Solid State Ionics 231 (2013) 1–4

Contents lists available at SciVerse ScienceDirect

Solid State Ionics

journal homepage: www.elsevier.com/locate/ssi

Thermodynamic stability of Ag_2Se from 350 to 500 K by a solid state galvanic cell

Dawei Feng, Pekka Taskinen [*], Fiseha Tesfaye

Aalto University School of Chemical Technology, Department of Materials Science and Engineering, Metallurgical Thermodynamics and Modelling Research Group, Vuorimiehentie 2K, PO Box 16200, FI-00076 Aalto, Finland

ARTICLE INFO

Article history:
Received 15 June 2012
Received in revised form 5 October 2012
Accepted 17 October 2012
Available online 27 November 2012

Keywords:
Silver selenide
Enthalpy and entropy of formation
Polymorphic phase transformation

ABSTRACT

The numerical values on the standard thermodynamic functions of Ag_2Se (naumannite) were determined by the electromotive force (EMF) method in a solid-state galvanic cell with superionic conductor $RbAg_4I_5$ as the solid electrolyte. Ag_2Se was synthesized from pure elements in evacuated quartz glass ampoules and examined to be homogenous by SEM and EDS. According to the experimental data on the EMF versus temperature, the analytical equations were obtained for the polymorphic forms of Ag_2Se. The temperature-dependent relationships of the Gibbs energy of formation of Ag_2Se in its polymorphic forms and the standard thermodynamic functions of compounds within the temperature range of 350–500 K were also evaluated. The temperature of phase transformation from α-Ag_2Se to β-Ag_2Se is determined experimentally to be 407.7 K and the enthalpy of phase transformation is 6.06 kJ mol^{-1}.

1. Introduction

Ag_2Se was reported in the literature for its remarkable magnetoresistance (MR) with promising applications, such as magnetic field sensors [1,2]. Nevertheless, the limited resource of selenium becomes the bottleneck for its extensive applications. Selenium exists as trace element accompanied with other nonferrous metals, making it difficult to be extracted from minerals directly. Significant fraction of selenium is extracted from anode slime, which is a byproduct of the electrolytic refining of copper [3]. The Ag–Se system and its properties, therefore, play significant roles in the smelting of copper anode slimes. However, the thermodynamic stability of Ag–Se binary system is poorly documented. Therefore, it is significant to know better the thermodynamic properties of the binary Ag–Se intermetallic compounds.

The polymorphism of silver selenide was discovered in 1888 by Bellati and Lussana [4]. The high-temperature structure was found by Rahlfs [5] to be body-centered cubic, while the ambient temperature polymorph naumannite [6] occurs in nature with orthorhombic structure [7]. A sharp change in resistivity occurs when Ag_2Se is transformed from the low-temperature orthorhombic form (α-Ag_2Se) to the high-temperature body centered-cubic form (β-Ag_2Se) [8].

Various methods have been used for determination of thermodynamic properties of silver selenide. Calorimetry was used by Banus [8] in 1964, Shukla et al. [9] in 1982 and Grønvold et al. [10] in 2002. Other method like vapor pressure [11] was also used. Furthermore, the EMF method is deemed to be direct, effective, and most accurate for determination of thermodynamic properties of reactions. The solid electrolyte AgI was first used in EMF measurements on silver selenide by Kiukkola and Wagner [12] in 1957. Later on, $RbAg_4I_5$was applied by Takahashi and Yamamoto [13] in 1970 for its excellent ionic conductivity. On the other hand, molten salt electrolyte, such as LiCl–KCl, was employed by Nasar and Shamsuddin [14] in 1997. Coulometric titration was made by Oehsen and Schmalzried [15] for silver selenide investigation in 1981. More recently, Beck and Janek [16] have investigated the stoichiometric silver selenide from 373 down to 173 K by coulometric titration. Voronin and Osadchii [17] used both solid and liquid electrolytes to investigate the thermodynamic properties of silver selenide. However, the available literature data on the thermodynamic properties obtained in different laboratories are inconsistent.

