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Phase Equilibria in the Systems ZnS–MnS, ZnS–CuInS_2, and MnS–CuInS_2

C. SOMBUTHAWEE,* S. B. BONSALL,† AND F. A. HUMMEL

Ceramic Science and Engineering Section, Materials Science and Engineering Department, The Pennsylvania State University Park, University Park, Pennsylvania 16802

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Using high purity ZnS, MnS, Cu_2S, and In_2S_3, the binary systems were examined between 400 and 1300°C using evacuated fused silica capsules to contain intermediate mixtures. X-Ray and microscopic examination of samples at room temperature permitted the probable phase relations to be established. The extent of the very important stability regions for zinc blende and wurtzite solid solutions was firmly established and in the system MnS–CuInS_2, the stability fields for the intermediate γ-MnS (wurtzite) solid solutions and CuInS_2 solid solutions were determined.

I. Introduction

The determination of the phase relationships in the binary systems ZnS–MnS, ZnS–CuInS_2, and MnS–CuInS_2 was motivated by the fact that certain compositions containing all three end members will produce yellow, orange, and maroon pigments of commercial quality. The yellow and orange pigments are candidates for the replacement of pigments based on the toxic CdS which has been a standard for many years. The phase relations were determined as an aid to the selection of composition, preparation, and processing of these pigments.

II. Literature

A. ZnS

The literature on ZnS is so extensive that it need not be reviewed here. The unit cell of zinc blende is face-centered cubic with $a = 5.4093$, space group $F\bar{4}3m$.[1] The transition to wurtzite occurs at 1020°C (*1*).

Wurtzite is a hexagonal[1] space group *C6mc* with lattice parameters $a_0 = 3.811$ and $c_0 = 6.234$. It melts at 1850°C at 150 atm (*2*). It can be converted to sphalerite if ground in a mortar (*3*).

B. MnS

Alabandite (or α-MnS) is the stable form of MnS (*4*). It is green, has the rocksalt structure with $a = 5.2236$ Å, and melts at 1600 ± 10°C.

β-MnS is a metastable red form which has the structure of cubic zinc blende with $a = 5.600$ Å. γ-MnS is a metastable red form which has the structure of hexagonal wurtzite with $a_0 = 3.976$ Å and $c_0 = 6.432$ Å. The metastable forms can be stabilized by formation of solid solutions with ZnS and CdS (*5*).

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* Miss C. Sombuthawee is now enrolled as a Ph.D candidate at Alfred University, Alfred, N. Y.

† Mr. S. B. Bonsall is in the research laboratory, North American Refractories Company, Curwensville, Pa.

[1] Wyckoff, "Crystal Structures," 2nd ed., Vol. I, Interscience, New York (1965).

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C. $CuInS_2$

$CuInS_2$ has the chalcopyrite structure[1] which is tetragonal, but its structure is essentially a superlattice on that of zinc blende with $a_0 = 5.517$ Å and $c_0 = 11.06$ Å (*6*). It can be obtained by direct reaction of Cu_2S and In_2S_3 by heat treatment at 900°C/48 hr (*7*).

In recent years, there has been a great interest in the I–III–VI_2 sulfides as semiconductors (*8*), thin films, and other uses. Many of these involve $CuInS_2$ (*9–14*) and other chalcopyrites. Even more recently the interest in chalcopyrites (*15–17*) has extended to structures of the II–IV–V_2 type such as $ZnSiP_2$ and $ZnGeP_2$.

D. ZnS–MnS

Kröger (*18*) found that solid solutions of MnS and ZnS (wurtzite) using KCl as a flux, extended to 52% MnS at 1180°C thereby lowering the zinc blende $\rightleftarrows$ wurtzite transition.

Juza *et al.* (*19*) prepared mixtures of ZnS and MnS either by precipitation or from the solid components by heating at 600°C. Compositions containing up to 10% MnS were solid solutions of the blende type, those containing 10–43% MnS were solid solutions of the wurtzite type and above 43% MnS, crystals of the NaCl and wurtzite type coexisted.

