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Solid-State Synthesis and X-ray Diffraction Studies of Na_2S

M. KIZILYALLI* AND M. BİLGİN

Middle East Technical University, Department of Chemistry, Ankara, 06531 Turkey

AND H. M. KIZILYALLI

Ankara University, Department of Physics, Ankara 06100 Turkey

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Na_2S was synthesized by a new solid–gas reaction of Na_2CO_3 with a sulfidizing gas mixture and a solid–solid reaction of carbon with Na_2SO_4. The reaction products were analyzed by X-ray powder diffraction and IR methods. Two new crystal modifications of Na_2S were identified in addition to the previously reported antifluorite structure. They were designated as cubic Form II and orthorhombic Form III. The approximate unit cell dimensions were found to be $a = 11.29$ Å for the cubic form and $a = 15.94$, $b = 16.00$, and $c = 16.18$ Å for the orthorhombic form.

Introduction

Almost all of the metals in the periodic table react with sulfur in various proportions forming sulfides and polysulfides. Although some crystallographic data can be found in Wyckoff's compilation (*1*), sulfides are still being intensively studied because of their outstanding electrical properties, such as fast ion conduction (*2*) in antifluorite-type structures or superconducting properties shown by Chevrel-type phases which are the ternary metal molybdenum sulfides (*3, 4*). In our energy-conscious world impetus for further research related to binary sulfides comes from the possibility of developing new solid-state batteries.

In sulfide formation, the preferred coordination of the cation depends on the size, charge, and electron configuration of the ions. The similarities of monosulfides and monoxides of alkali metals (lithium to rubidium) are also seen in their crystal structures which are antifluorite type.

Alkali metal sulfides are soluble in water and almost completely hydrolyzed in solution. However, hydrates of Na_2S can be crystallized from aqueous solutions. Na_2S forms two hydrates: $Na_2S \cdot 5H_2O$ (*5*) and $Na_2S \cdot 9H_2O$ (*6*).

Anhydrous Na_2S usually has been obtained by the reduction of Na_2SO_4 at 600–1100°C with various methods. Asphaltite, a waste from oil refineries (*7*), natural gas (*8*), solid carbon (*9*), natural gas in fluidized bed (*10*), and coke in air (*11, 12*) have been used as reductants.

Another recently reported way of obtaining Na_2S (*13*) was from waste gas containing SO_2 that was scrubbed at 70–90°C with a saturated solution of Na_2CO_3. The solu-

* To whom correspondence should be addressed.

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tion was filtered and the filtrate treated with methane, CH_4, at 300–400°C for the reduction of sulfite to sulfide. The mixture of sulfite and sulfide was heated in a rotary furnace at 500–900°C to complete the reaction.

Steck *et al.* (*14*) prepared Na_2S from $Na_2S \cdot 9H_2O$ in a vacuum desiccator at 150°C with P_2O_5 desiccant. Anhydrous Na_2S was prepared recently by Chiotti and Markuszewskii (*15*) by heating $Na_2S \cdot 9H_2O$ in vacuum at 650–700°C for 4 hr, then cooling overnight. None of these techniques lead to sufficiently pure material. Brauer (*16*) lists two possible methods of preparation:

(a) $2Na(s) + S(s) \rightarrow Na_2S(s)$ in liquid ammonia

(b) $Na_2S \cdot 9H_2O(s) \rightarrow Na_2S(s) + 9H_2O$.

Both of these methods were investigated by Walker (*17*) to prepare Na_2S of single crystal growing quality.

Preparation and handling of Na_2S must be carried out extremely carefully to avoid contamination and all operations should be done in an inert atmosphere. Considerable difficulty has been experienced in X-ray Laue photography. The samples deteriorated very rapidly. Laue photographs and X-ray powder diffraction data were not presented by Walker.

In this paper preparation of Na_2S by the interaction of Na_2CO_3 with a sulfidizing gas mixture containing CS_2, COS, and CO and small amounts of CO_2 and S_2 vapor are discussed.

