



Application of the Barium- β '-Alumina Solid-State Electrolyte to the Thermodynamic Study of the BaO-ZrO₂ System

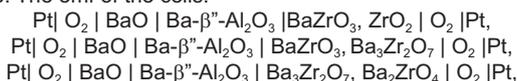
GRZEGORZ RÓG*, MIROSLAW M. BUĆKO, ANNA KOZŁOWSKA-RÓG

AGH University of Science and Technology, Faculty of Materials Science and Ceramics, Kraków, Poland

*e-mail: rog@uci.agh.edu.pl

Abstract

The standard molar Gibbs free energies of formation of BaZrO₃, Ba₂ZrO₄ and Ba₃Zr₂O₇ have been determined by the galvanic cells involving Ba- β '-alumina as a solid-state electrolyte. The emf of the cells:



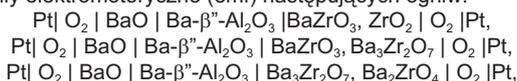
has been measured in the temperature range from 1073 to 1273 K.

The standard molar Gibbs free energies of formation of BaZrO₃, Ba₂ZrO₄, and Ba₃Zr₂O₇ from BaO and ZrO₂ have been calculated. The standard molar Gibbs free energies of formation of barium zirconates from elements have been estimated and compared with the data obtained by other authors.

Keywords: Barium zirconates, Gibbs free energy of formation, Solid-state galvanic cells, Thermodynamic functions

ZASTOSOWANIE ELEKTROLITU STAŁEGO Ba- β '-Al₂O₃ DO BADAŃ TERMODYNAMICZNYCH UKŁADU BaO-ZrO₂

Za pomocą ogniw galwanicznych, zawierających Ba- β '-Al₂O₃ jako elektrolit stały, oznaczono standardowe molowe entalpie swobodne tworzenia BaZrO₃, Ba₂ZrO₄ i Ba₃Zr₂O₇. Siły elektromotoryczne (emf) następujących ogniw:



zmierzono w zakresie temperatur od 1073 do 1273 K.

Obliczono standardowe molowe entalpie swobodne tworzenia BaZrO₃, Ba₂ZrO₄ i Ba₃Zr₂O₇ z BaO i ZrO₂. Oszacowano standardowe molowe entalpie swobodne tworzenia cyrkonianów baru z pierwiastków i porównano z wynikami innych autorów.

Słowa kluczowe: cyrkoniany baru, entalpia swobodna tworzenia, ogniwa galwaniczne z elektrolitem stałym, funkcje termodynamiczne.

1. Introduction

Three barium zirconates, BaZrO₃, Ba₂ZrO₄ and Ba₃Zr₂O₇, are formed at atmospheric pressure [1]. Materials based on barium zirconates operate at high temperatures and for that reason they should have high thermal stability. BaZrO₃ has been reported to be widely applied in electronic and ceramic industry [1, 2]. It has been also regarded as a candidate material for interface engineering of alumina fibre/alumina matrix composites [3]. Barium zirconates could be produced due to the interaction of fission products with zirconium alloy cladding [4]. Therefore, a knowledge of thermodynamic properties of barium zirconates, and thus, chemical reactivity of the compounds, would be important. Although thermodynamics of the BaO-ZrO₂ system has been studied exten-

sively, there is few literature data available. The standard molar Gibbs free energy of formation, $\Delta_f G_m^0$, of BaZrO₃ and Ba₂ZrO₄ has been determined as a function of temperature in the range (1774 to 1947) K, from the vapour pressure of BaO over (ZrO₂+BaZrO₃) and (BaZrO₃+Ba₂ZrO₄), by T. Matsui [5]. The measurements performed by S. Dash *et al.*, by the Knudsen mass-loss technique, have permitted $\Delta_f G_m^0$ of BaZrO₃ [6], Ba₂ZrO₄ [7], and Ba₃Zr₂O₇ [8] to be estimated, in the temperature range (1203 to 1347) K, (1566 to 1732) K and (1212 to 1361) K, respectively. A.S. Lvova and N.N. Feodosev have obtained thermodynamic data for BaZrO₃ from calorimetric measurements [9]. Other authors have been using solid-state galvanic cells to determine the $\Delta_f G_m^0$ values, in the temperature range (1180 to 1320) K [10] or (937 to 1150) K [11], for BaZrO₃ only. In our recent work

