

Structure and Channels of Cationic Conduction of Ag_8SnSe_6 Argyrodite

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The solid state materials with high ionic (superionic) and mixed electronic-ionic conductivity (solid electrolytes) belong to prospective materials of the near future [1]. Crystals of Ag_8SnSe_6 argyrodite, which we had grown by means of pseudosublimation method, served as the object of X-ray diffraction (XRD). The structure of the low-temperature β' -phase ($t = 20 \div 83^\circ\text{C}$, space group $Pmn2_1$) and the high-temperature γ -phase ($t = 83 \div 140^\circ\text{C}$, space group $F\bar{4}3m$) of Ag_8SnSe_6 were investigated by means of method of temperature XRD, and with the use of Frank-Kasper (FK) polyhedra modeling of their space structures has been carried out. Since it is ionic conduction that is characteristic of argyrodite type structures, the concept of partial occupation of crystallographic positions of Ag was used to describe the positions of Ag atoms in the structural model.

The refinement of the structure was carried out with the use WinCSD (Version 4.14) packet of software [2]. In the elementary cell of β' - Ag_8SnSe_6 argyrodite, there are 7 positions of Ag atoms, 4 of them are completely filled, and 3 are partially filled. The completely filled positions of Ag1 and Ag3 atoms in Ag_8SnSe_6 structure have tetrahedral surrounding of Se atoms, and the completely filled positions of Ag2 and Ag4 atoms have trigonal coordination of Se atoms. The partially occupied (Occ) positions of Ag in the structure β' - Ag_8SnSe_6 are situated in tetrahedral voids, which are formed by Se atoms. The Ag atoms with partially occupied positions (Ag5 (Occ = 0.921), Ag6 (Occ = 0.047), Ag7 (Occ = 0.102)), which form potential channels of conduction.

It is shown that the structure of the high-temperature γ -phase of Ag_8SnSe_6 can be represented with help of FK polyhedra. In the tetrahedral voids of pyramids and bi-pyramids of these FK polyhedra, there are three partially filled positions of Ag atoms: Ag1 (Occ = 0.3243), Ag2 (Occ = 0.301), Ag3 (Occ = 0.068). The structural elements (tetrahedra and triangular bi-pyramids) of γ -phase of Ag_8SnSe_6 , being joint by common faces, form continuous channels of conduction. The connection of such channels between each other by common tetrahedra lead to the existence of 3D network of ionic conduction.

1. International Technology Roadmap for Semiconductors (ITRS).
<http://www.itrs.net/home.html>. 2012.
2. L. Akselrud, Yu. Grin. WinCSD: software package for crystallographic calculations (Version 4.14) // J. Appl. Crystallogr.– 2014.– P. 47.