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THERMAL ANALYSIS DETERMINATION OF $A^{II}B^{VI}$ SOLID SOLUBILITY IN $A_2^{I}B^{VI}$

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ABSTRACT

Solid solubility of zinc and cadmium chalkogenides in copper and silver chalkogenides is determined by thermal analysis. Data on temperature dependence of solubility are presented. The data obtained provide description of phase equilibrium for binary systems below solidus.

INTRODUCTION

Solubility of soli components is usually determined by means of X-ray diffraction, microstructural analysis and microhardness measurements. These are rather cumbersome methods taking much time to prepare, anneal, treat and analyse the samples. Moreover, a single value of solubility is obtained by studying the whole compositional range of the compound. These three methods are applied for most of the systems.

Solubility of $A^{II}B^{VI}$ compounds in $A_2^{I}B^{VI}$ compounds can be reliably determined by differential thermal analysis. The point is that the ions of the copper and silver chalkogenides are highly mobile within the crystal lattice even at rather low temperatures (I). In this case the rate of diffusion due to the initiation and growth of the new phase centres is so high that in the process of cooling the state of the system remains close to thermodynamic equilibrium (2).

MEASURING METHODS

In the experiments, commercially available high-purity powders of zinc and cadmiumchalkogenides were used. Copper and silver chalkogenides were synthesized by sintering stoichiometric amounts of the initial components of special purity (99.999 %). The synthesis was carried out in double evacuated quartz ampoules at a temperature 50°C higher than the melting point of the compound. For research purposes, 5 g specimens at a composition from

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0 to 95 mole % $A^{II}B^{VI}$ were prepared. The lumps were placed in quartz tubes which were sealed off at I x 10^{-6} torr. The thermal analysis of specimens was carried out on the device based on the principle of Kurnakov's pyrometer. Temperature was measured by Pt-Pt/Rh thermocouple calibrated by points of fusion of reference substances. The temperature measurements ranged from 50 to 1300°C. Initial specimens were kept for 5 hours in the melts to achieve better homogenization after which the melt was cooled at a rate of 5 °C/min and the appropriate curves were plotted. In the course of cooling, the effects corresponding to the curves of liquidus as well as to the alloy break-down were shown on the curves of differential thermal analysis. The points corresponding to the solidus curve could be observed in heating the specimens. In the repeated experiments the results were reproduced within ± I °C.

RESULTS AND DISCUSSION

On the basis of the differential thermal analysis results fusibility diagrams were obtained for the systems Cu_2S - ZnS, Cu_2S - CdS, Cu_2Se-ZnSe, Cu_2Se-CdSe, Cu_2Te-ZnTe, Cu_2Te-CdTe, Ag_2Se-ZnSe, Ag_2Se-CdSe, Ag_2Te-ZnTe and Ag_2Te-CdTe. All the diagrams studied apply either to the simple eutectic type or to the peritectic type with limited solubility of solid components (3-7). The limit solubility of zinc and cadmium chalkogenides rises appreciably at elevated temperatures. As temperature decreases, the solubility lowers sharply. The data on the maximum solubility of solid components and minimal concentrations at which the solid solutions break-down was recorded are given in the Table.

The break-down of solid solutions exerts a strong exothermal effect on the cooling curves. The break-down heat averages I/3 of the fusion heat of $A^{I}_2B^{VI}$ compound. It has been found that the duration of annealing and variation of the rate of cooling do not affect the temperature of break-down. Some of the specimens were subject to X-ray diffraction analysis following thermal analysis. At room temperature, only pure copper, silver, zinc and cadmium chalkogenides were found in specimens. This means that the process of break-down is completed and the solubility data may be considered as quite reliable.

Table. Maximum solubility of $A^{II}B^{VI}$ compounds in solid $A_2^{I}B^{VI}$ and minimum concentration for which the solid solutions break-down was observed

System	Type of phase diagram	Maximum solubility mole % $A^{II}B^{VI}$	t, °C	Minimum concentration mole % $A^{II}B^{VI}$	t, °C
Cu_2S - ZnS	p	42	II85	2.5	740
Cu_2S - CdS	eu	53	IOII	2.5	395
Cu_2Se-ZnSe	p	55	II42	2.5	575
Cu_2Se-CdSe	eu	50	9I0	2.0	500
Cu_2Te-ZnTe	eu	5I	I038	I.5	545
Cu_2Te-CdTe	eu	47	842	2.0	535
Ag_2Se-ZnSe	eu	I2	850	I.0	545
Ag_2Se-CdSe	p	68	970	2.5	4I5
Ag_2Te-ZnTe	eu	29	880	I.0	530
Ag_2Te-CdTe	p	83	955	I.0	345

eu - eutectic type, p - peritectic type

CONCLUSIONS

Fusibility diagrams are constructed for the systems Cu_2S-ZnS, Cu_2S-CdS, Cu_2Se-ZnSe, Cu_2Se-CdSe, Cu_2Te-ZnTe, Cu_2Te-CdTe, Ag_2Se-ZnSe, Ag_2Se-CdSe, Ag_2Te-ZnTe, Ag_2Te-CdTe using the differential thermal analysis. For these systems the regions of the existence of $A_2^{I}B^{VI}$ based alloys are determined.

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