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The Fast Silver Ion Conducting Solid-State Electrolytes for Deriving Thermodynamic Data

Fiseha Tesfaye, Mykola Moroz, Oleksandr Reshetnyak, Daniel Lindberg, Pekka Taskinen and Leena Hupa

Abstract

The electromotive force (EMF) method was described and some characteristic examples from the past and recent literatures were reviewed. The important experimental procedures for a successful measurement of an EMF of different galvanic cells at a certain temperature and determination of the thermodynamic properties of chemical compounds from the obtained EMF values were described. A typical galvanic cell arrangement in a furnace was presented. The two most common types of AgI-based solid electrolytes, AgI and $RbAg_4I_5$, were discussed in detail. The ionic conduction mechanisms and the application of the solid electrolytes in the EMF cells were described. In this work, we have also conducted EMF measurements using the fast Ag^+ ion conducting solid-state electrolyte. The solid-state electrolyte Ag_3GeS_3I glass and the cathode material $Ag_4HgSe_2I_2$ were synthesized and electrochemical cell $(-)graphite|Ag|Ag_3GeS_3I$ glass$|Ag_4HgSe_2I_2|graphite(+)$ was assembled to measure the activity of Ag in the quaternary phase. The extremely low values of activity of silver in $Ag_4HgSe_2I_2$ in the temperature range 412–482 K indicate that $Ag_4HgSe_2I_2$ has superionic property. The obtained results and the determined thermodynamic values are presented and discussed.

Keywords: EMF method, solid electrolyte, silver iodide, thermal stability, Gibbs free energy

1. Introduction

Thermochemical data of chemical compounds is of great importance in the modeling of high temperature materials processing and their applications. Accurate thermodynamic data are important for meaningful modeling of phase equilibria and thermodynamics of multiphase material systems. These accurately determined thermodynamic properties and their chemical behaviors under different conditions promote improved extractive metallurgy of valuable metals and the design of novel multi-component functional materials.

Calorimetry, vapor pressure measurements and EMF methods are the main experimental techniques to investigate thermodynamic properties of phases and phase assemblages. Extensive reviews on these methods have been published in the past. For the determination of enthalpy, precisely, calorimetry is a well proven.

In the vapor pressure methods, partial pressures of individual components can be measured and the thermodynamic activities and partial Gibbs energies can be derived from them. When partial pressures can also be measured as a function of temperature, the partial enthalpies and entropies can be derived, although these derived quantities are usually less accurate than the directly measured partial Gibbs energies. Introduced by Kiukkola and Wagner [1] for solid-state thermodynamic investigations, the EMF method has proven to be direct, effective, and the most accurate method for determining the Gibbs free energies of formation, chemical potentials, thermodynamic activities and partial pressures in equilibrium conditions. Furthermore, the entropies and enthalpies of chemical reactions can be derived from the measured temperature versus EMF relations of the cell [2].

This paper reviews, updates and discusses the EMF method that applies the fast Ag^+ ion conducting solid electrolytes. Furthermore, we have also conducted EMF measurements using the fast Ag^+ ion conducting solid-state electrolyte. The solid electrolyte Ag_3GeS_3I glass and the cathode material $Ag_4HgSe_2I_2$ were synthesized and electrochemical cell was assembled to measure the activity of Ag in the quaternary phase $Ag_4HgSe_2I_2$. The obtained results and the determined thermodynamic values are presented in the subsequent sections.

1.1 Principles of the EMF method

In a galvanic cell for thermodynamic studies there is generally one electrode at which electrons would be consumed (the cathode) and one electrode at which electrons are produced (the anode) as the cell reaction proceeds. If the electrolyte system conducts electricity by the migration of ions only, then the electrons must move from cathode to anode via an external electronic conductor, which is usually Pt or Au or pure graphite lead. It is along this conductor that the electric potential which is generated by the cell reaction can be measured. Any meaningful thermodynamic investigation requires that the cell function in a complete reversible manner, i.e., no external current is flowing. This is usually assured by the use of high-resistance (above 10^{10} Ω) measuring devices, resulting in the measurement of an "open circuit" potential [3, 4].

In most practical high temperature systems, electrolytes usually have a small component of non-electrolytic conduction, which make the open circuit unattainable. In this case, in addition to ionic, electronic conduction will also takes place, because electrons can migrate through the electrolyte and permit the cell reaction to proceed at speed which is not determined by the resistance of the external electronic conductor. A real electrochemical system therefore has a potential which is given by Eq. (1) [4]:

$$E = \frac{RT}{zF} \int_{a_i'}^{a_i''} t_i \cdot dlna_i \tag{1}$$

where t_i is the transfer number of the ionic species, which is conducted through the electrolyte having the thermodynamic activity a_i' at one electrode and a_i'' at the other. When the electrolyte conducts significantly by electron migration, then the cell reaction can proceed spontaneously and one electrode is depleted of atoms while the other receives atoms.

It follows that the electrodes can only be maintained at a constant chemical potential of all components providing that equilibrium can be established more rapidly than the rate of arrival or loss of material at the electrode-electrolyte interface. Consider a cell which has two metal-metal oxide electrodes with a leaky

electrolyte. The electrode with the higher oxygen dissociation pressure can lose oxygen through the electrolyte by the arrival of electrons through the electrolyte to form oxygen ions, and hence the oxide is reduced at this electrode. At the other electrode, oxygen ions absorbed and the electrode is oxidized continuously. Providing the electrode reactions can accommodate this corrosion reaction as a result of metal-oxygen reactions at the electrodes which restore the original mixture at the electrode-electrolyte interface, and then the cell can be used for thermodynamic studies. Failing to do so, the EMF of the cell will drift continuously and results are difficult to interpret. At the higher temperatures, solid electrolyte systems can be permeable to gases, and interaction between electrodes and their surrounding gaseous atmospheres can also play an important role in making experiments difficult.

The porosity of a solid electrolyte depends very much upon the manufacturing method as well as on the temperature of the cell operation, and therefore no general description can be given of the conditions under which this effect could become significant. The effects of atmospheric reactions with electrode systems can be minimized, or eliminated to all practical extents, by providing samples of the electrode to the gas phase for pre-equilibration of the gas approaching the cell electrode and by separating the atmospheres surrounding the electrodes from one another.

The corresponding phenomena in molten salt electrolytes which can lead to drifting EMFs are reactions which result from the solubility of metals in the molten electrolyte, which confer electron conducting properties on the electrolyte, or the possibility of cations of more than one valency for a given cation in the melt. Both mechanisms can lead to the transport number of the ions less than unity and to oxidation/reduction reactions at the electrode [4].

