Convenient, low-energy synthesis of metal sulfides and selenides; PbE, Ag_2E, ZnE, CdE (E = S, Se)

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Reaction of elemental metal Pb, Ag, Zn and Cd with sulfur or selenium in liquid ammonia at room temperature for 2–12 h produces highly crystalline PbS, PbSe, Ag_2S, Ag_2Se and X-ray amorphous ZnS, ZnSe, CdS and CdSe in virtually quantitative yield.

The synthesis of binary metal sulfides and selenides of groups Ib, IIb and IVb has been the focus of much attention recently. These materials have an extensive array of commercial applications from semiconductors and pigments to luminescence devices.[1] Binary metal sulfides can be made by the direct reaction of the elements at high temperatures for prolonged time periods,[2] treatment of the element oxides with H_2S,[3] and by precipitation of the metal cation from aqueous solution by a source of S^{2-}.[4] Binary metal sulfides such as MoS_2 and WS_2 have been made using a solid-state metathesis reaction of anhydrous metal halide and sodium sulfide, the reaction being spontaneous on mixing reactive components.[5] Molecular precursor routes to metal sulfides have been developed by a number of groups both for bulk materials[6] and for coatings.[7] One intriguing development has been the reaction of zinc and copper with sulfur at the reflux temperatures of strongly coordinating solvents such as pyridine and *N*-methylimidazole, this forms $[M(S_6)(solv)_2]$ complexes that can be decomposed at 500 °C in the case of zinc to yield cubic ZnS.[8] Here we report the convienient one-step room-temperature preparation of both crystalline and amorphous metal sulfides and selenides at room temperature *via* elemental reactions in liquid ammonia.

Reaction of elemental lead or silver (*ca.* 1.0 mmol scale) with sulfur or selenium in liquid ammonia (15 ml) at room temperature in a Youngs thick-walled Teflon-in-glass pressure tube for 12 h affords crystalline PbS, PbSe, Ag_2S and Ag_2Se (Fig. 1, 2) in virtually quantitative yield [eqn. (1), (2)].

$$Pb(s) + S(am) \longrightarrow PbS \qquad (1)$$

$$2Ag(s) + S(am) \longrightarrow Ag_2S \qquad (2)$$

The silver and lead sulfides and selenides were characterised by X-ray powder diffraction[†] which showed perfect matches and indexed patterns with literature cell parameters.[9] Average crystallite sizes as determined by the Scherrer equation based on the XRD linewidths were in the range 500–1000 Å.[10] Scanning electron microscopy[‡] (SEM) analysis of the powder revealed agglomerates of particles. Energy dispersive analysis by X-rays (EDAX) shows the presence of only metal and chalcogenide with virtually uniform composition over many surface spots. Electron microprobe analysis showed excellent agreement in the case of PbS with the empirical formula however some traces of lead metal were also observed. Microanalysis reveals trace levels of nitrogen and hydrogen (typically 0.2% or less). IR and Raman analyses[§] are consistent with the formation of metal sulfides and selenides with vibrations at 600–250 cm^{-1}. Some samples showed very weak bands at 3200 and 1450 cm^{-1} corresponding to residual trace NH_2 groups.

The reaction of zinc and cadmium metals with sulfur and selenium in liquid ammonia proceeded analogously to that of lead and silver, the products were the expected colour of the metal chalcogenide. These materials were amorphous to X-rays but had the correct IR, Raman, EDAX and microanalytical signatures for the binary chalcogenides. The XPS spectrum of the CdSe powder showed binding energy shifts in agreement with literature values.[11] Heating the Zn and Cd powders to 300 °C for 2 h was sufficient to allow characterisation by X-ray powder diffraction as phase-pure ZnS, ZnSe, CdS and CdSe.

The reactions of elemental metal with sulfur and selenium at room temperature in liquid ammonia afford single-phase binary metal chalcogenides. The closest correlation would be the studies of Rauchfuss and coworkers[12] who have isolated discrete complexes by refluxing the elements in strongly coordinating donor solvents to isolate $[Zn(S_6)(tmeda)]$ and $[M(S_6)(Heim)_2]$ (M = Cu, Fe, Ni; tmeda = trimethylene-ethylenediamine, Heim = 2-ethylimidazole). Subsequent thermal decomposition of the complexes in the copper and zinc cases have led to good yields of the binary materials CuS and ZnS. The liquid-ammonia route developed here has the advantage of forming metal sulfides directly at room temperature and without recourse to thermolysis.

