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P–T–X Phase Equilibrium Study of New Solid Solution Systems, $Cd_{1-x}M_xS$ (M = Mg, Ca, Sr)

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Pressure, temperature, and composition phase equilibrium diagrams of new solid solution systems of the $Cd_{1-x}M_xS$ (M = Mg, Ca, Sr) type were investigated using the quenching method. The stable region for the rock-salt-type phase is widely extended toward the high-temperature/low-pressure region by substituting 10–20 mole% of Cd with Ca or Sr. Temperature and composition phase diagrams for each solid solution system were obtained at 2 GPa. The rock-salt-type phase stability is discussed in view of these phase relations.

Introduction

In preceding papers (*1*, *2*), it was found that rock-salt-type CdS, a high-pressure modification, can be retained by using metal monosulfide additives such as CaS, SrS, PbS, SnS, GeS, and rare earth sulfides. It was also deduced from a crystal chemical consideration that an additive with a larger ionic radius than Cd stabilizes rock-salt-type CdS. At the same time, the retained phases were found to be metal-substituted solid solutions.

The temperature and pressure conditions for synthesizing these new solid solutions were typically 2.0 GPa and 800°C. This temperature condition, according to Miller *et al.* (*3*), is well above the stable region limits of CdS-II , the rock-salt-type phase. This fact suggests that, by using these metal additives, the stable region of CdS-II is extended toward higher temperature regions.

Thus, the present work presents new phase diagrams, investigated by the quenching method, for the system $Cd_{1-x}Ca_xS$. In addition, the isobaric temperature–composition diagrams for three selected systems, $Cd_{1-x}M_xS$ (M = Ca, Sr, Mg), where the ionic radii of Ca and Sr are larger than that of Cd while that of Mg is smaller, are outlined.

Experimental

It was previously found that the solid solutions of rock-salt-type CdS with some selected alkaline earth monosulfides can be synthesized at pressures below 3.0 GPa (*1*). Therefore, a piston-cyclinder-type high-pressure cell proved useful in the present study. The piston-cylinder-type cell is considered to generate pressure much more hydrostatically than the girdle-type cell which was used in the preceding study (*1*).

A cross section of the cell is shown in Fig. 1. In order to make the pressure more hydrostatic, a glass cell was used. At elevated temperatures, glasses are expected to flow better than conventional solid pres-

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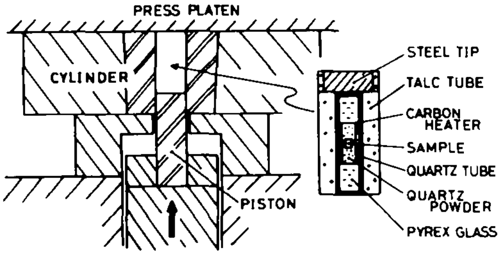

FIG. 1. Cross section of high-pressure cell.

sure-transmitting media such as pyrophyllite and talc. In the present study, the sample cell consisted of an external talc tube containing a graphite tube heater with graphite end disks. The graphite heater surrounds the end rods made of sodium borosilicate glass (or Pyrex glass) and a quartz tube containing the sample holder. the quartz tube is then filled with a quartz powder. The sample holder used was a platinum capsule for experiments below 800°C and a boron nitride capsule for those above 800°C.

The pressure and temperature calibrations were made in the same manner as described in the preceding paper (*1*). CdS and the other metal sulfides, with the exception of MgS, were all commerically obtained. Their stated purities were all 99.99%. MgS was prepared by heat-treating Mg metal (99.9% pure) with a stoichiometric amount of sulfur (99.999% pure) in a vacuum-sealed quartz tube at 600°C for 24 hr.

The starting sample materials were prepared by grinding a weighted mixture of CdS and a metal sulfide in acetone and drying.

In each series of high-pressure runs, the pressure and temperature were simultaneously raised to the desired level and maintained for 2 hr unless otherwise stated. Consequently, almost all reaction times were 2 hr. After a high-pressure run, the sample was recovered at room temperature and pressure. Then, the samples were X-rayed to identify the phases obtained.