Bethke and Barton (*20*) reported that a miscibility gap appeared at about 50 mole% between manganese-bearing wurtzite and MnS (NaCl structure). The limit of zinc blende stability was approximately 7 mole% MnS at 600°C.

E. ZnS–$CuInS_2$

Solid solutions in the system ZnS and $CuInS_2$ were prepared and studied crystallographically by Robbins and Miksovsky (*21*). All samples were prepared from appropriate mixtures of Cu, In, S, and ZnS. The mixtures were pressed into pellets, sealed in evacuated silica tubes, and heated at the rate of 10–20°C/hr between room temperature and 1200°C. The final temperature was maintained for 48 hr; then the power to the furnace was shut off and the ampoules were allowed to cool to room temperature. The addition of ZnS to $CuInS_2$ caused a decrease in cation ordering, resulting in a chalcopyrite–zinc blende transition at ~33 mole% ZnS. The presumably narrow region of two-phase coexistence was not delineated.

F. MnS–$CuInS_2$

No previous data could be found.

III. Experimental Procedure

High purity (at least 99.9%) ZnS, MnS, In_2S_3, and Cu_2S were used to make batches of 0.5 g which were weighed to an accuracy of 0.1 mg. Compositions were mixed in acetone in an agate mortar, dried in air, and encapsulated *in vacuo*. To accelerate reactions below 600°C, a salt flux with a mole ratio of 42KCl:58LiCl was used in some compositions.

A 20-c length of fused silica tubing (inside diameter 0.5 cm, wall thickness 1–2 mm) was sealed at one end by an oxygas flame, 0.5–0.1 g of batch was placed in the tube, and alumina wool was inserted in the tube above the sample. The wool prevented loss of sample during evacuation and overheating of the sample during sealing. Narrow capillaries were drawn just above the alumina wool, the open end was connected to a Welch Duo-Seal pump and evacuated for 1–2 min. With the pump running, the capillary was sealed off in the flame.

A. Heat Treatment

The capsules were placed in Thermolyne furnaces when the temperatures were below 1000°C, Globar furnaces when the temperatures were between 1000–1200°C, or a quench furnace when the temperatures were above 1200°C. The rate of heating was 10–20°C/hr to the desired equilibrium temperatures, which ranged from 310 to 1330°C.

Equilibirum times ranged from 15 min to 1 month.

Different quenching techniques were used to prevent explosion of the capsules. The general method used for temperatures under 1200°C (except those in the system ZnS–MnS), was to remove the capsule from the furnace with tongs and plunge in cold water. Samples heated above 1200°C were quenched in water directly from the quench furnace. For compositions in the system ZnS–MnS, samples heated to 850°C or below could be quenched by the general method, but those heated above 850°C were allowed to cool to room temperature in the furnace. It was found that these compositions could not be quenched in water from above 850°C without exploding.

Nickel filtered Cu*Kα* radiation from a Norelco X-ray diffractometer was used to identify phases present after the sample was quenched. Scanning was done in the range $2\theta = 60–20°$ at 1°/min. For measuring the solid solution limits, which relies on measurable shifts with compositions in the *d*-spacing of one or more X-ray peaks, scanning was done at $\frac{1}{4}$°/min.

IV. Results and Discussion

A. The System ZnS–MnS

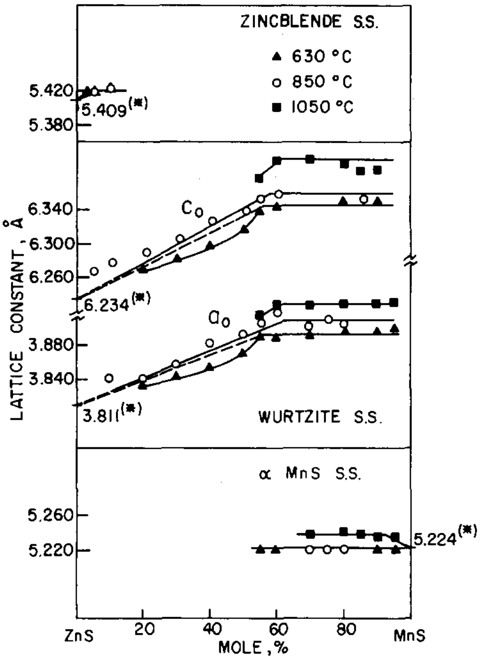

FIG. 2. Variation of room temperature lattice parameters with composition of zinc blende, wurtzite, and α-MnS solid solutions in the system ZnS–MnS after quenching from 1050, 850, and 630°C. [* refers to Wyckoff, "Crystal Structures," 2nd ed., Vol. I, Interscience, New York (1965)].

