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NEW QUATERNARY CHALCOGENIDES $Ag_{11}D^{IV}C^{III}_3S_{12}$

Lyudmyla Piskach*, Orysia Berezniuk, Lubomir Gulay, Yuri Kogut
Department of Chemistry and Ecology, Volyn National University, Lutsk, 43025, Voli Ave. 13

INTRODUCTION & AIM

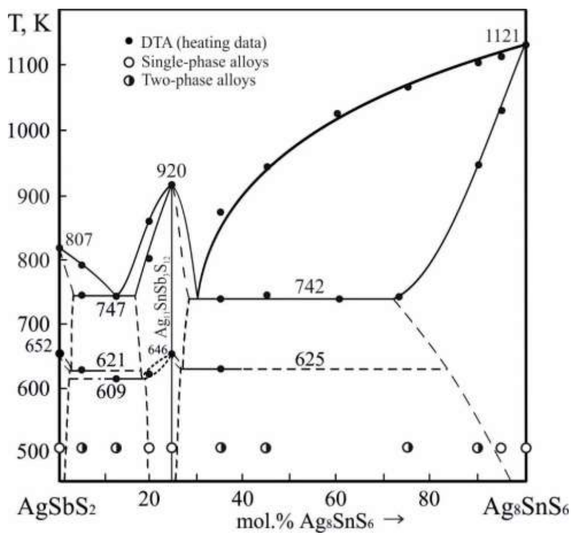
Ternary and quaternary silver chalcogenides are promising semiconductor materials due to valuable physical properties such as optical, electric, ionic conductivity. Antimony chalcogenides are of interest to the research for thermoelectric properties and optical absorption suitable for thin-film solar cells. Our investigation combining these two directions produced three new quaternary sulfides, $Ag_{11}GeSb_3S_{12}$, $Ag_{11}SnSb_3S_{12}$, and $Ag_{11}SnAs_3S_{12}$.

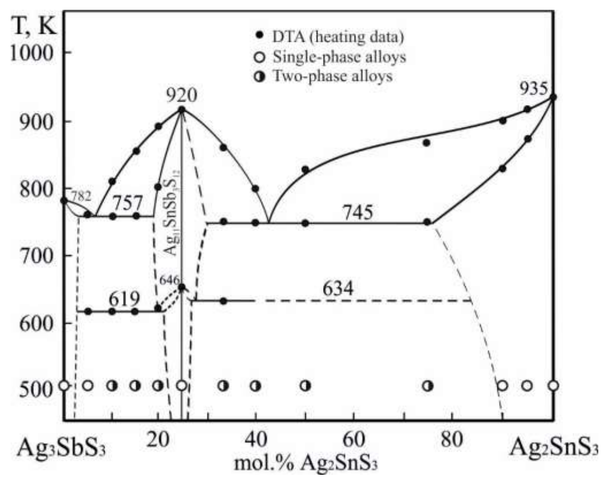
METHOD

The samples were synthesized from high-purity elements Ag, Ge, Sn, Sb, S and pre-made As_2S_3. The batches were heated to 670 K at the rate of 20 K/hr, kept for 24 hr, heated to the maximum temperature of 1170 K. After 10-hr exposure the alloys were slowly (10 K/hr) cooled to 500 K, annealed for 500 hr, and cooled with the furnace switched off.

