

Thermodynamic investigation of ZrO₂-BaO system

GONG Wei-ping(龚伟平), CHEN Teng-fei(陈腾飞), JIN Zhan-peng(金展鹏)

State Key Laboratory of Powder Metallurgy, Central South University, Changsha 410083, China

Received 28 June 2006; accepted 11 January 2007

Abstract: Thermodynamic description of ZrO₂-BaO system was developed using the available experimental information. Special attention was paid to the modelling of the perovskite phase BaZrO₃ by a temperature-dependent polynomial to fit the experimental thermodynamic properties. The liquid phases, C_{SS} (cubic ZrO₂ solid solution) and T_{SS} (tetragonal ZrO₂ solid solution) were modelled with Redlich-Kister formula. The compounds Ba₂ZrO₄ and Ba₃Zr₂O₇ were treated as stoichiometric phases and the BaO_{SS} and M_{SS} (halite BaO and monoclinic ZrO₂ solid solutions) were treated as pure compounds. Comparisons between the calculated and the measured phase diagram as well as the thermodynamic quantities indicate that the most reliable experimental information is satisfactorily accounted for by the present thermodynamic calculation.

Key words: ZrO₂-BaO system; thermodynamic description; perovskite phase; Redlich-Kister formula

1 Introduction

Doped with certain amount of MgO, CaO, SrO, BaO, Y₂O₃ or CeO₂, the disruptive martensitic phase transformation of pure ZrO₂ from monoclinic to tetragonal can be suppressed, thus the mechanical properties are greatly improved[1]. While the mechanical properties of partially stabilized zirconia(PSZ) or tetragonal zirconia polycrystals(TZP) with a smaller amount than needed to produce fully stabilized zirconia, are quite different from each other[2–4]. Obviously, the knowledge of the phase diagram and thermodynamic properties is of fundamental importance to define the processing conditions for making these materials and subsequent treatments to obtain optimal engineering properties. Associated with the sluggish kinetics at low temperatures, the formation of meta-stable phases, and the difficulties in conducting experiments at high temperatures, etc, the phase equilibria in ZrO₂-included systems have been proved to be difficult to determine with certainty. Since only calorimetry, the electromotive force and mass spectrometry are practicable, measurements of the thermodynamic properties in ZrO₂-included systems are also not easy from the experimental point of view. When the present investigation was initiated, the literature experimentally dealing with the ZrO₂-BaO system gave an incomplete

and confusing picture[5–8]. In this work, the Calphad technique was employed to determine the phase relations and thermodynamic properties in ZrO₂-BaO system with the aim to assess the thermodynamic properties of the various phases in the ZrO₂-BaO system and to provide the optimized thermodynamic parameters, which can reproduce the reliable experimental phase diagram, thermodynamic data and structural information satisfactorily.

2 Evaluation of experimental data in literature

2.1 Phase diagram information

PASCHOAL et al[6] and SHEVCHENKO et al[7] were responsible for the major contributions to understanding the ZrO₂-BaO liquidus phase diagram. By means of optical microscopy, X-ray diffraction(XRD) and differential thermal analysis(DTA) techniques, PASCHOAL et al[6] measured the liquidus in the BaO-rich side. Using the DTA method, SHEVCHENKO et al[7] constructed a series of the phase diagrams of ZrO₂/HfO₂-based systems, and the attention was paid to the ZrO₂-rich side. The ZrO₂-BaO liquidus equilibria reported by SHEVCHENKO et al[7] were in good agreement with those measured by WARTENBERG et al[8]. Based on the available experimental information, the ZrO₂-BaO system was characterized by BaZrO₃ and

Ba₂ZrO₄ compounds, in which BaZrO₃ melted congruently at (2 978±10) K, and Ba₂ZrO₄ decomposed peritectically at about 2 600 K. The present work was mainly based on these experimental data to set up the liquidus equilibria, on the grounds that the high-purity specimens were employed, and experimental procedures were well described.

