JOURNAL OF
Materials
CHEMISTRY

Solid-state and solution phase metathetical synthesis of copper indium chalcogenides

Claire J. Carmalt, Daniel E. Morrison and Ivan P. Parkin*

Department of Chemistry, Christopher Ingold Laboratories, University College London, 20 Gordon Street, London, UK WC1H 0AJ

Received 11th June 1998, Accepted 22nd July, 1998

Copper indium chalcogenides, of the type $CuInE_2$ (E = S, Se and Te), have been successfully prepared by solid-state and solution phase metathetical reactions of CuBr or $CuCl_2$, $InCl_3$ and the appropriate sodium chalcogenide (Na_2E). The copper indium chalcogenides were analysed by powder X-ray diffraction, scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDXA) and FTIR spectroscopy.

Copper indium chalcogenides, of formula $CuInE_2$ (where E = S, Se and Te), are chalcopyrite-type ternary semiconductors. These materials are suitable for high efficiency, radiation-hard solar cell applications,[1,2] and candidates for the cathode material of photochemical devices as a result of their high performance and high output stability.[3] There are many procedures available for preparing $CuInE_2$ thin films including evaporation,[4] sputtering,[5] multi- and single source chemical vapour deposition (CVD)[6,7] and spray pyrolysis.[8] However, it is difficult to maintain the stoichiometry during the deposition, especially in cases of deposition from the vapour phase and Cu deficient films of the type $CuIn_5S_8$ can result.[6–8] The conventional ceramic preparation of bulk $CuInE_2$ involves combination of the elements in specially strengthened quartz ampoules at 1150 °C for 3 days.[9]

In previous papers, we have demonstrated how metal chalcogenides and pnictides can be synthesised by the metathetical exchange reactions of compounds of the form Na_xE (E = chalcogen or pnictogen) with metal halides in the solid-state.[10] The driving force is the stability of the co-produced salt. During the reaction large amounts of heat are developed which in some reactions are high enough to decompose the product or yield some undesired phase. A lower temperature approach to these materials is found in solution phase metathetical reactions which have been developed by Kher and Wells[11] and focused on the preparation of III–V semiconductor materials. Recently, we have studied the preparation of In_2S_3 and In_2Se_3 *via* a solution phase metathetical route.[12]

We report here, an alternative rapid synthesis for copper indium chalcogenides of the type $CuInE_2$ (E = S, Se and Te), from the solid-state and solution phase reactions of copper(I) bromide or copper(II) chloride, indium(III) chloride and the appropriate sodium chalcogenide. A comparison is made between the solid-state and solution phase synthesis of $CuInE_2$, since in the latter the solution acts as a heat sink and a particle dispersant allowing lower temperatures to be used.

Experimental

All manipulations were performed under an inert atmosphere either using Schlenk techniques or in a Saffron Scientific inert atmosphere glove box. Toluene was dried over sodium and distilled from sodium under nitrogen prior to use. $CuCl_2$, CuBr and $InCl_3$ were obtained from Aldrich and used as supplied. Na_2E (E = S, Se or Te) were prepared by a modification of the literature procedure[13] from the reaction of sodium with the appropriate chalcogenide in refluxing toluene for 48 h. Thermolysis studies were performed in a Lenton Thermal Designs tube furnace. Powder XRD measurements were recorded on a Siemens D5000 transmission diffractometer using germanium monochromated Cu-Kα_1 radiation (λ = 1.5406 Å) as thin films. SEM profiles and EDXA were performed on a Hitachi S570. FTIR spectra were recorded on a Nicolet 205 spectrometer as CsBr pellets.

Solid–state metathesis reactions of CuBr, $InCl_3$ and Na_2E (E = S, Se or Te)

CuBr (0.090 g, 0.63 mmol) and $InCl_3$ (0.139 g, 0.63 mmol) were ground together thoroughly inside the glove box. Na_2E (1.30 mmol) was added and the powders were ground lightly together and then placed into an ampoule which was sealed under vacuum and heated to 500 °C for between 5 min and 48 h. This induced an exothermic reaction with some of the product spread along the inside walls (E = S) of the ampoule and a fused black material was obtained. The reaction mixture was allowed to cool to room temperature and the black solid was triturated with ethanol (2×20 cm^3), followed by distilled water (3×20 cm^3) and ethanol (2×20 cm^3) and dried *in vacuo*, (average yield 90%). The resulting powders were analysed by SEM/EDXA, powder XRD (Table 1) and FTIR spectroscopy.

