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J. Chem. Thermodynamics 40 (2008) 21–24

JCT

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Determination of the standard Gibbs free energies of formation of barium zirconates in the temperature range (1073 to 1273) K

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Received 7 February 2007; received in revised form 23 April 2007; accepted 4 June 2007
Available online 8 June 2007

Abstract

The standard molar Gibbs free energies of formation of $BaZrO_3$, and Ba_2ZrO_4 have been determined by solid-state galvanic cells involving a single crystal CaF_2 as a solid-state electrolyte. The e.m.f. measurements were performed in the temperature range (1073 to 1273) K. The average values of the standard molar enthalpy and the standard molar entropy of formation in the temperature range covered by the e.m.f. measurements have been also estimated. The results have been compared with those obtained by other authors.
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Keywords: Solid-state galvanic cell; CaF_2 electrolyte; E.m.f. measurements; Gibbs free energy of formation; $(BaO + ZrO_2)$

1. Introduction

The phase diagram of $\{xBaO + (1-x)ZrO_2\}$ has extensively been studied because of its interest in electronic and ceramic industry. The results have been discussed, in detail, in the paper by Dash *et al.* [1]. Three barium zirconates, $BaZrO_3$, Ba_2ZrO_4, and $Ba_3Zr_2O_7$ are formed at atmospheric pressure. Materials based on barium zirconates operate at high temperatures and for that reason they should have high thermal stability. Therefore, the knowledge of the thermodynamic properties of barium zirconates, and thus, the chemical reactivity of the compounds, would be important.

There is some literature concerning thermodynamic properties of barium zirconates. Matsui calculated the standard molar Gibbs free energy of formation, $\Delta_f G_m^\circ$ of $BaZrO_3$ and Ba_2ZrO_4 as a function of temperature in the range (298 to 2000) K from the measurements of vapor pressure of BaO over two-phase mixtures $(ZrO_2 + BaZrO_3)$ and $(BaZrO_3 + Ba_2ZrO_4)$ [2]. The measurements performed by Dash *et al.*, by the Knudsen mass-loss technique (KLM) allowed to estimate $\Delta_f G_m^\circ$ of $BaZrO_3$ [3], Ba_2ZrO_4 [4], and $Ba_3Zr_2O_7$ [5], in the temperature range (1203 to 1347) K, (1566 to 1732) K, and (1212 to 1361) K, respectively. Other authors used solid-state galvanic cells to determine thermodynamic data for $BaZrO_3$, in the temperature range (980 to 1120) K [6], (1180 to 1320) K [7], and (937 to 1150) K [8], respectively.

The aim of this work was to determine the $\Delta_f G_m^\circ$ for $BaZrO_3$ and Ba_2ZrO_4, by a solid-state galvanic cell method. However, in spite of numerous attempts we failed to prepare $Ba_3Zr_2O_7$. The following galvanic cells were set up:

$$\mathrm{Pt}|O_2(p = 50\ \mathrm{Pa})|BaO + BaF_2|CaF_2|BaF_2 + BaZrO_3 + ZrO_2|O_2(p = 50\ \mathrm{Pa})|\mathrm{Pt}, \qquad \text{(I)}$$

$$\mathrm{Pt}|O_2(p = 50\ \mathrm{Pa})|BaO + BaF_2|CaF_2|BaF_2 + Ba_2ZrO_4 + BaZrO_3|O_2(p = 50\ \mathrm{Pa})|\mathrm{Pt}. \qquad \text{(II)}$$

A fluorine ion conductor, CaF_2, generally applied in the e.m.f. measurements of many oxide systems with very low equilibrium pressure of oxygen, was used as a solid-state electrolyte [9]. BaF_2 was added to the half-cells in order to transform the potential of oxygen ions to that of fluorine ions. The e.m.f. was measured in the temperature range (1073 to 1273) K.

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0021-9614/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jct.2007.06.001

2. Experimental

Single crystal optical grade CaF_2 rods of 12 mm diameter, grown along $\langle 1\,1\,1 \rangle$ direction were purchased from Harshaw Chemical Company. Pellets of 2 mm thickness were cut from the rods. The starting materials for preparation of half-cells were $BaCO_3$, ZrO_2, and BaF_2 powders. All the substances were of reagent grade purity. The reactants were dried at $T = 570$ K before use. The right half-cells (I) and (II) were obtained in the following way. First, $(BaZrO_3 + ZrO_2)$ and $(Ba_2ZrO_4 + BaZrO_3)$ were prepared by high-temperature reaction $BaCO_3$ with ZrO_2, mixed in a respective mole ratio $BaO{:}ZrO_2$. Repeated grindings at the intermediate stage of the reaction were done. The X-ray diffraction analysis showed that $BaZrO_3$ and ZrO_2 or Ba_2ZrO_4 and $BaZrO_3$ were main phases, and indicated that BaO phase was absent in a respective mixture (figure 1). To the mixtures obtained, 5 mol% BaF_2 was added. The mixtures were pressed into pellets 3 mm thick and 12 mm in diameter, under pressure 300 MPa. The left half-cell in cells (I) and (II) was obtained by thermal decomposition of $BaCO_3$, to which 2 mol% BaF_2 was admixed. Then, the mixtures were pelletized. Compositions of the half-cell mixtures and the conditions of their heat treatment are presented in table 1. To separate the samples from moisture and CO_2 in the ambient atmosphere, they were stored in a desiccator under reduced pressure.

