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# MELTING TEMPERATURES OF THE $A^{I}B^{III}C^{VI}_2$ -TYPE ($A^{I}$-Cu,Ag; $B^{III}$-Al, Ga, In; $C^{VI}$-S, Se) COMPOUNDS AND PHASE DIAGRAMS OF THEIR SOLID SOLUTIONS

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## ABSTRACT

The phase diagrams of the $CuInS_{2x}Se_{2(1-x)}$, $CuAl_xGa_{1-x}Se_2$, $CuGa_xIn_{1-x}Se_2$, $AgGaS_{2x}Se_{2(1-x)}$, $AgGa_xIn_{1-x}S_2$, $CuGaS_{2x}Se_{2(1-x)}$, $CuGa_xIn_{1-x}S_2$ solid solutions are plotted using the differential thermal analysis (DTA). All investigated phase diagrams are characterized by a small crystallization range and belong to the first type phase diagrams according to Roseboom's classification. It has been found that there are solid phase transformations in the above mentioned solid solutions. The termodynamical analysis of investigated phase diagrams is performed.

## INTRODUCTION

There is scarce information in literature about phase diagrams of the ternary compounds $A^{I}B^{III}C^{VI}_2$ and their solid solitions. In /1,2/ the phase diagram of the $AgGaSe_2$-$AgGaS_2$ system has been plotted but the data are contradictory. Observations on phase equilibrium in the $CuInS_2$- $CuInSe_2$ system are reported in /3,4/. The data on other systems are not available.

The aim of this study is to investigate the phase diagrams of solid solutions of the ternary compounds $A^{I}B^{III}C^{VI}_2$. The apparatus for DTA is analogous to that described in /5/. The studies have been carried out on samples obtained by direct melting of the elemental components, a two-temperature technique and a chemical transport method. The composition and homogeneity of the ternary compounds and their solid solutions have been tested by chemical and X-ray analysis.

## RESULTS AND DISCUSSION

The phase diagrams of the $CuInSe_2$ - $CuInS_2$, $CuInS_2$ - $CuGaS_2$,

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$CuInSe_2$-$CuGaSe_2$, $CuGaSe_2$-$CuGaS_2$, $CuAlSe_2$-$CuGaSe_2$, $AgGaSe_2$-$AgGaS_2$, $AgGaS_2$-$AgInS_2$ solid solutions are plotted from the DTA data, some of them are given in Fig.1-4. The T-x phase diagrams are characterized by a small crystallization range and can be referred to the first type phase diagrams according to Roseboom's classification.

The $CuInSe_2$-$CuInS_2$ phase diagram is given in Fig.1. The presence of solid phase transformations is characteristic of both the $CuInSe_2$, $CuInS_2$ ternary compounds and their solid solutions. The phase transformations analogous to that taking place at 1083 K in $CuInSe_2$ and at 1284 K in $CuInS_2$ are observed in the $CuInS_{2x}Se_{2(1-x)}$ solid solutions over the whole composition range that indicates the identical nature of these transformations. The second phase transformation is detected for $CuInS_2$ (1313 K) and the above mentioned solid solutions in the composition range $0.7 \leqslant x \leqslant 1$.

Fig.2 gives the $CuInS_2$-$CuGaS_2$ system phase diagram. The solid phase transformations in the system are observed in the $0 \leqslant x \leqslant 0.5$ composition range. The temperature range of the second phase transformation is 3-5 K as in the case of the $CuInSe_2$-$CuGaSe_2$ system.