Both PASCHOAL et al[6] and SHEVCHENKO et al[7] did not report the compound Ba₃Zr₂O₇, while the available information on $\{(1-x)(\text{BaO})+x(\text{ZrO}_2)\}$ indicated the existence of Ba₃Zr₂O₇ in the ZrO₂-BaO system[8–9] and the phase diagram calculated by DASH et al[10] for $\{(1-x_1-x_2)(\text{Ba})+x_1(\text{Zr})+x_2(\text{O})\}$ indicated that Ba₃Zr₂O₇ co-existed with BaZrO₃ at 1 287 K. And more, Ba₃Zr₂O₇ was really prepared by the reaction of BaCO₃(s) and ZrO₂(s) in the mole ratio of 3/2 in an alumina boat at 1 300 K for 400 h in dry air[10] and was found at 1 650 K[11]. Consequently, special attention was paid to the compound Ba₃Zr₂O₇ in this work with the aim to understand the difference existing in Refs.[6–11].

The maximum solubility of BaO in c-ZrO₂ (cubic ZrO₂) and t-ZrO₂ (tetragonal ZrO₂) is 0.025 mol [7]. This small solubility of BaO in ZrO₂ benefits the mechanical properties of zirconia very much and the measured data [7] were used to evaluate the thermodynamic properties of C_{SS} (cubic ZrO₂ solid solution) and T_{SS} (tetragonal ZrO₂ solid solution). The very limited solubility of ZrO₂ in halite BaO (about 0.005 mol)[6–8] was ignored. No experimental data were reported for the solubility of BaO in m-ZrO₂ (monoclinic ZrO₂).

2.2 Structural and thermodynamic information

The structural behavior and the thermodynamic properties of the perovskite phase BaZrO₃ have been the subjects of many investigations associated with the technological application[12–19]. Using high-temperature X-ray diffractometry, MATHEWS et al[12] measured the cell parameters, unit-cell volumes and the coefficients of volume thermal expansion of the zirconia CaZrO₃, SrZrO₃ and BaZrO₃ in the temperature range from 298 to 1 675 K. The linear variation of the unit-cell volume and the cell parameters without any discontinuity indicated that the compound BaZrO₃ did not take place any phase transition, and the structure of BaZrO₃ was cubic. Using electromotive force, JOYAB et al[13] reported the enthalpies of formation of both SrZrO₃ and BaZrO₃ from the component oxides in the temperature range from 960 to 1 210 K. Based on the slope of electromotive force, SrZrO₃ was detected to undergo a structural transformation at about 1 123 K, while no structural transformation was detected for the compound BaZrO₃[13]. Because the experimental procedures were well controlled and the experimental results were

generally consistent with each other[12–13], the structure of BaZrO₃ was treated as cubic in the whole temperature range.

Several groups[13–19] investigated the thermodynamic properties of BaZrO₃. Using high-temperature differential calorimeter, NAGARAJAN et al[14] reported the enthalpy increments $H(T)-H(298)$ for BaZrO₃ from 1 000 to 1 700 K. Drop calorimetry was used by LEVITSKII[15], for $H(T)-H(298)$ measurements on BaZrO₃, respectively. BANERJEE et al[16] determined $H(T)-H(298)$ of BaZrO₃ by a precise high-temperature Calvet micro-calorimeter in the temperature range from 365.7 to 981 K. CORDFUNKE et al[17] also reported the enthalpy values for BaZrO₃ in their compilations. GOSPODINOV et al[18] reported enthalpy data for BaZrO₃ in the temperature range between 298 and 500 K by differential scanning calorimeter(DSC). These experimental data[14–16] except those of Ref.[18] were in good agreement with each other and join smoothly with the adiabatic measurements carried out by KING et al[19]. They were used to evaluate the Gibbs energy of BaZrO₃. Data from GOSPODINOV et al[18] were too high to have any physical meaning and were excluded in this work. The estimated data from CORDFUNKE et al[17] were not adopted, since they were directly connected with the thermodynamic parameters.

The estimated thermodynamic properties at 298 K, i.e. the enthalpy of formation of BaZrO₃ $\Delta_f H(298) = (-1\,768.58 \pm 2)$ kJ/mol[13,15], the molar heat capacity $C_p(298) = (101.71 \pm 0.31)$ J/(mol·K)[19] and the standard entropy $S^\theta(298) = (124.7 \pm 2)$ J/(mol·K)[19] were adopted so that the evaluation can be carried out practically, but a low weight factor was applied to them.