the $\Delta_r G_m^0$ values for BaZrO_3 and Ba_2ZrO_4 in the temperature range (1073-1273) K have been determined by the galvanic cells with CaF_2 electrolyte. However, such a determination for $\text{Ba}_3\text{Zr}_2\text{O}_7$ has not been successful [12]. Contrary to the work by A. Banerjee *et al.*, concerning the measurements of Gibbs free energy for barium uranates [13], we have failed to obtain stable emf values in the thermodynamic study of barium zirconates by the cells involving calcia stabilized zirconia electrolyte.

In the present work, the galvanic cells involving Ba- β -alumina as a solid-state electrolyte, were applied to the determination of thermodynamic properties of barium zirconates. The electrolytes of β -alumina related compounds are well known to show practically pure and relatively high ionic conductivity. They have been frequently used in thermodynamic investigations [14-17].

The following galvanic cells were set up:

Cell I



Cell II



Cell III



Though Ba- β -alumina does not exist in equilibrium with BaO and several intermediate barium aluminates could form at the interface between the electrolyte and the BaO electrode, metastable coexistence of these phases might be maintained, when the reactions between them occur after the stable emf is reached. The emf of the galvanic cells under study was a result of the difference in BaO activity at the electrodes. As it results from thermodynamic considerations, Ba- β -alumina is more stable than barium zirconates, and thus, any reaction between them could not take place in the cells. The composition of the half-cells was established according to the respective phase diagram [1]. The nonstoichiometry of the phases considered was neglected.

2. Experimental

Polycrystalline barium- β -alumina was prepared by an ion exchange of sodium- β -alumina in molten barium salt. Sodium- β -alumina samples were prepared from Na_2CO_3 , MgCO_3 and $\gamma\text{-Al}_2\text{O}_3$ powders by the method described previously [18]. The composition of the samples prepared corresponded to the formula $\text{Na}_{1.69}\text{Mg}_{0.66}\text{Al}_{10.33}\text{O}_{17}$. The ion-exchange experiments were performed in an α -alumina crucible filled by a eutectic salt mixture (62 mol% $\text{Ba}(\text{NO}_3)_2$ + 38 mol% BaCl_2). The sodium- β -alumina pellets were dipped in the fused salt bath, covered with an active carbon layer, and held there over 24 h. In such a way salt was separated from moisture in the ambient atmosphere. The temperature of the bath was 850 K. After exchange the pellets were treated with dilute nitric acid and then with anhydrous ethyl alcohol to remove surplus of the respective salt. The samples were dried under vacuum at the temperature of 800 K for 3 h and stored in a vacuum desiccator. The X-ray analysis of the samples revealed pure β -alumina phase (Fig. 1). Microscopic observations before and after the exchange showed that the pellets did not exhibit any considerable changes. The extent of ion exchange was determined by weighing pellets before and after the exchange experiment. It appeared to be larger than 95 %.

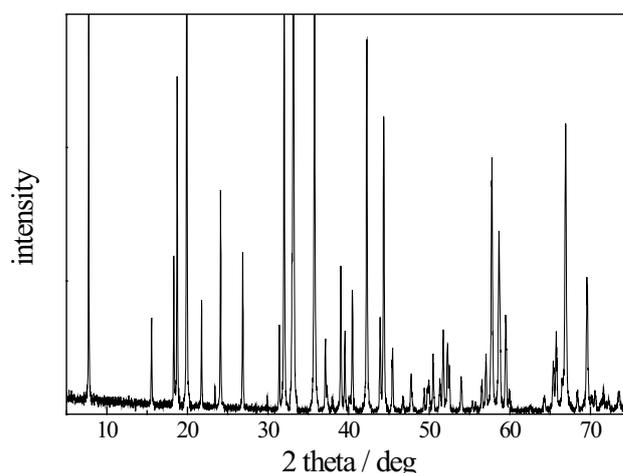


Fig. 1. X-ray diffraction pattern of the Ba- β -alumina sample.