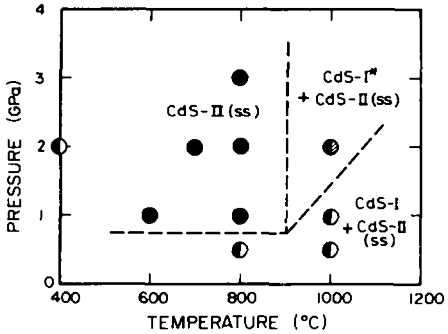

FIG. 2. Experimental results of $Cd_{1-x}Ca_xS$, x = 0.12.

Results

1. Pressure and Temperature Phase Diagram of $Cd_{1-x}Ca_xS$ System

The first series of experiments was carried out to investigate the pressure and temperature stability conditions of the $Cd_{1-x}Ca_xS$ system. The experimental results are shown in Figs. 2 and 3 for compositions $x = 0.12$ and $x = 0.06$, respectively. Three phases were identified by X-ray powder diffraction as previously illustrated (*1*). In these figures, the obtained phases are represented by symbols: ● CdS-II(ss) or rock-salt-type CdS in the form of solid solution; ○ CdS-I or wurtzite-type CdS; and ◎ CdS-I* or strained sphalerite. Mixed phases are represented by symbols such as ◐ or ◍. The results show that, at $x = 0.12$, a single phase of solid solution $Cd_{0.88}Ca_{0.12}S$ with a rock-salt structure can

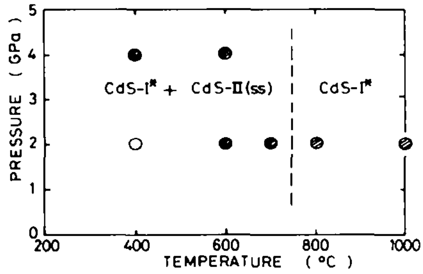

FIG. 3. Experimental results of $Cd_{1-x}Ca_xS$, x = 0.06.

be quenched at 1 GPa and above, and at 800°C and below. However, at higher temperatures or lower pressures, CdS-I or CdS-I* can be observed in addition to CdS-II(ss).

At $x = 0.06$, on the other hand, the single-phase region for CdS-II(ss) disappears while a mixed-phase region becomes predominant. Above 800°C, however, another single-phase region for CdS-I* begins to appear. It should be noted that at 400°C, the reaction time was extended to 12 hr in order to realize a complete reaction. However, the reaction still appears incomplete except for the sample with $x = 0.06$ reacted at 4 GPa.

2. *Isobaric Temperature and Composition Phase Diagrams of $\mathrm{Cd}_{1-x}M_xS$ (M = Ca, Sr, Mg) Systems*

Next, isobaric temperature and composition phase diagrams were determined for three solid solution systems, $\mathrm{Cd}_{1-x}M_x\mathrm{S}$ (M = Ca, Sr, Mg).

The experimental results are shown in Figs. 4, 5, and 6 for M = Ca, Sr, and Mg, respectively. In these figures, the same symbols as in Figs. 2 and 3 are used for the representation of the phases obtained. In addition, new symbols ■, ◗, and ◩ are used which represent the rock-salt-type solid solution of MS(ss) (M = Sr or Mg), the mixed phase of MS and CdS-II, and the mixed phase of MS and CdS-I*, respectively. In the figures, phase boundaries are shown on the basis of the present experimental results. Here, the boundary between CdS-II and CdS-I* at $x = 0.0$ or pure CdS was chosen to correspond to the phase boundary between CdS-II and III at 2.0 GPa in accordance with Miller *et al.* (*3*).

