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

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Systems of the type $M^IM^{III}S_2$ (chalcopyrite)–CdS (wurtzite) where M^I = Ag, Cu and M^{III} = Al, Ga, In were investigated to determine the regions of mutual solid solubility. It was found that the chalcopyrite structure could not tolerate extensive CdS substitution. When M^{III} was Al or Ga the solubility of $M^IM^{III}S_2$ in CdS was also very limited. However, when M^{III} = In ($r_{In^{3+}} \gg r_{Ga^{3+}} > r_{Al^{3+}}$), the solubility of M^IInS_2 in CdS was quite extensive (~50%). These results are consistent with a prior study on systems of the type $M^IM^{III}S_2$–ZnS which indicated that in sulfides, larger cations tend to result in the formation of new quaternary, wurtzite phases.

Structural relationships in systems of the type $M^IM^{III}S_2$–(chalcopyrite $I\bar{4}2d$)–ZnS (sphalerite $F\bar{4}3m$), where M^I = Cu, Ag and M^{III} = Al, Ga, In, have been reported. It was shown that when M^I = Cu there exists large regions of mutual solid solubility. However, when M^I = Ag, the sphalerite and related chalcopyrite phase were found to be relatively unstable with respect to the hexagonal wurtzite structure (*1*). It was further found that the stability or the tendency to form new compositions with the wurtzite phase was enhanced with increasing cationic radius of the M^{III} ion. It was concluded that the sphalerite and chalcopyrite structures, in sulfides, are relatively unstable and do not exhibit extensive solid solutions with compounds containing large cations. Instead, compositions with the wurtzite structure are stabilized by large cations.

In order to further study this effect we have investigated systems of the type $M^IM^{III}S_2$–CdS where M^I = Ag, Cu, and M^{III} = Al, Ga, In. In these systems the stability of the wurtzite (CdS) phase can be determined as a function of cation size in the chalcopyrites ($M^IM^{III}S_2$) which were used. The systems investigated were $AgAlS_2$–CdS, $CuAlS_2$–CdS, $AgGaS_2$–CdS, $CuGaS_2$–CdS, $AgInS_2$–CdS, and $CuInS_2$–CdS.

Experimental

All of the compositions were prepared from appropriate mixtures of Ag, Cu, Al, Ga, In, CdS, and S. The mixtures were pressed into pellets and sealed in evacuated silica tubes. The tubes were heated to 800°C at 10–15°C/hr, held at this temperature for 48 hr, and cooled over a period of 24 hr to room temperature. X-ray diffraction (Cu*Kα* radiation) was used to determine if the samples were single-phase. Samples which formed as a mixture of phases when heated at 800°C were reheated in silica tubes up to temperatures of 1000°C and quenched in air.

As expected, all of the systems with the exception of $AgInS_2$–ZnS showed two regions of solid solution with the chalcopyrite and wurtzite structures. The immiscibility regions contained materials with both structures. It has been reported (*2*) that $AgInS_2$ undergoes a chalcopyrite–wurtzite phase transition above 700°C. We found that firing at 800°C resulted in a mixture of phases instead of $AgInS_2$, with wurtzite and chalcopyrite phases. Compositions which formed with either wurtzite or chalcopyrite structures as a result of heating at 800°C were found to be stable when annealed at 600°C followed by cooling to room temperature over a period of 24 hr.

