SOLID STATE ROUTES TO CRYSTALLINE GROUP IIB CHALCOGENIDES. APPLICATIONS OF METATHESIS REACTIONS

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Abstract

Thermolysis (500°C) of mixtures of MCl_2 (M = Zn, Cd, Hg) and Li_2E (E = O, S, Se, Te) produces ME via an exothermic reaction. The ME compounds were characterised by microanalysis, scanning electron microscopy (SEM)/energy dispersive X-ray analysis (EDXA), FTIR and X-ray powder diffraction. Mixed metal-sulphides, $M_xM'_yS$ and metal sulphide-selenides, MS_xSe_y were made by reaction of ground powders of MCl_2, $M'Cl_2$ and Li_2S or $Li_2(S_{0.5}Se_{0.5})$.

Introduction

The group IIB metals form monochalcogenides many of which occur naturally, for example zinc blende, wurtzite, cinnabar and zincite.[1] They are important for a wide range of industrial applications including pigments, glasses, fungicides, enamels, cathode-ray tubes/radar screens, phosphors and semi-conductors.[2] Preparation of Group IIB chalcogenides can be achieved by direct combination of the elements at high temperature, by pyrolysis of appropriate metal salts and by precipitation techniques.[3]

Recent interest has centered on the development of systematic routes to new and existing advanced materials with controls on substance morphology, stoichiometry,

structure and properties. Plasma, MOCVD and sol-gel type processes have been developed with the object of increasing product purity, speed of preparation and most importantly, lowering the overall energy required for synthesis. This approach is also dominant in solid state reactions whereby Kaner[4] and others[5] have demonstrated that certain important metal chalcogenides and pnictides can be synthesised via metathesis reactions. Such reactions are invariably rapid, produce minimum impurity products, have low external energy consumption and have the potential to make a range of new reagents.

In this paper we demonstrate that Group IIB chalcogenides and mixed chalcogenides can be made via an exothermic solid state metathesis reaction.

Experimental

All reagents were handled under nitrogen using either a glove box or Schlenk line techniques. Glass ampoules (thick walled borosilicate or quartz glass) were annealed prior to use and flame dried under vacuum. Anhydrous metal halides were obtained from Aldrich Chemical Co. and from J. M. Blythe Colours under a loan agreement. Methanol was dried over 3Å molecular sieves. All solvents were degassed with nitrogen prior to use. Infra-red spectra were recorded on a Nicolet 205 (CsI) using KBr and CsI discs. X-ray powder diffraction (XRD) measurements were performed on a Siemens Diffractometer D5000 using nickel filtered CuK_α (λ = 1.5406Å) radiation, magnetic moment measurements were determined on a Johnson Matthey balance and SEM profiles on a Jeol JSM 820 instrument using a Kevex system[6] for energy dispersive X-ray analysis. Magnetic moments were determined using a Johnson Matthey balance. A Lenton Thermal Designs programmable tube furnace was used to initiate the reactions.

Lithium oxide was purchased from Aldrich Chemical Co. and used as supplied. Lithium chalcogenides Li_2X (X = S, Se, Te), Li_2(S, Se) and Li_2(Se, Te) were made by

combining the elements in the appropriate ratios in liquid ammonia and allowing the ammonia to evaporate after reaction had occured.

Preparation of Metal Chalcogenides ME (M = Zn, Cd, Hg; E = O, S, Se, Te)

Lithium chalcogenide Li_2E (1.0 mmol) and anhydrous metal halide (1.0 mmol) were carefully ground together under an atmosphere of nitrogen (a surface reaction between $CdCl_2$ and Li_2S occurs almost immediately), sealed in an ampoule and placed in a tube furnace at 550°C for 3 hours. After this time the ampoule was allowed to cool slowly to room temperature (2°c min^{-1}) removed from the oven and broken open. Trituration of the material with methanol (2 × 20 ml) or water (2 × 20 ml) followed by acetone (10 ml) and ether (10 ml) removed LiCl and left a coloured powder. The identity of the powder was confirmed as ME by X-ray powder diffraction (Table 1), microanalysis, FTIR, magnetic moment measurements, SEM/EDXA. Ceramic yields of metal chalcogenides varied from 80-90% dependent on the sample.

