

Preparation of and Phase Relationships in Systems of the Type $ZnS-M^I M^{III} S_2$ where $M^I = Cu, Ag$ and $M^{III} = In, Ga, Al$

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Solid solutions in systems of the type $M^I M^{III} S_2$ (tetragonal chalcopyrite structure when $M^I = Cu, Ag$ and $M^{III} = In, Ga, Al$)- ZnS (cubic sphalerite structure) were prepared and studied crystallographically. When $M^I = Cu$, there is extensive mutual solid solubility between $CuM^{III} S_2$ and ZnS , with no stabilization of a quaternary phase. However, when $M^I = Ag$, addition of ZnS to $AgM^{III} S_2$ causes wide regions of immiscibility with the formation of new quaternary compositions having the wurtzite structure. The stability of the wurtzite structure increases when larger cations are present.

Introduction

Chalcopyrites of the type $M^I M^{III} X_2^{VI}$ (e.g., $AgGaS_2$) were first prepared by Hahn (1). Crystals have been grown by Honeyman (2), Cound et al. (2), Lerner (4), Belova, Koshkin and Palatuik (5) and Kasper (6). Band gaps for the chalcopyrites and ZnS have been summarized (7, 8). Materials with the chalcopyrite and sphalerite structures are noncentrosymmetric and exhibit second harmonic generation (9). Recent studies on the nonlinear optic and semiconducting properties of chalcopyrites have been carried out by Tell, Shay and Kasper (10) and Boyd, Kasper and McFee (11) where it has been shown that chalcopyrites of the $CuGaS_2$ type have been prepared as both *p* and *n*-type semiconductors.

The crystal structures of cubic ZnS (sphalerite $F\bar{4}3m$) and chalcopyrites of the type $M^I M^{III} X_2^{VI}$ (tetragonal $I\bar{4}2d$) are related (12) as shown in Fig. 1. In Fig. 1 it can be seen that ordering of M^I and M^{III} on the cation sites in sphalerite results in an approximate doubling of the *a*-axis forming the tetragonal chalcopyrite structure. At temperatures above $1020^\circ C$ ZnS undergoes a cubic-hexagonal (wurtzite structure $C\bar{7}me$ where $a = 3.820$ and $c = 6.260$) phase transition (13-15).

It was decided to study the systems $M^I M^{III} S_2$ - ZnS (where $M^I = Cu, Ag$, and $M^{III} = In, Ga, Al$) in order to determine if materials with useful electric and optical properties could be generated

by preparing solid solutions of the end points. Apple (16) reported, in a study of the pseudo-binary $CuGaS_2$ - ZnS , that the addition of ZnS to $CuGaS_2$ lead to a decrease in cation ordering with a chalcopyrite-to-sphalerite phase transition at ~ 50 mole % ZnS . It was also reported that only ~ 5 mole % $AgGaS_2$ is soluble in ZnS (sphalerite) with the appearance of Ag_2S as an impurity phase on further addition of $AgGaS_2$.

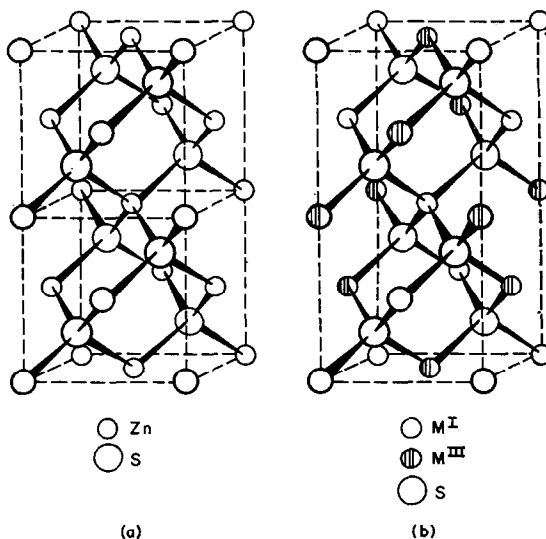


FIG. 1. Crystal structures of (a) ZnS (sphalerite) and (b) chalcopyrite.

As shown below, this latter result disagrees with our results and the addition of Ag-containing sulfide chalcopyrites to ZnS results in the formation of new quaternary compositions with the wurtzite structure.

