CRYSTALLIZATION OF SULFIDES FROM ALKALI POLYSULFIDE FLUXES

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Alkali polysulfides are solvents suitable for the synthesis of many metal sulfides from the metal and for crystal growth. Crystal plates, $\sim$ 2 cm diameter, of the antiferromagnetic (below 18 K) semiconductor $NaCrS_2$, and during controlled oxidation, crystals of $NaCrO_2$ and Cr_2O_3 have been obtained. CdS prepared from sodium polysulfide solution grows in the form of prisms, pyramids or plates depending on the growth temperature (respectively supersaturation) and added impurities. The CdS plates showed a very high dark resistivity and a strong photoconductivity effect. Other sulfides prepared from sodium polysulfide flux include ZnS, PbS, CuS, α-MnS, NiS_2, CoS_2, FeS_2, $NaInS_2$, $KFeS_2$, MoS_2, LaS_{2-x} and Cu_3VS_4. The sodium content of several sulfides varied from 30 to 450 ppm. Attempts to prepare thiospinels like $CdCr_2S_4$ from alkali polysulfide solvents have so far failed.

1. Introduction

Molten alkali sulfides have been used as solvents by Gaudin for the growth of Al_2O_3 [1]) and by Doelter[2]) (to obtain ZnS tetrahedrons), but these solvents have not found wide application since. However, Garner and White[3]) reported the preparation of small HgS crystals from Na_2S_4 and Na_2S_5 solutions while attempts by Bidnaya et al.[4]) to dissolve and grow CdS from Na_2S and from ammonium sulfides, were not successful.

Chlorides of the heavy metals like $CdCl_2$ and $PbCl_2$ have been used more frequently for the growth of sulfide crystals, although appreciable amounts of chloride may substitute for the sulfide ion since they are similar in size. As was shown by various workers, lead chloride shows good solubility for sulfides and is thus being used in crystal growth of sulfides, comparable to the use of lead fluoride in the growth of oxide crystals.

Increasing demands on purity and perfection of crystals for many applications necessitate the preparation of halide-free crystals, which should thus be grown from halide-free solvents if direct techniques (e.g. growth from stoichiometric melts or by sublimation) fail to result in crystals of the desired size and perfection. Sodium polysulfide melts have proven to be excellent solvents for the preparation and crystal growth of a variety of sulfides, and preliminary results are presented. The advantages of Na_2S_x solvents are the presence of a common anion and the insignificant incorporation of sodium into the grown sulfide crystals.

2. The alkali polysulfide melts

2.1. Li_2S

This system has recently been studied by Sharma[5]). Between Li_2S with a melting point of 1365 °C, and sulfur no further compounds exist. Between the monotectic at 65.5 mole% and 362 °C, and sulfur, a two-liquid region extends to about 850 °C. Using Temkin's model for molten salt mixtures and the calculated activities of Li_2S, Sharma expects species like S_2^{2-} at higher temperatures, towards the Li_2S composition, whereas at lower temperatures, near the monotectic, S_3^{2-} species should be predominant. Although compositions near the monotectic could be used as solvents for crystal growth, there seems to be no published work.

2.2. Na_2S–S

The phase diagram Na_2S–S was published earlier this century[6]) and is reproduced in ref. 3. The liquidus temperature decreases from Na_2S (978 °C) to the eutectic with Na_2S_4 at 69 wt% S and 230 °C, and the melting points and eutectics of Na_2S_4, Na_2S_5 and Na_2S_6 lie between 230 and 300 °C.

The potential application of a sodium–β-alumina–sulfur battery in automobiles prompted systematic investigations of the sodium polysulfide melts. Electrical conductivity and the electrode processes have been studied by Cleaver et al. and by South et al.[7]), and Cleaver and Davies[8]) reported on density, surface tension, viscosity and cryoscopy of Na_2S–S melts and

proved the existence of polysulfide ions in the sodium polysulfide melts; the sulfur activities of Na_2S_3, Na_2S_4 and Na_2S_5 melts are 0.04, 0.2 and 0.9, respectively.

