A Preparative and X-Ray Powder Diffraction Study of the Polysulfides Na_2S_2, Na_2S_4 and Na_2S_5

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Pure, well-crystallized samples of the Na-polysulfide phases Na_2S_2, Na_2S_4, and Na_2S_5 have been prepared by the reaction between anhydrous Na_2S and S(l) at elevated temperatures. These polysulfide phases were characterized by the X-ray powder diffraction method, and the following values of the cell parameters were obtained: for Na_2S_2 (with hexagonal symmetry), $a = 4.4869 \pm 0.0005$ Å, $c = 10.2210 \pm 0.0015$ Å, for Na_2S_4 (with tetragonal symmetry), $a = 9.5965 \pm 0.0008$ Å, $c = 11.7885 \pm 0.0016$ Å, and for Na_2S_5 (with orthorhombic symmetry), $a = 7.6505 \pm 0.0009$ Å, $b = 14.5036 \pm 0.0020$ Å, $c = 5.8430 \pm 0.0008$ Å.

In addition, metastable phases of Na_2S_4 and Na_2S_5 were prepared.

Knowledge of sulfide melts and the interaction between sulfur and sulfide melts is quite meagre. It thus appears fruitful to investigate alkali sulfide systems, where many different polysulfides are formed. In our department, work is progressing to establish conditions for the formation of Na-polysulfides and to determine their structures in solid and liquid state. In the system $Na_2S - S$ there exist three stable intermediate phases, Na_2S_2, Na_2S_4, and Na_2S_5. For a proper identification of the solid phases, X-ray powder photographs are most informative and significant.

Well-crystallized samples of high purity are needed for reliable and precise X-ray powder diffraction data. Consequently, the aim of this study was to find a convenient method for the preparation of pure, well-crystallized Na-polysulfide phases and to determine some characteristic data, primarily by accurate X-ray powder diffraction data.

EARLIER WORK

Preparation. Methods for the synthesis of pure Na_2S_2, Na_2S_4, and Na_2S_5 are described in Gmelin.[1] Two main methods are indicated: (1) the direct reaction of S(l) with anhydrous Na_2S at elevated temperatures; (2) the dissolution of stoichiometric amounts of Na_2S (or Na) and S in a solvent, most often ethanol or liquid NH_3, followed by evaporation and crystallization.

X-Ray powder diffraction investigations. The phase of Na_2S_2, stable at elevated temperatures (called β-Na_2S_2 by Feher and Berthold [2]) has been investigated by several groups: Klemm *et al.*,[3] Feher and Berthold,[2] Erämetsä and Karlsson [4] and by Föppl *et al.*,[5] the last-named study being the most extensive and included indexing of observed lines. It could be mentioned that the phase called α-Na_2S_2 (*cf*. Ref. 2) has appeared only in connection with preparation from ethanol solution.

Since the powder diffraction patterns from these earlier investigations were given in diagrammatic form only, which is quite unpractical from the point of view of identification, we found a re-determination and presentation of measured $\sin^2\theta$-values to be warranted.

The phases Na_2S_4 and Na_2S_5 were studied by Feher and Berthold,[2] who presented results merely in the form of "Strich-Diagramme" without any interpretation. Some years later, Erämetsä and Karlsson [4] indexed some lines of the powder pattern for Na_2S_4 but their meagre experimental values did not permit reasonable conclusions, which also can be shown by statistical considerations.[6]

PREPARATIVE WORK

Polycrystalline pure samples of Na_2S_2, Na_2S_4, and Na_2S_5 were prepared by the reaction between anhydrous Na_2S and elemental sulfur, according to the reaction formula

$$Na_2S(s) + nS(l) \rightarrow Na_2S_{n+1}(s,l)$$
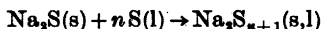
For these preparations commercial sulphur (spectrographically standardised sulphur crystals, Johnson and Matthey Chemicals) was used directly while pure anhydrous Na_2S had to be prepared. Anhydrous Na_2S and the Na-polysulfide phases are extremely hygroscopic and very sensitive to humid air oxidation. Therefore, all handling operations, such as weighings and mixings, were performed in a dry box, filled with purified and dried N_2, where the H_2O-content was kept at the level of $2-10$ ppm.

