

The system Ag-Au-Se: Phase relations below 405 K and determination of standard thermodynamic properties of selenides by solid-state galvanic cell technique

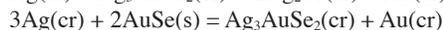
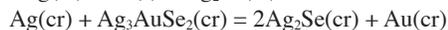
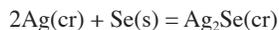
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ABSTRACT

The existence of the only ternary compound, Ag_3AuSe_2 (fischesserite), in the Ag-Au-Se system was confirmed by solid-state annealing method. The selenium analog of petrovskaita (AgAuS) was not observed under the experimental conditions (in the temperature range of 350–773 K and own vapor pressure).

The solid-state reactions



were studied by the electromotive force (EMF) technique in all solid-state galvanic cells with Ag_4RbI_5 as a solid electrolyte. The experiments were run in a dry argon gas flow at atmospheric pressure.

The following standard thermodynamic properties of the stable phases were determined at 298.15 K and 1 bar (10^5 Pa):

$$\Delta_f G^\circ(\text{Ag}_2\text{Se, low naumannite}) = -49470 (\pm 130) \text{ J/mol},$$

$$S^\circ(\text{Ag}_2\text{Se, low naumannite}) = 149.99 (\pm 0.56) \text{ J/(K}\cdot\text{mol)};$$

$$\Delta_f G^\circ(\text{Ag}_2\text{Se, high naumannite}) = -47430 (\pm 290) \text{ J/mol},$$

$$S^\circ(\text{Ag}_2\text{Se, high naumannite}) = 169.01 (\pm 0.78) \text{ J/(K}\cdot\text{mol)};$$

$$\Delta_f G^\circ(\text{Ag}_3\text{AuSe}_2, \text{fischesserite}) = -86450 (\pm 320) \text{ J/mol},$$

$$S^\circ(\text{Ag}_3\text{AuSe}_2, \text{fischesserite}) = 290.80 (\pm 1.26) \text{ J/(K}\cdot\text{mol)};$$

$$\Delta_f G^\circ(\beta\text{-AuSe}) = -4110 (\pm 1300) \text{ J/mol};$$

$$S^\circ(\beta\text{-AuSe}) = 75.49 (\pm 3.55) \text{ J/(K}\cdot\text{mol)}.$$

The phase transition point for low naumannite-high naumannite was determined at $T_{\text{trs}} = 405.4$ K, with the enthalpy of transition of $\Delta_{\text{trs}}H = -7713 (\pm 550) \text{ J/mol}$.

Keywords: Thermodynamic data, naumannite, fischesserite, AuSe, EMF-method, solid-state galvanic cell