

## STRAIGHTFORWARD SOLID-SOLID SYNTHESIS OF METALLIC SULFIDES.

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### ABSTRACT

*In this paper the authors report and discuss a new alternative for the preparation of metallic sulfides. An easy, simple, low-temperature, solid-solid one-pot reaction reacts solid thiourea with metallic salt or oxide to produce the sulfides. The reaction temperature ranges from room to 200°C. The synthesis is clean and leaves no waste to be disposed. Ab initio experiments allowed the preparation of copper, chromium, manganese, mercury, zinc, nickel, iron, silver, tin, antimony, lead, bismuth and rare earth sulfides. As a highlight it is mentioned the synthesis of the cadmium sulfide, made at 80°C, resulting the sulfide as a yellow powder, with good flowability. This sulfide could have several applications, among them as in solar cells and as yellow pigment for paints, especially paint for paved surfaces in streets and highways. The method is fast, safe and quantitative. The sulfides were characterized by several techniques, among them x-ray diffraction, x-ray fluorescence and thermal analysis.*

**Key Words:** solid-state reaction, thiourea, metal sulfides, cadmium sulfide.

## INTRODUCTION

The main methods to prepare metallic sulfides are:

- The direct reaction of the elements, for example,  $\text{Li}_2\text{S}$  produced by reacting elemental sulfur with the metal in the absence of oxygen or reacting lithium with sulfur in liquid ammonia<sup>(2)</sup>. Sodium and potassium monosulfides can also be prepared by the reaction of sulfur with the liquid ammonia solutions of the metals.
- The reaction of anhydrous  $\text{H}_2\text{S}$  with the metal, as for instance Li reacting with  $\text{H}_2\text{S}$  in tetrahydrofuran; or reaction of the metal with hydrogen sulfide at high temperature, as for example the synthesis of  $\text{Ga}_2\text{S}_3$  passing hydrogen sulfide over gallium metal at  $950^\circ\text{C}$ .
- Reaction of metals with mercury (II) sulfide, as the rubidium and cesium mono-sulfides preparation case.
- Reduction at elevated temperature ( $750^\circ\text{C}$  to  $1000^\circ\text{C}$ ) of sulfates by carbon, carbon monoxide or pure hydrogen or hydrogen generated by the cracking of natural gas, as is the case of the industrial production of  $\text{Na}_2\text{S}$  and  $\text{K}_2\text{S}$ .
- Barium sulfide is another important commercial sulfide product obtained by the reduction of barite (barium sulfate) with coal at high temperatures. Barium sulfide is an important source of barium compounds.
- Reaction of anhydrous salts or metallic oxides with a stream of hydrogen sulfide at high temperature ( $1000^\circ\text{C}$ ). Magnesium sulfide for instance is prepared by heating anhydrous magnesium chloride in a stream of hydrogen sulfide at  $1050^\circ\text{C}$ . Cadmium sulfide is prepared from  $\text{CdSO}_4$  with  $\text{H}_2\text{S}$  at high temperature<sup>(5)</sup>.
- The preparation of transition metal sulfides by a vapor phase reaction of the metal halide with hydrogen sulfide at elevated temperatures. The reaction of  $\text{TiCl}_4$  with hydrogen sulfide proceeds at  $450^\circ\text{C}$  as indicated by the following equation<sup>(9)</sup>:  
$$\text{TiCl}_4 + 2 \text{H}_2\text{S} = \text{TiS}_2 + 4 \text{HCl}$$

The elevated temperatures are necessary for achieving favorable reaction rates.

Many metallic sulfides are obtained by aqueous methods, using the precipitation of the cations with  $\text{H}_2\text{S}$  in acid solutions or alkali sulfide like sodium or

ammonium sulfide for the precipitation of the sulfides in alkaline solutions. The solid sulfide must be filtered and then dried.

Some syntheses are made using carbon disulfide as source of sulfur. The  $\text{CS}_2$  vapor is passed over the element, at high temperature ( $1000^\circ\text{C}$ ). Silicon carbide,  $\text{SiC}$ , can be obtained by this method.

