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High-Pressure Synthesis of Rock-Salt Type CdS Using Metal Sulfide Additives

KENZO SUSA, TOSHIO KOBAYASHI, AND SATOSHI TANIGUCHI

Central Research Laboratory, Hitachi Ltd., Tokyo 185, Japan

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The retention of the high-pressure phase for CdS with the rock-salt structure is investigated in the presence of metal sulfide additives. The most effective metal sulfides for the retention are CaS, SrS, PbS, SnS, GeS, and rare earth sulfides. X-Ray measurements of lattice parameters indicate that the retained CdS phases are metal-substituted solid solutions. The retention properties are discussed from the crystal chemistry point of view.

Introduction

Cadmium sulfide (CdS) with a rock-salt structure, that is, a high-pressure modification, can be obtained by applying high pressure to normal wurtzite form CdS at room temperature. However, as pressure is reduced, the phase reconverts to the original low-pressure phase. Corll (*1*) first succeeded in retaining the rock-salt phase by starting with unannealed and severely strained materials precipitated from $CdCl_2$ solutions. Miller *et al.* (*2*) have also reported that the rock-salt phase can be retained with starting materials precipitated from a solution containing chloride ions.

Malyushitskaya *et al.* (*3*) have obtained high-pressure phase CdS by cooling the apparatus before the pressure is released. They have also been able to retain this phase at room temperature by using a mixture of CdS and NaCl as the starting materials. However, complete retention is rather difficult with these methods and usually requires very high pressures for permanent conversion. Another possible approach to retaining high-pressure phase CdS is to add selected metal sulfides to the starting material as reported by Miller *et al.* (*2*), who used MnS as an additive. They have obtained the rock-salt phase from starting materials containing at least 20 mole% MnS without using cadmium chloride impurities.

In order to expand understanding of this area, the possibilities of retaining rock-salt phase CdS in the presence of metal sulfide additives have been investigated further. This paper describes the experimental results regarding additives which effectively enhance the retention of rock-salt phase CdS.

Further investigations on pressure–temperature–composition phase relations and semiconductive properties of these retained samples have also been carried out. These results have been reported recently (*4, 5*).

Experimental

A girdle type, high-pressure apparatus with a bore diameter of 15 mm was used in

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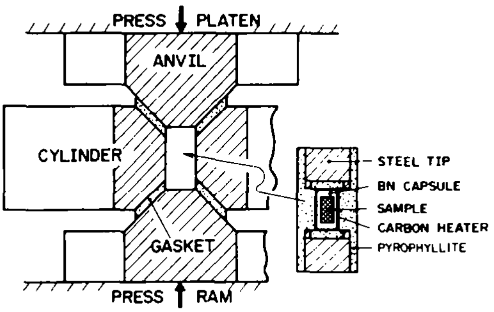

FIG. 1. Cross section of high-pressure cell.

the present study. A sketch of the apparatus and the sample-cell assembly is shown in Fig. 1. Pyrophyllite was used as the pressure-transmitting medium and a carbon tube as the resistance heater. A sleeve of boron nitride was inserted inside the carbon tube to prevent direct contact of the sample with the carbon heater. A carbon disk was placed at each end of the carbon tube to ensure good electrical contact with the molybdenum metal disk. In addition, a nickel ring, containing a pyrophyllite disk, was placed on each metal disk and then attached to the steel tip.

Sample pressure was calibrated using the known pressure-induced electrical resistivity changes of such metals as bismuth and thallium. The sample pressure was then coordinated with the pressure measured on an external oil gauge. Temperature was calibrated for input ac power by inserting a Pt–13% RhPt thermocouple in the high-pressure chamber. No pressure correction was made on the emf of the thermocouple.

The CdS and most metal sulfides used in this study were commercially obtained. When not commercially available, metals or metal oxides were sulfurized before mixing with CdS. X-Ray powder diffraction patterns of the starting CdS revealed sharp diffraction lines for the wurtzite structure. The starting materials were prepared by grinding a weighed mixture of CdS and a sulfide additive in acetone and then drying.

High-pressure runs were carried out under various conditions ranging from 1–4 GPa, 500–1000°C, and 0.5–15 hr. The system was first brought to a desired pressure, and then the temperature was raised. After completion of the reaction, the temperature was reduced to room temperature by cutting off the power supply. Then, the pressure was gradually reduced to atmospheric pressure. Phase identification was made using the X-ray powder diffraction technique.

