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The use of hexamethyldisilathiane for the synthesis of transition metal sulfides

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Abstract

The reaction of $TiCl_4$ with hexamethyldisilathiane in diethyl ether at room temperature affords black precipitates which upon annealing under H_2S at 800 °C results in the formation of crystalline TiS_2. Similarly, reaction of MCl_5 (M = Nb, Ta, Mo) with $S(SiMe_3)_2$ in diethyl ether at room temperature or toluene at reflux results in the initial formation of black precipitates $M_xS_yCl_zSi_pC_qH_r$. Annealing of these precipitates under static vacuum at 550 or at 800 °C under H_2S affords MS_2. The black precipitates and metal sulfides produced under all annealing conditions were analysed by powder X-ray diffraction, scanning electron microscopy, energy dispersive X-ray analysis and Raman spectroscopy.

Keywords: Metal sulfide; Molecular precursor; Diethyl ether; Annealing

1. Introduction

Transition metal disulfides (MS_2) are of interest for many technological applications. They are suitable for use as high-temperature lubricants, hydrogenation catalysts, and batteries due to weak van der Waals interactions between adjacent layers in the MS_2 lattice [1–4]. In addition, these materials display a wide range of electronic properties, for example, they are semiconductors (TiS_2, MOS_2) or superconductors (TaS_2) [5]. There are a number of procedures available for preparing MS_2 thin films. TiS_2 thin films have been prepared via dual [6] and single source chemical vapour deposition (CVD) [7], radio frequency sputtering [8] and activated reactive evaporation [9]. NbS_2 films have, to our knowledge, only been prepared using physical deposition processes [10]. In contrast, a number of techniques for the preparation of MoS_2 thin films have been reported including dual [11] and single source CVD [7], chemical vapour transport [12] and pulsed laser evaporation [13].

Bulk metal disulfides (MS_2) have been prepared by direct reaction of the elements [14], solid-state metathesis reactions [15] and chemical vapour transport using iodine as a transport agent (TiS_3) [16]. Amorphous MS_2, has also been prepared via the solution phase metathetical reaction of MCl_x ($x = 4$, M = Ti, Mo; $x = 5$, M = Nb) with Li_2S [17]. More recently, solution based approaches to MoS_2 have been reported, for example the hydrothermal reaction between $Na_2S_2O_3$ and Na_2MoO_4 resulted in the formation of amorphous MoS_2 [18,19]. After annealing at 350 °C crystalline MoS_2 was produced [18]. Recently, we reported the preparation of crystalline TiS_2 via a novel thio 'sol–gel' process using titanium(IV) thiolate precursors as the metal source [20].

A potential low temperature route to MS_2 involves the reaction of hexamethyldisilathiane with metal chlorides. A report by Jenkins and Willey showed that the equimolar reaction between $TiCl_4$ and $S(SiMe_3)_2$ resulted in the formation of $TiSCl_2$ [21]. However, reports by Schleich, Martin and co-workers showed that when metal chlorides (e.g. $TiCl_4$, $MoCl_5$, $MoCl_4$) were reacted

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with excess $S(SiMe_3)_2$ amorphous precipitates were isolated [22–25]. Annealing of the precipitates afforded the metal sulfide which in some examples was contaminated with a large percentage of oxide or resulted in the formation of non-stoichiometric sulfides (by powder XRD). The composition of the initial precipitates was not fully analysed. Nevertheless, these reports indicate that this procedure could be an excellent route to metal sulfides and warrants further investigation.

In this paper, we report a detailed investigation into the reaction of MCl_x ($x = 4$, M = Ti; $x = 5$, M = Nb, Ta, Mo) with $S(SiMe_3)_2$. We report on the effect of different annealing conditions; static vacuum, dynamic vacuum and processing under an H_2S atmosphere. In particular the static vacuum methods offers a convenient comparatively low temperature approach to the formation of metal sulfides without the use of H_2S.

2. Experimental

All manipulations were performed under a dry, oxygen-free dinitrogen atmosphere using standard Schlenk techniques or in a Mbraun Unilab glove box. Owing to the toxic nature of H_2S all of the experiments were carried out in a well-ventilated fume cupboard. All solvents were distilled from appropriate drying agents prior to use (sodium–toluene and diethyl ether). All reagents were procured commercially from Aldrich and used without further purification. Microanalytical data were obtained at University College London.

2.1. Physical measurements

Raman spectra were acquired on a Renishaw Raman System 1000 using a helium–neon laser of wavelength 632.8 nm. The Raman system was calibrated against the emission lines of neon. Powder XRD measurements were recorded on a Siemens D5000 transmission diffractometer using germanium monochromated Cu Kα_1 radiation ($\lambda = 1.5406$ Å) as powders. Unit cell parameters were determined by the Unit Cell indexing programme. Scanning electron microscopy (SEM) profiles and energy dispersive X-ray analysis (EDX) were performed on a Hitachi S570 instrument using the KEVEX system. Thermolysis studies were performed in a Carbolite tube furnace.