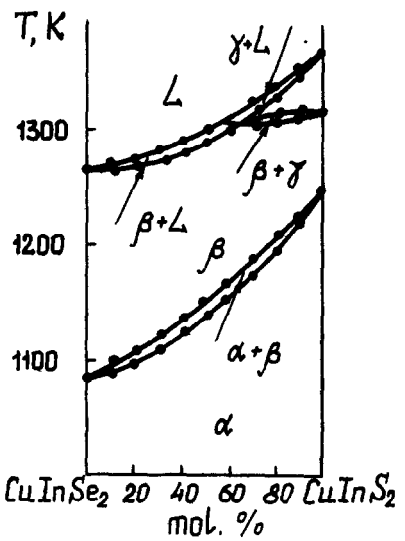


Fig.1

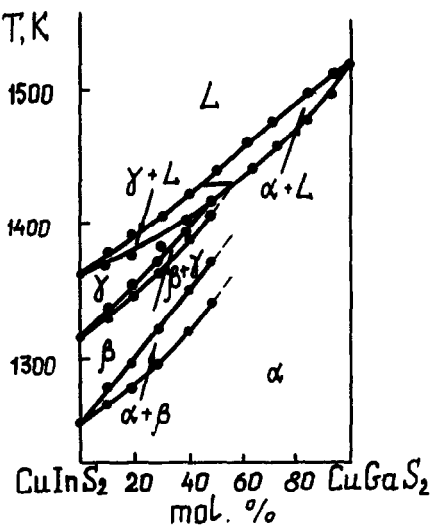


Fig.2

The phase diagram of the $CuInSe_2$-$CuGaSe_2$ system is given in Fig.3. The solid phase transformations are observed for the $CuInSe_2$, $CuGaSe_2$ (1320 K) ternary compounds and their solid solutions over the whole range of composition that indicates the identical nature of these transformations. The solid phase transformation is observed for the compositions with $0 \leqslant x \leqslant 0.5$ in the $CuGaS_{2x}Se_{2(1-x)}$ solid solutions (Fig.4) and for compositions with $0 \leqslant x \leqslant 0.3$ for the $CuAl_xGa_{1-x}Se_2$ solid solutions. Contrary to other investigated systems in the phase diagram of the $CuAlSe_2$-$CuGaSe_2$ system there is a common point at 33 mol.% $CuGaSe_2$ that is characteristic of the systems with close melting temperatures of the initial components ($T_m$ = 1336 K for $CuAlSe_2$ and $T_m$= 1345 K for $CuGaSe_2$).

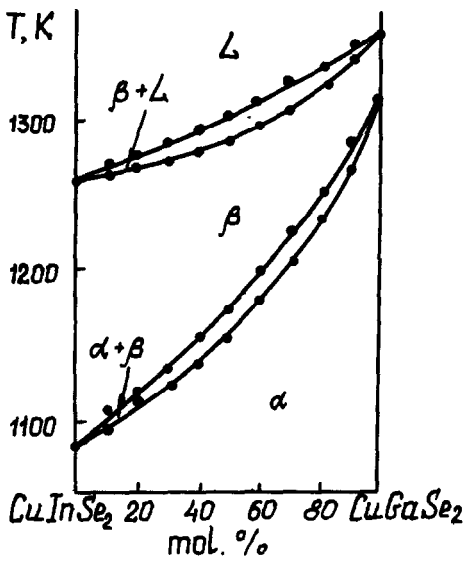


Fig.3

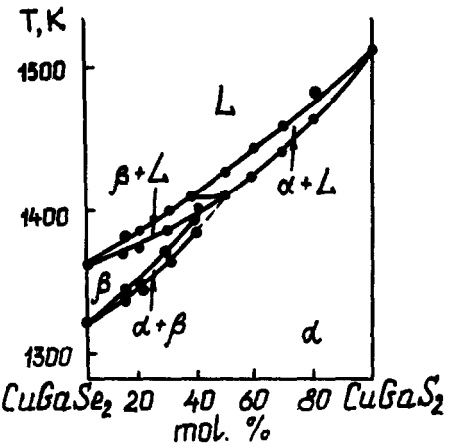


Fig.4

In the phase diagram for $AgGaSe_2$-$AgGaS_2$ the crystallization range is 10-15 K as in the case of other investigated systems. In 90 mol.% $AgInS_2$-10mol.% $AgGaS_2$ solid solution the solid phase transformation is observed, the analogous transformation of $AgInS_2$ is detected at 958 K.

The nature of the solid phase transformations in the investigated ternary $A^{I}B^{III}C^{VI}_2$ compounds and their solid solutions can be accounted for in terms of the concepts of cation-cation and cation-anion disorderings given in /6/. It can be assumed that the solid state transformations observed at 1083, 1313, 1248 K for the $CuInSe_2$, $CuGaSe_2$, $CuInS_2$ compounds and their solid solutions correspond to the cation-cation disordering. The solid phase transformation at 1363 K in $CuInS_2$ and that in the $CuInS_{2x}Se_{2(1-x)}$ $CuGa_xIn_{1-x}S_2$ correspond to the cation-anion disordering. Thermal effect observed at 958 K for $AgInS_2$ is of different nature. $AgInS_2$ is the only compound of the $A^{I}B^{III}C^{VI}_2$ family which can exist in two ordered structures: chalcopyrite and orthorombic ones. The orthorhombic structure can be easily obtained by quenching from the temperature exceeding that of phase transition to room temperature.

Using the obtained experimental results for the $CuInSe_2$-$CuInS_2$, $CuInS_2$-$CuGaS_2$, $CuInSe_2$- $CuGaSe_2$, $CuGaSe_2$-$CuGaS_2$ systems the termodynamical analysis of phase equilibriums was carried out that made it possible to determine the interaction parameters for liquid ($k^l$) and solid ($k^s$) phases. From the obtained interaction parameters values the solidus and liquidus curves are calculated in approximation of the theory of regular and ideal solutions using the known equations of phase equilibriums. The calculated values in approximation of the theory of regular solutions (solid lines in figers) coincide with the experimental data.

REFERENCES

1 J.C. Mikkelsen, J. Appl. Phys. 49 (1978) 426
2 V.V. Badiakov et al., Kristallografiya 26 (1981) 537
3 T.V. Tiagunova, F.F. Harahorin, E.N. Holina, Izv. AN SSSR. Neor. mat. 13 (1977) 46
4 E.N. Holina, V.B. Ufimtsev, A.S. Timoshin, Izv. AN SSSR, Neor. mat. 15 (1979) 1918
5 N.N.Belevich et al., No 5466-80 Dep. VINITI (1980)
6 L.S. Palatnik, V.M.Koshkin, L.P. Galchinetskii, FTT 4 (1962) 2365