1.2 The EMF method with solid-state electrolytes

Electrochemical cells with solid-state electrolytes for thermodynamic studies typically consist of a solid electrolyte between the reference and the cathode electrodes [2]. These electrodes are connected to wires, which are usually Pt or Au, for measuring the EMF of the cell. In thermodynamic measurements, the EMF must be measured under open circuit conditions. This is usually assured by the use of high impedance ($R > 10^{10}$ Ω) measuring devices, which enable measurement of an "open circuit" EMF [3, 5]. Utilization of the EMF technique for thermodynamic investigation of metallic systems, and its basic principles and the main requirements has been recently discussed in detail by a few researchers [2, 3, 5–9].

The EMF technique is a direct method that enables one to determine the Gibbs energies of formation, chemical potentials, thermodynamic activities or partial pressures precisely [10, 11]. Furthermore, the entropies and enthalpies of reactions can be calculated from the temperature dependence of EMF of the cell. Electrochemical cells with solid electrolytes consist in most cases of a solid electrolyte between two electrodes [11]. A typical galvanic cell arrangement for thermodynamic measurements is shown in **Figures 1** and **2**.

The alumina sheaths indicated in **Figure 2** should press the cell from both directions to insure good contact at the interfaces. Flow of the protective gas (Ar) must always be away from the reference electrode. The design of the galvanic cell should be such that the reaction of interest harnesses the cell reaction and the Gibbs energy for the reaction could be calculated from the EMF of the galvanic cell. One of the criteria for the application of this method is that the electrolyte is a pure ionic conductor under the very experimental conditions.

For instance, in experimental investigation of Ag-based compounds below 713 K, solid-electrolytes $RbAg_4I_5$ and AgI are the two widely known and used
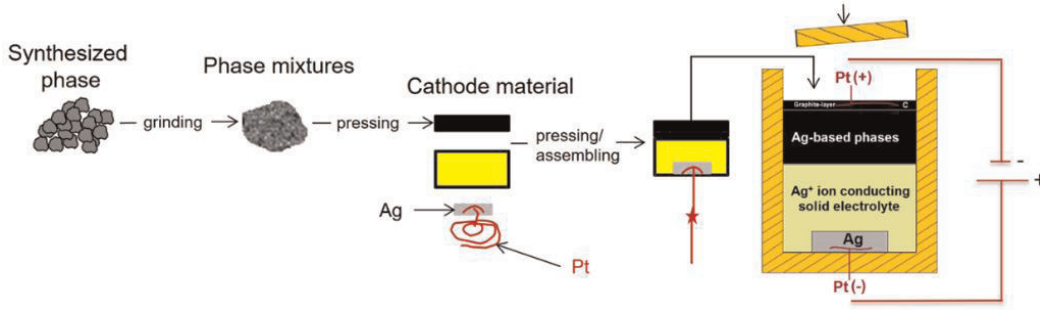
Figure 1.
Illustration showing preparation of galvanic cells for the solid-state EMF experiments.
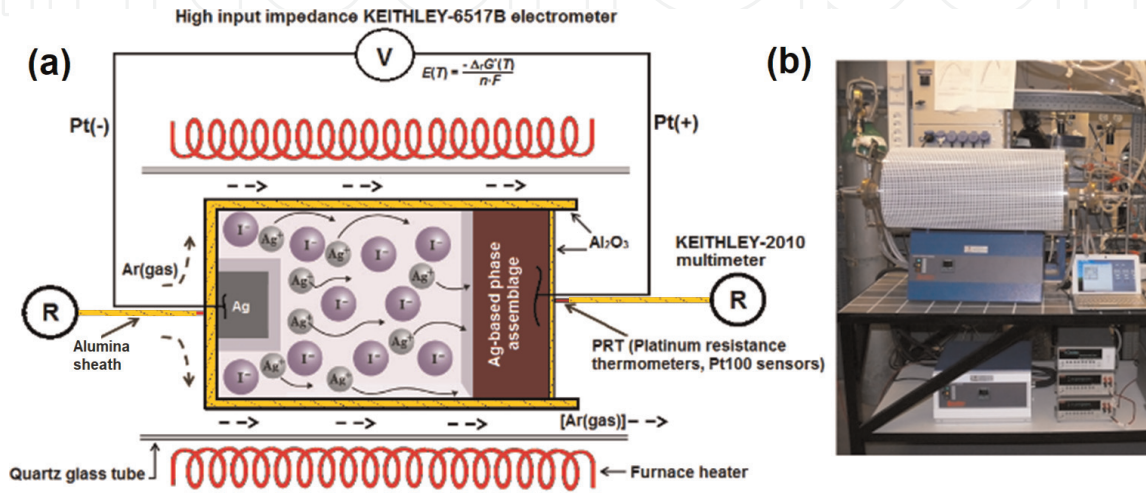
Figure 2.
(a) Schematic diagram of the experimental setup for an EMF-measurements in a horizontal tube furnace; [12]. (b) A picture of a high-temperature electrochemical stations for thermodynamic measurements in the laboratory.

superionic conductors of silver ion. For example, to determine the Gibbs energies of formation of the compound Ag_5Te_3 at different temperature conditions galvanic cells are constructed as cells in Eqs. (2) and (3):

$$Ag|RbAg_4I_5|Ag_5Te_3, Te \quad 300 < T/K < 505 \tag{2}$$

$$Ag|AgI|Ag_5Te_3, Te \quad 420 < T/K < 713 \tag{3}$$
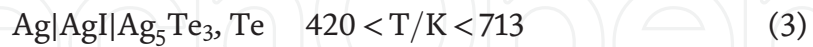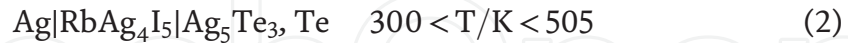
Current flows from the right to the left. Temperature ranges for accurate measurements are those in which the electrolytes are superionic conductors. At equilibrium conditions, the virtual cell reaction in both cells is expressed as Eq (4):

$$5Ag + 3Te = Ag_5Te_3 \tag{4}$$

Based on the EMF of the galvanic cells, at certain temperatures, it is possible to determine the thermodynamic properties by using the basic thermodynamic equations at constant pressure.