Preparation of pure, anhydrous Na_2S. In the starting material, recrystallized $Na_2S \cdot 9H_2O$ (Merck, *p.a.*), there are several impurities caused by air oxidation, in particular $Na_2S_2O_3$, Na_2SO_3, Na_2S_2, and NaOH. The total impurity content amounts normally to about $1-2$ %. To obtain pure, anhydrous Na_2S, the following procedure was used. The main part of the hydration water was removed according to Kapylov [7] by slowly heating under vacuum to 300°C. To remove the remaining water and all the impurities mentioned, a second heat treatment at about 900°C was followed. Predried Na_2S was intimately mixed with about 10 % Na_2S_2 and the mixture put into a carbon boat, which then was placed in a tube-furnace. A gas mixture containing about 50 % H_2 and 50 % N_2, both carefully purified from O_2 by passage through hot activated Cu on kieselguhr, from CO_2 with concentrated NaOH-solution and from H_2O by passage through $P_2O_5(s)$, was constantly passed through the furnace. The temperature was then slowly raised to 900°C and kept there for about $5-10$ h. Under these conditions, Na_2S_2 and H_2 will firstly transform NaOH to Na_2S and H_2O and then H_2 will react with excess Na_2S_2 as well as with the oxygen-containing species to form Na_2S, H_2O and H_2S. It should be noticed that the addition of Na_2S_2 to the predried Na_2S is necessary to remove NaOH from the final product.

The anhydrous product thus obtained is quite white and the analysis according to Bethge [8] indicated a value of 100.0 ± 0.2 % of Na_2S. It could be mentioned that the white colour is a strong indication of high purity; *e.g.*, the presence of about 0.1 % polysulfide will give a faint but distinct discolouration.

Preparation of pure Na_2S_2, Na_2S_4, and Na_2S_5. Stoichiometric amounts of anhydrous Na_2S and S were carefully mixed by grinding and then put into a pyrex tube which was evacuated and sealed. A heat treatment procedure as indicated in Table 1 proved to yield quite pure and well-crystallized products for all the three Na-polysulfide phases.

Some comments to the suggested preparation method may be justified: It is favourable that the reactions occur at moderate temperatures yielding solid polysulfides, since the melted polysulfides will attack the glass walls. This procedure is also recommended in order to avoid high sulfur pressure in the tube with risk of explosion. However, to ensure complete reactions the temperature is raised for a relatively short time so that a homogeneous melt will be obtained. A treatment period of $\frac{1}{2}$ h gave no indication of

Table 1. Heat treatment procedure for the preparation of Na-polysulfides.

Moment	Reaction temp. (°C)	Reaction time (h)	Comments
Step 1	200 – 230	10 – 12	Solid-state reaction, 80 – 90 % conversion
Step 2	300 – 500	$\frac{1}{2}$	Liquid state reaction, complete conversion
Step 3	200 – 220	1 – 10	Tempering until complete crystallization

corrosion. On cooling, the polysulfides generally form a glass. A well-crystallized phase will be obtained after crushing at room temperature and tempering in a sealed tube at about 200°C.

The melting points, which are given in Table 5, were determined in connection with phase equilibria studies of the system $Na_2S - S$ to be described elsewhere. The colours indicated (see Table 5) are those for coarse, polycrystalline samples.

Table 2. X-Ray powder diffraction data for Na_2S_2 at 24°C taken with $CuK\alpha_1$-radiation ($\lambda = 1.54051$ Å) and using $Pb(NO_3)_2$ ($a = 7.8572$ Å) as an internal standard.