Results

Various kinds of metal monosulfides were selected on the basis of their crystal structures and group in the periodic table. Many monosulfides, the crystal structures of which under atmospheric pressure are of the rock-salt type, were chosen based on the hints provided by the study on the CdS–MnS system (*2*). They include sulfides of Mg, Ca, Sr, and Ba from group $\mathrm{II_a}$; rare earth metals of Eu, Gd, Ho, and Yb; Pb from group $\mathrm{IV_b}$; and Mn from the transition metal group. Furthermore, sulfides of elements such as Sn, Ge, and Si from group $\mathrm{IV_b}$ and Fe and Cr from the transition metal group were also chosen although their crystal structures were not of the rock-salt type. Finally, sulfides of Zn and Hg from group $\mathrm{II_b}$, the same group as Cd, were also used.

The experimental results are summarized in a composition chart shown in Fig. 2. The composition, x, represents the mole fraction of an additive in the initial mixture of CdS and the metal sulfide. Solid circles indicate the cases where a rock-salt type single phase was obtained, while open circles indicate the cases where no rock-salt structure phase was observed. Half-filled circles indicate the cases where the rock-salt form was identified among multiple phases. The pressure and temperature conditions in these experiments were 2.0 GPa and 800°C, respectively.

As expected, most of the additives with

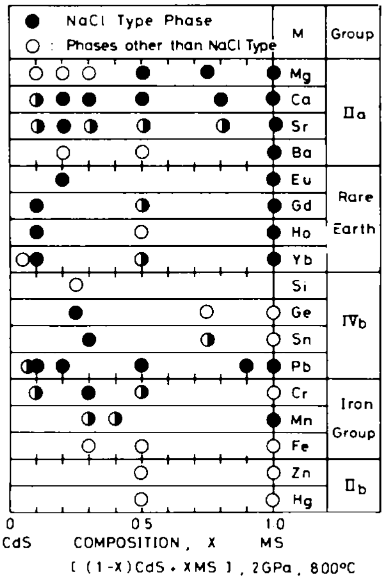

FIG. 2. Summary of the experimental results. ●, single phases with rock-salt type crystal structures; ○, phases other than rock-salt type structure; ◑, mixed phases containing rock-salt structure.

rock-salt type structures are effective for retaining rock-salt type CdS when 10 to 30 mole% is used. The most effective additives were found to be PbS, rare earth sulfides, and most alkaline earth sulfides.

The samples always gave a highly distorted wurtzite type X-ray diffraction pattern whenever the rock-salt form was not or was only partially obtained with CdS-rich compositions. The diffraction patterns for various structures are illustrated in Fig. 3. The distorted phase is denoted by CdS-I* and is shown in Fig. 3b. The diffraction patterns of CdS-I (wurtzite type used as a starting material) and CdS-II (completely retained rock-salt type) phases are also shown in Figs. 3a and c, respectively. CdS-I* is considered to be formed by a phase transformation from CdS-II or CdS-III (another high-pressure phase reported by Miller *et al.* (*2*)) when reducing the pressure and temperature.

The retained samples of rock-salt form CdS had a black or very dark red color and gave a very sharp X-ray diffraction pattern. Lattice constants calculated from the X-ray diffraction patterns were plotted against composition in Fig. 4. Extrapolation of the observed lattice constants for $x = 0.0$, or pure CdS, from the cases of CaS and PbS, gave a value of $a = 5.43$ Å. This is in good agreement with the results obtained by Miller *et al.* (*2*). The lattice constant variations with composition seem to obey Vegard's law, a linear relation with composition. These observations suggest that the retained phase, CdS-II, is a metal-substituted solid solution. Thus, in the cases of PbS and CaS, solid solutions are formed for all compositions. However, in the case of SrS, a miscibility gap seems to exist within the $0.3 \leqq x < 0.95$ composition range under the present experimental conditions.

No rock-salt phase was observed in the obtained samples in the case of MgS at compositions $x \leqq 0.3$. However, a single phase of CdS-I* was always observed. This, consequently, indicates that a single phase of CdS-II or III existed under high-pressure conditions. On the other hand, BaS provided a different behavior. At compositions of $x = 0.2$ and 0.5, a mixture of CdS-I* and an unknown phase was obtained, although the rock-salt form was observed for pure BaS.

