



Thermodynamic study in the Ag–Sb–S system by the EMF method



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ABSTRACT

In this study, thermodynamic properties of AgSbS₂ and Ag₃SbS₃ have been determined by the advanced EMF method. All the measured phases have been carefully synthesized in evacuated quartz glass ampoules. The synthesized phases were analyzed by the SEM–EDS and DSC techniques. Solid state electrochemical cells of the type (Ag|AgI|Ag–Sb–S-compounds in equilibrium) were applied in EMF measurements. Independent experimental apparatuses were applied to prove the reproducibility of the measured EMF values. The measured *E* vs. *T* relations were analyzed, and thermodynamic functions of AgSbS₂ and Ag₃SbS₃ have been determined. Accurate thermodynamic properties of both phases including data in new temperature ranges have been obtained. The results were compared with the available literature data and discussed.

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1. Introduction

Power generation through the thermoelectric effect is a subject of increasing interest both scientifically and commercially. Thermoelectric materials can directly and reversibly convert waste heat into electrical energy, and will play a significant role in the future energy management plans [1]. The performance of thermo-electric materials is quantified as a function of temperature by a dimensionless figure of merit, $ZT = \sigma S^2 T / (\kappa_{el} + \kappa_{lat})$, where σ , S , T , κ_{el} and κ_{lat} are the electrical conductivity, Seebeck coefficient, temperature, electronic thermal conductivity, and lattice thermal conductivity, respectively [1]. Apart from the traditional chalcogenide materials, cubic I–V–VI₂ (where I = Cu, Ag, Au; V = As, Sb, Bi; and VI = S, Se, Te), semiconductors are renowned for their intrinsically low κ_{lat} due to the strong anharmonicity of the bonding arrangements in these compounds [2]. AgSbS₂ and Ag₃SbS₃ are typical members of this I–V–VI₂ family. For instance, AgSbS₂ is known for its good thermoelectric properties, particularly, its solid solution AgPb_xSbS_{2+x} with cubic NaCl structure has desirable features for efficient *ZT* thermoelectric materials for solar thermal power generation [3]. In addition, the Ag–Sb-sulfosalts have also emerged as promising novel functional materials for other applications as well. For example, beside their thermoelectric properties, AgSbS₂ and Ag₃SbS₃ are also good candidates for optical applications

[4–7]. As an important part of chalcogenide semiconductor materials, pyrrargyrite (Ag₃SbS₃) is an attractive substance for different optoelectronic and data storage applications [8].

Currently, most of the available sulfide ores are low-grades and also becoming increasingly complex. Silver and antimony bearing sulfides and sulfosalts are encountered in these complex ore minerals for the production of base metals and are also common sources of silver. Among the Ag–(Sb, Bi, As)-based sulfosalts, miargyrite (AgSbS₂) and pyrrargyrite (Ag₃SbS₃) are dominantly associated with high-grade silver ores [9]. Miargyrite is also an economically important source of silver [10]. In order to modify their operating flow sheets and strategies for processing more complex feed materials economically, valuable metal producers are in need of thermodynamic data of phases and phase assemblages which are common in these complex ore minerals in the processing. Therefore, accurate thermodynamic data concerning the ternary phases in the Ag–Sb–S system determined within this study have considerable fundamental and practical importance in many aspects of material science and extractive metallurgy.

Reliable thermodynamic data are essential for accurate quantitative modeling of the stabilities of the sulfosalts and their chemical behavior in the presence of other equilibrium phases. In order to compile an accurate thermodynamic database of the equilibrium Ag–Sb–S-ternary phases only few experimental studies have been published. Babanly et al. [11] determined the thermodynamic properties of AgSbS₂ and Ag₃SbS₃ below 383 K by the EMF method. Bryndzia and Kleppa [12] determined the phase transition

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properties of both AgSbS_2 and Ag_3SbS_3 . Therefore, the purpose of this experimental investigation was to study thermodynamic properties of the Ag–Sb–S ternary phases accurately and also to contribute new experimental thermodynamic data in the temperature and compositional ranges that have not been experimentally studied before.

Miargyrite (AgSbS_2) exists in two polymorphic forms. The low temperature phase, α - AgSbS_2 , is monoclinic and is stable below $T = (653.0 \pm 5) \text{ K}$ [12]. The high temperature phase β - AgSbS_2 , is cubic and stable above 653 K [13,14]. However, the existence of a third form, the intermediate γ - AgSbS_2 phase, has been reported [15].

Schönau and Redfern [16] reported that Ag_3SbS_3 undergoes a phase transition at $T = 490 \text{ K}$. However, no such transition was observed in the experimental EMF data of this study, as the measured EMF data is notably linear over the claimed phase transition temperature. Furthermore, no DSC values were found in the literature verifying that Ag_3SbS_3 undergoes a phase transition at $T = 490 \text{ K}$. Thus, the impact of the phase transition has not been taken into account in the derivation of the thermodynamic quantities.

2. Materials and methods

All the substances used in this study have been listed in Table 1 together with the corresponding purities and countries of manufacture.

