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

Evgeniy G. Osadchii* and Ekaterina A. Echmaeva

Institute of Experimental Mineralogy, Russian Academy of Sciences, Chernogolovka, Moscow District, 142432, Russia

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 petrovskaite (AgAuS) was not observed under the experimental conditions (in the temperature range of 350–773 K and own vapor pressure).

The solid-state reactions

$2Ag(cr) + Se(s) = Ag_2Se(cr)$
$Ag(cr) + Ag_3AuSe_2(cr) = 2Ag_2Se(cr) + Au(cr)$
$3Ag(cr) + 2AuSe(s) = Ag_3AuSe_2(cr) + Au(cr)$

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):

$\Delta_f G°(Ag_2Se$, low naumannite) = –49470 (±130) J/mol,
$S°(Ag_2Se$, low naumannite) = 149.99 (±0.56) J/(K·mol);
$\Delta_f G°(Ag_2Se$, high naumannite) = –47430 (±290) J/mol,
$S°(Ag_2Se$, high naumannite) = 169.01 (±0.78) J/(K·mol);
$\Delta_f G°(Ag_3AuSe_2$, fischesserite) = –86450 (±320) J/mol,
$S°(Ag_3AuSe_2$, fischesserite) = 290.80 (±1.26) J/(K·mol);
$\Delta_f G°(\beta$-AuSe) = –4110 (±1300) J/mol;
$S°(\beta$-AuSe) = 75.49 (±3.55) J/(K·mol).

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

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