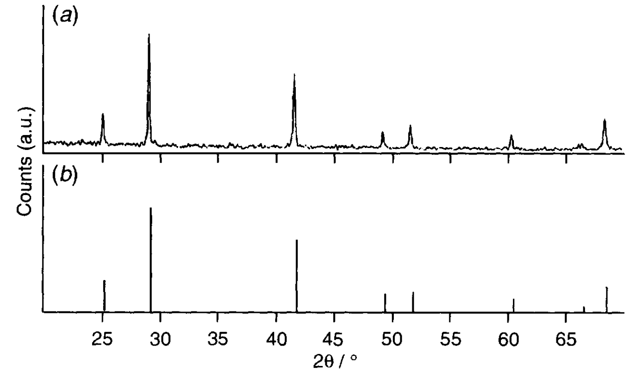

Fig. 1 (*a*) X-Ray powder diffraction pattern of the product from the reaction of Pb(s) and Se(s) in liquid ammonia at room temperature for 12 h; (*b*) standard stick pattern for PbSe

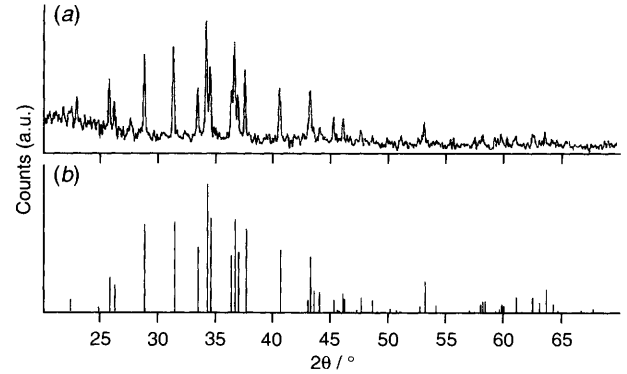

Fig 2 (*a*) X-Ray powder diffraction pattern of the product from the reaction of Ag(s) and S(am) in liquid ammonia at room temperature for 12 h; (*b*) standard pattern for Ag_2S

Some elements are known to react slowly with chalcogenides in the solid state at room temperature, however the reaction is surface limited and in most cases slow. Liquid ammonia does acquire various colours during the reaction ranging from green to blue to red and the metal and sulfur seem to dissolve in the solution and reprecipitate back out as the metal sulfide. It is known that sulfur does dissolve in liquid ammonia to form a complex series of sulfur–nitrogen and sulfur anions (S_6^{2-}, S_4^-, S_4N^-, S_7N^-) and it is likely that one of these species is a sufficiently strong oxidising agent to oxidize the metal and form the binary sulfide.[13].

The reaction of selenium with elemental metals (Pb, Ag, Zn, Cd) in liquid ammonia proceeds with no detectable solution species. It is probable that ammonia acts not only as a transport medium by which the elements can combine but also as a surface cleaning reagent that scrubs and removes the passivating oxide layer on the surface of the metals that would otherwise prevent reaction. Combination of the elements in other solvents such as water, thf, acetone, CH_2Cl_2 and CS_2 did not lead to the formation of metal chalcogenides. Further studies are in progress to determine the scope of the reaction.

CAUTION: Reactions in liquid ammonia at room temperatures in Teflon-in-glass pressure vessels have been known to explode. All reactions should be conducted with blast proof netting around the reaction vessels and behind a safety screen.

Footnotes

† XRPD patterns were obtained on a Siemens D5000 transmission diffractometer using germanium-monochromated Cu-Kα (1.5406 Å) radiation.

‡ FTIR spectra were obtained on a Nicholet 205 (CsI) using pressed KBr or CsI discs, Raman spectra obtained on a Dilor XY spectrometer using the 514.53 nm line of an argon laser (50 mW) as the excitation source.

§ SEM/EDAX measurements were made on a Hitachi S4000 instrument.

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