2. Experimental requirements

In EMF measurements for the determination of thermodynamic properties, it is important to ascertain the conditions under which the electrolyte shows the best

T (K)	E (mV)	T (K)	E (mV)
412.87	91.37	450.12	109.26
415.36	92.65	452.59	111.16
417.85	93.92	455.07	112.81
420.34	95.41	457.54	113.85
422.84	96.26	460.21	114.85
425.31	97.97	462.58	115.91
427.80	98.71	465.26	117.04
430.28	100.51	468.12	118.04
432.77	100.95	470.34	119.37
435.25	102.41	472.54	120.86
437.73	103.75	475.22	121.71
440.21	105.14	477.62	122.78
442.69	106.4	479.75	124.80
445.17	107.23	482.21	125.58
447.64	108.61	—	—

Table 1.
A summary of experimental values of EMF vs. T obtained in the electrochemical cell in Eq. (17).

performance. The main problems for successful electrochemical cell operation are selection of a suitable electrolyte and the exact identification of the single reversible process occurring at each electrode. The corresponding electrolyte should provide purely ionic conductivity in the temperature range where it is used, i.e., one single ion should be responsible for establishing the potential. A well-defined reversible reaction is required to establish the potential. Practically, there are many additional requirements [3, 5]:

- the equilibrium potential at a given temperature should be established within a reasonable time,

- after temperature changes, the same equilibrium potential has to be established regardless of whether the temperature has been increased or lowered, and

- following polarization of the cell by a potential imposed from outside, again the same equilibrium potential has to be established.

In addition, there are a number of purely experimental requirements that have to be considered, especially in measurements at high temperatures [5, 9]:

- any reaction between electrodes and electrolyte or between electrodes and lead wires must be negligible,

- if lead wires of different materials are used it is necessary to consider the corresponding thermal-EMF,

- any temperature gradient in the cell should be avoided;

- reactions between crucible materials and electrodes or electrolyte should be excluded,

- concentration changes due to the vapor pressure of the electrodes must be taken into consideration,

- any direct exchange of matter between the two electrodes (e.g., via the gas phase) has to be excluded, and

- any electrical interference between the furnace in which the cell is heated and the cell itself should be avoided, either by a proper winding of the furnace or by appropriate grounding.

Thermal-EMF and temperature gradients can be minimized by using similar lead material at both electrodes and by placing the cell within the constant heating zone of the experimental assembly, respectively [9]. Proper design of the galvanic cells and their flexibility in the furnace while measurements are conducted will also help to minimize temperature differences at both ends of the electrodes, as described in [12]. In this work, all these experimental requirements were fulfilled.

2.1 Ag$^+$ ion conducting solid electrolytes

Solid electrolytes are solid phases, which transfer electric charge by moving ions only. Good ionic conductivity requires a large amount of movable ions and a lot more free sites in the lattice than movable ions, so that the jump probability is as high as possible. The solid electrolytes can be oxides, halides, iodides, sulfides and other types of solid materials. For example, in the AgI-based electrolytes electrical current is carried by Ag$^+$ ions.
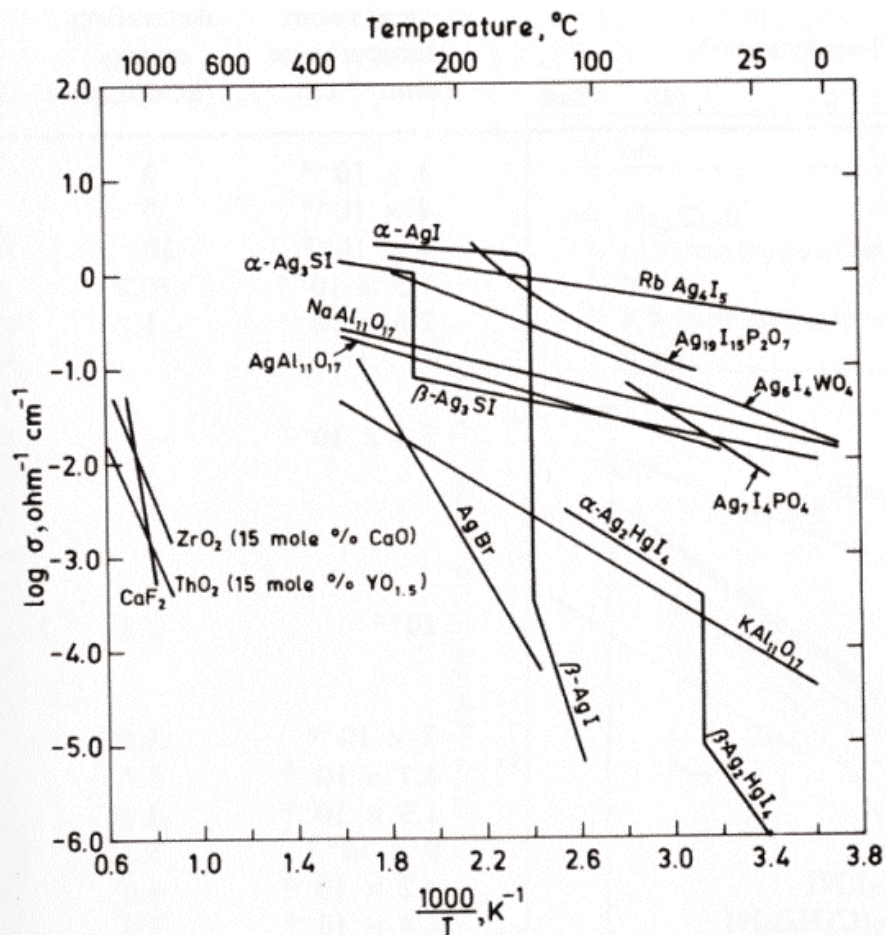
Figure 3.
The ionic conductivity of some solid electrolytes as a function of temperature [2].

Recently, the importance of solid electrolytes has increased remarkably due to their role in various applications. They are commonly used in electrochemical cells to measure chemical potentials of gases, liquids and solids. Detailed theory and practical applications of the solid electrolytes have been discussed in many review papers [3, 6, 13–22]. **Figure 3** shows ionic conductivity of some of the solid electrolytes in different temperature regions.

One of the most important criteria for a solid electrolyte to be used in EMF cells for thermodynamic studies is that it should be a purely ionic conductor, or at least has only a negligible contribution of electronic conduction. Thus, if electric current is carried solely by moving ions, the ion transference number t, in Eq. (5), should be >0.99 at a given experimental conditions [3, 4].

$$t = \frac{\sigma(ion)}{\sigma(ion) + \sigma(electronic)} \tag{5}$$

where σ(ion) is ionic conductivity and σ(electronic) is electronic conductivity.

