

Crystallization and Phase Transition of Solid Solutions in the $\text{Cu}_8\text{GeX}_6\text{-Ag}_8\text{GeX}_6$ (X-S, Se) Systems

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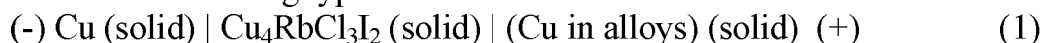
Copper and silver chalcogenides with germanium are particular interest because possess ionic conductivity and are perspective materials for photoelectrodes, electrochemical converters of solar energy, ionselective sensors, photoelectro-chemical imaging etc.

Ternary compounds $\text{Ag}_8^{\text{I}}\text{GeX}_6$ ($\text{A}^{\text{I}}\text{-Cu}$, Ag, Sn; XS, Se) have phase transition. Their high-temperature modifications are isostructural and crystallize in cubic ($F\text{-}43m$) system, however low-temperature ones crystallize in orthorombic or hexagonal system. This allows us to expect the formation of wide series of solid solutions in $\text{Cu}_8\text{GeS}_6\text{-Ag}_8\text{GeS}_6$ (A) и $\text{Cu}_8\text{GeSe}_6\text{-Ag}_8\text{GeSe}_6$ (B) systems.

This work is devoted to investigation of phase relations in the systems (A) and (B) and some properties of solid solutions.

Starting compounds were synthesized from high-purity elements (at least 99.999 wt.% purity) in sealed silica ampoules under vacuum (10^{-2} Pa). Synthesis was carried out in a two-zone furnace. Samples of the systems (A) and (B) were prepared by melting of the pre-synthesized compounds in sealed silica ampoules under vacuum followed by homogenizing annealing at 900 K for about 500 h.

DTA, XRD and EMF measurements were employed to analyze the samples. The XRD data were collected using a Bruker D8 ADVANCE diffractometer (Cu-K α radiation). DTA of the equilibrated alloys was carried out using a NETZSCH 404 F1 Pegasus system. For the EMF measurements, the reversible cells of following type were assembled:



EMF was measured by the compensation method in the temperature range of 295–380 K with the accuracy of ± 0.1 mV, using the high-resistance universal B7-34A digital voltmeter.

Based on experimental data the T-x diagrams, concentration dependences of crystal lattice parameters, microhardness and EMF measurements are constructed.

It was shown that both systems are characterized by continuous series of solid solutions between high temperature modifications and limited solid solutions based on their low-temperature ones. Formation of solid solutions decreases the temperature of polymorphic transitions of compounds down to room and low.