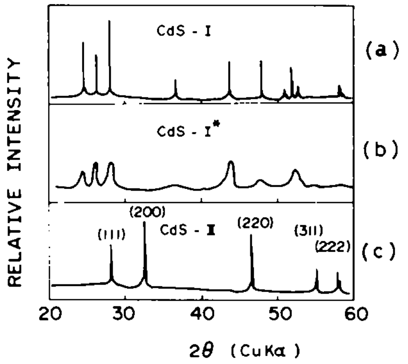

FIG. 3. Typical X-ray powder diffraction patterns of phases. (a) CdS-I: wurtzite-type starting material. (b) CdS-I*: strained wurtzite type. (c) CdS-II: a completely retained rock-salt type.

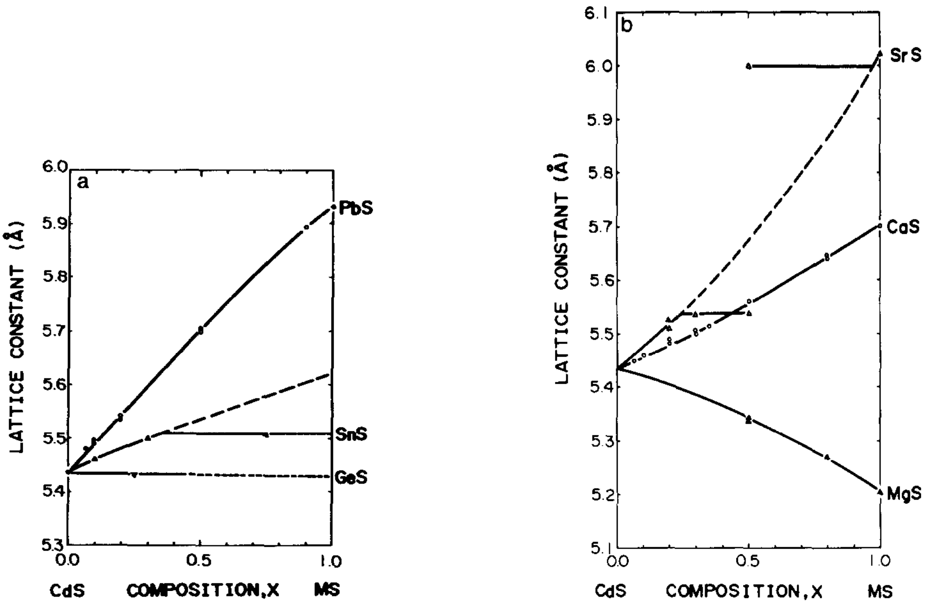

FIG. 4. Lattice constants versus composition of additives in retained rock-salt phase. (a) $Cd_{1-x}M_xS$ (M = Pb, Sn, Ge) systems. (b) $Cd_{1-x}M_xS$ (M = Sr, Ca, Mg) systems.

Rare earth sulfides seem to work as effective additives at about 10 mole% compositions, as seen in Fig. 2. However, at high additive concentrations, such as $x = 0.5$, a rock-salt single phase was hard to obtain and, instead, the Th_3P_4 structure tended to be more stable. For sulfides of group IV_b, SnS and GeS additives seem to work as effectively as PbS and form solid solutions with CdS-II. However, there seems to exist a solubility limit in both cases. With SiS, on the other hand, at $x = 0.25$, a mixed phase of CdS-I* and monoclinic Cd_4SiS_6 was obtained and seems to be ineffective for retaining the CdS-II phase.

For the transition metal sulfides, CrS yielded a single phase of CdS-II at $x = 0.3$; a mixed phase of CdS-I* and CdS-II at $x = 0.1$; and another mixed phase of CdS-II and an NiAs structure at $x = 0.5$. MnS, on the other hand, seems to be less effective than CrS. At $x = 0.3$ and even at 0.4, a mixture of CdS-I* and CdS-II was obtained. FeS was not effective and always gave a mixed phase of CdS-I* and NiAs form.

Sulfides of group II_b elements, ZnS and HgS, were confirmed to be ineffective for retaining the CdS-II phase. When 50 mole% of ZnS was added, a mixed phase of CdS-I* and zinc blende was obtained. In addition, for HgS at $x = 0.5$, a mixed phase of CdS-I* and cinnabar was obtained. In both cases, the X-ray diffraction patterns of additive sulfides were sharp and did not show any indication of solid solubility.

Discussion

It was surprising to find cases where a metal monosulfide, the crystal structure of which is not of the rock-salt type, can still be an effective additive for retaining the CdS-II phase. SnS, GeS, and CrS are such cases. On the other hand, there are some cases, such as MgS and BaS, which have rock-salt type crystal structures but are not effective additives.