2.2. Reaction of $TiCl_4$ and $S(SiMe_3)_2$ in diethyl ether

$TiCl_4$ (0.52 cm^3, 4.74 mmol) was added dropwise to a stirred mixture of $S(SiMe_3)_2$ (2 cm^3, 9.48 mmol) and diethyl ether (40 cm^3). The solution turned red immediately on addition of $TiCl_4$. After 1 min the reaction mixture turned dark brown and a precipitate started to form. The mixture was stirred for 15 h at room temperature. The resulting black precipitate was allowed to settle and the colourless liquid was syringed off, washed with diethyl ether (10 ml) and the remaining solid dried in vacuo (0.81 g). The sample was annealed on a ceramic boat under a constant stream of H_2S gas at 800 °C for 6 h. The initial precipitate and annealed solid was analysed by powder XRD, SEM/EDXA and Raman spectroscopy, Table 1.

2.3. Reaction of MCl_5 (M = Mo, Nb, Ta) and $S(SiMe_3)_2$ in diethyl ether

$S(SiMe_3)_2$ (2 cm^3, 9.48 mmol) was added dropwise to a stirred red solution of $MoCl_5$ (1.04 g, 3.80 mmol) in diethyl ether (35 cm^3). A black/brown precipitate formed immediately and the mixture was stirred for 15 h at room temperature. The resulting black precipitate was allowed to settle and the colourless liquid was syringed off and the remaining solid was washed with diethyl ether (10 cm^3) and dried in vacuo (0.78 g). The black precipitate was annealed under H_2S at 800 °C as described above. The precipitates and annealed powders were characterised by powder XRD, EDXA/SEM and Raman, Table 1.

2.4. Reaction of MCl_5 (M = Nb, Ta, Mo) and $S(SiMe_3)_2$ in refluxing toluene

In a typical experiment, $S(SiMe_3)_2$ (1.32 cm^3, 6.25 mmol) was added dropwise to a stirred slurry of MCl_5 (2.5 mmol) in toluene (20 cm^3). The formation of a black precipitate (black/green for $NbCl_5$) was observed immediately on addition of $S(SiMe_3)_2$. The reaction mixture was stirred for 4 h at reflux and then allowed to cool to room temperature. The resulting black precipitate was allowed to settle and the colourless liquid was syringed off and the remaining solid was dried in vacuo (0.325 g (Nb); 0,361 g (Mo); 0.625 g (Ta)). The black precipitate was annealed in one of two ways; (i) under dynamic vacuum at 550 °C for 4 h; (ii) at 550 °C for 4 h in a sealed ampoule. Some sublimation of impurities to the cooler parts of the ampoule was noted in the sealed ampoule experiments. The precipitates and annealed products were characterised by powder XRD, EDX/SEM and CHN microanalysis, Table 1. Selected samples were examined by Raman Spectroscopy.

2.5. Reaction of $NbCl_5$/$TaCl_5$ and $S(SiMe_3)_2$

$S(SiMe_3)_2$ (1.32 cm^3, 6.25 mmol) was added dropwise to a stirred slurry of a mixture of $NbCl_5$ (0.34 g, 1.25 mmol) and $TaCl_5$ (0.45 g, 1.25 mmol) in toluene (20 cm^3). Formation of a black precipitate was observed immediately on addition of $S(SiMe_3)_2$. The reaction mixture was stirred for 12 h at room temperature. The resulting blue/black precipitate was allowed to settle and

Table 1
Analytical data for the reaction of hexamethylsisilathiane (HMDST) with MCl_x (M = Ti, $x = 4$; M = Nb, Me, Ta, $x = 5$) under various annealing conditions