The Gibbs energies of formation of BaZrO₃ relative to the pure oxides in the temperature range from 960 to 1 210 K, and from 1 180 to 1 320 K were determined by JOYAB et al[13] and LEVITSKII[15] using electromotive force, respectively. JOYAB et al[13] also reported the enthalpies of formation of BaZrO₃ from the component oxides in the temperature range from 960 to 1 210 K, which were in good agreement with the value at 1 060 K reported by MUROMACHI et al[20]. These data were not used in the optimization. However, they were compared with the calculated results in order to check the final modelling.

For the compounds Ba₂ZrO₄ and Ba₃Zr₂O₇, the enthalpies of formation from the component oxides at 298 K were determined[11, 21]. These data were adopted to optimize the parameters of the compounds.

All temperatures quoted in this work were converted into the International Temperature Scale of 1990[22]. The thermodynamic functions were calculated at the normal constant pressure.

3 Thermodynamic models

The Gibbs energy function $G_{\phi,i}^{\ominus}(T) = G_{\phi,i}(T) - H_i^{\ominus}$ for the component i ($i = \text{ZrO}_2, \text{BaO}$) in the phase ϕ is expressed by

$$G_{\phi,i}^{\ominus} = a + bT + cT \ln T + dT^2 + eT^{-1} + fT^3 + gT^7 + hT^{-9} \quad (1)$$

where H_i^{\ominus} is the molar enthalpy of the component i at 298.15 K and 101 325 Pa in its standard element reference state, and T is the absolute temperature. The last two terms in Eqn.(1) are used only outside the ranges of stability, the term gT^7 is relative to the liquid below the melting point and hT^{-9} to the solid phases above the melting point.

In the present work, the Gibbs energy functions of pure ZrO_2 , $G_1^{\ominus}(\text{ZrO}_2)$, $G_c^{\ominus}(\text{ZrO}_2)$, $G_t^{\ominus}(\text{ZrO}_2)$ and $G_m^{\ominus}(\text{ZrO}_2)$, were taken from the assessments of DU et al[23]. The Gibbs energy functions of BaO , $G_1^{\ominus}(\text{BaO})$ and $G_h^{\ominus}(\text{BaO})$ were consistent with those used by LU et al[24], which were little different from those of SGTE substance database since some modification was made. Here, l denotes liquid, c, t and m stand for cubic, tetragonal and monoclinic ZrO_2 , respectively, h represents halite BaO . The Gibbs energy functions employed in this work are expressed as

$$G_1^{\ominus}(\text{ZrO}_2) = \begin{cases} -1040370 + 382.6904T - 67.506T \ln T - 0.0049133T^2 + 635630T^{-1} + 2.978 \times 10^{-22}T^7 & (298 \text{ K} \leq T \leq 2983 \text{ K}) \\ -1060705.8 + 538.008T - 87.864T \ln T & (2983 \text{ K} \leq T \leq 6000 \text{ K}) \end{cases} \quad (2)$$

$$G_c^{\ominus}(\text{ZrO}_2) = \begin{cases} -1125234.1 + 496.72262T - 80T \ln T & (298 \text{ K} \leq T \leq 2983 \text{ K}) \\ -1151298.9 + 568.29043T - 87.864T \ln T + 4.87454 \times 10^{33}T^{-9} & (2983 \text{ K} \leq T \leq 6000 \text{ K}) \end{cases} \quad (3)$$

$$G_t^{\ominus}(\text{ZrO}_2) = \begin{cases} -1124404.1 + 495.89773T - 80.2998T \ln T + 0.00108741T^2 & (298 \text{ K} \leq T \leq 2983 \text{ K}) \\ -1161302.3 + 571.87337T - 87.864T \ln T + 8.71 \times 10^{33}T^{-9} & (2983 \text{ K} \leq T \leq 6000 \text{ K}) \end{cases} \quad (4)$$

$$G_m^{\ominus}(\text{ZrO}_2) = \begin{cases} -1125386.9 + 411.83491T - 67.5063T \ln T - 0.00491334T^2 + 635630T^{-1} & (298 \text{ K} < T < 2983 \text{ K}) \\ -1139046.7 + 564.80249T - 87.864T \ln T - 5.46242 \times 10^{33}T^{-9} & (2983 \text{ K} \leq T \leq 6000 \text{ K}) \end{cases} \quad (5)$$