$h\,k\,l$	I_{obs}	$10^5 \sin^2\theta_{obs}$	$10^5\Delta$	d_{calc}, Å
0 0 2	v w	2262	− 10	5.110
1 0 0	m	3931	2	3.886
1 0 1	s	4495	− 2	3.632
1 0 2	s s	6213	12	3.093
1 0 3	s s	9045	4	2.562
1 1 0	s s	11815	27	2.243
1 1 4	m	13015	− 1	2.135
1 1 2	w	14052	− 8	2.054
2 0 0	v w	15716	− 1	1.943
2 0 1	w	16274	− 11	1.909
2 0 2	m	17993	4	1.816
1 0 5	s	18146	19	1.809
0 0 6	v w	20443	− 2	1.703
2 0 3	m	20832	3	1.688
2 0 4	w	24789	− 15	1.547
2 1 0	v v w	27500	− 5	1.469
2 1 1	v w	28065	− 8	1.454
2 1 2	m	29778	1	1.412
2 0 5	s	29938	23	1.408
1 1 6	w	32229	− 4	1.357
2 1 3	m	32608	− 9	1.349
3 0 0	s	35374	10	1.295
0 0 8	v w	36343	− 4	1.277
2 1 4	m	36583	− 9	1.273
2 1 5	m	41710	7	1.193
1 1 8	w	48130	− 5	1.110

Table 3. X-Ray powder diffraction data for Na_2S_4 at 23°C taken with $CuK\alpha_1$-radiation ($\lambda = 1.54051$ Å) and using $Pb(NO_3)_2$ ($a = 7.8570$ Å) as an internal standard. The accepted (h,k,l)-values satisfy the condition $h + k + l = 2n$.

$h\ k\ l$	I_{obs}	$10^5\sin^2\theta_{obs}$	$10^5\varDelta$	d_{calc}, Å
1 0 1	m	1061	−10	7.443
2 0 0	v v w	2571	−6	4.798
1 1 2	w	2991	−5	4.450
2 1 1	s s	3654	6	4.033
2 0 2	w	4278	−6	3.721
1 0 3	m	4482	−4	3.637
2 2 0	v w	5178	25	3.393
3 0 1	s s	6230	6	3.087
3 1 0	v w	6437	−5	3.033
0 0 4 }	m	6840	10	2.947
2 2 2 }			−21	2.940
2 1 3	s s	7068	6	2.898
3 1 2	s s	8152	3	2.698
3 2 1	w	8805	4	2.596
2 0 4	v w	9414	7	2.511
4 0 0	m	10298	−7	2.399
4 1 1	s	11368	−9	2.283
2 2 4	s	11984	1	2.225
3 2 3	s	12220	4	2.203
4 2 0	v v w	12894	11	2.146
3 1 4 }	w	13285	13	2.114
3 3 2 }			−17	2.112
2 1 5	w	13892	−1	2.066
4 2 2	m	14590	0	2.017
4 1 3	v w	14793	1	2.003
3 0 5	s	16494	25	1.898
4 0 4	m	17157	21	1.861
2 0 6	m	17955	10	1.818
5 1 2	m	18456	1	1.793
3 2 5	m	19060	14	1.764
5 0 3	v v w	19960	15	1.724
4 4 0	s	20613	1	1.697
4 1 5	m	21611	−12	1.656
3 1 6	m	21806	−3	1.649
5 3 0	m	21920	20	1.646
5 2 3	s	22522	0	1.623
5 1 4 }	v w	23584	6	1.586
5 3 2 }			−23	1.585
2 1 7	v w	24158	19	1.568
6 1 1	v w	24287	28	1.564
6 0 2	v w	24878	−18	1.544
5 0 5	v w	26790	15	1.489
3 3 6	v v w	26971	8	1.483
4 4 4 }	v w	27445	3	1.470
6 2 2 }			−21	1.470
6 1 3	s	27679	5	1.464
4 2 6	v w	28251	0	1.449
5 3 4	v v w	28713	−17	1.437
3 2 7	v w	29291	−1	1.423
2 0 8	v v w	29872	−26	1.409

Table 3. Continued.

5 4 3	v w	30239	− 12	1.400
5 1 6	m	32102	− 14	1.359
6 2 4	w	32581	− 14	1.349
6 3 3	w	32860	− 33	1.344
7 1 2	v v w	33929	− 16	1.322
6 4 2⎫ 1 0 9⎭	w	35240	38 17	1.298
5 4 5	w	37076	− 5	1.265
4 0 8⎫ 7 1 4⎭	v w	37657	10 25	1.256 1.233
7 3 2	v w	39061	− 5	1.232
6 3 5	v v w	39648	− 10	1.223
4 2 8	v v w	40199	− 5	1.215
6 5 3	v w	43124	− 9	1.173

Table 4. X-Ray powder diffraction data for Na_2S_5 at 24°C taken with $CuK\alpha_1$-radiation ($\lambda = 1.54051$ Å) and using $Pb(NO_3)_2$ ($a = 7.8572$ Å) as an internal standard.