The half-cells I – III involving barium zirconates were prepared by the standard solid-state reaction technique. The starting substances were BaCO_3 and ZrO_2 . After drying they were mixed in appropriate proportions, ground and preheated. The resulting products were pulverized thoroughly and pressed into pellets of 12 mm in diameter and 3 mm thick. Then the pellets were sintered. The conditions of heat treatment are given in Table 1 for each half-cell, respectively. X-ray analysis of the half-cells revealed the desired phases only, as it is shown in Fig. 2. One face of each half-pellet was covered by Pt paste and fired at $T = 1223$ K. The half-cell and the electrolyte pellets were assembled in a simple spring-loaded alumina holder, according to the respective cell arrangement. The cell was inserted into the electrical furnace. The procedure used in the present work was similar to that described earlier [19].

Table 1. The preparation conditions for the half-cells of the cells I, II, and III. T_p and t_p are temperature and time of preheating, respectively; T_s and t_s are temperature and time of final sintering, respectively.

| The half cell | BaO [mol%] | T_p , [K] | t_p , [h] | T_s , [K] | t_s , [h] |
|---|------------|-------------|-------------|-------------|-------------|
| $\text{BaZrO}_3, \text{ZrO}_2$ | 32.5 | 1300 | 10 | 1470 | 1.5 |
| $\text{BaZrO}_3, \text{Ba}_3\text{Zr}_2\text{O}_7$ | 57.5 | 1230 | 10 | 1350 | 1.5 |
| $\text{Ba}_2\text{ZrO}_4, \text{Ba}_3\text{Zr}_2\text{O}_7$ | 62.5 | 1350 | 16 | 1570 | 2 |

The emf measurements were carried out in the temperature range (1073 to 1273) K in air. The emf was measured when its value was steady for 3 h. The reversible behavior of the galvanic cells was tested by passing a small current (not exceeding 20 μA) through the cell and noting whether the observed voltage returned to its original value. No side-reactions between the electrode materials and the electrolyte after the emf experiments were observed.

3. Results and discussion

The half-cell and overall-cell reactions can be written as follows.

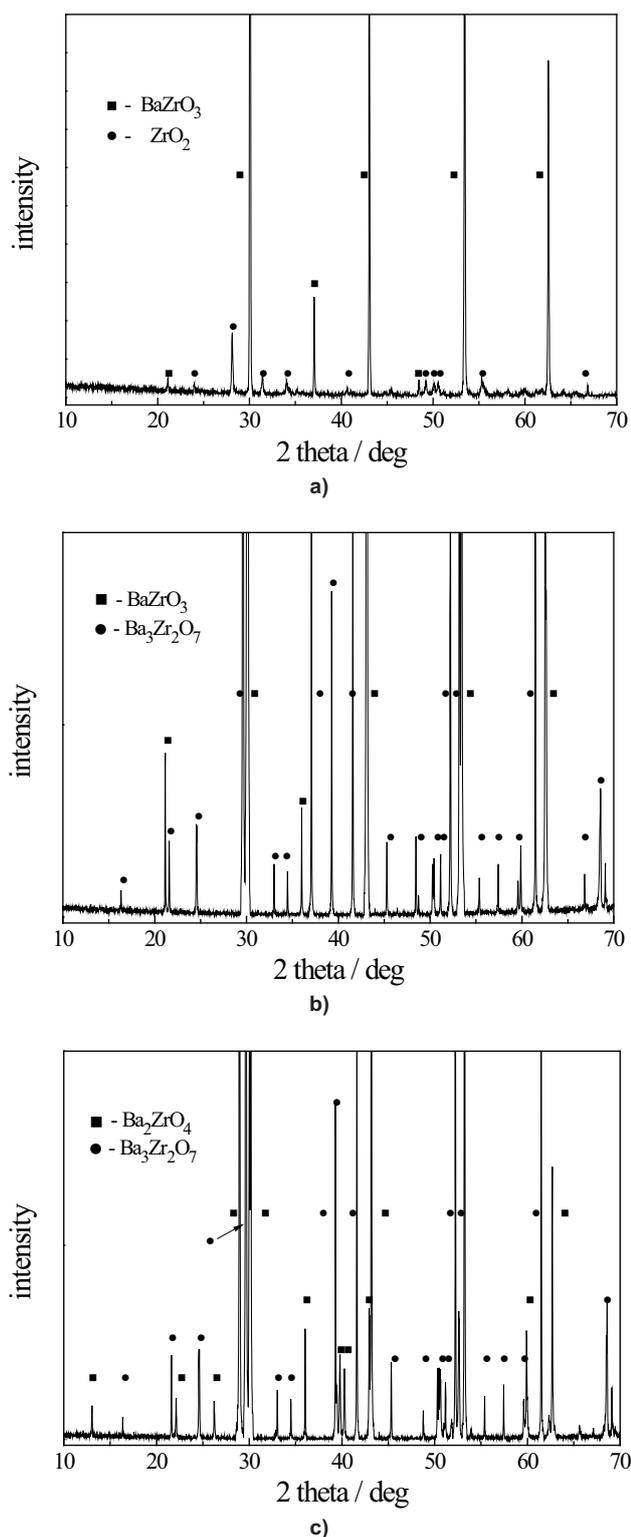
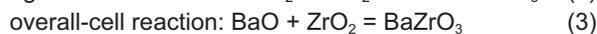
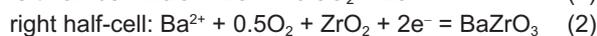
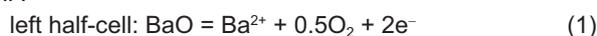
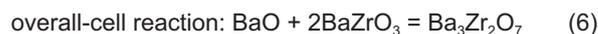
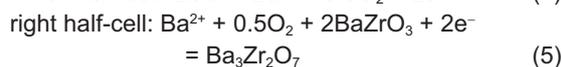
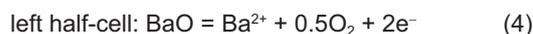


