Phase Equilibria in the Solid Region of the System Manganese Selenide–Cadmium Selenide*

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The temperature–composition phase diagram for the solid region of the MnSe–CdSe system has been investigated by X-ray diffraction and optical reflectance measurements on annealed samples over a range 500–1100°C. The small degree of solid solution on the MnSe-rich side compared to the large CdSe-rich one-phase region could be explained by the differences in structural and bonding properties of the components. The lattice parameters of compositions in the one-phase regions can be expressed for the MnSe-rich cubic phase by the equation

$$a_0 = 5.462 + 0.202 \cdot N,$$

and for the CdSe-rich hexagonal phase by the equations

$$a_0 = 4.173 + 0.124 \cdot N$$

and

$$c_0 = 6.822 + 0.193 \cdot N,$$

where N is the mole fraction of CdSe.

Introduction

The considerable interest in the chemistry of II–VI and related compounds is partially due to their useful solid state properties. In recent years some aspects of solid solutions of these compounds have been investigated (*1–6*). In general, when both components have the same crystal structure their physical properties vary continuously from one component to the other (*7*). Less is known about the synthesis and behavior of mixed systems with a miscibility gap. Such systems should be of practical importance since the properties of the alloys can differ significantly from either end component. This may be attributed to the difference in structures. It is therefore desirable to establish accurate phase diagrams of these alloys. This was done for the MnS–CdS system (*8*) in previous work. The results

are in agreement with similar studies by Cook (*9*). In his work on the mixed selenide system (*9*) the region close to and above the liquidus line was mainly studied and the results were not corrected for a small sulfur content of the CdSe samples.

The present work covers a temperature range 500–1100°C. The phase boundaries are determined on annealed samples by X-ray diffraction techniques and by optical reflectance measurements. Emphasis has been placed on the use of high purity and well-characterized materials and on the establishment of high temperature equilibria.

Experimental

Starting Materials

The pure compounds MnSe and CdSe were prepared by chemical transport reaction (*10*) using iodine as a transport agent. In case of MnSe (*11, 12*) stoichiometric amounts of manganese (99.99 + %) and selenium (99.999 %) were sealed with a known amount of in vacuo sublimed iodine in quartz tubes at a pressure of less than 10^{-6} Torr. The system

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was transported in the temperature gradient 875 → 840°C. The quartz tubes used throughout this work were outgassed under high vacuum ($< 10^{-6}$ Torr) at temperatures between 900 and 1000°C for 12–18 hours. Chemical analysis of the transport product by EDTA titration (13) and X-ray diffraction patterns verified that the material was stoichiometric (Mn (expt) = 41.10%; Mn (calcd) = 41.03%) and had the NaCl-type structure (a_0 (expt) = 5.463 Å; a_0 (lit) = 5.462 Å (14)). CdSe was prepared under similar conditions from cadmium (99.999%) and selenium by chemical transport with iodine in the temperature gradient 950 → 850°C. EDTA titration (13) showed stoichiometric composition within experimental error limits (Cd (expt) = 58.60%; Cd (calcd) = 58.74%), and X-ray diffraction patterns verified the wurtzite modification of CdSe with lattice parameters ($a_0 = 4.298$ Å, $c_0 = 7.016$ Å) in agreement with literature (15) values ($a_0 = 4.2985$ Å, $c_0 = 7.0150$ Å). Based on radioactive tracer studies by Schäfer and Odenbach (16) the amount of iodine incorporated into the transported materials is estimated to be less than 10^{-2} mole %. Emission spectrographic analysis of the pure compounds revealed that the total mean impurity content of spectroscopically detectable elements was about 4×10^{-2} wt %.

Preparation of Solid Solutions

Finely powdered samples of MnSe and CdSe were thoroughly mixed in various molar ratios and compressed into pellets of about 6 mm in diameter and 2 mm in height at a pressure of 13.5 kbar. This procedure yielded packing densities up to 0.96. The pellets were sealed under high vacuum ($< 10^{-6}$ Torr) in quartz ampules of 12 mm in inner diameter and 50 mm in length. After an appropriate annealing time at constant temperature the tubes were removed from the furnace and quenched in air. This procedure was sufficient to maintain the high temperature equilibrium.