The polysulfides of the larger alkali ions have not been investigated in detail; they are also potential solvents although the tendency of compound formation increases with ionic radius.

3. Experimental

As starting materials, the hydrated sodium sulfide $Na_2S \cdot 9H_2O$ (Merck), high-purity sulfur and the appropriate metal, generally as coarse powder, were used in the open system. For the pressure system Na_2S_4 was premelted from $Na_2S \cdot 9H_2O$ and sulfur, and was dried at about 350 to 400 °C.

The hydrated sodium sulfide decomposes by losing water at 48 °C. Above 110 °C its structure consists of a nearly octahedral configuration of six water molecules around the sodium ions, and chains of these octahedra are connected by hydrogen bonds with sulfide ions surrounded by 12 H_2O molecules [Bedlivy and Preisinger[9]]. By dehydration, the hydrate shell is successively reduced and replaced by Na–S bonds[9]. Absolutely dry sodium polysulfides are prepared from the elements dispersed in boiling toluene following a recipe by Cleaver et al.[7]).

Pyrex and silica containers as reported earlier[3,7]) are not adequate in the temperature range of 400–1000 °C when used for the crystallization of the sulfides. Instead, alumina and mullite-based ceramics were used in our experiments. The crucible of 60 mm diameter, filled with the metal, $Na_2S \cdot 9H_2O$ and S and covered with a lid was placed into a simple commercial muffle furnace as shown diagrammatically in fig. 1. Occasionally, a baffle was used in order to reduce the dissolution and reaction at the beginning of the experiments. The space around and above the crucible is filled with coarse corundum powder in order to reduce the oxidation of the melt by air. During heating, excess sulfur evaporates and removes residual oxygen and water by reaction to SO_2 and H_2S, respectively, thus requiring the furnace to be placed in a hood with good ventilation.

The temperature is set by a variable transformer which is connected to a stabilized power supply, and the thermocouple shown in fig. 1 is used to record the temperature. Cooling is adjusted by a motor driven variable transformer, the cooling rates being 5–25 °C/
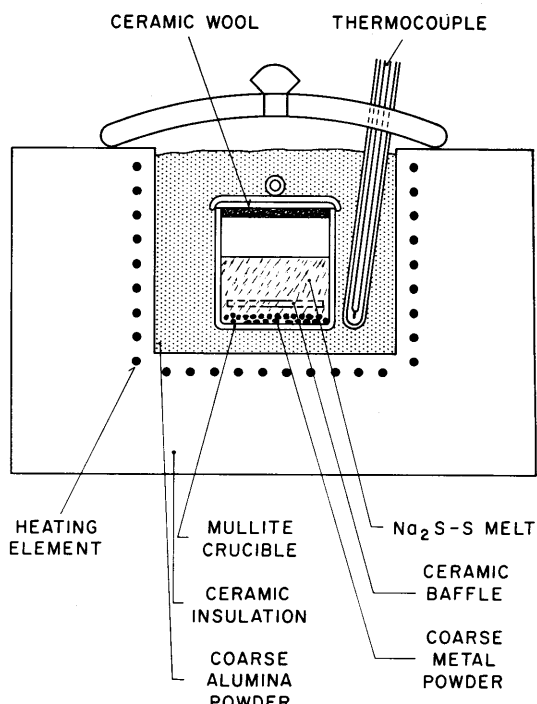

Fig. 1. Arrangement of crucible with alkali polysulfide melt in the muffle furnace.

hr. After cooling to room temperature, the sodium polysulfide is dissolved in cold water in order to separate the metal sulfide crystals; the poisonous sulfide is removed by aqueous $KMnO_4$ solution or precipitated with $ZnCl_2$ solution.

Several metal sulfides like those of the rare earths, Nb and Ta, could not be obtained by this simple technique and had to be prepared in an oxygen-free atmosphere. Premelted Na_2S_4 or Na_2S_5 were used in this case, and a pressure apparatus described by Robertson et al.[10]) was applied for argon pressures of 4–10 atm.