In order to reach a generalization, the experimental results were replotted against ionic radius for each group in the periodic

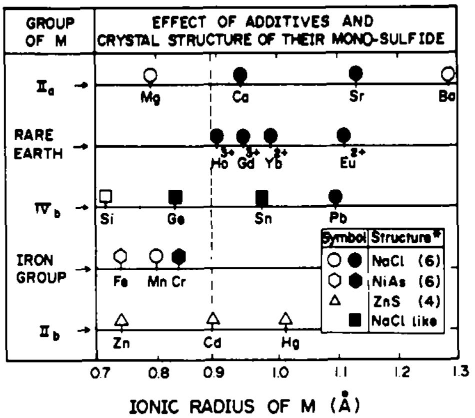

FIG. 5. Effects of additives on rock-salt type CdS synthesis. Solid symbols, rock-salt form retained; open symbols, no rock-salt form retained. Coordination numbers are shown in parentheses.

table as shown in Fig. 5. The ionic radius of each divalent metal ion was taken from the empirical crystal radii proposed by Pauling (*6*). In the figure, the solid symbols represent cases where the rock-salt form of CdS was successfully retained for a composition in the $x \leqq 0.3$ range. The open symbols represent cases where the rock-salt form was not obtained as a single phase for the same composition range. Each symbol represents the crystal structure of the additive monosulfides as indicated.

Generally, most of the effective elements have larger ionic radii than cadmium, according to this figure. However, there are some exceptions. The ionic radius of Cr is smaller than that of Cd but Cr is still effective for retention. It should be noted that the ionic radius of Cr is closer to that of Cd than is that of Mn or Fe. In addition, the crystal structure of CrS is of the NiAs type which is the same as the rock-salt type from the viewpoint of coordination number. A similar argument can be made for Ge, the ionic radius of which is closer to that of Cd than is that of Si. Furthermore, the crystal structure of GeS is rock-salt-like.

Ba is another exception because the ionic radius is larger than that of Cd and the crystal structure of BaS is rock-salt type, yet it is not an effective additive. It should be noted, however, that the ionic radius is too big to form a solid solution with CdS-II. This is expected because, in the case of Sr, there is a miscibility gap over a wide composition range in the rock-salt form.

From these ionic radius conditions, HgS should be regarded as an effective additive. However, the crystal structure of HgS is a zinc blende form or related structure which probably helps to stabilize the fourfold coordination.

As a result of these factors, the following empirical rule can be derived. Additive elements are effective for retaining CdS-II if their ionic radii are larger than or close to that of Cd, and the crystal structure of their monosulfides is of the rock-salt or rock-salt-like type. The ionic radius conditions for retaining CdS-II can be further explained by the radius ratio of cation to sulfur anion (Cd/S).

When a hard sphere model is applied to CdS, the radius ratio of cations to anions is $0.97/1.84 = 0.528$. This value is greater than 0.414, the critical value above which sixfold coordination is stable (*6*). Consequently, CdS ought to be stable in the sixfold coordinated or rock-salt structures. However, the real bond is much stronger and has a covalent character, so the Cd–S bond is directed toward fourfold coordination under atmospheric conditions. When high pressure is applied to CdS, both Cd cations and S anions shrink. Here the anion shrinkage is expected to be larger than that of the cations because anions are generally more bulky, and thus more compressible, than cations. Therefore, the Cd/S radius ratio is expected to increase with applied pressure, producing conditions favorable to the sixfold coordinated or rock-salt type structure.

On the other hand, the average ionic radius of metal ion sites is considered to vary with the degree of substitution, when a metal ion replaces some of the Cd in CdS to form a solid solution. If a metal ion larger than the Cd ion is substituted, the radius ratio of the average metal ion to the anion is expected to increase with the degree of substitution. This increase is also expected to stabilize structures with higher coordination numbers. However, this situation is reversed if a smaller metal ion than the Cd ion is substituted. This discussion, about the similar effects on rock-salt structure stabilization of high-pressure application and substitution of larger cations for Cd, qualitatively explains the present experimental observations for obtaining high-pressure form CdS.

Conclusion

Attempts have been made to retain the high-pressure modification of CdS, the rock-salt structure, using various metal monosulfide additives. It was found that additives of less than 30 mole% are effective for retaining CdS-II if their cation radii are larger than or close to that of cadmium. In addition, the monosulfides must have rock-salt type or rock-salt-like crystal structures. It was also found from X-ray measurements of lattice parameters that the retained phases are metal-substituted solid solutions. The ionic radius requirement for retention can be explained by introducing the radius ratio of cations to sulfur anions. The radius ratio increases with applied pressure and with degree of substitution.

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