CRYSTAL STRUCTURE AND SYNTHESIS OF Ag_3AsS_3 : Ho

Marchuk O.V. [1], *Smitiukh O.V.* [1], *Fedorchuk A.O.* [2]

[1] Department of Chemistry and Technology, Lesya Ukrainka Volyn National University, Potapova St., 9, Lutsk

[2] Department of Inorganic and Organic Chemistry, Lviv National University of Veterinary Medicine and Biotechnologies, Pekarska St., 50, 79010 Lviv, Ukraine

Marchuk.Oleg@vnu.edu.ua

Prostitute crystals (Ag_3AsS_3) have been known as natural minerals for many years [1]. Beginning from 70s last century, it was investigated as potential material for electronics because it is piezo- and pyroelectric, as well as thermo- and photosensitive semiconductor [2]. In the region of low temperatures they belong to semiconductor ferroelectrics, and at high temperatures to superionic conductors. The crystals Ag_3AsS_3 possess high optical anisotropy and transparency in IR region [3]. They are described with low coefficient of hardness (2-2.5 AU on the Moss scale) and easily machinable. Obtained after grinding the crystals are resistant to non-aggressive weather conditions [4]. It is worth noting that optical properties of doped prostitute are not investigated enough.

The crystal structure of Ag_3AsS_3 belongs to non-centrosymetric one and is described by presence of prismatic and tetrahedral cavities. Thus, properties of the material will be improved due to doping of the structure with atoms of rare-earth elements. Such points expand the possibilities of application of the materials.

In present work, we present theoretical substantiation of the possibility of doping prostitute (Ag_3AsS_3) and partial experimental results (x-ray phase analysis of obtained samples).

In the Ag_3AsS_3 (Pearson Symbol *hR*42, SG 161) [3] crystal structure As atoms occupy trigonal prismatic cavities and take place closer to the base of the prism. Thereby, the interatomic distances As-S (opposed base and face-centered atoms) are over the sum of ionic radii. Visualization of the crystal structure has been done by using VESTA [5] program.

The crystal structure of Ag_3AsS_3 may be considered as group packing of atoms $[AsS_3]^{3-}$ that behaves as a separate anionic group since their second coordination surrounding [6] (SCS) is rhombododecahedron (cuboctahedron with two additional atoms against opposite quadrangular faces) that indicates to close packing of such groups of atoms (Fig.1). Ag atoms occupy octahedral voids within the SCS. By contact with five anions $[AsS_3]^{3-}$ the second coordination surrounding of Ag atoms is described by flattened octahedron where cation atoms locate between two opposed S atoms. The distances from prism centre to S atoms are commensurate with the distance of R-S in chalcogenide compounds. Given the above, R atoms as doping impurities occupy statistical position of silver atoms in the crystal lattice of the compound Ag_3AsS_3 (Pearson Symbol *hR*42, SG 161). In order to confirm the possibility of doping of proustite with R atoms, we synthesized samples that contained 0.3, 0.6 and 0.9 at. %. Ho. The samples were synthesized from elementary substances (Ag, Ho, S) and

previously obtained As_2S_3 of at least 99.99 wt.% purity in quartz containers in an MP-30 programmable electric muffle furnace. The containers were evacuated to a residual pressure of 10^{-2} Pa and soldered in oxygen-gas burner flame. The alloys were synthesized step-wise as follows: heating the mixtures to 873 K at the rate of 12 K/h; exposure for 2 h; cooling to 473 K at the rate of 12 K/h; homogenizing annealing for 500 h at 473 K. After reaching the equilibrium state of the synthesized alloys, the amouples were quenched into room-temperature water without breaking. The diffraction patterns (Fig.2) for X-ray phase analysis were recorded at a DRON 4-13 diffractometer over range of $10° \le 2\Theta \le 70°$ (CuKα radiation, scan step 0.05°, 5 s exposure in each point).