In any case where $t < 0.99$, an accurate knowledge of the conductivity of the solid electrolyte becomes important [3]. When solid electrolytes are used for EMF measurements, one additional experimental requirement has to be fulfilled: a good and reliable contact between electrodes and electrolyte in order to obtain stable and reversible EMF values. In the thermodynamic studies of silver-based alloys and compounds, $RbAg_4I_5$ and AgI are two widely used fast ionic conductors of Ag^+ ions. These electrolytes were also used in our study by the EMF method. Properties of the solid electrolytes and their usage limits in the EMF method are reviewed in Section 2.2.1.

2.1.1 Properties of AgI and RbAg₄I₅

Crystalline forms γ-, β- and α-AgI are stable at ambient pressure conditions. The β-AgI $\rightarrow$ α-AgI phase transition takes place at 420 K, accompanied with a significant increase in ionic conductivity [10, 23–25]. At the phase transition temperature, the ionic conductivity of α-AgI is 1.31 S cm^{-1} [26]. As shown in **Figure 4**, the superionic compound $RbAg_4I_5$ is thermodynamically stable within the temperature range
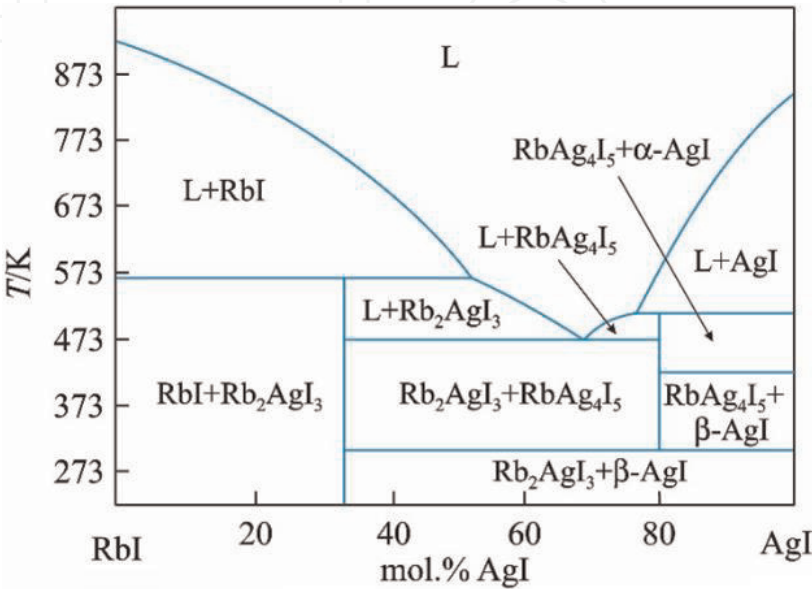
Figure 4.
The phase diagram of RbI–AgI system [27].

300–505 K and in the AgI rich region coexists with the β- and α-AgI phases [27]. At about 300 K, RbAg$_4$I$_5$ shows a high ionic conductivity of $\sim$0.21 S cm^{-1} [28]. Therefore, RbAg$_4$I$_5$ can be used as an electrolyte even close to room temperature (>300 K) [24, 29]. Ag$^+$ is the moving ion in both AgI-based solid electrolytes. In general, the AgI-based electrolytes possess a large amount of free sites for the Ag$^+$ ions to move.

Ionic conductivity in solid electrolytes is usually due to lattice defects, and in AgI-based electrolytes these defects are caused by large cation disorders [3, 25]. Chemical diffusion occurs in the presence of concentration or chemical potential gradient and it results in net transport of mass. For example, when local differences in stoichiometry equilibrate, metal or non-metal ions and electrons diffuse simultaneously. These phenomena are described by the chemical diffusion coefficient D [2]. At low-temperatures, the ionic conductivity generally follows the Arrhenius-type temperature dependence [24, 25, 30].

AgI-based electrolytes possess a large amount of free sites for the Ag$^+$ ions to move. Due to the presence of these excess sites for Ag$^+$ ions [31] and quasi-molten state of Ag$^+$ ions in the structure [24], as well as the presence of passageways for Ag$^+$ ions which are formed by the face-sharing tetrahedral [32]; α-AgI is a fast ionic conductor of Ag$^+$ ions. In α-RbAg$_4$I$_5$, iodide ions are arranged in a similar structure as manganese atoms are in β-Mn, so that one unit cell, which includes RbAg$_4$I$_5$, contains 56 tetrahedral sites, such that Ag$^+$ ions can move freely in the lattice. The large Rb$^+$ ions are surrounded by highly distorted iodide octahedral and are not mobile [26, 28]. Therefore, the structure of superionic compounds can be treated as two-component system where exist the highly mobile ions like molten sublattice and another type of ions in fixed positions that formed a framework and determined the mechanical properties of the sample.

The ion transference number of α-AgI in the temperature range 420–713 K is 1 ± 0.01 [33]. Below its melting temperature, at T_m = 505 K, α-RbAg$_4$I$_5$ is a high ionic conductor of Ag$^+$ ions with negligible electronic conduction [24, 35].

Based on various conductivity data and/or EMF data, Patterson [34] has shown that in the electrolytic conduction domain of AgI, the chemical potential of silver in AgI changes only slightly. Using the compiled thermodynamic data of Barin [36], we calculated activities of silver (a_{Ag}) in AgI at $P_{I_2(g)} = 1$ atm (for the dissociation reaction 2AgI $\rightleftarrows$ 2Ag + I$_2$(g)), as a function of temperature. According to results from our analysis, the a_{Ag} in AgI varied between 2.5•10^{-9} at 420 K, 1.2•10^{-7} at 500 K and 3.6•10^{-5} at 700 K. Thus, the chemical potential of silver in AgI does not change significantly, in its ionic conduction domain. Therefore, the solid electrolytes AgI and RbAg$_4$I$_5$ can be safely used in their respective pure ionic conduction domains (420–713 and 298–505 K, respectively) for EMF cells in the experimental thermodynamic studies of silver-based phases. The super ionic conducting temperature range of α-AgI (420–713 K) may be increased by adding PbI$_2$, in the lower temperature region.

AgI is a photosensitive material. According to the calculated curves shown in **Figure 7**, which was calculated by the HSC chemistry software [37] below 773 K, AgI reaction with H$_2$O, O$_2$(g), H$_2$(g) and S$_2$(g) is not spontaneous. However, its relative sensitiveness to the H$_2$(g) is clear.

