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Phase equilibria in the $Ag_{2/3}Cd_{1/3}$–Te system

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The T–X phase diagram of the polythermal $Ag_{2/3}Cd_{1/3}$–Te section in the Ag–Cd–Te system has been determined. Using X-ray diffraction, differential thermal and metallographic analyses, as well as microhardness and density measurements, 23 phase fields have been found, 8 of which were monophasic. The phase diagram is characterized by two non-variant peritectic and one peritectoidal equilibria. Two intermediate phases have been established: A (at 55 at % Te) with several polymorphic transitions, and B (at 25 at % Te).

1. Introduction

Investigation of complex systems containing semiconductors with different properties, for example Ag_2Te (a narrow-gap type) and CdTe (a wide-gap type), allows new phases to be found with interesting behaviour suitable for applications [1]. The ternary Ag–Cd–Te system has been studied along the Ag–Te, Ag–Cd and Cd–Te sections [2]. In order to establish the physico-chemical interactions in this system we have also studied the Ag_2Te–CdTe [3], Ag–CdTe [4] and Cd–Ag_2Te [5] sections. They are characterized by intermediate phases with constant or variable composition, as well as limited solid solutions on the basis of Ag, Cd, Ag_2Te and CdTe. The present work is a continuation of these investigations and concerned the phase equilibria along the $Ag_{2/3}Cd_{1/3}$–Te section. This particular section was chosen after analysis of the previous results [3–5].

2. Experimental procedure

The $Ag_{2/3}Cd_{1/3}$ phase and the $(Ag_{2/3}Cd_{1/3})_{100-x}Te_x$ ($0 \leq x \leq 100$) samples were synthesized by heating the elements (purity 99.99%) inside evacuated and sealed quartz ampoules in a rocking furnace. The melt was heated up to 1000 °C with vibrational stirring for 3 h and cooled to room temperature. The phase diagram was specified by a complex application of different methods. To identify the phases, X-ray diffraction analysis was carried out using a TUR-M61 diffractometer (CuK_α radiation with a nickel filter) and the phase transition temperatures were determined by differential thermal analysis (DTA). The microstructure was studied by the metallographic method. To achieve better development of the phases, the following solutions were chosen: for $Ag_{2/3}Cd_{1/3}$-rich samples, $NH_4OH:H_2O_2:H_2O = 1:1:1$; $t^\circ = 30\,^\circ C$; $\tau = 30$ s; for tellurium-rich ones, $(HF:HNO_3:CH_3COOH = 3:5:6$; $t^\circ = 25\,^\circ C$; $\tau = 20$ s). We did not succeed in developing microstructure of the compositions in the range 50–75 at % Te. The density, d, was measured by a picnometric technique in toluene, and the microhardness, $\bar{H}_\mu$, using a Vickers microindentor [3–5].

3. Results

The X-ray diffraction data of the system studied are presented in Fig. 1 as a schematic diagram, and the phase transitions temperatures are given in Table I. For the $(Ag_{2/3}Cd_{1/3})_{45}Te_{55}$ composition new lines appeared, which indicates formation of a new A-phase. Shift of these lines in the interval 50–60 at % Te was not observed, i.e. the range of homogeneity was below ± 5% compared to the composition of the A-phase. Tellurium lines exist in the interval 65–100 at % Te and $Ag_{2/3}Cd_{1/3}$ lines at 0–30 at % Te. This supposes the presence of two phases at room temperature: ($Ag_{2/3}Cd_{1/3}$ + A) and (Te + A).

The microhardness studies show that $\bar{H}_\mu$ varies linearly in the intervals 0–3 and 96–100 at % Te, indicating the presence of limited solid solutions based on $Ag_{2/3}Cd_{1/3}$ and Te, respectively (Fig. 2). In the range 52–58 at % Te, only the A-phase exists, while in the ranges 5–50 and 60–90 at % Te, ($Ag_{2/3}Cd_{1/3}$ + A) and (A + Te) exist, respectively. This conclusion is confirmed by the two established values of $\bar{H}_\mu$ in each of the above concentration intervals.

The character of variation in density in the ranges $0 \leq x \leq 5$ and $95 \leq x \leq 100$ gives proof of the existence of limited solid solutions based on $Ag_{2/3}Cd_{1/3}$ and Te, while in the ranges $5 \leq x \leq 55$ and $55 \leq x \leq 95$ it indicates the presence of two phases (Fig. 3).

4. Discussion

The T–X phase diagram of the polythermal $Ag_{2/3}Cd_{1/3}$–Te section in the ternary Ag–Cd–Te system was determined on the basis of X-ray diffraction, differential thermal and metallographic analyses and measurement of the microhardness and density. It is characterized by 23 phase fields, 8 of which are monophasic (Fig. 4).