A conventional method of preparation of metal sulfides is by reaction of the corresponding metal oxide with a sulfidizing agent such as hydrogen sulfide, at elevated temperatures<sup>(3)</sup>. Frequently oxalates or carbonates are used as precursors, since the formation of an oxide in situ yields a reactive intermediate.

### ***The importance of cadmium sulfide.***

The use of cadmium sulfide as a light detector in a CdS cell was advocated since several years<sup>(8)</sup>. Designs and schematic diagrams of filter photometers using cadmium sulfide detectors are shown. Cadmium sulfide photoconductive cells are commercially available<sup>(7)</sup>.

The applications of semi-conducting electronic devices go from transistorized radios to the most complicated computational systems. Thin films of semi-conducting CdS are deposited on glass substrates by using different techniques. Cadmium sulfide has its band gap energy in the visible spectrum and it is a widely used semi-conducting in optical electronic devices.

Due to its use in solar energy conversion and enhanced nonlinear optical properties, CdS is one of the most studied semi-conductor materials. Bulk CdS is a direct band-gap semi-conductor, with a relative dielectric constant of 5.7.

Since cadmium sulfide and zinc sulfide exhibit sensitivity towards electromagnetic and corpuscular radiations, they are widely used in electronics. By doping them with other metals the sulfides become luminescent. Cadmium and zinc sulfides are doped with rare earth and copper for the synthesis of luminescent compounds. The luminescent properties of lanthanide-activated CdS with Cu as a co-dopant are described by Apperson<sup>(1)</sup>. Cadmium sulfide silver-activated has been used as a phosphor.

Cadmium sulfide has uses in the fabrication of window materials for solar cells.

### ***Analytical applications.***

Metathesis of CdS with  $\text{AgNO}_3$  containing tracer  $^{110}\text{Ag}$  is followed by collection

of Ag<sub>2</sub>S on a membrane filter and gamma counting in a NaI(Tl) well counter.

Certain metal sulfides are used in small amounts to prepare sulfur dioxide for mass spectrometer analysis of the determination of <sup>34</sup>S/<sup>32</sup>S ratio. A mixture of the metallic sulfide with copper oxide (CuO or Cu<sub>2</sub>O) as oxygen donor is heated to generate sulfur dioxide<sup>(6)</sup>.

Metal sulfides are used as selective solid membrane electrodes. Different silver selective membrane electrodes have been most extensively used for silver estimation.

Filter paper impregnated with cadmium sulfide or zinc sulfide was used for the adsorption selectivity of a number of metal ions<sup>(6)</sup>.

### ***A novel alternative preparation of metallic sulfides.***

In this paper the authors report an easy, simple, low temperature, solid-solid one-pot reaction to prepare metallic sulfides. Reacting the metallic carbonates, other salts and oxides with solid thiourea at low temperature (from room temperature to 200°C) the obtaining of the sulfides is straightforward.

Cadmium sulfide was the first product obtained by the method<sup>(4)</sup>. The author's findings were confirmed by cadmium sulfide synthesis. Ab-initio experiments allowed the preparation of copper, chromium, manganese, mercury, zinc, nickel, iron, silver, tin, antimony, lead, bismuth, platinum metals and rare earth sulfides. Cadmium sulfide was the first product obtained by the method here reported and characterized by chemical, x-ray diffraction, x-ray fluorescence and thermal analyses.

## **EXPERIMENTAL**

### ***Apparatus.***

Microwave oven, domestic model, 2.450MHz, 750W, 120V;

Electrical oven, 220V.

### ***Reagents.***

Cadmium carbonate, cadmium oxide and thiourea were reagent grade.

### ***Exploratory experiments.***

The first synthesis experiments were made in exploratory character, to know the behaviour of the oxides and salts of the metals in contact with the thiourea in a solid-

solid reaction. Experiments were accomplished in different temperatures, being obtained with easiness the corresponding sulfides. Several sulfides were obtained in temperatures relatively low by this method. The cadmium sulfide was obtained with extreme easiness in temperature below 150°C, even at room temperature.