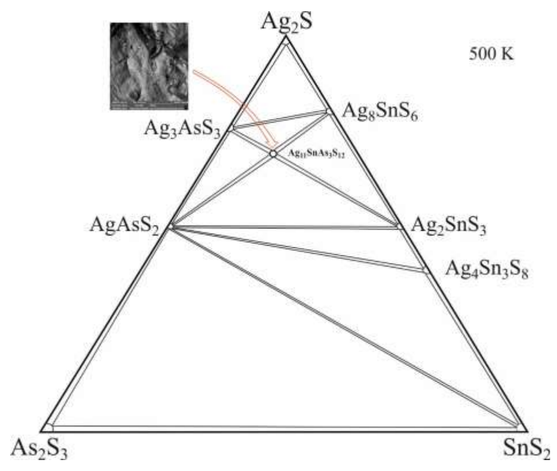
RESULTS & DISCUSSION

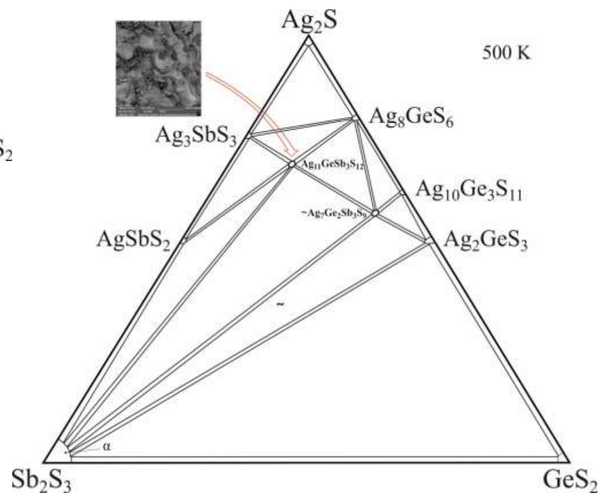
$Ag_{11}SnSb_3S_{12}$ forms at the intersection of $AgSbS_2$–Ag_8SnS_6 and Ag_3SbS_3–Ag_2SnS_3 at the component ratio 1:3 in either expression [1]. These sections are quasi-binary, and their phase diagrams with the formation of the quaternary compound are presented. The quaternary thiosalt melts congruently at 920 K and has a polymorphous transition at 646 K and a modest (5 mol.%) homogeneity region.

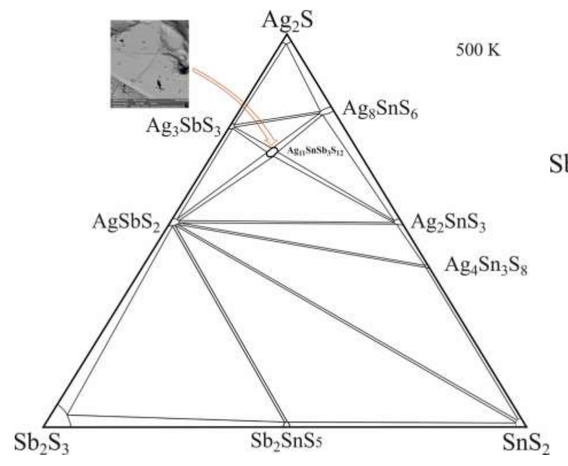




Presented further are the isothermal sections at 500K of quasi-ternary sulfide systems where the new quaternary compounds, $Ag_{11}GeSb_3S_{12}$, $Ag_{11}SnSb_3S_{12}$, and $Ag_{11}SnAs_3S_{12}$, form at the analogous intersections.

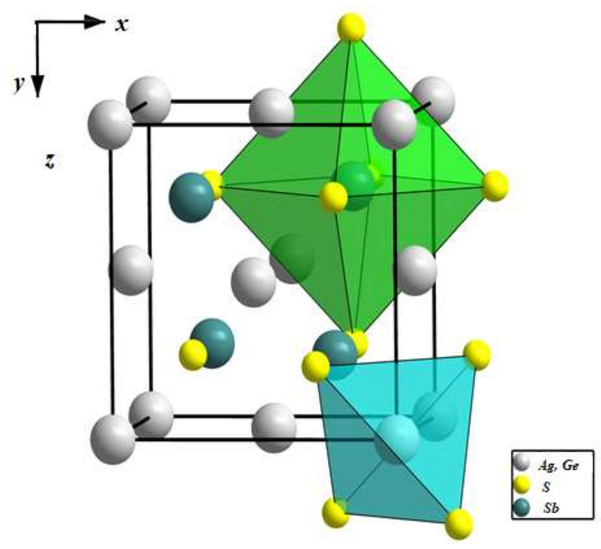






Inserts show SEM images of investigated compounds (x800).

The crystal structure of $Ag_{11}GeSb_3S_{12}$ was studied by powder X-ray structural analysis (DROM 4-13 diffractometer, CuKα radiation, angle range $10°\leq 2\Theta \leq 100°$, scan step 0.02°, 10 s exposure in each point). The diffraction pattern was indexed in the cubic symmetry, space group *I-43m*, the lattice parameter a=0.54127(2) nm.



Sulfur atoms form three-layer closest packing, the statistical mixture of Ag and Ge atoms occupies one half of the octahedral voids, and Sb atoms occupy one quarter of the tetrahedral voids.

FUTURE WORK / REFERENCES

Further investigation of the crystal structure of two other compounds as well as the study of optical absorption and electrophysical properties to quantify the practical prospects of these compounds as materials is pending.

[1] Berezniuk, O.P., Kogut, Y.M., Gulay, L.D., Piskach L.V. Phase Equilibria in the Ag_2S–Sb_2S_3–SnS_2 System and the Novel Quaternary Chalcogenide $Ag_{11}Sb_3SnS_{12}$. *J. Phase Equilib. Diffus.* **45**, 723–731 (2024). https://doi.org/10.1007/s11669-024-01126-7