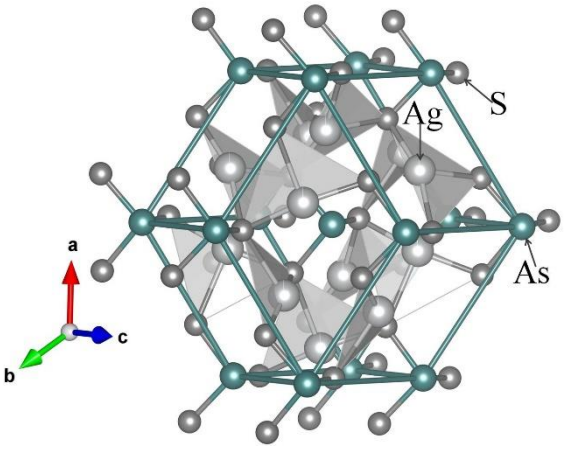

Fig. 1. The second coordination surrounding of $[AsS_3]^{-3}$ in the structure Ag_3AsS_3

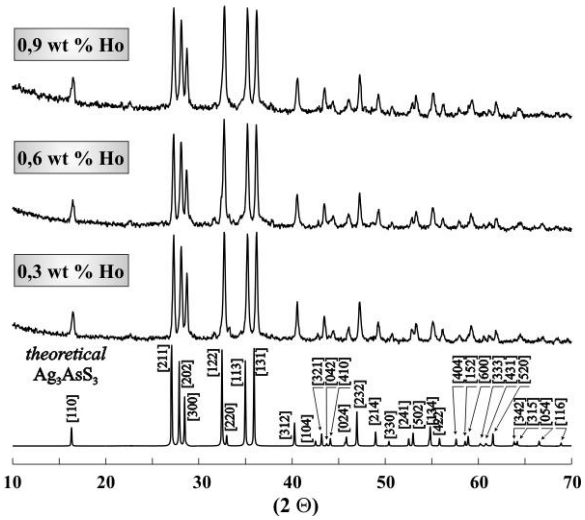

Fig. 2. Theoretical (for Ag_3AsS_3) and experimental diffractograms of Ho-doped proustite

Conclusion. The Ag_3AsS_3 crystal structure was analyzed by the theory of SCS. The synthesis of holmium-doped polycrystalline samples of the synthetic analogue of the mineral Proustite was carried out. According to the phase analysis, the obtained samples are one-phase. The next step of the research of the received chalcogenides will concern measurements of physical properties which are necessary for clarification of perspective spheres of application of researched materials.

References:

1. Kharbish S. Spectral-structural characteristics of the extremely scarce silver arsenic sulfosalts, proustite, smithite, trechmannite and xanthoconite: μ-Raman spectroscopy evidence // Spectrochiica Acta Part A: Molecular and Biomolecular Spectroscopy. – 2017. – Vol. 177. – P.104-110.
2. Schönau K.A., Redfern S. A. T. High-temperature phase transitions, dielectric relaxation, and ionic mobility of proustite, Ag_3AsS_3, and pyrargyrite, Ag_3SbS_3 // J. Appl. Phys. – 2002. – Vol. 92(12). – P.7415-7424.
3. Gagor A., Pawłowski A., Pietraszko A. Silver transfer in proustite Ag_3AsS_3 at high temperatures: Conductivity and single-crystal X-ray studies // J. Solid State Chem. – 2009. – Vol. 182(3). – P.451-456.

4. Hulme K. F., Jones O., Davies P. H., Hobden M. V. Synthetic proustite (Ag_3AsS_3): a new crystal for optical mixing // Appl. Phys. Lett. 1967. – Vol. 10(4). – P.133-135.
5. Momma K., Izumi F. VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data // J. Appl. Crystallogr. – 2011. – Vol. 44. – P.1272-1276.
6. Fedorchuk A.O., Parasyuk O.V., Kityk I.V. Second anion coordination for wurtzite and sphalerite chalcogenide derivatives as a tool for the description of anion sub-lattice // Mat. Chem. Phys. – 2013. – Vol. 139. – P.92-99.