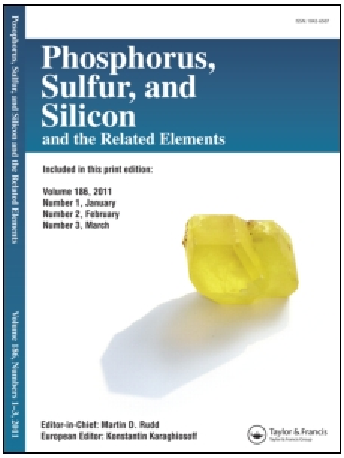

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The Synthesis of Sodium Sulfide Pentahydrate, $Na_2S{\cdot}5H_2O$, Through a Solid-Gas Reaction of Sulfidizing Gas Mixture with Sodium Carbonate, Na_2CO_3

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In this study, the sulfidization of Na_2CO_3 *was investigated by using a solid-gas reaction under a sulfidizing gas mixture, which consisted of COS,* CS_2*, and* S_2 *gases.*

Sodium sulfide pentahydrate, $Na_2S{\cdot}5H_2O$*, was prepared from sodium carbonate,* Na_2CO_3*, via a sulfidizing gas mixture by a solid-gas reaction under the cooling of a nitrogen atmosphere. The observed phase was found to be the pentahydrated form of sodium sulfide. This crystalline form was determined by X-ray powder diffraction (XRD) technique. Since sodium sulfide is strongly hygroscopic, the pentahydrated crystalline form was observed in XRD measurements for all repeated experiments. The crystal unit cell parameters of the synthesized product were in excellent agreement with values given in the JCPDS card number 18-1249. The sodium sulfide pentahydrate has an orthorhombic crystal structure with the unit cell parameters of* $a = 6.475$, $b = 12.55$, $C = 8.655\,\text{Å}$*, space group, Cmcm and* $Z = 4$.

Keywords Sodium sulfide pentahydrate; solid-gas reactions; synthesis; X-ray powder diffraction

INTRODUCTION

During the last few decades, the synthesis and characterization of a new binary, ternary, and quaternary type of metal sulfides has received

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Address correspondence to Halil Guler, Balikesir University, Chemistry Department, Faculty of Science, Balikesir, Turkey. E-mail: hguler@balikesir.edu.tr considerable attention. The advancing attempts and efforts in this area are driven in part by important technological applications found for many of these materials as well as their remarkable diversity in structure and properties.[1–15]

Sodium sulfide, Na_2S, is industrially used in various fields. It is used as a raw material of cure lividity, a cure blue in the dye making and dyestuff industry, and as a dye agent in solving thion dye in the dye printing industry.[16] It is used to reduce nitrified objects and man-made fibers, to carry out hydrolytic decomposition to make raw hide depilated in the tanning industry,[16,17] to make into febrifugal medicine, to synthesize sodium thiosulfate and sodium hydrosulfide in the medicine and chemistry industry,[16] and to control environmental remediation processes.[18] It is also used as mordant in dying cotton fabric in the textile industry,[16] as a digest agent in the paper industry,[16] as a flotation collector agent in mining industry,[19] and as a bath chemical and silver recovering agent from photographic wastes in the photography industry.[20,21]

In addition to industrial-scale usage, sodium sulfide, Na_2S, also has been used in recent scientific research activities. For example, Bandaranayake et al.[22] used it to synthesize CdS by thermal annealing at a high temperature. Vandecruys et al.[23] used it to prepare a solid-state sensor for H_2S as an auxiliary electrode. To obtain the CdS nanocrystals and to investigate their optical properties in the presence of polyethylene tethered chains, Umezu et al.[24] utilized sodium sulfide. In order to synthesize the di-butyl sulfide, Wang and Tseng[25] reacted sodium sulfide with bromobutane as a phase transfer catalysis. Delfini et al.[26] took avantage of sodium sulfide to decontaminate tailings from colemanite processing. Baláž et al.[27] achieved the synthesis of ZnS, CdS, and PbS nanoparticles by a mechanochemical route from corresponding acetates and sodium sulfide. Pan et al.[28] obtained the PbS nanocrystals from sodium sulfide by micromoulding in capillaries. Guan et al.[29] carried out photo catalytic H_2 evolution under visible light irradiation on a CdS/ETS4 zeolite composite as well.