Mixed Metal Chalcogenide Preparation $M_xM'_yS$

The same procedure as outlined above was used except equal molar quantities of the pre-ground metal halides MCl_2 and $M'Cl_2$ and Li_2S were combined in the glass ampoules and placed under vacuum prior to thermolysis.

Mixed Chalcogenide Metal Preparations $ME_xE'_y$ (E, E′ = S, Se; Se, Te)

The same procedure as outlined above was used, except $Li_2(E_xE'_y)$ was used as the starting material.

Results and Discussion

The solid state reaction of anhydrous group IIB chlorides with lithium chalcogenides in sealed ampoules at 500°C produces crystalline group IIB chalcogenides

in good yield, Eqn. 1.

$$Li_2E + MCl_2 \xrightarrow{500°C} ME + 2LiCl \qquad \text{Eqn.1}$$

(M = Zn, Cd, Hg; E = O, S, Se, Te)

The products from the reaction were contained as a fused mass with LiCl partially sublimed onto the walls of the ampoules. The bulk product was washed with methanol or water, acetone and ether and identified as ME by powder X-ray diffraction[7] (Table 1). A representative pattern for CdTe is shown in Figure 1. The EDXA step analysis of the metal chalcogenides after trituration showed no chlorine present (1% detection limit) and the product standardised as composition ME (Figure 2). No lithium (less than 0.1%) was found in the ME powders by microanalysis. Evaporation of the methanol or aqueous washings produced a white solid confirmed as LiCl by powder XRD, EDXA and lithium flame test.

Table 1., X-ray powder diffraction data from the reaction of Li_2E and MCl_2.

Reagents	Phase detected by XRD	Colour	lattice type	Literature[7] *a* value/ Å	Observed *a* value/ Å	X-tallite size/ Å
$ZnCl_2 + Li_2O$	ZnO (Zincite)	white	hexagonal	3.25 [c = 5.21]	3.26 [c = 5.16]	370
$ZnCl_2 + Li_2S$	ZnS (wurtzite)	white	hexagonal	3.82 [c = 6.26]	3.84 [c = 6.12]	120
$ZnCl_2 + Li_2Se$	ZnSe	yellow	cubic	5.67	5.65	220
$ZnCl_2 + Li_2Te$	ZnTe	red	cubic	6.10	6.04	280
$CdCl_2 + Li_2O$	CdO (monteponite)	grey	cubic	4.69	4.67	300
$CdCl_2 + Li_2S$	CdS (wurtzite)	yellow	hexagonal	4.14 [c = 6.71]	4.11 [c = 6.68]	350
$CdCl_2 + Li_2Se$	CdSe (zinc blende)	red	hexagonal	4.30 [c = 7.01]	4.29 [c = 6.99]	320
$CdCl_2 + Li_2Te$	CdTe (zinc blende)	grey	cubic	6.49	6.47	400
$HgCl_2 + Li_2O$	HgO (montroydite)	brown	orthorhombic	5.53 [b = 6.61, c = 3.52]	5.56 [b = 6.64, c = 3.54]	200
$HgCl_2 + Li_2S$	HgS (zinc blende)	red	hexagonal	4.15 [c = 9.50]	4.15 [c = 9.43]	280
$HgCl_2 + Li_2Se$	HgSe (zinc blende)	grey	cubic	6.09	6.03	320
	+ $[Hg_3Se_2Cl_2]$	cream	cubic	-	9.04	
$HgCl_2 + Li_2Te$	HgTe (zinc blende)	grey	cubic	6.46	6.43	400
	+ $[Hg_3Te_2Cl_2]$		cubic	[9.33]	[9.28]	

