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# Low Temperature Synthesis of Transition Metal Sulfides

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The various techniques for the low temperature synthesis of transition metal sulfides are discussed. The advantages of methods using precursors which already contain metal sulfur linkages are treated, and the properties of the sulfides produced are compared with those prepared by high temperature methods.

## Introduction

A major interest of solid state chemists has been the development of novel synthetic methods for the low temperature preparation of transition-metal sulfides. The traditional method used to prepare these compounds involves the direct combination of the elements in evacuated silica tubes. Complete reaction requires the use of high temperatures for long periods of time. To ensure homogeneity, it is necessary to expose fresh metal surface to the chalcogen periodically. This is accomplished by one of two methods. The sample can be removed from the tube intermittently and ground under an inert atmosphere, or it can be mechanically shaken while it is still sealed in the evacuated tube. Direct combination of the elements can result in homogeneous, single-phase materials, but the products are highly crystalline and have low surface areas. These features are undesirable for certain applications, e.g., in catalytic processes. A number of ternary compounds in which anion substitution has been achieved (e.g., $CoP_xS_{2-x}$ (*1*), $CoAs_xS_{2-x}$ (*2*), and $CoSe_xS_{2-x}$ (*3*)) have also been prepared by direct combination of the elements.

Another method for the preparation of transition metal chalcogenides is by a vapor phase reaction of the metal halide with hydrogen sulfide at elevated temperatures. The reaction of $TiCl_4$ with hydrogen sulfide proceeds at 450°C as indicated by the following equation (*4*):

$$TiCl_4 + 2H_2S \xrightarrow{450^\circ C} TiS_2 + 4HCl.$$

The elevated temperatures are necessary for achieving favorable reaction rates. However, the products obtained by this method have low surface areas and are well-crystallized.

In this paper, a number of novel synthetic techniques for the low temperature prepara-

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tion of transition-metal chalcogenides are discussed. The compounds selected are those that have been of particular interest from the point of view of potential catalyst applications or because of their unique magnetic/structural properties.

## Low Temperature Syntheses and Properties of the Transition-Metal Sulfides $Co_9S_8$, $Ni_3S_2$ and $Fe_7S_8$

Delafosse *et al.* (*5–8*) have shown that sulfides of nickel and cobalt can be prepared by heating their anhydrous sulfates in a stream of $H_2/H_2S$ at low temperatures. However, there was no report of the experimental conditions used to obtain the phases $Ni_3S_2$ or $Co_9S_8$, which are of importance as hydrodesulfurization catalysts. It has been shown (*9, 10*) that both $Co_9S_8$ and $Ni_3S_2$ permit little variation from ideal stoichiometry.

Synthetic samples of the low-temperature phase of $Fe_7S_8$ have been prepared by Lotgering (*11*), and magnetic measurements confirmed the conclusions of other investigators (*12–14*) that the spontaneous magnetism of $Fe_7S_8$ represents a ferrimagnetic structure that is based upon an ordering of iron vacancies. This can be represented by the formula

$$\overrightarrow{Fe_4}\,[\overleftarrow{Fe_3}\,\square]S_8$$

Bertaut (*13*) discussed the ferrimagnetic behavior of naturally occurring $Fe_7S_8$ samples in terms of the ordering of iron vacancies as well as of spins. In a study by Pasquariello *et al.* (*15*), a quenched sample of $Fe_7S_8$ showed a temperature-independent susceptibility from liquid nitrogen to room temperature, which was considered to be consistent with a random distribution of iron vacancies. The observed magnitude of $25 \times 10^{-6}$ emu/g for the susceptibility of the quenched sample was what was anticipated for an antiferromagnet well below $T_N$. The annealed samples of $Fe_7S_8$ showed strong field-dependent behavior (i.e., large spontaneous magnetization) which coincided with the appearance of superlattice lines in the X-ray diffraction patterns. These observations were consistent with the Bertaut model for vacancy ordering in ferrimagnetic $Fe_7S_8$.

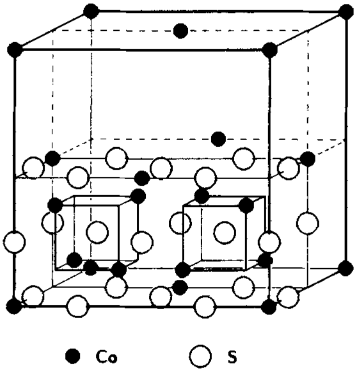


FIG. 1. FCC unit cell of $Co_9S_8$. One-fourth is shown in detail.