This gas mixture was obtained by Owen *et al.* (*18*) when SO_2 was passed through activated charcoal at 1000, 1200, and 1400 K. The equilibrium constants of the following equations and the partial pressures of the gases were calculated with respect to the reaction temperature by the method of successive approximations:

$$SO_2 + 2C \rightarrow COS + CO$$

$$2COS \rightarrow 2CO + S_2$$

$$C + S_2 \rightarrow CS_2$$

$$2COS \rightarrow CO_2 + CS_2.$$

The change in partial pressures with respect to temperature was reported in a previous publication (*19*).

Welch proposed that this reducing and sulfidizing gas mixture could be used to prepare metal sulfides (*20*). The sulfides of iron and copper, namely, bornite, cubanite, stoichiometric and nonstoichiometric chalcopyrite (*19*), and CdS (*21, 22*) were prepared previously in our laboratory by this method. If unreduced sulfur dioxide is present in the gaseous mixture the following side reaction may occur:

$$Na_2CO_3 + SO_2 \rightarrow Na_2SO_4 + CO.$$

In this work we also tried to synthesize Na_2S by the reaction of Na_2SO_4 with carbon in the solid state or by the dehydration of $Na_2S \cdot 5H_2O$ and determined X-ray powder patterns of the products for comparison.

Structure of $Na_2S \cdot 5H_2O$ and Anhydrous Na_2S

The X-ray powder diffraction data of $Na_2S \cdot 5H_2O$ were published by Bedlivy and Preisinger (*5*). The structure is orthorhombic (space group: *CmCm*) with the unit cell parameters, $a = 6.479$, $b = 12.55$, and $c = 8.655$ Å (JCPDS Card No. 18-1249). Sodium ions are coordinated by six and four H_2O molecules and form layers. These layers are linked to each other by hydrogen bonding.

The X-ray powder diffraction data of anhydrous Na_2S were reported by Zintl and Harder (*23*) and indexed with an fcc structure (space group: *Fm3m* JCPDS Card No. 23-441) with $a = 6.539$ Å (*24*). Although numerous workers have investigated and synthesized Na_2S, the X-ray powder diffraction data have received little attention due to peculiarities of sulfide crystal structures. Sulfide structures are considered as comprising two substructures, one com-

posed of the large sulfur anions and the other composed of the small metallic cations (*25*). The former substructure is based on a fcc lattice. In the sulfide structures which have been studied by Morimoto *et al.* (*25*), the sulfur atoms remain at the fcc positions and the symmetry of the sulfur substructure is truly cubic. The cation substructure is based on a larger cell.

The metal ions are quite mobile and migrate through the structure as the temperature changes. They can settle along the body diagonal of the cube at $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ positions with tetrahedral or $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ with octahedral sulfur coordination. On cooling from the high temperature form the cations are ordered such that the unit cell changes. The size of the cell and the crystal structure depend on both composition and cooling rate. In some cases metastable forms are also obtained.

Experimental

Materials and Instrumentation

The starting materials were reagent grade Na_2CO_3, Na_2SO_4, $Na_2S \cdot 5H_2O$, and carbon powder (Merck or Riedel). Na_2CO_3 and Na_2SO_4 were dried at 100°C before use. Nitrogen, technical grade sulfur dioxide, coke, and activated charcoal were obtained locally.

Spectroscopic grade KBr was used as a pellet material and a Perkin Elmer 1430 ratio recording IR spectrophotometer was employed for taking IR spectra.

Either an Enraf nonius Diffractis 582 type of diffraction generator and Guinier de Wolff Camera No. II or a Philips diffractometer and PW 1050/25 goniometer were employed with Cu$K\alpha$ radiation for X-ray diffraction studies.

Heat Treatments of Na_2SO_4 and $Na_2S \cdot 5H_2O$

To facilitate comparison of X-ray and IR data of the products obtained in solid-state reactions, these chemicals were heat treated under the same conditions as those of the reaction products and X-ray and IR data were recorded.