Solid–state metathesis reactions of $CuCl_2$, $InCl_3$ and Na_2E (E = S, Se or Te)

$CuCl_2$ (0.070 g, 0.52 mmol) and $InCl_3$ (0.120 g, 0.54 mmol) were ground together thoroughly inside the glove box. Na_2E (1.30 mmol) was added and the powders were ground lightly together and then placed into an ampoule which was sealed under vacuum and heated to 500 °C for between 5 min and 48 h. This induced an exothermic reaction with some of the product spread along the inside walls of the ampoule (E = S) and the formation of a black partly fused product. The reaction was allowed to cool to room temperature and the black solid was triturated as described above and dried *in vacuo* (average yield 90%). The resulting powders were ana-

Table 1 X-Ray powder diffraction data[a] for $CuInE_2$ prepared by routes (i)–(iv)

Product	Route (i)	Route (ii)	Route (iii)	Route (iv)	Lit.[14]
$CuInS_2$	$a = 5.519$	$a = 5.522$	$a = 5.516$	$a = 5.524$	$a = 5.52$
	$c = 11.108$	$c = 11.133$	$c = 11.114$	$c = 11.106$	$c = 11.12$
$CuInSe_2$	$a = 5.776$	$a = 5.779$	$a = 5.781$	$a = 5.780$	$a = 5.782$
	$c = 11.603$	$c = 11.612$	$c = 11.613$	$c = 11.608$	$c = 11.619$
$CuInTe_2$	$a = 6.20$	$a = 6.19$	$a = 6.20$	$a = 6.19$	$a = 6.18$
	$c = 12.40$	$c = 12.40$	$c = 12.39$	$c = 12.40$	$c = 12.36$

[a] Unit cell dimensions *a*, *c* in Å (±0.004 Å).

lysed by SEM/EDXA, powder XRD (Table 1) and FTIR spectroscopy.

Solution phase reactions of CuBr, $InCl_3$ and Na_2E (E = S, Se or Te)

CuBr (0.186 g, 1.30 mmol) and $InCl_3$ (0.280 g, 1.30 mmol) were ground together thoroughly inside the glove box. Na_2E (2.60 mmol) was added and the powders were ground lightly together and then placed into a Schlenk flask. Toluene (20 cm^3) was added *via* syringe and the reaction mixture was heated to reflux for 72 h. The resulting slurry was allowed to settle and the toluene was syringed off and the remaining black solid was triturated as described above and dried *in vacuo* (average yield 90%). The resulting powders were analysed by SEM/EDXA, powder XRD (Table 1) and FTIR spectroscopy. The black solids were annealed at 500 °C for 24 h and reanalysed by powder XRD and SEM/EDXA.

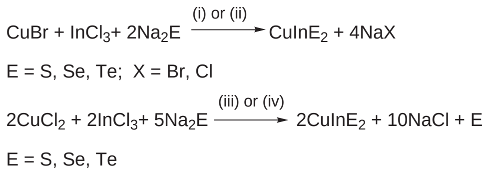
Solution phase reactions of $CuCl_2$, $InCl_3$ and Na_2E (E = S, Se or Te)

$CuCl_2$ (0.174 g, 1.30 mmol) and $InCl_3$ (0.28 g, 1.30 mmol) were ground together thoroughly inside the glove box. Na_2E (2.60 mmol) was added and the powders were ground lightly together and then placed into a Schlenk flask. Toluene (20 cm^3) was added *via* syringe and the reaction mixture was heated to reflux for 72 h. The resulting slurry was allowed to settle and the toluene was syringed off and the remaining solid was triturated as described above and dried *in vacuo* (average yield 90%). The resulting powders were analysed by SEM/EDXA, powder XRD (Table 1) and FTIR spectroscopy. The black solids were annealed at 500 °C for 24 h and reanalysed by powder XRD and SEM/EDXA.