Both $Co_9S_8$ and $Ni_3S_4$ were prepared from $CoSO_4 \cdot 7H_2O$ and $NiSO_4 \cdot 6H_2O$ (*15*). The sulfates were predried at 135°C for 4 hrs and then heated first at 250°C for 1 hr in a dry nitrogen atmosphere, followed by a 2–4 hr treatment in a 40/1 (v/v) $H_2/H_2S$ atmosphere at 525°C. The $Fe_7S_8$ was prepared from predried $FeSO_4 \cdot nH_2O$ by heating in a 10/1 $H_2/H_2S$ atmosphere at 325°C, followed either by quenching or slow cooling the product to give either random or ordered distribution of the vacancies.

$Co_9S_8$ crystallizes in the space group *Fm3m*. The cubic close packing of sulfur atoms in this compound results in a cubic cell $a$ = 9.923(1)Å (*16*). In $Co_9S_8$, cobalt atoms occupy 1/8 of the available octahedral and 1/2 of the tetrahedral sites. One out of every nine cobalt atoms is in an octahedral position, with the rest occupying pseudo-tetrahedral sites. Single crystals of $Co_9S_8$ were grown by chemical vapor transport with iodine as the transport agent (*16*). The crystals were determined to be cation

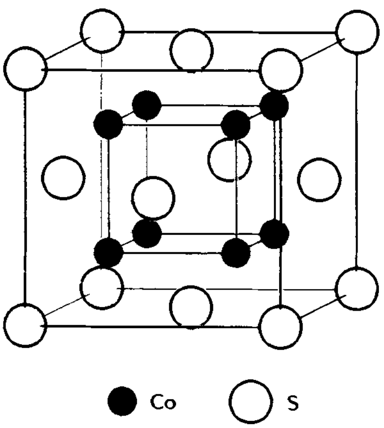


FIG. 2. Cubic cluster of tetrahedral Co(II) in $Co_9S_8$.

deficient having a composition of $Co_{8.85}S_8$. $Co_9S_8$ was observed to be metallic and Pauli paramagnetic (*15*). The unit cell is shown in Fig. 1, and an important feature of the structure is the presence of three metal–metal bonds that extend from each tetrahedral cobalt to form cube clusters of tetrahedral cations (Fig. 2). The metallic behavior of $Co_9S_8$ is a result of metal–metal interactions, both direct and indirect (*16*).

The low temperature rhombohedral form of $Ni_3S_2$ is stable below 556°C (*10*). The unit cell has the symmetry of the space group $R32(D_3^7)$ and the dimension $a$ = 5.738(2), $c$ = 7.126(2) (*15*). There are three nickel atoms and two sulfur atoms per unit cell as shown in Fig. 3. The nickel atoms are in pseudo-tetrahedral positions formed by their coordination with four sulfur atoms.

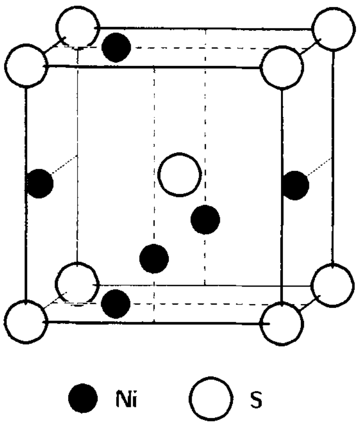


FIG. 3. Unit cell of $Ni_3S_2$.

$Fe_7S_8$ can be considered a derivative of FeS which has the layered NiAs structure (Fig. 4). In $Fe_7S_8$ one-eighth of the iron atoms have been removed. Random distribution of the vacancies results in a unit cell which is hexagonal. However, when the vacancies order among alternate layers of iron atoms, the unit cell is monoclinic (Fig. 5). Slow-cooling or annealing of $Fe_7S_8$ samples results in ordering of these vacancies.

## Low Temperature Preparation of Sulfides with the Pyrite Structure

Bouchard has used (*17*) coprecipitated mixed crystal sulfates to prepare solid solutions of the type $Fe_xCo_{1-x}S_2$, $Co_xNi_{1-x}S_2$, and $Cu_xNi_{1-x}S_2$. The mixed sulfates were precipitated out of aqueous solution by their addition to 10 times their volume of acetone. The products were filtered and heated at 300°C for 6 hrs in a $H_2S/N_2 = 1/1$ atmosphere. The resulting sulfides were quenched to room temperature. The particle size was determined by X-ray diffraction line broadening to be ~ 500 Å. The critical step of the preparation is the low-temperature treatment with $H_2S$. Such products gave single-phase, well-crystallized sulfides when heated to higher temperatures.