Experimental Methods

The systems investigated were CuAlS₂-ZnS, CuGaS₂-ZnS, CuInS₂-ZnS, AgInS₂-ZnS, AgGaS₂-ZnS and AgAlS₂-ZnS.

All of the samples were prepared from appropriate mixtures of Ag, Cu, In, Ga, Al, ZnS and S. The mixtures were pressed into pellets and sealed in evacuated silica tubes. The tubes were heated at the rate of 10–15°C/hr between room temperature and 800°C. This temperature was maintained for 48 hr at which time the power to the furnace was shut off and the ampoules were allowed to cool to room temperature. All of the samples were examined by X-ray diffraction using CuK α radiation. Materials which did not form as single phase samples were reannealed at various temperatures up to 1200°C.

Results

1. Systems Where M^I = Cu

In all of the pseudo-binaries containing Cu^I the addition of ZnS to CuM^{III}S₂ simply resulted in a decrease in cation ordering, resulting in a chalcopyrite-sphalerite transition. The presumably narrow two phase coexistence regions were not delineated. No new quaternary phases appeared by our method of preparation.

For the CuAlS₂-ZnS system, the chalcopyrite-sphalerite transition takes place at ~65 mole % ZnS. Unit cell parameters as a function of composition are shown in Fig. 2.

Our results for the CuGaS₂-ZnS system were the same as those previously reported by Apple (16).

For the CuInS₂-ZnS system the chalcopyrite-sphalerite transition occurs at ~33 mole % ZnS. Unit cell parameters as a function of composition are also shown in Fig. 2.

2. Pseudo-binaries Containing Ag

The addition of ZnS to AgM^{III}S₂ did not lead to simple extensive terminal solid solutions as in the Cu-containing systems. Instead it was found that new quaternary phases with the wurtzite structure formed when M^{III} = In, Ga, or Al.

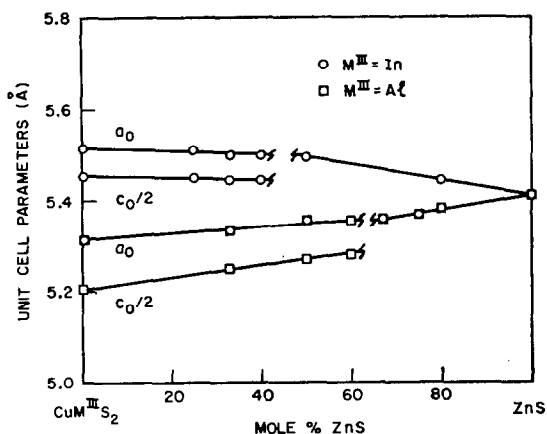


FIG. 2. Unit cell parameters in the systems CuInS₂-ZnS and CuAlS₂-ZnS.

a. *The AgAlS₂-ZnS System.* As shown in Fig. 3, the chalcopyrite structure is maintained for additions of ZnS to AgAlS₂ in amounts up to 20 mole % on annealing up to 1000°C. Beyond 20 mole % ZnS, a two phase region exists and the phases present were identified as having chalcopyrite and wurtzite structures. This two phase region exists between approximately 20 and 83 mole % ZnS depending on preparation temperature. A composition containing 75 mole % ZnS (Zn₃AgAlS₅) exhibited

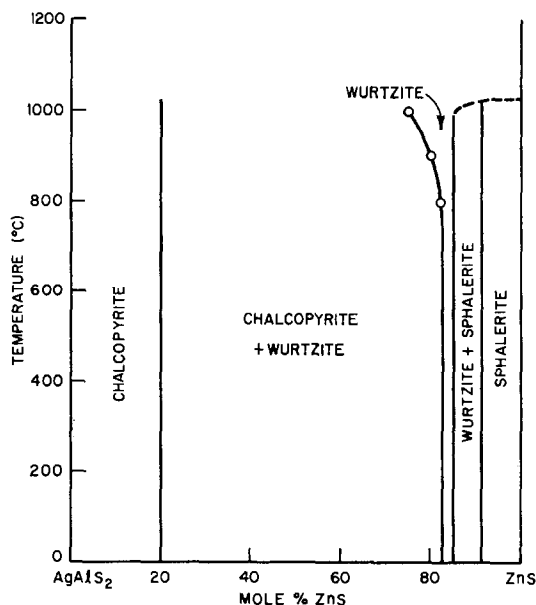


FIG. 3. Proposed phase diagram for the pseudo-binary AgAlS₂-ZnS below 1020°C based on powder X-ray data only.

