Mat. Res. Bull., Vol. 23, pp. 857-868, 1988. Printed in the USA.
0025-5408/88 $3.00 + .00

NOVEL LOW TEMPERATURE SYNTHESIS OF TITANIUM SULFIDE

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(Received March 17, 1988; Communicated by A. Wold)

ABSTRACT

Amorphous titanium sulfides were synthesized by the direct reaction between dry organic sulfurizing agents and $TiCl_4$. A detailed discussion is given about the reactivity of $TiCl_4$ with each sulfurizing agent. All of the usual crystalline titanium sulfides phases (Ti_3S_4, TiS_2, TiS_3) were also synthesized by simply heating the obtained amorphous powder or by heating this powder in the presence of sulfur. These reactions occurred very rapidly and allowed for the simple synthesis of all the crystalline phases.

MATERIALS INDEX: titanium, sulfides, tert-butylsulfide,
tert-butylmercaptan, hexametyldisilthiane

INTRODUCTION

The direct high temperature synthesis of titanium sulfide ($TiS_{1.3}$--->TiS_3) is based on the reaction of titanium metal and sulfur in the necessary quantities at controlled temperature (1,2,3,4). However, this reaction is slow unless elevated temperatures are used. At these elevated temperatures the S/Ti ratio is limited by the pressure/temperature phase diagram.

It has been known for many years that TiS_2 and non stoichiometric TiS_2 could be produced by the reaction between $TiCl_4$ and H_2S at temperatures greater than 400°C (i.e., gas phase reactions) (1). At low temperature (room temperature), Chianelli and Dines (5) observed that $TiCl_4$ and H_2S does not interact. There is technological interest in an efficient low cost preparation technique for TiS_2 primarily as an active cathode material for lithium batteries (6,7). Chianelli and Dines (5) showed that amorphous TiS_2 could be prepared at low temperatures by reacting $TiCl_4$ with ionic sulfides (Li_2S, Na_2S, etc.) when the $TiCl_4$ was dissolved in a polar solvent:

$$TiCl_4 + 2Li_2S \text{--->} TiS_2 + 4LiCl$$

The amorphous TiS_2 prepared in this way is coprecipitated with ionic halides which have to be removed to obtain a pure product. In addition this requires the use of meticulously dry solvent or TiO_2 and TiOCl will be prepared.

In this work we report on the reactivity of $TiCl_4$ with different organic sulfurizing agents and the formation of amorphous titanium sulfides. Schleich and Martin (8) synthesized amorphous molybdenum sulfides at room temperture by reacting halides with hexamethyldisilthiane (HMDST):

$$MoX_n + n/2(CH_3)_3SiSSi(CH_3)_3 \text{---->} MoS_{n/2} + n(CH_3)_3SiX.$$

It was this work which initiated our interest in the use of organic sulfurizing agents to prepare inorganic sulfides. In order to better understand the reactions leading to the formation of titanium sulfides, we have used several different organic sulfurizing agents. These reagents present different sulfur bonding properties. In this article we will report on the reactions of $TiCl_4$ with:

1. H_2S where the sulfur is bonded to two protons,
2. Tert-butyl mercaptan [$(CH_3)_3CSH$], where one of the protons has been replaced by a tert-butyl group,
3. Ditert-butyl sulfide [$(CH_3)_3CSC(CH_3)_3$], where both protons have been replaced by the tert-butyl groups,
4. Ditert-butyl disulfide [$(CH_3)_3CS\text{-}SC(CH_3)_3$], where a disulfide bridge is introduced between the tert-butyl groups.
5. Hexamethyldisilthiane (HMDST) $(CH_3)_3SiSSi(CH_3)_3$ where trimethyl silyl groups have replaced the protons.

Except for H_2S, all of these reagents react with $TiCl_4$ at room temperature and lead to the formation of amorphous titanium sulfides. In addition, we also report on using these amorphous materials as precursors for the rapid formation of crystalline titanium sulfides.

Experimental

A - Synthesis of Amorphous Titanium Sulfides

Amorphous titanium sulfides were synthesized by the direct reaction between dry organic sulfurizing agents and $TiCl_4$. The organic sulfurizing agents were obtained from either Fluka Chemical Corporation or Aldrich Chemicals. All the reagents were fractionally distilled under dry argon after refluxing with calcium hydride to remove water. For each reagent, the material used for the reaction was collected over a two degree range of its boiling point as shown in table I.