Reaction conditions	Analysis of initial precipitate[a]	Annealing conditions	Composition of product after annealing[a]	XRD of annealed product[b] (cell edges in nm)
$TiCl_4$+HMDST (RT, diethyl ether)	$Ti_{1.0}S_{1.2}Cl_{0.5}C_{0.4}H_{1.0}$	800 °C, H_2S	TiS_2	TiS_2[c]; $a = 0.340(1)$, $c = 0.571(1)$
$TiCl_4$+HMDST (reflux, toluene)	$Ti_{1.0}S_{1.4}Cl_{0.2}C_{0.7}H_{1.3}$	550 °C, dynamic vacuum	$TiS_{1.1}O_{0.9}$	TiS_2[c]; $a = 0.340(1)$, $c = 0.571(1)$ (TiO_2–anatase)
$TiCl_4$+HMDST (reflux, toluene)	$Ti_{1.0}S_{1.4}Cl_{0.2}Si_{0.2}C_{0.7}H_{1.3}$	550 °C, static vacuum	TiS_2	X-ray amorphous
$NbCl_5$+HMDST (RT, diethyl ether)	$Nb_{1.0}S_{1.2}Cl_{0.4}C_{0.5}H_{0.7}$	800 °C, H_2S	NbS_2	NbS_2[d]; $a = 0.334(1)$, $c = 1.787(1)$
$NbCl_5$+HMDST (reflux, toluene)	$Nb_{1.0}S_{2.4}Si_{0.2}Cl_{0.1}C_{0.8}H_{1.4}$	550 °C, dynamic vacuum	$NbS_{1.2}O_{0.8}$	X-ray amorphous
$NbCl_5$+HMDST (reflux, toluene)	$Nb_{1.0}S_{2.4}C_{0.8}H_{1.4}$	550 °C static vacuum	NbS_2	NbS_2[d]; $a = 0.334(1)$, $c = 1.786(1)$
$MoCl_5$+HMDST (RT, diethyl ether)	$Mo_{1.0}S_{2.9}Cl_{1.0}C_{1.4}H_{2.8}$	800 °C, H_2S	MoS_2	X-ray amorphous
$MoCl_5$+HMDST (reflux, toluene)	$Mo_{1.0}S_{1.9}Si_{0.1}C_{1.5}H_{2.4}$	550 °C, dynamic vacuum	$MoS_{1.1}O_{0.9}$	X-ray amorphous
$MoCl_5$+HMDST (reflux, toluene)	$Mo_{1.0}S_{1.9}Si_{0.1}C_{1.5}H_{2.4}$	550 °C static vacuum	MoS2	X-ray amorphous
$TaCl_5$+HDMST (RT, diethylether)	$Ta_{1.0}S_{1.01}Si_{3.0}C_{0.8}H_{1.3}$	800 °C, H_2S	$TaS_2Si_{0.5}$	TaS_2[e]; $a = 0.336(1)$, $c = 0.578(1)$
$TaCl_5$+HDMST (reflux, toluene)	$Ta_{1.0}S_{1.01}Si_{0.3}C_{0.6}H_{1.3}$	550 °C, dynamic vacuum	$TaS_{0.2}Si_{0.4}O_{0.4}$	X-ray amorphous
$TaCl_5$+HDMST (reflux, toluene)	$Ta_{1.0}S_{1.0}Si_{0.3}C_{0.6}H_{1.3}$	550 °C static vacuum	$TaS_{0.1}Si_{0.25}O_{1.6}$	X-ray amorphous

Note that in the final products elements present at trace levels (1-2 atom%) are not shown.

[a] Ti, Nb, Mo, Ta, S, Cl, Si and O determined by EDX and C and H by microanalysis.

[b] The absence of cell data in some entries implies that no useful XRD data was obtained in these cases.

[c] Literature [PDF 15-0853] TiS_2 $a = 0.34049$, $c = 0.56912$ nm [Note, a cubic TiS_2 is known $a = 9.800$ Å; PDF 36-1406].

[d] Literature [PDF 38-1367] NbS_2 $a = 0.33352(2)$, $c = 1.7867(2)$ nm [Note, a separate NbS_2 entry $a = 0.3320(1)$, $c = 1.1945(4)$ nm; PDF 41-980].

[e] Literature TaS_2 [PDF 2-137] $a = 0.3385$, $c = 0.590$ nm

the colourless liquid was syringed off and the remaining solid was washed with toluene (10 ml) and dried in vacuo (0.49 g). *Analytical data for the precipitate:* Found C, 7.44; H, 0.77. The precipitate was also characterised by powder XRD and EDX/SEM. The blue/black precipitate was annealed under H_2S at 800 °C as described above.

3. Results and discussion

3.1. Synthesis and characterisation

The reaction of a range of metal halides with 2 equiv. of hexamethyldilsilathiane (HDMST) in diethyl ether at room temperature or toluene at reflux produced black precipitates of various compositions (Table 1). The precipitates were annealed in one of three ways, by heating in H_2S at 800 °C, by heating to 550 °C under static vacuum and by heating to 550 °C under dynamic vacuum. It was found that the annealing conditions had a great effect on the products obtained.