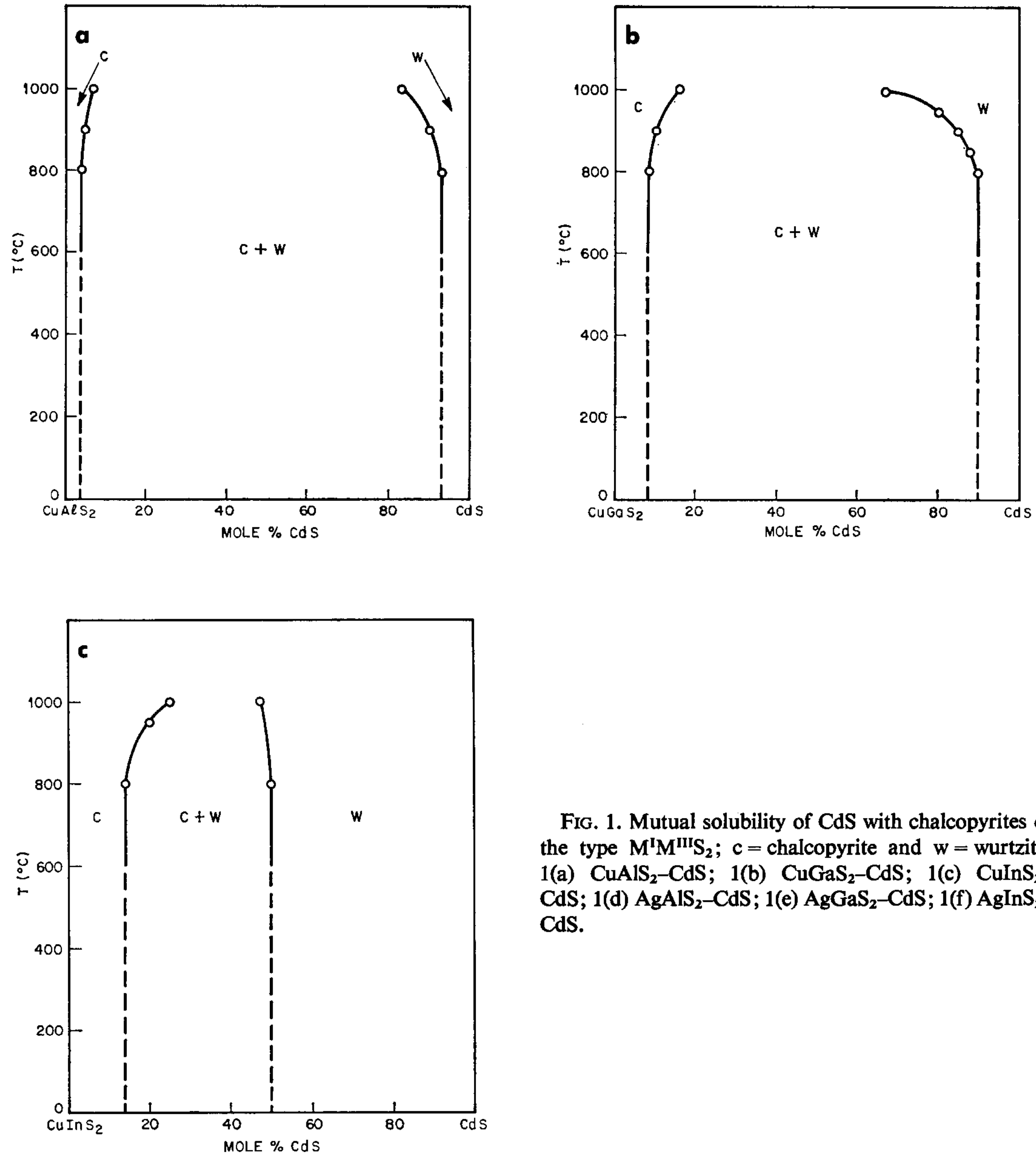

FIG. 1. Mutual solubility of CdS with chalcopyrites of the type $M^IM^{III}S_2$; c = chalcopyrite and w = wurtzite. 1(a) $CuAlS_2$–CdS; 1(b) $CuGaS_2$–CdS; 1(c) $CuInS_2$–CdS; 1(d) $AgAlS_2$–CdS; 1(e) $AgGaS_2$–CdS; 1(f) $AgInS_2$–CdS.