In RbAg$_4$I$_5$ iodide ions are arranged in very same way as in manganese atoms are in β-manganese, so that one unit cell, which includes four RbAg$_4$I$_5$, contains 56 tetrahedra sites, so that Ag$^+$ ions can move freely in the lattice. The RbAg$_4$I$_5$ electrolyte has a wider temperature stability range and do not be affected by moisture [11]. The ionic conductivity of RbAg$_4$I$_5$ is illustrated in **Figure 3**.

The thermodynamic stability of $RbAg_4I_5$ is an important property that must be considered in any long term application. $RbAg_4I_5$ is unstable at temperatures below 300 K where it decomposes into $AgI + Rb_2AgI_3$, as shown in **Figure 4**.

Therefore the conducting phase would be nonexistent at low temperature. However, it was found that this reaction requires a catalyst such as H_2O vapor in order to initiate. By handling the materials in a dry atmosphere and hermetically sealing the batteries, the conducting phase has been maintained in devices for 5 years at temperatures below 300 K.

The synthesis of $RbAg_4I_5$ is straightforward. One method involves intimately mixing stoichiometric amounts of RbI and AgI, adding sufficient H_2O to form a thick fluid paste, and then removing the H_2O by air drying at slowly increasing temperatures, finally drying and combining the remaining reactant phases at a temperature between 483 and 502 K that is between the eutectic and the incongruent melting point [38]. By performing this reaction process over a 2 day period, single phases $RbAg_4I_5$ is formed. The materials is then powdered and stored in a vacuum oven at 343 K to prevent any environmental degradation [39].

2.1.2 Properties of superionic Ag-based glassy electrolytes

Another class of superionic materials is superionic glassy electrolytes (SGE). Inorganic SGE have a number of advantages compared to crystal compounds. Some advantages include easier regimes of synthesis, absence of grain boundaries, isotopic properties, single ion conductivity, etc. [40, 41]. In the vicinity of the glass transition temperature (T_g) the glassy material becomes very soft. It is mean a good contact between the electrolyte and electrodes. In contrast to the crystal compounds such as AgI and $RbAg_4I_5$ some glassy materials have the high values of ionic conductivity at room temperature [42]. The high ionic conductivity in SGE can be explained by the presence of open free space in the glass structure [42]. Moreover, using the glass matrix we can fixed the high ionic conductivity modification of superionic phase in the temperature range where it is metastable [43]. For example, at crystallization of $AgI-Ag_2O-M_xO_y$ (M = B, Ge, P, Mo) glasses that include the high concentration of silver iodide, the α-AgI phase was successfully stabilized in a glass matrix. As a result, the value of ionic conductivity for this material at room temperature is found $\sigma = 10^{-1}$ S cm^{-1} [43, 44].

The glass formation regions in the GeS_2-Ag_2S and GeS_2-Ag_2S-AgI systems were investigated in [45]. It was found that glasses from these regions are purely ionic (Ag^+) conductors. The influence of the silver iodide addition on conductivity of different sulfide based glasses has been established. The maximum value of conductivity and minimum value of activation energy for the sample with highest content of AgI (52.3 mol%) is found to be $\sigma \sim 10^{-2}$ S cm^{-1} and $E_a = 0.25$ eV, respectively at room temperature. The mechanism of the Ag^+ diffusion in AgI based superionic glasses has been investigated by using NMR method [46]. The NMR time scale shows that all Ag^+ ions are moving by hopping from one iodine ion to the other.

Moroz et al. [47] investigated the glass forming region in the Ag_2GeS_3-AgBr system. The formation of the Ag_3GeS_3Br glassy phase has been established for the first time. Based on results of electrical conductivity measurements it was established that Ag_3GeS_3Br glass is purely ionic conductor and belong to class of superionic materials. The model of the drift motion of ions has been proposed. According to [48], the glass forming region in the $Ag_3GeS_3Br-AgBr$ system is found to be 0–52 mol% GeS_2. In this system the new quaternary phase $Ag_3Ge_2S_5Br$ (space group $P2_13$, $a = 1.016702(7)$ nm, $Z = 4$ [49]) has been synthesized for the first time.

It can be obtained in both crystalline and glassy state. Electronic structure calculations support the experimental results. The electrical conductivity measurements of glassy and crystalline samples were performed by direct current probe method using different constructions electrochemical cells. It was found that the glassy materials are purely ionic conductors [48, 49].

The purely ionic conductivity in the wide temperature range and simple method of obtaining glassy materials make them interesting for different applications. For example, Ag_2GeS_3, Ag_3GeS_3Br, and Ag_3GeS_3I glassy materials were used as ion selective membranes in electrochemical cells to calculate the thermodynamic functions of some superionic compounds [50–53].

2.2 Thermodynamics of electrochemical cells

For an electrochemical cell with a solid-electrolyte and elements M and Z:

$$M\ (solid, Liq)|electrolyte\ (M^{+n}\ or\ M^{-n})|\ M_xZ_{1-x}(solid, Liq) - Z, \tag{6}$$
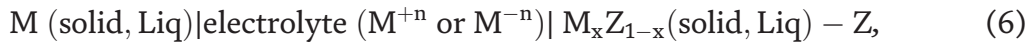
at equilibrium, the incorporation of M^{+n} or M^{-n} at the interface into the cathode (M_xZ_{1-x}(solid, Liq)-Z) or the overall electrochemical reaction of the electrochemical cell can be expressed by a virtual electrochemical cell reaction Eq. (7).

$$M^{+n}\ or\ M^{-n} + Z = M_xZ_{1-x}. \tag{7}$$
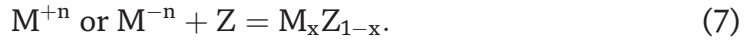
The amount of work, other than the work for volume expansion, which is necessary for the transfer of 1 mole of element M in a valence state n from its pure state into a M-Z-compound, is related to the transfer of a charge $n{\cdot}F$ by;

$$\mu_M(M - Z - compound(s)) - \mu_M^{\circ}(M) = -n \cdot F \cdot E_{EMF}, \tag{8}$$

or

$$\Delta_r G^{\circ} = -n \cdot F \cdot E_{EMF} \tag{9}$$

where μ_A is the chemical potential of substance M in the M-N-compound(s) and μ_M° is the standard chemical potential of substance M in pure substance M, which is 1. $\Delta_r G°$ is the change in the Gibbs energy of the reaction, E is the electromotive force produced by the cell in volts, F is the Faraday constant, 96485.332896 C mol^{-1} [54] and n is the number of electrons involved in the virtual electrochemical cell reaction.