In all of the reactions between $S(SiMe_3)_2$ and MCl_x (M = Ti, $x = 4$; M = Nb, Mo, Ta; $x = 5$) a black precipitate was formed on reagent combination. Two different solvent systems were explored for the reaction; stirring in diethyl ether at room temperature and refluxing in toluene. In either case the composition of the precipitates as determined by energy dispersive analysis by X-rays EDX over several areas and by bulk combustion analysis (CHN) was fairly uniform consisting primarily of metal and sulfur but with some additional chlorine, carbon, hydrogen and silicon contaminants. For example for M = Ti the precipitate had an empirical formula of $Ti_{1.0}S_{1.2}Cl_{0.5}Si_{0.1}C_{0.4}H_{1.0}$ if formed in diethyl ether and $Ti_{1.0}S_{1.4}Cl_{0.2}Si_{0.2}C_{0.7}H_{1.3}$ from toluene. These compositions are consistent with the partial elimination of $ClSiMe_3$ from the reaction of $TiCl_4$ and $S(SiMe_3)_2$. Presumably this reaction does not go to completion before the product precipitates out of solution and is consistent with some Ti–Cl bonds remaining intact together with some Ti–$SSiMe_3$ linkages, Scheme 1. The precipitates formed had similar composition whether derived at room temperature in diethyl ether or from refluxing toluene.

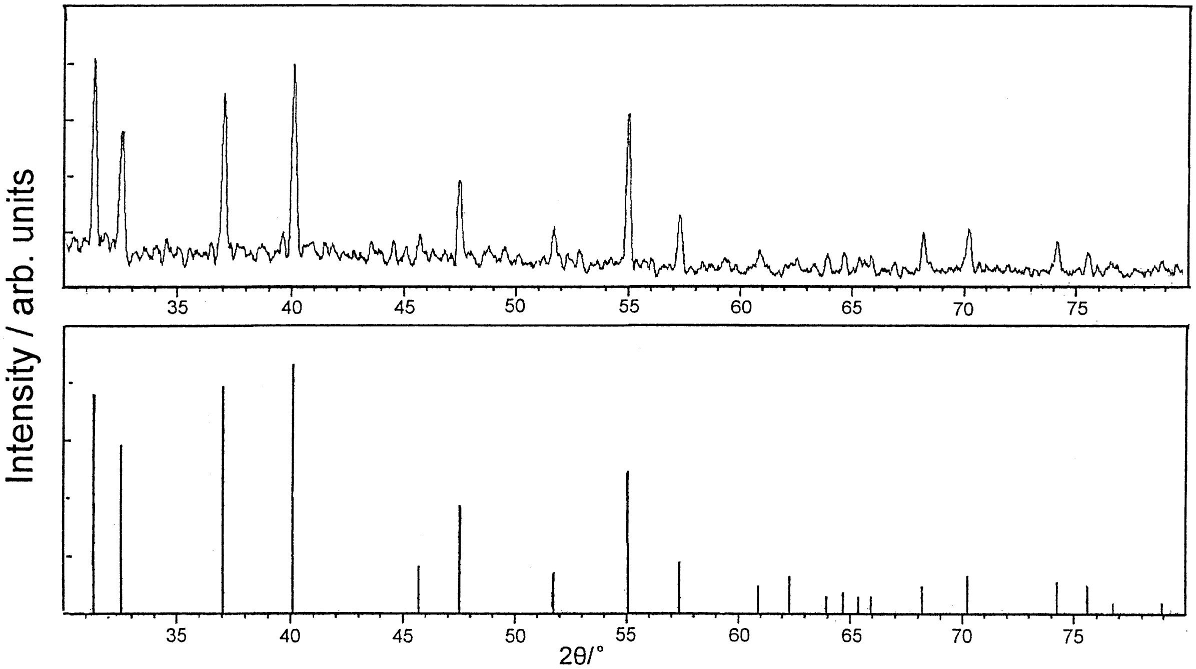
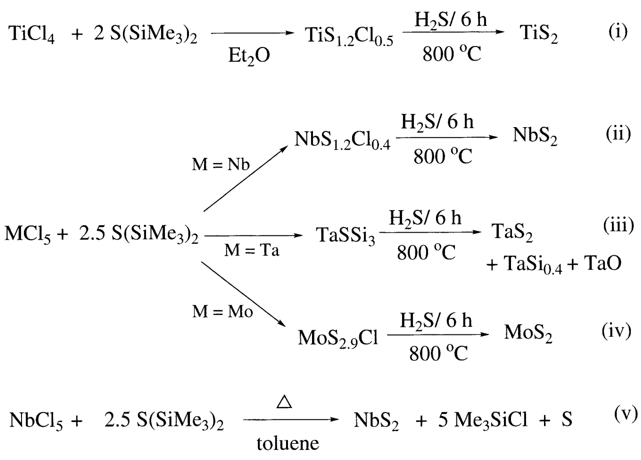


Fig. 1. Top trace: X-ray powder diffraction pattern of NbS_2 prepared from $NbCl_5$ and HMDST after annealing at 800 °C under H_2S for 6 h. Bottom trace: literature stick pattern for NbS_2

All of the black precipitates decomposed in air with the evolution of H_2S. They were also amorphous to X-rays with the exception of the reaction for $M = Ti$ in refluxing toluene where nanocrystalline TiS_2 was identified with a crystallite size from line broadening studies of less than approximately 100 nm [20]. SEM analysis of all precipitates showed an agglomerated structure with no evidence for crystallites.