Results

Solid–state synthesis

Thermolysis of a pre-ground mixture of sodium chalcogenide, copper(I) bromide and indium(III) chloride at 500 °C induces an exothermic reaction [Scheme 1, route (i)]. Similarly, an exothermic reaction resulted from the thermolysis of a pre-ground mixture of sodium chalcogenide, copper(II) chloride and indium(III) chloride at 500 °C [Scheme 1, route (iii)]. In the sulfide cases for both route (i) and (iii), the reaction spreads material throughout the containment vessel. No thermal flash or synthesis wave[10] was observed for any of the reactions. In all cases a colour change from green to dark grey–black occured during the reaction. The initiation temperature of the reaction was difficult to gauge, however, significant colour change to grey had occurred at 200 °C. The reaction went to completion after just 5 min heating at 500 °C producing a product that was comparable to that obtained after 48 h at 500 °C. Powder XRD of the material[14] reveals the formation of sodium halide and $CuInE_2$. Trituration with ethanol and distilled water removes the sodium halide and the residue was pumped to dryness *in vacuo*. The powder patterns of this material showed that a single phase of tetragonal $CuInE_2$ had formed (Table 1) with a typical crystallite size from the X-ray line broadening of 300–400 Å. Fig. 1(a) shows the powder X-ray diffraction pattern of $CuInSe_2$ prepared *via* route (iii). The X-ray powder diffraction patterns of $CuInE_2$ were indexed and gave exact matches to literature measurements.[14] The EDXA data showed good agreement to a 1 : 1 : 2 ratio of Cu : In : E over a number of spots. Fig. 2(a) shows an SEM image of $CuInSe_2$ prepared by route (iii) which showed irregular shaped agglomerated particles of dimension *ca.* 15–30 μm. The FTIR spectra of the copper indium chalcogenides showed two broad bands centered at *ca.* 520 and 410 cm^{-1}.



Scheme 1 *Conditions*: (i) solid-state metathesis at 500 °C; (ii) solution phase metathesis in refluxing toluene; (iii) solid-state metathesis at 500 °C; (iv) solution phase metathesis in refluxing toluene.

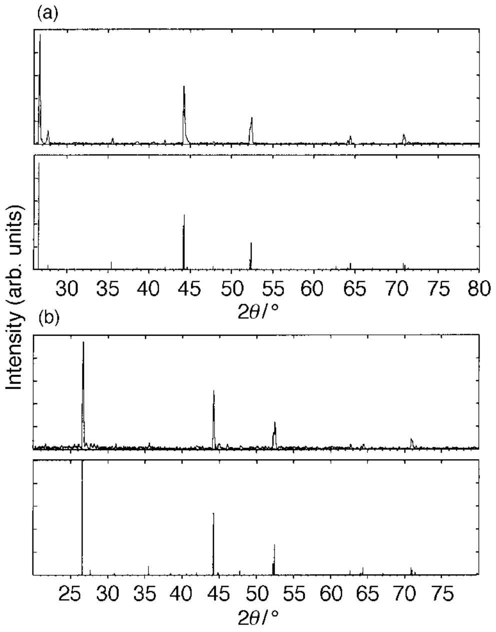


Fig. 1 (a) Top trace; X-ray powder diffraction pattern of $CuInSe_2$ prepared from the solid-state metathesis reaction of $CuCl_2$, $InCl_3$ and Na_2Se [route (iii)]. Bottom trace; literature stick pattern for $CuInSe_2$. (b) Top trace; X-ray powder diffraction pattern of $CuInSe_2$ prepared from toluene reflux of $CuCl_2$, $InCl_3$ and Na_2Se after annealing at 500 °C for 48 h. Bottom trace; literature stick pattern for $CuInSe_2$.

Solution phase synthesis

The reaction between a pre-ground mixture of sodium chalcogenide, copper(I) bromide and indium(III) chloride in refluxing toluene results, after trituration with ethanol and distilled water (to remove the sodium halide formed), in the formation of $CuInE_2$ [Scheme 1, route (ii)]. Similarly, the reaction between a pre-ground mixture of sodium chalcogenide, copper(II) chloride and indium(III) chloride in refluxing

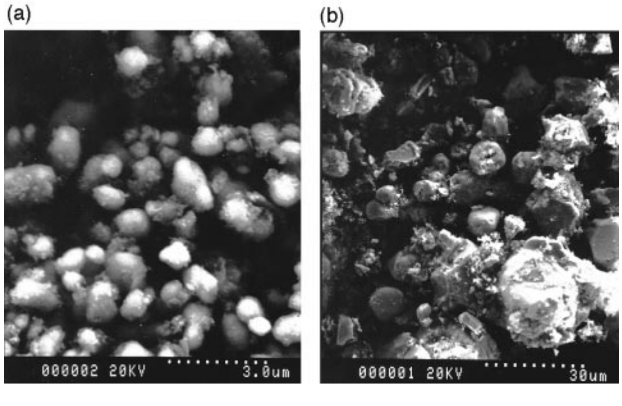


Fig. 2 (a) SEM of $CuInSe_2$ prepared by solid-state metathesis reaction of $CuCl_2$, $InCl_3$ and Na_2Se [route (iii)]. (b) SEM of $CuInSe_2$ prepared from toluene reflux of $CuCl_2$, $InCl_3$ and Na_2Se after annealing at 500 °C for 48 h [route (iv)].

