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Phase diagrams of the $Cu_{1.95}(Ag_2)Te$–ZnTe(CdTe) quasibinary systems and liquidus surfaces of the $Cu_{1.95}(Ag_2)Te$–ZnTe–CdTe quasiternary systems

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Phase diagrams of the quasibinary systems $Cu_{1.95}(Ag_2)Te$–ZnTe, $Cu_{1.95}(Ag_2)Te$–CdTe and the vertical sections $Cu_{1.95}(Ag_2)Te$–$Zn_xCd_{1-x}Te$ (x = 0.2, 0.4, 0.6 and 0.8) have been constructed using methods of physico-chemical analysis. The liquidus surfaces of the quasiternary systems $Cu_{1.95}Te$–ZnTe–CdTe and Ag_2Te–ZnTe–CdTe have been determined based on experimental data. Both liquidus surfaces include two fields of primary crystallization, corresponding to $Zn_xCd_{1-x}Te$ solid solutions and copper or silver telluride.

Liquidus surface / Solid solution / Copper telluride / Silver telluride / Traveling heater method

Introduction

High-quality single crystals of the $Zn_xCd_{1-x}Te$ solid solution can be obtained by crystallization from the melt using the traveling heater method (THM). The crystallization temperature is decreased by 100-200 °C if a solvent is used, which improves the quality of the obtained crystals. These crystals could be used as substrates for the epitaxial growth of $Cd_xHg_{1-x}Te$ films. In order to better understand the use of $Cu_{1.95}Te$ and Ag_2Te as solvents, we decided to investigate the phase relations in the quasiternary systems $Cu_{1.95}Te$–ZnTe–CdTe and Ag_2Te–ZnTe–CdTe and construct their liquidus surfaces.

Experiments

The $Cu_{1.95}(Ag_2)Te$–ZnTe and $Cu_{1.95}(Ag_2)Te$–CdTe quasibinary systems and eight vertical sections $Cu_{1.95}(Ag_2)Te$–$Zn_xCd_{1-x}Te$ (x = 0.2, 0.4, 0.6 and 0.8) were investigated for the construction of the liquidus surfaces of the $Cu_{1.95}(Ag)_2Te$–ZnTe–CdTe quasiternary systems. The investigations were made using differential thermal (DTA) and microstructural (MSA) analyses and X-ray diffraction (XRD). Zinc telluride of extra grade quality was used for these experiments. Cadmium, copper and silver tellurides were synthesized from high-purity elements containing more than 99.999 at.% of Cd, Cu, Ag and Te, respectively, by alloying in evacuated quartz ampoules. An individual synthesis technique was used for each telluride [1,2]. The samples were held for 10-20 hours at a temperature 50 °C higher than the melting point and were then slowly cooled to room temperature. The obtained Ag_2Te and CdTe phases had the stoichiometric composition. Excess Te was extracted on the surface when copper and tellurium were alloyed in the ratio 2:1. To determine the homogeneity region of copper telluride, a series of ingots within the composition range from $Cu_{1.88}Te$ to Cu_2Te were synthesized. By microstructural investigation it was determined that the ingots of copper telluride were single-phase in the range from $Cu_{1.90}Te$ to $Cu_{1.98}Te$. For the investigation of phase equilibria, copper telluride of composition $Cu_{1.95}Te$ was used.

The differential thermal analysis was carried out by means of a device analogous to Kurnakov's pyrometer. 5 g ingots containing an appropriate mixture of binary components were placed in an evacuated Stepanov's quartz ampoule, held for 2-3 hours at the temperature 1300 °C for their homogenization and after that the thermal analysis was carried out. A Pt-Pt/Rh thermocouple, calibrated according to the reference points, was used for the temperature measurement and the uncertainty did not exceed 2 °C. The points corresponding to the liquidus were determined with the help of cooling thermograms, and the solidus was constructed using the heating thermograms after annealing for 20 hours at temperatures near the corresponding eutectic temperatures. An increase of the annealing time did not influence the temperatures of the phase transitions. The decomposition of the solid solution ranges of the copper and silver tellurides was clearly given by the DTA method. This is connected with the fact that all copper and silver chalcogenides have very high mobility in the crystal lattice even at relatively low temperatures. Therefore the rate of the diffusion process is so fast that on cooling the system is in a state near the thermodynamic equilibrium. The liquidus surfaces of the quasiternary systems $Cu_{1.95}Te$–ZnTe–CdTe and Ag_2Te–ZnTe–CdTe were constructed using the liquidus of the quasibinary systems, which bound the above-mentioned systems, and of vertical sections. Isotherms were drawn at intervals of 50 °C.