$Na_2CO_3 + SO_2 \rightarrow Na_2SO_4 + CO$ Reactions

The reaction of Na_2CO_3 and SO_2 to check the formation of Na_2SO_4 and to determine its diffraction data was attempted at 750°C.

Preparation of Na_2S by Solid-State Reactions

Appropriate quantities of Na_2SO_4 and C to obtain the stoichiometric formula, Na_2S, were crushed and throughly mixed in an agate mortar. The mixture was then put into a porcelain boat and placed in the middle of a horizontal tubular furnace. Reactions were carried out at 350 to 800°C for about 2 hr in a dry N_2 atmosphere. N_2 gas was used to remove O_2 from the system and to avoid the side reaction:

$$Na_2SO_4 + C + O_2 \rightarrow Na_2CO_3 + SO_3.$$

Reaction of Na_2CO_3 with the Sulfidizing Gas Mixture

The methods and apparatus used in obtaining data herein reported were given in detail in a previous publication and need only be summarized briefly (*19, 22*).

A horizontal tubular furnace and a silica tube of 2.5 cm inside diameter and 60 cm length were used as a reaction chamber. A silica tube of the same size filled with coke or activated charcoal and inserted vertically in a tubular furnace comprised the reduction chamber. SO_2 gas was bubbled through the vertical furnace at the rate of two bubbles per second. A weighed amount of Na_2CO_3 in a porcelain boat was inserted into the horizontal furnace. The system was flushed with N_2 to remove O_2, then the sulfidizing gas mixture was introduced into the reaction chamber and the furnace heated to the desired temperature. After the reaction

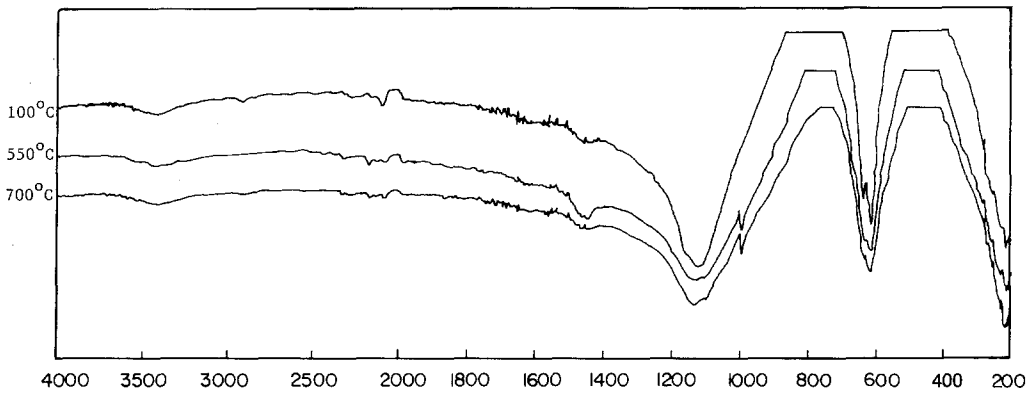

FIG. 1. IR spectra of sodium sulfate treated at different temperatures.

was complete the samples could be either quenched by withdrawal of the porcelain boat from the furnace into a region at ambient temperature while remaining in the sulfidizing gas or N_2 atmosphere, or cooled slowly in the furnace.

Results and Discussion

X-ray and IR Results of Na_2SO_4 and Heat Treated Forms

X-ray diffraction data of Na_2SO_4 obtained by reaction of Na_2CO_3 with SO_2 agreed very well with the data of reagent grade Na_2SO_4. The 550° and 750°C forms gave the same diffraction patterns. The experimental orthorhombic lattice parameters $a = 5.59$, $b = 8.92$, and $c = 6.95$ Å (space group: *CmCm*) are in good agreement with those reported by Frevel (*26*) and Fischmeister (*27*). The infrared spectrum of Na_2SO_4 and heated forms is shown in Fig. 1. The IR spectrum of sulfate ion was reported by Ross and Nakamato (*28, 29*). The following frequences (in cm^{-1}) were given:

ν_1	ν_2	ν_3	ν_4
983	450	1105	611

where ν_1 and ν_2 are only Raman active. It is clear from Fig. 1 that ν_3 and ν_4 are IR active and appear strongly in the spectra. On heating, Raman active ν_1 also appears since the symmetry of the SO_4^{2-} ion was lowered from Td to C_{3v} or C_{2v} (*30*). Ions of the formula XO_4^{2-} are tetrahedral but distort upon heating in such a way that there are two long and two short X–O bonds so the symmetry turns out to be C_{2v}. On the other hand the IR spectra of sodium sulfate are given by Gadsden (*31*) with the following frequencies (cm^{-1}): 1135–1130 (vs), 1116–1095 (vs), 991 (vw, sharp), 725 (w), 640–635 (s), 620–615 (s). These agreed quite well with Fig. 1.

X-ray Powder Diffraction and IR Results of $Na_2S \cdot 5H_2O$ and Heat Treated Forms

The X-ray powder diffraction data of $Na_2S \cdot 5H_2O$ (Riedel) were obtained and compared with the literature data (JCPDS Card No. 18-1249). The spacings observed in this work agreed quite well with the data of Bedlivy and Preisinger (*5*), but it was observed that the data also contain some lines due to NaHS (JCPDS Card No. 3-645) and Na_2SO_3 (JCPDS Card 37-1488). The pattern was indexed in the orthorhombic system and the unit cell parameters were calculated to be $a = 6.48$, $b = 12.54$, and $c = 8.66$ Å.

Figure 2 shows the previously unre-

ported IR spectrum of $Na_2S \cdot 5H_2O$. The IR spectrum of metal sulfides depends on S–S stretching or metal–S stretching vibrations (*32*) due to the covalent nature of the bonds. Any sulfide absorption bands that arise usually occur below 400 cm^{-1} in the low frequency region, but there is no simple correlation (*31*). However, the frequency of the vibration decreases with increasing atomic weight of the cation. In hydrated inorganic salts, the presence of lattice or coordinated water gives rise to lattice vibrations in the low frequency region in addition to 3550–3200 cm^{-1} antisymmetric and symmetric OH^- stretching and 1630–1600 H–O–H bending modes. Librational modes occur between 300–600 cm^{-1}. Coordinated water is also expected to show other modes. Rocking, wagging, and the metal–oxygen stretching vibrations appear at 900, 768, and 673 cm^{-1}, respectively (*33*). The water twisting vibration is only Raman active. These frequencies depend on coordination as well as hydrogen bonds in the crystal, so these two effects must be carefully differentiated, since there is no definite borderline between the lattice and the coordinated water.

The following probable modes were assigned to the bands observed in Fig. 2.

(cm^{-1})	Remarks
270	Sulfide lattice vibration
550	Librational mode of water
626	SO_3^{2-} (ν_2) (*29–34*)
670	Na–O stretching vibration
870	δ-S–H (*35*) or rocking mode of coordinated water
892	SO_3^{2-} (ν_3)
900	$NaHS \cdot xH_2O$ (*36*)
1000–1138	SO_3^{2-} (ν_1)
1450	$NaHS \cdot xH_2O$

These observations together with the X-ray data showed that the commercial $Na_2S \cdot 5H_2O$ oxidized partially to Na_2SO_3.

The X-ray and IR data of $Na_2S \cdot 5H_2O$ dried in vacuum (1 mbar) at room temperature are given in Table I and Fig. 3, respectively. The formula of the vacuum dried product was found to be $Na_2S \cdot 1.17H_2O$ by mass loss. Comparison of the two samples revealed that as the water content decreased, the X-ray and IR data changed considerably. Examination of the X-ray data showed that the product is a mixture of the pentahydrate (JCPDS Card No. 18-1249) and antifluorite-type Na_2S (JCPDS card No. 23-441), but the intensities and the *d* spacings of Na_2S lines do not fit properly to the reported data. The pattern may also contain some NaHS and Na_2SO_3 reflections.

