

## Phase Studies and Hydrothermal Syntheses in the System Mercury Sulfide-Manganese Sulfide

A. PAJACZKOWSKA\* AND A. RABENAU†

*Max-Planck-Institut für Festkörperforschung, 7 Stuttgart 80, Germany*

Received December 6, 1976

$\beta$ -HgS forms solid solutions with MnS while retaining the sphalerite structure. The solubility limit as determined from lattice constant measurements is 37.5 mole% MnS at 600°C. No detectable solubility of HgS in rocksalt type MnS was observed. Small single crystals 0.1 to 2.0 mm in size of  $\alpha$ -HgS,  $\text{Hg}_{1-x}\text{Mn}_x\text{S}$ ,  $\alpha$ -MnS, and  $\gamma$ -MnS were obtained by hydrothermal syntheses in aqueous solutions of HCl/H<sub>2</sub>S, NH<sub>4</sub>Cl, and NH<sub>4</sub>SCN.

### 1. Introduction

Investigations of the systems ZnS-MnS (1) and CdS-MnS (2, 3) have been reported in the literature. In both cases MnS has an extended range of solubility in the respective group IIB sulfide. In this paper results on the HgS-MnS system are given together with hydrothermal growth experiments.

The tetrahedral structure ( $\beta$ -HgS, sphalerite), common to IIB sulfides, is stable at high temperatures and transforms to the red cinnabar structure ( $\alpha$ -HgS) at 345°C (4). The melting point of  $\beta$ -HgS is reported to be 825°C (4). The equilibrium pressure at this temperature as calculated from the curve of solubility of HgS in Hg (5) is about 70 bar.

Manganese sulfide occurs in three modifications: the stable green  $\alpha$ -MnS with rocksalt structure and two pink metastable tetrahedral structures,  $\beta$ -MnS (sphalerite type), and  $\gamma$ -MnS (wurtzite type). The melting point of  $\alpha$ -MnS is given as 1610°C (6).

Crystals of  $\alpha$ -HgS have been obtained by hydrothermal syntheses, e.g., from HCl solutions (7, 8) and Na<sub>2</sub>S solutions (9). Chemical

transport reactions have been used to grow  $\alpha$ -MnS above 800°C (10).  $\gamma$ -MnS crystals have been obtained from silica gels (11).

### 2. Experimental Methods

Finely powdered  $\alpha$ -HgS and  $\alpha$ -MnS (99.9 Cerac) were thoroughly mixed in molar ratios and pressed into pellets at a pressure of approximately 13 kbar. Coarse pieces of the pellets were introduced into fused silica ampoules, avoiding free space as much as possible in order to decrease the influence of the vapor phase formed during annealing. The evacuated and sealed ampoules were subjected to heat treatments at 300 and then 600°C each for 3 days. After each cycle the samples were quenched in water. The sintered material was ground, examined by powder diffraction, and again pressed into pellets. The samples were assumed to be in equilibrium if in two successive cycles no changes in the lattice constants were observed. A few additional cycles were run with the maximum temperature of 300°C, the region of stability of  $\alpha$ -HgS (cinnabar).

Lattice constants were determined by X-ray powder technique, using Ni-filtered CuK $\alpha$  radiation. Silicon was used as a standard (Si,  $a_0 = 5.43086 \text{ \AA}$ ). The uncertainty in the

\* On leave from Institute of Physics, Polish Academy of Sciences, 02-668 Warsaw, Al. Lotnikow 32/46, Poland.

† Author to whom correspondence should be addressed.

