

PHASE EQUILIBRIA IN THE Ag_2Te – Cd SYSTEM

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The phase diagram of the Ag_2Te – Cd system, which is a polythermal section of the ternary system Ag – Cd – Te , was established by means of DTA and metallographic analysis. The diagram contains 32 phase regions, including the polymorphic modifications of Ag_2Te , solid solutions based on Ag_2Te and Cd , and two intermediate phases with variable compositions: $\text{Ag}_2\text{Cd}_{1+x}\text{Te}$ and $\text{Ag}_2\text{Cd}_{3+x}\text{Te}$.

The semiconductors Ag_2Te and CdTe and their solid solutions are comparatively new. These materials are very interesting in practice, because their physical, physico-chemical and optical properties may be varied smoothly and in very wide ranges, depending on the composition.

The purpose of the present paper is to study the phase diagram of the system Ag_2Te – Cd . This system is a polythermal section of the ternary system Ag – Cd – Te , for which data are not available in the literature. In the ternary system Ag – Cd – Te , the state diagrams of the systems Ag – Te [1], Ag – Cd [2], Cd – Te [3], CdTe – Ag [4] and Ag_2Te – CdTe [5] are known.

Experimental

Samples of the system Ag_2Te – Cd in the range 0–100 at.% Cd were obtained by direct monotemperature synthesis at $1000 \pm 20^\circ$, with vibrational stirring of the melt during 2 hours. All samples were annealed for 240 h at $100 \pm 10^\circ$.

The samples were subjected to phase analysis X-ray diffraction. A TUR–M61 diffractometer, CuK_α radiation and a Ni-filter were used.

The DTA was carried out at a heating rate of 10 deg min^{-1} with a derivatograph. Al_2O_3 was used as a standard substance. The microstructure and the microhardness were studied on previously-prepared well-polished sections. A MIM–7 microscope and a PMT–3 microhardnessmeter at loadings of 10 and 20 g were used for this purpose.

Different etching solutions (Table 1) were investigated for developing of the microstructure.

Table 1 Compositions of etching solution

Composition of the samples, at.% Cd	Composition of etching solution	Etching		Results*
		time, s	temperature, °C	
(100% Ag ₂ Te)	HNO ₃ :CH ₃ COOH:H ₂ O = 3:1:1	10	40	A
20	NH ₄ OH:H ₂ O ₂ = 3:2	15	20	B
40	HNO ₃ :CH ₃ COOH:H ₂ O = 2:1:1	25	20	B
55	3 g NH ₄ NO ₃ + 10 ml (28%) NH ₄ OH + 5 ml H ₂ O	15	20	B
60	NCl:H ₂ O = 2:1	5	40	A
70 ÷ 95	HCl:H ₂ O = 1:1	5	40	B
100 (Cd)	13 g NH ₄ NO ₃ + 4 g NH ₄ Cl + 35 ml (28%) NH ₄ OH + 100 ml H ₂ O	15	20	A

A* – develops the grain boundaries; B* – develops the phases.

Results and discussion

Results of X-ray diffraction measurements are presented schematically in Fig. 1. The shift of the lines in the concentration ranges 0–5 and 95–100 at.% Cd towards diminishing of the interplane distances indicates the existence of limited solid solutions based on Ag₂Te and Cd.

New lines in the concentration intervals 55–70% and 85–90 at.% Cd indicate the formation of new phases with variable compositions.

