Cu_8SiS_6–Ag_8SiSe_6 SYSTEM: PHASE EQUILIBRIA AND HIGH ENTROPY ALLOYS

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Argyrodite-type compounds are complex copper and silver chalcogenides that are environmentally benign and exhibit a wide range of functional properties. Many of these phases attract interest due to high thermoelectric performance in the intermediate temperature range, as well as photoelectric and optical properties, which make them promising multifunctional energy materials. Argyrodite compounds undergo polymorphic phase transitions at relatively low temperatures (≤530 K). The low-temperature modifications crystallize in ordered structures with lower symmetry, whereas the high-temperature modifications adopt a cubic lattice. In high-temperature phases, Cu^+ and Ag^+ cations are statistically distributed over several crystallographic sites, resulting in high ionic mobility and increased configurational entropy. Simultaneous substitution in both the cation (A^I) and anion (X) sublattices increases structural disorder in the crystal lattice and enhances configurational entropy, leading to the formation of thermodynamically stable single-phase solid solutions based on argyrodite-type high-entropy alloys.

The aim of the present work is to investigate phase equilibria in the Cu_8SiS_6–Ag_8SiSe_6 system and to identify possible high-entropy phases. For this purpose, the Cu_8SiS_6 and Ag_8SiSe_6 compounds were first synthesized. The synthesis was carried out by co-melting high-purity elemental components in evacuated quartz ampoules using a two-zone heating regime. After synthesis and identification of the initial compounds, the Cu_8SiS_6–Ag_8SiSe_6 alloys were prepared by co-melting of parents compounds in various proportions. The obtained alloys were annealed at 800 K for 500 hours. The synthesized samples were investigated by differential thermal analysis (DTA) and X-ray diffraction (XRD). DTA measurements were performed using a NETZSCH 404 F1 Pegasus instrument, while XRD patterns were recorded on a Bruker D2 PHASER diffractometer ($CuK\alpha_1$ radiation). The obtained diffraction patterns were analyzed using the Topas V3.0 Software (Bruker), and the lattice parameters of alloys were calculated.

Based on the DTA and XRD results the phase diagram of the title system was plotted. It was established that the Cu_8SiS_6–Ag_8SiSe_6 system forms a continuous series of solid solutions based on the high-temperature cubic modifications of the initial compounds, whereas only limited solid-solution regions are observed for their low-temperature modifications. The formation of solid solutions leads to a decrease in the polymorphic transition temperatures of the initial compounds. As a result, all alloys in the Cu_8SiS_6–Ag_8SiSe_6 system within the 10–90 mol % Ag_8SiSe_6 composition range are single-phase and crystallize in a cubic structure (Sp. Gr. *F-43m*). Samples containing 34–66 mol % Ag_8SiSe_6 of this phase can be considered as high-entropy alloys.