3.2. Annealing the samples

Annealing of all of the precipitates at 800 °C under a flow of H_2S formed crystalline powders that gave X-ray diffraction patterns for TiS_2, NbS_2, TaS_2 and MoS_2 (Fig. 1). Indexing the powder patterns gave cell constants identical to those in the literature, Fig. 1. SEM showed that the H_2S treated powders consisted of platelets (size ≈2 μm) that were agglomerated into larger agglomerates (size ≈10 μm), this is illustrated for $M = Ti$ in Fig. 2. Raman analysis showed the patterns



$$TiCl_4 + 2\,S(SiMe_3)_2 \xrightarrow[Et_2O]{} TiS_{1.2}Cl_{0.5} \xrightarrow[800\ ^{\circ}C]{H_2S/\,6\ h} TiS_2 \quad (i)$$

$$MCl_5 + 2.5\,S(SiMe_3)_2 \xrightarrow{M = Nb} NbS_{1.2}Cl_{0.4} \xrightarrow[800\ ^{\circ}C]{H_2S/\,6\ h} NbS_2 \quad (ii)$$

$$MCl_5 + 2.5\,S(SiMe_3)_2 \xrightarrow[M = Ta]{} TaSSi_3 \xrightarrow[800\ ^{\circ}C]{H_2S/\,6\ h} TaS_2 + TaSi_{0.4} + TaO \quad (iii)$$

$$MCl_5 + 2.5\,S(SiMe_3)_2 \xrightarrow{M = Mo} MoS_{2.9}Cl \xrightarrow[800\ ^{\circ}C]{H_2S/\,6\ h} MoS_2 \quad (iv)$$

$$NbCl_5 + 2.5\,S(SiMe_3)_2 \xrightarrow[toluene]{\triangle} NbS_2 + 5\,Me_3SiCl + S \quad (v)$$

Scheme 1.

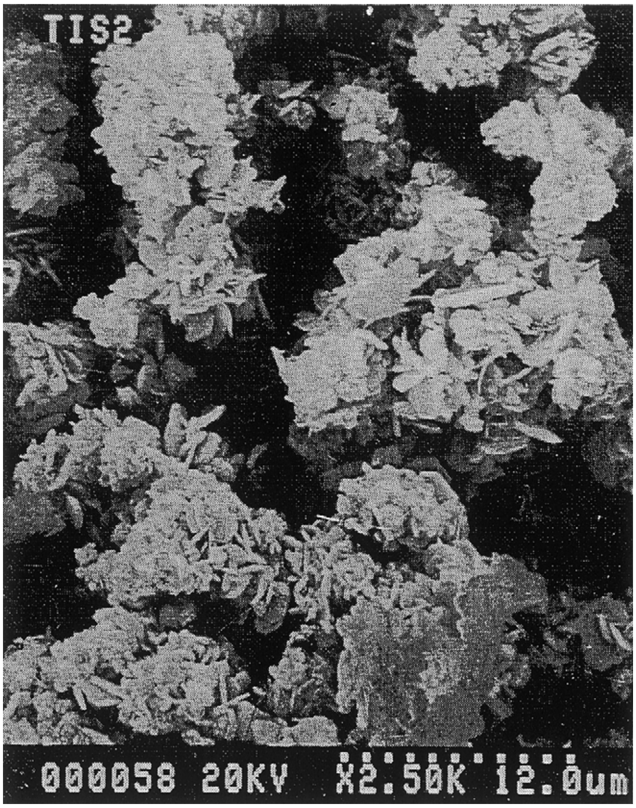


Fig. 2. SEM of the sample prepared from the reaction of HMDST and $TiCl_4$ in diethyl ether after annealing at 800 °C under a flow of H_2S.