Two non-variant peritectic equilibria, at 38 at % Te (with a peritectic point at 890 ± 10 °C) and at 95 at % Te (with a peritectic point at 450 ± 10 °C), respectively, as well as one peritectoidal equilibrium at 25 at % Te (with a peritectoidal point at 530 ± 10 °C) have been established. Two intermediate phases were found, A-phase (at 55 at % Te), formed by the interaction of the limited solid solutions based on $Ag_{2/3}Cd_{1/3}$ and Te, and B-phase (at 25 at % Te), formed by the peritectic reaction between the A-phase and the limited solid solution based on $Ag_{2/3}Cd_{1/3}$ (at 530 ± 10 °C).

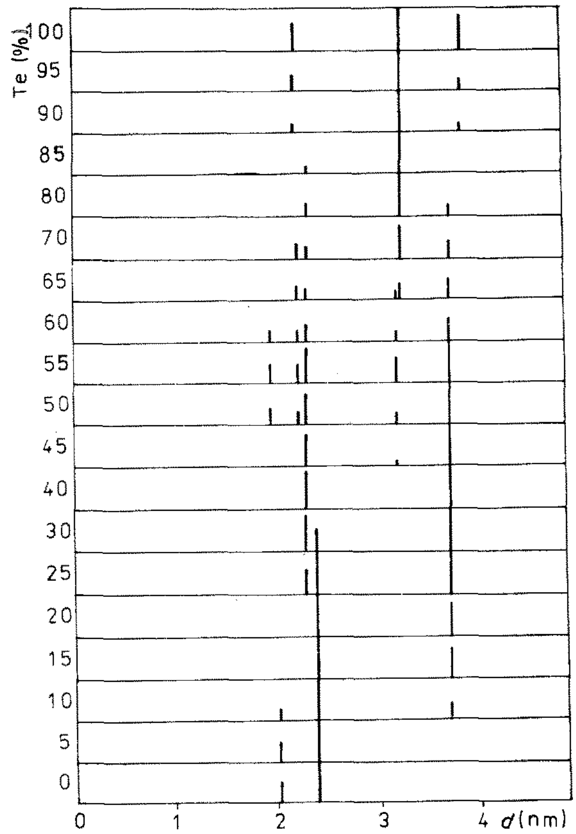

Figure 1 Schematic diagram of the X-ray diffraction lines.

The A-phase exists from room temperature to 980 ± 10 °C (at which it melts congruently), and the B-phase in the range 305–530 °C.

The A-phase undergoes several polymorphic transitions at different temperatures, depending on the

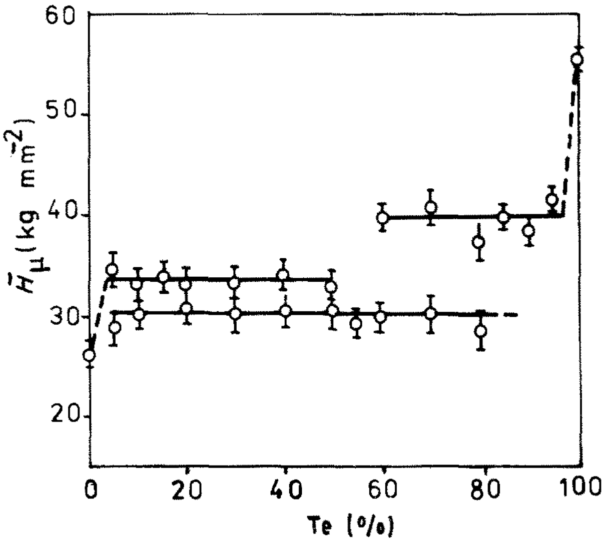

Figure 2 Compositional dependence of the microhardness.

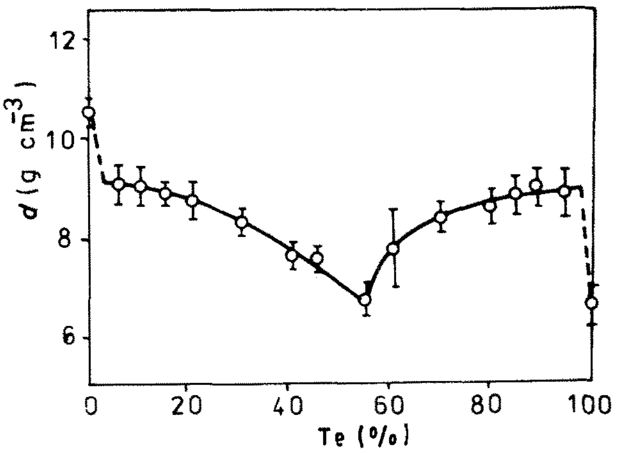

Figure 3 Compositional dependence of the density.