The diagram shown in Fig. 1 is based on the data given in Table I. The lattice constants shown in Fig. 2 indicate that only limited solubility exists between zinc blende and MnS rocksalt structure. At 630°C, about 5% MnS is soluble in zinc blende and at 1050°C, about 8% ZnS is soluble in MnS.

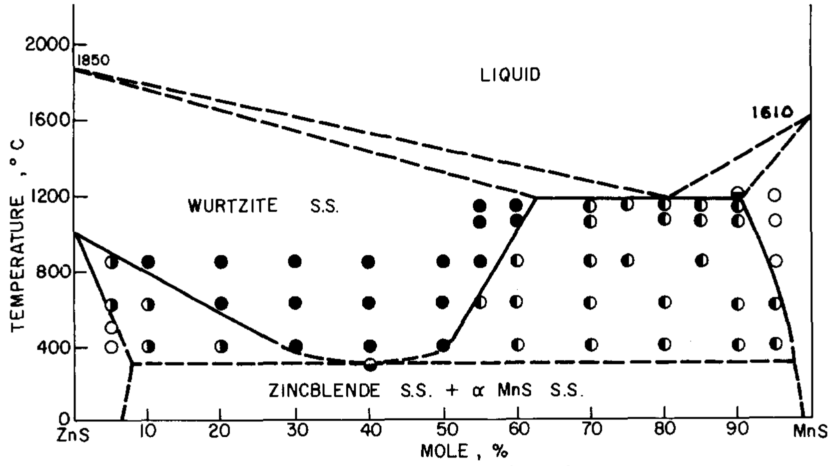

FIG. 1. The system ZnS–MnS.