The vacuum dried product was then heated very slowly at 50°, 75°, and 100°C to avoid melting. The low temperature removal of water was quite difficult, so the specimens were heated again to constant weight in the temperature range 500–800°C. The IR data proved that water was still present at 500°C and was practically re-

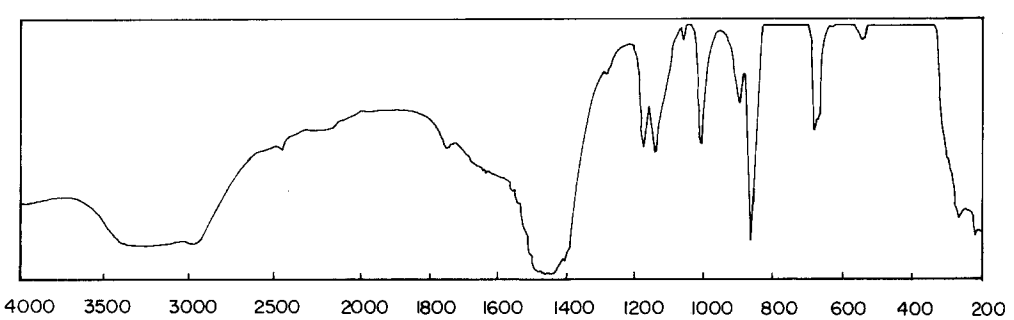

FIG. 2. IR spectrum of $Na_2S \cdot 5H_2O$.

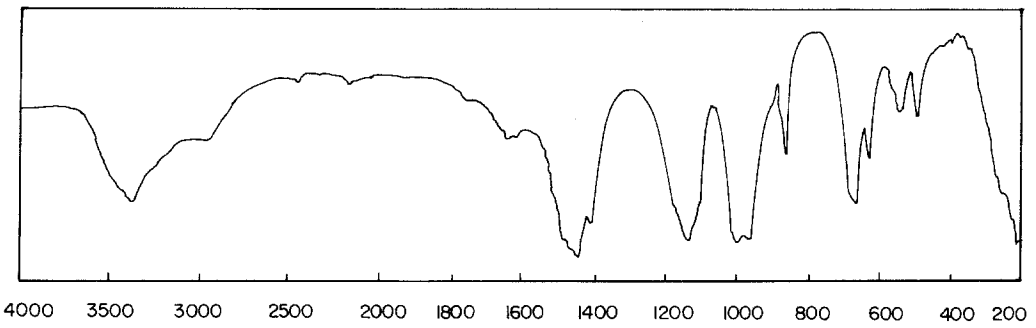

FIG. 3. IR spectrum of vacuum dried $Na_2S \cdot 5H_2O$.

TABLE I

X-RAY DIFFRACTION DATA OF VACUUM DRIED $Na_2S \cdot 5H_2O$

I/I_0	d(Å)	I/I_0	d(Å)
5	5.29	40	2.045
5	3.99	40	2.006
20	3.70–Na_2S	40	1.9649–Na_2S
5	3.65	40	1.9375
5	3.51	15	1.9084
10	3.25–Na_2S	80	1.8766–Na_2S
35	3.196	50	1.8625
5	3.079	15	1.8039
10	2.940	10	1.7874
20	2.829	10	1.7664
35	2.746	5	1.7374
100	2.694	5	1.7250
50	2.659	20	1.6894
75	2.611	20	1.6509
5	2.501	25	1.6474
40	2.478	10	1.6313–Na_2S
40	2.453	20	1.6045
5	2.429	10	1.5901
35	2.371	25	1.5583
45	2.311–Na_2S	25	1.5436
20	2.284	10	1.5245
25	2.241	20	1.4974–Na_2S
25	2.182	10	1.4629
10	2.144	5	1.4508
40	2.114	15	1.4447
		15	1.3894
		15	1.3474
		25	1.3187–Na_2S

Note. Formula calculated as $Na_2S \cdot 1.17H_2O$ Rad. CuKα (λ = 1.54178 Å).

moved at 700–800°C (Fig. 4). Theoretical and calculated weight loss agreed quite well at this stage.

