Polyhedron Vol. 12, No. 24, pp. 2961–2964, 1993
Printed in Great Britain

0277–5387/93 $6.00+.00

METATHESIS ROUTES TO TIN AND LEAD CHALCOGENIDES

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(*Received* 16 *June* 1993; *accepted* 15 *July* 1993)

Abstract—Thermal initiation (550°C) of a mixture of SnI_4 and Li_2E produces SnE_2 ($E = O$, S, Se). Similarly, $PbCl_2$ and Li_2E' produces PbE' ($E' = O$, S, Se, Te) via an exothermic solid state metathesis reaction. The PbE' and SnE_2 compounds were characterized by microanalysis, SEM/EDAX, FT-IR spectroscopy, magnetic moment measurements, X-ray powder diffraction and, in the case of tin, by solid state NMR.

Tin and lead chalcogenides are found as minerals and manufactured for semi-conductors, mosaic golds, pigments, photo-conductors and radio receivers.[1] Traditionally they are made by high temperature combination of the elements, by solution precipitation methods or by reaction of H_2E ($E = S$, Se, Te) on the metal.[2]

Self-propagating high temperature synthesis (SHS) methods to materials have been developed by Russian chemists[3] in the 1960s. These process involve initiating a solid-state reaction between pressed discs of the elements by means of an electric filament or an oven. Kaner *et al.*[4] and others[5] have utilized a similar idea by synthesizing transition metal chalcogenides via a solid state metathesis reaction involving sodium chalcogenides and metal halides. These syntheses have a number of advantages, firstly the reaction can be extremely rapid (2–3 s), secondly the by-product NaCl is easily removed by trituration, thirdly high purity crystalline products are produced and fourthly the reaction requires low energy initiation. Modifications to this technique have allowed control of crystallite size and morphology.[6]

Here we outline an extension of solid state metathesis reactions to main group metals in the synthesis of tin and lead chalcogenides.

EXPERIMENTAL

All reactions and preparations were carried out *in vacuo* or in a dinitrogen-filled dry box. Glass ampoules were made out of pyrex glass and were either flame dried *in vacuo* or heated to 400°C for 6 h prior to reaction. All solvents were degassed with dinitrogen. Methanol was distilled from MgI_2 and stored over 3 Å molecular sieves prior to use. Metal halides and Li_2O were purchased from Aldrich Chemical Co. and used as supplied. Lithium chalcogenides, Li_2S, Li_2Se and Li_2Te, were made by combining lithium and the chalcogenide in liquid ammonia followed by evaporation of the ammonia and thermolysis of the residue to 550°C for 10 h. X-ray powder diffraction patterns were obtained using a Seimens D5000 diffractometer using nickel filtered copper K_α ($\lambda = 1.5406$ Å) radiation; SEM and electron microprobe analysis on a Jeol JSM 820 equipped with Kevex program,[7] FT-IR as pressed KBr discs on a Nicolet 205 (CsI); magnetic susceptibility measurements were determined on a Johnson Matthey balance. Solid state ^{119}Sn MAS NMR spectra were obtained at 111.862 MHz at a spin rate of 12.25 kHz on the SERC machine at Durham University with chemical shift measurements given relative to $Sn(CH_3)_4$. Ultrasound sonication was achieved at 20 kHz using a Soniprep ultrasonic gun. Thermal initiation of the reactions was performed in a Lenton Thermal Design tube furnace.

Preparation of tin and lead chalcogenides

Lithium chalcogenide and anhydrous metal halide (SnI_4 or $PbCl_2$) were ground together using an agate pestle and mortar in a dinitrogen-filled dry box (such that the ratio of lithium to halide was 1 : 1). The powder was added to a thick-walled glass

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ampoule, sealed under vacuum and sonicated with an ultrasonic gun for 10 min. The ampoule was then wrapped in glass wool and placed in a conventional oven at 550°C for 5 h. The ampoule was removed from the oven, allowed to cool to room temperature and opened in a glove box. Trituration of the grey, orange or yellow solid with methanol, aqua regia, water or dilute HCl for 1 h produced a fine precipitate and a cloudy layer (Table 1). Evaporation of the methanol filtrate produces crystals of a white solid identified as LiCl or LiI by X-ray powder diffraction, lithium flame test and chlorine/iodine EDAX analysis. The coloured powders were identified as tin or lead chalcogenides by X-ray powder diffraction (Table 1), EDAX analysis, magnetic moment measurements, FT-IR and ^{119}Sn NMR. Ceramic yields, based on the metal after THF trituration, varied from 20% (Pb_2O_2Cl) to 80% (PbSe, SnS_2) depending on the sample.