Results and discussion

According to literature data [3,4], ZnTe and CdTe form a complete series of solid solutions with zinc-blende structure and the lattice parameter follows Vegard's law.

The quasibinary system $Cu_{1.95}Te$–ZnTe is characterized by a eutectic phase diagram with limiting mutual solid solubility of the binary components and polymorphic transformations of the solid solution based on Cu_2Te (Fig. 1). The eutectic crystallizes at 1038 °C and contains 53 mol.% ZnTe [1]. The solid solubility of zinc telluride in copper telluride reaches 51 mol.% at the eutectic temperature, and decreases sharply with decreasing temperature (the solid solubility is 10 mol.% ZnTe at 700°C) [5]. The solid solution with face-centered cubic structure based on the high-temperature modification β-$Cu_{2-x}Te$ transforms at 527 °C according to a eutectoid reaction into a solid solution with hexagonal structure based on β^{III}-$Cu_{2-x}Te$. The eutectoid composition corresponds to 3 mol.% ZnTe. Thermal effects at 195, 310 and 360 °C, which correspond to the phase transitions of the copper telluride from α-$Cu_{2-x}Te$ with hexagonal structure to β^{I}- and β^{III}-$Cu_{2-x}Te$ with cubic structures, were detected on the heating curves for all ingots in the $Cu_{1.95}Te$–ZnTe system [6]. The solid solubility on the ZnTe side was determined using XRD and MSA. It was found that the maximum solid solubility does not exceed 3 mol.% $Cu_{1.95}Te$.

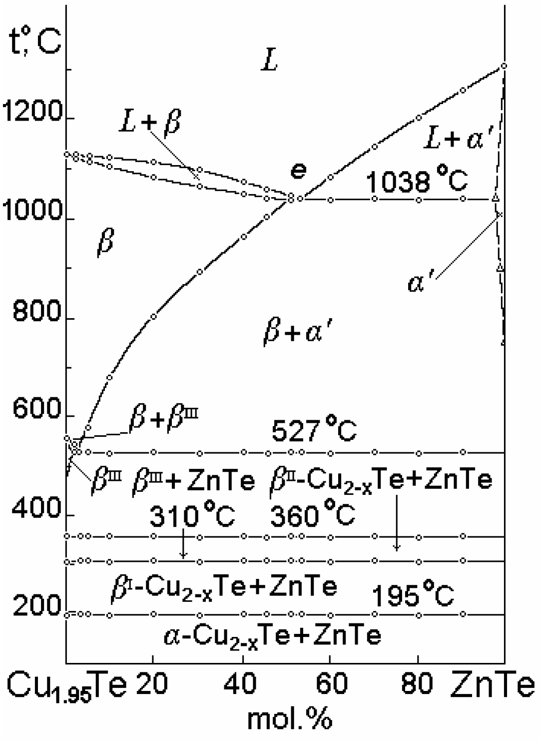

Fig. 1 Phase diagram of the quasibinary system $Cu_{1.95}Te$–ZnTe.

The quasibinary system $Cu_{1.95}Te$–CdTe is also described by a phase diagram of the eutectic type with limited solid solutions in the solid state and polymorphic transformations (Fig. 2).