The proper choice of the annealing temperature was found to be critical in order to obtain X-ray patterns with well-resolved back reflections necessary for accurate lattice parameter calculations. Test runs showed that 500°C was the optimum temperature for CdSe-rich solid solutions to yield high quality X-ray diagrams without using a prohibitively long time to establish equilibrium. Lattice constants for compositions of the hexagonal one-phase region were determined on samples equilibrated at 500°C. The one-phase line of the MnSe-rich solid solutions was established by

annealing mixtures with 5, 10, 15, and 20 mole % CdSe at temperatures between 500 and 1100°C.

To ensure equilibrium, all samples were subjected to repeated annealing cycles of one week each. The cell dimensions were calculated after each cycle and the results after the third annealing agreed within the limits of error with those after the second heating. A qualitative but sensitive test of equilibrium is the observation of the homogeneity of the color of the powdered solid solution. The color changes across the visible spectrum as a function of composition, which is related to changes in the band structure of the solid. Typical local concentration gradients observed after the first heating cycle had disappeared after the second one. After removing the quartz tubes from the furnace the inside wall showed a very thin layer of sublimate. X-ray examination showed that the material was pure CdSe. A determination of the amount of sublimate revealed that the effect on the composition of the solid solution was negligibly small (< 0.1 mole % CdSe), so that the final composition agreed with the nominal weights of MnSe and CdSe used.

X-Ray Diffraction

X-ray diffraction techniques were used to determine the degree of solid solution from the change in lattice parameters as a function of composition and the appearance of a second phase. This procedure was used to establish the solubility limit of the MnSe-rich cubic phase at various temperatures between 500 and 1100°C. For the CdSe-rich hexagonal phase this method was used at 500°C. To obtain the solubility limits of this phase at other temperatures mixed samples of composition within the two-phase region were annealed at different temperatures. The equilibrium lattice parameters of the hexagonal phase were used to determine the hexagonal phase boundary. The absence of any additional reflections in all X-ray patterns verified that no other crystallographic phases but the NaCl and the wurtzite structure were present. Debye–Scherrer powder photographs were taken in a 114.59-mm-diameter camera with Ni-filtered CuKα-radiation. The lattice parameters for the MnSe-rich solid solutions with NaCl structure were calculated by the extrapolation method as described by Cullity (17) and Buerger (18) using high angle reflections. For the evaluation of lattice parameters of the CdSe-rich wurtzite-type solid solutions Buerger's reciprocal lattice method (19) was used. By choosing proper reflections the cell constants a_0 and c_0 were calculated and averaged. These values

were used to obtain an initial c/a ratio, and lattice constants from each reflection were calculated with the following equations:

$$a = d[4/3(h^2 + hk + k^2) + l^2/(c/a)^2]^{\frac{1}{2}} \qquad (1)$$

and

$$c = d[4/3(h^2 + hk + k^2)(c/a)^2 + l^2]^{\frac{1}{2}} \qquad (2)$$

The a and c values thus obtained were plotted against the Nelson and Riley (20) function $\frac{1}{2}(\cos^2\theta/\sin\theta + \cos^2\theta/\theta)$ to give a more precise c/a ratio. This re-iteration process was applied twice and the lattice constants obtained by the last cycle agreed precisely with the prior calculated values.

Reflectance Measurements

An independent method to determine the solubility limits of the hexagonal phase in this system is offered by optical measurements. It has been fully described by Fochs (21) that the change in absorption in the diffuse reflectance of powdered materials in the visible region of the spectrum is directly related to the promotion of charge carriers across the band gap of the solid solution. As a result of work reported elsewhere (22) the variation of the energy gap with composition in the CdSe-rich hexagonal one-phase region can be described by the expression

$$E_G = 2.78 - 1.08 \cdot N, \qquad (3)$$

where N is the mole fraction of CdSe and E_G is given in electron volts. The use of reflectance measurements to determine the energy gap of the CdSe-rich phase is based on the fact that the MnSe-rich phase has a high absorption coefficient so that any large change in the percent reflectance can be attributed solely to the CdSe-rich phase in a homogeneous mixture containing both phases. For this purpose measurements of the diffuse reflectance were made on powdered samples containing 40 mole % CdSe (two-phase region) which were equilibrated at various temperatures. The absorption edge is obtained by extrapolation of the two linear portions of the reflectance curve at the low-wavelengths knee and converted into the energy gap in electron volts. This value corresponds to the energy gap of the CdSe -rich phase (22). The composition of this phase is obtained with the particular energy gap value and Eq. (3) by solving for N.