Fig. 2. X-ray diffraction patterns of the samples: a) $\text{BaZrO}_3 + \text{ZrO}_2$, b) $\text{BaZrO}_3 + \text{Ba}_3\text{Zr}_2\text{O}_7$ and c) $\text{Ba}_3\text{Zr}_2\text{O}_7 + \text{Ba}_2\text{ZrO}_4$.

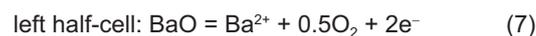
Cell I



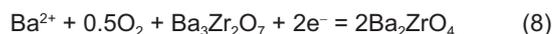
Cell II



Cell III



right half-cell:



overall-cell reaction:



The standard Gibbs free energy of respective cell reaction, ΔG_i^0 ($i = 1, 2$ or 3 for the cell I, II, III, respectively), was calculated by the relation

$$\Delta G_i^0 = -2F \cdot E_i \quad (10)$$

where E_i is the emf of the i -th cell, F is the Faraday constant. The emf of these cells could be calculated as linear functions of temperature in the entire range; the equations:

$$E_1/\text{mV} = (575.5 \pm 0.2) - (0.101 \pm 0.001) \cdot (T/\text{K}) \quad (11)$$

$$E_2/\text{mV} = (183.6 \pm 0.7) - (0.079 \pm 0.004) \cdot (T/\text{K}) \quad (12)$$

$$E_3/\text{mV} = (179.9 \pm 0.1) - (0.063 \pm 0.001) \cdot (T/\text{K}) \quad (13)$$

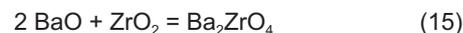
resulted from the least-squares fit. The values of emf measured with an accuracy ± 0.1 mV at the temperatures (1073, 1123, 1173, 1223, and 1273) K are given in Table 2.

Table 2. The emf values of the studied cells: E_1 - cell I, E_2 - cell II and E_3 - cell III, as a function of temperature.

| T [K] | E_1 [mV] | E_2 [mV] | E_3 [mV] |
|-------|-----------------|----------------|-----------------|
| 1073 | 466.8 ± 0.5 | 98.9 ± 1.0 | 112.3 ± 0.5 |
| 1123 | 461.3 ± 0.4 | 94.3 ± 0.9 | 109.2 ± 0.4 |
| 1173 | 456.7 ± 0.6 | 90.2 ± 0.7 | 106.2 ± 0.2 |
| 1223 | 451.6 ± 0.5 | 85.8 ± 0.6 | 102.7 ± 0.3 |
| 1273 | 446.3 ± 0.4 | 83.3 ± 0.4 | 99.8 ± 0.2 |

It is worth noting that the emf measured in this work and the previous one obtained from the galvanic cells involving Ba- β "-alumina electrolyte prepared by solid-state sintering route does not differ much from each other.