TABLE I

COMPOSITIONS, HEAT TREATMENTS, AND PHASES PRESENT IN THE SYSTEM ZnS–MnS

Composition (mole% MnS)	Heat treatment (°C)	Phases present	Color
+ 1% flux	400/20 days	Zinc blende s.s.	Light cream
5	500/7 days	Zinc blende s.s.	Light cream
	630/72 hr	Zinc blende s.s. + wurtzite s.s.	Light cream
	850/72 hr	Zinc blende s.s. + wurtzite s.s.	Light cream
10 + 1% flux	400/20 days	Zinc blende s.s. + wurtzite s.s.	Cream
10	630/72 hr	Zinc blende s.s. + wurtzite s.s.	Cream
	850/72 hr	Wurtzite s.s.	Cream
20 + 1% flux	400/20 days	Zinc blende s.s. + wurtzite s.s.	Cream
20	630/72 hr	Wurtzite s.s.	Cream
	850/72 hr	Wurtzite s.s.	Cream
30 + 1% flux	400/20 days	Wurtzite s.s.	Cream
30	630/72 hr	Wurtzite s.s.	Cream
	850/72 hr	Wurtzite s.s.	Cream
40 + 2% flux	310/30 days	Zinc blende s.s. + wurtzite s.s. + α-MnS s.s.	Cream
40 + 1% flux	400/20 days	Wurtzite s.s.	Orange
40	630/72 hr	Wurtzite s.s.	Orange
	850/72 hr	Wurtzite s.s.	Orange
50 + 1% flux	400/20 days	Wurtzite s.s.	Orange
50	630/72 hr	Wurtzite s.s.	Orange
	850/72 hr	Wurtzite s.s.	Orange
55	650/72 hr	Wurtzite s.s. + α-MnS s.s.	Brownish orange
	850/72 hr	Wurtzite s.s.	Orange
	1075/½ hr	Wurtzite s.s.	Orange
	1150/½ hr	Wurtzite s.s.	Orange
60 + 1% flux	400/20 days	Wurtzite s.s. + α-MnS s.s.	Orange
60	630/72 hr	Wurtzite s.s. + α-MnS s.s.	Orange brown
	850/72 hr	Wurtzite s.s. + α-MnS s.s.	Orange
	1075/½ hr	Wurtzite s.s.	Orange
	1150/½ hr	Wurtzite s.s.	Orange
70	630/72 hr	Wurtzite s.s. + α-MnS s.s.	Brown
	850/72 hr	Wurtzite s.s. + α-MnS s.s.	Brown
	1075/½ hr	Wurtzite s.s. + α-MnS s.s.	Brown
	1150/½ hr	Wurtzite s.s. + α-MnS s.s.	Orange
75	850/72 hr	Wurtzite s.s. + α-MnS s.s.	Light brown
	1150/½ hr	Wurtzite s.s. + α-MnS s.s.	Brown
80	630/72 hr	Wurtzite s.s. + α-MnS s.s.	Green
	1080/2 hr	Wurtzite s.s. + α-MnS s.s.	Brown
	1150/½ hr	Wurtzite s.s. + α-MnS s.s.	Brown
85	850/72 hr	Wurtzite s.s. + α-MnS s.s.	Brown
	1080/2 hr	Wurtzite s.s. + α-MnS s.s.	Brown
	1150/½ hr	Wurtzite s.s. + α-MnS s.s.	Brown
90 + 1% flux	400/20 days	Wurtzite s.s. + α-MnS s.s.	Greenish brown
90	630/72 hr	Wurtzite s.s. + α-MnS s.s.	Greenish brown
	1080/2 hr	Wurtzite s.s. + α-MnS s.s.	Brown
	1150/½ hr	Wurtzite s.s. + α-MnS s.s.	Brown
	1200/½ hr	α-MnS s.s. + liquid	Green
95 + 1% flux	400/20 days	Wurtzite s.s. + α-MnS s.s.	Green
95	630/72 hr	Wurtzite s.s. + α-MnS s.s.	Green
	850/72 hr	α-MnS s.s.	Green
	1080/2 hr	α-MnS s.s.	Dark green
	1200/½ hr	α-MnS s.s.	Dark green

The outstanding feature of the diagram is the very large region of wurtzite solid solution which extends to about 60% MnS at 1050°C. It is apparently stable over a wide temperature range from 400°C to the subsolidus temperatures indicated in the diagram. One composition containing 40% MnS and 60% ZnS was held for a month at 310°C in the presence of 2% LiCl–KCl flux. The composition contained mainly wurtzite, but some zinc blende and some rocksalt MnS were also present indicating that either (1) equilibrium was probably not yet achieved, or (2) that 310°C is very close to the true eutectoid temperature where all three phases should coexist.

The lattice constants show a variation with the temperature of heat treatment and quenching temperature, increasing with temperature as might be expected. The variation of a_0 and c_0 with composition at 850°C is reasonably linear. At 650°C, considerable variation from linearity is observed, probably due to incomplete reaction and poor crystallinity.

B. The System ZnS–CuInS$_2$

The diagram shown in Fig. 3 is based on the data given in Table II. Additions of CuInS$_2$ to ZnS have little effect on the zinc blende ⇄ wurtzite inversion temperature up to 20% CuInS$_2$. At 30–40% CuInS$_2$, there is a definite increase in the transition temperature. The lattice parameters of the zinc blende and wurtzite solid solutions are shown in Fig. 4. The wurtzite parameters show a considerable deviation from linearity. Due to the difficulty of differentiating zinc blende and chalcopyrite, Robbins and Miksovsky (*21*) did not accurately determine the upper limit of the zinc blende solid solution and merely suggested a transition region in the neighborhood of 33% ZnS. The same difficulty was experienced in this work and the limit of 80% CuInS$_2$ must be regarded as tentative.

