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, Ag₃AuSe₂ (fischesserite), in the Ag-Au-Se system was confirmed by solid-state annealing method. The selenium analog of petrovskait (AgAuS) was not observed under the experimental conditions (in the temperature range of 350–773 K and own vapor pressure).

The solid-state reactions

\[ 2\text{Ag}(cr) + \text{Se}(s) = \text{Ag}_2\text{Se}(cr) \]
\[ \text{Ag}(cr) + \text{Ag}_3\text{AuSe}_2(cr) = 2\text{Ag}_2\text{Se}(cr) + \text{Au}(cr) \]
\[ 3\text{Ag}(cr) + 2\text{AuSe}(s) = \text{Ag}_3\text{AuSe}_2(cr) + \text{Au}(cr) \]

were studied by the electromotive force (EMF) technique in all solid-state galvanic cells with Ag₄RbI₅ 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 (10⁵ Pa):

\[ \Delta G^\circ(\text{Ag}_2\text{Se}, \text{low naumannite}) = -49470 (±130) \text{ J/mol}, \]
\[ S^\circ(\text{Ag}_2\text{Se}, \text{low naumannite}) = 149.99 (±0.56) \text{ J/(K·mol)}; \]
\[ \Delta G^\circ(\text{Ag}_2\text{Se}, \text{high naumannite}) = -47430 (±290) \text{ J/mol}, \]
\[ S^\circ(\text{Ag}_2\text{Se}, \text{high naumannite}) = 169.01 (±0.78) \text{ J/(K·mol)}; \]
\[ \Delta G^\circ(\text{Ag}_3\text{AuSe}_2, \text{fischesserite}) = -86450 (±320) \text{ J/mol}, \]
\[ S^\circ(\text{Ag}_3\text{AuSe}_2, \text{fischesserite}) = 290.80 (±1.26) \text{ J/(K·mol)}; \]
\[ \Delta G^\circ(\beta\text{-AuSe}) = -4110 (±1300) \text{ J/mol}; \]
\[ S^\circ(\beta\text{-AuSe}) = 75.49 (±3.55) \text{ J/(K·mol)}. \]

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

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

INTRODUCTION

The class of selenides, and selenides of noble metals in particular (including system Ag-Ga-Se), are rare but characteristic minerals of the Ag-Au-S-Se-Te hydrothermal deposits. The existence of low-temperature silver selenide—naumannite—has been known for a long time (Earley 1950). Fischesserite (Ag₃AuSe₂) was discovered (Johan et al. 1971) in the carbonate veins of Predborice, Bohemia, Czechoslovakia (now Czech Republic), where it was associated with naumannite, clausthalite (PbSe), benzianite (Cu₂Se), gold, and other selenides. The phase AgAuSe was synthesized by Nekrasov et al. (1990). Gold selenide (AuSe) was never found in the nature. The only gold and silver selenide Ag₃AuSe₂ occurs in many gold-silver deposits, and its thermodynamic properties are very important in understanding geochemistry, transport, and deposition of gold.

The objectives of the present study are to explore the phase relations in the Ag-Au-Se system below the temperature of the α-β transition in Ag₂Se and to determine the standard thermodynamic properties of fischesserite, naumannite, and β-AuSe using electromotive force (EMF) measurements in solid-state galvanic cells. This method has proved to be direct, effective, and most accurate for determination of molar free energy and molar entropy change in reactions (Kiukkola and Wagner 1957a, 1957b).

Ag-Au-Se system and marginal systems. This ternary system Ag-Au-Se has not been studied experimentally. However, its marginal binary and pseudo-binary sections were studied quite intensely (Karakaya and Thompson 1990; Wiegers 1976; Rabenau et al. 1971; von Oehsen and Schmalzried 1981). The results of these works provide the relatively complete picture of low-temperature phase relations in the ternary system (Fig. 1a).

The system Ag-Se. The Ag-Se binary phase diagram was