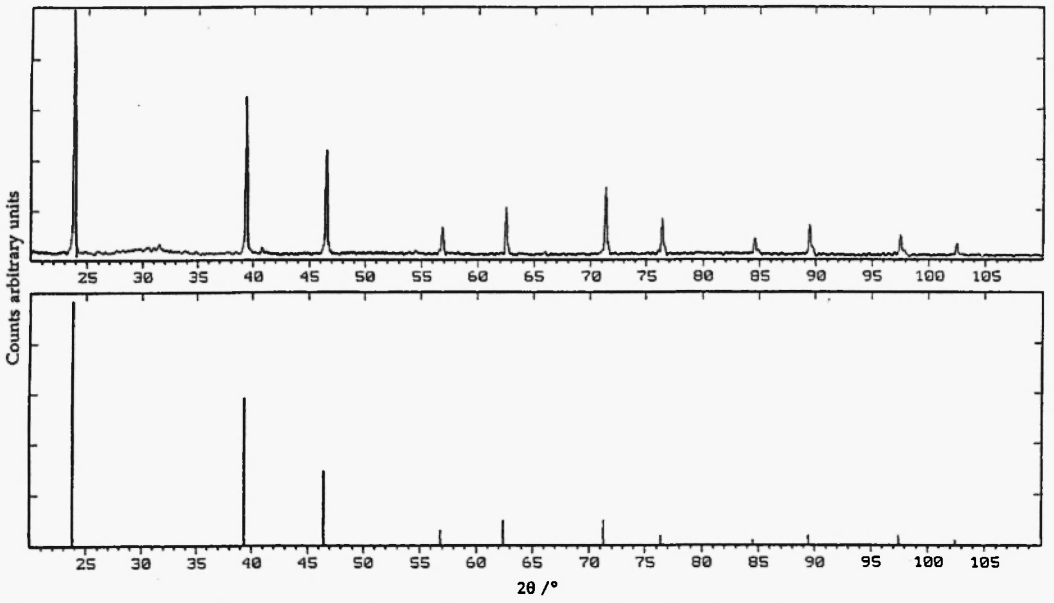
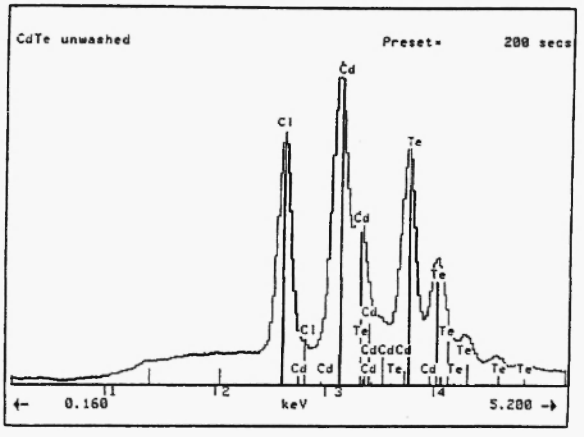


fig 1., X-ray powder diffraction pattern of material obtained from reaction of $CdCl_2$ with Li_2Te; lower trace standard for CdTe.

(a)



(b)

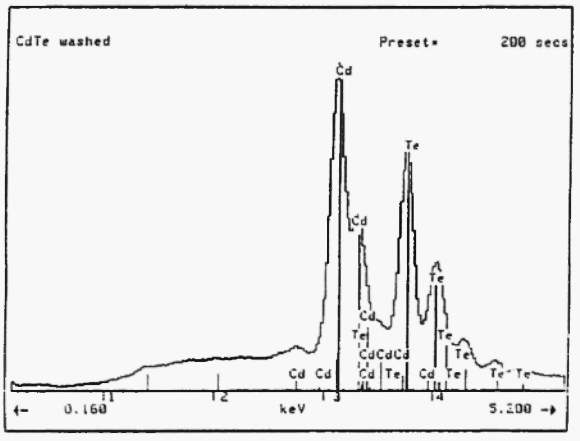


fig 2., EDXA elemental profile for CdTe before (a) and after (b) trituration.