The melting point of CuInS$_2$ has not been reported. Attempts were made to obtain a reasonable figure for the solid ⇋ liquid transition by special experiments in sealed silica tubes. After eight attempts, the melting point was estimated to be around 1265°C. At 1280°C, the sample had obviously been liquid and at 1260°C, the sample was sintered to a very hard condition making further grinding extremely difficult.

The extent of solid solution of ZnS in CuInS$_2$ is uncertain and is either small or negligible. The a_0 and c_0 lattice parameters shown in Fig. 4 are inconsistent, but collectively they suggest an increase over the

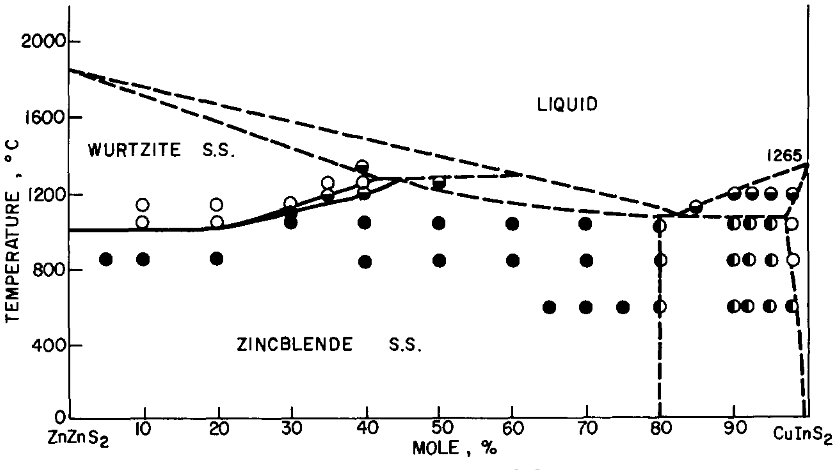

FIG. 3. The system ZnS–CuInS$_2$.

TABLE II

COMPOSITIONS, HEAT TREATMENTS AND, PHASES PRESENT IN THE SYSTEM ZnS–$CuInS_2$

Composition (mole% $CuInS_2$)	Heat treatment (°C)	Phases present	Color
5	850/72 hr	Zinc blende s.s.	Bright yellow
10	850/72 hr	Zinc blende s.s.	Yellow
	1050/72 hr	Wurtzite s.s.	Yellow
	1150/2 hr	Wurtzite s.s.	Yellow
20	850/72 hr	Zinc blende s.s.	Orange
	1050/72 hr	Wurtzite s.s.	Orange
	1150/2 hr	Wurtzite s.s.	Orange
30	850/72 hr	Zinc blende s.s.	Dark red
	1050/72 hr	Zinc blende s.s.	Dark red
	1100/2 hr	Zinc blende s.s.	Reddish brown
	1150/2 hr	Wurtzite s.s.	Reddish brown
35	1200/½ hr	Zinc blende s.s. + wurtzite s.s.	Reddish brown
	1250/¼ hr	Wurtzite s.s.	Reddish brown
40	850/72 hr	Zinc blende s.s.	Brown
	1050/72 hr	Zinc blende s.s.	Brown
	1200/½ hr	Zinc blende s.s. + wurtzite s.s.	Brown
	1250/½ hr	Wurtzite s.s.	Brown
	1330/¼ hr	Wurtzite s.s. + liquid	Brown
50	850/72 hr	Zinc blende s.s.	Brown
	1050/72 hr	Zinc blende s.s.	Brown
	1250/¼ hr	Zinc blende s.s. + liquid	Brown
60	850/72 hr	Zinc blende s.s.	Black
	1050/72 hr	Zinc blende s.s.	Black
65	600/72 hr	Zinc blende s.s.	Black
70	600/72 hr	Zinc blende s.s.	Black
	850/72 hr	Zinc blende s.s.	Black
	1050/72 hr	Zinc blende s.s.	Black
75	600/72 hr	Zinc blende s.s.	Black
80	600/72 hr	Zinc blende s.s. + $CuInS_2$ s.s.	Black
	850/72 hr	Zinc blende s.s. + $CuInS_2$ s.s.	Black
	1050/72 hr	Zinc blende s.s. + $CuInS_2$ s.s.	Black
85	1150/½ hr	$CuInS_2$ s.s. + liquid	Black
90	600/72 hr	Zinc blende s.s. + $CuInS_2$ s.s.	Black
	850/72 hr	Zinc blende s.s. + $CuInS_2$ s.s.	Black
	1050/72 hr	Zinc blende s.s. + $CuInS_2$ s.s.	Black
92	600/72 hr	Zinc blende s.s. + $CuInS_2$ s.s.	Black
	850/72 hr	Zinc blende s.s. + $CuInS_2$ s.s.	Black
	1050/72 hr	Zinc blende s.s. + $CuInS_2$ s.s.	Black
95	600/72 hr	Zinc blende s.s. + $CuInS_2$ s.s.	Black
	850/72 hr	Zinc blende s.s. + $CuInS_2$ s.s.	Black
	1050/72 hr	Zinc blende s.s. + $CuInS_2$ s.s.	Black
	1200/½ hr	$CuInS_2$ s.s. + liquid	Black
98	600/72 hr	Zinc blende s.s. + $CuInS_2$ s.s.	Black
	850/72 hr	$CuInS_2$ s.s.	Black
	1050/72 hr	$CuInS_2$ s.s.	Black
	1200/½ hr	$CuInS_2$ s.s. + liquid	Black
100	1200	$CuInS_2$	Black
	1120	$CuInS_2$	Black
	1180	$CuInS_2$	Black
	1230	$CuInS_2$	Black
	1250	$CuInS_2$	Black
	1260	$CuInS_2$	Black
	1280	$CuInS_2$ s.s. + liquid	Black