The parameters of interest studied were: reaction temperature, melting point of the mixture, ratio of mass thiourea / sulfide precursor and time of reaction. The temperature of reaction was studied intensively, from room temperature up to 300°C interval. It was used electrical oven and bath oil. The studies were made using a microwave oven, domestic type, with 2.45GHz power, to verify the effectiveness of the reaction.

The compounds obtained were characterized by x-ray diffraction to verify the formation of the sulfides. For the cadmium sulfide, its synthesis can also be verified visually as well.

#### ***Cadmium carbonate-thiourea mixture as function of temperature and heating time.***

The behaviour of stoichiometric mixtures of cadmium carbonate and thiourea were studied as function of time and temperature. The samples were submitted to 60°C, 65°C, 80°C, 90°C, 100°C, 110°C and 120°C respectively into the electrical oven at time periods from 1 minute to several hours. In all experiments the yellow cadmium sulfide was formed. The reaction threshold was observed at about 60°C, the reaction being somewhat slow. As the temperature is raised, the reaction became more rapid. The cadmium sulfide obtained at lower temperature is light yellow and at higher temperature became orange-yellow. At 80°C and beyond the reaction is quite rapid and if maintained at this temperature for more time, the product melts. In several experiments at 100°C it was observed that the cadmium sulfide is ready formed in the first minute. From 65°C to 80°C in all experiments the product was a nice powder, with high flowbility. Beyond 80°C it is required the control of reaction time to avoid the melting at the cadmium sulfide if thiourea excess is used.

Keeping the cadmium carbonate-thiourea from 60°C to 80°C during 2 to 24 hours the cadmium sulfide is canary-yellow and has easy flowbility.

#### ***Cadmium carbonate-thiourea mixture as function of water.***

It was observed that the humidity accelerates the reaction, even at room temperature and at higher temperatures. Compound synthesized starting from

mixtures with addition of water presented a time reaction lower than the experiments done with mixtures of the anhydrous solids.

It was also observed that the presence of little amount of water in the cadmium carbonate-thiourea mixture, only sufficient to wet the powder, accelerates the reaction resulting the cadmium sulfide. The mixture when exposed to the laboratory atmosphere absorbs humidity and the appearance of the yellow cadmium sulfide was recognized. Even the small percentage of water in common ethanol is sufficient to promote the synthesis. In this case, after the preparation of the cadmium sulfide, the product is easily dried.

Performing the synthesis using an excess of thiourea the addition of ethanol promoted the reaction and allows the removal of the excess thiourea as well.

### ***Synthesis of cadmium sulfide using excess of thiourea.***

It was studied the effect of the excess of one of the reagents (thiourea and the metallic compound) in the synthesis processes. The syntheses were made using stoichiometric amounts of the reagents and also excess of one of them, usually 10 to 15% in mass. For the excess of the metal salts was not obtained significant results; therefore emphasis was given to the tests with thiourea excess.

It was studied the effect of the excess of reagents in the synthesis of the sulfides being verified that when there is a thiourea excess, it happens the melt of the mixture sulfide of cadmium-thiourea, with probable formation of an eutectic.

The thiourea excess after synthesis can be removed by washing the sulfide with water. This treatment doesn't offer any difficulty, since the thiourea is completely soluble in water.

The cadmium sulfide synthesized in low temperatures (80-85°C) was washed to remove the thiourea excess, dried to 80°C and later heated in the electric oven to 400°C for two hours. There was not alteration of the composition. Then an excess of thiourea was added to the dried CdS and heated again, the melt happening when the temperature reaches the mark of 115°C. It is concluded that the thiourea addition reduces the melting point of the mixture CdS-thiourea.

In table 1 are the observations for the formation of CdS as function to the time and reaction temperatures. A mixture of cadmium carbonate and thiourea was used (10% of excess over the stoichiometric value).

The same study was accomplished for mixture of cadmium carbonate and

thiourea using stoichiometric proportion of the reagents instead of thiourea excess. In this case, the melt was not observed in any of the experiments.