The FTIR spectra of the triturated metal chalcogenides showed weak, broad bands in the region 800-200 cm^{-1} corresponding to metal-chalcogen stretching vibrations[8]. The SEM analysis of the pre-triturated material showed a smooth surface profile due to LiCl coatings; washing with methanol or water removed this coating and revealed a finely divided porous surface corresponding to submicron particles. The ME materials were all diamagnetic as expected.

The X-ray powder patterns of the metal chalcogenides showed that the high temperature modifications were formed. The crystallite size, as determined from the Scherrer[9] equation, varied from 150-400Å. The crystallite size, crystal form and sublimed LiCl all indicate that temperatures in excess of 1000°C are generated in the reaction.

The reaction of MCl_2 with Li_2E is exothermic, as determined by Hess law[10] calculations with $\Delta H_f \approx$-75 to -150 kJ mol^{-1}. The reaction required thermal initiation at oven temperatures of 500°C; however, once initiated the heat of reaction was sufficient to partially sublime the by-product LiCl (bpt 1300°C) and produce a relatively crystalline metal chalcogenide. The reaction between MCl_2 (M = Zn, Hg) and Li_2E could not be initiated by either vigorous grinding or by means of a hot filament, in contrast to studies of some transition metal halides and metal pnictides[4,5]. In the metal oxide cases, thermal initiation of the reaction occured at c.a. 300-350°C as determined by differential scanning calorimetry (DSC) analysis.[5] The difference in temperature between that of the tube furnace oven and the DSC initiation temperature is probably due to poor thermal contact and temperature gradients in the oven.

The product ME, as formed in Equation 1, showed that the reaction proceeded without any redox chemistry and was a simple metathesis exchange. The driving force for the reaction is the extra stability of the products resulting from the formation of two moles of lithium chloride. Exception to this reactivity was observed for the reaction of $HgCl_2$

with Li_2Se and Li_2Te which produced small amounts of $Hg_3Se_2Cl_2$ and $Hg_3Te_2Cl_2$ (ca 15%) respectively. No evidence for the formation of elemental chalcogenide or the evolution of any gases was observed for these reactions.

Reaction of $Li_2(E,E')$ (E,E'= S, Se; Se, Te) with metal dichloride (Table 2) proceeds analogously to the binary reactions described in Eqn. 1. The EDXA step analysis of the triturated products revealed an uneven distribution of the chalcogens across the surface morphology. This can also be related to a slight broadening of the powder XRD patterns for MS_xSe_y (typically $MS_{0.6}Se_{0.4)}$ and thus 'enrichment' of sulphur compared to selenium and selenium compared to tellurium in the mixed species. The vapour pressure decreases from sulphur to tellurium at elevated reaction temperatures

Table 2., X-ray powder diffraction data from the reactions of MCl_2 and $Li_2(S_{0.5}Se_{0.5})$ and $MCl_2/M'Cl_2$ with Li_2S.

Reagents	Phase detected by XRD	Colour	Lattice type	Literature a value/ Å	Observed a value/ Å	X-tallite size/ Å
$ZnCl_2$ + $Li_2(S_{0.5}Se_{0.5})$	ZnS_xSe_y	off white	hexagonal	ZnSe 4.00 [c = 6.55] ZnS 3.82 [c = 6.26]	3.90 [c = 6.50]	100
$CdCl_2$ + $Li_2(S_{0.5}Se_{0.5})$	CdS_xSe_y	dark red	hexagonal	CdSe 4.30 [c = 7.01] CdS 4.14 [c= 6.71]	4.20 [c = 6.88]	280
$HgCl_2$ + $Li_2(S_{0.5}Se_{0.5})$	HgS_xSe_y	grey	cubic [HgSe]	6.09	5.96	300
$HgCl_2$ + $Li_2(Se_{0.5}Te_{0.5})$	$Hg_3(Se_xTe_y)Cl_2$	grey	cubic	[$Hg_3Se_2Cl_2$] 9.04 [$Hg_3Te_2Cl_2$] 9.33	9.13	280
$ZnCl_2/CdCl_2/Li_2S$	$Zn_{0.78}Cd_{0.22}S$	yellow	hexagonal	3.92 [c = 6.41]	3.93 [c = 6.42]	150
$ZnCl_2/HgCl_2/Li_2S$	$Zn_{0.39}Hg_{0.61}S$	black	cubic	5.80	5.80	260
$CdCl_2/HgCl_2/Li_2S$	HgS	grey	hexagonal	4.15 [c =9.50]	4.16 [c = 9.48]	