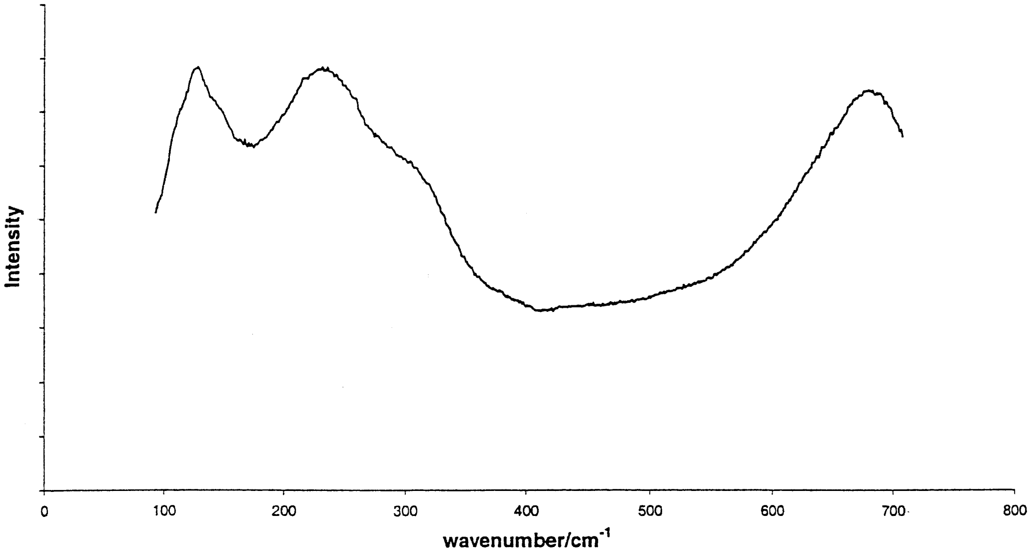


Fig. 3. Raman spectrum for NbS_2 prepared from $NbCl_5$ and HMDST after annealing at 800 °C under H_2S for 6 h.

expected for MS_2 (M = Ti, Nb, Ta, Nb) with notably no evidence for the presence of a second phase such as MO_2. The Raman spectra of NbS_2 and MoS_2 formed in this study are shown in Figs. 3 and 4.

The treatment with H_2S at high temperature is quite drastic. It ensured that all of the impurities noted in the initial product were removed in the processing and that a single-phase crystalline metal sulfide was isolated. However, it could be claimed that the H_2S is the source of the sulfur in the final product and that the tailored Me_3SiCl elimination chemistry is largely unimportant; a number of metal oxides (and even a couple of the metal halides) treated under equivalent conditions would form the same sulfide phases as those observed here. To counter this argument two further sets of annealing experiments were investigated at lower temperature, and

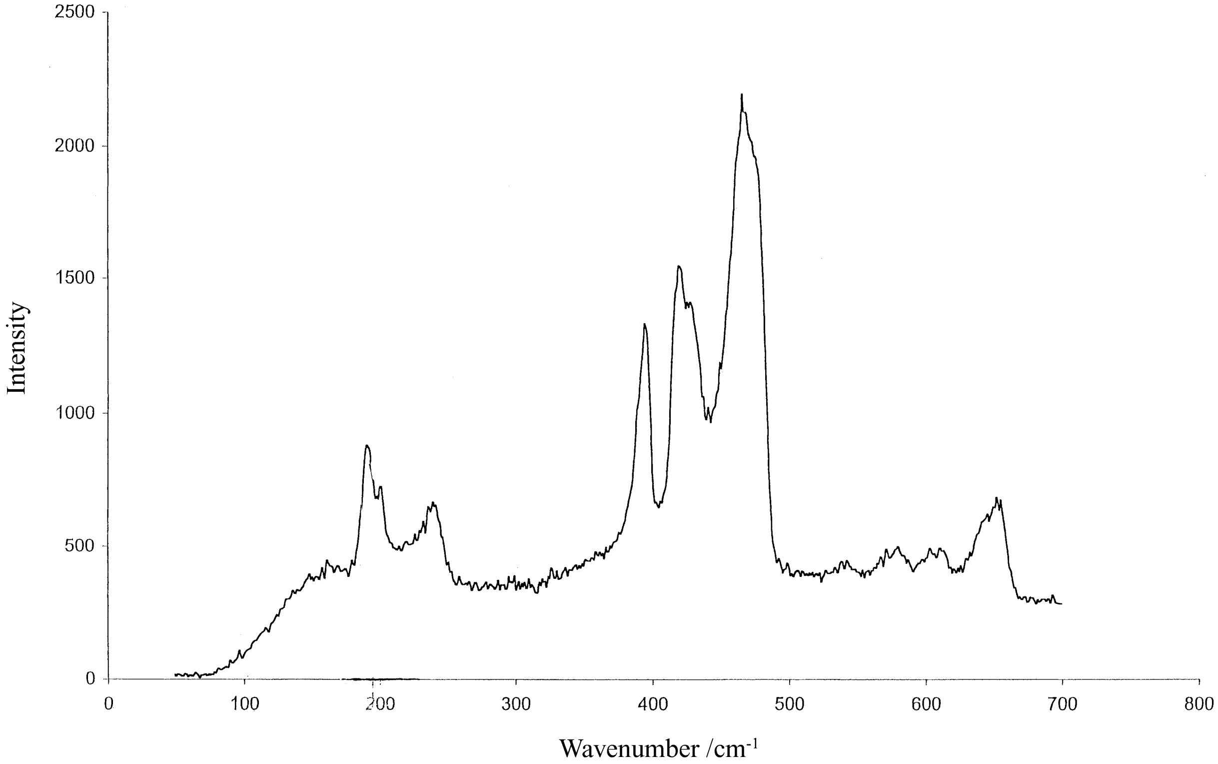


Fig. 4. Raman spectrum for MoS_2 prepared from $MoCl_5$ and HMDST after annealing at 800 °C under H_2S for 6 h.

importantly, without the use of a secondary sulfur source such as H_2S.

