Journal Name

ARTICLE

A Simple Route to Complex Materials: the Synthesis of Alkaline Earth – Transition Metal Sulfides

dReceived 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Mundher Al-Shakban,[a] Peter D. Matthews[b] and Paul O'Brien[a,b*]

A simple, low-temperature synthesis of a family of alkaline earth metal chalcogenide thin films is reported. These materials have previously only been produced from demanding, high temperature, high pressure reactions. The decomposition of calcium, barium and copper xanthates leads to the clean formation of CaS, BaS, $CaCu_2S_2$, β-$BaCu_2S_2$ and β-$BaCu_4S_3$.

The synthesis of potentially useful complex materials is a key area for research, and one class of these, metal chalcogenides, are of particular interest to the semiconductor industry. Transition metal chalcogenides have been shown to make promising photovoltaic devices, energy storage, electronics and lubricants.[1–8] The introduction of an alkaline earth metal to make a mixed metal chalcogenides produces a broad variety of structures with distinctive properties.[9–15]

Metal chalcogenides often provide significant synthetic challenges and syntheses often require very high temperatures and/or pressures. Synthetic routes that involve more benign conditions will represent a major step forward. The mixed alkaline earth/transition metal compound $CaCu_2S_2$ has previously only been synthesized by a challenging ammonothermal process,[16] whilst $BaCu_2S_2$ has been reported via a hydrothermal method or in a flux of potassium thiocyanate.[17,18] Here we report a much simpler approach making use of metal xanthates in melt reactions.

There are numerous ways to deposit thin films of metal chalcogenides, though it is undoubtedly true that the simpler the better if industrial applications are to be realised. We have previously discussed chemical bath deposition (CBD),[19,20] as well as aerosol-assisted chemical vapour deposition (AA-CVD)[21,22] as being general than metal-organic (MO-CVD) or other CVD techniques, as the precursor does not have to be volatile, which is a requirement for MO-CVD.[23,24] Mitzi has previously proposed 'dimensional reduction', which involves dismantling an extended metal-anion framework by reacting it with an ionic reagent resulting in dissolution. The resulting solution may be deposited and annealed to generate a thin film. This method results in high quality films,[25–27] but also relies extensively on toxic hydrazine, limiting its usefulness.[7] The method that we have applied here is simpler in its elegance – we have spin coated single source precursors onto a substrate (a method that can be extended to any type of material, or size of substrate), and thermally decomposed it to generate clean metal sulfides.[28,29]

We, and others, have previously described the use of metal xanthates [$M(S_2COR)_x$] (M = transition metal, R = alkyl chain) to generate nanostructured metal sufides via AA-CVD, melt reactions and hot-injection syntheses.[29–39] Metal xanthates are a good choice as single-source precursors to metal sulfides, as they decompose cleanly at low temperature. One potential decomposition pathway is the Chugaev elimination mechanism (Scheme 1), from which the only by-products are gases that are readily removed from the reaction system.[40]

We report here the simple, low-temperature synthesis of AS, ACu_2S_2 and ACu_4S_3 (A = Ca or Ba; Figure 1) from [$Ca(S_2CO^iPr)_2(^iPrOH)_3$] (**1**) [$Ba(S_2CO^iPr)_2$] (**2**) and [$(PPh_3)_2Cu(S_2CO(CH_2)_2OMe)$] (**3**). The calcium and copper xanthates were synthesized according to literature methods,[41,42] whilst we report a novel barium xanthate (see Supporting Information for full details).

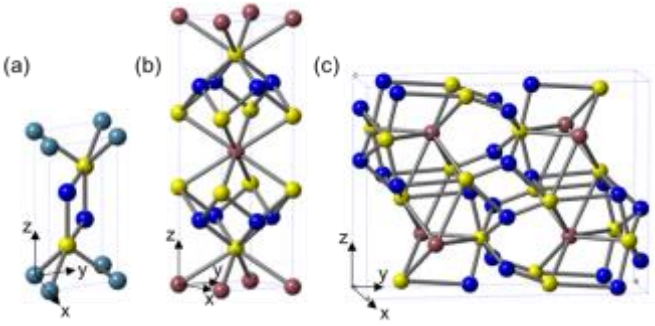

Figure 1. Schematic drawing of the unit cells of (a) $CaCu_2S_2$, (b) β-$BaCu_2S_2$ and (c) β-$BaCu_4S_3$. Teal = Ca, brown = Ba, blue = Cu, yellow = S.