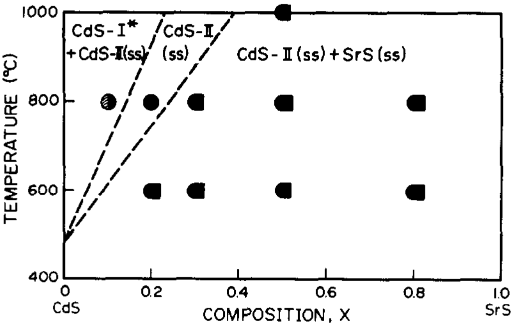

FIG. 5. Experimental results of $\mathrm{Cd}_{1-x}\mathrm{Sr}_x\mathrm{S}$, at 2 GPa.

In the CdS–CaS system in Fig. 4, a wide single-phase region for CdS-II(ss) exists and the range narrows with increasing temperature. At less than 15 mole% of CaS, there exists a narrow two-phase region for CdS-I* and CdS-II(ss), and another single-phase region for CdS-I*. This single-phase region seems to be more stable at higher temperatures. It should correspond to CdS-III which is said to be stable only at high pressures and temperatures (*3*).

In the CdS–SrS system seen in Fig. 5, the

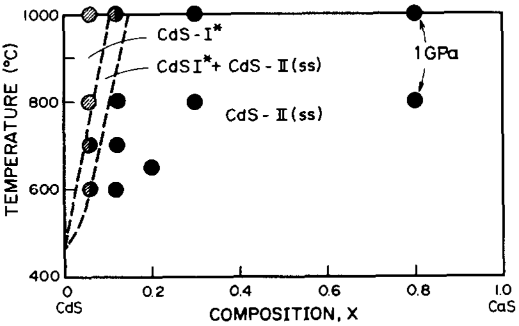

FIG. 4. Experimental results of $\mathrm{Cd}_{1-x}\mathrm{Ca}_x\mathrm{S}$, at 2 GPa.

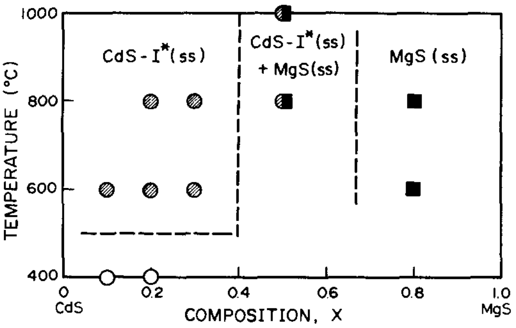

FIG. 6. Experimental results of $\mathrm{Cd}_{1-x}\mathrm{Mg}_x\mathrm{S}$, at 2 GPa.

single-phase region for CdS-II(ss) seems quite narrow compared with that for the Ca case. In addition, a wide miscibility gap seems to exist between CdS-II(ss) and SrS(ss). The behavior of the CdS-rich region, however, seems to be similar to that of the Ca case.

In the CdS–MgS system, a wide single-phase region for CdS-I* is observed at higher temperatures than about 500°C. At a composition around $x = 0.5$, there exists a miscibility gap between CdS-I* and MgS(ss). A boundary line for MgS(ss) single phase lies between $x = 0.5$ and 0.8.

3. Pressure Dependences of CdS Solubility in Alkaline Earth Sulfides

The solid solubilities of CdS in the three alkaline earth sulfides of $M_{1-y}Cd_yS$ were determined at 800°C. The solubility was measured using the lattice parameter variations with composition as determined in the previous work (*1*). The solubility limit can be determined when mixed phases are observed. The solubility limits are plotted against pressure in Fig. 7. At atmospheric pressure, the solubiities and solubility differences are small; the CdS solubilities in CaS and MgS are about 8 and 7 mole%, respectively, and in SrS, the solubility is less than 1 mole%.

At elevated pressures, however, there exists a remarkable difference between them. In the Ca case, a single phase was obtained even at 0.5 GPa, and a true solubility limit curve could not be determined. Thus, the solubility curve is represented by a broken line. Contrary to this, in the Sr case, there is small pressure dependence of the solubility and, even at 2 GPa, the solubility remains below 10 mole%. In the Mg case, on the other hand, at 3 GPa, the solubility reached about 50 mole%. This means that a nearly single-phase solid solution can be obtained at 3 GPa, with a composition of $x = 0.5$.