Organic Sulfurizing Agent	Temperature of Collection of Material for the reaction (°C)
$(CH_3)_3$ SiSSi $(CH_3)_3$	160-162
$(CH_3)_3$ CSSC $(CH_3)_3$	200-202
$(CH_3)_3$ CSC $(CH_3)_3$	148-150
$(CH_3)_3$ CSH	62-65

Table I: Boiling Point of Organic Sulfurizing Agents

The collected reagents were transferred into the reactor under dry nitrogen. Prior to this transfer the glassware was dried by heating under dry nitrogen for one hour. The titanium tetrachloride was used as obtained from Aldrich Chemicals. Because of the extreme reactivity of $TiCl_4$ with water, care had to be taken in introducing it to the organic sulfurizing reagent. This was accomplished by using a stainless steel transfer tube under dry argon. All the reactions proceeded spontaneously and exothermically. A brownish - blackish precipitate was formed in all cases and this was separated BY filtration (fritted glass), followed by washing with dichloromethane. The filtered product is heated under vacuum or inert gas to remove adsorbed residue.

B - Synthesis of Crystalline Titanium Sulfides

The crystalline titanium sulfides were synthesized either by heating the samples in vacuum or by the direct reaction between the amorphous powder obtained by method (A) and sulfur. The reactions were carried out in evacuated quartz tubes heated for 10 hours. Different stoichiometries were obtained by varying the temperature and the sulfur vapor pressure.

Results and Discussion

A - Synthesis of Amorphous Titanium Sulfides

1. Synthesis from $TiCl_4$ and HMDST

The reaction with HMDST occurs spontaneously and exothermically in a wide temperature range (0°C ---> 150°C). A black precipitate is formed which can be readily separated by filtration. The collected liquid was analyzed by proton nuclear magnetic resonance. The results indicate the formation of magnetic resonance. The results indicate the formation of trimethylsilyl chloride $(CH_3)_3$ SiCl (Fig. 1)

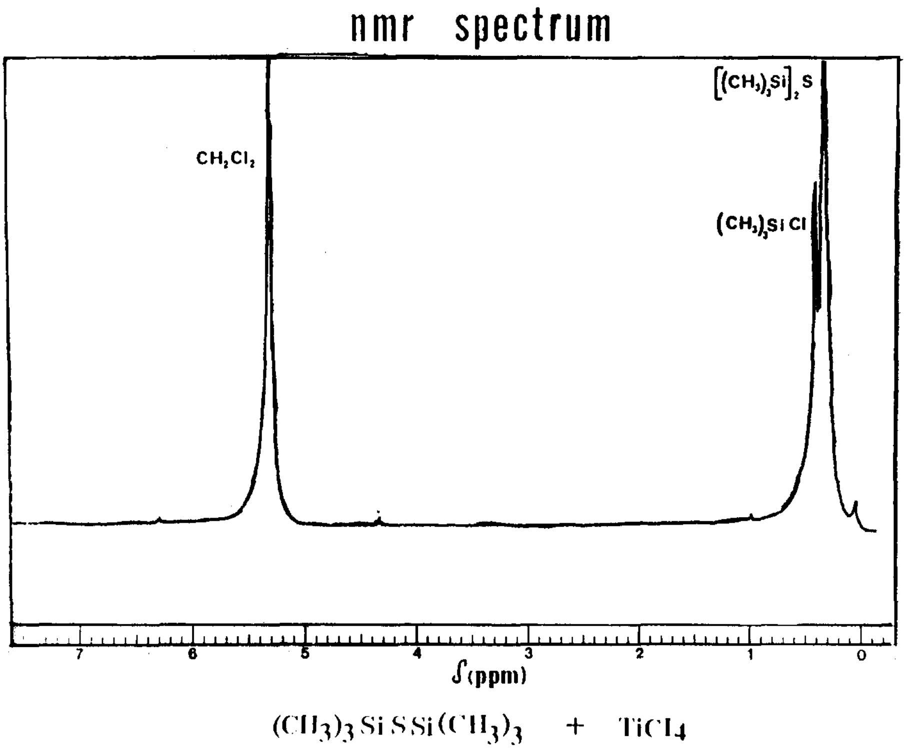

Fig.1: Proton N.M.R. spectrum of the liquid phase collected from the reaction of $TiCl_4$ with HMDST.