[a] *School of Materials, University of Manchester, Oxford Road, Manchester M13 9PL, UK. E-mail: paul.o'brien@manchester.ac.uk; Fax: +44 (0)161 275 4616; Tel: +44 (0)161 275 4653*
[b] *School of Chemistry, University of Manchester, Oxford Road, Manchester, M13 9PL, UK.*
† *Electronic Supplementary Information (ESI) available: materials and methods, TGA, GIXRD, Raman and SEM/EDX data. See DOI: 10.1039/c000000x/*

The Ca and Ba xanthates were synthesized from the insertion of CS_2 into the metal-alkoxide bond, according to the procedure of Bezougli *et al.*[41] (Equation 1). The Cu xanthate was prepared from CuCl, PPh_3 and potassium 2-methoxyethylxanthate by a method that we have previously reported.[42]

$$A + {}^{i}PrOH \xrightarrow{-H_2} A({}^{i}PrO)_2 \cdot x\,{}^{i}PrOH \xrightarrow{CS_2} A(S_2CO{}^{i}Pr)_2 \cdot x\,{}^{i}PrOH \quad (1)$$

An assessment of the thermogravimetric profile of **1**, **2** and **3** (ESI Figure S1) suggests that the complexes breakdown cleanly in the region of 225-250 °C and 100-125 °C respectively. The final weight of the residue is in good agreement with the formation of CaS, BaS and CuS respectively. The suggested breakdown pathway is shown in Scheme 1.

Scheme 1. A generalised breakdown mechanism proposal for the xanthate precursors. M = Ca, Ba or Cu, L = ^{i}PrOH or PPh_3, R = ^{i}Pr or 2-methoxyethyl.

Thin films of the metal sulfides were prepared by spin-coating a solution of the precursor xanthates in dry THF onto a clean glass slide, followed by thermolysis in a tube furnace under an inert nitrogen atmosphere (ESI Table S1).

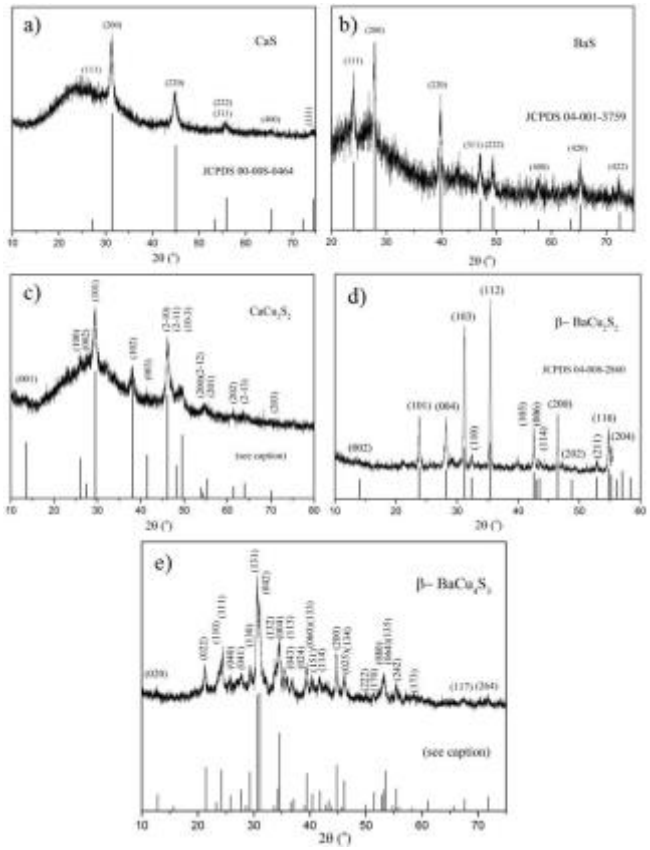

Figure 2. The grazing incidence X-ray diffraction (GIXRD) patterns of the thin films. (a) cubic CaS and reference pattern JCPDS 00-008-0464, (b) cubic BaS and reference pattern JCPDS 04-001-3579, (c) hexagonal $CaCu_2S_2$ and reference pattern generated from Purdy's work,[16] (d) β-$BaCu_2S_2$ with reference pattern JCPDS 04-008-2860 and (e) orthorhombic β-$BaCu_4S_3$ and reference pattern generated from Iglesias's work.[43]