$h\ k\ l$	I_{obs}	$10^5\sin^2\theta_{obs}$	$10^5\varDelta$	d_{calc}, Å
0 2 0	m	1128	0	7.252
0 1 1	v w	2015	− 5	5.420
1 2 0	v v w	2150	8	5.263
1 0 1	m	2756	5	4.644
1 1 1	s	3037	4	4.422
1 2 1	s	3882	2	3.911
2 0 0	w	4055	0	3.825
0 3 1	s	4275	− 1	3.725
2 1 0	s	4338	1	3.699
0 4 0	m	4521	8	3.626
1 3 1	s	5291	1	3.349
2 0 1	v w	5797	5	3.200
2 1 1	m	6077	3	3.125
2 3 0	m	6594	1	3.000
2 2 1	s	6926	5	2.928
0 5 0	v w	7060	9	2.901
1 4 1	s s	7265	0	2.858
1 0 2	w	7974	9	2.729
1 5 0⎫ 0 2 2⎭	m	8079	− 14 0	2.712 2.710
1 1 2	w	8250	3	2.682
2 3 1	s	8339	8	2.669
2 4 0	v w	8551	− 16	2.632
0 5 1	v w	8786	− 3	2.598
0 6 0	m	10155	1	2.417
2 4 1	m	10306	1	2.399
2 0 2	v w	11014	8	2.322
3 1 1⎫ 1 6 0⎭	v w	11147	4 − 20	2.308 2.305
2 1 2	v v w	11305	17	2.293
3 2 1	m	11993	4	2.225
2 2 2	v w	12131	− 3	2.211
1 4 2	v w	12475	− 2	2.181
2 5 1	m	12848	5	2.149

Table 4. Continued.

2 6 0	m	14217	9	2.043
1 5 2	w	15014	− 2	1.988
3 0 2	v w	16062	− 12	1.921
3 2 1	m	16366	10	1.905
1 1 3	v v w	16932	− 4	1.872
0 6 2	w	17101	− 4	1.862
1 2 3	v w	17802	20	1.827
4 0 1	v w	17945	− 11	1.818
0 8 0	w	18050	− 1	1.813
2 5 2			− 7	1.813
3 3 2	w	18610	− 2	1.785
2 7 1	v v w	19630	18	1.739
2 1 3	w	19978	01	1.723
3 4 2	m	20590	3	1.698
2 6 2	v w	21158	− 1	1.674
1 4 3			3	1.674
2 8 0	v w	22102	− 3	1.638
4 4 1	w	22476	7	1.625
0 5 3	v v w	22685	− 6	1.617
4 5 0	v v w	23272	3	1.597
4 1 2	v w	23468	17	1.591
2 8 1	v w	23844	1	1.577
1 9 0			− 15	1.577
2 4 3	w	24212	5	1.566
0 9 1	v w	24582	− 1	1.554
2 7 2	v w	24829	3	1.546
0 8 2	v w	25018	16	1.540
4 5 1			11	1.540
1 6 3	v w	26794	− 13	1.488
5 1 1	v w	27338	− 23	1.473
4 4 2	v w	27672	− 10	1.464
0 1 4	v v w	28109	22	1.453
4 6 1			− 1	1.453
1 0 4	v w	28807	− 11	1.435
2 8 2	v w	29045	11	1.429
3 4 3	v v w	29260	− 6	1.424
5 4 0	w	29875	21	1.410
3 7 2			− 19	1.409
4 7 0	v v w	30036	− 2	1.405
1 7 3	v w	30466	− 8	1.395
5 4 1	v w	31592	0	1.370
3 5 3	v w	31824	10	1.366
2 10 1	v w	33995	− 2	1.321
3 6 3	v w	34933	17	1.304
6 3 0	v w	39034	4	1.233
5 0 3	w w	40994	13	1.203
6 4 0			− 10	1.203

Metastable phases. We have found a metastable phase for each of Na_2S_4 and Na_2S_5. These are formed from subcooled liquid Na_2S_4 and Na_2S_5, respectively. The metastable phases undergo transitions to corresponding stable phases after some weeks, even at room temperatures. For the metastable phase of Na_2S_4 it was possible to take an X-ray powder photograph, which showed a very large number of diffraction lines and which was quite different from those of the other Na-polysulfide phases.