RESULTS AND DISCUSSION

Reaction of SnI_4 or $PbCl_2$ with Li_2E (E = O, S, Se, Te) produces tin or lead chalcogenides and lithium halide via an exothermic solid-state metathesis reaction:

$$SnI_4+2Li_2E \xrightarrow{500°C} SnE_2+4LiI \ (E = O, S, Se) \quad (1)$$

$$PbCl_2+Li_2E \xrightarrow{500°C} PbE+2LiCl \ (E = S, Se, Te) \quad (2)$$

$$PbCl_2+Li_2O \xrightarrow{500°C} Pb_2O_2Cl+LiCl+[Pb]. \quad (3)$$

After thermolysis the product was contained in fused grey, gold or orange lumps which showed a smooth morphology by SEM indicative of a coating of sublimed LiCl. Metal, chalcogenide and chloride were detected by EDAX analysis, which is consistent with the formation of a metal chalcogenide that contains amorphous lithium chloride on the surface. The metal chalcogenides were purified by trituration with methanol, aqua regia or dilute HCl (Table 1) to remove the LiCl, tin metal and unreacted metal halide, respectively. Characterization was by X-ray powder diffraction, magnetic moment measurement and solid state ^{119}Sn NMR spectroscopy.

The SEM profile of the triturated metal chalcogenides showed a rough porous surface, whilst the EDAX step analysis revealed only metal and chalcogen with no halide present (2–3% detection limit, except for Pb_2O_2Cl, where Cl was observed). The FT-IR spectra of the metal chalcogenides were featureless in the range 4000–400 cm^{-1}. No lithium (<0.1%) was detected by microanalysis for the triturated powders. The solid state ^{119}Sn NMR spectrum of SnS_2 showed a single resonance at −764 ppm, indicating that only one environment for tin is present in the lattice and that no detectable free tin is produced from the reaction of SnI_4 and Li_2S.

The X-ray powder diffraction data for the metal chalcogenides formed from reaction of Li_2E and $SnI_4/PbCl_2$ are summarized in Table 1. In general, after a reaction time of 4 h at 550°C, a crystalline metal chalcogenide was formed.[8] The crystalline size as determined by the Scherrer equation[9] based on the powder XRD line widths varied from 300 to 600 Å. The metal chalcogenides after trituration had no crystalline lithium halide present and showed the material as a single phase, SnE_2 or PbE.

Table 1. Crystallographic and experimental data from the reaction of SnI_4 and $PbCl_2$ with Li_2E (E = O, S, Se, Te)

Reagents	Work-up	Colour	Crystalline phase detected	Literature **a** spacing[8] (Å)	Observed **a** spacing (Å)	Crystalline size (Å)
SnI_4+Li_2O	aqua regia	white	SnO_2[a] (tetragonal)	4.738	4.727	450
SnI_4+Li_2S	methanol	gold	SnS_2 (hexagonal)	3.639	3.627	450
SnI_4+Li_2Se	methanol	grey	$SnSe_2$ (hexagonal)	3.810	3.793	400
$PbCl_2+Li_2O$	water	orange	Pb_2O_2Cl (tetragonal)	3.910	3.908	350
$PbCl_2+Li_2S$	methanol	grey	PbS (cubic)	5.936	5.908	600
$PbCl_2+Li_2Se$	methanol	grey	PbSe (cubic)	6.124	6.088	500
$PbCl_2+Li_2Te$	dilute HCl	grey	PbTe (cubic)	6.459	6.437	450
$PbCl_2+Li_2$(Se, Te)	dilute HCl	grey	Pb_2(Se, Te)		6.24	300
$PbCl_2+Li_2$(S, Se)	dilute HCl	grey	Pb_2(S, Se)		5.99	450
SnI_4+Li_2(S, Se)	dilute HCl	grey	Sn(S, Se)		3.71	400

[a] Before trituration tin metal was also detected by XRD.

In general, the reaction of SnI_4 or $PbCl_2$ with Li_2E involves no redox chemistry, with the metal in the same oxidation state as the starting material. The reaction times and crystallinity of the products were comparable for all the chalcogens studied; however, the yield of Pb_2O_2Cl was considerably lower than the rest at 20%. Formation of Pb_2O_2Cl involves oxidation at the metal and may form from a dispropotronation reaction with formation of some lead metal, although this was not detected by XRPD.

Analogous studies of reaction of sodium chalcogenides with transition metal halides showed that initiation can be achieved at room temperature by light grinding of the reagents.[4] No initiation of the reaction of $PbCl_2$ or SnI_4 and Li_2E could be achieved either by grinding or mixing the reagents or by means of a heated filament. The reactions required heating at 450–500°C to initiate; however, the presence of sublimed LiCl (b.p. = 1300°C) and occasional warping/pitting of the ampoules indicates that these reactions are exothermic and it is this that provides for a relatively rapid reaction generating crystalline products.

