



Thermodynamic study of MgO–Sb₂O₃ system and the stability functions of magnesium antimonite



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ABSTRACT

In this study, the standard Gibbs free energy of formation of MgSb₂O₄ has been determined by means of the solid-oxide electrolyte EMF technique. A pure-oxygen reference electrode was applied for the first time to this system in an oxygen concentration cell. The EMF values, temperature and the prevailing pressure of the following galvanic cell were measured:



The standard Gibbs free energy of the virtual cell reaction $2\text{Sb(l)} + 3/2\text{O}_2\text{(g)} + \text{MgO(s)} = \text{MgSb}_2\text{O}_4\text{(s)}$ was determined to be:

$$\Delta_f G^\circ / (\text{kJ} \cdot \text{mol}^{-1}) \pm 2.97 = -734.96 + 0.2645T/\text{K} \quad (906 \leq T/\text{K} \leq 1148).$$

The standard Gibbs free energy of formation of solid MgSb₂O₄ from its pure component oxides $\text{Sb}_2\text{O}_3\text{(l)} + \text{MgO(s)} = \text{MgSb}_2\text{O}_4\text{(s)}$ was determined to be:

$$\Delta_f G^\circ_{\text{MgSb}_2\text{O}_4} / (\text{kJ} \cdot \text{mol}^{-1}) \pm 3.00 = -52.75 + 0.0253T/\text{K} \quad (929 \leq T/\text{K} \leq 1148).$$

The standard Gibbs free energy of formation of solid MgSb₂O₄ from the elements $\text{Mg(l)} + 2\text{Sb(l)} + 2\text{O}_2\text{(g)} = \text{MgSb}_2\text{O}_4\text{(s)}$ was determined to be:

$$\Delta_f G^\circ_{\text{MgSb}_2\text{O}_4} / (\text{kJ} \cdot \text{mol}^{-1}) \pm 18.2 = -1392 + 0.4055T/\text{K} \quad (973 \leq T/\text{K} \leq 1148).$$

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1. Introduction

Exhaustion of high-grade copper ores leads to implication into processing of lower-quality copper ores and concentrates with significant concentration of trace elements such as antimony. This fact causes potentially decline of anode copper quality and interferes with electro-refining [1]. Besides academic interest, thermodynamic properties of magnesium antimonite are essential from industrial viewpoint for antimony elimination during copper smelting and refining processes utilizing MgO. On the other hand, antimony has been found to be a critical raw material for the EU due to the fact that China accounts for a high share of the world-wide production, low recycling rate and low substitutability of antimony. Therefore antimony is potentially a valuable co-product in the copper industry; moreover, it has numerous applications such as the production of micro capacitors [2].

No reliable phase diagram information on the system MgO–Sb₂O₃ has been presented in the literature. The existence of one ternary oxide with a chemical formula MgSb₂O₄ and tetragonal crystal structure with following lattice parameters $a = 0.8476$ nm, $c = 0.5938$ nm has been reported [3]. It has been determined that MgSb₂O₄ can be in equilibrium with MgO as well as Sb can coexist with both phases MgSb₂O₄ and MgO [4,5]. It is related to a higher thermodynamic stability of MgO compared to Sb₂O₃.

Previous research on the standard Gibbs free energy of formation of MgSb₂O₄ has been conducted by utilizing the electromotive force (EMF) method [4–6]. Katayama *et al.* [4] and Kemori *et al.* [5] employed similar galvanic cells with a Pt-air reference electrode. The cells differ from each other in the applied solid electrolytes: yttria stabilized zirconia (YSZ) [4] and calcia stabilized zirconia (CSZ) [5], respectively. The observed results from these studies agree satisfactorily. Another study by Raghavan [6] utilized the EMF technique with a MgF₂ solid electrolyte. The measurements by Raghavan were performed at higher temperatures and a direct comparison of his primary results with [4,5] is not possible. However, there is a discrepancy among the reported results, especially at

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temperatures slightly above the melting point of antimony trioxide, Sb_2O_3 .

Filling this discrepancy in earlier observations and increasing the accuracy of the standard Gibbs free energy of formation of MgSb_2O_4 , the solid-oxide electrolyte EMF technique was applied in this study to MgSb_2O_4 saturated with MgO and metallic antimony, employing the pure oxygen gas reference electrode and state-of-the-art equipment.

2. Experimental

The magnesium antimonite MgSb_2O_4 was synthesized by a ceramic route from an equimolar mixture of Sb_2O_3 and MgO (table 1). Both starting materials were in a fine powder form. The denoted mixture was pelletized at a pressure of about 0.25 GPa and heated under flowing inert atmosphere of N_2 in an alumina crucible at $T = 973$ K for 24 h. Heat-treated sample was analyzed by X-ray powder diffraction analysis to confirm the formation of the ternary compound. The single phase was determined within 0.05 mass fraction XRPD detection limit of a second phase.