$$G_1^{\ominus}(\text{BaO}) = \begin{cases} -504636.303 + 126373.536T^{-1} + 212.590092T - 45.367112T \ln T - 0.0088301228T^2 + 9.53812533 \times 10^{-7}T^3 & (298 \text{ K} \leq T \leq 900 \text{ K}) \\ -507499.47 + 390471.8T^{-1} + 251.681742T - 51.308392T \ln T - 0.003335694T^2 + 7.57304 \times 10^{-9}T^3 & (900 \text{ K} \leq T \leq 2286 \text{ K}) \end{cases} \quad (6)$$

$$G_h^{\ominus}(\text{BaO}) = \begin{cases} -563212.303 + 126373.536T^{-1} + 238.213889T - 45.367112T \ln T - 0.0088301228T^2 + 9.53812533 \times 10^{-7}T^3 & (298 \text{ K} \leq T \leq 900 \text{ K}) \\ -566075.47 + 390471.8T^{-1} + 277.305539T - 51.308392T \ln T - 0.003335694T^2 + 7.57304 \times 10^{-9}T^3 & (900 \text{ K} \leq T \leq 2286 \text{ K}) \\ -584226.131 + 398.668889T - 66.944T \ln T & (2286 \text{ K} \leq T \leq 3000 \text{ K}) \end{cases} \quad (7)$$

$$G_c^{\ominus}(\text{BaO}) = G_h^{\ominus}(\text{BaO}) + 29624.35 \quad (298 \text{ K} \leq T \leq 3000 \text{ K}) \quad (8)$$

$$G_t^{\ominus}(\text{BaO}) = G_h^{\ominus}(\text{BaO}) + 50739.69 \quad (298 \text{ K} \leq T \leq 3000 \text{ K}) \quad (9)$$

Due to the lack of experimental information, the Gibbs energies of the hypothetical meta-stable ZrO_2 and BaO were expressed relative to those of their stable structures:

$$G_{c(t,m)}^{\ominus}(\text{BaO}) = G_h^{\ominus}(\text{BaO}) + A_1 + B_1 \quad (10)$$

$$G_h^{\ominus}(\text{ZrO}_2) = G_m^{\ominus}(\text{ZrO}_2) + A_2 + B_2 \quad (11)$$

where the coefficients A_i and B_i ($i=1, 2$) are to be assessed by checking their influence on the calculated phase equilibria.

The liquid phase and solid solutions C_{SS} and T_{SS} were described by Redlich-Kister polynomials. The Gibbs energy for the liquid was expressed by

$$G_{l,m} - H^\ominus = (1-x)G_1^\ominus(\text{ZrO}_2) + xG_1^\ominus(\text{BaO}) + RT \cdot [x \ln x + (1-x) \ln(1-x)] + x(1-x)[a_0 + b_0T + (1-2x)(a_1 + b_1T) + \dots] \quad (12)$$

where H^\ominus is the abbreviation of $(1-x)H^\ominus(\text{ZrO}_2) + xH^\ominus(\text{BaO})$, R is the gas constant, and x is the molar fraction of BaO. The interactive parameters a_0 , b_0 , a_1 and b_1 are to be optimized. The C_{SS} and T_{SS} were described by an analogous equation. Due to the very limited solubility of ZrO_2 in halite BaO and BaO in m- ZrO_2 , the BaO_{SS} (halite BaO solid solution) and M_{SS} (monoclinic ZrO_2 solid solution) were treated as pure compounds in this work.

The compounds Ba_2ZrO_4 and $\text{Ba}_3\text{Zr}_2\text{O}_7$ were modelled as stoichiometric phases due to the very limited information. The Gibbs energy of Ba_2ZrO_4 was given by

$$G^\ominus(\text{Ba}_2\text{ZrO}_4) = A_3 + B_3T + 2G_h^\ominus(\text{BaO}) + G_m^\ominus(\text{ZrO}_2) \quad (13)$$

where A_3 and B_3 are connected with the enthalpy and entropy of formation from pure oxides in solid state, which will be evaluated in the course of optimization. The analogous equation, Eqn.(14) can be written for the Gibbs energy of $\text{Ba}_3\text{Zr}_2\text{O}_7$:

$$G_s^\ominus(\text{Ba}_3\text{Zr}_2\text{O}_7) = A_4 + B_4T + 3G_h^\ominus(\text{BaO}) + 2G_m^\ominus(\text{ZrO}_2) \quad (14)$$

Since there were experimental thermodynamic data for BaZrO_3 in a wide temperature range[12–19], it was preferable to express its Gibbs energies relative to the SER state, and the following equation was used:

$$G_s^\ominus(\text{BaZrO}_2) = a_1 + b_1T + c_1T \ln T + d_1T^2 + e_1T^{-1} \quad (15)$$

where the coefficients c_1 , d_1 and e_1 can be evaluated mainly from the measured enthalpy increments[14–16].