The Gibbs energies of our isobaric equilibrium reactions were calculated directly from the measured E_{EMF} vs. T relations, by using the basic thermodynamic Eq. (9) of an electrochemical cell. In a similar way, the entropies, enthalpies and heat capacities of the studied virtual reactions were calculated using Eqs. (10)–(12).

$$\Delta_r S° = -n \cdot F \cdot \left(\frac{\partial E_{EMF}}{\partial T}\right), \tag{10}$$

$$\Delta_r H^{\circ} = -n \cdot F \cdot \left[E_{EMF} - \left(\frac{\partial E_{EMF}}{\partial T}\right) \cdot T\right], \tag{11}$$

$$\Delta_r C_P = -n \cdot F \cdot \left(\frac{\partial^2 E_{EMF}}{\partial^2 T}\right) \cdot T \tag{12}$$

2.2.1 Gibbs energy of formation

By definition, the reaction of formation of a species A can be written as:

$$mM + nN + \ldots \rightleftarrows aA \tag{13}$$

where a, n, m etc. are stoichiometric coefficients, and the standard Gibbs energy of formation is:

$$\Delta_f G^\circ = G^\circ_{\text{products}} - G^\circ_{\text{reactants}} = aG^\circ_A - mG^\circ_M - bG^\circ_N - \tag{14}$$

The standard Gibbs energies of formation of the studied multicomponent phases were calculated by combining the Gibbs energies of the virtual electrochemical cell reactions (calculated according to Eq. (9)) and the standard Gibbs energies of the pure components, for which literature data are available. The standard entropies of pure compounds have been calculated by:

$$S^\circ_A = \Delta_f S^\circ_A + S^\circ_M + S^\circ_N + \ldots \tag{15}$$

Gibbs energy of phase transition at the transformation temperature T_{tr} can be expressed by:

$$\Delta_{tr} G^\circ = \Delta_{tr} H^\circ - \left(\frac{\Delta_{tr} H^\circ}{T_{tr}}\right) \cdot T. \tag{16}$$

The high or low temperature experimental points can be extrapolated to low or high temperatures, respectively, by using the Gibbs energies of phase transitions expressed by Eq. (16). Two types of electrolyte are used in thermodynamic measurements: liquid electrolytes and solid electrolytes, each with characteristic advantages and disadvantages. In the following chapter, experimental study with the solid-state electrolyte is presented.

3. Experimental section

The phases were synthesized from the pure elements Ag (99.999 wt%), Hg (99.99 wt%), Se (99.999 wt%), and I_2 (99.999 wt%). The synthesis and annealing were performed in an evacuated quartz glass ampoules with a total residual pressure of <1 Pa. Ag_2Se and HgI_2 compounds were obtained by cooling the melt mixtures of the corresponding elements, at the rate of 2 K min^{-1}, to room temperature. The $Ag_4HgSe_2I_2$ compound was obtained by cooling the melted mixture of Ag_2Se and HgI_2 in the molar ratio 2:1 to room temperature. The thermodynamic equilibrium of $Ag_4HgSe_2I_2$ crystals powdered to particle size ≤5 μm was achieved by two-stage annealing at 510 and 400 K for 500 h. The synthesized material was analyzed by the SEM-EDS technique. The SEM-EDS analyses confirmed the existence of a homogenous quaternary phase with a composition of $Ag_4HgSe_2I_2$. Results of the SEM-EDS analysis are presented in **Figure 5**.

The potential-forming processes were performed by cell in Eq. (17):

$$(-) \text{ graphite}|Ag|Ag_3GeS_3I \text{ glass}|Ag_4HgSe_2I_2|\text{graphite} (+), \tag{17}$$
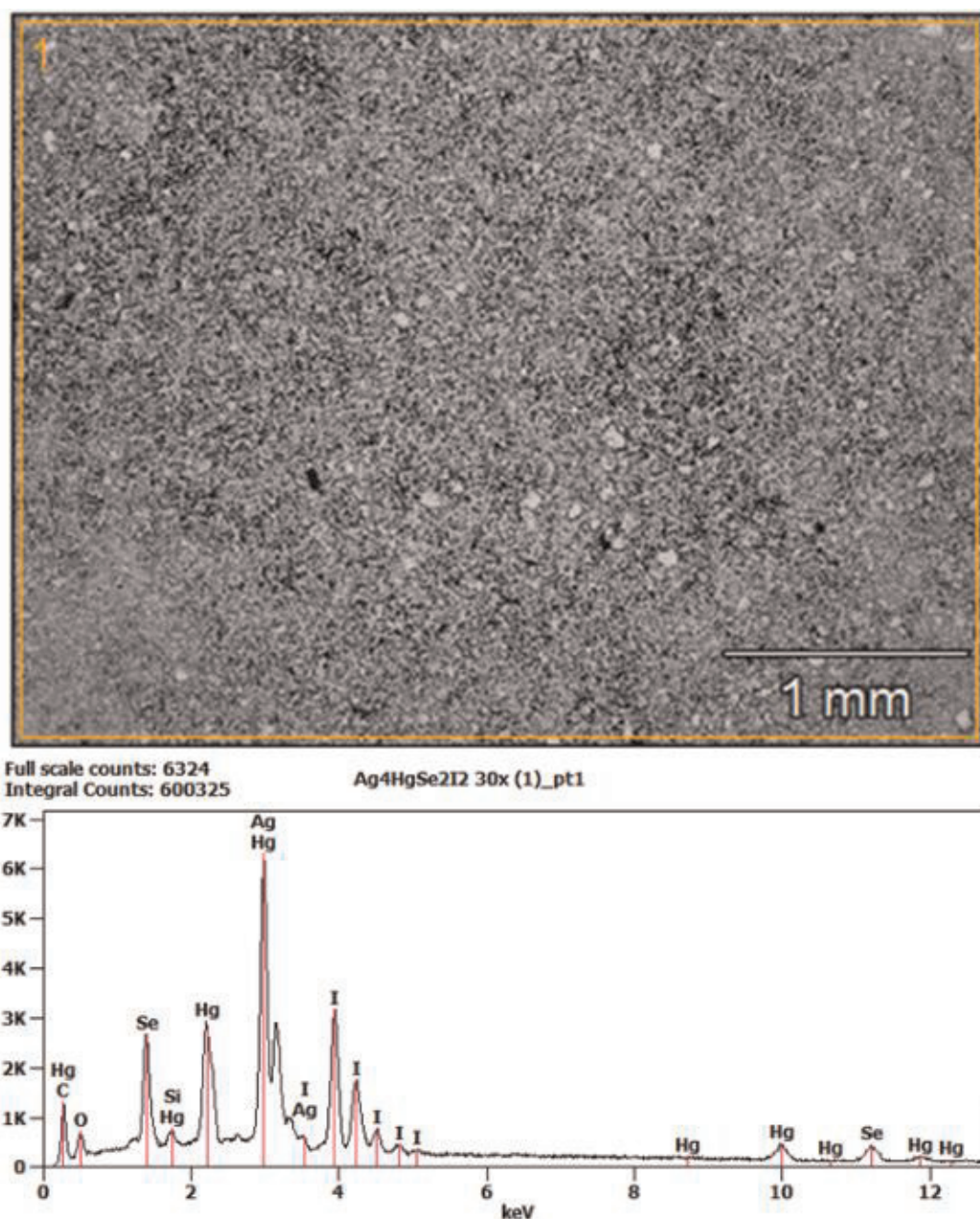
Figure 5.
The SEM-EDS analysis of the synthesized phase Ag$_4$HgSe$_2$I$_2$. Traces of Si and O peaks are as a result of the quartz glass SiO$_2$ ampoule particles after depressurization and crushing operation to remove the synthesized sample.
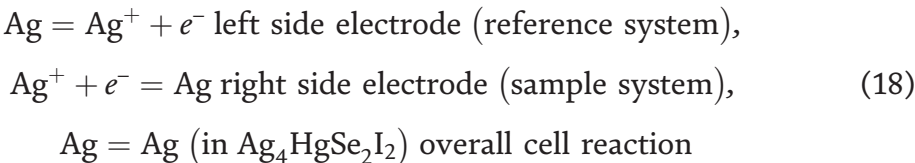
where Ag$_3$GeS$_3$I glass is the solid electrolyte with fast Ag$^+$ ion conductivity [45], Ag$_4$HgSe$_2$I$_2$ is the cathode material. Ag$_3$GeS$_3$I glass, as well as Ag$_3$GeS$_3$Br [48], belongs to the category of superionic materials [55]. The linear dependencies of the EMF of the electrochemical cell on temperature were used to determine the standard thermodynamic properties of Ag$_4$HgSe$_2$I$_2$.