The peak observed at δ = 5.3 p.p.m. corresponds to the reference (CH_2Cl_2) and the peak at δ = .35 p.p.m. corresponds to excess HMDST. The degassed powder is amorphous to X-rays. This powder transform to crystalline TiS_2 when the temperature is greater than 200°C, as demonstrated by powder X-ray diffraction (Fig. 2). Heating at temperatures greater than 500°C, results in the liberation of sulfur and the formation of non stoichiometric TiS_2. These results allow us to express the reaction between hexamethyldisilthiane and $TiCl_4$ as the following:

$$TiCl_4 + 2(CH_3)_3SiSSi(CH_3)_3 \text{ ----> } TiS_2 + 4(CH_3)_3SiCl.$$

The reaction occurs without oxidation or reduction and is based on an exchange between the sulfur bonded to a trimethylsilyl group and the chloride bonded to the titanium. The same phenomenon was observed in the reaction between HMDST and molybdenum halides (8).

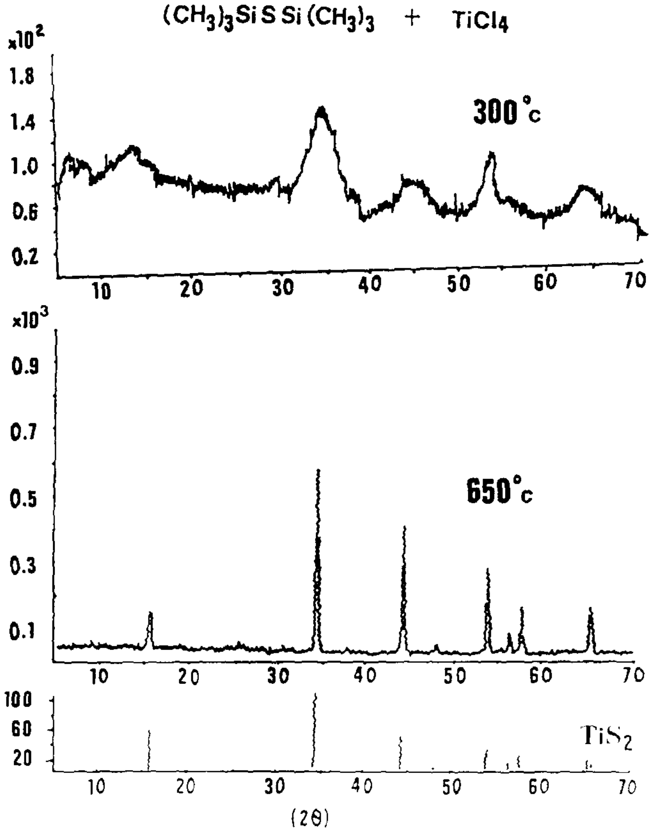

Fig. 2: X-ray diffractograms of the powder obtained from the reaction of $TiCl_4$ with HMDST after heating at 300°C for 10 hours.

2. Synthesis from $TiCl_4$ and ditert-butyl disulfide.

In this reaction $TiCl_4$ and ditert-butyl disulfide are reacted at temperatures ranging from 20°C to 150°C. The reaction proceeds spontaneously and exothermically. A brown powder precipitates from the solution. It appears that the reaction temperature can substantially change the precipitate particle size. Indeed when the reaction is performed at 150°C, the particles readily pass through a medium porosity glass filter. In this case the liquid was removed by evaporation under vacuum at 150°C. The degassed powder is amorphous to X-rays. After heating under vacuum at temperatures greater than 200°C this powder transforms to crystalline TiS_2 as determined by powder X-ray diffraction (Fig. 3)