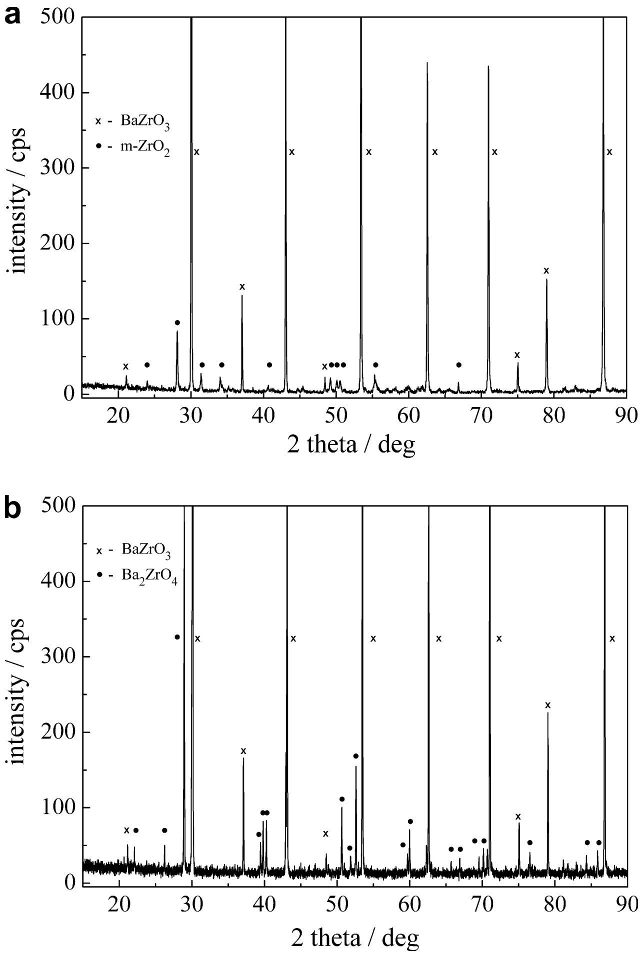

FIGURE 1. X-ray powder patterns of $(BaZrO_3 + ZrO_2)$ (a) and $(Ba_2ZrO_4 + BaZrO_3)$ (b).

One face of each half-cell pellet was covered by Pt paste and fired at $T = 1223$ K. The half-cell and electrolyte pellets were assembled in a simple spring-loaded alumina holder according to the respective cell arrangement. The cell was inserted in an electrical furnace. The procedure applied in the present work was similar to that described by us earlier [10]. The e.m.f. measurements were carried out in the temperature range (1073 to 1273) K. Dry argon containing oxygen ($p(O_2) = 50$ Pa) was passed through the furnace during the measurements. The e.m.f. was read on the high ohmic voltmeter with an accuracy of ±0.1 mV. The time taken for the cell to attain equilibrium was no longer than 50 min. The e.m.f. values maintained practically stable during a whole measurement time (about 3 h). The reversibility of each cell was checked by passing small currents (about 20 μA) through the cell in either direction for 120 s and noting if the e.m.f. returned to its original value. No side-reaction between the electrode materials and the electrolyte was observed.

3. Results and discussion

The galvanic cells under study could be regarded as reversible cells with respect to fluorine ions and their e.m.f. was a result of a difference in BaO activity at the electrodes. The choice of CaF_2 rather than BaF_2 as a solid electrolyte was dictated by the fact that the ionic conduction domain, defect chemistry, and transport properties of CaF_2 were better known than those of BaF_2. CaF_2 as a less thermodynamically stable compound than BaF_2, could react with BaO. However, metastable coexistence of BaO and CaF_2 phases might be maintained in the galvanic cells when the reaction occurs after the stable e.m.f. was reached.

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

Cell (I)

$$\text{Left half-cell: } BaO + 2F^- = BaF_2 + 0.5O_2 + 2e^- \qquad (1)$$

$$\text{Right half-cell: } BaF_2 + 0.5O_2 + ZrO_2 + 2e^- = BaZrO_3 + 2F^- \qquad (2)$$

$$\text{Overall-cell reaction: } BaO + ZrO_2 = BaZrO_3 \qquad (3)$$

Cell (II)

$$\text{Left half-cell: } BaO + 2F^- = BaF_2 + 0.5O_2 + 2e^- \qquad (4)$$

$$\text{Right half-cell: } BaF_2 + 0.5O_2 + BaZrO_3 + 2e^- = Ba_2ZrO_4 + 2F^- \qquad (5)$$

$$\text{Overall-cell reaction: } BaO + BaZrO_3 = Ba_2ZrO_4 \qquad (6)$$

The standard Gibbs free energy of respective overall-cell reaction, ΔG_i° ($i = 1$ or 2) was calculated by the relation

$$\Delta G_i^\circ = -2FE_i, \qquad (7)$$