Components of the electrochemical cells in powder form were pressed at 10^8 Pa through a 2 mm diameter hole arranged in the fluoroplast matrix up to density $\rho = (0.93 \pm 0.02) \cdot \rho_0$, where ρ_0 is the experimentally determined density of cast alloys. To eliminate possible defects of plastic deformation during the pressing of alloys, we performed five-fold thermal cycling of electrochemical cells in the range of 400–470 K, with heating and cooling rates of 2 K min^{-1}. The electrochemical cells were heated in a resistance furnace similar to that described in [12] filled with a mixture of H$_2$ and Ar (both 0.9999 volume fraction) in a molar ratio of 1:9, with $P = 1.2 \cdot 10^5$ Pa. Argon gas was purified from traces of oxygen in a quartz glass tube by passing it through copper foil heated at 673 K. The flow of gas at the rate of

$2 \cdot 10^{-3}$ m^3 h^{-1} had the direction from the positive to the negative electrodes of the electrochemical cells. The temperature was maintained with an accuracy of ± 0.5 K. The EMF values of the cells were measured using the voltmeter U7–9 electrometric amplifier (Ukraine) with an input impedance of above 10^{12} Ω. The equilibrium in electrochemical cells at each temperature was achieved within 2 h. The equilibrium was considered to have been reached when the EMF values were constant or their variations were not significant (below $\Delta E = \pm 0.2$ mV or $\pm$ 0.1 mV for electrochemical cells (A)). The dependences of the EMF of the cells on temperature $E(T)$ were analyzed by the method described in [56, 57].

4. Results and discussion

The activity of silver in Ag$_4$HgSe$_2$I$_2$ compound was investigated using the electrochemical cell in Eq. (17). The electrochemical process in this cell can be written as follows:

$$\text{Ag} = \text{Ag}^+ + e^- \text{ left side electrode (reference system),}$$

$$\text{Ag}^+ + e^- = \text{Ag right side electrode (sample system),} \qquad (18)$$

$$\text{Ag} = \text{Ag (in Ag}_4\text{HgSe}_2\text{I}_2) \text{ overall cell reaction}$$

The temperature dependences of the EMF of the cell (17) are shown in **Table 1** and **Figure 6**.

The relationship of *EMF* vs. *T* measured with electrochemical cell (17) was approximated by Eq. (19):
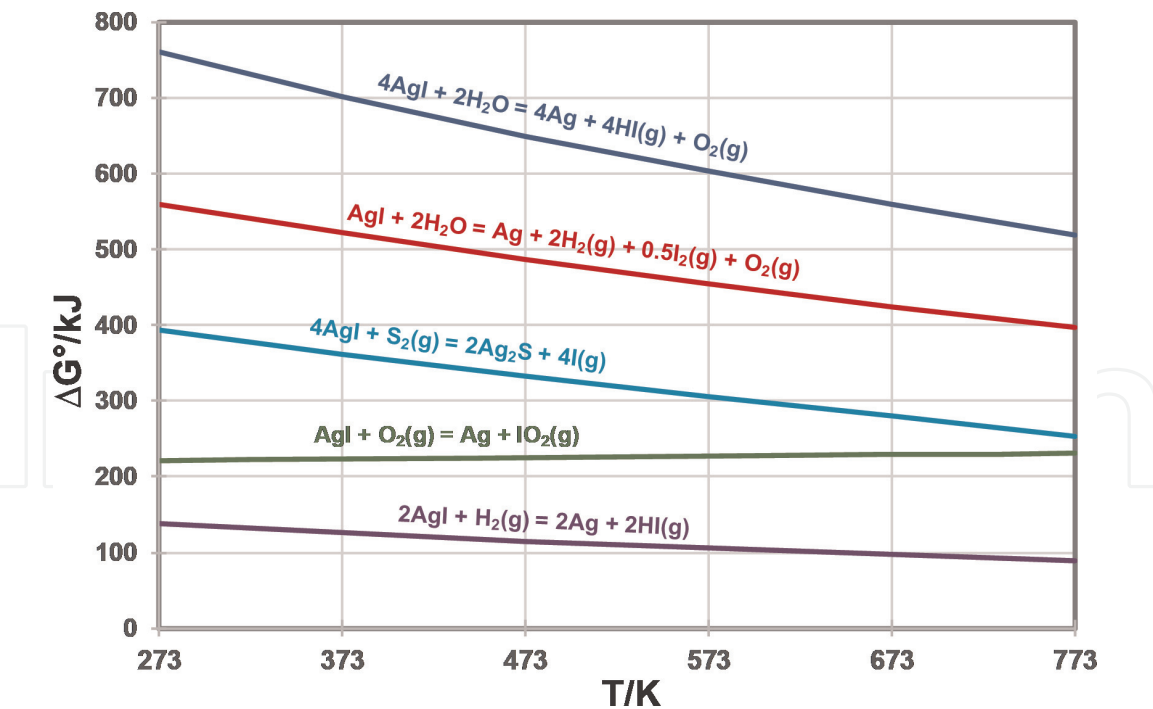
$$E/\text{mV} = (-110.178 \pm 1.244) + (488.66 \pm 2.78) \cdot 10^{-3} T/\text{K} \quad 412 \leq T/\text{K} \leq 482 \quad (19)$$