4 Optimization procedure

The Thermo-calc software package was used to optimize the thermodynamic parameters. The critically selected experimental data were employed with some certain weights, and the weights can be changed systematically until most of the experimental data were accounted for within the claimed uncertainty limits.

Optimization was started with the perovskite phase BaZrO_3 . By using the measured thermodynamic data [14–16] selected in the above section, the numerical values of the coefficients c_1 , d_1 and e_1 in Eqn.(15) describing the Gibbs energy function of BaZrO_3 could be critically evaluated. Once c_1 , d_1 and e_1 have been estimated, the coefficients a_1 and b_1 in Eqn.(15) could be

estimated from the reported heat capacity, entropy, and enthalpy of formation of BaZrO_3 at 298 K[13, 19]. The obtained coefficients were subjected to further optimization, the calculated thermodynamic properties of BaZrO_3 at 298 K were compared with the literature available data[13,15, 19–20] in Table 1.

Table 1 Estimated thermodynamic properties of perovskite phase BaZrO_3 at 298 K compared with measured values

Data source	$\Delta_f H/$ (kJ·mol ⁻¹)	$S/$ (J·mol ⁻¹ ·K ⁻¹)	$C_p/$ (J·mol ⁻¹ ·K ⁻¹)
This work	-1 775.61	124.62	101.78
Ref.[19]	-1 768.58[13]	124.7±2	101.71±0.31

Since the liquidus has been measured over a wide composition and temperature region[6–8], the optimization for its thermodynamic parameters is very important to the successful description of the ZrO_2 -BaO system. And since there are not any independent data for the liquid phase, such as experimental enthalpy of the mixture, the C_{SS} , T_{SS} and Ba_2ZrO_4 should be modelled to reproduce the liquidus throughout the system. In this case, a suitable number of the thermodynamic parameters for each phase was really important to the optimization. It was found that the parameters a_0 , b_0 , a_1 and b_1 in Eqn.(12) should be introduced to describe the properties of the liquid satisfactorily. For the C_{SS} and T_{SS} phases, the experimental data were few, so the regular substitutional parameters were introduced to describe the relative properties. The coefficients A_3 and B_3 in Eqn.(13), were used to describe the compounds Ba_2ZrO_4 . With most of experimental data[5–8] reproduced quite well, special attention was paid to the compound $\text{Ba}_3\text{Zr}_2\text{O}_7$ to check the possibility of its existence. Because there were not any phase diagram data about the compound $\text{Ba}_3\text{Zr}_2\text{O}_7$, the estimated enthalpy of formation of $\text{Ba}_3\text{Zr}_2\text{O}_7$ from the component oxides at 298 K[11] was used to optimize the coefficients A_4 and B_4 in Eqn.(14).

All the thermodynamic parameters were finally evaluated together and slight adjustments were made to give the best description of the system.

5 Results and discussion

The present evaluated thermodynamic parameters of the ZrO_2 -BaO binary system are as follows:

The interaction parameters of liquid:

$$a_0 = -357\,817.66, b_0 = 73.4$$

$$a_1 = -282\,549.78, b_1 = 93.9$$

The interaction parameters of the C_{SS} phase:

$$a_0 = -104\,672.96, b_0 = -8.4$$

The interaction parameters of the T_{SS} phase:

$$a_0 = -94\,433$$

Gibbs energy of BaZrO_3 :

$$G_s^\ominus(\text{BaZrO}_3) = -1\,818\,096.5 + 688.86\,T - 119.3\,T \ln T - 0.006\,44\,T^2 + 948\,187.2\,T^{-1}$$

Gibbs energy of Ba_2ZrO_4 :

$$G_s^\ominus(\text{Ba}_2\text{ZrO}_4) = -209\,954.8 + 15.9T + 2G_h^\ominus(\text{BaO}) + G_m^\ominus(\text{ZrO}_2)$$