On the other hand, the present concern about the greenhouse effect, pollution, renewable energy, and a durable society has incited researchers to find better ways of using limited energy resources at our disposal. This resulted in the development of fuel cells, solar cells, and heat pumps, to mention only a few. At the same time, energy efficiency has a huge potential for the reduction of energy consumption and CO_2 reduction. In recent years, much effort has been put into the development of heat-driven solid-sorption chemical heat pumps and heat transformers[30] for heating as well as cooling purposes. The working principle of this apparatus is based on the exothermic absorption and endothermic desorption of vapor in solids, e.g., water in silica or zeolites[31] and ammonia in metal salts[32] or in carbon.[33] The thermal effects, and thus the attainable energy densities, are much larger, about one order of magnitude, in the case of chemisorptions, e.g., hydration of metal salts, than in the case of physisorption, e.g., water in silica. In this context, Boer et al.[34] investigated the structural, thermodynamic, and phase properties of the Na_2S–H_2O system that might be used in a waste heat-driven solid-vapour absorption heat pump for cooling purposes in buildings and industrial processes.

In a general framework, for the synthesis of metal chalcogenides, the following methods have been commonly used: (1) a gas-phase reaction between elements or compounds and gaseous H_2X ($X = S$, Se and Te), (2) solid-state reactions, (3) chemical bath deposition and precipitation, and (4) pyrolysis of single source precursors.[35] However, over the years, different sulfidizing methods for the synthesis of various metal sulfides have been intensively investigated and successfully applied. Among these, the outstanding method was of Welch,[36] Kızılyallı and Kızılyallı,[4] Kızılyallı et al.,[8] and Guler et al.[8,12,14,15] The cited methods involve solid-gas reactions. Generally, all these reactions require high temperatures (~500°C or higher). Commercially, the Na_2S is prepared from Na_2SO_4 by the reduction with C, CO, or H_2 at elevated temperatures.[37] Moreover, it is difficult to obtain sufficiently pure material by this method. Therefore, the process is now out of date; it does not meet modern requirements to the environmental protection and to the product quality and is characterized by low utilization of the raw material. Instead of the process cited, in recent years, modern methods were developed based on desulfurizing natural gas and reducing barium sulfate.[38]

In context of obtaining pure sodium sulfide, Brauer[39] proposed two possible methods of preparation:

1. $2Na(s) + S(s) \rightarrow Na_2S(s)$ (liq. ammonia), and
2. $Na_2S.9H_2O \rightarrow Na_2S(s) + 9H_2O(g)$.

The reaction shows that any excess of sulfur in the reaction number 1 can lead to a number of sulfides. In the past, preparing a metal sulfide types of compounds, a different route had been proposed by Welch.[36] In his method, metal sulfides were synthesized by the sulfidization of metal oxides under a sulfidizing gas mixture. This sulfidizing and reducing gas mixture could be simply obtained by passing sulfur dioxide through activated charcoal at the temperature of 750°C.

Regarding characterization studies, the crystal structure of anhydrous Na_2S has been reported as a fluorite type with as Na-S distance of 2.83 Å.[5,41–44] Buhrer and Bill[45] measured the phonon frequencies and elastic constants of Na_2S using a neutron-scattering technique and reported its crystal structure as an antifluorite type based on their own measurements. In another study, Vegas et al.[46] investigated the phase transitions in Na_2S at high pressures. De Boer et al.[34] investigated the structural, thermodynamic, and phase properties of a $Na_2S.9H_2O$ system using X-Ray Power Diffraction (XRD), TG/DTA, melting point, and vapor pressure determinations. On the other hand, the ionic and photo sensitive nature of $Na_2S.7H_2O$ was established.[47] The interaction of $Na_2S.7H_2O$ with lanthanum oxides and chlorides in either the solid state or in solution in the presence of sun light was also investigated.[47] New complexes of the type $[Ln(SH)(OH)_2(H_2O)]$ were reported as well by Lakshimi et al.[47]

Since it has been realized that methods based on Welch's proposal[36] could be successfully applied to the synthesis of metal sulfide compounds with pure forms, it was also plausible to use the same method and reactions for the sodium sulfide synthesis in the present study.