TABLE I  
HYDROTHERMAL EXPERIMENTS:  $\text{Hg}_{1-x}\text{Mn}_x\text{S}^a$

Run	Starting materials (mole %)	Solvent	Degree of fill (%)	Temperature (°)	Time (days)	Remarks
1	100 $\alpha$ -HgS	1 M HCl saturated $\text{H}_2\text{S}$	30	470	3	$\alpha$ -HgS $\leq$ 0.1 mm
2	100 $\alpha$ -HgS	5 wt % $\text{NH}_4\text{Cl}$ + 5 wt % $\text{NH}_4\text{SCN}$	30	470	3	$\alpha$ -HgS $\leq$ 0.1 mm
3	90 $\alpha$ -HgS + 10 $\alpha$ -MnS	5 wt % $\text{NH}_4\text{Cl}$ + 5 wt % $\text{NH}_4\text{SCN}$	30	470	3	$\text{Hg}_{0.92}\text{Mn}_{0.08}\text{S} \leq$ 0.1 mm
4	80 $\alpha$ -HgS + 20 $\alpha$ -MnS	5 wt % $\text{NH}_4\text{Cl}$ + 5 wt % $\text{NH}_4\text{SCN}$	30	470	3	$\text{Hg}_{0.82}\text{Mn}_{0.17}\text{S} \leq$ 0.1 mm
5	70 $\alpha$ -HgS + 30 $\alpha$ -MnS	5 wt % $\text{NH}_4\text{Cl}$ + 5 wt % $\text{NH}_4\text{SCN}$	30	470	3	$\text{Hg}_{0.80}\text{Mn}_{0.20}\text{S} \leq$ 0.1 mm
6	60 $\alpha$ -HgS + 40 $\alpha$ -MnS	5 wt % $\text{NH}_4\text{Cl}$ + 5 wt % $\text{NH}_4\text{SCN}$	30	470	3	$\text{Hg}_{0.70}\text{Mn}_{0.30}\text{S} \leq$ 0.1 mm + $\alpha$ -MnS
7	50 $\alpha$ -HgS + 50 $\alpha$ -MnS	5 wt % $\text{NH}_4\text{Cl}$ + 5 wt % $\text{NH}_4\text{SCN}$	30	470	3	$\text{Hg}_{0.69}\text{Mn}_{0.31}\text{S} \leq$ 0.1 mm + $\alpha$ -MnS
8	50 $\alpha$ -HgS + 50 $\alpha$ -MnS	5 wt % $\text{NH}_4\text{Cl}$ + 5 wt % $\text{NH}_4\text{SCN}$	30	470	10	$\text{Hg}_{0.69}\text{Mn}_{0.31}\text{S} \leq$ 2 mm + $\alpha$ -MnS
9	70 $\alpha$ -HgS + 30 $\alpha$ -MnS	1 M HCl saturated $\text{H}_2\text{S}$	70	370	3	$\text{Hg}_{0.84}\text{Mn}_{0.16}\text{S} \leq$ 0.1 mm + $\alpha$ -MnS
10	70 $\alpha$ -HgS + 30 $\alpha$ -MnS	5 wt % $\text{NH}_4\text{Cl}$	70	370	3	$\text{Hg}_{0.84}\text{Mn}_{0.16}\text{S} \leq$ 0.1 mm + $\alpha$ -MnS + $\gamma$ -MnS
11	70 $\alpha$ -HgS + 30 $\alpha$ -MnS	5 wt % $\text{NH}_4\text{Cl}$ + 5 wt % $\text{NH}_4\text{SCN}$	70	370	3	$\text{Hg}_{0.84}\text{Mn}_{0.16}\text{S} \leq$ 0.1 mm + $\alpha$ -MnS

<sup>a</sup> Sphalerite-type solid solution.

TABLE II  
HYDROTHERMAL EXPERIMENTS: FORMATION OF  $\gamma$ -MnS

Nutrient	Solvent wt % $\text{NH}_4\text{Cl}$	Degree of fill (%)	Temperature (°)	Time (days)	Remarks
$\alpha$ -MnS	3, 5 <sup>a</sup> , 8, 20, 30	30 <sup>a</sup> , 70	250, 370, 470 <sup>a</sup>	3, 10 <sup>a</sup>	Nutrient = $\alpha$ -MnS, platelets of $\gamma$ and $\alpha$ -MnS on the wall (approximately 1:1)
$\beta$ + $\gamma$ -MnS	5	30	470	3	Nutrient = $\alpha$ -MnS, platelets of $\gamma$ and $\alpha$ -MnS on the wall (approximately 1:1)
	5	70	470	3	
	5	30	250	3	

<sup>a</sup> Best conditions for  $\gamma$ -MnS crystals,  $\leq$  0.2 mm.

measurements was calculated by means of the least-squares method.