Gibbs energy of $\text{Ba}_3\text{Zr}_2\text{O}_7$:

$$G_s^\ominus(\text{Ba}_3\text{Zr}_2\text{O}_7) = -361\,924.9 + 30.3T + 3G_h^\ominus(\text{BaO}) + 2G_m^\ominus(\text{ZrO}_2)$$

A comparison between the calculated ZrO_2 - BaO phase diagram and that measured by ADAMSON et al [5–8] is shown in Fig.1. The calculated invariant reaction temperatures are compared with the experimental ones [5–8] in Table 2. It can be seen from Table 2 that the present modelling can account for the measured invariant temperatures [5–8] quite well. The eutectoid reactions $T_{SS} \rightleftharpoons M_{SS} + \text{BaZrO}_3$ at 1 454 K and the peritectoid reaction $\text{Ba}_3\text{Zr}_2\text{O}_7 \rightleftharpoons \text{Ba}_2\text{ZrO}_4 + \text{BaZrO}_3$ at 1 650 K are the results of calculations. These reactions are not easy to be experimentally detected because of the following reasons: 1) it is not easy to detect $\text{Ba}_3\text{Zr}_2\text{O}_7$ from Ba_2ZrO_4 or BaZrO_3 due to the near composition; 2) it is very difficult for oxides to achieve equilibrium at a low temperature such as 1 454 K. Better knowledge on the phase equilibria at low temperatures is useful for further refinement of the ZrO_2 - BaO system.

In Fig.2, the calculated $H(T) - H(298)$ for BaZrO_3 is compared with the experimental values [14–16]. The agreement between the calculated and measured values of $H(T) - H(298)$ is acceptable within the experimental

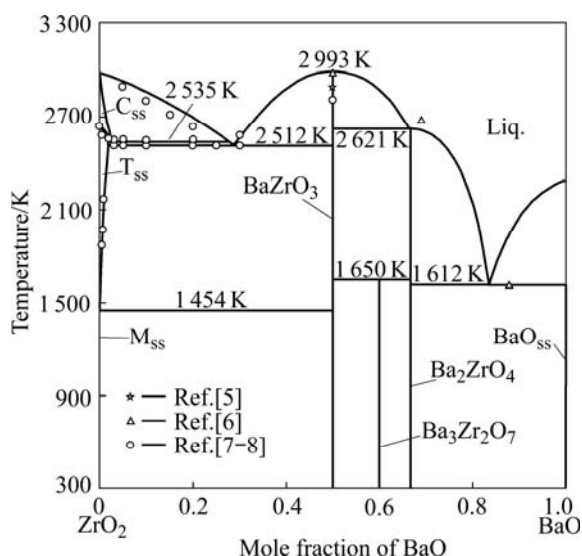


Fig.1 Comparison between calculated ZrO_2 - BaO phase diagram and experimental data in Refs.[5–8]

Table 2 Comparison between calculated and measured coordinates of invariant temperatures in ZrO_2 - BaO system

Equilibrium	Invariant temperature/K			
	Ref.[5]	Ref.[6]	Ref.[7–8]	This work
$L + T_{SS} \rightleftharpoons C_{SS}$			2 553	2 535
$L \rightleftharpoons T_{SS} + \text{BaZrO}_3$			2 513	2 512
$L \rightleftharpoons \text{BaZrO}_3$	2 978	2 978	2 893	2 993
$L + \text{BaZrO}_3 \rightleftharpoons \text{Ba}_2\text{ZrO}_4$		$\approx 2\,673$		2 621
$L \rightleftharpoons \text{Ba}_2\text{ZrO}_4 + \text{BaO}_{SS}$		1 608		1 612
$\text{BaZrO}_3 + \text{Ba}_2\text{ZrO}_4 \rightleftharpoons \text{Ba}_3\text{Zr}_2\text{O}_7$				1 650
$T_{SS} \rightleftharpoons M_{SS} + \text{BaZrO}_3$				1 454