Phase diagrams (up to 1000°C) for all six of the systems investigated are shown in Figs. 1 (a–f). Unit cell parameters for all of the compositions prepared are shown in Table I. As shown in Table I the substitution of CdS in chalcopyrites of the type $CuM^{III}S_2$ leads to increasing unit cell parameters. The magnitude of these changes decrease as the size of the M^{III} ion increases. Small changes are observed when chalcopyrites of the type $AgM^{III}S_2$ are used.

As seen in Figs. 1(a–f) the region of formation of the wurtzite structure increases greatly when M^{III} = In. The homogeneity range of the chalcopyrite structure is relatively unaffected by the identity of the M^I and M^{III} cations.

Discussion

The small increase in solid solubility of CdS in $M^IM^{III}S_2$ with increasing size of the M^I and

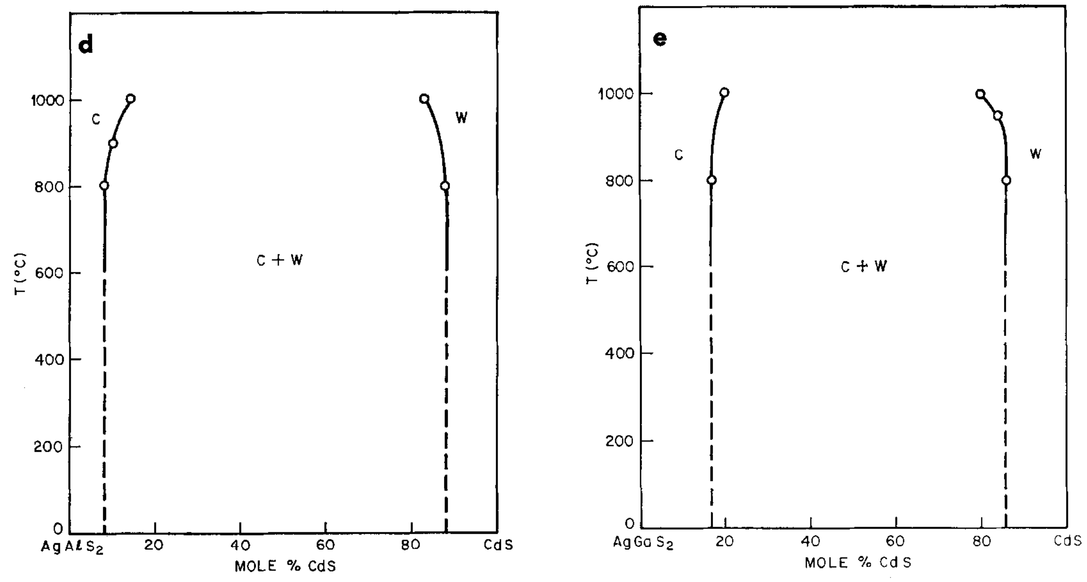

TABLE I

Crystallographic Data of Materials in the Systems $M^IM^{III}S_2$–CdS Where M^I = Ag, Cu and M^{III} = Al, Ga, In[a]

Mole %			a_0 (Å)	c_0 (Å)	c/a
$CuAlS_2$	CdS				
96	4	c	5.343	10.570	1.98
95	5	c	5.344	10.483	1.96
93	7	c	5.34	10.424	1.95
17	83	w	4.031	6.573	1.63
10	90	w	4.078	6.637	1.63
7	93	w	4.108	6.678	1.63
$CuGaS_2$	CdS				
92	8	c	5.361	10.497	1.96
90	10	c	5.369	10.511	1.96
84	16	c	5.380	10.545	1.96
33	67	w	3.937	6.457	1.64
20	80	w	3.978	6.499	1.63
15	85	w	4.028	6.562	1.63
12	88	w	4.050	6.587	1.63
10	90	w	4.077	6.630	1.63
$CuInS_2$	CdS				
90	10	c	5.536	11.072	2.00
86	14	c	5.550	11.081	1.99
80	20	c	5.562	11.093	1.99
75	25	c	5.573	11.000	1.99
60	40	w	3.969	6.485	1.63
50	50	w	3.997	6.541	1.64
25	75	w	4.049	6.604	1.63
10	90	w	4.100	6.697	1.63