1 decomposes cleanly at 300 °C to form cubic CaS, with the grazing incidence X-ray diffraction (GIXRD) pattern agreeing well with phase formed being that of oldhamite (JCPDS 00-08-0464, Figure 2a). The unit cell of a = 5.699(2) Å is a close match to the literature (a = 5.694 Å). The decomposition of the barium xanthate **2** requires higher temperatures to form a pure phase. At 550 °C, cubic BaS is formed (Figure 2b) - the unit cell is a = 6.392(6) Å, which is a good match with the literature (a = 6.388 Å). CaS and BaS both adopt the cubic structure of NaCl. **3** forms orthorhombic chalcocite $Cu_{1.73}S$ (JCPDS 00-009-0328, ESI Figure S3) at 300 °C, with a unit cell of a = 11.810(1) Å, b = 27.020(7) Å and c = 13.435(1) Å.

In order to generate the mixed alkaline earth/transition metal compounds the appropriate molar ratios of **1**/**2** and **3** were dissolved in dry THF and spin coated onto glass slides and annealed in a N_2 atmosphere. For the Ca-Cu system an annealing temperature of 300 °C was used. The GIXRD pattern of the obtained films matches that of hexagonal $CaCu_2S_2$ as reported by Purdy[16] (Figure 2c) and the unit cell parameters of a = 3.949(3) Å, c = 6.520(3) Å are consistent with that data.[16] Comparing the Raman spectra of this film with that of $Cu_{1.73}S$ (the structure produced from the decomposition of **3**) indicates that there is no chalcocite contamination of the calcium copper sulfide film (ESI Figure S10). In the $CaCu_2S_2$ structure, planes of double layer, puckered six member Cu-S rings are separated by Ca^{2+} (Figure 1a). Energy-dispersive X-ray spectroscopy (EDX) analysis gives a formula consistent with that of $CaCu_2S_2$ and EDX mapping reveals a homogenous dispersion of the elements (ESI Figure S5 and Table S4).

Unlike $CaCu_2S_2$, which exists as only one phase, there are two phases for $BaCu_2S_2$: an α (orthorhombic) and a β (tetragonal) phase. We find at 550 °C, the temperature required to breakdown **2**, that we form a mixture of α- and β-$BaCu_2S_2$ from a 2:1 ratio of **3**:**2** (ESI Figure S2). Increasing the temperature to 650 °C leads to a loss of the orthorhombic phase, leaving pure tetragonal β-$BaCu_2S_2$ (Figure 2d, JCPDS 04-008-2860) with a unit cell of a = 3.907(3) Å, c = 12.648(3) Å (literature values: a = 3.907 Å, c = 12.640 Å). Note that in this case we switched to a silicon substrate to reflect the high temperature of deposition. Compositional analysis by EDX indicates an appropriate ratio of Ba:Cu:S, which is evenly distributed across the sample (ESI Figure S6 and Table S4).

