

**THERMODYNAMIC INVESTIGATION OF THE  $\text{Ag}_7\text{B}^{\text{IV}}\text{Se}_5\text{I}$  COMPOUNDS  
AND  $\text{Ag}_{8-x}\text{B}^{\text{IV}}\text{Se}_{6-x}\text{I}_x$  ( $\text{B}^{\text{IV}}\text{-Ge, Sn}$ ) SOLID SOLUTIONS  
BY THE EMF METHOD WITH SOLID ELECTROLYTE**

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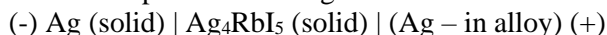
Compounds of the argyrodite family and related phases are of considerable interest as environmentally safe, multifunctional materials exhibiting thermoelectric, photovoltaic, and optical properties, as well as high ionic conductivity.

In this work, the thermodynamic properties of the  $\text{Ag}_7\text{B}^{\text{IV}}\text{Se}_5\text{I}$  compound and solid solutions  $\text{Ag}_{8-x}\text{B}^{\text{IV}}\text{Se}_{6-x}\text{I}_x$  ( $\text{B}^{\text{IV}}\text{-Ge, Sn}$ ) were studied for the first time using the EMF method with a solid  $\text{Ag}^+$  conducting electrolyte  $\text{Ag}_4\text{RbI}_5$ .

The compounds  $\text{Ag}_8\text{GeSe}_6$ ,  $\text{Ag}_8\text{SnSe}_6$ ,  $\text{Ag}_7\text{GeSe}_5\text{I}$ , and  $\text{Ag}_7\text{SnSe}_5\text{I}$  were synthesized by co-melting stoichiometric mixtures of high-purity elemental substances ( $\text{Ag}$ -rod, 99.997%;  $\text{Ge}$ -ingot, 99.999%;  $\text{Sn}$ -ingot, 99.999%;  $\text{Se}$ -granules, 99.999%;  $\text{I}_2$ -powder, 99.999%) in evacuated ( $10^{-2}$  Pa) sealed quartz ampoules. Considering the high saturated vapor pressures of iodine ( $T_b = 457$  K) and selenium ( $T_b = 958$  K) at the melting temperatures, the syntheses were performed in a two-zone inclined furnace.

The phase purity of all synthesized parent compounds was confirmed by X-ray diffraction (XRD) and differential thermal analysis (DTA), and the results were consistent with literature data. For the investigations, alloys of various compositions were prepared from the presynthesized and identified compounds.

EMF measurements were performed using concentration cells of the type



Linear temperature-dependent EMF equations were obtained in the temperature range of 300–390 K based on the experimental data. For the EMF measurements, a high-impedance digital voltmeter Keithley 2100 6½, with an input resistance of  $10^9 \Omega$ , was used. Analysis of the EMF data for electrochemical cells of type (1) showed that, within the studied temperature range, the EMF isotherms are linear functions of temperature. Using the obtained equations for the temperature dependence of the EMF, the partial thermodynamic functions of silver in the alloys were calculated. Based on the solid-phase equilibria data in the  $\text{Ag}_2\text{Se-AgI-B}^{\text{IV}}\text{Se}_2$  system, a fragment of the quaternary phase diagram of the  $\text{Ag-B}^{\text{IV}}\text{-Se-I}$  system was constructed. This diagram was used to formulate the equations of the potential-forming reactions corresponding to the synthesized alloys. Based on these reactions, the standard thermodynamic functions of formation and the standard entropies of the  $\text{Ag}_7\text{B}^{\text{IV}}\text{Se}_5\text{I}$  compound and the solid solutions  $\text{Ag}_{8-x}\text{B}^{\text{IV}}\text{Se}_{6-x}\text{I}_x$  ( $x = 0.2, 0.4, 0.6, 0.8$ ) were calculated.