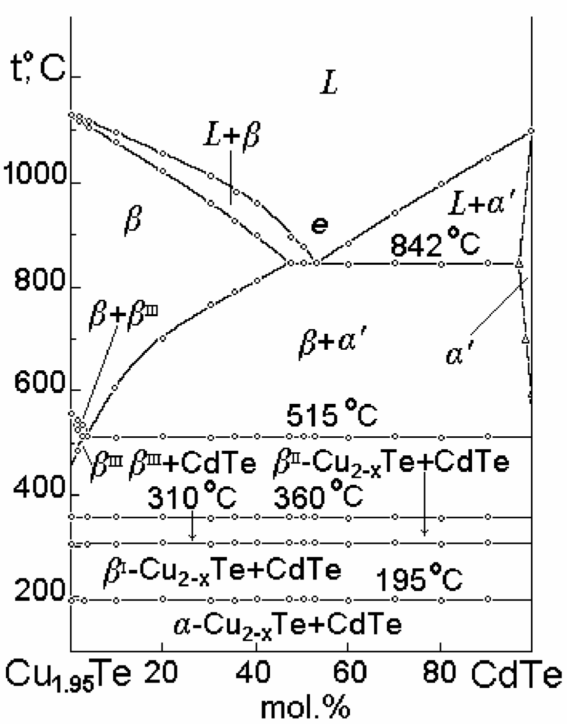

Fig. 2 Phase diagram of the quasibinary system $Cu_{1.95}Te$–CdTe.

The temperature 842 °C and composition 53 mol.% CdTe correspond to the eutectic point [1]. The solid solubility of CdTe in $Cu_{1.95}Te$ reaches 47 mol.% at the eutectic temperature and decreases abruptly with decreasing temperature and is equal to 6 mol.% at 600 °C [5]. The solid solution based on the high-temperature modification β-$Cu_{2-x}Te$ with face-centered cubic structure transforms at 515 °C through a eutectoid transformation into the solid solution based on β^{III}-$Cu_{2-x}Te$ with hexagonal structure. As in the previous system, thermal effects at 195, 310 and 360 °C, which correspond to the phase transitions of the copper telluride, were detected on the heating curves for all ingots in the $Cu_{1.95}Te$–CdTe system. The solid solubility of $Cu_{1.95}Te$ in CdTe is not higher than 3 mol.%.

The phase diagram of the Ag_2Te–ZnTe quasibinary system belongs to the eutectic type of phase diagrams with limited solid solubility (Fig. 3). The eutectic crystallizes at 880 °C and contains 32 mol.% ZnTe [2]. Silver telluride has three polymorphic modifications: the low-temperature α-modification with a monoclinic structure transforms at 145 °C into the β-modification with a f.c.c. lattice, which in turn transforms at 802 °C into the high-temperature γ-modification with a b.c.c. lattice. Zinc telluride forms solid solutions with all silver telluride modifications. A solid solution based on γ-Ag_2Te exists within the interval from 0 to 29 mol.% ZnTe [5] and is transformed into the solid solution based on β-Ag_2Te on decreasing the temperature, according to a eutectoid reaction. The eutectoid point is located at 713 °C and 11 mol.% ZnTe. The solid solubility of zinc telluride in β-Ag_2Te reaches 9 mol.%, but its solid solubility in α-Ag_2Te is negligible. The solid solutions based on β- and γ-Ag_2Te are separated by a cigar-shaped region where they coexist. The solid solubility of γ-Ag_2Te in zinc telluride is equal to 2 mol.% at the eutectic temperature and decreases to 0.5 mol.% at 700 °C.

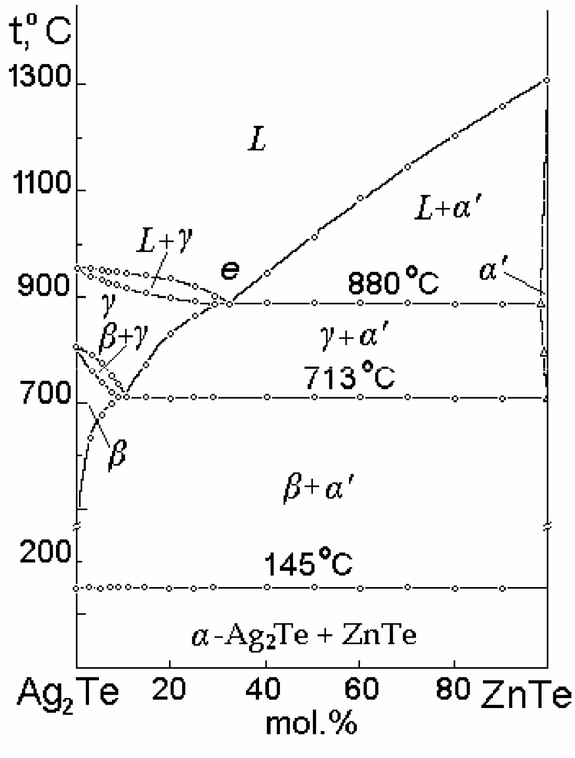

Fig. 3 Phase diagram of the quasibinary system Ag_2Te–ZnTe.