TABLE I Phase transition temperatures of the $Ag_{2/3}Cd_{1/3}$–Te system

	Te (at %)	Thermal effects (°C)							
1	0	–	–	–	–	–	–	745	785
2	5	–	–	380	–	–	–	750	805
3	10	–	305	–	–	530	–	755	810
4	15	150	–	–	–	–	–	770	825
5	20	150	–	–	–	–	630	780	–
6	25	150	305	–	–	530	660	800	830
7	30	145	305	335	–	530	–	763	–
8	40	150	–	–	–	535	–	895	925
9	45	150	–	–	–	535	–	–	–
10	50	–	310	330	–	–	735	850	970
11	55	150	–	335	–	–	–	–	975
12	60	120	–	245	–	485	–	850	–
13	70	125	–	245	–	485	–	–	850
14	80	130	–	245	450	–	–	–	755
15	85	125	–	235	450	–	–	–	695
16	90	–	–	230	455	490	–	–	585
17	95	–	–	235	455	–	–	–	505
18	100	–	–	–	–	–	–	–	455

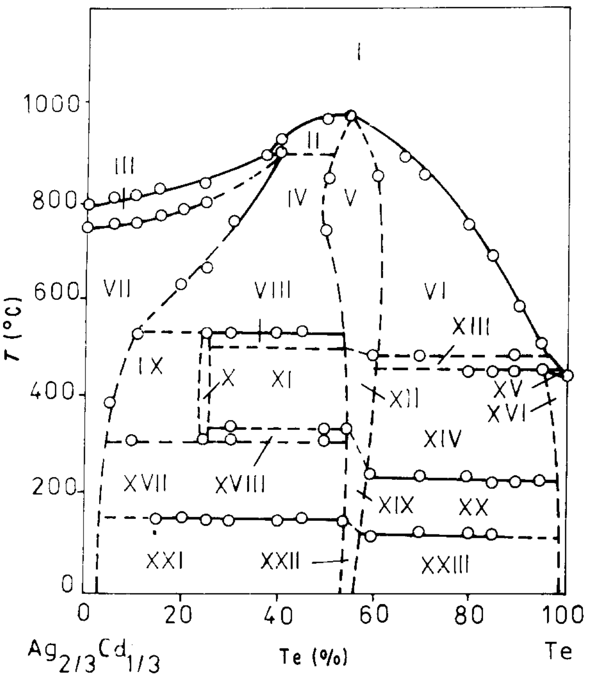

Figure 4 Phase diagram of the $Ag_{2/3}Cd_{1/3}$–Te system: (I) liquid, (II) liquid + δ – A, (III) liquid + ε – $Ag_{2/3}Cd_{1/3}$, (IV) ε – $Ag_{2/3}Cd_{1/3}$ + δ – A, (V) δ – A, (VI) δ – A + liquid, (VII) ε – $Ag_{2/3}Cd_{1/3}$ (solid solution based on $Ag_{2/3}Cd_{1/3}$), (VIII) B + δ – A, (IX) ε – $Ag_{2/3}Cd_{1/3}$ + B, (X) intermediate B-phase, (XI) B + γ – A, (XII) γ – A, (XIII) γ – A + liquid, (XIV) γ – A + κ – Te, (XV) κ – Te + liquid, (XVI) κ – Te (solid solution based on Te), (XVII) ε – $Ag_{2/3}Cd_{1/3}$ + β – A, (XVIII) B + β – A, (XIX) β – A, (XX) β – A + κ – Te, (XXI) ε – $Ag_{2/3}Cd_{1/3}$ + α – A, (XXII) α – A, (XXIII) α – A + κ – Te.

composition, x. The transition temperatures decrease at the point of deviation from the stoichiometric composition with increasing tellurium content. The opposite tendency is observed with decreasing tellurium content. The temperature intervals, in which the modifications belonging to the A-phase exist, are α–A from room temperature to 120–150 °C, β–A from 120–150 °C to 240–330 °C, γ–A from 240–330 °C to 480–500 °C, and δ–A from 480–500 °C to 980 °C.

The homogeneity region of the A-phase expands with increasing temperature and reaches its largest size at about 800 °C, for 49–61 at % Te. This is also confirmed by the slight endothermal effects on the DTA curves of the compositions containing 50 and 60 at % Te.

We did not succeed in "freezing" the B-phase nor in determining its homogeneity region, nor in obtaining information about the structure.

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