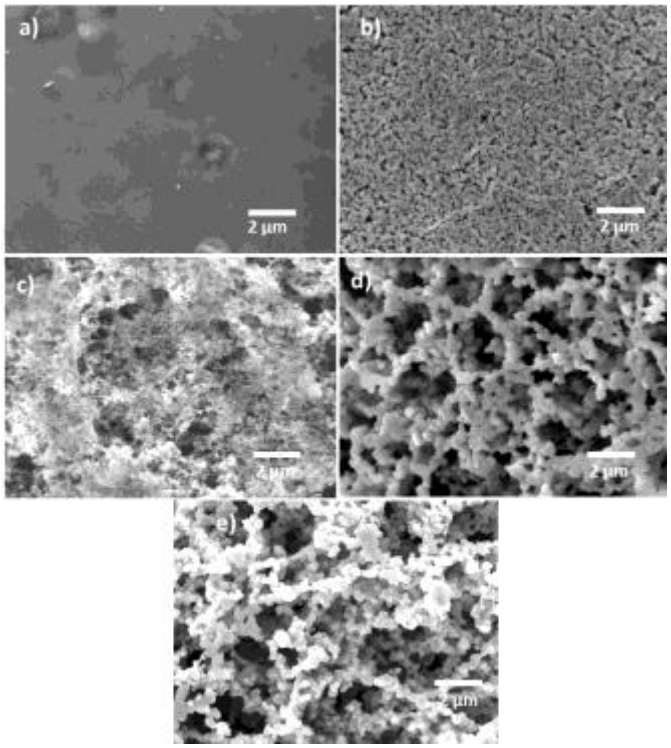

Figure 3. SEM images of thin films of (a) CaS, (b) BaS, (c) hexagonal $CaCu_2S_2$ (d) β-$BaCu_2S_2$ and (e) β-$BaCu_4S_3$.

$CaCu_2S_2$ is the only known calcium copper sulfide, but for the barium family there is another: $BaCu_4S_3$. This also has an α and β phase, though in this case they are both orthorhombic.[44] The structure consists of BaS_6 triangular face sharing trigonal prisms (Figure 1c). The key difference between the α and β phases is that S caps a rectangular face in α-$BaCu_4S_3$ and a triangular face in β-$BaCu_4S_3$.[43,44] Previous work has focused on the synthesis of these materials through a vapour transport method, and Iglesias *et al.* noted an α to β phase transition at 640 ± 10°C.[43,44] We have successfully synthesized the high temperature phase, β-$BaCu_4S_3$, at 580 °C on glass (Figure 2e). The unit cell of a = 4.053(1) Å, b =13.848(3) Å and c = 10.377(2) Å agrees with the literature values of a = 4.058 Å, b = 13.863 Å and c = 10.373 Å and the EDX analysis is consistent with the target formula (ESI Figure S7 and Table S4).

It is clear from the GIXRD patterns that there is a broad hump in the CaS, BaS and $CaCu_2S_2$ spectra in the 25-30° region. This is due to the glass signal showing through from beneath the film. We have calculated the penetration depth, which is the thickness of the sample contributing to 99% of the diffracted intensity for a given incident angle, for our samples in ESI Table S3. The penetration depths for the samples are larger than the thickness of the films (ESI Figure S4), which explains why we see the broad glass signal.

There is little difference in the morphology of the films that can be discerned by scanning electron microscopy (SEM), other than that of CaS (Figure 3). The alkaline earth metal-copper sulfides consist of conjoined spheres 0.1-0.5 µm in diameter, whereas CaS appears to be much smoother. Optical images of the films (ESI Table S1) indicate that the CaS/BaS films are a lighter brown colour, whilst the others are a dark black.

The TGA data (ESI Figure S1) indicates that there is unlikely to be much carbon residue left in the films, as the final decomposition percentage is in good agreement with the clean formation of CaS, BaS and CuS. We probed the samples for C inclusion through EDX by depositing the films on a Si substrate (as glass is known to contain carbon) and coated them with an Au/Pt target. The binary systems (CaS, BaS and CuS) all contain ~0.1 at.% C, whereas the ternary barium-copper films contain ~0.3 at.% C (ESI Table S5 and ESI Figure S9). The use of EDX to determine carbon content quantitatively is notoriously difficult, however, these values suggest that only a very small amount of C is included in the final film.

In summary, we have presented a simple, efficient route to three complex alkaline earth metal-copper sulfides; $CaCu_2S_2$, β-$BaCu_2S_2$ and β-$BaCu_4S_3$. This synthesis has been achieved by a melt reaction of calcium isopropylxanthate and the novel compounds barium isopropylxanthate and bis(triphenylphosphine)copper 2-methoxyethylxanthate.

Acknowledgements

The authors would like to acknowledge the Iraqi Culture Attaché in London for financial support (M.A.S.) and the EPSRC (Doctoral Prize for P.D.M., grant EP/M507969/1). Some of the equipment used in this study were provided by the Engineering and Physical Sciences Research Council (Core Capability in Chemistry, EPSRC grant number EP/K039547/1). We thank Prof. D. Michael P. Mingos (University of Oxford) for helpful discussions.