**TABLE 1.** Synthesis of cadmium sulfide as function of the time and reaction temperature for mixtures CdCO<sub>3</sub>, and excess of thiourea.

<i>Temperature</i>	<i>Time</i>	<i>Observations</i>
<i>Room temp. (20-25°C)</i>	<i>24 hours</i>	<i>Any change in the mixture coloration</i>
	<i>2 months</i>	<i>Fine very clear yellow powder</i>
	<i>2 years</i>	<i>Fine powder of intense yellow coloration</i>
<i>65°C</i>	<i>2 hours</i>	<i>Fine very clear yellow powder with predominance of the reagents</i>
	<i>24 hours</i>	<i>Fine very clear yellow powder</i>
<i>80°C</i>	<i>2 hours</i>	<i>Fine clear yellow powder</i>
	<i>24 hours</i>	<i>Fine yellow powder a little more intense</i>
<i>100°C</i>	<i>1 minute</i>	<i>Beginning of the synthesis</i>
	<i>10 minutes</i>	<i>Fine yellow powder</i>
	<i>30 minutes</i>	<i>Fine yellow powder</i>
	<i>1 hour</i>	<i>Fine yellow powder with some melted spots</i>
	<i>2 hours</i>	<i>Fine yellow powder with larger area of the melted mass</i>
<i>110°C</i>	<i>1 minute</i>	<i>Beginning of the melting</i>
	<i>1 hour</i>	<i>Melt of the mixture with orange coloration</i>

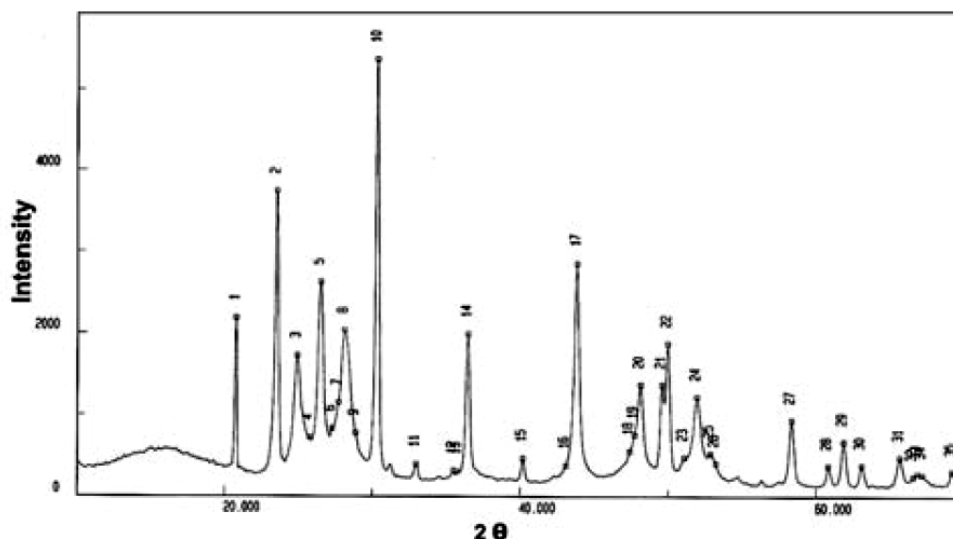
### ***Oxygen atmosphere effect.***

As the most preparation experiments were made in open vessels, the effect of the natural oxygen in the oven atmosphere was studied. The x-rays diffraction spectra for several samples allowed to conclude that from 80°C to 400°C no oxygen effect (formation of cadmium oxide or cadmium oxysulfide) was observed.