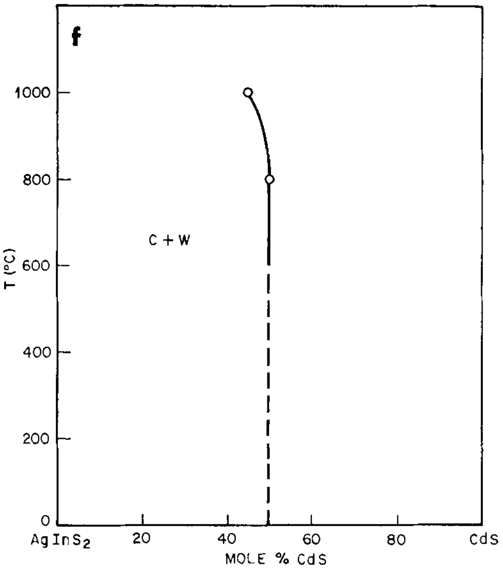

TABLE I—*continued*

Mole %			a_0 (Å)	c_0 (Å)	c/a
$AgAlS_2$	CdS				
93	7	c	5.730	10.243	1.79
90	10	c	5.731	10.243	1.79
87.5	12.5	c	5.733	10.241	1.79
17	83	w	4.077	6.641	1.63
12	88	w	4.094	6.660	1.63
10	90	w	4.107	6.676	1.63
7	93	w	4.115	6.700	1.63

TABLE I—*continued*

Mole %			a_0 (Å)	c_0 (Å)	c/a
$AgGaS_2$	CdS				
90	10	c	5.750	10.360	1.80
83	17	c	5.751	10.361	1.80
75	25	c	5.755	10.362	1.80
20	80	w	4.055	6.613	1.63
16	84	w	4.073	6.640	1.63
14	86	w	4.082	6.653	1.63
10	90	w	4.100	6.668	1.63
$AgInS_2$	CdS				
44	56	w	4.110	6.696	1.63
40	60	w	4.111	6.698	1.63
25	75	w	4.117	6.701	1.63
10	90	w	4.133	6.726	1.63

[a] c = chalcopyrite and w = wurtzite.

M^{III} ions is probably due to an increase in the ability of a larger chalcopyrite unit cell to accommodate the large Cd^{2+} ion. However, these changes are small and the stability of the chalcopyrite phase remains very limited with respect to CdS addition. Conversely the stability of the wurtzite phase seems to be very dependent on the size of the M^{III} ion. Cu^+ and Cd^{2+} have similar ionic radii and Ag^+ is slightly larger than Cd^{2+}. Al^{3+} and Ga^{3+} are considerably smaller than Cd^{2+} which leads to a very limited region of solid solubility of $M^I(Al,Ga)S_2$ in CdS. When M^{III} = In both ions in the chalcopyrite phase (M^I and M^{III}) are commensurate in size with Cd^{2+} and the region of solid solubility of $M^IM^{III}S_2$ in CdS is greatly enhanced. These results are in agreement with the previously described work (*1*) on the systems $M^IM^{III}S_2$–ZnS in which it was postulated that the stability of the wurtzite phase was enhanced (over that of the sphalerite and chalcopyrite phases) when $M^IM^{III}S_2$ contained the larger cations ($r_{\mathrm{Ag}^+} > r_{\mathrm{Cu}^+}$ and $r_{\mathrm{In}^{3+}} \gg r_{\mathrm{Ga}^{3+}} > r_{\mathrm{Al}^{3+}}$). The variation of unit-cell parameters (Table I) within the systems described in this work are all consistent with the ionic radii of the cations involved.

In this work we have been making reference to ionic radii only. The interpretation of the results would be unchanged if covalent radii were used since the size relationships between the ions remains essentially the same.

References

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