Hess' law calculations[10] of the reaction of metal halide and lithium chalcogenide indicate that the reaction is exothermic with $\Delta H \approx -200$ kJ mol^{-1}. The primary driving force for the reaction is due to the large lattice energy of the co-product LiX, which accounts for up to 80% of the reaction enthalphy.

Reaction of SnI_4 with mixed lithium chalcogenides $Li_2Se_{0.5}S_{0.5}$ proceeds analogously to the reactions to produce binary SnE_2 materials. The X-ray diffraction patterns of the mixed $Sn(S_xSe_y)$ materials are intermediate between and slightly broader than the patterns observed for the corresponding binary SnS_2, $SnSe_2$ materials. The EDAX step analysis of the mixed tin chalcogenide showed constant ratios of sulphur and selenium, indicating that an intermixed species was formed. Similar behaviour is observed for the reactions with $PbCl_2$ and $Li_2Se_{0.5}S_{0.5}$, $Li_2Se_{0.5}Te_{0.5}$ which formed the mixed species $PbSe_xS_y$ and $PbSe_xTe_y$, respectively. The composition of the mixed lead chalcogenide species as assessed from the lattice spacing, **a** (assuming Vegards' law[11]) and the EDAX analysis indicates that species of composition close to $PbSe_{0.5}S_{0.5}$ and $PbSe_{0.5}Te_{0.5}$ were formed. A representative powder pattern for $PbSe_{0.5}S_{0.5}$ is shown in Fig. 1.

Kaner[4] has suggested that reaction of MCl_5 and $Li_2S_xSe_y$ may proceed by formation of the salt LiCl, co-reduction to the metal and chalcogen followed by recombination of the metal and chalcogen promoted by the heat of reaction. This accounts for the slight differences in chalcogen ratio in a range of reactions.[12] The mixed chalcogenide reactions to form PbS_xSe_y showed that $x = y$. However, the amount of selenium incorporation (as assessed by EDAX and **a** value) was found to be slightly lower than that of sulphur, in agreement with Kaner's findings. Interestingly, reaction of SnI_4 with Li_2O formed some tin metal in the reaction, unlike the reactions for Li_2S and Li_2Se. If the partial reduction to the elements followed by recombination mechanism was correct, then combination of tin metal with O_2 (g) would be expected to be less likely than with sulphur or selenium.

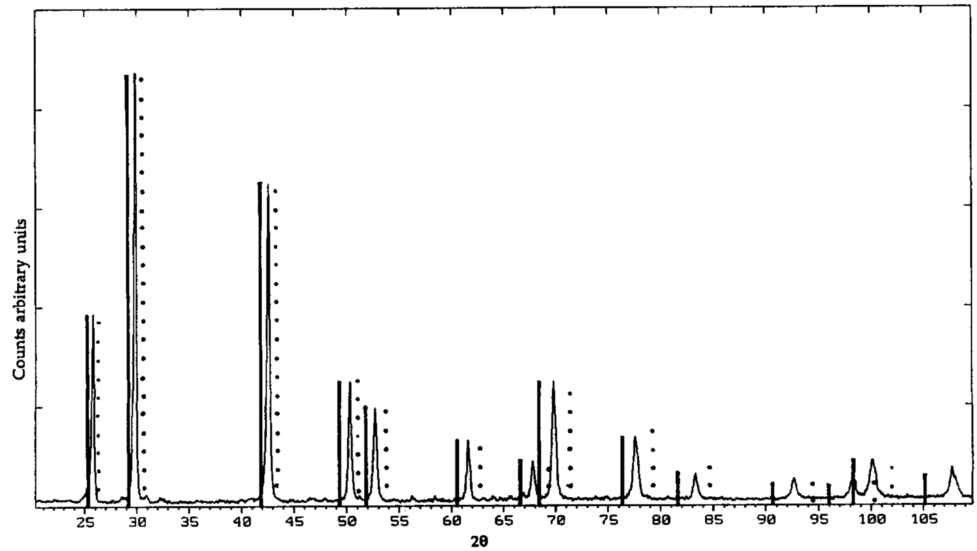

Fig. 1. X-ray powder diffraction pattern from reaction of $Li_2(Se, S)$ and $PbCl_2$; standard patterns for PbS (—) and PbSe (···).

CONCLUSION

Solid state metathesis reactions offer a route to crystalline tin and lead chalcogenides via an exothermic reaction. The reactions are at lower temperature and reasonably rapid, requiring shorter annealing times than conventional preparations. The purity of the metal chalcogenide is high, with the by-product lithium halides either subliming out during the course of the reaction or being removed by trituration.

Acknowledgements—The Royal Society, Nuffield Trust, Leverhulme Trust, SERC (Fellowship to A.T.R.). Dr Apperley is thanked for obtaining the solid state NMR spectra.

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