Chianelli and Dines (*18*) have reported a novel technique for the preparation of a number of transition-metal dichalcogenides. These sulfides of group IV, V, and VIB were synthesized in non-aqueous solutions at room temperature by the reaction between the anhydrous transition metal chloride and either lithium sulfide or ammonium hydrogen sulfide. The products obtained by this method were poorly crystallized and had high surface areas. The synthetic method

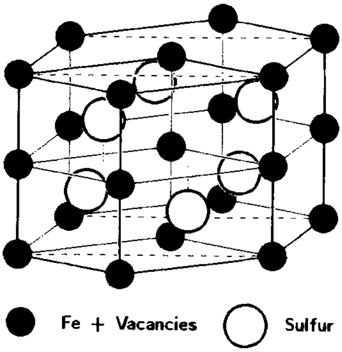


FIG. 4. Hexagonal structure of disordered $Fe_7S_8$. The primitive hexagonal and pseudo-orthorhombic unit cells are indicated.

can be represented by the following equations:

$$MX_4 + 2A_2S \xrightarrow[\text{ambient temp and pressure}]{\text{solvent}} MS_2 + 4AX \quad (1)$$

and

$$MX_5 + \frac{5}{2}A_2S \xrightarrow[\text{ambient temp and pressure}]{\text{solvent}} MS_2 + 5AX + \frac{1}{2}S. \quad (2)$$

In the first reaction, the metal (IV) halide reacts with a sulfide source to form a metal disulfide and a halide salt. The disulfides $ZrS_2$, $HfS_2$, $VS_2$, $MoS_2$, and $TiS_2$ have been prepared by this method. In the second redox reaction, the metal (V) state is reduced to metal (IV); examples of this process are $TaS_2$ and $NbS_2$. A polar solvent free of oxygen and water is used in order to prevent the formation of a transition-metal oxide or hydroxide. The solvents which were used were ethylacetate or tetrahydrofuran, and the chalcogenide source was an ammonium or alkali-metal sulfide. Passaretti *et al.* (*19*) reported the synthesis of amorphous $RuS_2$ by the reaction of anhydrous $RuCl_3$ and $NH_4HS$ in 2-methoxyethyl ether at room temperature. The product was filtered and extracted with methanol, then heated in a stream of $H_2S$ at 250°C. The final product was amorphous, but began to crystallize as a pyrite phase when annealed at temperatures greater than 350°C. The extent of crystallinity was directly related to the annealing temperature. At 825°C, a well-crystallized product was obtained.

Amorphous $RuS_2$ as well as $OsS_2$, $PtS_2$, and $PdS_2$ were also prepared by the reaction of the anhydrous hexachlorometallate (IV) with hydrogen sulfide at various temperatures (*20*). The starting materials and reaction conditions are given in Table I.

A sample of $CoS_2$ was prepared by sulfurizing $Co(NH_3)_6Cl_2$ for 2 hrs at room temperature (*21*). The ammonium chloride was removed by extracting the product in a soxhlet extractor with methanol for 24 hrs. The product was annealed for 4 days at 800°C in a sealed silica tube with 10% by weight of excess sulfur. The sulfur-to-cobalt ratio was obtained by thermogravimetric analysis to give a value of 1.99 : 1.

Schleich and co-workers have prepared a number of amorphous transition metal sulfides by a novel low-temperature technique (*22–24*). The process involves the reaction

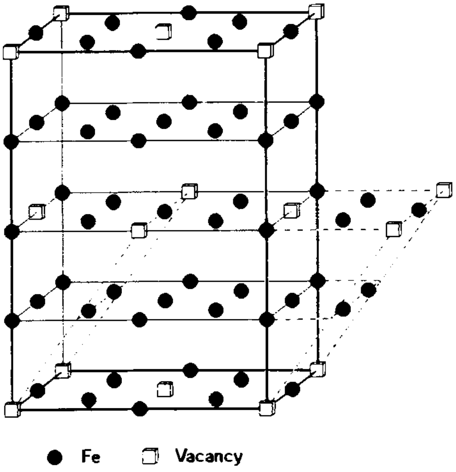


FIG. 5. Ordering of vacancies in $Fe_7S_8$. The monoclinic unit cell is indicated.