The IR spectra of $Na_2S \cdot 5H_2O$ dried in vacuum (Fig. 3) have frequencies common with $Na_2S \cdot 5H_2O$ except for the split bands at 540 and 1000 cm^{-1}. The IR spectra of the compound heated at 500°, 700°, 750°, and 800°C are given in Figs. 4a,b,c,d. It was observed that the band at 1450 cm^{-1} progressively disappears as the temperature increases. This band was attributed to NaHS (*36*) and we assumed that H–S was destroyed upon heating. The bands due to SO_3^{2-} also disappeared after 500°C, and strong bands of SO_4^{2-} were observed in spectra 4b, c, and d.

The X-ray powder patterns of $Na_2S \cdot 5H_2O$ heated at 300°, 400°, 500°C were very complicated and contained a number of phases including Na_2S (Form I), NaHS, and Na_2SO_3. The product heated at 550°C does not contain NaHS and Na_2SO_3. A new phase which we assumed to be a different cubic crystal modification of Na_2S (Form II, a = 11.29 Å) was observed together with strong Na_2SO_4 lines.

Since the sample heated at 800–850°C gave a very complicated pattern with strong Na_2SO_4 reflections, it was assumed that anhydrous Na_2S cannot be easily obtained through heating the pentahydrate. Utmost

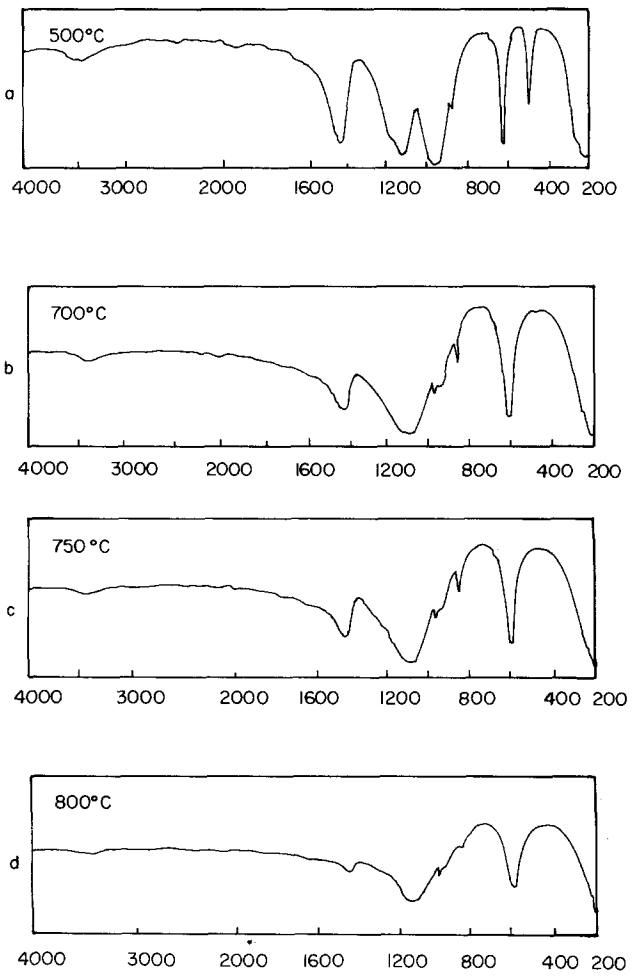

FIG. 4. IR spectra of $Na_2S \cdot 5H_2O$ heated at different temperatures.

care should be taken to avoid contamination.

X-ray and IR Results of Na_2S Obtained from Na_2SO_4 + C Solid-State Reactions

The experiments were performed at 350, 450, 500, 550, and 800°C for 2 hr and at 900°C for 1 hr. The X-ray powder patterns of the products proved that the optimum condition for preparing Na_2S was 2 hr heating time at 800°C. A new type of structure was observed together with weak Na_2SO_4 lines (see the following paragraph and Table II). The IR spectra of this product were about the same as that of $Na_2S \cdot 5H_2O$ heated at 800°C (Fig. 4d) showing the presence of Na_2SO_4 bands.