Results

The lattice parameters and axial ratios of compositions of the one-phase regions of the system are listed in Table I. It is found that the lattice para-

meters change linearly with composition within the limits of experimental error. Applying a linear least-squares analysis to the data the lattice constants of the one-phase compositions can be expressed for the MnSe-rich cubic phase by the equation

$$a_0 = 5.462 + 0.202 \cdot N, \qquad (4)$$

and for the CdSe-rich hexagonal phase by the equations

$$a_0 = 4.173 + 0.124 \cdot N \qquad (5)$$

and

$$c_0 = 6.822 + 0.193 \cdot N, \qquad (6)$$

where N is the mole fraction of CdSe.

Assuming that Vegard's law holds for a complete substitution of Mn^{2+} for Cd^{2+} in the hexagonal phase Eqs. (5) and (6) yield lattice parameters for MnSe in the wurtzite structure, namely $a_0 = 4.173$ Å and $c_0 = 6.822$ Å. These values are in general agreement with literature (23) data ($a_0 = 4.12$ Å, $c_0 = 6.72$ Å). A similar evaluation of Eq. (4) yields a lattice parameter for CdSe in the NaCl structure, $a_0 = 5.664$ Å. Mariano and Warekois (24) studied the high-pressure transformation of CdSe from the wurtzite to the NaCl-type modification and obtained a value for a_0 of 5.49 Å determined at a pressure of 32 kbar. Rooymans (25) reported a value of 5.54 Å for the lattice parameter of CdSe with NaCl structure at a pressure of 30 kbar. The trend in these values could suggest that in addition to the rearrangement of atoms to form a structure of higher coordination the interatomic distances are reduced due to the applied pressure. The value obtained in

TABLE I

LATTICE PARAMETERS AND AXIAL RATIOS OF COMPOSITIONS IN THE ONE-PHASE REGIONS OF THE MnSe–CdSe SYSTEM

Composition Mole % CdSe	NaCl Structure a_0 (Å)	Wurtzite Structure		
		a_0 (Å)	c_0 (Å)	c/a
0	5.462			
5	5.472			
10	5.483			
15	5.492			
50		4.236	6.919	1.633
60		4.247	6.938	1.633
70		4.261	6.958	1.633
80		4.272	6.973	1.632
90		4.285	6.997	1.633
100		4.298	7.016	1.632
	±0.001	±0.001	±0.003	±0.001

TABLE II

AVERAGE LATTICE PARAMETERS OF COMPOSITIONS IN THE TWO-PHASE REGION
AND CORRESPONDING SOLUBILITY LIMITS CALCULATED WITH Eq. (4) FOR THE
CUBIC PHASE AND WITH Eq. (5) FOR THE HEXAGONAL PHASE

| Temperature °C | Cubic Phase[a] | | Hexagonal Phase[b] | | |
	a_0 (Å)	Solubility Limit Mole % CdSe	$a_0{}^c$ (Å)	c_0 (Å)	Solubility Limit Mole % CdSe
500	5.469	3.5 ± 0.5	4.234	6.916	49.2 ± 2
640	5.473	5.4 ± 0.5	4.236	6.912	50.8 ± 2
800	5.482	9.9 ± 0.5	4.236	6.918	50.8 ± 3
960	5.491	14.4 ± 0.5	4.234	6.916	49.2 ± 3
1100	5.501	19.3 ± 1.0	4.234	6.917	49.2 ± 5

[a] The error limit of the lattice parameter of the cubic phase is ±0.001 Å up to 960° and ±0.002 Å at 1100°C.

[b] The errors in the a parameter of the hexagonal phase change from ±0.001 Å at 500° to ±0.003 Å at 1100°C.

[c] Only the a parameters were used to determine the solubility limits.

this work by a Vegard law extrapolation is based on ideal substitution at room pressure which does not consider possible compressibilities of the atoms at higher pressures.