RESULTS AND DISCUSSION

Preparation and Characterization of Na_2S

On the experimental practice, the Na_2S was prepared through a solid-gas reaction of a sulfidizing gas mixture of COS, CS_2, and S_2 with the reactant of Na_2CO_3 and cooling under a nitrogen atmosphere. According to Welch's[36] proposal, products in the sulfidizing gas mixture could be explained as follows:

$$SO_2(g) + 2C(s) \rightarrow COS(g) + CO(g)$$

$$2COS(g) \rightarrow CS_2(g) + CO_2(g)$$

$$2COS(g) \rightarrow 2CO(g) + S_2(g)$$

$$C(s) + S_2(g) \rightarrow CS_2(g)$$

When a metal oxide, MO or a metal carbonate (in this case Na_2CO_3) is heated in the flow of a sulfidizing gas mixture, the following reactions could take place:

$$2MO(s) + CS_2(g) \rightarrow 2MS(s) + CO_2(g)$$

$$MO(s) + COS(g) \rightarrow MS(s) + CO_2(g)$$

$$2MO(s) + 2CO(g) + S_2(g) \rightarrow 2MS(s) + 2CO_2(g)$$

$$2Na_2CO_3(s) + CS_2(g) \rightarrow 2Na_2S(s) + 3CO_2(g)$$

$$2Na_2CO_3(s) + 2COS(g) \rightarrow 2Na_2S(s) + 4CO_2(g)$$

$$2Na_2CO_3(s) + 2CO(g) + S_2(g) \rightarrow 2Na_2S(s) + 4CO_2(g)$$

In this study the previous reactions were adopted for sodium sulfide synthesis.

The XRD pattern of the product is given in Figure 1. As shown, it is consistent with the sodium sulfide pentahydrate compound, $Na_2S.5H_2O$. The detailed XRD parameters of the $Na_2S.5H_2O$ were reported in JCPDS, card no. 18-1249. The sodium sulfide pentahydrate has an orthorhomic crystal structure with the unit cell parameters of $a = 6.475$, $b = 12.55$, $c = 8.655$ Å, space group, Cmcm and $Z = 4$. The observed experimental and JCPDS card "d" values are given in Table I for comparison. Since the sodium sulfide, Na_2S, is strongly hygroscopic material, we had observed the hydrate instead of the anhydrate form.

In XRD measurements of the compound obtained from repeated experiments, it was seen that both the initial product and those remaining in the desiccator for a long time (approximately one year) were stable with the pentahydrated crystalline form of the sodium sulfide.

The following conclusions could be deduced from this work:

- The chemical reactions have taken place between the sodium carbonate, Na_2CO_3, and the sulfidizing gas mixture (COS, CS_2, S_2) under the inert nitrogen gas atmosphere with cooling process.
- The powder crystalline form of sodium sulfide pentahydrate, $Na_2S.5H_2O$, was prepared purely by a solid-gas reaction. It was characterized by the XRD technique, and the XRD data were in excellent agreement with the JCPDS card no. 18-1249.

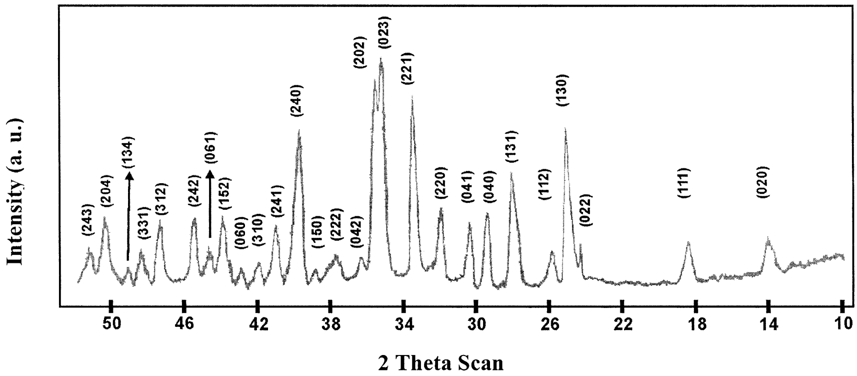

FIGURE 1 The XRD pattern of the synthesized product, $Na_2S{\cdot}5H_2O$.