The technique described in detail by Rabenau and Rau (12) was used for hydrothermal syntheses. Experimental data are given in Tables I and II. Besides  $\alpha$ -MnS and  $\alpha$ -HgS, a mixture of  $\beta$ -MnS and  $\gamma$ -MnS was used as starting material, the latter being obtained by coprecipitation (13). The composition of the mixed crystals was derived from the lattice constants and confirmed by atomic absorption analysis and electron microprobe. A precession camera and a single-crystal diffractometer were used for the identification of the crystals obtained by hydrothermal syntheses. For an estimation of  $T$ - $P$ - $C$ - $V$  values, data of solvents, published by Ikornikova, were considered (14).

### 3. Results

#### *X-Ray Measurements*

Whereas the sphalerite phase of pure  $\beta$ -HgS could not be quenched, it was found to be possible for the solid solution  $\text{Hg}_{1-x}\text{Mn}_x\text{S}$ . The measurements could, therefore, be performed at room temperature.

With increasing manganese content the lattice parameter  $a_0$  of the  $\text{Hg}_{1-x}\text{Mn}_x\text{S}$  sphalerite type mixed crystal was observed to decrease (Fig. 1). The linearity of the curve is in accord with Vegard's law. From the extrapolated value of the curve and the  $a_0$  value in the two-phase region the limit of solubility is found to be 37.5 mole% MnS at

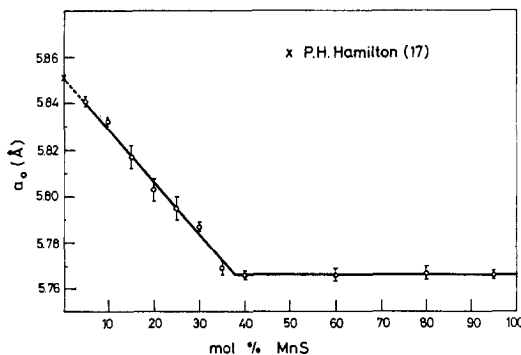


FIG. 1. Lattice parameter vs composition in the HgS–MnS system at 600°C.

600°C. Within the limits of error no change of the lattice parameter of rocksalt type MnS was observed, indicating a negligible solubility of HgS in  $\alpha$ -MnS.

The results of the 300°C annealing experiments within the stability range of  $\alpha$ -HgS are not included in Fig. 1. Changes in lattice parameters were within the limits of error. Since the lines of  $\alpha$ -MnS disappeared after annealing in the 5 and 10 mole% MnS sample but were detectable at 20 mole% MnS, it can be concluded that the solubility limit for cinnabar,  $\alpha$ -HgS, is around 10 mole% MnS.

Two types of crystals were formed in the hydrothermal experiments with pure MnS (Table II): platelets,  $\leq 0.2$  mm which were orange-yellow in transmitting light, and green platelets and pyramids  $\leq 0.5$  mm. The orange-yellow crystals proved to be  $\gamma$ -MnS (wurtzite type) grown along the  $c$  axis, some of them being twinned. The green crystals were  $\alpha$ -MnS (rocksalt type). Both platelets and pyramids exhibit [111] faces. The lattice parameters are in agreement with literature data (15). No crystals of  $\beta$ -MnS (sphalerite type) were observed.

#### *Hydrothermal Syntheses of Mixed Crystals*

The experiments show (Table I) that hydrothermal syntheses and growth of mixed crystals of different compositions within the range of solid solution  $\text{Hg}_{1-x}\text{Mn}_x\text{S}$  is possible. An aqueous solution of 5 wt%  $\text{NH}_4\text{Cl}$  + 5 wt%  $\text{NH}_4\text{SCN}$  proved to be a suitable solvent. As in the case of the dry process the sphalerite phase is retained although the cooling rate is much slower. Again, the pure phase  $\beta$ -HgS could not be obtained (runs 1 and 2). The composition of the mixed crystal was found to be different from that of starting material. The experiments show, however, that a relation must exist between the composition of the liquid phase and that of the corresponding mixed crystal (runs 3–8). Under these conditions the limit of solubility is found to be 31 mole% MnS. The kind of solvent seems to have no influence on the liquid–solid equilibrium (runs 9–11). It is more probable, however, that the temperature has an influence on the equilibrium (run 11 as com-



FIG. 2. Crystals of  $\text{Hg}_{0.7}\text{Mn}_{0.3}\text{S}$ ; mm scale.

pared with run 5).<sup>1</sup> Although no efforts have been made to optimize the size of the crystals, run 8 compared with run 7 shows that longer heat treatment results in larger crystals (Fig. 2).