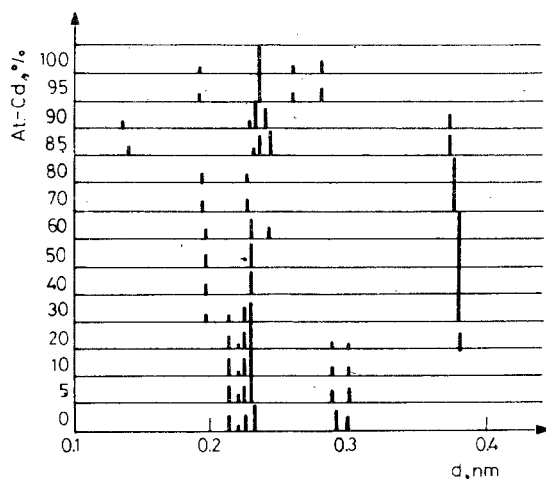


Fig. 1 Scheme of X-ray diffractograms of the Ag₂Te-Cd system

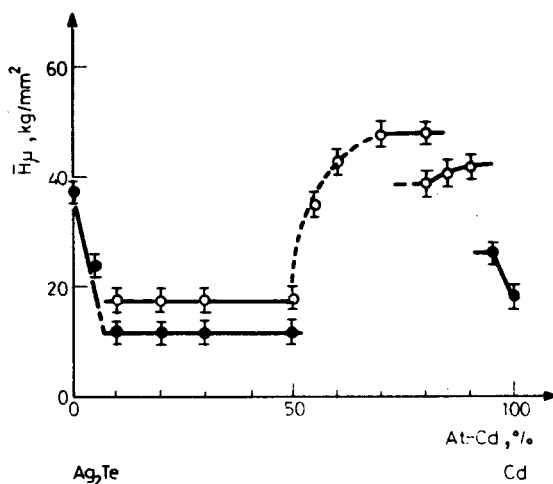


Fig. 2 Microhardness of samples of the Ag_2Te -Cd system

The dependence microhardness vs. composition for the investigated system is shown in Fig. 2.

The phase diagram of the system Ag_2Te -Cd was constructed from the results of DTA, X-ray phase analysis and metallographic analysis (Fig. 3).

The phase diagram of the system Ag_2Te -Cd may be characterized by 32 phase regions; a nonvariant monotectic equilibrium $L_2 \xrightleftharpoons{800 \pm 10^\circ} L_1 + \varepsilon''$ with monotectic point at about 57 at.% Cd; a eutectic reaction $L_1 \xrightleftharpoons{735 \pm 10^\circ} \gamma_0 + \gamma''$ with eutectic point at about 37 at.% Cd; eutectoidal decomposition $\gamma_0 \xrightleftharpoons{480 \pm 10^\circ} \beta + \gamma'$ with eutectoidal point at about 25 at.% Cd; a metatectic equilibrium $\varepsilon'' \xrightleftharpoons{500 \pm 10^\circ} \varepsilon' + L$ with metatectic point at about 94 at.% Cd; two peritectic reactions $L_1 + \varepsilon'' \xrightleftharpoons{755 \pm 10^\circ} \gamma''$ and $\varepsilon' + L \xrightleftharpoons{340 \pm 10^\circ} \eta$; and two peritectoidal reactions $\gamma'' + \varepsilon'' \xrightleftharpoons{520 \pm 10^\circ} \varepsilon'$ and $\beta + \gamma' \xrightleftharpoons{160 \pm 10^\circ} \alpha$.

Conversion of the intermediate phase ε'' into ε' (from a disordered to an ordered state) may be achieved, depending on the composition, either through the peritectoidal reaction $\gamma'' + \varepsilon'' \xrightleftharpoons{520^\circ} \varepsilon'$, through the metatectic reaction $\varepsilon'' \xrightleftharpoons{500} \varepsilon' + L$.

Lowering of the temperature causes broadening of the phase width of the ε' -phase up to about 82–92 at.% Cd at room temperature (approximate composition $\text{Ag}_2\text{Cd}_{5+x}\text{Te}$ at $0.12 \leq x \leq 6.5$).