TABLE I The Observed and Literature (JCPDS 18-1249) "d" Values for $Na_2S{\cdot}5H_2O$

I	d	d_{obs}	h k l
20	6.30	6.26	0 2 0
10	4.80	4.79	1 1 1
5	3.56	3.56	0 2 2
80	3.50	3.51	1 3 0
5	3.46	3.46	1 1 2
60	3.250	3.254	1 3 1
20	3.130	3.132	0 4 0
20	2.950	2.945	0 4 1
10	2.8700	2.8756	2 2 0
50	2.7306	2.7303	2 2 1
100	2.6200	2.6213	0 2 3
100	2.5900	2.5981	2 0 2
5	2.5400	2.5414	0 4 2
10	2.3900	2.3921	2 2 2
5	2.3400	2.3382	1 5 0
60	2.2500	2.2529	2 4 0
30	2.1800	2.1759	2 4 1
5	2.1300	2.1270	3 1 0
5	2.0900	2.0103	0 6 0
40	2.0600	2.0579	1 5 2
10	2.0300	2.0290	0 6 1
20	1.9980	1.9900	2 4 2
20	1.9110	1.9112	3 1 2
10	1.8720	1.8697	3 3 1
5	1.8450	1.8448	1 3 4
20	1.8020	1.8022	2 0 4
10	1.7780	1.7728	2 4 3

- In light of this study, it could be proposed that the compound $Na_2S.5H_2O$ could be prepared purely through a sulfidizing gas mixture by a solid-gas reaction under cooling of a nitrogen atmosphere.
- The $Na_2S.5H_2O$ has many potential applications in industry, scientific researches, and particularly in heat-pump systems.

EXPERIMENTAL

All chemicals were of analytical grade and supplied from Merck Company. The gases were passed through $CaCl_2$ for the removal of water.

A Philips diffractometer with a PW1050/25 goniometer was used for taking X-ray diffraction of the powders with CuK_α ($\lambda = 1.54178$ Å)

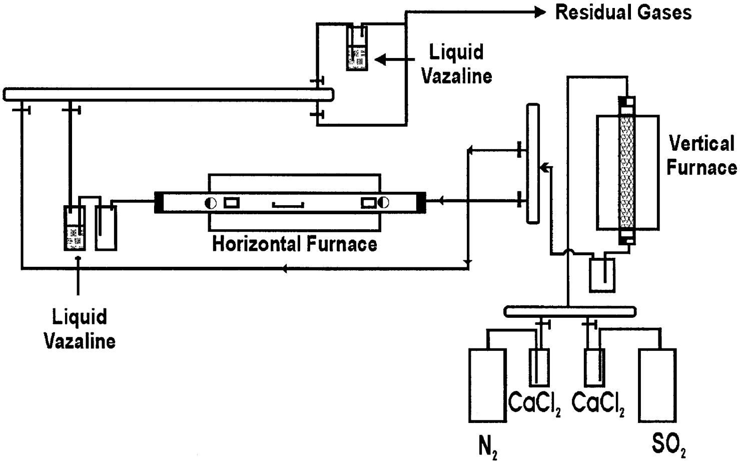

FIGURE 2 Flow sheet of the solid-gas system.

radiation. Forty kV potential and 20 mA current was used for producing X-ray radiation.

Solid-Gas Reaction System

The schematic diagram of a solid-gas reaction system used in this work is given in Figure 2. On the system, a horizontal tubular furnace with a silica tube of 4 cm in diameter and 60 cm in length was used as a reaction chamber. A vertical tube filled with activated charcoal in the furnace was used as a reduction chamber. The temperature control was made with a Cr-Ni thermocouple using a temcometer type of heat control system. Polyethylene tubes with glass connections and glass valves were used in the system. In order to prevent gas leakage, a silicone type of adhesive material was employed at connections of the system.

The procedure applied in solid-gas sulfidizing reaction is as follows. The reactant, sodium carbonate, was ground into fine particles in an agate mortar by crushing until a homogeneous mixture was obtained. Then, this powder was put into the porcelain boat crucible of fixed weight, initially weighed, and the crucible was placed into the center of a ceramic tube in the horizontal reaction furnace. The ambient oxygen was removed by flowing nitrogen gas until reaching a desired reaction temperature. The gas-flow rate was adjusted in such a way so that a rate of 15–20 bubbles per min was achieved. When the system arrived at the desirable temperature, the flow of nitrogen in a vertical tube furnace was adjusted to 700°C and stopped while SO_2 gas was introduced. The optimized reaction times of 3 h were observed. At the end of the reaction times, the SO_2 flow was terminated, and a flow of nitrogen gas was initiated. The N_2 flow was continued until the system reached an ambient temperature. After cooling, the closed system was opened, and the crucible was removed together with contents from the furnace. The crucible was finally weighted, and the final product was ground well in an agate mortar. In order to ensure reproducibility, the experiment was repeated three times. The phase characterization was done by the XRD technique.

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