The standard molar Gibbs free energies, $\Delta_f G_{\text{ox}}^0$, for the reactions of formation of barium zirconates from starting oxides:



as functions of temperature were calculated by the formulae:

$$\Delta_f G_{\text{ox}}^0(\text{BaZrO}_3) = -2F \cdot E_1 \quad (17)$$

$$\Delta_f G_{\text{ox}}^0(\text{Ba}_2\text{ZrO}_4) = -F \cdot (2E_1 + E_2 + E_3) \quad (18)$$

$$\Delta_f G_{\text{ox}}^0(\text{Ba}_3\text{Zr}_2\text{O}_7) = -F \cdot (2E_1 - E_2) \quad (19)$$

The following equations were obtained:

$$\Delta_f G_{\text{ox}}^0(\text{BaZrO}_3) = -(111.05 \pm 0.04) + (18.49 \pm 0.29) \cdot 10^{-3} \cdot T \quad (20)$$

$$\Delta_f G_{\text{ox}}^0(\text{Ba}_2\text{ZrO}_4) = -(146.12 \pm 0.13) + (33.19 \pm 0.80) \cdot 10^{-3} \cdot T \quad (21)$$

$$\Delta_f G_{\text{ox}}^0(\text{Ba}_3\text{Zr}_2\text{O}_7) = -(257.53 \pm 0.10) + (51.14 \pm 1.86) \cdot 10^{-3} \cdot T \quad (22)$$

The temperature-independent term in equations (20) - (22) gives the average value of the standard molar enthalpy of formation (from oxides) of respective barium zirconate, $\Delta_f H_{\text{ox}}^0$, in the temperature range covered by the emf measu-

Table 3. The values of the standard molar Gibbs free energy of formation (from oxides) of barium zirconates, $\Delta_f G_{1073,ox}^0$, determined by a solid-state galvanic cell method at $T = 1073$ K. The average values of the standard molar enthalpy, $\Delta_f H_{ox}^0$, and the standard molar entropy, $\Delta_f S_{ox}^0$, of formation (from oxides) of barium zirconates in the temperature range covered by emf measurements.

| Compound | $\Delta_f G_{1073,ox}^0$, [kJ·mol ⁻¹] | $\Delta_f H_{ox}^0$, [kJ·mol ⁻¹] | $\Delta_f S_{ox}^0$, [J·mol ⁻¹ ·K ⁻¹] | T, [K] | Reference |
|--|--|---|---|--------------|-----------|
| BaZrO ₃ | -90.1 | -111.0 | -19.5 | 1073 to 1273 | this work |
| | -71.7 | -99.7 | -26.1 | 1180 to 1320 | 10 |
| | -52.2 | -105.2 | -49.1 | 937 to 1150 | 11 |
| | -84.9 | -109.5 | -23.0 | 1073 to 1273 | 12 |
| Ba ₂ ZrO ₄ | -110.5 | -146.1 | -33.2 | 1073 to 1273 | this work |
| | -107.6 | -142.8 | -32.8 | 1073 to 1273 | 12 |
| Ba ₃ Zr ₂ O ₇ | -202.6 | -257.5 | -51.1 | 1073 to 1273 | this work |

rements. However, the temperature-dependent term in these equations represents the standard molar entropy, $\Delta_f S_{ox}^0$, of formation (from oxides). The values of $\Delta_f G_{ox}^0$ calculated for $T = 1073$ K, $\Delta_f H_{ox}^0$, and $\Delta_f S_{ox}^0$ together with respective data obtained by other authors by emf method are presented in Table 3. The differences in the data given in Table 3 might be mainly due to the different electrolytes used as well as to the different temperature range in the emf measurements.