and the rate of solid state diffusion of the chalcogens into a flux containing the metal halide will also be dependent on the reaction scale with larger quantites allowing for greater intermixing (the larger scale reactions are better insulated against heat loss).

Reaction of $ZnCl_2$ with $Li_2(S_{0.5}Se_{0.5})$ and $CdCl_2$ with $Li_2(S_{0.5}Se_{0.5})$ results in a fully intermixed products (hexagonal lattice) with lattice parameters intermediate between those for ZnS/ZnSe and CdS/CdSe (fig., 3a) respectively. The powder XRD pattern for the reaction of $HgCl_2$ with $Li_2(S_{0.5}Se_{0.5})$ showed the product adopted the HgSe lattice with a reduced unit cell, indicating incorporation of sulphur into the lattice. Interestingly the product from $HgCl_2$ and $Li_2(Se_{0.5}Te_{0.5})$ exhibits a cubic lattice and corresponds to the phase $Hg_3(Se,Te)_2Cl_2$.

Combinations of Group IIb metal halides with Li_2S resulted in intermixed products, with the lower melting point halide ($ZnCl_2$< $HgCl_2$< $CdCl_2$) being enriched in the final product, e.g., $Zn_{0.78}Cd_{0.22}S$ (fig., 3b). Thus the temperature attained during the reaction has a determining effect on the stoichiometry of the product. Significantly the mixture of $CdCl_2/HgCl_2$ with Li_2S yields only HgS after trituration, as confirmed by EDXA and powder XRD.

It seems likely that a series of $ME_xE'_y$ species can be formed by this route.

