Nonstoichiometry of Zinc Selenide

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In the present study the homogeneity limits of zinc selenide in equilibrium with zinc melt have been investigated. The equilibrium concentration of the excess Zn in ZnSe has been determined by the extraction method. The concentration of excess Zn in ZnSe decreases when the temperature and pressure of zinc vapor are decreased. Electrically inactive defects form under these conditions. © 1993 Academic Press, Inc.

Introduction

In single crystals of zinc selenide that were grown from melt or from the vapor phase, inclusions of the outer phase appear during the cooling of the crystals. One possible reason for this is the disintegration of the supersaturated solution into its components. In order to estimate the maximum possible concentration of these inclusions, information about homogeneity limits of the compound is necessary. The same information is also desirable to determine the range of point defect concentrations, since the optical, photoelectric, and luminescent properties of materials in many cases depend on the concentration of these defects. Since no quantitative estimates of the homogeneity limits of zinc selenide have been published

the purpose of this work is to determine the homogeneity limits of zinc selenide in equilibrium with zinc melt. According to [1], the deviation from stoichiometry under such conditions probably is no higher than $1-2 \times 10^{-4}$ mole percent. For the determination of such small concentrations, the extraction method has been used [2].

Experimental

Powdered zinc selenide (mean dimensions of crystals, 20 μm; content of admixture, less than 1×10^{-4} mass%), and argon (high purity) were used.

Zinc selenide was successively annealed at 1170 K in a quartz ampoule in vacuum (pressure of residual gas, less than 1×10^{-1} Pa), in zinc vapor (at 9×10^4 Pa), and under conditions of congruent evaporation. The duration of each annealing stage was 1 hr,

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and the duration of the whole process of annealing was 4 hr.

The residual zinc and selenium phases, present in the industrial preparation, were removed during the annealing process. Prior to the experiment the oxidized surface of metallic zinc was removed by a solution of nitric acid in redistilled water.

The saturation of crystals of zinc selenide in zinc vapor was carried out in a quartz ampoule in vacuum (under 1×10^{-1} Pa) or in an argon atmosphere ($0.3-0.7 \times 10^5$ Pa). The overall pressure could be regulated by varying the quantity of ZnSe added to the ampoule. These conditions made it possible to vary the rate of mass transport of zinc, and to study its effect on the experimental results.

A portion of the inside surface of the ampoules was deliberately graphitized, to absorb any residual oxygen present. Zinc selenide (5–20 g) was placed at one side of the ampoule, and zinc or a mixture of zinc and zinc selenide in the mole ratio 1:1 was placed on the other side. The mixture provided better control over the homogeneity limits.

The determination of the homogeneity limits of zinc selenide was carried out while the temperature of the zinc selenide/zinc mixture was maintained, with an error of ±2 K, 2–5 K below the temperature of the saturated zinc selenide sample. This largely eliminated the uncontrolled volatilization of zinc to the saturated crystals. The determination of concentration of the excess Zn in ZnSe within the homogeneity limits was carried out while the temperature of the zinc melt was kept below the temperature of the saturated crystals.

The error of the temperature measurements was ±2 K. The pressure of zinc vapor above the crystals of zinc selenide was calculated using the results of Ref. [3] and from the known melting point of zinc. After annealing, the ampoules were quenched in water to freeze in the high-temperature configuration.

We measured the concentration of the excess Zn in ZnSe in two stages. The zinc condensate was first removed from surface of samples and from the walls of that part of the ampoule into which zinc had been placed.

The part of the ampoule with the sample was cut away and placed in another ampoule. This ampoule was annealed at T = 870 K in vacuum. Zinc volatilized to the cold end of the ampoule but did not escape from the ZnSe crystals kept at room temperature. Zinc volatilized for approximately 20 min, after which no additional volatilization of zinc was noted. The excess zinc was extracted for approximately 1 hr from crystals during the anneal by the above-mentioned method, while the temperature of the sample was kept at 1070 K. The amount of zinc and selenium in the condensate was determined by well established spectrophotometric methods, calibrated against known standards [4]. The detection limit for zinc is 0.3 μg and for selenium is 1.5 μg; the errors in the determination did not exceed ±6%. The quantity of selenium in the condensate did not differ from the quantity of zinc by more than 5%.

Results and Discussion

The results of the determination of excess zinc in ZnSe are shown in Table 1. The data for samples 1–6, 9, and 10 were taken when zinc/zinc selenide mixtures were used in place of zinc. These results can be fitted to the equation

$$X_{Zn}/P_{Zn} = 1.816 \times 10^{-9} \exp(-933.9/T). \quad (1)$$

Equation (1) was tested by varying the mass of samples (5–20 g), the time of annealing, and the cooling rate. This established that the measured concentrations are close to the equilibrium concentrations. It follows that the solubility of Zn in AnSe is retrograde.

TABLE I

THE CONCENTRATION OF EXCESS Zn IN ZnSe

No.	T (K)	$P_{Zn} \times 10^5$ (Pa)	τ (hr)	Gas	$X_{Zn} \times 10^5$ (mole Zn/mole ZnSe)		$\Delta\%$
					Expt	Calcd	
1	1173	0.90	30	Ar	8.32	7.37	+13.0
2	1173	0.90	20	Ar	9.33	7.37	+26.6
3	1223	1.46	15	Ar	10.2	12.3	−17.1
4	1223	1.46	15	Ar	9.32	12.3	−24.2
5	1273	2.28	10	Ar	19.9	19.9	0.0
6	1273	2.28	10	Ar	20.7	19.9	+4.0
7	1273	0.19	6	Vacuum	1.57	1.66	−5.4
8	1273	0.039	12	Ar	0.29	0.34	−14.7
9	1323	3.44	6	Ar	34.2	30.8	+11.7
10	1323	3.44	6	Vacuum	37.2	30.8	+21.4

Note. Nos. 1–6, 9, and 10 are the homogeneity limits of the ZnSe phase.

According to Eq. (1) the concentration of excess Zn in ZnSe decreases when the temperature and pressure of zinc vapor decrease. Therefore, when the crystals are cooled, a disintegration of the supersaturated solution can occur and the concentration of Zn in ZnSe crystals can reach several hundredths of a mole%. The concentration of excess Zn is much higher than the concentration of the electrons in the conducting region [5].

Thus, either self-compensation of charged defects occurs or electrically inactive defects are formed. The latter case is more probable if one considers the proportional variation of X_{Zn} with P_{Zn}. In this case formation of Zn_i^x or V_{se}^x according to Ref. [6] is possible via

$$Zn^v = Zn_{Zn}^x + V_{se}^x \qquad (2)$$

$$Zn^v = Zn_i^x. \qquad (3)$$
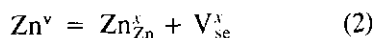
Here the subscripts designate the sites and x designates electrically neutral species.

In both cases $X_{zn} \sim P_{Zn}$. The equilibrium constant of reaction (2) or (3) is determined by the equation

$$K_{2(3)} = \exp(-933.9/T - 8.613). \qquad (4)$$

Thus, the enthalpy at the reaction is given by $\Delta H_{2(3)} = +0.081$ eV, and the entropy by $\Delta S_{2(3)} = -8.61 \, k_B$ (k_B is the Boltzmann constant).

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