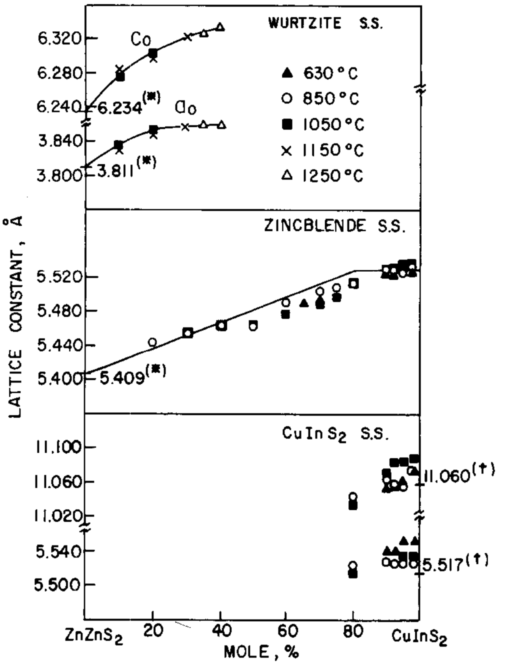

FIG. 4. Variation of room temperature lattice parameters with composition of zinc blende, wurtzite, and $CuInS_2$ solid solutions in the system ZnS–$CuInS_2$ after quenching from five temperature levels. [†, Ref. (*21*).]

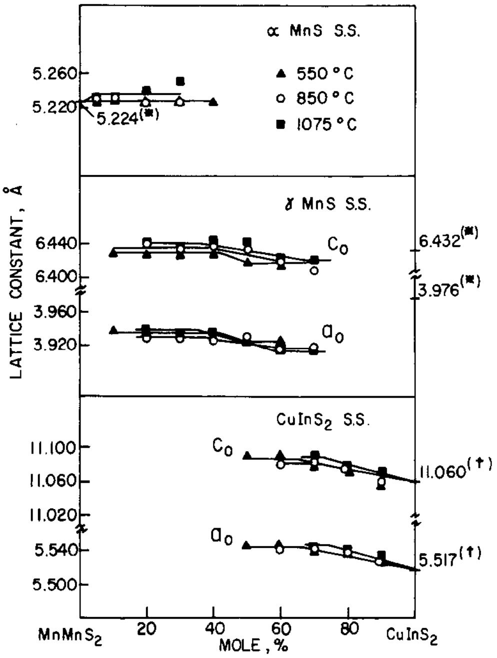

FIG. 6. Variation of room temperature lattice parameters with composition of α-MnS, γ-MnS, and $CuInS_2$ solid solutions in the system MnS–$CuInS_2$ after quenching from 1075, 850, and 550°C. [* refers to Wyckoff, "Crystal Structures," 2nd ed., Vol. I, Interscience, New York (1965; † to Ref. (*21*).]

parameters for pure $CuInS_2$ (in the range from 0–5% $ZnZnS_2$).