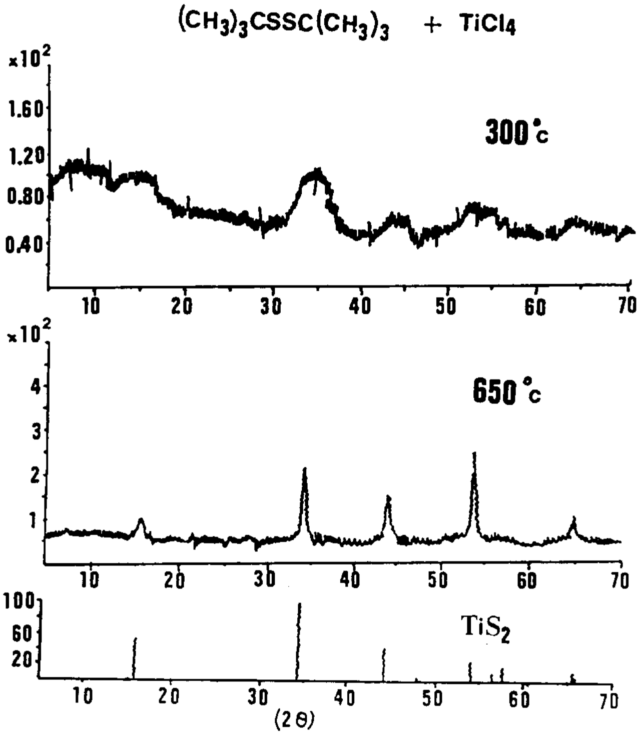

Fig.3: X-ray diffractograms of the powder obtained from the reaction of $TiCl_4$ with ditert-butyl disulfide at 150°C after heating at 300°C and 650°C for 10 hours.

N.M.R. analysis of the liquid phase indicates the formation of tert-butyl chloride $(CH_3)_3CCl$ (Fig. 4); however, this spectrum is not as clear as the spectra of reactions using HMDST. We observe a very small peak at $\delta = 1.35$ p.p.m. in addition to the peaks related to the reference (CH_2Cl_2) and the excess ditert-butyl disulfide. Although the X-ray results show that the reaction occurs without reduction of Ti^{4+}. This reaction may be more complex than a simple exchange between the sulfur - tert-butyl bonds and the chloride - titanium bonds. The cleavage could occur at the middle of the S-S bond which could create tert-butyl sulfide as a by-product. A proton magnetic resonance peak would be expected at $\delta = 1.35$ p.p.m. for this compound which could well explain our observed spectrum.

The powder collected from the same reaction performed at room temperature has also been studied. Figure 5 shows the X-ray powder diffraction spectrum of this material after heating for 10 hours at 650°C

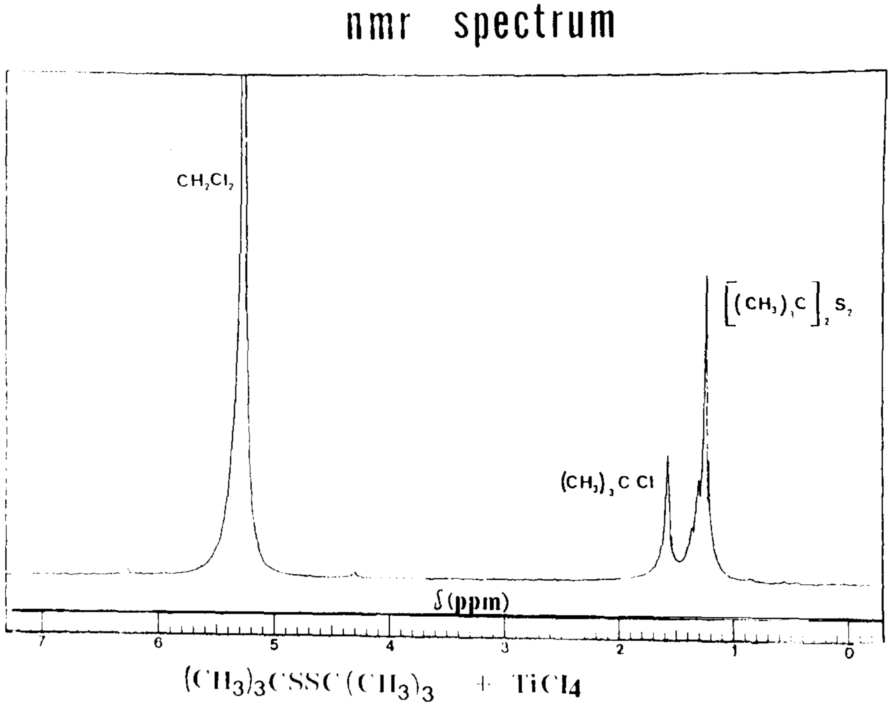

Fig.4: Proton N.M.R. spectrum of the liquid phase collected from the reaction of $TiCl_4$ with ditert-butyl disulfide.