The objective of the present study is to determine the thermodynamic stability of naumannite experimentally, by using electromotive force (EMF) measurements in solid-state galvanic cells at low temperatures. Ag_2Se(cr) is the only intermediate phase in the Ag–Se system and it exists in two polymorphs, α and β. The α-polymorph (low naumannite) is stable below 406 K. The temperature range from 350 to 500 K was chosen in order to obtain thermodynamic data for both α-Ag_2Se (stable below 406 K) and β-Ag_2Se (stable above 406 K) in equilibrium with pure selenium.

2. Experimental

2.1. Material synthesis

Silver powder from Alfa Aesar (99.99% in purity) and selenium powder from Koch–Light Laboratories Ltd (99.999% in purity) were used for synthesis of the intermetallic Ag_2Se phase.

The Ag_2Se intermetallic compound was prepared by a direct synthesis from the elements. The Ag and Se powders were mixed in mole ratio 2:1 together and sealed in an evacuated quartz glass ampoule. Then the

---

[*] Corresponding author. Tel.: +358 40 5017411; fax: +358 9470 22798.
E-mail address: pekka.taskinen@aalto.fi (P. Taskinen).

0167-2738/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.ssi.2012.10.013

ampoule was heated up from room temperature to 673 K at a rate of 4 K/min and kept for 2 days. After that it was heated to 873 K and then kept at that temperature for 2 days. Finally, it was heated to 1173 K (the melting point of Ag_2Se) and kept there for 1 h, and then cooled down to room temperature.

The resulting phase mixture from the synthesis was examined to be homogenous by SEM and EDS. The compounds were ground with 1% atomic excess of selenium and pressed uniaxially to obtain a pellet of 6 mm in diameter and 2 mm in thickness, under pressure of about 0.1 G Pa.

The solid electrolyte, $RbAg_4I_5$, was synthesized according to the method described by Owens and Argue [18]. Weighing of 0.8 mole fraction of silver iodide from Alfa Aesar (99.9% in purity) and 0.2 mole fraction of rubidium iodide from Alfa Aesar (99.8% in purity) was followed by mixing. The mixture was sealed in a glass tube under vacuum, and heated at 220 °C for 2 h. Then after being cooled down and maintained at 160 °C for 15 h, thereby $RbAg_4I_5$ was obtained.

2.2. Temperature and EMF measurements

Constant temperature profile inside a Lenton tube furnace type LTF 12/50/610 was located by measurements using a moveable thermo-resistance. Schematic illustration of the experimental furnace for carrying out measurements with the solid electrolytes is shown in Fig. 1. During the EMF-measurements, temperatures on both ends of the galvanic cell were measured using two PT100 sensors (platinum resistance thermometers, PRT). The PRTs, with tolerance class B 1/10 DIN, i.e. ± 0.03 °C variation at 0 °C, according to the manufacturer, were calibrated in a mixture of ice and water at 0 °C. The obtained resistance values above 100 Ω (Ro = 100.026 Ω and Ro = 100.03 Ω, respectively) were added to a program based on LabVIEW software code from National Instruments that records the temperature values from each PRT. The accuracy of temperature and EMF readings reaches 0.0001 K and 0.001 mV, respectively.

The identical platinum wires for the EMF-measurements were used and the lead wires from the PT100 sensors for temperature measurements were connected to a KEITHLEY-6517B/electrometer/high resistance meter and a KEITHLEY-2000-multimeter, respectively. Input impedance of the electrometer for EMF-measurements was $2 \cdot 10^{14}\,\Omega$, which allows the cells to function in a reversible way. The measured EMF-values and temperatures were simultaneously transferred to a computer through an IEE-488-GPIB-cable and a KEITHLEY-KUSB-488A USB-to-GPIB interface adapter, and the readings were recorded by the software giving two measured values every 5 s.