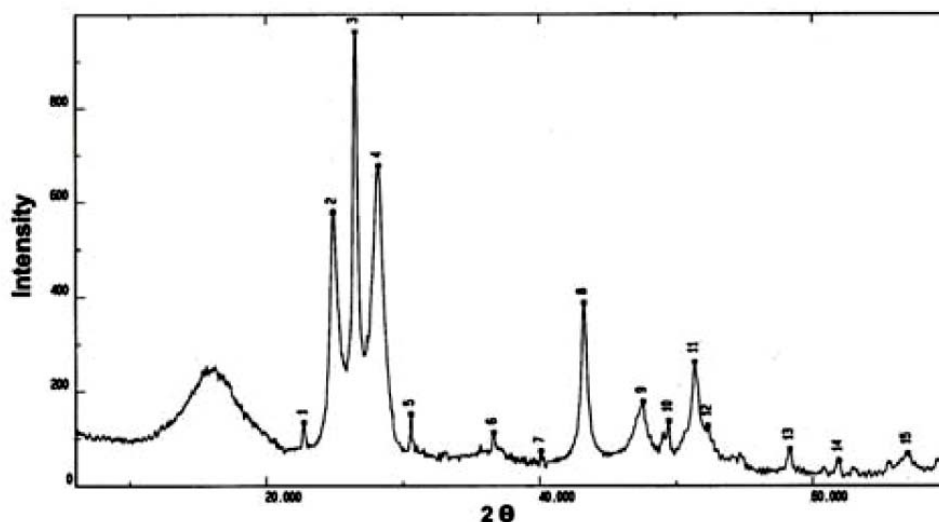
### ***Characterization of CdS.***

Efforts toward the characterization of the cadmium sulfide synthesized by the new technique here reported was achieved by x-ray fluorescence analysis (cadmium sulfide determination), thermal analyses, melting point determination and x-ray diffraction analyses. By thermal analyses was possible to observe that the oxidation process of CdS started beyond 450°C.

The figures 1 and 2 depict the identification of the CdS by x-ray diffraction method.



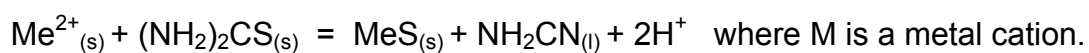
**Figure 1.** X Ray diffraction spectrum of the CdS synthesized at 80°C.



**Figure 2.** X-Ray diffraction spectrum of the CdS synthesized at 100°C in stoichiometric proportion of the reagents, washed and dried.

### ***Mechanism.***

The method comprises a simple operation of reaction between two solids according with the reaction:



Thiourea is a fairly strong reducing agent and in acidic medium it is oxidized to formamidine disulfide,  $\text{H}_2\text{N,HN=C-S-S-C-NH}_2$ , which exists as a salt (ion) in solution.

The basic properties of thiourea are extremely weak, as shown by an inappreciable change in the pH of a dilute strong acid solution to which thiourea has

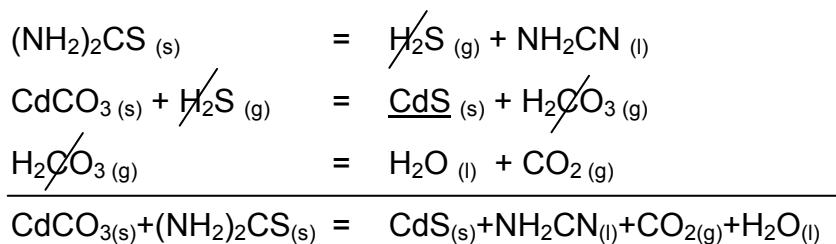


been added (basic ionization constant probably less than  $10^{-15}$  in aqueous solution).

Thiourea is stable in solution at room temperature but decomposes slowly at higher temperatures. One of the hydrolysis products is hydrogen sulfide.

Interpretation of sulfide formation reactions involving solid thiourea and metal oxide or metal carbonate, especially elucidation of the nature of the direct reaction between both, it is not the main scope of the present work.

The mechanism proposed for the cadmium sulfide synthesis is the following:



## RESULTS AND DISCUSSION

Due to the fact that the cadmium sulfide has a yellow characteristic coloration, it was easy to verify the formation of this compound. This fact was confirmed by the characterization analyses.

The sulfides synthesized in initial solid phase as described in this work, were obtained with the autogenous pH of the mixtures of the reagents. There was not pH adjustment for the mixtures, staying all about 7,0.