Annealing of the precipitates formed from reaction of MCl_x ($M = Ti$, $x = 4$; $M = Nb$, Ta, Mo, $x = 5$) and $S(SiMe_3)_2$ in toluene at 550 °C under dynamic vacuum invariably formed a mixed phase product, Table 1. Notably the sulfur content of the products decreased from that observed in the initial precipitate and some oxidation was noted. The attendant silicon, chlorine, chlorine and hydrogen in the initial precipitate disappeared to detection limits (approximately less than 1–2 atom%) in the annealing stage presumably as they combined to form volatile components that were pumped out of the system. The empirical formulas found in the annealed products were $TiS_{1.1}O_{0.9}$; $NbS_{1.2}O_{0.8}$; $MoS_{1.1}O_{0.9}$ and $TaS_{0.2}Si_{0.4}O_{0.4}$. Analysis of the products by Raman and XRD showed direct evidence for a bi-phasic mixture of MO_2 and MS_2 phases; for example for $M = Ti$ anatase TiO_2 was observed along with TiS_2 by both techniques. Hence annealing under dynamic vacuum showed a loss of sulfur from the products and a degree product oxidation. The fact that sulfur remained bound to the metals in the MS_2 phase showed that the precipitates formed from reaction of MCl_x and $S(SiMe_3)_2$ can be a useful precursor to metal sulfides. The oxidation of the products observed under dynamic vacuum is probably due to a slight ingress of air during the procedure.

Annealing of the precipitates in a static vacuum at 550 °C for 4 h was more successful. In each case partial sublimation of material onto the cooler parts of the ampoule was noted. The EDX analysis of the residue showed that a homogeneous single phase of composition TiS_2, NbS_2 or MoS_2 could be readily obtained. X-ray powder diffraction showed that crystalline materials were formed that could be indexed to the MS_2 phases. Typical crystallite sizes were in the range 50–100 nm as determined by line broadening studies [20]. The phases seen by XRD correlated well with the Raman analysis. The static method of annealing was more successful than the dynamic one and notably showed no evidence for oxide formation. In this method all of the elements in the final metal sulfide powder come from the initial precipitate. The loss of the impurity elements from the initial precipitate occurs because they sublimed out from the precipitate to the cooler parts of the ampoule.

The reactions of $TaCl_5$ and $S(SiMe_3)_2$ in both ether and toluene were somewhat anomalous. The initial precipitates contained significantly more silicon than the comparable reactions involving titanium, niobium and molybdenum. Further annealing under dynamic or static vacuum produced a product with very little sulfur incorporation and significant silicon and oxygen. It was only annealing under very forcing conditions (ie H_2S, 800 °C) that enabled isolation of TaS_2. It would thus appear that the elimination chemistry at the tantalum centre does not follow the same pattern as the other elements in this study. Considering the close relationship in chemical properties between niobium and tantalum this is somewhat puzzling.

As noted in Section 1 some previous work has been reported on the reaction of titanium and molybdenum halides and $S(SiMe_3)_2$ [22,23]. In these studies the initial precipitates were amorphous as we have reported here, however the elemental composition was not reported. We have shown here that the reaction of $S(SiMe_3)_2$ and metal halides forms products containing predominantly metal and sulfur but that there are significant amounts of the other elements found in the initial precipitates. The previous work also found that annealing at 650 °C was required and that the metal sufide products were often contaminated with metal oxides [24]. We have shown here that the annealing temperature can be reduced to 550 °C and provided that a static vacuum system is employed single phase metal sulfides can form under these conditions. Further we have extended the range of reactions to other metal halides. Notably, in all reactions save that of $M = Ta$ the MS_2 product is favoured in the reactions. This is despite the initial reagent mixture containing 2.5 equiv. of sulfur for each metal atom ($M = Mo$, Nb) and that a wide range of stable metal sulfide stoichiometries are available for all the elements studied, for example for $M = Nb$; $Nb_{1\text{-}x}S$, NbS, Nb_3S_4, $Nb_{1+x}S_2$, NbS_2 and NbS_3.

