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Crystal growth, structural and electrical properties of $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeS}_5\text{I}$ superionic solid solutions

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Abstract

$\text{Cu}_7\text{GeS}_5\text{I}$ and $\text{Ag}_7\text{GeS}_5\text{I}$ crystals belong to the family of compounds with argyrodite structure and they are known as superionic conductors. The studies of the influence of cationic substitution on the physical properties of solid solutions based on $\text{Cu}_7\text{GeS}_5\text{I}$ and $\text{Ag}_7\text{GeS}_5\text{I}$ crystals are interesting both from fundamental and application point of view. Therefore the aim of this paper is to develop growth technology as well as to investigate structural and electrical properties of $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeS}_5\text{I}$ solid solutions.

The specificity of the modified technique of $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeS}_5\text{I}$ crystals growth, as in the case of individual compounds obtaining, is that the into ampoule there were loaded the elementary initial products Ag, Cu, Ge, S and pre-synthesized AgI (CuI), additionally purified by directional solidification from the melt. This allows us to obtain the single crystals of solid solutions with accurately given stoichiometric composition in the whole concentration range. The crystal growth regime of directional solidification from the melt of $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeS}_5\text{I}$ solid solutions consists of several stages. In the first stage the $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeS}_5\text{I}$ synthesis is conducted. The temperature of both zones increases to 673 K within 6 hours. Hereupon the 24-hour exposure is carried out, which is necessary for complete sulphur combination, the vapor pressure of which at ~ 720 K is 0.1 MPa, and the rapid temperature increase can cause depressurization of the ampoule. Then, temperature increases during the day to the maximum temperature values of 1323 K for "hot" upper zone and 973 K for "cold" lower zone. After reaching the corresponding temperature in upper zone the solid solution melting takes place, and at higher temperatures the melt homogenization is realised. The temperature in the melt zone is maintained on 50 K above the melting point to prevent the substance partial thermal dissociation. After that the 24-hour exposure is maintained at which the full homogenization of melt takes place.

The structural studies were carried out with powder method using diffraction patterns obtained on a DRON-3 diffractometer (conventional θ - 2θ scanning method, Bragg angle $2\theta \cong 10$ - 60° , Ni-filtered CuK_α radiation). It was determined that compounds and solid solutions based on them crystallize in $F\bar{4}3m$ cubic crystal system. The compositional dependence of cubic lattice parameter at cation substitution was obtained. It is shown that the increase of Ag content leads to the increase of cubic lattice parameter in $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeS}_5\text{I}$ solid solutions.

Electrical properties of $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeS}_5\text{I}$ solid solutions with $x = 0, 0.25, 0.5, 0.75$ were investigated by the impedance spectroscopy. The measurements were performed in the temperature range 300 – 360 K and in the frequency range 10 Hz – 10 GHz. It is shown that the total electrical conductivity of $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeS}_5\text{I}$ decreased at $T = 300$ K with the increase of stoichiometric parameter x . The highest electrical conductivity value $\sigma_{100\text{Hz}} = 4.3$ S/m (activation energy $\Delta E = 0.17$ eV) was observed for $\text{Cu}_7\text{GeS}_5\text{I}$. The complex impedance plots were fitted with Zview software. The frequency dependences of the real part of complex conductivity at various temperatures for $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeS}_5\text{I}$ crystals were analysed. The temperature dependences of the real part of complex conductivity for $(\text{Cu}_{1-x}\text{Ag}_x)_7\text{GeS}_5\text{I}$ crystals were described by Arrhenius law.