C. The System MnS–$CuInS_2$

The diagram shown in Fig. 5 is based on the data given in Table III. The lattice constants of the rocksalt MnS solid solution, the intermediate γ-MnS or wurtzite solid solution and the relatively large region of $CuInS_2$ (chalcopyrite) solid solution are shown in Fig. 6. The unusual stabilization of the wurtzite

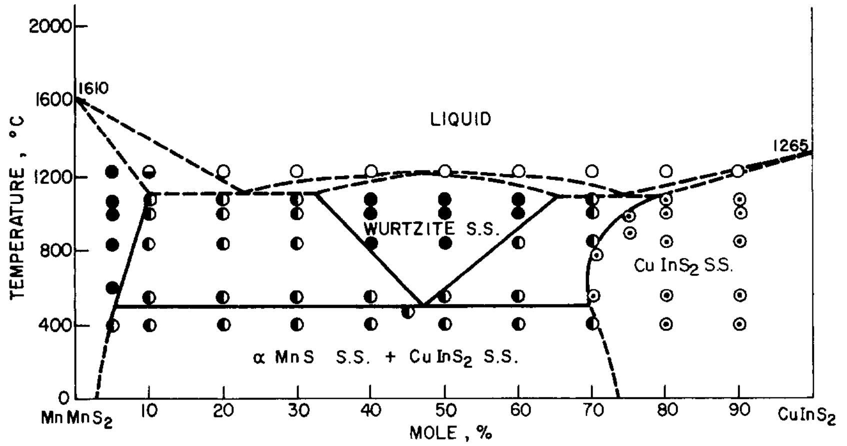

FIG. 5. The system MnS–$CuInS_2$.