4. Crystal growth experiments

4.1. $NaCrS_2$ ($NaCrO_2$, Cr_2O_3), $KCrS_2$, $NaInS_2$

Sodium chromium sulfide has been prepared by Schneider[11]) in 1873, by melting a chromium compound in sodium carbonate or Na_2CO_3–K_2CO_3 melts with excess sulfur, and by slow cooling. This procedure has been used by Rüdorff and Stegemann[12]) and is described in the handbook of Hecht[13]). However, experiments by several crystal growers including ones from this laboratory, showed that the growth of large $NaCrS_2$ crystals would be extremely difficult from carbonate

melts. On the other hand, with the following procedure, using sodium polysulfide as solvent, large $NaCrS_2$ crystals are easily obtained.

Coarse chromium powder (4.5 g) is placed on the bottom of the crucible, then 10 g sulfur is added and at the top 60 g $Na_2S \cdot 9H_2O$. The crucible is closed with a 2 mm thick plate of ceramic wool which just fits into the crucible, covered with a ceramic lid, and placed into the arrangement of fig. 1. The furnace is heated to 1000 ± 30 °C, held at temperature for 2 hr, and then cooled at 25 °C/hr to 300 °C at which temperature the power is shut off. After dissolution of the solvent in water hexagonal plates of $NaCrS_2$ of 2 to 20 mm diameter and of 0.1 to 1 mm thickness, were obtained. The crystals show metallic reflectivity and small transparency in the red for platelets of about 1 μm thickness. $NaCrS_2$ exhibits antiferromagnetic ordering at 18 K, and the antiferromagnetic phase diagram and an anomalously large band gap shift near the Néel temperature have been measured by Blazey and Rohrer[14]).

$NaCrS_2$ slowly decomposes at room temperature in air. The decomposition at high temperatures starts after crystal growth, especially when the temperature of the growth system is held above 1000 °C for extended times. In that case, sizeable crystals of $NaCrO_2$ and Cr_2O_3 are obtained.

Pure $NaCrS_2$ is relatively soft; this fact in combination with easy cleavage parallel (001), makes sample machining very difficult. By doping with silver, brittle $NaCrS_2$ crystals were prepared, and the analyses of several different crystals indicate a solubility of 2.25 $\pm$ 0.25 % Ag for the growth conditions given.

Large sodium indium sulfide $NaInS_2$ crystals are prepared similarly, except that the maximum temperature has to be lower, i.e. about 750 to 800 °C. Potassium chromium sulfide $KCrS_2$ is obtained when potassium sulfide is used instead of $Na_2S \cdot 9H_2O$, and a maximum temperature of 1000 °C should be applied.

4.2. CdS

Cadmium sulfide has been synthesized and grown from various solvents: from $CdCl_2$ by Durocher[15]), from K_2CO_3 by Schüler[16]), from $CaCl_2$–CaF_2–BaS by Deville and Troost[17]), from metal halides by Viard[18]), from $CdCl_2$ by Bidnaya et al. and by Haworth and Lake[19]), from $PbCl_2$ by Linares[20]), from metals by Harsy and by Rubenstein[21]) and from cadmium by

Lorenz and by Hemmat and Weinstein[22]). However, other crystal growth techniques, from the melt and from the vapour phase [Kaldis[23])], have been favoured because of the unsatisfactory quality of the flux-grown CdS crystals. Cadmium sulfide grown from metallic solution is non-stoichiometric (sulfur deficiency), and CdS grown from halide solvents contains appreciable amounts of incorporated halide ions. By using Na_2S_x fluxes, better crystal quality is expected because of the common anion and because of the high sulfur activity in the Na_2S_x melts (with x larger than 4) which minimises non-stoichiometry.

