Argirodito tipo Cu_7PS_6 kristalų struktūra ir elektrinės savybės

Structural and electrical properties of argyrodite-type Cu_7PS_6 crystal

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Cu_7PS_6 compound belongs to argyrodite-type solid electrolytes [1]. Phase diagram of a quasibinary $Cu_2S–P_4S_{10}$ system was studied in [2]. Cu_7PS_6 compound is formed with a large excess of S^{2-} anions and in a simplified case its structure can be viewed as a Cu_2S matrix containing isolated $[PS_4]^{3-}$ ions. Its high-temperature modification contains disordered subsystem of metal ions that are characterized by high ionic conductivity due to a considerable mobility of monovalent cations while with cooling an ordered phase is formed. In Cu_7PS_6 a phase transition is observed at 515 K from the high-temperature phase with $F\bar{4}3m$ symmetry to the low-temperature phase with $P2_13$ symmetry. Calorimetric studies of Cu_7PS_6 showed no phase transitions in the temperature range of 100–400 K, the linear temperature dependence of specific heat capacity being an evidence for strong anharmonicity [3].

To our knowledge, no detailed studies of the crystal structure and charge transport in Cu_7PS_6 have been carried out so far. Therefore, a detailed investigation of the structural and electrical properties of Cu_7PS_6 argyrodite-type superionic conductor is of great interest.

Cu_7PS_6 crystals were grown using direct crystallization from melt (Bridgman-Stockbarger technique). The synthesis of Cu_7PS_6 compound was performed in the following way: heating at a rate of 50 K/h to 673 ± 5 K, ageing at this temperature for 24 h, then heating to 973 ± 5 K, ageing at this temperature for 72 h, further heating of the melting zone up to 1380 ± 5 K that is by 50 K above the melting temperature with 24 h ageing. The ageing resulted in nucleation. The annealing of the formed seeds was performed for 48 h. The growth rate was kept at 3 mm/day. The annealing zone temperature was 973±5 K and the annealing duration was 48 h. As a result, Cu_7PS_6 crystals with the length of 45–50 mm and 10– 2 mm in diameter were obtained.

Cu_7PS_6 was investigated using X-ray powder diffraction technique. Cu_7PS_6 crystallizes into cubic structure (space group $P2_13$ (No.198), lattice parameter a = 9.6706(1) Å, Z = 4), which is identical to β-Cu_7PSe_6. The crystal structure of the Cu_7PS_6 contains cation–anion coordination shell of four different types: $[PS_4]$, $[CuS_4]$, $[CuS_3]$, and $[CuS_2]$. The split position of a copper atom, resulting in two 12b positions (Cu2 and Cu3) with partial site occupancies was determined.

Electrical parameters of Cu_7PS_6 crystal were studied in the frequency range 10–10^{10} Hz and temperature interval 296–351 K by coaxial line impedance spectrometer set-up [1]. Two relaxation processes were found in the spectra of Cu_7PS_6 crystal electric properties. The conductivity dispersion regions are related to these processes. The first one is observed in the frequency range from about 10 kHz up to about 100 MHz, while the other dispersion was found above 3 GHz frequency. Both dispersions reveal themselves as maxima of the complex resistivity imaginary part. The maximum of imaginary part of complex resistivity corresponds to relaxation frequency, which increases with increasing temperature. In the frequency range from about 10 MHz up to 1 GHz a well-defined dispersion of dielectric permittivity was found, while in the frequency ranges below 10 MHz and above 1 GHz dielectric permittivity decrease slightly with increasing frequency. A gradual decrease of high frequency ε' from 26.3 to 23 was observed in the studied temperature range. At room temperature and at 1 kHz frequency the conductivity value is $1.77 \cdot 10^{-3}$ S/m while at high frequency of 1 GHz the conductivity reaches 5 S/m. The corresponding conductivities' activation energies were found to be 0.17 eV and 0.08 eV, respectively. Cu^+ ions and electrons/holes contribute to the conductivity in Cu_7PS_6 crystal.

Keywords: crystal growth, X-ray diffraction, impedance spectroscopy, charge transport.

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