In order to check whether the $\Delta_f G_{ox}^0$ values are consistent with thermodynamic requirements, the molar Gibbs free energies of mixing, $\Delta_M G^0$ (at $T = 1073$ K), calculated according to the formulae:

$$\Delta_M G^0 (\text{BaZrO}_3) = 1/2 \Delta G_{ox}^0 (\text{BaZrO}_3) \quad (23)$$

$$\Delta_M G^0 (\text{Ba}_2\text{ZrO}_4) = 1/3 \Delta G_{ox}^0 (\text{Ba}_2\text{ZrO}_4) \quad (24)$$

$$\Delta_M G^0 (\text{Ba}_3\text{Zr}_2\text{O}_7) = 1/5 \Delta G_{ox}^0 (\text{Ba}_3\text{Zr}_2\text{O}_7) \quad (25)$$

are presented in Fig. 3 as the functions of mole fraction of BaO, x , in the respective barium zirconate. Similar plots could also be shown for other temperatures. The shapes of these curves indicate the internal consistency (in the limit of error) of our results.

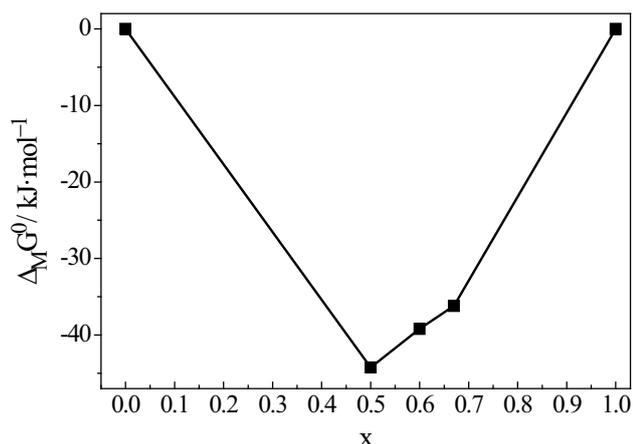


Fig. 3. The molar Gibbs free energy of mixing, $\Delta_M G^0$, as a function of x in $\{x\text{BaO} + (1-x)\text{ZrO}_2\}$, $T = 1073$ K.

Since the standard Gibbs free energy data for barium zirconates, existing so far in literature, had been referred to the reactions of their formation from elements, the results obtained in the present work were recalculated in order to compare them to those obtained by other authors. To these calculations, the values of the standard Gibbs free energy, $\Delta_f G_m^0$, of formation of BaO and ZrO₂ were taken from the

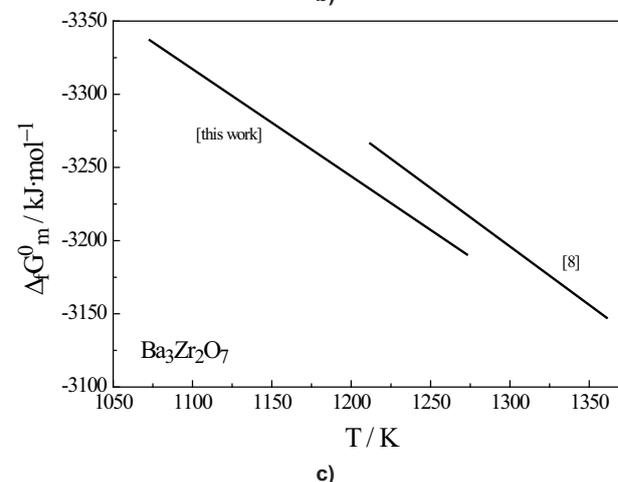
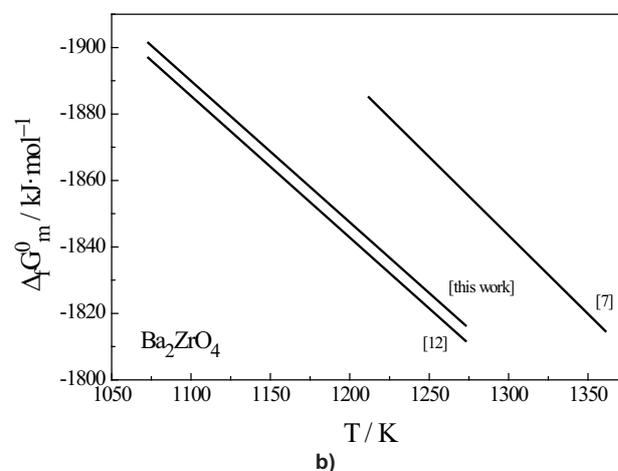
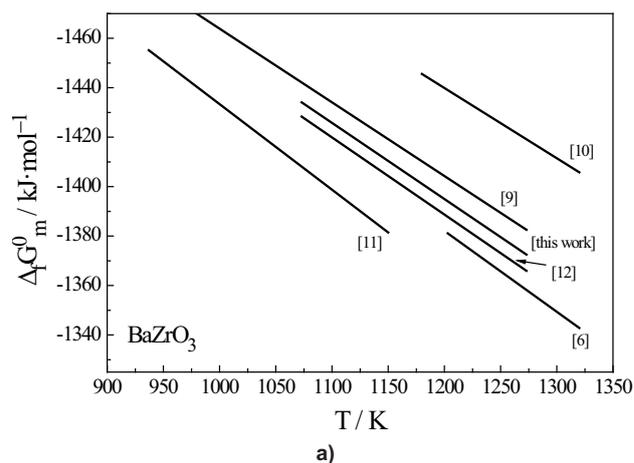


