) and appear less speherical but still rounded at the edges. Lattice fringes can be clearly observed in the high resolution TEM (HR-TEM) images (Figure 4, right) of both the Cu_3BiS_3 and $AgBiS_2$.

In both samples, the particles isolated appear to be aggregated however, clear SAED patterns were obtained for both AgBiS₂ and Cu₃BiS₃ (Figures S17 and S18). The AgBiS₂ SAED pattern could be indexed to the cubic phase of AgBiS₂ (*Fm*3*m*, *a*=*b*=*c*= 5.648 Å).^[34–36] The SAED pattern collected from the Cu₃BiS₃ sample shows individual bright spots, indicative of a crystalline material. Although no obvious ring patterns were observed, various *d*-spacings could be calculated from the bright spots, which match well with the orthorhombic phase of Cu₃BiS₃ (*P*₂₁2₁2₁, *a*=7.723, *b*=10.395 and *c*=6.716 Å).^[35,37]



Figure 4. TEM images of the Cu₃BiS₃ (top) and AgBiS₂ (bottom) isolated from the microwave reaction of [{Bi(3-MBDT)₃}₂·C₇H₈] (**3**₂·C₇H₈) with CuCl or AgNO₃. High resolution TEM images (right) show the clear lattice fringes observed in each sample.

Bulk analysis, in the form of powder X-ray diffraciton (PXRD) was used to further confirm the purity of the samples analysed by TEM. Figures 5, 6 and 7 show the

PXRD patterns of synthesized AgBiS₂ and Cu₃BiS₃ nanoparticles as well as Au; formed from the microwave irradiation of $[{Bi(3-MBDT)_3}_2 \cdot C_7 H_8]$ (3₂·C₇H₈) with AgNO₃, CuCl and HAuCl₄ respectively. The experimental patterns (black) match well with their corresponding standard PXRD patterns (red). This bulk analysis supports the TEM, SAED and EDX analysis of the mixed metal sulfide nanoparticles. The observed diffraction peaks suggest that these materials are pure AgBiS₂, Cu₃BiS₃ and Au, containing no traces of side products or monometallic sulfides. The black solids isolated from the reactions of the remaining complexes (1, 2, 4-6) with either AgNO₃ or CuCl show comparable PXRD patterns with $AgBiS_2$ (Figures S19 – S23) and Cu_3BiS_3 (Figures S24 - S28).



Figure 5. Comparison of the powder X-ray diffraction pattern of standard AgBiS₂ (red)^[34] and synthesised AgBiS₂ nanoroparticles from [{Bi(3-MBDT)₃₂·C₇H₈] (3₂·C₇H₈) (black).



Figure 6. Comparison of the powder X-ray diffraction pattern of standard Cu_3BiS_3 (red)^[38] and synthesised Cu_3BiS_3 nanoparticles from [{Bi(3-MBDT)₃}₂·C₇H₈] (3₂·C₇H₈) (black).



Figure 7. Comparison of the powder X-ray diffraction pattern of standard metallic Au (red)^[39] and synthesised Au from [{Bi(3-MBDT)₃}₂·C₇H₈] (32.C7H8) (black).

We have discovered a novel method for the formation of nanoparticles of the ternary group 11 bismuth sulfides, AgBiS₂ and Cu₃BiS₃ under mild conditions using bismuth dithioates as reactive single-source precursors of Bi and S. The attempted synthesis of the gold analogue using a similar method resulted only in reduction of Au from +III (in HAuCl₄) to +I (as the gold dithioate), and ultimately to agglomerated Au(0) on gentle heating.

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Keywords: bismuth • nanoparticles • mixed metal sulfides • dithioate ligands • microwave

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