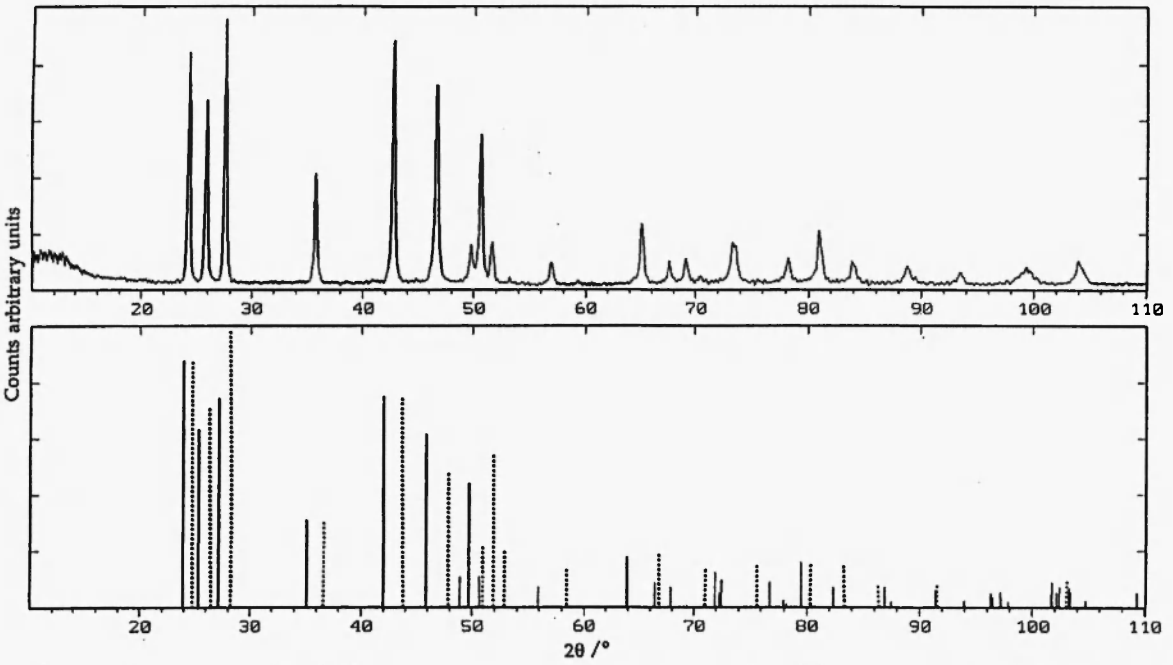


fig 3a., X-ray powder diffraction pattern of material obtained from reaction of $CdCl_2$ with $Li_2(S_{0.5}Se_{0.5})$; lower trace standards for CdS (····) and CdSe (--).

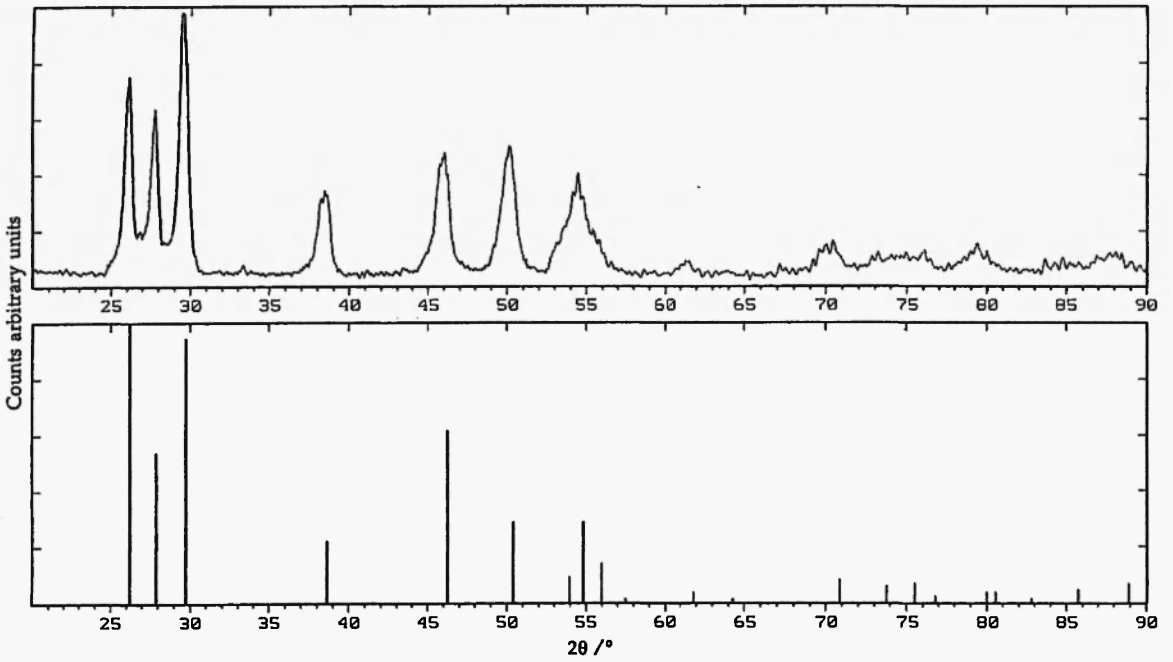


fig 3b., X-ray powder diffraction pattern of material obtained from reaction of $ZnCl_2$ and $CdCl_2$ with Li_2S; lower trace standard for $Zn_{0.78}Cd_{0.22}S$.

Conclusion

The metathesis reactions to form Group IIb chalcogenides are reasonably rapid and at lower initiation temperature (500°C) than many conventional preparations. The purity of the product ME is also high as the by-product lithium halide can be easily removed by methanol or aqueous trituration.

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