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The CdS-MnS and CdSe-MnSe Phase Diagrams

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The CdS-MnS and CdSe-MnSe phase diagrams were determined by lattice constant measurements, visual examination of quenched specimens, and DTA. Melting points are 1258° ± 2°C for CdSe, 1397° ± 2° for CdS, and 1460° ± 8° for MnSe. The solid solution limit of MnS in CdS (wurtzite type) is 49 mole % MnS at 800° and 44% MnS at 1385°; the limit of CdS in MnS (rock salt type) is 11.5% CdS at 800° and 37% CdS at 1390°. The solid solution limit of MnSe in CdSe is 50% MnSe at 700° and 44% MnSe at 1175°; the limit of CdSe in MnSe is 5% at 700° and 19% at 1265°. The phases recovered after application of high pressure are also reported.

I. Introduction

There has been recent interest in the transition with pressure from wurtzite-type structure to rock salt-type structure in CdS and CdSe and in the way in which the transition pressure varies with solid solution. Preliminary work indicated that manganese lowered the transition pressure.[1] Therefore, the CdS-MnS and CdSe-MnSe phase diagrams were investigated to determine the optimum composition dependence of the transition pressure.

Limited information was found in the literature. Melting points have been reported for three of the four end-members: 1475°[2] and 1405° ± 10°C[3] for CdS, 1610° ± 3°C[4] for MnS, and 1239°,[5] 1258°,[6] and 1268°C[7] for CdSe. The melting points of CdS and CdSe have been checked in this study. The principal work on solid solution was that of Kröger[8] on the system ZnS-CdS-MnS, for which the equilibrium phases were determined only at 900°C. Therefore, the shape of the CdS-MnS diagram could not be deduced from Kröger's data. However, his results suggest that the ZnS-MnS and CdS-MnS systems may be quite similar in form. He quotes Schnaase[9] to the effect that CdS-MnS solid solutions can be made in all proportions by room-temperature precipitation, although the lattice constant data of Schnaase do not fully confirm this. No other solid solution data on CdS-MnS or CdSe-MnSe were found.

II. Materials and Experimental Techniques

The starting materials were luminescent grade CdS and CdSe* and 99.9% MnS and MnSe.† The CdS and CdSe were purified by sintering in vacuo at 850°, followed by sintering in argon at 1200°C. The final level of metallic impurities in each was probably less than 10 ppm, and the nonmetallic impurities (except for sulfur), initially 0.10 to 0.15%, were substantially reduced.[7] X-ray fluorescent analysis of the CdSe showed that it contained 2.7 at.% sulfur replacing selenium. None of the data in the phase diagram have been corrected for the sulfur content. The MnS and MnSe were checked by spectrographic analysis, which showed that each metallic impurity was well under 0.1%. The materials were heated in an

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atmosphere of sulfur or selenium, respectively, in an attempt to improve stoichiometry.

Fifty grams of various ratios of CdS and MnS or CdSe and MnSe powders of <50-mesh size were hand-mixed and were then reacted for 18 to 24 hr at 1140° to 1175°C in evacuated sealed fused silica ampuls containing practically no unfilled space to reduce the likelihood of separation of volatile constituents. The furnace had a long, even hot zone. The cooled ampuls were broken, a sample was taken to test for completeness of reaction by X-ray diffraction, and the remaining sample was reground to pass a 60-mesh screen. Since one component was volatile, intimate mixing was not needed if sufficient time was allowed for the volatile component to diffuse into the other.

Several techniques were used to determine the phase diagram. In one, 1-g samples were sealed under vacuum in fused silica ampuls with as small a free volume as possible, put into a preheated furnace at a specific temperature which was monitored by a calibrated thermocouple placed with its bead next to the sample, and quenched into liquid nitrogen. Liquid nitrogen was chosen despite its poor heat capacity and heat transfer properties since water would react with the sample if the ampul cracked while hot, and it was feared that organic liquids might explode. After the sample was quenched, the ampul was broken and examined for signs of more than one phase or of liquid. The solid phases were identified and their lattice constants were determined by X-ray diffraction (on film). Standard curves of lattice constant versus composition were established within the area of solid solution of each phase and were used to establish solid solution limits for those compositions and temperatures at which more than one phase was in equilibrium. The lattice constants were plotted against the Nelson-Riley function[10] and extrapolated to $\theta = 90°$. Vegard's law was assumed to apply for the curves of lattice constant versus composition and did hold within experimental error where checks were available. Most of the error resulted from the mixing of a volatile compound with a nonvolatile one, with the result that the compounds tended to separate slightly if the temperature varied.