To see if this route could be used to form a novel mixed metal sulfide one test system was studied.

3.3. Mixed metal sulfides

Reaction between $NbCl_5$, $TaCl_5$ and 5 equiv. of $S(SiMe_3)_2$ was carried out in toluene. A black precipitate formed immediately on addition of $S(SiMe_3)_2$. After work up, powder XRD of the precipitate [26] revealed that it was X-ray amorphous. Analysis showed that the precipitate was contaminated with small amounts of carbon and hydrogen. The precipitate was annealed at 800 °C under H_2S for 6 h. EDX analysis on the annealed powder showed good agreement with a 0.5:0.5:2 ratio of Nb:Ta:S over a number of areas. These EDAX data (Table 1) suggested that the product $Nb_{0.5}Ta_{0.5}S_2$ is a complete solid solution of NbS_2 and TaS_2. The powder XRD showed that the material adopted the hexagonal TaS_2 lattice with some significant shifts in line position, consistent with the formation of a solid solution [26]. Fig. 5 shows the powder XRD pattern of $Nb_{0.5}Ta_{0.5}S_2$ prepared via this route and shows a typical crystallite size from the X-ray broadening of 890 Å. This material is to our knowledge a new phase. No evidence was seen for a bi-phasic mixture of components.

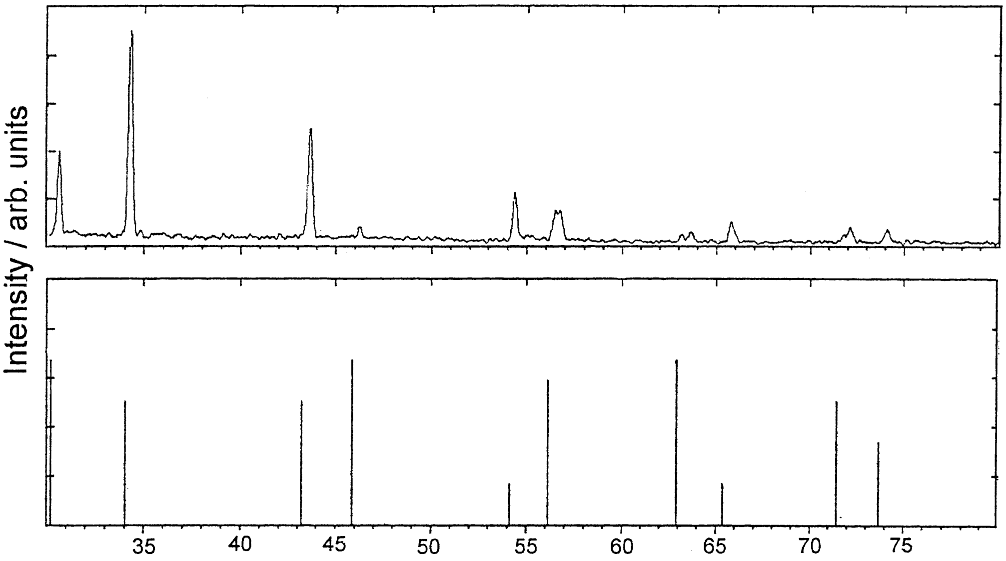


Fig. 5. Top trace: X-ray powder diffraction pattern of $Nb_{0.5}Ta_{0.5}S_2$ prepared from $NbCl_5$, $TaCl_5$ and HMDST after annealing at 800 °C under H_2S for 6 h. Bottom trace: literature stick pattern for TaS_2.

4. Conclusions

Reactions of metal halides with $S(SiMe_3)_2$ formed black amorphous precipitates that when annealed under H_2S or static vacuum result in the formation of single phase crystalline TiS_2, NbS_2 and MoS_2. Elemental analysis of the initial precipitates indicates that they are somewhat contaminated with $SiMe_3$ and Cl groups. This is probably as the reaction is extremely fast and precipitation effectively removes partly reacted material. Despite extensive reaction times or temperatures the initial precipitate remains unchanged by further processing. However the annealing process can remove these contaminants at temperatures as low as 550 °C provided it is done in a static vacuum. Products prepared under dynamic vacuum were shown to be bi-phasic mixtures of MO_2 and MS_2. Surprisingly the analogous reaction of $TaCl_5$ and $S(SiMe_3)_2$ did not form TaS_2 unless very forcing conditions were applied (800 °C, H_2S) as the products annealed under static or dynamic vacuum at 550 °C contained significant amounts of silicon. This indicates that the decomposition pathway adopted for Nb and Ta species in these reactions are subtly different. Despite this a new mixed metal sulfide $Nb_{0.5}Ta_{0.5}S_2$ was readily prepared by this method. It would seem that this method has potential for the synthesis of a wide range of mixed metal sulfides. Further studies are planned.

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