Conflicts of Interest

There are no conflicts of interest to declare.

Notes and references

1. P. D. Matthews, P. D. McNaughter, D. J. Lewis and P. O'Brien, *Chem. Sci.*, 2017, **8**, 4177–4187.
2. K. Woo, Y. Kim and J. Moon, *Energy Environ. Sci.*, 2012, **5**, 5340–5345.
3. Y.-C. Wang, D.-Y. Wang, Y.-T. Jiang, H.-A. Chen, C.-C. Chen, K.-C. Ho, H.-L. Chou and C.-W. Chen, *Angew. Chem. Int. Ed.*, 2013, **52**, 6694–6698.
4. D. J. Lewis, P. Kevin, O. Bakr, C. A. Muryn, M. A. Malik and P. O'Brien, *Inorg. Chem. Front.*, 2014, **1**, 577–598.
5. A. A. Tedstone, D. J. Lewis and P. O'Brien, *Chem. Mater.*, 2016, **28**, 1965–1974.
6. Q. H. Wang, K. Kalantar-Zadeh, A. Kis, J. N. Coleman and M. S. Strano, *Nat. Nanotechnol.*, 2012, **7**, 699–712.
7. D. B. Mitzi, *Adv. Mater.*, 2009, **21**, 3141–3158.
8. S.-L. Li, K. Tsukagoshi, E. Orgiu and P. Samorì, *Chem. Soc. Rev.*, 2015, **45**, 118–151.
9. S.-M. Kuo, Y.-M. Chang, I. Chung, J.-I. Jang, B.-H. Her, S.-H.