<sup>1</sup> In order to get comparable pressures at the temperatures involved, the degree of fill has to be adapted.

#### *Hydrothermal Syntheses of $\gamma\text{-MnS}$*

During the hydrothermal experiments metastable  $\gamma\text{-MnS}$  (wurtzite type) was occasionally observed (Table I, run 10). In order to clarify the situation runs with the pure  $\text{MnS}$  phases were made. The most significant results of these experiments are summarized in Table II. Aqueous solutions of  $\text{NH}_4\text{Cl}$  as solvents

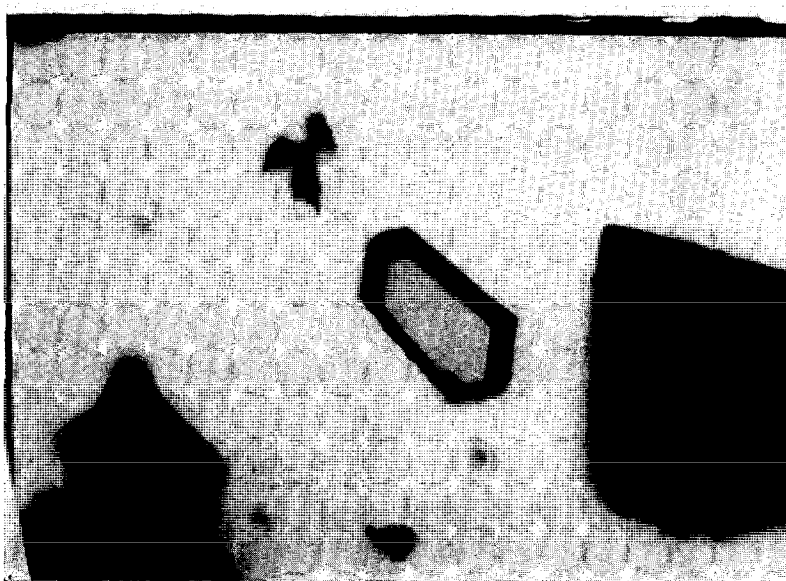


FIG. 3. Crystal of  $\gamma\text{-MnS}$ ; 0.1 mm in length.

showed this effect. After the experiments, the walls of the ampoule in the somewhat colder part above the nutrient were covered with platelets of  $\alpha$ -MnS and  $\gamma$ -MnS in approximately the same amount. The remaining part of the nutrient was always  $\alpha$ -MnS, either from the beginning or by transformation of  $\beta$ - and  $\gamma$ -MnS into  $\alpha$ -MnS. The formation of  $\gamma$ -MnS crystals did not seem to be quantitatively influenced by the nutrient ( $\alpha$ -,  $\beta$ -,  $\gamma$ -MnS), the concentration of the  $\text{NH}_4\text{Cl}$  solution, the degree of fill, or the temperature. The quality and size of the crystals (Fig. 3), however, depends on these conditions.

#### 4. Discussion

With this work the last of three IIB sulfide–manganese sulfide systems has been investigated. A discussion of the phase studies should also include, therefore, the systems ZnS–MnS and CdS–MnS. At 600°C the IIB element can be replaced by manganese to 43, 44.3, and 37.5 at% for ZnS (1), CdS (3), and HgS, respectively, while retaining a tetrahedral structure of the  $\text{IIB}_{1-x}\text{Mn}_x\text{S}$  solid solution. The quantitative difference in these figures may be understood by comparing the ionic radii of the IIB elements with that of manganese. MnS is least soluble in HgS since the Hg radius matches least favorably the Mn radius. The tetrahedral coordination which manganese exhibits in these solid solutions is not found for the stable form  $\alpha$ -MnS which has a rocksalt structure but is realized in two metastable modifications,  $\beta$ -MnS, sphalerite type, and  $\gamma$ -MnS, wurtzite type. This coordination is stabilized, however, in the IIB sulfide host lattice and this stabilization is maintained to a high manganese content, as shown by the figures.

A detectable solubility of the IIB sulfide in the rocksalt-type manganese sulfide has been observed only for CdS. It has been found to 6 mole% CdS in  $\alpha$ -MnS at 600°C and increases strongly with increasing temperature (3). Cadmium is the only IIB element for which an octahedral coordination in chalcogenides has been observed. For example, for the high-pressure phase of CdS

(16) as well as for CdO under normal conditions, both have the rocksalt structure. This may be the reason for the exceptional situation in the CdS–MnS system.