2.1. Synthesis and sample preparation

Each sample was synthesized by mixing starting materials Ag_2S , Sb_2S_3 and Sb with such a ratio that the content of the sample was in equilibrium with the desired three phase field, as presented in Fig. 1. The test electrodes containing the three phases were synthesized in evacuated quartz glass ampoules, which were flushed with high purity argon before final evacuation and the sealing of the ampoule. After a number of trials, the clean three phase containing samples were obtained after annealing samples at $400 \text{ }^\circ\text{C}$ for 6 days, melting the samples at $540 \text{ }^\circ\text{C}$ for 15 min and finally annealing the samples at $410 \text{ }^\circ\text{C}$ for 4 weeks. The content of each ampoule was confirmed separately after synthesis by SEM–EDS analysis to confirm that only the desired phases were present in each test electrode.

After the synthesis, porous samples were pressed again into pellets to improve diffusion and electrical conductivity inside the electrode. A short piece of Pt wire was pressed together with the synthesized sample. The reference electrode of the cell was formed by bending a piece of silver plate around a short platinum wire. The connection to the Pt wire was ensured by squeezing silver sheet around the Pt wire. Finally, the experimental cell arrangement was formed by pressing the sample electrode, AgI powder and the reference electrode all together into one pellet, to maintain

Table 1

Provenance and purities of the materials used in this study.

Manufacturer	Substance	Country of manufacture	Mass fraction purity
Alfa Aesar	Ag (plate)	Germany	0.999
Alfa Aesar	Ag_2S	Germany	0.999
Alfa Aesar	Sb	Germany	0.99999
Alfa Aesar	AgI	Germany	0.99999
Alfa Aesar	Sb_2S_3	Germany	0.999
Alfa Aesar	Re	Germany	0.9997
AGA	Ar	Finland	0.99999
Johnson-Matthey Noble Metals	Pt	UK	0.9999
Friatec	α - Al_2O_3	Germany	0.995

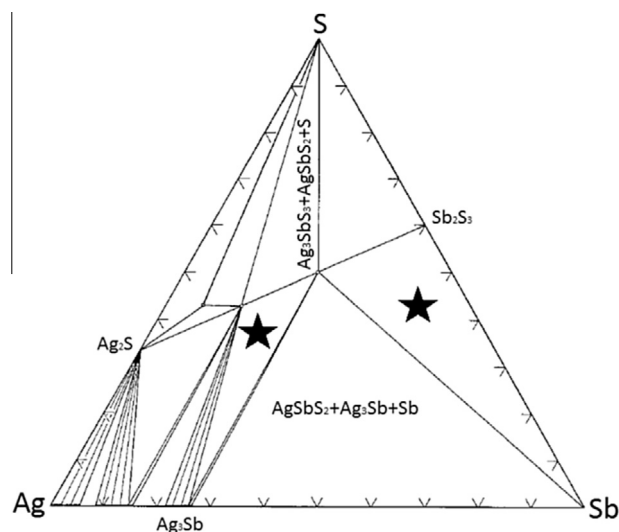


Fig. 1. Modified phase diagram of Ag–Sb–S system in 673 K initially presented in paper of Kleighin and Honea [17]. The composition of the test electrodes of the experimental cells (C) and (D) have been illustrated with star symbols.

unrestricted connection between the components. The electrical connections to the electrodes were formed by skimming off the ends of the short Pt wires out from the cell arrangement. The arrangement has been presented in B fraction of Fig. 2.

After the first experimental runs, the reference electrode was contaminated by evaporated phases of the test electrode. For this reason, in the following cell arrangements the reference electrode was pressed together with powdery AgI electrolyte so that the reference electrode was completely covered by a protective electrolyte layer as presented in the A insert of Fig. 2.

In one of the cell arrangements (cell (B)), short rhenium lead wire was used to avoid undesired chemical reactions between the pure antimony in the sample electrode and the platinum lead wire. The electrical connection to the test electrode was formed by pressing it towards a spirally shaped rhenium wire during the experiments. However, no difference in the measured EMF was obtained between the cell arrangements with Pt and Re lead wire materials, as presented in Fig. 3.

2.2. Symmetrical cell arrangement

The method of estimating the systematic error as a function of temperature and temperature gradient of an electrochemical cell arrangement by applying symmetrical cell measurements have been presented previously by Aspiala et al. [18]. The parasitic voltage of the experimental arrangement, resulting from thermovoltage, was measured by symmetrical cell arrangement:

$$(\pm)\text{Pt, Ag|AgI|Ag, Re, Pt}(\pm), \quad (\text{A})$$

The dimensions and structure of the symmetrical cell (A) were equal to the actual experimental cells, so that the measured EMF of the cell (A) is comparable to the systematic error of the actual EMF cells. The EMF of the symmetrical cell was measured as a function of temperature (T) and temperature gradient over the cell (ΔT) and quadratic equation was fitted to the measured set of data. The equation describing the EMF of the cell (A) was used to compensate the systematic error from the actual EMF data as:

$$f_{\text{error}}/(\text{mV}) = 2.214 - 0.007194T + 0.3541\Delta T + 5.767 \cdot 10^{-6}T^2 + 4.708 \cdot 10^{-5}T \cdot \Delta T + 0.008583\Delta T^2 \quad (\text{1})$$

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