We note the existence of TiO_2 (both rutile and anatase) in addition to TiS_2. This can be explained by the fact that the reaction was not complete after several hours at room temperature, and exposure to air during filtration caused rapid hydrolysis of unreacted chlorides.

3. Synthesis from $TiCl_4$ and ditert-butyl sulfide or tert-butyl mercaptan

In this reaction $TiCl_4$ and ditert-butyl sulfide or tert-butyl mercaptan are reacted neat or within a solvent at temperatures ranging from 20°C to 150°C. A brown precipitate is formed and separated by filtration. N.M.R. analysis of the liquid phase indicated the formation of tert-butyl chloride as well as many other organic by-products (Fig. 6,7).

For each reaction, the degassed powder (amorphous to x-rays) was heated under vacuum at temperatures greater than 200°C for 10 hours. The x-ray powder diffraction patterns indicated the formation of crystalline Ti_3S_4 (Fig. 8)

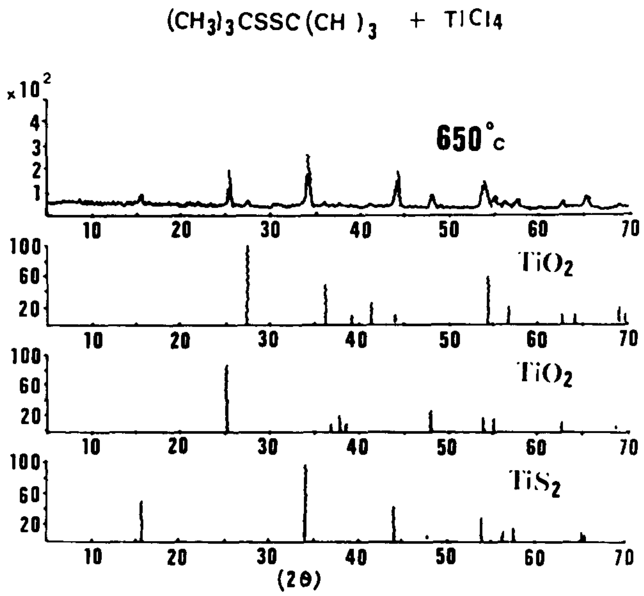

Fig. 5: X-ray diffractogram of the powder obtained from the room temperature reaction between $TiCl_4$ and ditert-butyl disulfide after heating at 650°C for 10 hours.

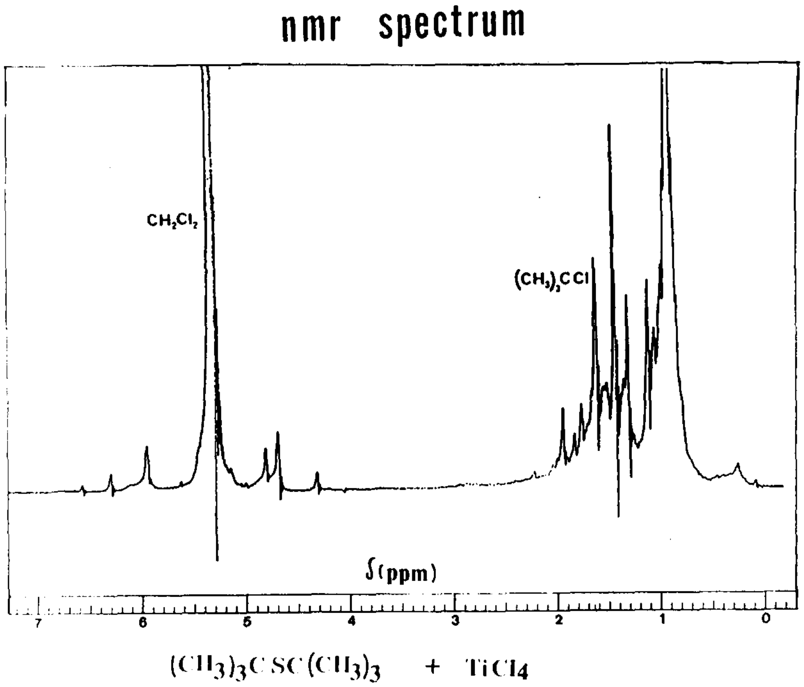

Fig.6: Proton N.M.R. spectrum of the liquid phase collected after the reaction between $TiCl_4$ and ditert-butyl sulfide.