The phase diagram of the system Ag_2Te–CdTe belongs to the peritectic type (Fig. 4). The peritectic point is situated at 955 °C and 76 mol.% CdTe [2]. The solid solution based on γ-Ag_2Te contains 83 mol.% CdTe at the peritectic temperature [5]. It is characterized by a minimum at 928 °C and 32 mol.% CdTe. On decreasing the temperature this solid solution transforms into a solid solution based on β-Ag_2Te according to a eutectoid reaction. The eutectoid point is located at 532 °C and 13.5 mol.% CdTe. The maximum solid solubility of CdTe in β-Ag_2Te is equal to 12 mol.% and abruptly decreases with decreasing temperature. Cadmium telluride, like zinc telluride, stabilizes the high-temperature modification of silver telluride γ-Ag_2Te and enlarges its field of existence at lower temperatures. The solid solubility on the cadmium telluride side is negligible and equals 2.5 mol.% Ag_2Te at the peritectic temperature and decreases to 0.5 mol.% at 700 °C. The solid solution based on CdTe differs from that given in [7], where probably not all of the investigated ingots were in equilibrium.

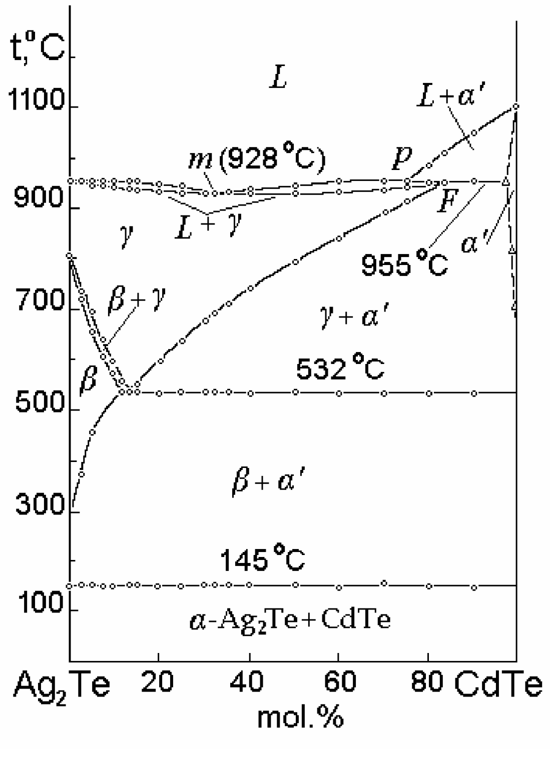

Fig. 4 Phase diagram of the quasibinary system Ag_2Te–CdTe.

In the investigated vertical sections, as in the quasibinary systems, there is only considerable solid solubility on the copper and silver telluride sides. The solid solubility of copper and silver telluride in CdTe and ZnTe is not very high and does not exceed 3 mol.%. The liquidus surfaces of the quasiternary systems $Cu_{1.95}Te$–ZnTe–CdTe and Ag_2Te–ZnTe–

CdTe were constructed using experimental data on the phase relations in the quasibinary systems $Cu_{1.95}(Ag_2)Te$–ZnTe and $Cu_{1.95}(Ag_2)Te$–CdTe and vertical sections $Cu_{1.95}(Ag_2)Te$–$Zn_xCd_{1-x}Te$ (x = 0.2, 0.4, 0.6 and 0.8).

The liquidus surface of the quasiternary system $Cu_{1.95}Te$–ZnTe–CdTe (Fig. 5) contains two fields of primary crystallization: the fields of primary crystallization of the $Cu_{2-x}Te$ and $Zn_xCd_{1-x}Te$ solid solutions. These fields are separated by the line of secondary crystallization $\boldsymbol{e_1e_2}$, which connects the eutectics in the quasibinary systems based on copper telluride. The eutectic of the quasibinary system $Cu_{1.95}Te$–CdTe is the lowest melting point in this quasiternary system.

