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CRYSTAL GROWTH OF SULFIDE MATERIALS FROM ALKALI POLYSULFIDE LIQUIDS

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ABSTRACT

The fluids experiment system has been designed for low temperature solution growth, nominally aqueous solution growth. The alkali polysulfides, compositions in the systems $\text{Na}_2\text{S-S}$ and $\text{K}_2\text{S-S}$ form liquids in the temperature range of 190 to 400°C. These can be used as solvents for other important classes of materials such as transition metal and other sulfides which are not soluble in aqueous media. Among these materials are luminescent and electroluminescent crystals whose physical properties are sensitive functions of crystal perfection and which could, therefore, serve as test materials for perfection improvement under microgravity conditions.

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INTRODUCTION

Crystal growth from solvents has conventionally been divided into three "techniques": solution growth, in which the system pressure is atmospheric or thereabouts and the temperature ranges up to 100°C or a little more; hydrothermal growth, in which the use of confining pressure of 100 or more MPa allows aqueous solutions to be used at temperatures of several hundred degrees centigrade, and flux growth, in which the pressure is again ambient, but the solvent is a fused salt and growth takes place at temperatures above 600 - 800°C. Solution growth and flux growth, although identical in form and process, are regarded as separate crystal growth techniques because of the large gap in temperature between the top of the operating range of water and organic solvents in open systems and the bottom of the flux range dictated by the 600 - 800°C melting points of the fused salts.

The Fluids Experiment System has been devised for experiments with solution growth (among other things) and depends on optical systems to record and transmit information about the crystal growth process. Conventional flux systems are unsuitable not only because of the high temperatures involved but also because thermal emission and the optical opacity of many of the solvents would preclude the optical observations that are at the core of the system design.

The criteria for crystal growth in space should include the following: (i) the crystals should be of technological importance; (ii) the properties that make the crystal important should depend in a sensitive way on crystal perfection. Growth in microgravity conditions is not likely to be a cost-effective way of improving elemental purity, for example. Crystals whose optimum performance demands low dislocation densities, absence of voids and inclusions, absence of segregated impurities on dislocations and grain boundaries, are the ones to which research efforts should be directed. Such properties as dielectric loss, luminescence, domain switching, and electrical conductivity meet these criteria.

The number of materials whose solubility in aqueous or organic solvents is such that solution growth is feasible is somewhat limited. There would be an advantage to extending the range of crystal growth experiments by extending the temperature range and extending the list of useful solvents.

This paper discusses the potential for crystal growth from alkali polysulfide solvents. These are liquids whose composition can be continuously varied by changing alkali-to-sulfur ratios and with liquidus temperatures in the range of 200 - 400°C. Their potential application is to chalcogenide materials, of which those intended for electroluminescent display application might be of immediate interest.

ALKALI POLYSULFIDE LIQUIDS

The alkali sulfides K_2S and Na_2S have melting points in the range of 900°C and as such could be used as molten salt solvents in normal flux growth although little use seems to have been made of them. They are normally available in hydrated form and the difficulty in eliminating the water may have discouraged their use as fluxes. When sulfur is added to the alkali sulfides, there is a dramatic lowering of the liquidus surface (Figure 1). There is formed a distinct series of polysulfides, some of which melt congruently in the range of 250 to 450°C. As Figure 1 indicates, there is some disagreement about the details of the phase diagram but the existence of Na_2S_2 , Na_2S_3 , Na_2S_4 , and Na_2S_5 seems to be certain. Equivalent phases exist in the K_2S -S system although no phase diagram was found in the literature.

The polysulfides provide a wide range of low-melting liquids of varying properties. By using eutectic compositions, melting points as low as 200°C can be achieved.

The Fluids Experiment System is designed around various optical systems to monitor the growth of crystals and therefore requires the use of transparent solvents. The alkali sulfides are colorless and form transparent liquids. Addition of sulfur to form the polysulfide liquids imparts a yellow color, but the liquids appear to be transparent. More data on this point are needed.