The average times for the beginning of reaction of stoichiometric mixtures of thiourea and cadmium carbonate as function of the temperature were studied. The results of synthesis studies can be observed in Table 2.

**TABLE 2.** Average times for the reaction of stoichiometric mixtures of thiourea and  $\text{CdCO}_3$  as function of the temperature.

<i>Temperature</i>	<i>Times of the reaction</i>
<i>Room temperature (20-25°C)</i>	<i>&gt; 2 months</i>
<i>65°C</i>	<i>24 hours</i>
<i>80°C</i>	<i>2 hours</i>
<i>100°C</i>	<i>10 minutes</i>
<i>150°C</i>	<i>1 minute</i>
<i>200°C</i>	<i>1 minute</i>

### ***Synthesis of the cadmium sulfide at room temperature.***

The formation of the cadmium sulfide starting from the mixture of cadmium carbonate and thiourea does react to room temperature. In this case the reaction is slower, but it proceeds continually along the time. After 2 months of reaction, the mixture presented a very clear yellow coloration, being visible the formation of the CdS, although the characterization by x-rays diffraction is not still possible in this stage to observe with clarity. After an aging of 7 months it is possible to characterize the CdS by x-rays diffraction.

It was made a detailed study at room temperature and the formation of the CdS was observed during 4 years. In this period there was formation of 98,2% of the CdS, without heating and free from humidity. In agreement with the results obtained by x-ray fluorescence characterization (98,2%), it is concluded that the formation was total, without any type of induction of the reaction, just the simple contact of the reagents.

CdS synthesized at 100°C by 1 hour using stoichiometric proportions of the mixtures has specific mass of 4,83 g.cm<sup>-3</sup> ( $\pm 0,01$ ).

### **CONCLUSION**

The main purpose of this work is to report a new technique for metallic sulfides synthesis. By means of the solid-solid reaction using thiourea and a metal carbonate or another metal compound, the authors propose a new inorganic sulfide synthesis.

The use of thiourea and thioacetamide and other hydrogen sulfide generators by hydrolysis from hot acidic or alkaline media have been published. The solid-state reaction like the one reported in this paper was not published before.

One important aspect of the use of H<sub>2</sub>S in the preparation of metallic sulfides is the need to eliminate the hydrogen sulfide in the firing stage. Hydrogen sulfide is relatively expensive; its use requires specialized furnace equipment at high cost.

The authors claim the development of a novel synthetic method using low-temperature preparation of metal sulfides. In many sulfides preparation the complete reaction requires the use of high temperatures for long periods of time in evacuated reaction reactors.

Direct combination of the sulfide forming compound (thiourea) and the metallic carbonate or oxide simplified the metallic sulfides preparation without aqueous

solutions as it is discussed here. This technique yields cadmium sulfide of high quality, the first product studied by the authors, in a short time. This method is also applicable to the synthesis of other metal sulfides. Another advantage would result using the proposed technique: an improved purity of the prepared sulfide, since the synthesis does not use chloride salts for instance, the final product is not contaminated by anions. During the preparation of the cadmium sulfide no odor of the unpleasant H<sub>2</sub>S smell was scent. Finally another advantage must be claimed: the synthesis has no waste to be disposed.

Summarizing, this work demonstrates a potential technique for the preparation of metallic sulfides using thiourea and an oxide or carbonate of the metal in a one-step solid-solid reaction. The sulfide thereof prepared has no anionic impurities, as is the case when the conventional preparation of metallic sulfides is made employing salts of the metals of interest.

In spite the fact that the mechanism of the direct reaction between thiourea and cadmium carbonate or oxide has not been completely elucidated, the results of this investigation substantiate the proposal made in this study. It is assumed, provisionally, that the cadmium compound react directly and immediately with a stoichiometric amount of thiourea, to give pure cadmium sulfide. A number of possible sulfide preparations from metal carbonate or oxide can be proposed on the basis of the present study.

Future research must include investigation of the preparation of many other metal sulfides.

## ACKNOWLEDGMENT

The authors thank the researchers of the Ipen x-ray laboratories by the help in the characterization of the sulfides.

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