TABLE III

Compositions, Heat Treatments, and Phases Present in the System MnS–$CuInS_2$

Composition (mole% $CuInS_2$)	Heat treatment (°C)	Phases present	Color
5	400/12 days	α-MnS s.s. + $CuInS_2$ s.s.	Green
	600/72 hr	α-MnS s.s.	Dark green
	850/45 hr	α-MnS s.s.	Black
	1020/2 hr	α-MnS s.s.	Black
	1050/2 hr	α-MnS s.s.	Black
	1230/½ hr	α-MnS s.s.	Black
10	400/12 days	α-MnS s.s. + $CuInS_2$ s.s.	Dark green
	550/92 hr	α-MnS s.s. + γ-MnS s.s.	Black
	850/45 hr	α-MnS s.s. + γ-MnS s.s.	Black
	1020/2 hr	α-MnS s.s. + γ-MnS s.s.	Black
	1075/2 hr	α-MnS s.s. + γ-MnS s.s.	Black
	1220/2 hr	α-MnS + liquid	Black
20	400/12 days	α-MnS s.s. + $CuInS_2$ s.s.	Dark green
	550/92 hr	α-MnS s.s. + γ-MnS s.s.	Black
	850/45 hr	α-MnS s.s. + γ-MnS s.s.	Black
	1020/2 hr	α-MnS s.s. + γ-MnS s.s.	Black
	1075/2 hr	α-MnS s.s. + γ-MnS s.s.	Black
	1220/2 hr	Liquid	Black
30	400/12 days	α-MnS s.s. + $CuInS_2$ s.s.	Black
	550/92 hr	α-MnS s.s. + γ-MnS s.s.	Black
	850/45 hr	α-MnS s.s. + γ-MnS s.s.	Black
	1020/2 hr	α-MnS s.s. + γ-MnS s.s.	Black
	1075/2 hr	α-MnS s.s. + γ-MnS s.s.	Black
	1200/½ hr	Liquid	Black
40	400/12 days	α-MnS s.s. + $CuInS_2$ s.s.	Black
	50/92 hr	α-MnS s.s. + γ-MnS s.s.	Black
	850/45 hr	α-MnS s.s.	Black
	1020/2 hr	α-MnS s.s.	Black
	1075/2 hr	α-MnS s.s.	Black
	1220/½ hr	Liquid	Black
45	480/92 hr	α-MnS s.s. + $CuInS_2$ s.s.	Black
50	400/12 days	α-MnS s.s. + $CuInS_2$ s.s.	Black
	550/92 hr	α-MnS s.s. + γ-MnS s.s.	Black
	850/45 hr	α-MnS s.s.	Black
	1020/2 hr	α-MnS s.s.	Black
	1075/2 hr	α-MnS s.s.	Black
	1220/½ hr	Liquid	Black
60	400/12 days	α-MnS s.s. + $CuInS_2$ s.s.	Black
	550/92 hr	α-MnS s.s. + γ-MnS s.s.	Black
	850/45 hr	α-MnS s.s. + γ-MnS s.s.	Black
	1020/2 hr	α-MnS s.s.	Black
	1075/2 hr	α-MnS s.s.	Black
	1220/2 hr	Liquid	Black
70	400/12 days	α-MnS s.s. + $CuInS_2$ s.s.	Black
	550/92 hr	$CuInS_2$ s.s.	Black
	800/72 hr	$CuInS_2$ s.s.	Black
	850/45 hr	α-MnS s.s. + $CuInS_2$ s.s.	Black
	1020/2 hr	α-MnS s.s. + $CuInS_2$ s.s.	Black
	1075/2 hr	α-MnS s.s. + $CuInS_2$ s.s.	Black
	1220/½ hr	Liquid	Black
75	900/72 hr	$CuInS_2$ s.s.	Black
	1020/2 hr	$CuInS_2$ s.s.	Black
80	400/12 days	$CuInS_2$ s.s.	Black
	550/92 hr	$CuInS_2$ s.s.	Black
	850/45 hr	$CuInS_2$ s.s.	Black
	1020/2 hr	$CuInS_2$ s.s.	Black
	1075/2 hr	$CuInS_2$ s.s.	Black
	1220/½ hr	Liquid	Black
90	400/12 days	$CuInS_2$ s.s.	Black
	550/92 hr	$CuInS_2$ s.s.	Black
	850/45 hr	$CuInS_2$ s.s.	Black
	1020/2 hr	$CuInS_2$ s.s.	Black
	1075/2 hr	$CuInS_2$ s.s.	Black
	1220/½ hr	Liquid	Black

structure in the central region of the system was unexpected, even though a metastable, hexagonal γ form of MnS has been reported. Although the relationships at the liquidus are very tentative due to formidable experimental difficulties with the silica tubes at temperatures around 1200°C, the lower limit of stability of the intermediate solid solution around 500°C is well established. Samples at 400°C were heated for 12 days and those at 550°C for 92 hr.

V. Summary and Conclusions

A. In the system ZnS–MnS, MnS lowers the zinc blende to wurtzite transition temperature to less than 400°C, creating a very large field of stability of wurtzite solid solutions which extends to 60% MnS at 1150°C.

B. In the system ZnS–$CuInS_2$, the opposite effect is observed. A concentration of 40% $CuInS_2$ raises the zinc blende to wurtzite inversion temperature to 1250°C, creating a very large field of stability of zinc blende solid solutions which extends to about 80% $CuInS_2$ at 1050°C. This effect might be expected due to the close relationship of the zinc blende and chalcopyrite structures. A substantial region of stability for wurtzite solid solution also characterizes the diagram.

C. In the system MnS–$CuInS_2$, two outstanding features emerged: (1) the intermediate region of γ-MnS or wurtzite solid solution, and (2) the relatively extensive $CuInS_2$ solid solution. It is noteworthy that the six-coordinated MnS participates in the stabilization of two different four coordinated structures, wurtzite and chalcopyrite.

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