Viscosities have been measured on liquids in the Na_2S -S system by Cleaver and Davies [3] (Figure 2) as a function of temperature and composition. It can be seen that the viscosity varies by about a factor of four over the temperature range that would be used for crystal growth and that the viscosity

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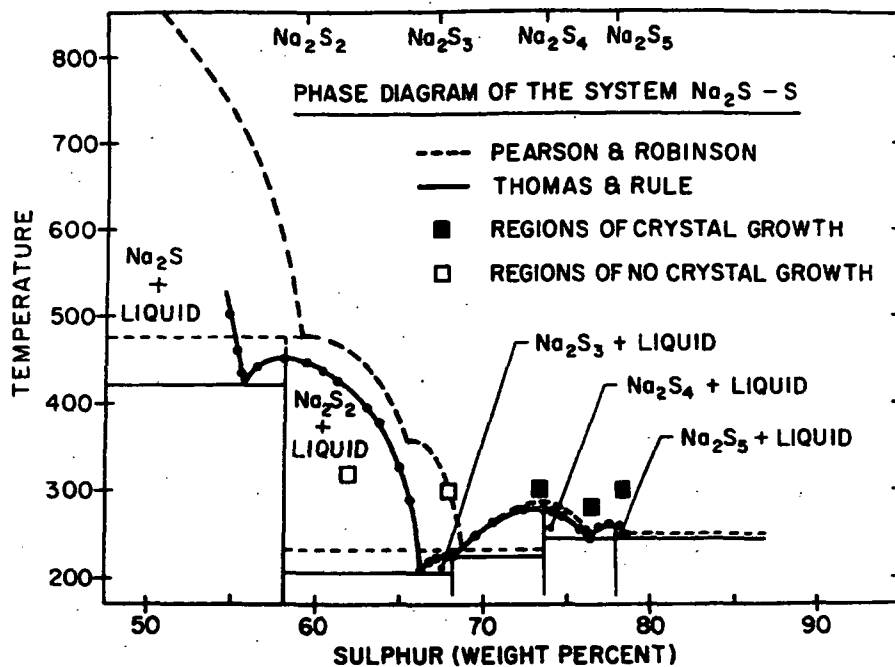


Figure 1. Phase diagram for the system $\text{Na}_2\text{S}-\text{S}$. Compiled from data in references [1] and [2].

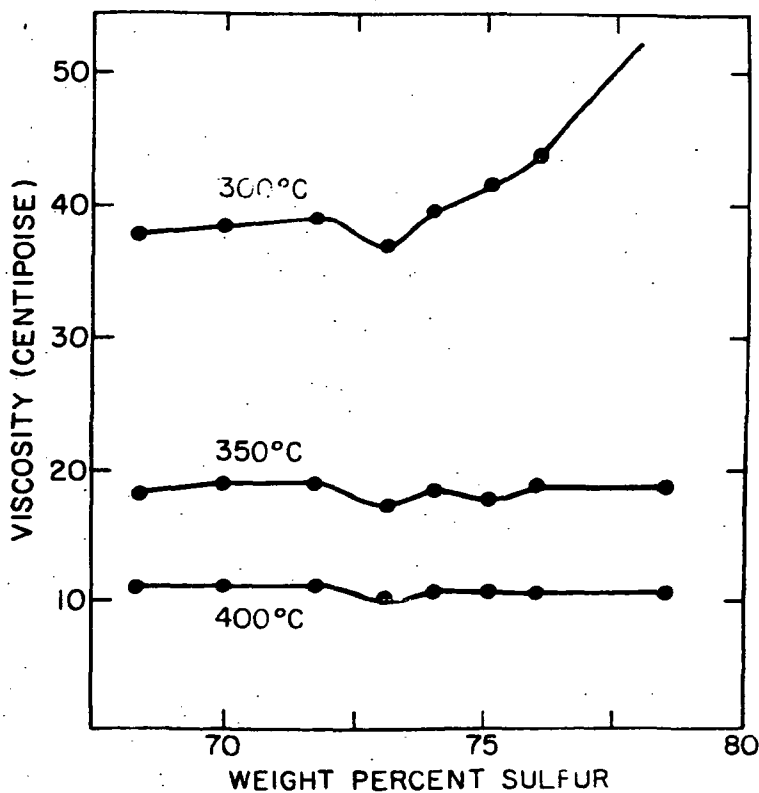


Figure 2. Viscosity of $\text{Na}_2\text{S}-\text{S}$ melts calculated from [3].

is remarkably independent of composition especially at the higher temperatures. The viscosity data indicate that fluid motion in a growth cell will be qualitatively similar to fluid motion of aqueous solutions at lower temperatures. The electrical conductivity data of Cleaver et al. [4] suggest that these are ionic liquids, not network structures, in spite of the polymerization of the sulfur groups. Further data on liquid structure would also be useful.

