THERMODYNAMIC STUDY OF THE $BiS_{1-x}Se_xI$ AND $Bi_{19}S_{27(1-x)}Se_{27x}I$ SOLID SOLUTIONS

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Chalcohalides of the arsenic subgroup elements and the phases on their basis have recently attracted considerable attention from researchers due to their functional properties, including thermoelectric, optical, etc., as well as Rashba-type semiconducting characteristics. These properties enhance the potential of such materials for application in various devices in the fields of quantum computing and spintronics [1, 2].

In this work, the thermodynamic properties of the $BiS_{27(1-x)}Se_{27x}I$ and $BiS_{1-x}Se_xI$ solid solutions formed in the Bi_2S_3-Bi_2Se_3-BiI_3 system is investigated.

At the initial stage, experimental studies of solid-phase equilibria in the Bi_2S_3-Bi_2Se_3-BiI_3 system were carried out. To this end, the relevant binary and ternary compounds were synthesized in advance. The synthesis was conducted in a two-zone inclined furnace to accommodate the high vapor pressures of elemental iodine, sulfur, and selenium. To prepare alloys of various compositions in the studied system, the synthesized and identified starting compounds were melted at 850 K in evacuated quartz ampoules. The alloys were subsequently homogenized by stepwise annealing at 650 K for 300 hours and 370 K for 100 hours. Differential thermal analysis (multichannel device based on a TC-08 thermocouple recorder), powder X-ray diffraction technique (Bruker D2 PHASER), and electromotive force measurements (Keithley 2100 6½-digit multimeter) were employed to systematically characterize of all the alloys.

For thermodynamic investigations the following type concentration cells:

(−) Bi (solid) / liquid electrolyte, Bi^{3+} / (Bi in alloy) (solid) (+)

were composed and their EMF was measured over the temperature range 300-370 K. An ionic liquid (morpholine formate) containing $BiCl_3$ was employed as the electrolyte. Analysis of the experimental data revealed a linear dependence of EMF on temperature for all samples. The data were processed using the least-squares method, yielding linear E–T relationships. Based on these equations, the partial molar functions of bismuth in the alloys were calculated at 298 K. By integrating the Gibbs–Duhem equation, the standard thermodynamic functions of formation ($\Delta_f G°$, $\Delta_f H°$, $\Delta_f S°$) and standard entropies for the $BiS_{1-x}Se_xI$ and $Bi_{19}S_{27(1-x)}Se_{27x}I$ solid solutions were calculated.

1. B. Peng, K. Xu, H. Zhang, et al., Adv. Theory Simul, 2018, 1(1), 1700005.
2. G. Landolt, S.V. Eremeev, Y.M. Koroteev, et al., Phys. Rev. Lett, 2012, 109, 116403.