For the growth of CdS 1.5 g Cd, 60 g $Na_2S \cdot 9H_2O$ and 20 g S are placed into a crucible arrangement as described above. The furnace is heated in about three hours to 700 °C and kept at that temperature for three hours; it is then cooled by approximately 25 °C/h to room temperature. After dissolving the sodium polysulfide, prisms of $10 \times 1 \times 1$ mm and hexagonal plates of $4 \times 4 \times 0.1$ mm were obtained. The growth conditions show an appreciable effect on the habit of the CdS crystals. At growth temperatures below 720 °C prisms are formed from pure Na_2S_x flux; above 750 °C thin hexagonal plates are favoured. Growth of thin prisms is also found at high cadmium to solvent ratios, and replacement of $Na_2S \cdot 9H_2O$ by K_2S as well as addition of lead (→ PbS) favours formation of pyramids and of prisms of more than 1 mm diameter.

The observations concerning flux-grown CdS crystals may be compared with the results of flux growth of ZnS by Parker and Pinnell[24]) who obtained feathery crystals from KCl flux at 789 °C, plates at 810 °C and tetrahedrons at 850 °C. An explanation of the habit modifications observed in flux growth of sulfides has not yet been found.

The degree of supersaturation (influenced by the growth temperature through rate of metal dissolution, transport of CdS^{x-}_{1+x} complexes and evaporation of sulfur) and the effect of impurities at the growing faces, are the most likely causes of habit modification.

The temperature dependence of the morphology of vapour-grown CdS was studied by Boyd and Shivonen[25]), and Bulakh[26]) claimed a relation of the habit on the element ratio Cd:S in front of the growing crystal and on the growth temperature. He made the assumption that the degree of supersaturation which presumably depends on the equilibrium ratio of different

TABLE 1

Sulfides prepared from alkali polysulfide fluxes

	Sodium impurity* (ppm)	Habit, size (mm)	Structure type, space group	ASTM No.
$NaCrS_2$		Hex. plates, $20 \times 20 \times 0.2$	$\alpha\text{-}NaFeO_2$, R$\bar{3}$m	10-292
$NaInS_2$		Hex. plates, $15 \times 15 \times 0.2$	$\alpha\text{-}NaFeO_2$, R$\bar{3}$m	—
$KCrS_2$		Hex. plates, $2 \times 2 \times 0.1$	$\alpha\text{-}NaFeO_2$, R$\bar{3}$m	10-290
$KFeS_2$	210	Prisms, $10 \times 0.2 \times 0.2$	chain structure, C2/c	3-103
CdS	30–160	Prisms, $15 \times 1 \times 1$; Hex. plates, $3 \times 3 \times 0.1$	wurtzite, P6_3mc	6-0314
CuS	450	Plates, $2 \times 2 \times 0.1$	covellite, P6_3/mmc	6-464
ZnS	35	Tetrahedra, 1	sphalerite, F$\bar{4}$ 3m	5-566
ZnS	35	< 1	wurtzite, P6_3mc	12-688
$\alpha\text{-}MnS$		< 1	NaCl, type, Fm3m	6-0518
PbS	195	Cubes, 1	NaCl, type, Fm3m	5-592
FeS_2	65	Pentagon. dodecahedra, $3 \times 3 \times 2$	pyrite, Pa3	6-0710
CoS_2		Octahedra, 1	pyrite, Pa3	3-0772
NiS_2		Octahedra, 1	pyrite, Pa3	11-99
NbS_2		Plates, 2×0.2	hexagonal	—
MoS_2		Plates	molybdenite, C6/mmc	17-744
LaS_{2-x}		< 1		16-688, 16-689
Cu_3VS_4		~ 1	sulvanite, P$\bar{4}$ 3m	11-104

* The analyses of sodium by neutron activation analysis were kindly provided by Dr. L. Rybach (ETH Zurich); in CdS the sodium was determined by emission spectometry and by flame photometry.

Cd_xS_y complexes, is responsible for habit modifications. Kaldis[23]) demonstrates in his review on growth of CdS crystals by sublimation and chemical vapour transport, the morphology dependence from growth temperature, iodine concentration and growth rates. He also showed that nucleation and growth rates of CdS can be controlled by optimizing the conditions of growth from vapour, whereas this goal has not yet been achieved in flux growth.