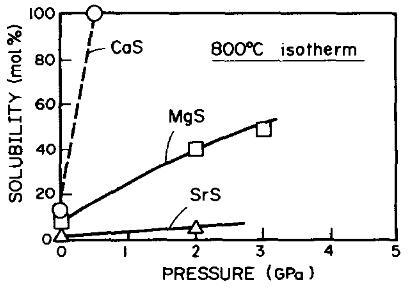

FIG. 7. Isothermal solid solubilities of CdS in alkaline earth metal sulfides.

Discussion

The phase represented by CdS-I* is characterized by a broad X-ray powder diffraction pattern as illustrated in the preceding paper (*1*). This phase is formed when the high-pressure phase CdS-III, rather than the CdS-II phase, is not successfully quenched. The result is deduced from Fig. 4, where a mixed phase of CdS-I* and CdS-II(ss) was observed at 700°C and below which changed to a single phase of CdS-I* at 800°C and above. This change makes it possible to assume that CdS-I* results from the high-temperature phase CdS-III (*3*).

These phase relations are summarized by the isobaric temperature–composition phase diagram for 2.0 GPa, as shown in Fig. 8. Here the three selected systems are shown together. In this diagram, CdS-I* was again assumed to be the phase not successfully quenched from the CdS-III phase. In the figure, II_C and II_M represent solid solutions based on CdS-II and metal sulfide MS, respectively.

For M = Sr, there exists a mixed-phase region of $II_C + II_M$ or a miscibility gap. However, for M = Ca, a solid solution of CdS-II(ss) single phase exists in essentially all composition ranges. This difference should be attributed to the ionic radius difference between Sr and Ca. On the other hand, the CdS-III stable region is limited to a narrow high-temperature, and CdS-rich

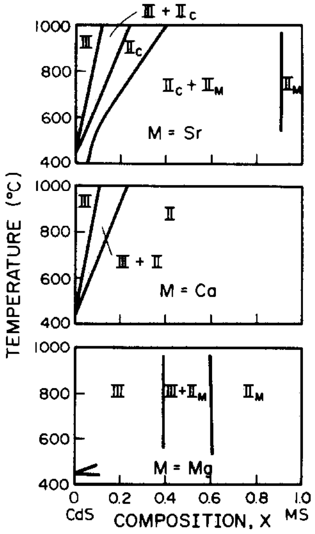

FIG. 8. Isobaric temperature–composition phase diagrams of the $Cd_{1-x}M_xS$ (M = Sr, Ca, Mg) systems at 2 GPa.

composition region. Phase II_C or II_M becomes stable over a wide composition range for these conditions.

For M = Mg, the composition diagram is essentially the same as for the previous two cases. However, phase III is stable over a wider composition range than in the previous cases. Consequently, the CdS-II(ss) phase of Cd-rich composition cannot exist under these conditions. This difference in the phase diagram appears to be due to the fact that the ionic radius of Mg is smaller than that of Cd, while the radii of Ca and Sr are larger than that of Cd.

Conclusions

Pressure, temperature, and composition phase diagrams for new solid solution systems of $Cd_{1-x}M_xS$ (M = Sr, Ca, Mg) were investigated using the quenching method. As a result, the following conclusions were reached.

(1) By substituting 10–20 mole% of CdS with CaS or SrS, the cation radii of which are larger than that of Cd, the stable region of the rock-salt-type phase is extended to higher temperatures and lower pressures.

(2) Substitution with MgS, the cation radius of which is smaller than that of Cd, is not effective for stabilizing the rock-salt-type phase of CdS-rich composition.

(3) In the CdS–CaS system, a solid solution with the rock-salt structure can generally be obtained with any composition at 2.0 GPa. However, in the case of a CdS–SrS system, a wide miscibility gap exists for the same pressure condition.

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