CRYSTAL GROWTH

If the alkali polysulfides are to be used as low temperature fluxes, two criteria must be met: (1) There must be an extensive liquid range between the polysulfide composition and material to be grown. In this range the liquidus should vary smoothly to permit uniform growth by slow cooling, and there should be no compounds formed between the flux liquid and the material to be grown; (2) The liquids should be "good" fluxes. This latter criterion is difficult to state specifically because it is not clear just what properties PbO , PbF_2 , Bi_2O_3 , alkali tetraborates, etc. possess that makes them such universal solvents for flux growth of crystals at higher temperatures. One criterion, perhaps, is that the material to be grown should not form complexes with the liquid. The energy necessary to break up the complexes acts as an additional barrier to crystal growth, raises the necessary supersaturation, and thus increases the possibility of spontaneous nucleation of many small crystals rather than continuous growth of a few large crystals.

Few data are available on the solubilities of materials in the alkali polysulfide liquids. One demonstrated case where crystals can be grown from these liquids is that of mercuric sulfide [5]. The phase relations (Figure 3) show a smooth liquidus curve giving a good range from crystal growth. Mercuric sulfide occurs in two polymorphic forms: cinnabar, a deep red optically active material is stable below $344^\circ C$; metacinnabar, a black semiconductor with the sphalerite structure, is stable at higher temperatures. The phase relations given in Figure 3 show that it is possible to grow the low temperature form over the specified temperature-composition interval without formation of metacinnabar.

The likely candidates for crystal growth from alkali polysulfide liquids are binary and ternary sulfides of various kinds. Figure 4 illustrates some solubility data for four transition metal monosulfides replotted from the

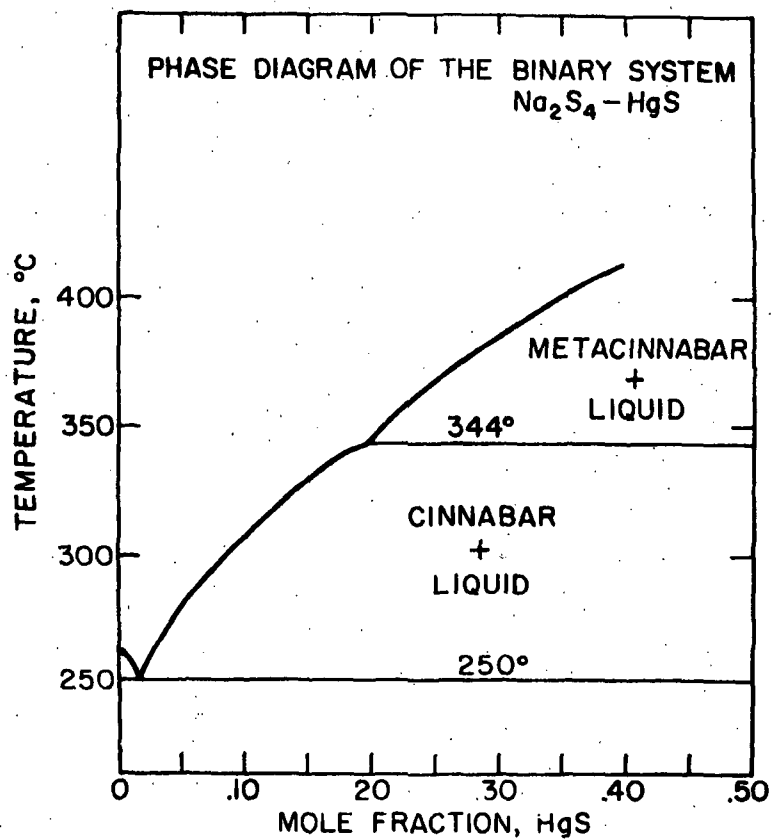


Figure 3. Phase diagram along the join $\text{Na}_2\text{S}_4\text{-HgS}$ in the ternary system Na-Hg-S. Adapted from [5].