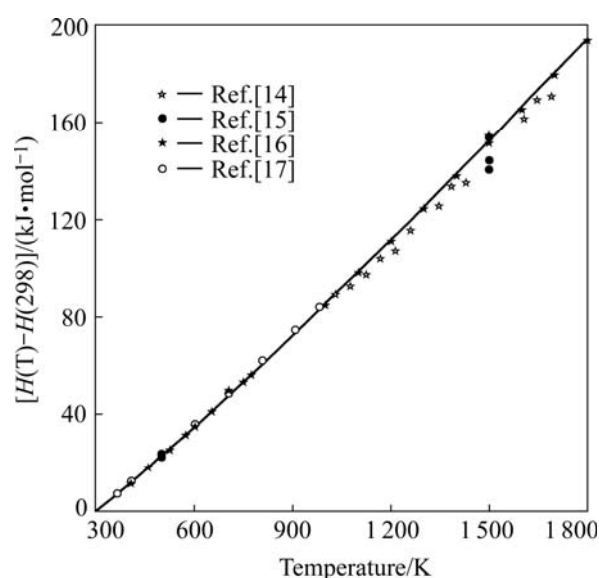


Fig.2 Comparison of calculated $H(T) - H(298)$ of BaZrO_3 with measured data [14–16]

uncertainties.

The calculated Gibbs energy and enthalpy of formation for BaZrO_3 from the pure oxides are compared with the experimental data [13, 15, 19–20] in Tables 3 and 4, respectively. The calculation can describe these experimental data reasonably although they are not used in the present optimization.

Table 3 Gibbs energy of formation of BaZrO_3 from component oxides compared with measured values in Refs.[13, 15]

Temperature/K	$G/(\text{kJ}\cdot\text{mol}^{-1})$		
	Ref.[13]	Ref.[15]	This work
1 000	-129.55	-136.4 ± 4	-128.543
1 100	-129.73	-136.6 ± 4	-128.573
1 200	-129.91	-136.8 ± 4	-128.572

The present calculated enthalpy of formation for the compounds Ba_2ZrO_4 and $\text{Ba}_3\text{Zr}_2\text{O}_7$ from the component oxides at 298 K are compared with the literature data in Table 5, a good agreement is obtained.

Table 4 Enthalpy of formation of BaZrO₃ from component oxides compared with measured values in Refs.[13, 20]

Temperature/K	$H/(\text{kJ}\cdot\text{mol}^{-1})$		
	Ref.[13]	Ref.[20]	This work
298	-125.56 ± 2		-126.93
1 085	-127.76 ± 2		-128.23
1 060		-123.9 ± 4	-128.28

Table 5 Comparison of enthalpy of formation for Ba₂ZrO₄ and Ba₃Zr₂O₇ from component oxides at 298 K

Compound	$H/(\text{kJ}\cdot\text{mol}^{-1})$	
	Ref.[20]	This work
Ba ₂ ZrO ₄	$-2\,421.3 \pm 1$	-2 406.7
Ba ₃ Zr ₂ O ₇	$-4\,204.3 \pm 5.7$	-4 207.4

6 Conclusions

1) The thermodynamic function of the perovskite phase BaZrO₃ is critically evaluated with all reliable experimental data reproduced within the estimated experimental uncertainty. A set of reasonable and self-consistent thermodynamic parameters for the ZrO₂-BaO binary system is obtained. The calculated phase diagram and thermodynamic properties data are in good correspondence with the experimental information.

2) The compound Ba₃Zr₂O₇ decomposes to Ba₂ZrO₄ and BaZrO₃ at 1 650 K. Thermodynamic and phase diagram measurements on Ba₃Zr₂O₇ are useful for further refinement of the compound and the ZrO₂-BaO system.