toluene results, after trituration with ethanol and water, in the formation of $CuInE_2$ [Scheme 1, route (iv)]. Powder XRD of the material[14] revealed it was X-ray amorphous. However, the EDXA data showed good agreement to a 1:1:2 ratio of Cu:In:E over a number of spots with no halide or sodium detected. The washings from the reaction on evaporation yielded sodium halide salts. The amorphous $CuInE_2$ was annealed at 500 °C for 24 h. The powder patterns of the annealed material showed that single phase tetragonal $CuInE_2$ had formed (Table 1). Fig. 1(b) shows a powder X-ray diffraction pattern of $CuInSe_2$ prepared *via* route (iv) in Scheme 1. The EDXA data showed good agreement with the pre-annealed material with a 1:1:2 ratio of Cu:In:E over a number of spots. Fig. 2(b) shows the SEM image of $CuInSe_2$ prepared from solution phase metathesis reaction [route (iv)]; this showed spherical particles of size *ca.* 5 μm. The FTIR spectra of the copper indium chalcogenides were comparable to those prepared by the solid-state route with bands at *ca.* 520 and 410 cm^{-1}.

Discussion

The results from the solid–state and solution phase reactions are very similar with both routes leading to crystalline $CuInE_2$ in high yields. The quality of the $CuInE_2$ formed from either route was comparable, although the solution phase routes resulted in the formation of smaller and more even particle sizes. The solution phase reactions offer a low temperature route to these materials and enables X-ray amorphous $CuInE_2$ to be obtained.

In solution the solvent acts as a heat sink to absorb reaction energy. No detectable colour was observed in the solution, however, the reagents gradually darkened during the course of the reaction. At reflux in toluene the reaction is best described as a slow solid-state reaction which is thermally assisted by the solvent. Previous work has shown that metathesis reactions between a solid reagent and a neat liquid metal halide occur extremely rapidly with a thermal flash, often on contact.[10] This ease of initiation is a consequence of overcoming the solid-state diffusion barrier. In the reactions studied here in solution neither of the initial reagents has measurable solubility in the solvent. The refluxing solvent allows fresh surfaces of the solid-state reactants to combine together and this coupled with the long reaction time allowed the solid-state diffusion barrier to be overcome and since the reaction temperatures were low the products were X-ray amorphous. The oxidation state of the copper halide appears to be of no importance to the reactivity either in solution or the solid-state since copper(I) bromide produced the same results as copper(II) chloride. It is also worth noting that no Cu deficient $CuIn_5S_8$ phase was identified by any of the routes described.

Thermodynamic considerations

Solid-state metathesis reactions have been utilised for the synthesis of a large range of binary materials.[10] Solid-state metathesis reactions have often been found not to lead readily to ternary materials.[10] Phase segregation of the binary components often features and requires the powders to be heated for extensive time periods to ensure formation of a ternary phase. The solid-state metathesis formation of $CuInE_2$ is unusual in that the ternary phase is formed directly in the reaction (500 °C, 5 min) indicating that it is the kinetic product. The reaction is driven by the lattice energy of the co-produced salt. Hess's law calculations indicate that the reactions to form $CuInE_2$ have an exothermicity of the order of 400 kJ mol^{-1}.[15] This is just below the threshold in exothermicity required for a propagation wave (thermal flash).[10]

Conclusions

Solid-state and solution phase metathetical reactions of CuBr or $CuCl_2$, $InCl_3$ and the appropriate sodium chalcogenide (Na_2E) offer a convenient route to the formation of good quality $CuInS_2$, $CuInSe_2$ and $CuInTe_2$. The solid-state metathesis reactions are at significantly lower temperatures (500 °C as compared with 1150 °C) and shorter reaction times (5 min *vs.* 3 days) than conventional preparative routes to $CuInE_2$. Solution phase metathesis reactions also form $CuInE_2$ with the solvent acting as a heat sink to absorb reaction energy and enabling X-ray amorphous $CuInE_2$ to be obtained. Both solution and solid-state metathesis routes form single phase $CuInE_2$ with no $CuIn_5E_8$.