The liquidus and solidus were determined mostly by DTA. The DTA equipment was standardized against the melting point of 99.9+% silicon taken as 1412°C[11] (three determinations on 99.9 to 99.99% material are reported from 1411° ± 2° to 1415° ± 2°[11-13]) and the melting point of gold, 1064.5°.[14] The DTA data are believed to be accurate to ±5° for the pure compounds and to ±10° for the solid solutions. The observed melting points are accurate within ±2° for CdS and CdSe. Where the melting point was sharp, values for solid solutions should be as accurate as those for pure compounds, but many solutions did not melt sharply. Probably all the plotted melting points are accurate within ±10°.

III. Results

The phase diagrams are shown in Fig. 1. Because devitrification of the fused silica prevented accurate determinations on the high-manganese end of each diagram, dashed curves are shown. In both diagrams solid solution in the rock salt phase* increased with temperature as is usual, whereas solid solution in the wurtzite phase decreased slightly with temperature. The maximum solid solution attained in the wurtzite structure was 49% MnS at 800°C for CdS-MnS and 50% MnSe at 700° for CdSe-MnSe. The limiting composition of the rock salt phase increases from 11.5% CdS at 800° to 37% CdS at 1390°, and from 5% CdSe at 700° to 19% CdSe at 1265°. The liquidus and solidus are not widely enough separated on the left side of Figs. 1(*A*) and (*B*) to be distinguished.

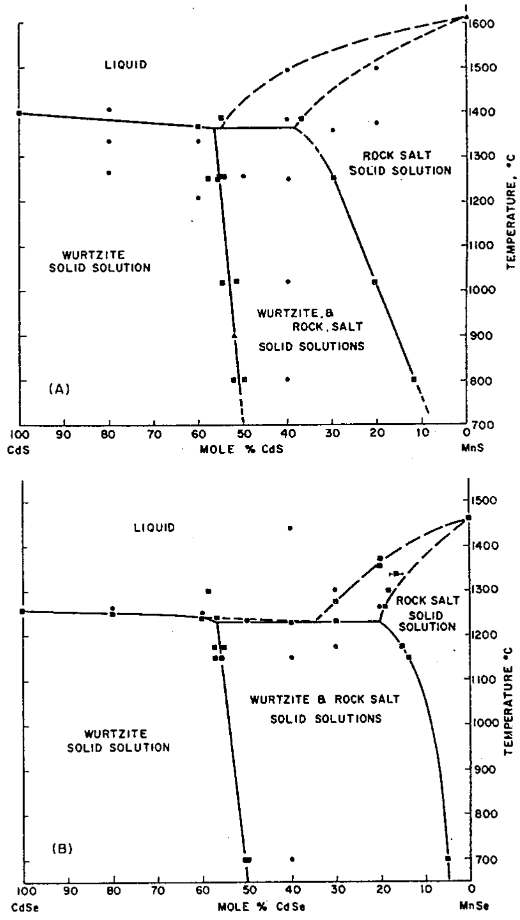

Fig. 1. Phase diagrams for (*A*) CdS-MnS and (*B*) CdSe-MnSe. ▲ Points from Refs. 4 and 8, ■ determined phase boundary, and ● composition not on a phase boundary, including those used to determine the solid solution limits.

They are estimated to be within 5° of each other for both systems. The minimum melting point in Fig. 1(*A*) is 1365° ± 10° and in Fig. 1(*B*) is 1231° ± 5°.

The melting point of MnS was not checked because of experimental difficulties. The melting point of MnSe was 1460° ± 8° by quenching. The melting point of CdSe is 1258° ± 2° by quenching and 1259° ± 4° by DTA. The melting point of CdS was 1397° ± 2° by quenching and 1401° ± 5° by DTA. For CdSe the value of Mason and O'Kane[6] was confirmed. For CdS the melting point of 1475° reported by Addamiano[2] was much too high, but the value determined by Sysoev *et al.*[3] was confirmed.

The lattice constants used to determine the compositions are shown in Table I. For the wurtzite structure, a_0 is more accurate than c_0 because 75% of the lines contribute more to a_0 than c_0.

IV. Phases Present after Exposure to High Pressure

Transition pressures on samples of some of the compositions studied were measured by Corll,[1] who used a high-pressure belt apparatus.[15,16] The samples were subjected to at least 45 kbars on each application, which was well in excess of the transition pressures. Subsequently, the samples were examined to determine the phases present after transformation to the rock salt structure. These phases do not necessarily represent equilibrium composition at 1 atm but were obtained under a given set of conditions. The results are plotted in

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* In the following discussion, the phase isostructural to the mineral wurtzite is referred to as the wurtzite phase, the phase isostructural to the mineral sphalerite (zinc blende) as the sphalerite phase, and the phase isostructural to rock salt (halite, NaCl) as the rock salt phase.