the wurtzite structure when annealed at 1000°C for 18 hr followed by quenching the sealed ampoules in air. The composition containing 80 mole % ZnS (Zn_4AgAlS_6) formed with the wurtzite structure after a 900°C anneal and air quenching. Compositions between 83 and 86 mole % ZnS exhibit the wurtzite structure when prepared at 800°C and cooled slowly to room temperature. Mixtures containing 86–91 mole % ZnS formed a mixture of wurtzite and sphalerite phases. From 91 to 100 mole % ZnS only the sphalerite phase was present as determined by powder X-ray methods. Samples containing 83–100 mole % ZnS were heated only at 800–900°C as annealing over 1000°C would bring about wurtzite formation throughout this region since the sphalerite–wurtzite transition in ZnS takes place above 1020°C (13, 14). Unit cell parameters for this system are shown in Table I.

b. AgGaS₂–ZnS. The addition of ZnS leads to same type of phase relationships as is observed for AgAlS₂–ZnS (Fig. 4). Between 0 and 14 mole % ZnS the chalcopyrite structure is maintained. Mixtures containing 14–66 mole % ZnS form with both chalcopyrite and wurtzite phases present. When quenched from 1000°C the sample containing 66% ZnS (Zn_2AgGaS_4) forms with the wurtzite structure. This is also true of the sample with 75% ZnS (Zn_3AgGaS_5) when quenched from 900°C. Between 77 and 83% ZnS the wurtzite structure is the stable phase. From 83 to 91% mixtures of the wurtzite and sphalerite phases are formed following which the sphalerite phase is formed. Unit cell parameters are shown in Table I.

c. AgInS₂–ZnS. AgInS₂ can be prepared with the chalcopyrite structure below 700°C. Above 700°C various papers report different transitions

TABLE I
CRYSTALLOGRAPHIC PROPERTIES OF MATERIALS IN THE PSEUDO-BINARIES $AgM^{III}S_2-ZnS^a$

M^{III}	ZnS (mole %)	Formula	System	<i>a</i> (Å)	<i>c</i> (Å)	<i>c/a</i>
Al	0	AgAlS ₂	c(tetragonal)	5.731	10.246	1.79
	10	ZnS·9AgAlS ₂	c(tetragonal)	5.731	10.250	1.79
	20	ZnS·4AgAlS ₂	c(tetragonal)	5.732	10.255	1.79
	80	4ZnS·AgAlS ₂	w(hexagonal)	3.836	6.290	1.64
	83	5ZnS·AgAlS ₂	w(hexagonal)	3.843	6.294	1.64
	86	6ZnS·AgAlS ₂	w(hexagonal)	3.842	6.293	1.64
	91	10ZnS·AgAlS ₂	s(cubic)	5.420		
	92	12ZnS·AgAlS ₂	s(cubic)	5.418		
	100	ZnS	s(cubic)	5.410		
Ga	0	AgGaS ₂	c(tetragonal)	5.759	10.304	1.79
	10	ZnS·9AgGaS ₂	c(tetragonal)	5.755	10.300	1.79
	14	ZnS·6AgGaS ₂	c(tetragonal)	5.754	10.298	1.79
	67	2ZnS·AgGaS ₂	w(hexagonal)	3.859	6.337	1.64
	75	3ZnS·AgGaS ₂	w(hexagonal)	3.856	6.321	1.64
	80	4ZnS·AgGaS ₂	w(hexagonal)	3.852	6.312	1.64
	83	5ZnS·AgGaS ₂	w(hexagonal)	3.851	6.306	1.64
	91	10ZnS·AgGaS ₂	s(cubic)	5.428		
	92	12ZnS·AgGaS ₂	s(cubic)	5.425		
	100	ZnS	s(cubic)	5.410		
	In	50	ZnS·AgInS ₂	w(hexagonal)	3.950	6.473
67		2ZnS·AgInS ₂	w(hexagonal)	3.908	6.405	1.64
75		3ZnS·AgInS ₂	w(hexagonal)	3.882	6.356	1.64
83		5ZnS·AgInS ₂	w(hexagonal)	3.872	6.337	1.64
87.5		7ZnS·AgInS ₂	w(hexagonal)	3.866	6.330	1.64
92		12ZnS·AgInS ₂	s(cubic)	5.449		
93		13ZnS·AgInS ₂	s(cubic)	5.443		
97		30ZnS·AgInS ₂	s(cubic)	5.426		
100		ZnS	s(cubic)	5.410		

^a c = chalcopyrite, w = wurtzite and s = sphalerite.