X-ray and IR Results of the Reaction Na_2CO_3 + Sulfidizing Gas Mixture

Several different sets of experiments were performed at 700°, 750°, and 800°C for 1,2,3,4,5, and 12 hr heating periods with cooling under a dry nitrogen of sulfidizing gas atmosphere. Of the experimental conditions studied to prepare Na_2S, the optimum

TABLE II

X-RAY DIFFRACTION DATA OF Na_2S AT 800–850°C (FORM III)

I/I_0	d(Å)	Remarks
50	11.276	
5	8.154	
10	6.549	
5	5.626	
10	5.366	
5	5.111	
5	5.039	
10	4.635	$+Na_2SO_4$
10	4.250	
10	3.969	
3	3.890	Na_2SO_4
5	3.746	$+Na_2SO_4$
5	3.655	
5	3.583	$+Na_2SO_4$
5	3.499	$+Na_2SO_4$
15	3.421	
15	3.402	
10	3.190	Na_2SO_4
40	3.074	$+Na_2SO_4$
10	2.910	
60	2.831	
3	2.797	Na_2SO_4
1	2.733	
5	2.694	
25	2.660	
100	2.584	
5	2.521	
10	2.495	
90	2.442	
90	2.432	
70	2.382	$+Na_2SO_4$
25	2.211	
5	2.194	
5	2.153	
5	2.144	$+Na_2SO_4$
5	2.114	
30	2.076	
15	1.9930	
15	1.9649	$+Na_2SO_4$
10	1.8934	
5	1.8711	
5	1.7906	
5	1.7841	
5	1.7554	
10	1.7292	
15	1.7202	
10	1.7077	
5	1.6260	$+Na_2SO_4$
5	1.6090	
5	1.6104	
5	1.5801	$+Na_2SO_4$
5	1.5453	
5	1.4764	
5	1.4588	$+Na_2SO_4$
5	1.3481	
5	1.3109	

Note. Rad. Cu$K\alpha$ orthorhombic, a = 15.94, b = 16.00, c = 16.18 Å.

was 12 hr heating time at 700°C and slow cooling in the sulfidizing gas atmosphere. Activated charcoal (6–12 mesh) instead of coke in the reduction chamber increased the Na_2S yield. The X-ray powder diffraction data were about the same as those obtained from the Na_2SO_4 + C reactions. At 700°C the product was found to be a mixture of two phases (Forms II and III) but at 800°C only Form III was observed. The intensities of Na_2SO_4 lines are very weak and are not consistent with Na_2SO_4 data, but the IR spectra are the same as that of Fig. 4d showing the presence of SO_4^{2-} ions.

The powder pattern of Form III is recorded in Table II. The whole system could be indexed on a large pseudocubic (orthorhombic) unit cell with approximate unit cell parameters a = 15.94, b = 16.00, and c = 16.18 Å. The sulfur content of the compound was 39.9% compared with the theoretical value of 41.08% (*37*). These results, together with X-ray and IR data, proved the presence of SO_4^{2-} impurity in the Na_2S product.

In conclusion we have shown that Na_2S can be prepared through solid–gas reactions which have not been reported before. In these reactions care should be taken to avoid diffusion of oxygen into the system and formation of Na_2SO_4 (*38*).

A new orthorhombic crystal modification of Na_2S was observed (Form III) and a cu-

bic modification of it with an approximate 11.29 Å unit cell parameter was predicted (Form II) in this work. The cell parameter relations between the antifluorite type of Na_2S (Form I), Form II, and Form III are found to be:

(i) $a_{\text{Form I}} \cdot \sqrt{2} \sim a_{\text{Form II}}$

(ii) $a_{\text{Form II}} \cdot \sqrt{3} \sim a_{\text{Form III (pseudocubic)}}$.

Further research is going on in our laboratories to clarify these difficult sets of phase relationships in sodium sulfide structures and to refine the unit cell parameters.

Acknowledgments

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