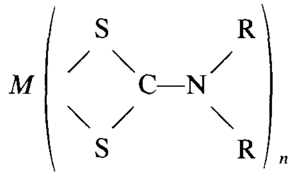
TABLE I

PREPARATION OF PLATINUM METAL DICHALCOGENIDES

| Disulfide | Starting material | Temp. of reaction (°C) | Reaction time (hr) | Temp. of anneal (°C) | Length of anneal (days) |
|---|---|---|---|---|---|
| $RuS_2$ | $(NH_4)_2RuCl_6$ | 180 | 4 | 800 | 4 |
| $OsS_2$ | $(NH_4)_2OsCl_6$ | 220 | 3 | 800 | 4 |
| $PtS_2$ | $(NH_4)_2PdCl_6$ | 110 | 2 | 750 | 6 |
| $PdS_2$ | $(NH_4)_2PtCl_6$ | 130 | 1 | 700 | 5 |

between metal halides $MX_n$ ($M$ = Ta, Nb, Mo; $X$ = Cl, F) and organic sulfur compounds such as hexamethyldisilthane (HMDST), ditert-butyldisulfide (DTBDS), ditert-butylsulfide (DTBS), and tert-butylmercaptan (TBMC). Crystalline sulfides were obtained by heating the amorphous powders in vacuum or by direct reaction of the amorphous products with sulfur. These reactions were carried out in evacuated silica tubes. Different stoichiometries were obtained by changing the temperature and partial pressure of sulfur.

It has recently been discovered (*25*) that metal-dithiocarbamate complexes may be used as precursors to metal-sulfide materials as shown in the following equation:



$$\xrightarrow{H_2S} MS_x + CS_2 + NHR_2.$$

The dithiocarbamates are well-known coordination complexes (*26*) and are easily prepared. They decompose under hydrogen sulfide at temperatures slightly below their melting points. Further heating in the range of 400–600°C serves to produce metal-sulfide phases that correspond to those obtained by direct combination of the elements at higher temperatures. Oftentimes several distinct metal-sulfide phases are accessible by controlling the partial pressure of sulfur in the higher temperature step.

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## References

1. H. Nahigian, J. Steger, R. J. Arnott, and A. Wold, *J. Phys. Chem. Solids* **35,** 1349 (1974).
2. J. C. Mikkelson and A. Wold, *J. Solid State Chem.* **3,** 39 (1971).
3. V. Johnson and A. Wold, *J. Solid State Chem.* **2,** 109 (1970).
4. A. H. Thompson, F. R. Gamble, and C. R. Symon, *Mater. Res. Bull.* **10,** 915 (1975).
5. D. Delafosse and P. Barrett, *C.R. Acad. Sci. Paris* **251,** 2964 (1960).
6. D. Delafosse, M. Abon, and P. Barrett, *Bull. Soc. Chim. Fr.* **164,** 110 (1961).
7. D. Delafosse and P. Barret, *C.R. Acad. Sci. Paris* **252,** 280 (1961).
8. D. Delafosse and P. Barret, *C.R. Acad. Sci. Paris* **252,** 888 (1961).
9. K. Kim, K. Dwight, A. Wold, and R. R. Chianelli, *Mater. Res. Bull.* **16,** 1319 (1981).
10. G. Kullerud and R. A. Yund, *J. Petrol.* **3**(1) 126 (1962).
11. F. K. Lotgering, *Philips Res. Rep.* **11,** 190 (1956).
12. L. Néel, *Rev. Mod. Phys.* **25,** 58 (1953).
13. E. F. Bertaut, *Bull. Soc. Fr. Miner. Crystallogr.* **79,** 276 (1956).
14. R. Benoit, C. R. Hebd, Seances Acad. Sci., **234,** 2174 (1952).
15. D. M. Pasquariello, R. Kershaw, J. D.

PASSARETTI, K. DWIGHT, AND A. WOLD, *Inorg. Chem.* **23,** 872 (1984).

*16.* V. RAJAMANI AND C. T. PREWITT, *Can. Miner.* **13,** 75 (1975).

*17.* R. J. BOUCHARD, *Mater. Res. Bull.* **3,** 563 (1968).

*18.* R. R. CHIANELLI AND M. B. DINES, *J. Inorg. Chem.* **17,** 2758 (1978).

*19.* J. D. PASSARETTI, R. C. COLLINS, AND A. WOLD, *Mater. Res. Bull.* **14,** 1167 (1979).

*20.* J. D. PASSARETTI, R. B. KANER, R. KERSHAW, AND A. WOLD, *Inorg. Chem.* **20,** 501 (1981).

*21.* J. D. PASSARETTI, K. DWIGHT, A. WOLD, W. J. CROFT, AND R. R. CHIANELLI, *Inorg. Chem.* **20,** 2631 (1981).

*22.* D. M. SCHLEICH AND M. J. MARTIN, *J. Solid State Chem.* **64,** 359 (1986).

*23.* A. BENSALEM AND D. M. SCHLEICH, *Mater. Res. Bull.* **23,** 857 (1988).

*24.* A. BENSALEM AND D. M. SCHLEICH, *Mater. Res. Bull.* **25,** 349 (1990).

*25.* R. D. PIKE AND A. WOLD, to be submitted.

*26.* D. COUCOUVANIS, *Prog. Inorg. Chem.* **26,** 301 (1979).