Our crystals of CdS were light yellow, very brittle and showed a high dark resistivity not so far observed in vapour or melt-grown crystals. Platelets of CdS gave dark resistivities of 10^{11} to 6×10^{12} Ω cm which in the light of a focused 30 V lamp, decreased by factors of 10^4 to 1.5×10^5. Chemical analyses gave 30 to 160 ppm sodium impurities. The role of alkalis in CdS has been discussed by Tell[27]) who was not able to unravel the effect of various alkalis alone.

In case of codoping with donors, sodium acts as "acceptor" but all experiments to prepare p-CdS were unsuccessful.

Possibly the high resistivity of our sodium doped flux-grown CdS crystals is due to substitutional sodium introducing an acceptor level in the crystal, in analogy to the high resistivity found in Li-doped ZnO where substitutional Li is known to act as acceptor. Upon

irradiation, a hole is trapped at a nearest neighbour oxygen, which was established by ESR absorption experiments of Schirmer[28]).

Polycrystalline CdS is used as a photoconductor, photoresistor and for other optoelectronic purposes and thus is produced in relatively large quantities. According to Weisbeck[29]) several steps in the fabrication process are necessary in order to obtain CdS material of homogeneous doping and crystallite size. Instead one ought to consider the polysulfide solvents for direct preparation of doped crystalline CdS powder or layers[30]), with metallic cadmium or any cadmium compound as a starting material and with the addition of the appropriate dopants. Habit and size of the crystallites are controlled by the degree of supersaturation and agitation. Although cubic CdS may be precipitated from aqueous solutions as was shown by Jackson[31]), experiments to prepare cubic CdS from Na_2S_x solutions failed, even at temperatures below the transition range of 310 to 370 °C reported by Hartmann[32]).

4.3. OTHER SULFIDES CRYSTALLIZED FROM Na_2S_x SOLUTIONS

In addition to the crystals already discussed, in table 1 further sulfides are listed which have been crystallized from sodium polysulfide solutions, generally as small

crystals in preliminary experiments. The appropriate metal, $Na_2S \cdot 9H_2O$ and sulfur were used as starting materials with the exception of $KFeS_2$ where K_2S had been added to the flux. All sulfides have been synthesized in the temperature range of 400 to 1000 °C in the arrangement of fig. 1, except for NbS_2 and LaS_{2-x} which have been prepared under argon pressure as described above. The latter sulfide was not homogeneous, the X-ray powder diagram showed $LaS_{1.75-1.80}$(ASTM 16-698) and $LaS_{1.94}$(ASTM 16-688). The sulfides were identified by X-ray powder diagrams obtained with the focusing Guinier–De Wolff camera and by comparison with the ASTM X-ray powder diffraction file.

As in the case of $NaCrS_2$, other experiments at high temperatures and long running times produced oxides, for instance $NaNbO_3$, $NaTaO_3$, SnO_2 and ZrO_2. Experiments to synthesize sulfides of spinel type failed so far. Using Cd and Cr in the Na_2S_x melts, only CdS and $NaCrS_2$ formed in the temperature range investigated (500–900 °C) instead of the desired $CdCr_2S_4$.

5. Discussion

Sodium polysulfide melts have been demonstrated to be suitable solvents for the growth of crystals as proven for the examples of $NaCrS_2$, CdS and $NaInS_2$. A fairly general applicability of the alkali polysulfides for the preparation of metal sulfides is evident.

By optimizing the experimental conditions the sulfides given in table 1 and others can, presumably, be grown to larger sizes than the crystals obtained in our preliminary experiments. Many sulfides show features of unstable growth like dendrites and inclusions which are undoubtedly due to the fast cooling rates used. Sulfur evaporation has to be kept small and the temperature program for maximum stable growth rates[33] be applied in order to achieve control of nucleation and stable growth.

Generally, metal sulfides of high oxidation states are obtained which is explained by the high activity of sulfur in the polysulfide melts and by the relatively low growth temperatures. The use of alkali polysulfides other than Na_2S_x reported here is suggested, as is the extension to the corresponding selenide systems.

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