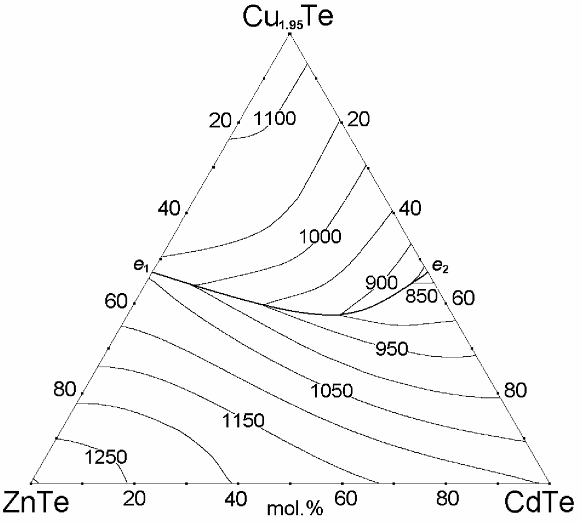

Fig. 5 Liquidus surface of the quasiternary system $Cu_{1.95}Te$–ZnTe–CdTe.

The liquidus surface of the quasiternary system Ag_2Te–ZnTe–CdTe (Fig. 6) has also two fields of primary crystallizations: the fields of primary crystallization of the solid solution based on Ag_2Te and the field of $Zn_xCd_{1-x}Te$ solid solution. These fields are separated by the line of secondary crystallization ***ep***, which connects the eutectic in the quasibinary system Ag_2Te–ZnTe and the peritectic in the quasibinary system Ag_2Te–CdTe. The liquidus surface ascends sharply from the line of secondary crystallization in the direction of the high-temperature melting component (ZnTe). The eutectic of the quasibinary system Ag_2Te–ZnTe is the lowest melting point in the Ag_2Te–ZnTe–CdTe quasiternary system.

Conclusions

The phase diagrams of the quasibinary systems $Cu_{1.95}Te$–ZnTe, $Cu_{1.95}Te$–CdTe, Ag_2Te–ZnTe and Ag_2Te–CdTe have been constructed using methods of physico-chemical analysis. The eight vertical sections $Cu_{1.95}(Ag_2)Te$–$Zn_xCd_{1-x}Te$ (where x = 0.2, 0.4, 0.6 and 0.8) were constructed with the help of the differential thermal analysis. The liquidus surfaces of the quasiternary systems $Cu_{1.95}Te$–ZnTe–CdTe and Ag_2Te–ZnTe–CdTe were constructed based on experimental data obtained on studying the quasibinary systems and vertical sections.

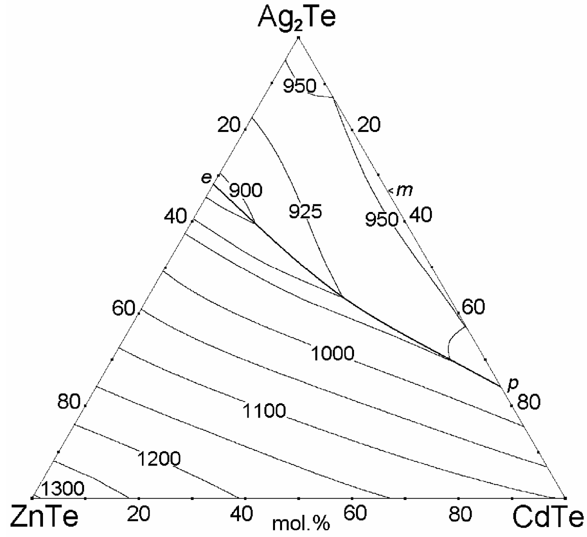

Fig. 6 Liquidus surface of the quasiternary system Ag_2Te–ZnTe–CdTe.

Based on this study, optimal compositions and temperatures were chosen to grow single crystals by the traveling heater method, using the constructed liquidus surfaces.

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