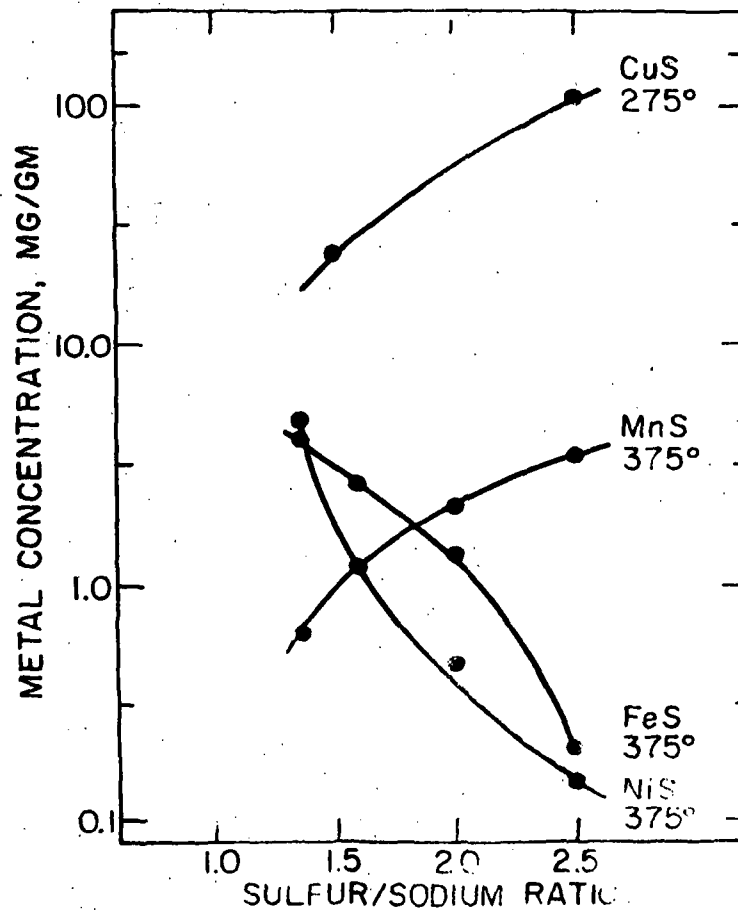


Figure 4. Solubility curves (at temperatures shown) for transition metal sulfides in $\text{Na}_2\text{S-S}$ melts as a function of melt composition. Adapted from [6].

solubility data of Bailey and Skeaff [6]. Of the four compounds chosen for investigation, two have direct and two have retrograde solubility as a function of the sulfur/sodium ratio in the melt. Melt composition is obviously important and could be chosen to give the greatest solubility. The solubility of CuS is about an order of magnitude higher than the solubility of MnS, FeS, and NiS at the optimum flux composition. Certainly the Na_2S_5 -CuS join meets the first criterion for crystal growth.

DEVELOPMENT OF SULFIDE GROWTH EXPERIMENTS

Let us return now to the statement made in the introduction. The number of substances that are suitable for growth from low temperature aqueous solutions and at the same time are of strong technological interest is quite limited. The overall design concept for the Fluids Experiment System suggests 400 to 500°C as an absolute upper limit beyond which optical systems could not be used because of the thermal radiation background. This paper suggests that there is at least one family of solvents from which crystals could be grown in the intermediate temperature range. However, knowledge of these systems is very primitive and two categories of research and development would be required before such growth experiments in microgravity could be contemplated.

The present Fluids Experiment System was designed to operate only to 100°C with a possible extension to 200°C. It would be necessary to review the FES design to determine whether it could be adapted for operation at higher temperatures without complete redesign of the system.

The case for the alkali polysulfide melts as growth media is predicated on the idea that these liquids could be used to grow complex sulfides among which are important luminescent and electrooptic materials for which a high degree of crystal perfection would be desired. Research necessary before prototype growth experiments could be designed include

1. Determination of phase equilibria in the K_2S -S system where lower melting liquids might be expected.
2. Determination of the optical properties of the liquids, particularly absorption in the visible regions.
3. Determination of solubility curves for selected binary and ternary sulfides as a function of temperature and polysulfide liquid composition.

4. Experiments to determine cooling regimes necessary to produce single crystals of selected materials.
5. Optimization of crystal growth conditions in ground-based experiments.
6. Determination of the crystal perfection of materials obtained from solution growth as compared with alternative preparation techniques such as melt growth or chemical vapor deposition.

Only after these steps have been taken could a final materials selection be made and a growth-in-space experiment designed.

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