Yang, J. B. Ketterson, M. G. Kanatzidis and K.-F. Hsu, *Chem. Mater*, 2013, **25**, 2427–2433.
10. K. Feng, W. Yin, Z. Lin, J. Yao and Y. Wu, *Inorg Chem*, 2013, **52**, 11503–11508.
11. A. Mesbah, E. Ringe, S. Lebègue, R. P. Van Duyne and J. A. Ibers, *Inorg. Chem.*, 2012, **51**, 13390−13395.
12. A. Mesbah, S. Lebègue, J. M. Klingsporn, W. Stojko, R. P. Van Duyne and J. A. Ibers, *J. Solid State Chem.*, 2013, **200**, 349–353.
13. A. Mesbah, J. Prakasha and J. A. Ibers, *Dalton Trans.*, 2016, **45**, 16067–16080.
14. M.-C. Chen, L.-M. Wu, H. Lin, L.-J. Zhou and L. Chen, *J Am Chem Soc*, 2012, **134**, 6058–6060.
15. A. Assoud, N. Soheilnia and H. Kleinke, *Chem. Mater*, 2005, **17**, 2255–2261.
16. A. P. Purdy, *Chem. Mater.*, 1998, **10**, 692–694.
17. Z. Ma, F. Weng, Q. Wang, Q. Tang, G. Zhang, C. Zheng, R. P. S. Han and F. Huang, *RSC Adv.*, 2014, **3**, 28937–28940.
18. J. Huster and W. Bronger, *Z. Anorg. Allg. Chem*, 1999, **625**, 2033–2040.
19. D. S. Boyle, P. O'Brien, D. J. Otway and O. Robbe, *J. Mater. Chem.*, 1999, **9**, 725–729.
20. D. S. Boyle, O. Robbe, D. P. Halliday, M. R. Heinrich, A. Bayer, P. O'Brien, D. J. Otway and M. D. G. Potter, *J. Mater. Chem.*, 2000, **10**, 2439–2441.
21. D. J. Lewis, A. A. Tedstone, X. L. Zhong, E. A. Lewis, A. Rooney, N. Savjani, J. R. Brent, S. J. Haigh, M. G. Burke, C. A. Muryn, J. M. Raftery, C. Warrens, K. West, S. Gaemers and P. O'Brien, *Chem. Mater.*, 2015, **27**, 1367−1374.
22. J. Akhtar, M. Afzaal, M. A. Vincent, N. A. Burton, I. H. Hillier and P. O'Brien, *Chem. Commun.* , 2011, **47**, 1991–1993.
23. M. A. Malik, M. Afzaal and P. O'Brien, *Chem. Rev.*, 2010, **110**, 4417–4446.
24. P. Marchand, I. A. Hassan, I. P. Parkin and C. J. Carmalt, *Dalton Trans.*, 2013, **42**, 9406–9422.
25. D. B. Mitzi, L. L. Kosbar, C. E. Murray, M. Copel and A. Afzali, *Nature*, 2004, **428**, 299–303.
26. D. B. Mitzi, M. Copel and C. E. Murray, *Adv. Mater.*, 2006, **18**, 2448–2452.
27. D. J. Milliron, D. B. Mitzi, M. Copel and C. E. Murray, *Chem. Mater.*, 2006, **18**, 581–590.
28. M. Al-Shakban, P. D. Matthews, N. Savjani, X. L. Zhong, Y. Wang, M. Missous and P. O'Brien, *J. Mater. Sci.*, 2017, **52**, 12761–12771.
29. E. A. Lewis, P. D. McNaughter, Z. Yin, Y. Chen, J. R. Brent, S. A. Saah, J. Raftery, J. A. M. Awudza, M. A. Malik, P. O'Brien and S. J. Haigh, *Chem. Mater.*, 2015, **27**, 2127–2136.
30. M. Afzaal, C. L. Rosenberg, M. A. Malik, A. J. P. White and P. O'Brien, *New J. Chem.*, 2011, **35**, 2773.
31. P. S. Nair, T. Radhakrishnan, N. Revaprasadu, G. A. Kolawole and P. O'Brien, *J. Mater. Chem.*, 2003, **22**, 3129–3135.
32. M. Afzaal, M. A. Malik and P. O'Brien, *J. Mater. Chem.*, 2010, **20**, 4031–4040.
33. E. A. Lewis, S. Haigh and P. O'Brien, *J. Mater. Chem. A*, 2014, **2**, 570–580.
34. P. D. McNaughter, S. A. Saah, M. Akhtar, K. Abdulwahab, M. A. Malik, J. Raftery, J. A. M. Awudza and P. O'Brien, *Dalton Trans.*, 2016, **45**, 16345–16353.
35. P. D. Matthews, M. Akhtar, M. A. Malik, N. Revaprasadu and P. O'Brien, *Dalton Trans.*, 2016, **45**, 18803–18812.
36. N. Alam, M. S. Hill, G. Kociok-Köhn, M. Zeller, M. Mazhar and K. C. Molloy, *Chem. Mater.*, 2008, **20**, 6157–6162.
37. J. M. Clark, G. Kociok-Köhn, N. J. Harnett, M. S. Hill, R. Hill, K. C. Molloy, H. Saponia, D. Stanton and A. Sudlow, *Dalton Trans.*, 2011, **40**, 6893–6900.
38. T. Lutz, A. MacLachlan, A. Sudlow, J. Nelson, M. S. Hill, K. C. Molloy and S. A. Haque, *Phys. Chem. Chem. Phys.*, 2012, **14**, 16192–16196.
39. T. Rath, A. J. MacLachlan, M. D. Brown and S. A. Haque, *J. Mater. Chem. A*, 2015, **3**, 24155–24162.
40. M. A. Buckingham, A. L. Catherall, M. S. Hill, A. L. Johnson and J. D. Parish, *Cryst. Growth Des.*, 2017, **17**, 907–912.
41. I. K. Bezougli, A. Bashall, M. McPartlin and D. M. P. Mingos, *J. Chem. Soc., Dalt. Trans.*, 1998, 2671–2677.
42. M. Al-Shakban, P. D. Matthews, G. Deogratias, P. D. McNaughter, J. Raftery, I. Vitorica-Yrezabal, E. B. Mubofu and P. O'Brien, *Inorg. Chem.*, 2017, **56**, 9247–9254.
43. J. E. Iglesias, K. E. Pachali and H. Steinfink, *Mater. Res. Bull.*, 1972, **7**, 1247–1258.
44. Z. Eliezer and H. Steinfink, *Mater. Res. Bull.*, 1976, **11**, 385–388.