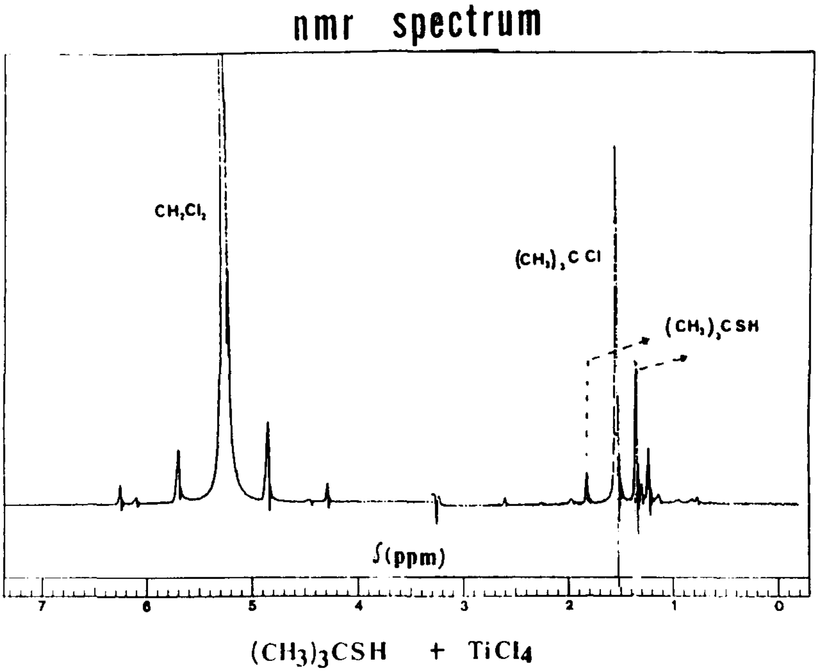

Fig.7: Proton N.M.R. Spectrum of the liquid phase collected after the reaction between $TiCl_4$ and tert-butyl mercaptan

We note that during the reactions using either of these two reagents that the titanium is reduced. This may be due to the formation of free radicals which can react with the titanium chloride. Electron paramagnetic resonance studies are underway to clarify this phenomenon.

B. Synthesis of Crystalline titanium Sulfides

We have prepared crystalline titanium sulfides by direct combination of the obtained amorphous powder and excess sulfur in evacuated quartz tubes heated at different temperatures using either:

i. constant tube temperature
ii. cold tip gradient temperature (cold end of tube outside furnace).

Using these processes, we can obtain different sulfur vapor pressures and subsequently different titanium sulfides. The results are listed in table II.

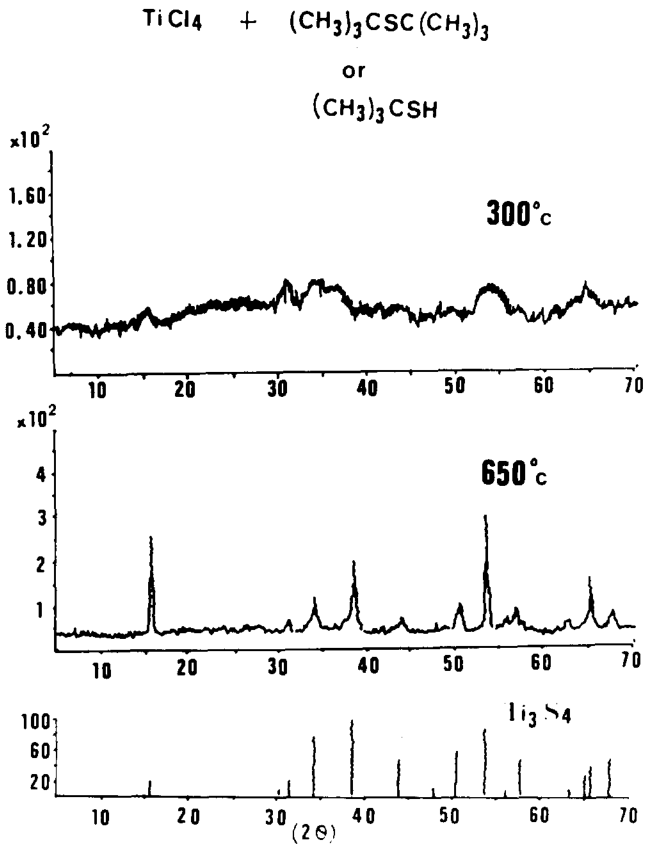

Fig.8: X-ray diffractograms of the powder obtained from the reactions between either ditert-butyl sulfide or tert-butyl mercaptan after heating at 650°C.