The test electrode was comprised of three phases: Sb, MgSb_2O_4 and MgO. The applied mole ratio of the phases was varied from 6:1:1 to 10:1:1, respectively, among the four similar experimental galvanic cells used. Preparing the test electrode, antimony metal lumps (table 1) were ground in an agate mortar and mixed with two other compounds in a powder form. Before the measurement, the three-phase mixture was placed in a closed-end zirconia solid electrolyte tube (table 1) for further homogenization by heating in inert argon atmosphere at $T = 910$ K for 24 h. The protective atmosphere was provided with a steady purified argon flow controlled by a rotameter. The argon was purified from its initial purity (table 1) by passing it through a Ti-packed tube furnace at $T = 873$ K.

The experimental setup has been described and outlined in detail previously [7]. The experiments were performed in a vertical Lenton LTF 16/-/450 tube furnace. The temperature profile along the height of the furnace was measured prior to the EMF measurements, with the aim to place the cell accurately within the isothermal zone. Moreover, the amount of the sample was minimized in order to avoid a temperature gradient over the cell. Prior to the EMF measurements, temperatures below and above the cell were measured with calibrated S-type thermocouples (Johnson-Matthey Noble Metals) and the temperature difference between them was verified to be less than 1 K within the whole experimental temperature range. During the EMF measurements, the cell temperature was measured from the bottom of the zirconia tube with the same type of thermocouple, connected to a Keithley 2010 DMM multimeter. The cold junction compensation was performed by a PT100 resistance thermometer (SKS-Group, Finland, tolerance class B 1/10), connected to a Keithley 2000 DMM multimeter.

The pure oxygen reference electrode was arranged in such a way that the steady oxygen (table 1) flow inside the gas tight mullite

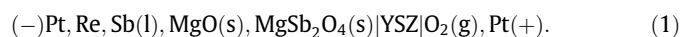
working furnace tube, and outside the solid-electrolyte zirconia tube, was controlled by a digital mass flow controller, Aalborg DFC26 (USA). Due to the solid electrolyte zirconia tube being inserted in the mullite tube, it also separated the oxygen reference electrode and the argon protective atmosphere of the test electrode. The pressure of oxygen in the reference electrode was measured as a sum of the ambient pressure plus the pressure difference, taking place due to the bubble counter connected to the oxygen outlet. The prevailing atmospheric pressure was measured with a Vaisala PTU300 (Finland). The pressure difference was measured with a Beamex MC2 calibrator (Finland).

The identical platinum (table 1) wires (0.25 mm in diameter) for the EMF measurements were connected to a Keithley 6517B electrometer. Its input impedance is $2 \cdot 10^{14} \Omega$ allowing the cells to function in a reversible way [8]. The contact between the anode Pt lead wire and the three-phase sample in the zirconia tube was provided inserting a rhenium wire tip into the test electrode. Rhenium was applied due to the absence of reaction with antimony [4,5]. The short Re-wire tip (0.5 mm in diameter, 20 mm long) was spot-welded to the end of the Pt lead wire in order to prevent a reaction between platinum and molten antimony. To avoid a reaction with vaporized antimony, the platinum lead wire was inserted into a thin (0.5 mm in diameter) alumina tube and then sheathed by another alumina tube with a bigger diameter. The Pt-Re junction point was sealed with alumina-cement in the end of the bigger alumina tube, in such a way that only Re-wire tip was uncovered. The end of cathode Pt lead wire was made as a circular contact, which was pressed toward the closed end of the zirconia tube. The experimental galvanic cell was shielded from external electromagnetic fields by a grounded Faraday cage.

The measured EMF and temperature values were simultaneously transferred to a computer and recorded at a rate of one data-point per 5 s. The experimental data points were recorded when the equilibrium was achieved. The equilibrium was considered to have been established when the EMF values at isothermal conditions were constant or varied within less than 0.1 mV for several hours. Achieving steady EMF values at a new temperature took from few hours up to few days, depending on temperature.

3. Results and discussion

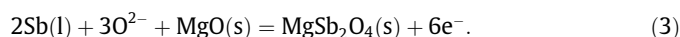
In order to determine the standard Gibbs free energy of formation of magnesium antimonite MgSb_2O_4 , the independent EMF values of four similar galvanic cells were measured within experimental temperature range by heating and cooling the furnace. The galvanic cell (1) as well as its virtual cell reaction (4) have been illustrated below:



The two half-cell reactions of the oxygen concentration cell are:



and



Therefore the net cell reaction for the formation of one mole of magnesium antimonite is:



Table 2 shows the experimental data collected during the measurements of four identical galvanic cells in this work. The EMF values reported were obtained by applying the median filter for signal-noise discrimination and averaging 200 data points (1 ks), recorded after having the achieved equilibrium. The values reported for temperature and the prevailing pressure of the reference electrode are

TABLE 1
Purities and sources of materials used in the present study.

Chemical	Source	Mass fraction purity
Sb	Cerac Inc., Milwaukee, Wisconsin (USA)	0.99999
Sb_2O_3	Koch-Light Laboratories Ltd (England)	0.99995
MgO	Sigma-Aldrich (USA)	0.99995
O_2	AGA (Finland)	0.9995
Ar	AGA (Finland)	0.99999
N_2	AGA (Finland)	0.99998
Pt	Johnson-Matthey Noble Metals (England)	0.9999
Re	Alfa Aesar (Germany)	0.9997
ZrO_2	Friatec (Germany)	Doped by 0.085 of Y_2O_3
Al_2O_3	Friatec (Germany)	

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