References

- [1] RUFF O, EBERT F. Refractory ceramics (I): The form of zirconium dioxide [J]. *Z Anorg Allg Chem*, 1929, 180: 19–41.
- [2] GARVIE R C, HANNINK R H, PASCOE R T. Ceramic steel [J]. *Nature*, 1975, 258: 703–704.
- [3] PORTER D L, HEUER A H. Mechanisms of toughening partially stabilized zirconia (PSZ) [J]. *J Am Ceram Soc*, 1977, 60: 183–184.
- [4] GUPTA T K, LANGE FF, BECHTOLD J H. Effect of stress-induced phase transformation on the properties of polycrystalline zirconia containing metastable tetragonal phase [J]. *J Mater Sci*, 1978, 13: 1464–1470.
- [5] ADAMSON M G, AITKEN E A, CAPUTI R W. Experimental and thermodynamic evaluation of the melting behavior of irradiated oxide fuels [J]. *J Nuclear Materials*, 1985, 130: 349–365.
- [6] PASCHOAL J O A, KLEYKAMP H, THÜMMER F. Phase equilibria in the pseudo-quaternary BaO-UO₂-ZrO₂-MoO₂ system [J]. *J Nuclear Materials*, 1987, 151: 10–21.
- [7] SHEVCHENKO A V, LOPATO LM, GERASIMYUK G I, ZAITSEVA Z A. Reactions in the systems hafnium dioxide-strontium oxides, hafnium dioxide-barium oxide and zirconium dioxide-barium oxide in the regions with a high content of a hafnium dioxide (zirconium dioxide) [J]. *Izv Akad Nauk SSSR Neorg Mater*, 1987, 23(9): 1495.
- [8] WARTENBERG H V, GURR W. A compilation of phase-rule diagrams of interest to the ceramist and silicate technologist [J]. *Z Anorg Allg Chem*, 1931, 196: 374–383.
- [9] APPENDINO P, RAMONDA G. New compounds in the barium oxide-zirconium oxide system [J]. *Ann Chim*, 1971, 61(1): 61–65.
- [10] DASH S, SINGH Z, PRASAD R, SOOD D D. The standard molar Gibbs free energy of formation of Ba₃Zr₂O₇ (s) [J]. *J Chem Therm*, 1994, 26: 737–744.
- [11] MARUSHKIN K N, ALIKHANYAN A S, GRINBERG Y K, KURTASOV O V, GORGORAKI V I. Vapor composition in the barium oxide-zirconium dioxide system and thermodynamic properties of barium zirconates [J]. *Zh Nerg Khim*, 1989, 34(6): 1592–1597.
- [12] MATHEWS M D, MIRZA E B, MOMIN A C. High-temperature X-ray diffractometric of CaZrO₃, SrZrO₃ and BaZrO₃ [J]. *J Mater Sci Lett*, 1991, 10: 305–306.
- [13] JOCAB K T, WASEDA Y. Potentiometric determination of the Gibbs energies of formation of SrZrO₃ and BaZrO₃ [J]. *Metall Mater Trans*, 1995, 26B: 775–781.
- [14] NAGARAJAN K, SAHA R, BABU R, MATHEWS C K. Thermodynamic functions of barium and strontium zirconates from calorimetric measurements [J]. *Therm Acta*, 1985, 90: 297–304.
- [15] LEVITSKII V A. Thermodynamics of double oxides (I): Some aspects of the use of CaF₂-type electrolyte for thermodynamic study of compounds based on oxides of alkaline earth metals [J]. *J Solid State Chem*, 1978, 25: 9–22.
- [16] BANERJEE A, DASH S, PRASAD R, SOOD D D. Enthalpy increments of strontium and barium zirconates [J]. *Therm Acta*, 1997, 298: 59–64.
- [17] CORDFUNKE E H P, KONINGS R J M. Enthalpy increments of barium zirconate, BaZrO₃, and an assessment of its thermochemical properties [J]. *Therm Acta*, 1989, 156: 45–51.
- [18] GOSPODINOV G G, MARCHEV V M. The temperature relations of the thermodynamic quantities of Ca, Sr, Ba, and Pb zirconates [J]. *Therm Acta*, 1993, 222: 137–141.
- [19] KING E G, WELLER W W. Thermochemistry and Thermodynamic Properties of Substances [R]. US Bur Mines Rept 5571 Invest, 1960.
- [20] MUROMACHI E T, NAVROTSKY A. Energetics of compounds (A²⁺B⁴⁺O₃) with the perovskite structure [J]. *J Solid State Chem*, 1988, 72: 244–256.
- [21] DASH S, SINGH Z, PRASAD R, SOOD D D. The determination of the standard molar Gibbs free energy of formation of Ba₂ZrO₄ [J]. *J Chem Therm*, 1994, 26: 745–750.
- [22] THOMAS H P. The international temperature scale of 1990 (ITS-90) [J]. *Metrologia*, 1990, 27: 3–10.
- [23] DU Y, JIN Z P. Optimization and calculation of the ZrO₂-MgO system [J]. *Calphad*, 1991, 15(1): 63–73.
- [24] LU X G, JIN Z P. Thermodynamic assessment of the BaO-TiO₂ quasibinary system [J]. *Calphad*, 2000, 24(3): 319–338.

(Edited by CHEN Wei-ping)