C. J. C. acknowledges the Royal Society for a Dorothy Hodgkin Fellowship and London University Central Research Fund. D. E. M. thanks the CVCD for an ORS award.

References

1 R. W. Birkmire and E. Eser, *Annu. Rev. Mater. Sci.*, 1997, **27**, 625; M. I. Schimmel, O. L. Bottechia and H. Wendt, *J. Appl. Electrochem.*, 1998, **28**, 299; G. C. Park, H. D. Chung, C. D. Kim, H. R. Park, W. J. Jeong, J. U. Kim, H. B. Gu and K. S. Lee, *Sol. Energy Mater. Sol. Cells*, 1997, **49**, 365; T. Watanabe and M. Matsui, *Jpn. J. Appl. Phys., Part 1*, 1996, **35**, 1681.

2 *Ternary Chalcopyrite Semiconductors: Growth, Electronics, Properties and Applications*, ed. J. L. Shay and J. H. Wernik, Pergamon, Oxford, 1976, pp. 110–187.

3 D. Cahen, G. Dagan, Y. Mirovsky, G. Hodes, W. Giriat and M. Lubke, *J. Electrochem. Soc.*, 1985, **132**, 1062.

4 Y. Yamamoto, T. Yamaguchi, T. Tanaka, N. Tanahashi and A. Yoshida, *Sol. Energy Mater. Sol. Cells*, 1997, **49**, 399; Y. L. Wu, H. Y. Lin, C. Y. Sun, M. H. Yang and H. L. Hwang, *Thin Solid Films*, 1989, **168**, 113.

5 C. C. Landry, J. Lockwood and A. R. Barron, *Chem. Mater.*, 1995, **7**, 699; S. P. Grindle, C. W. Smith and S. D. Mittleman, *Appl. Phys. Lett.*, 1979, **35**, 24; S. V. Krishnaswamy, A. S. Manocha and J. R. Szedon, *J. Vac. Sci. Technol., Part A*, 1983, **1**, 510.

6 M. Gossla, T. Hahn, H. Metzzner, J. Conrad and U. Geyer, *Thin Solid Films*, 1995, **268**, 39; H. L. Hwang, C. Y. Sun, C. S. Fang, C. H. Chang, M. H. Cheng, H. H. Yang, H. H. Liu and H. Tunan-Mu, *J. Cryst. Growth*, 1981, **55**, 116.

7 R. Nomura, Y. Sekl and H. Matsuda, *J. Mater. Chem.*, 1992, **2**, 765; R. Nomura, Y. Sekl, K. Konishi and H. Matsuda, *Appl. Organomet. Chem.*, 1992, **6**, 685; J. McAleese, P. O'Brien and D. J. Otway, *Chem. Vap. Deposition*, 1998, **4**, 94.

8 Y. D. Tembhurkar, *Bull. Mater. Sci.*, 1997, **20**, 1011; R. Nomura, K. Kanaya and H. Matsuda, *Chem. Lett.*, 1988, 1849; A. N. Tiwari, D. K. Pandya and K. L. Chopra, *Thin Solid Films*, 1985, **130**, 217.

9 D. Suri, K. Nagpal and G. Chadha, *J. Appl. Crystallogr.*, 1989, **22**, 578.

10 I. P. Parkin, *Chem. Soc. Rev.*, 1996, 199.

11 S. S. Kher and R. L. Wells, *Chem. Mater.*, 1994, **6**, 2056.

12 C. J. Carmalt, D. E. Morrison and I. P. Parkin, *J. Mater. Sci. Lett.*, submitted.

13 J. C. Fitzmaurice and I. P. Parkin, *New. J. Chem.*, 1994, **18**, 825.

14 PDF–2 database, 1990, International Center for Diffraction Data, Swarthmore, PA, 19081, 1990; H. Hahn, *Z. Anorg. Chem.*, 1953, **271**, 153.

15 *Materials Thermochemistry*, ed. O. Kubaschewski, C. B. Alcock and P. J. Spiner, Pergamon, Oxford, 6th edn., 1993.

Paper 8/04430I