As described in [29], the Gibbs energy of reaction of the electrochemical cell (17) as expressed by Eq. (20) is the difference of the chemical potential (μ) of silver in Ag$_4$HgSe$_2$I$_2$ and in the standard state (pure silver):

$$\Delta_r G_r^\circ = \mu_{\text{Ag}}\left(\text{Ag}_4\text{HgSe}_2\text{I}_2\right) - \mu_{\text{Ag}}^\circ = -EF. \qquad (20)$$
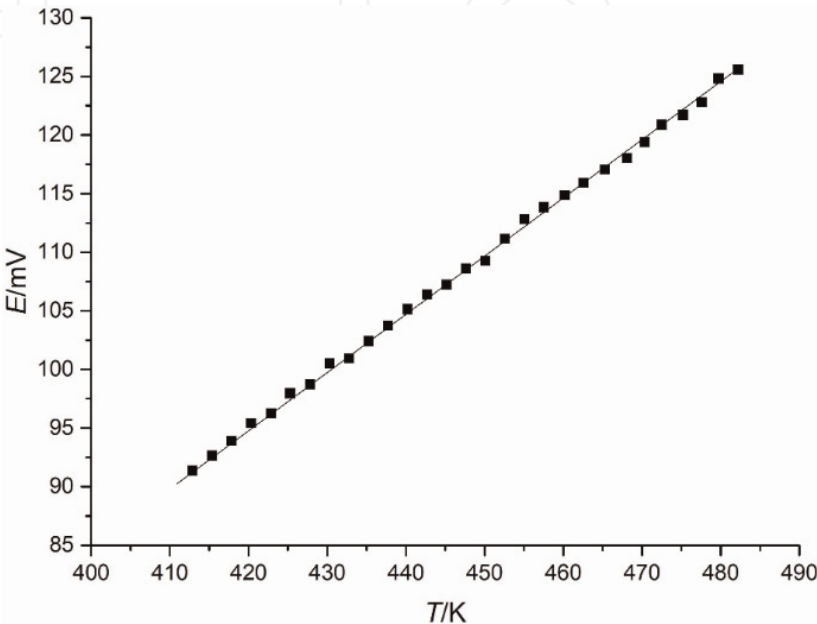
Figure 6.
The temperature dependence of EMF vs. T of electrochemical cell [17].

Figure 7.
Gibbs energies of reaction of AgI with $H_2O(g)$, $O_2(g)$, $H_2(g)$, and $S_2(g)$, as a function of temperature.

Using the relation

$$\mu_{Ag} = \mu_{Ag}^\circ + RT\ln a_{Ag}, \tag{21}$$

the activity of silver a_{Ag} in $Ag_4HgSe_2I_2$ is determined to be:

$$a_{Ag} = e^{-\frac{E_2 F}{RT}} = e^{-\frac{[(-110.178 \pm 1.244) + (488.66 \pm 2.78)\cdot 10^{-3}T]F}{RT}} \quad 412 \leq T/K \leq 482. \tag{22}$$

According to Eq. (22), the activity of silver in $Ag_4HgSe_2I_2$ compound varies between 0.075 and 0.048 in temperature range 412–482 K and decrease in accordance with the exponential law. The decrease of a_{Ag} in $Ag_4HgSe_2I_2$ with increasing temperature indicates that an increase of Ag^+ cations in the quasi-free state due to the release of the one-type capture levels [30]. Such low values of a_{Ag} indicate that $Ag_4HgSe_2I_2$ is superionic phase in the temperature range 412–482 K.

5. Summary and conclusions

Deficiencies in reliable and reproducible data have been deriving the quest for accurate experimentation. Experiences in different experimental techniques are also extremely important to the modeler to get an idea as to the errors involved in the various experimental data available in literature. This would minimize the uncertainties in thermodynamic assessments and modeling.

EMF-method is one of the versatile methods to obtain the thermodynamic data of different chemical compounds in equilibrium conditions. Since its introduction, in the late 1950s, it has been widely used to determine the thermodynamic properties of oxides, sulfides, intermetallic and several other material systems. This chapter focused on the thermodynamic investigation of solid-state materials, however, the method is applicable to investigate liquid and gas phases as well. It is the most accurate method to determine the Gibbs energies of alloys and compounds.

In studies that apply the EMF technique, selection of an appropriate electrolyte plays the key role. It is important to ascertain the conditions under which the electrolyte shows the best performance. The super ionic conducting temperature range of α-AgI is 420–713 K and that of $RbAg_4I_5$ is 298–505 K. In addition to the superionic properties even at room temperature, $RbAg_4I_5$ is more moisture resistant than AgI.

$Ag_4HgSe_2I_2$ compound was synthesized through a peritectic reaction $L + \beta$-$Ag_2Se \leftrightarrow Ag_4HgSe_2I_2$ at T = 917 K. Using the EMF method, standard thermodynamic properties of $Ag_4HgSe_2I_2$ and activity of silver in it are determined for the first time. The extremely low values of activity of silver in $Ag_4HgSe_2I_2$ in the temperature range 412–482 K are indicative of the superionic nature of the quaternary compound.

Acknowledgements

Conflict of interest

The authors declare no conflict of interest.

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