Nothing is known yet about the physical properties of the solid solution  $\text{Hg}_{1-x}\text{Mn}_x\text{S}$ . Such measurements require crystals of defined composition. It could be shown that hydrothermal syntheses in an aqueous solution of  $\text{NH}_4\text{Cl} + \text{NH}_4\text{SCN}$  fulfills this necessary requirement. This method has the advantage that it allows crystal syntheses and growth at temperatures below 500°C. In this way experimental difficulties can be avoided due to the increasing decomposition pressure of mercury sulfide at higher temperatures.

The formation of crystals of the metastable wurtzite ( $\gamma$ -MnS) modification under hydrothermal conditions has up to now been observed only in pure  $\text{NH}_4\text{Cl}$  solutions. The crystals grow from the solution, that is, from that part of the nutrient which has been dissolved together with crystals of  $\alpha$ -MnS. In the case for which the nutrient consists of  $\beta$ -MnS and  $\gamma$ -MnS, the undissolved part has transformed to  $\alpha$ -MnS. It is, therefore, unlikely that  $\gamma$ -MnS is the stable phase under these conditions. The occurrence of metastable phases under hydrothermal conditions has been reported occasionally. Christensen and Brccch (18) obtained metastable rhombohedral  $\text{In}_2\text{O}_3$  in the system  $\text{In}_2\text{O}_3\text{--H}_2\text{O--Na}_2\text{O}$ . Also in this case, it was not possible to draw conclusions from the experiments as to how parameters should be chosen to avoid the formation of the stable modification.  $\gamma$ -MnS crystals have also been grown in sodium silicate gels (11). The authors conclude that this phase is stabilized by the incorporation of silicon. In the hydrothermal experiments the addition of silicon had no influence on the results. At the present state of investigations the growth of metastable  $\gamma$ -MnS is still an open question.

#### References

1. R. JUZA, A. RABENAU, AND G. PASCHER, *Z. Anorg. Allg. Chem.* **285**, 61 (1956).
2. H. WIEDEMEIER AND A. KHAN, *Trans. Met. Soc. AIME* **242**, 1969 (1968).

3. W. R. COOK, JR., *J. Amer. Ceram. Soc.* **51**, 518 (1968).
4. G. KULLERUD, Carnegie Institute, Washington, *Yearbook* **64**, 194 (1964-65).
5. A. PAJACZKOWSKA AND Z. DZIUBA, *J. Crystal Growth* **11**, 21 (1971).
6. ZEN-ICHI SHIBATA, *Techn. Repts., Tohoku Imp. Univ.* **7**, 279 (1928).
7. H. RAU AND A. RABENAU, *Solid State Commun.* **5**, 331 (1967).
8. A. PAJACZKOWSKA, *J. Crystal Growth*, **7**, 93 (1970).
9. S. D. SCOTT AND H. L. BARNES, *Mat. Res. Bull.* **4**, 897 (1969).
10. H. WIEDEMEIER AND A. G. SIGAI, *J. Crystal Growth* **6**, 67 (1969).
11. A. SCHWARTZ, A. TAUBER, AND J. R. SHAPPIRO, *Mat. Res. Bull.* **2**, 375 (1967).
12. A. RABENAU AND H. RAU, in "Inorganic Syntheses," Vol. XIV (A. Wold and J. K. Ruff, Eds.), p. 160, McGraw-Hill, New York (1973).
13. H. LUX, in "Handbuch der Präparativen Anorganischen Chemie" (G. Brauer Ed.), p. 1270, F. Enke, Stuttgart (1962).
14. N. JU. IKORNIKOVA, "Gidrotermalniy Sintez Kristallov w Chloridnykh Sistemach," Nauka, Moskva (1975).
15. F. MEHMED AND H. HARALDSEN, *Z. Anorg. Allgem. Chem.* **235**, 193 (1938).
16. W. L. ROTH, in "Physics and Chemistry of II-VI Compounds" (M. Aven and J. S. Prener, Eds.), p. 135, Wiley, New York (1967).
17. P. H. HAMILTON, *Semiconductor Prod. Solid State Technol.* **7**, 15 (1964).
18. A. N. CHRISTENSEN AND N. C. BROCH, *Acta Chem. Scand.* **21**, 1046 (1967).