The average lattice parameters of mixed compositions within the two-phase region equilibrated at different temperatures and the corresponding solubility limits are given in Table II. The composition of the phase boundaries was calculated from the equilibrium lattice constants of the corresponding phases with Eqs. (4) and (5). The individual data are plotted in Fig. 1. The solubility limit of the hexagonal phase is based on the a parameters only since they can be determined more precisely than the c parameter. For this purpose the composition closest to the phase boundary (40 mole % CdSe) was used for the final evaluation. Corresponding reflections in X-ray diagrams of compositions with lower CdSe content were too weak for a reliable evaluation. The temperature-composition phase diagram is given in Fig. 2.

It was observed in this work that with increasing annealing temperature the back reflections in the X-ray patterns became more diffuse. This contributes to the errors in lattice parameters and solubility limits at higher temperatures. Fischer and Paff (26) explained similar observations in the ZnSe–CdS system through the occurrence of strain in the particles due to rapid quenching. As a part of this investigation equilibrated solid solution samples of MnSe–CdSe were annealed for one month at 800°C and cooled to room temperature over a period of several days with no apparent improvement of

the X-ray diffraction patterns. A possible explanation for the diffuseness of the back reflections could be the presence of polymorphic modifications in these materials. It is known that II–VI compounds crystallize in a variety of polymorphic and polytypic forms (27). This is due to the fact that the thermodynamic stabilities of different close packed arrange-
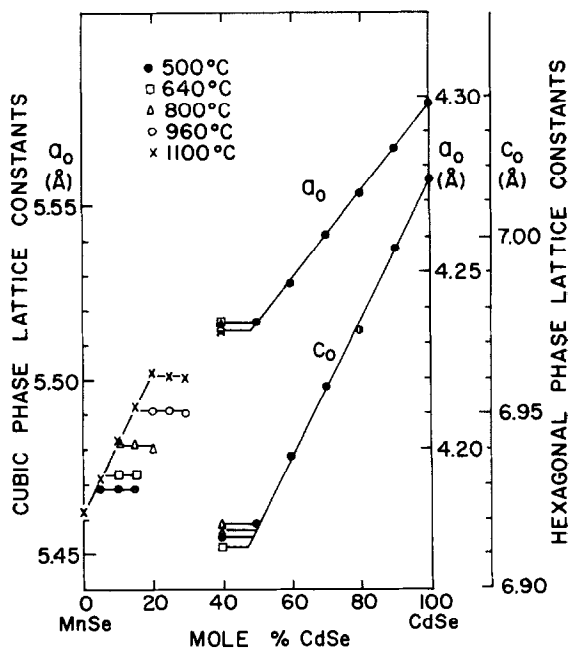

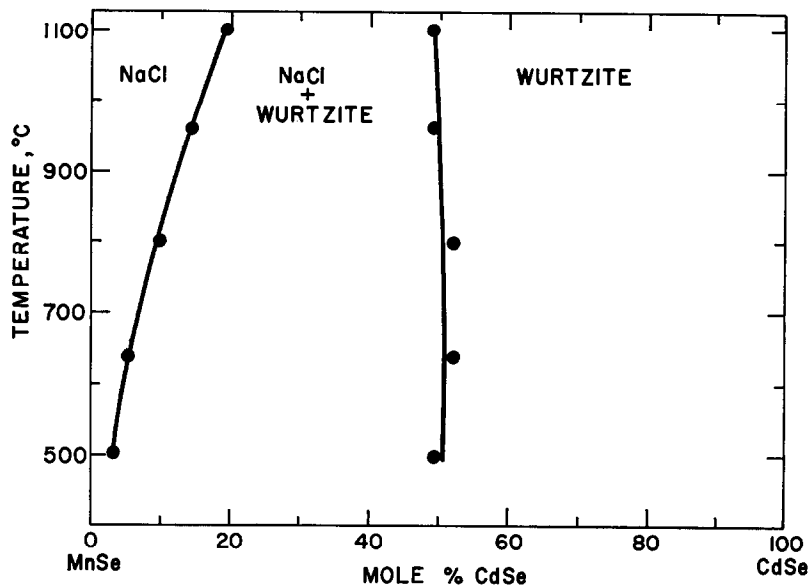FIG. 1. Isothermal lattice parameter-composition plots in the MnSe–CdSe system.