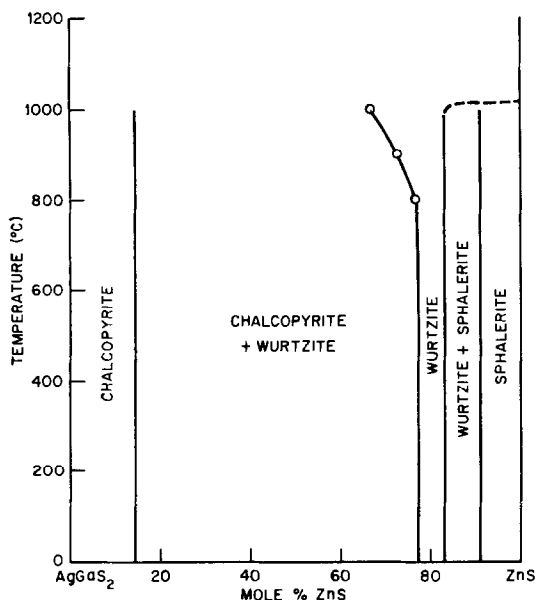


FIG. 4. Proposed phase diagram for the system AgGaS_2 -ZnS below 1020°C based on powder X-ray data only.

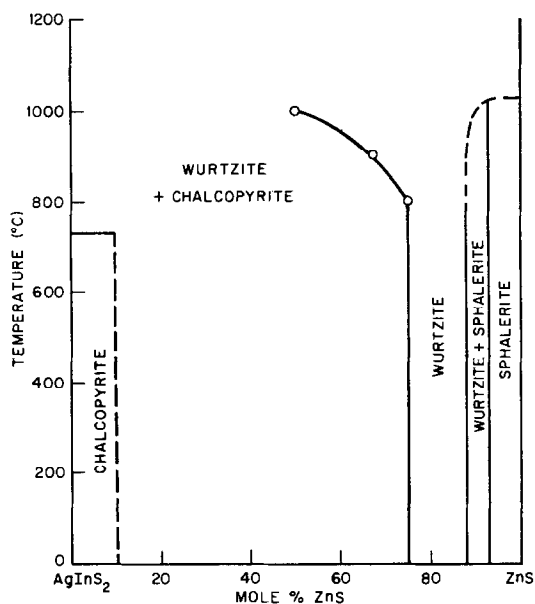


FIG. 5. Proposed phase diagram for the AgInS_2 -ZnS system below 1020°C based on powder X-ray data only.

including chalcopyrite to wurtzite (17) and chalcopyrite to αNaFeO_2 [$R\bar{3}m$ (18)]. In this work we found mixtures of wurtzite and chalcopyrite to form at preparation temperature up to 1000°C . The addition of ZnS to AgInS_2 caused no change up to 50 mole % ZnS. A sample containing 50 mole % ZnS and AgInS_2 exhibited the wurtzite structure when air quenched from 1000°C (Fig. 5). As shown in Fig. 5 the stable wurtzite region extends from ~ 75 to 88 mole % ZnS. This is followed, as in the two previous systems, by a two phase region which consists of wurtzite and sphalerite phases between 88 and 93% ZnS. From here to 100% ZnS the sphalerite phase is stable. Unit cell parameters of materials in the sphalerite and wurtzite regions are shown in Table I.

Discussion

It has been shown that below 1000°C the addition of ZnS to Cu-containing sulfide chalcopyrites simply introduce cation disorder leading to a chalcopyrite-sphalerite phase transition with extensive terminal solid solution formation. The ternary chalcopyrite does not stabilize the ZnS wurtzite phase to temperatures below 1000°C .