Table I. Lattice Constants of End-Members and Solid Solutions

Composition	a_0 (A)	c_0 (A)
CdS	4.1367 ± 0.0003	6.7161 ± 0.0005
$Cd_{0.6}Mn_{0.4}S$	4.077 ± .002	6.613 ± .004
Solid solution limit at 800°C ($Cd_{0.51}Mn_{0.49}S$)	4.0627 ± .0004	6..5919 ± .0008
MnS	5.2228 ± .0003	
$Cd_{0.2}Mn_{0.8}S$	5.2679 ± .0009	
Solid solution limit at 1390°C ($Cd_{0.37}Mn_{0.63}S$)	5.307 ± .001	
CdSe	4.2972 ± .0003	7.0065 ± .0005
$Cd_{0.6}Mn_{0.4}Se$	4.2453 ± .0004	6.9160 ± .0008
Solid solution limit at 700°C ($Cd_{0.50}Mn_{0.50}Se$)	4.2326 ± .0007	6.9018 ± .0015
MnSe	5.4626 ± .0005	
$Cd_{0.15}Mn_{0.85}Se$	5.4960 ± .0009	
Solid solution limit at 1265°C ($Cd_{0.19}Mn_{0.81}Se$)	5.5046 ± .0002	

Fig. 2. Because the X-ray diffraction pattern was diffuse, presumably because of imperfections introduced by the pressure, lines near $\theta = 90°$ were very weak, and the error limits tended to be much larger for those than for the original mixes. The lattice constant appeared to expand after the sample was ground, but this effect may not exceed the experimental error.

In the CdSe-MnSe system, the wurtzite phase transformed under pressure to the rock salt phase and converted to the sphalerite phase when the pressure was released, except near the wurtzite phase solid solution limit where the rock salt phase remained. As a result, there were two rock salt phases in some of the samples after pressure release. The phase with the smaller lattice constant (~5.47 A) was the limiting rock salt solid solution present before pressure application. The phase with the larger lattice constant (5.56 A) resulted from high-pressure conversion of the limiting wurtzite solid solution; this lattice constant is that predicted for $Cd_{0.5}Mn_{0.5}Se$ if it could be synthesized at ordinary pressure in a single-phase rock salt structure.

Similar results were obtained after exposure of the CdS-MnS system to pressure, except that the compositions with at least 80% CdS partly or wholly reverted to the wurtzite structure rather than to the sphalerite structure. This is understandable, since the tetrahedra in CdS are more distorted than those in CdSe. (In the sphalerite phase there is no distortion.) Near the solid solution limit, two rock salt phases were again observed after pressure release. The rock salt phase with the larger lattice constant again resulted from conversion of the wurtzite phase under pressure, whereas the rock salt phase with the smaller lattice constant represented the limiting solid solution under the original conditions of formation.

Corll[1] showed that the substitution of manganese for cadmium in CdS and CdSe caused a lowering of the pressure of transformation from wurtzite to rock salt structure. The results of this study established the limit to which the pressure can be lowered in these systems, as determined by the maximum amount of manganese that can be added to the wurtzite structure.

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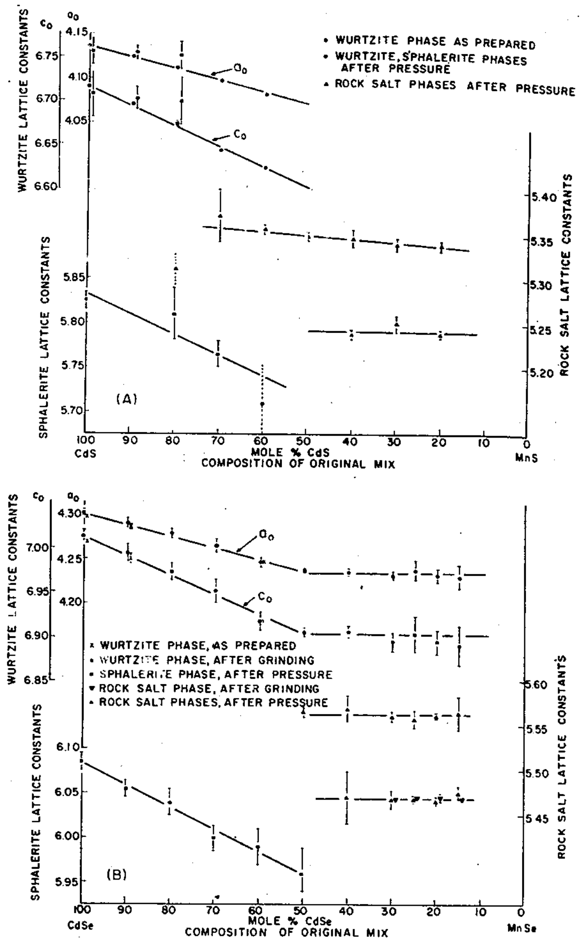

Fig. 2. Lattice constants of solid solutions before and after pressure. (*A*) CdS-MnS and (*B*) CdSe-MnSe. Data points for which no error limit is shown are more accurate than the point diameter. Some data points are slightly offset laterally for clarity.