We can observe that the constant temperature method permitted us to prepare crystalline TiS_3 in the temperature range 300 - 500°C. At 525°C the TiS_3 is contaminated by TiS_2. Above 525°C the sulfur pressure is insufficient to prepare TiS_3. Using the cold tip method, we synthesized crystalline TiS_2 at temperatures greater than 400°C. At 400°C TiS_2 is contaminated by TiS_3 and at 300°C we obtained pure crystalline TiS_3.

CONCLUSION

Amorphous titanium sulfides can be prepared rapidly at low temperatures using the reaction between organic sulfurizing agents and $TiCl_4$. Thus we prepared pure amorphous TiS_2 using HMDST, a procedure previously developed for the preparation of the amorphous molybdenum sulfides. We have again confirmed that the reaction using this reagent maintains the oxidation state of

Temperature of the Titanium Phase (°C)	Obtained Cystalline (Constant Temperature Tube)	Obtained Crystalline Phase (Cold Tip)
650	TiS_2	TiS_2
600	TiS_2	TiS_2
550	TiS_2	TiS_2
525	TiS_2 + TiS_3	TiS_2
500	TiS_3	TiS_2
450	TiS_3	TiS_2
425	TiS_3	TiS_2
400	TiS_3	TiS_2 + TiS_3
300	TiS_3	TiS_3

Table II: The Composition of the Titanium Sulfide Formed Depending on Temperature and Atmosphere.

the starting metal halide. The reaction using this reagent is certainly not limited to molybdenum and titanium salts, and we expect to study several different metathesis reactions between transition metal halides and HMDST in order to prepare other transition metal sulfides. Meanwhile this reagent presents certain practical inconveniences. In particular, it has a pungent odor which resembles commercial mercaptans added to natural gas. The difficulties associated with this odor as well as the relatively high cost of this reagent impelled us to search for other organic sulfurizing agents for the preparation of amorphous titanium sulfide.

Thus we have been able to prepare amorphous TiS_2 using ditert-butyl disulfide, a reagent which is far less costly and also has little odor. However, the reactions using HMDST are undoubtedly the simplest and easiest to understand. In order to better understand the reactions leading to the formation of titanium sulfides, we have studied several sulfurizing reagents. Thus starting with H_2S in which the sulfur is bonded to two proton we observe no reaction. Upon replacing one proton with a tert-butyl group in tert-butyl mercaptan, the reaction proceeds spontaneously to the formation of a reduced titanium sulfide as well as several organic by-products. The same result is obtained for the reaction using the ditert-butyl groups. It therefore appears likely that the tert-butyl group is responsible for the reduction of the Ti^{4+}. The addition of a disulfide linkage between the tert-butyl groups appears to prevent the reduction and allow for the formation of amorphous TiS_2. It is our hypothesis at this stage that the disulfide may act as a scavenger for tert-butyl radicals which would otherwise reduce the titanium. However, this reduction process may be useful in one specifically wishes to prepare metal sulfides in low valence states.

Amorphous powders obtained from all of our low temperature reactions can either be used in their natural state, or because of their highly reactive nature, be rapidly converted to crystalline sulfides by simply heating. They can be converted to compounds with a greater sulfur to titanium ratio by heating in the presence of non-toxic, inexpensive sulfur. The particular titanium compound formed will depend on the precursor, the temperature and the atmosphere. It is possible to readily prepare any of the usual crystalline titanium sulfide phases (Ti_3S_4, TiS_2, TiS_3).

ACKNOWLEDGMENTS

The authors wish to thank Ms. Y.H. Ko and Dr. A. Srivastava for their technical assistance. We also wish to acknowledge the NSF - Solid State Program, Condensed Matter Sciences Section, Division of Materials Research, DMR 8602666 and NSF: US-France Cooperative Science Program INT 8413961 for supplying funds allowing us to perform this work.

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