Where the chalcopyrite involved contains Ag, as the monovalent ion, the compositional regions of sphalerite and chalcopyrite stability are extremely limited with the apparent stabilization of the wurtzite phase.

The differences observed in Cu- vs Ag-containing pseudo-binaries, i.e., the stabilization of the wurtzite phase, can be discussed in terms of the monovalent ion as a first approximation. For ZnS the sphalerite phase is of limited stability as illustrated by the sphalerite-wurtzite phase transition which takes place at temperatures in excess of 1020°C . Ag-containing chalcopyrites may gain stability from the cation ordering which is present. However, this stabilization is also marginal as shown by the instability of AgInS_2 above 700°C . Therefore in these pseudo-binaries the large ionic radius of Ag in contrast to Cu favors the formation of the wurtzite structure.

This hypothesis is strengthened by the observation that the size of the wurtzite region decreases with smaller trivalent cations as shown in Figs. 3, 4 and 5. The largest wurtzite region occurs in AgInS_2 -ZnS followed by AgGaS_2 -ZnS and finally by AgAlS_2 -ZnS where $r_{\text{In}^{III}} < r_{\text{Ga}^{III}} < r_{\text{Al}^{III}}$ (tetrahedral radii). Although these phase relationships are discussed only in terms of the size of the cations it is understood that other factors which include electronegativity (which is related to ionic size) are operative. However, consideration of factors other than size are beyond the scope of this work.

Finally, the study of these systems has resulted in a new group of stable wurtzite materials

exhibiting the noncentrosymmetric wurtzite structure. Crystals have been grown (19) by chemical vapor transport and their nonlinear optical properties will be determined. In the Ag(Ga, Al)S₂-ZnS system the crystals are transparent yellow. In the AgInS₂-ZnS wurtzite region crystal colors range from transparent orange to yellow with increasing ZnS.

References

1. H. HAHN, G. FRANK, W. KLINGER, A. MEYER, and A. D. STÖIGER, *Z. Anorg. Allg. Chem.* **271**, 153-170 (1953).
2. W. N. HONEYMAN, *J. Phys. Chem. Solids* **30**, 1935-1940 (1969).
3. V. M. COUND, P. H. DAVIES, K. F. HULME, and D. ROBERTSON, *J. Phys. C* **3**, L83 (1970).
4. L. S. LERNER, *J. Phys. Chem. Solids* **27**, 1-8 (1966).
5. D. K. BELOVA, V. M. KOSHKIN, and L. S. PALATUIK, *Izv. Akad. Nauk SSSR, Neorg. Mater.* **3**, 617 (1967).
6. H. KASPER, *Mat. Res. Symp.*, 5th, Gaithersburg, MD, Oct. 18021 (1971).
7. N. A. GORYUNOVA, "The Chemistry of Diamond-Like Semiconductors," MIT Press, Cambridge, MA (1965).
8. L. I. BERGER and V. C. PROCHUKHAN, "Ternary Diamond-Like Semiconductors," Consultants Bureau, New York (1969).
9. M. V. HOBDEN, *Acta Crystallogr. Sect. A* **24**, 676 (1968)
10. B. TELL, J. SHAY, and H. M. KASPER, unpublished data.
11. G. D. BOYD, H. M. KASPER, J. H. MCFEE, *IEEE J. Quantum electron.* **7**, 563 (1971).
12. A. F. WELLS, "Structural Inorganic Chemistry," p. 531. Oxford University Press, London (1962).
13. E. T. ALLEN and J. L. CRENSHAW, *Z. Anorg. Chem.* **79**, 125 (1913).
14. G. KULLERUD, *Nor. Geol. Tidsskr.* **32**, 64 (1953).
15. W. L. ROTH, *G. E. Res. Lab. Rep.* RL-256 M, Schenectady, NY (1960).
16. E. F. APPLE, *J. Electrochem. Soc.* **105**, 251 (1958).
17. H. HAHN, G. FRANK, W. KLINGER, A. MEYER, and G. STORGER, *Z. Anorg. Allg. Chem.* **271**, 153 (1956).
18. K. J. RENGE, M. KEUBLER, and A. WEISS, *Z. Naturforsch. B* **24(8)**, 1060-1061 (1969)
19. V. G. LAMBRECHT, JR., unpublished data.