X-RAY POWDER DIFFRACTION INVESTIGATIONS

Apparatus. Powder photographs were taken with $CuK\alpha_1$-radiation in a Guinier-Hägg type camera ($\lambda = 1.54051$ Å) with $Pb(NO_3)_2$ ($a = 7.8575$ Å at 25°C) as internal standard. To prevent disturbance from moisture, the samples were enclosed between two tapes. Conc. H_2SO_4 was placed in the camera and vacuum applied.

The powder diffraction lines were measured using the technique, described by Hägg,[9] with a scale printed on the film prior to development. The observed values of $\sin^2\theta$ and of relative intensities, I, are given in Tables 2, 3, and 4 for the polysulfides Na_2S_2, Na_2S_4, and Na_2S_5, respectively. The intensities were visually estimated following the 6-fold scale: ss = very strong, s = strong, m = medium, w = weak, vw = very weak, vvw = extremely weak. In Tables 2 − 4 are also given the calculated quantities d_{calc} and $\varDelta = (\sin^2\theta_{obs} - \sin^2\theta_{calc})$.

Indexing. To be able to index the $\sin^2\theta_{obs}$-values for Na_2S_4 and Na_2S_5 a general indexing method was developed. By this method, which is an extension of the method suggested by de Wolff,[10] the indexing procedure can be performed without any *a priori* values of the cell parameters and of the symmetry. The reciprocal cell parameters thus obtained were used in a computer program, PIRUM,[11] for a least-squares refinement of the cell dimensions. Values of the refined cell parameters are given in Table 5 (the errors indicated are 3 standard deviations).

It can be mentioned that many of the $\sin^2\theta$-values obtained for Na_2S_4 can be indexed with a cubic unit cell with $a = 16.64$.

Using observed density values (see Table 5) the number of formula units, Z, in the unit cells were obtained. The densities were determined by means of the flotation method,[12] using mixtures of CCl_4 and $CHBr_3$ as immersion mediums. At a later stage in our work we succeeded in preparing single crystals of Na_2S_4 from ethanol solution. Weissenberg and rotation photographs around [100] and [001] showed the crystals to be tetragonal with the approximate

Table 5. Colour, melting point, density and crystal data for each of the stable phases Na_2S_2, Na_2S_4, and Na_2S_5.

Phase	Colour	Melting-point (°C)	Density (g/cm³)	Crystal symmetry	Formula units	Cell parameters
Na_2S_2	Yellow	482 ± 2	$d_{obs} = 2.02$ $d_{calc} = 2.05$	Hexagonal	$Z = 2$	$a = 4.4869 \pm 0.0005$ Å $c = 10.2210 \pm 0.0015$ Å $V = 178.20$ Å³
Na_2S_4	Olive-green	294 ± 2	$d_{obs} = 2.12$ $d_{calc} = 2.13$	Tetragonal	$Z = 8$	$a = 9.5965 \pm 0.0008$ Å $c = 11.7885 \pm 0.0016$ Å $V = 1085.6$ Å³
Na_2S_5	Brick-red	265 ± 3	$d_{obs} = 2.08$ $d_{calc} = 2.11$	Ortho-rhombic	$Z = 4$	$a = 7.6505 \pm 0.0009$ Å $b = 14.5036 \pm 0.0020$ Å $c = 5.8430 \pm 0.0008$ Å $V = 648.34$ Å³

unit cell dimensions $a = b = 9.60$ Å, $c = 11.79$ Å, which agrees quite well with the results obtained from the powder data (cf. Table 5). However, the occurrence of reflection satellites on the photographs as well as some extra powder diffraction lines may indicate an OD-structure. An extended structural investigation of this phase is in progress.

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