FIG. 2. Temperature-composition phase diagram of the MnSe–CdSe system.

ments do not depend strongly on the specific order of the layers within the sequence of the hexagonal and cubic structures. Because of extensive poly-typism in these compounds gross defect structures associated with intergrowth of several crystal forms are frequently encountered (27). This can lead to a random distribution of small regions of cubic order in a wurtzite stacking causing a lower intensity of the major reflections, a slight contraction of the unit cell in the cubic regions, and diffuse X-ray patterns. The reason that the diffuseness of lines predominates at higher temperatures in the MnSe–CdSe system could be that the entropy contribution to the free energy of the structure resulting from a random distribution of layer sequences of zinc blend type within the hexagonal (wurtzite) structure becomes more dominant with increasing temperature.

The results of measurements of the diffuse reflectance of powdered samples in the two-phase region of this system are summarized in Table III. As discussed elsewhere (22) the uncertainty of the extrapolated absorption edges is less than ± 10 nm. With the computed energy gap the composition of the phase boundary is calculated with Eq. (3). The solubility limits obtained by this method agree within the limits of experimental error with the results from X-ray diffraction studies.

Discussion

The distribution of phases in the MnSe–CdSe system is analogous to the corresponding sulfide system (8). The CdSe-rich hexagonal phase is considerably wider than the MnSe-rich cubic phase. This could be explained by the fact that MnSe exists in three crystallographic modifications: NaCl structure (28) ($a_0 = 5.462$ Å), zinc blend structure (29) ($a_0 = 5.82$ Å), and wurtzite structure (23) ($a_0 = 4.12$ Å, $c_0 = 6.72$ Å). The stable modification of CdSe at room pressure is the wurtzite structure (23) ($a_0 = 4.30$ Å, $c_0 = 7.02$ Å). Based on this one would expect that MnSe can be easily accommodated in the CdSe host lattice since it requires only a rearrangement of the MnSe structure to a metastable modification with a change in

TABLE III

Solubility Limits of the Hexagonal Phase Calculated with Eq. (3) from Energy Gap Values of Samples Containing 40 Mole % CdSe (Two-Phase Region) Equilibrated at Various Temperatures

(Energy Gap Values are from Room Temperature Reflectance Measurements.)

Temperature °C	λ_{edge} (nm)	Energy Gap (eV)	Solubility Limit Hexagonal Phase Mole % CdSe
500	545 ± 10	2.27 ± 0.04	47 ± 3.7
640	545 ± 10	2.27 ± 0.04	47 ± 3.7
800	545 ± 10	2.27 ± 0.04	47 ± 3.7
960	555 ± 10	2.23 ± 0.04	51 ± 3.7
1100	550 ± 10	2.25 ± 0.04	49 ± 3.7

bonding from octahedral to tetrahedral configuration. The electronic structure of manganese permits both configurations with s-p-d and s-p orbitals, respectively. In order for cadmium to form octahedral bonds in the NaCl-type structure, higher d-orbitals have to be used which is energetically unfavorable. This structure type can only be obtained for CdSe through the application of high pressure. These bonding properties explain the existence of only the wurtzite modification of CdSe at room pressure and the narrow range of solid solubility of CdSe in MnSe.

It is interesting to note that the solubility limit of the hexagonal phase corresponds to approximately 50 mole % CdSe (i.e., an equal distribution of Mn^{2+} and Cd^{2+} ions) and that it is little temperature dependent. This suggests the possibility of an ordered stable arrangement and the existence of a super-lattice for the alloy composition at the phase-boundary. X-ray patterns obtained with CuKα-radiation did not show any additional reflections which could have been interpreted as superlattice lines. The back region of the solid solution X-ray diagrams is masked by the fluorescence of manganese. X-ray diffraction patterns of alloys containing 50 mole % CdSe obtained with chromium radiation using a vanadium filter gave no indication of superlattice lines either. This result, however, does not exclude the existence of ordering in the solid solution, since even the most intense superlattice lines of an ordered alloy are very weak compared to the major reflections of the pattern.

Acknowledgments

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