Most measurements were performed by heating and cooling the cell in steps from 1 to 10 °C. To reach steady state EMF reading, it took from few hours up to two weeks. The equilibriums were considered to be reached when the EMF-values were constant, or their variations were not significant (<0.1 mV) and they were oscillating about a certain value for several hours. Temperature differences between the two electrodes of the EMF cell were controlled to be much less than 1 °C ($0.1 < T(°C) < 0.8$), by manually adjusting the horizontal position of the galvanic cells and observing the real-time temperature readings over the cell from the highly accurate PRTs. The uncertainty of temperature and EMF was established to be ± 0.5 K and ± 0.1 mV, respectively. Thus, the possible thermoelectric effect generated in the cell EMF by the temperature gradients is negligible.

Functionality of the experimental electrochemical system was tested by measuring the EMF of the symmetric cell Ag | Ag^+ | Ag, which theoretically should not result in any measurable EMF or electric potential difference. The equilibriums in this study were considered reproducible when the EMF readings in heating and cooling coincided, and another galvanic cell with the same chemical composition resulted in the same EMF-values.

In this particular cell design, the resistance thermometers are connected to each end of the cell, in order to record the temperature exactly on the anode and cathode, thus eliminating the temperature errors of measurements.

Gas flow of dry argon (99.999% Ar) to the EMF cell was purified before introduction to the cell, by passing through an auxiliary furnace with titanium wire at 900 K for removing oxygen traces. Owing to these improvements, the accuracy of EMF measurement and its stability as a function of time was very good, allowing also very long measuring campaigns for each experimental cell.

2.3. EMF cell

The measurements were performed on the solid state galvanic cell when one mole silver selenide is formed from solid pure silver and selenium, and its virtual cell reaction is given by (*A*).

The virtual reaction of the electrochemical cell is

$$2\,\mathrm{Ag}\,(s) + \mathrm{Se}\,(s) = \mathrm{Ag_2Se}\,(s)\ (A).$$

The EMF of the cell

$$(-)\mathrm{Pt}|\mathrm{Ag(s)}|\mathrm{RbAg_4I_5(s)}|\mathrm{Ag_2Se(s)},\ \mathrm{Se(s,1)}|\mathrm{Pt}(+)$$

was measured in a temperature range of 350 K–500 K, under the ambient atmospheric pressure.

The Gibbs energy change of the cell reaction, except for the work of volume expansion, is related to the reversible EMF of reaction (*A*) by the Nernst equation

$$\Delta\overline{G}_{\mathrm{Ag_2Se}} = -zFE \qquad (1)$$

where E is the electromotive force produced by the cell and F is the Faraday constant (96,485 $\mathrm{C \cdot mol^{-1}}$) and the number of elementary changes transferring in the virtual cell reaction (*A*) is $z = 2$.The other fundamental thermodynamic properties of Ag_2Se at selenium saturation can be derived from the general properties of Gibbs energy and its functional relationships with temperature [19]:

$$\Delta\overline{S}_{\mathrm{Ag_2Se}} = zF\left(\frac{\partial E}{\partial T}\right)_P \qquad (2)$$

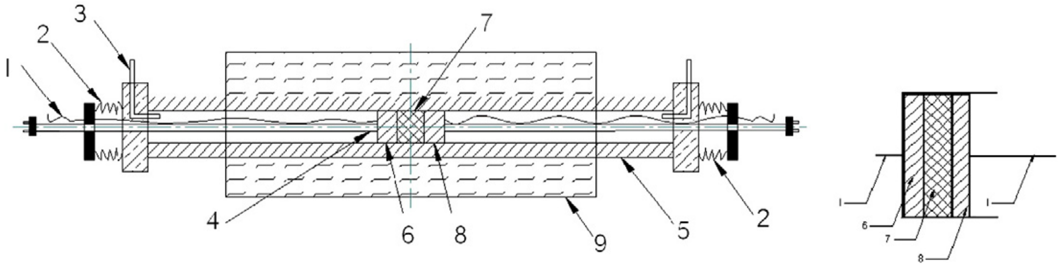

Fig. 1. Schematic illustration of an experimental furnace for carrying out measurements with the solid electrolytes (1) platinum wire, (2) spring, (3) inert gas inlet/outlet, (4) PRT, (5) furnace tube of quartz glass, (6) sample system, (7) solid electrolyte, (8) reference system, and (9) Lenton tube furnace.