Fig. 4. Temperature dependence of the standard Gibbs free energy, $\Delta_f G_{ox}^0$, of the formation of barium zirconates from elements: a) BaZrO₃, b) Ba₂ZrO₄ and c) Ba₃Zr₂O₇.

thermochemical tables [20], and calculated as linear functions of temperature:

$$\Delta_f G_m^0(\text{BaO}/\text{kJ}\cdot\text{mol}^{-1}) = -55.7 + 0.103(T/\text{K}) \quad (26)$$

$$\Delta_f G_m^0(\text{ZrO}_2/\text{kJ}\cdot\text{mol}^{-1}) = -1095.9 + 0.186(T/\text{K}) \quad (27)$$

Then, the following equations enabling the standard Gibbs free energy of formation (from elements) for barium zirconates to be estimated, were derived:

$$\Delta_f G_m^0(\text{BaZrO}_3) = \Delta_f G_{\text{ox}}^0(\text{BaZrO}_3) + \Delta_f G_m^0(\text{BaO}) + \Delta_f G_m^0(\text{ZrO}_2) \quad (28)$$

$$\Delta_f G_m^0(\text{Ba}_2\text{ZrO}_4) = \Delta_f G_{\text{ox}}^0(\text{Ba}_2\text{ZrO}_4) + 2 \cdot \Delta_f G_m^0(\text{BaO}) + \Delta_f G_m^0(\text{ZrO}_2) \quad (29)$$

$$\Delta_f G_m^0(\text{Ba}_3\text{Zr}_2\text{O}_7) = \Delta_f G_{\text{ox}}^0(\text{Ba}_3\text{Zr}_2\text{O}_7) + 3 \cdot \Delta_f G_m^0(\text{BaO}) + 2 \cdot \Delta_f G_m^0(\text{ZrO}_2) \quad (30)$$

Considering equations (25)-(27), $\Delta_f G_m^0$ was calculated as a linear function of temperature:

$$\Delta_f G_m^0(\text{BaZrO}_3) = -1764.6 + 0.308 \cdot T \quad (31)$$

$$\Delta_f G_m^0(\text{Ba}_2\text{ZrO}_4) = -2357.4 + 0.425 \cdot T \quad (32)$$

$$\Delta_f G_m^0(\text{Ba}_3\text{Zr}_2\text{O}_7) = -4234.7 + 0.799 \cdot T \quad (33)$$

The changes of $\Delta_f G_m^0$ with temperature are illustrated in Fig. 4, together with the data reported by other authors [6-12]. The plots in Fig. 4 show that the results obtained in this work for BaZrO₃ and Ba₂ZrO₄ are in quite reasonable agreement with the values determined recently by us with the galvanic cells involving CaF₂ electrolyte [12]. As it can be seen in Fig. 4, the $\Delta_f G_m^0$ values determined in this work do not differ significantly from presented in [6, 8, 9]. However, $\Delta_f G_m^0$ values obtained by us and those for BaZrO₃ given in [10, 11] as well as for Ba₂ZrO₄ given in [7], show considerable discrepancies. Such differences might be due to the experimental methods employed and/or to the different temperature range covered by the measurements.

4. Conclusions

The solid-state galvanic cells involving Ba-β"-alumina as an electrolyte turned out to be applicable to the thermodynamic study on BaO-ZrO₂ system. It could be concluded that Gibbs free energies of formation of barium zirconates, obtained in this way, were reliable.

Acknowledgments

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