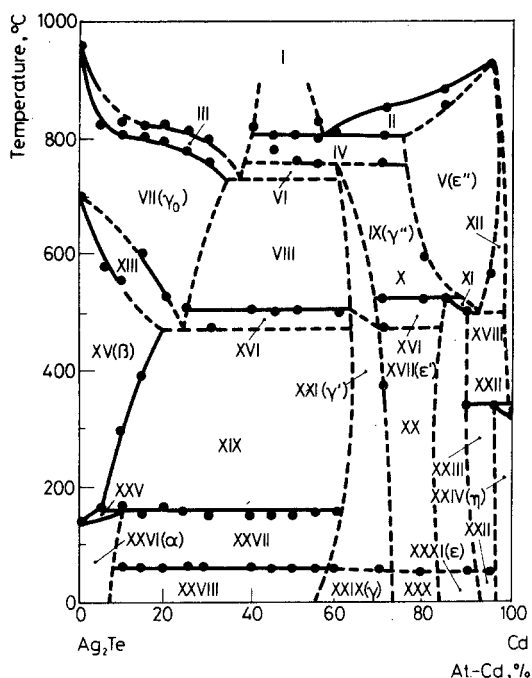


Fig. 3 Phase diagram of the Ag_2Te -Cd system

The influence of temperature on the γ -phase, formed in the peritectic reaction $L_2 + \varepsilon'' \xrightleftharpoons{755^\circ} \gamma$, is analogous. At room temperature, this phase exists from 52 to 72 at.% Cd, with the approximate composition $\text{Ag}_2\text{Cd}_{1+x}\text{Te}$ at $0.88 \leq x \leq 1.57$.

The phases η and α are solid solutions based on Cd and Ag_2Te , with a maximum solubility of Ag_2Te in Cd and of Cd in Ag_2Te of about 5% at room temperature.

Two polymorphic transitions were observed in the γ -phase: the low-temperature $\gamma \rightleftharpoons \gamma'$ transition $60 \pm 5^\circ$, and the high-temperature $\gamma' \rightleftharpoons \gamma''$ transition at 500° (from the side rich in Ag_2Te) and at 470° (from the side rich in Cd). The phase transition $\varepsilon \rightleftharpoons \varepsilon'$ was observed at $50 \pm 5^\circ$.

Conclusions

Investigation of the phase equilibria in the system Ag_2Te -Cd by studying the dependence composition vs. property revealed the complex character of the chemical interaction. 32 phase regions were observed, due to the Ag_2Te polymorphism and the tendency of Ag and Cd to form intermediate phases with

variable compositions [2]. The formation of two intermediate phases was found: $\text{Ag}_2\text{Cd}_{1+x}\text{Te}$ (through a peritectic reaction) and $\text{Ag}_2\text{Cd}_{1+x}\text{Te}$ (through peritectoid and metatectic reactions).

References

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Zusammenfassung — Das Phasendiagramm des Systems $\text{Ag}_2\text{Te}-\text{Cd}$, eines polythermen Schnittes im ternären System $\text{Ag}-\text{Cd}-\text{Te}$, wurde aus DTA- und metallographischen Ergebnissen konstruiert. Das System besteht aus 32 Ein- und Zweistoffgebieten, darunter den polymorphen Modifikationen des Ag_2Te , festen Lösungen auf Basis Ag_2Te bzw. Cd , und ternären Phasen mit den variablen Zusammensetzungen $\text{Ag}_2\text{Cd}_{1+x}\text{Te}$ und $\text{Ag}_2\text{Cd}_{5+x}\text{Te}$.

Резюме — С помощью ДТА и металлографического анализа установлена фазовая диаграмма для системы $\text{Ag}_2\text{Te}-\text{Cd}$, являющейся только политермической частью тройной системы $\text{Ag}-\text{Cd}-\text{Te}$. Диаграмма содержит тридцать две фазовые области, включая полиморфные модификации Ag_2Te , твердые растворы на основе Ag_2Te и Cd , а также промежуточные тройные фазы переменного состава $\text{Ag}_2\text{Cd}_{1+x}\text{Te}$ и $\text{Ag}_2\text{Cd}_{5+x}\text{Te}$.