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Thermodynamic properties of ternary barium oxides ☆

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Abstract

The vapor pressure over the two-phase mixture of $CeO_2 + BaCeO_3$ has been measured by mass spectrometry in the temperature range 1774–1947 K. BaO(g) only was identified as being the main gas species. From the vapor pressure of BaO(g) over $CeO_2 + BaCeO_3$, the standard molar enthalpy of formation of $BaCeO_3$ has been determined by second and third law treatments and is compared with those values calculated by the use of Aronson's semiempirical equation in this study and obtained previously by solution calorimetry. The standard molar Gibbs energies of formation of $BaCeO_3$, $BaZrO_3$ and Ba_2ZrO_4 have also been determined as a function of temperature from the respective vapor pressures of BaO(g) over $CeO_2 + BaCeO_3$ in this study and those over $ZrO_2 + BaZrO_3$ and $BaZrO_3 + Ba_2ZrO_4$ previously determined by the present author and co-workers. The experimental values of the standard molar Gibbs energy of formation and the standard molar enthalpy of formation of other ternary barium oxides such as $BaMoO_3$, $BaMoO_4$, $BaUO_3$, $BaUO_4$, $BaTiO_3$, Ba_2TiO_4, $BaThO_3$ and $BaPuO_3$ are summarized and the latter is compared with calculated values from Aronson's equation. The relative stability of barium perovskite oxides is briefly discussed from the Goldschmidt tolerance factors and the molar enthalpies of formation of the perovskite oxides from the constituent binary oxides.

Keywords: Goldschmidt tolerance factor; Heat capacity; Ternary barium oxide; Thermodynamics; Vapour pressure

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1. Introduction

Two groups of fission-produced compounds are generally found in irradiated oxide fuels [1]. One group, often described as the "white inclusion", is metallic precipitate consisting of molybdenum, technetium, ruthenium, rhodium and palladium. The other phase encountered is mainly composed of a multicomponent perovskite-type oxide phase with composition ABO_3. Here A represents fission-produced elements such as barium and strontium, whereas B denotes zirconium, molybdenum and rare earth metals produced by fission, and uranium and plutonium from the fuel. The composition of these phases depends largely on the fission yield, the temperature gradient in the fuel pin, the burnup and so on. The titanium perovskite phase is also of importance as one of the main phases in the ceramics (synroc, i.e. synthesized rock) designed for solidification of high-level nuclear waste. The thermodynamic properties of these ternary perovskite oxides are very important for the understanding of the thermal stability. Few thermodynamic studies have, however, been reported for the perovskite-type and the related oxides containing barium at high temperatures [2-9]. For $BaCeO_3$ only the enthalpy measurement using a high temperature differential calorimeter [4] and the standard molar enthalpy of formation by solution calorimetry [9] have been reported.

In the present study, the vapor pressure over the two-phase mixture of $CeO_2 + BaCeO_3$ was measured by mass spectrometry in the temperature range 1774-1947 K in an attempt to derive the standard molar enthalpy of formation and the standard molar Gibbs energy of formation of $BaCeO_3$. The standard molar Gibbs energies of formation of $BaZrO_3$ and Ba_2ZrO_4 have also been determined as a function of temperature using the vapor pressures over the two-phase mixtures of $ZrO_2 + BaZrO_3$ and $BaZrO_3 + Ba_2ZrO_4$, repectively, previously measured by the present author and co-workers [8] and are compared with those of other ternary barium oxides. The standard molar enthalpies of formation of $BaCeO_3$, $BaZrO_3$, Ba_2ZrO_4, $BaTiO_3$, Ba_2TiO_4, $BaMoO_3$, $BaMoO_4$, $BaUO_3$, $BaUO_4$, $BaThO_3$ and $BaPuO_3$ are summarized to compare with those calculated from Aronson's semiempirical equation. The relative stabilities of the barium perovskite oxides are briefly discussed from the Goldschmidt tolerance factors and the molar enthalpies of formation from the constituent binary oxides.

2. Experimental

The $BaCeO_3$ powder was prepared by heating a mixture of 99.99% pure powder of $BaCO_3$ and CeO_2 supplied by Rare Metallic Co. Ltd., Japan, at 1373 K for 30 h in air, after which the powder was pressed into a pellet. The pellet was finally heated at 1473 K for 20 h in air. The $BaCeO_3$ powder prepared by pulverizing the pellet and CeO_2 powder was used for the vapor pressure measurement. Before and after the vapor pressure measurement, the X-ray diffraction pattern of the sample powder confirmed the presence of two phases: perovskite-type $BaCeO_3$ and fluorite-type CeO_2.

The vapor pressures were measured with a time-of-flight mass spectrometer (CVC model MA-2) equipped with a molybdenum Knudsen cell lined with rhenium in a tungsten holder. The sample was heated in the tungsten holder by electron bombardment. The molybdenum cell lined with rhenium was used in order to avoid chemical interaction between barium cerates and the Knudsen cell. The Knudsen cell is of 7 mm internal diameter, 7 mm height and the diameter of the effusion orifice is 0.5 mm. The electron energy used to ionize the gaseous species was 14 eV. The absolute pressure was determined by comparing the intensity of the ionic current of BaO^+ with that of silver over pure silver metal used as a standard. The values of the atomic ionization cross sections of silver, barium and oxygen were taken from the table by Mann [10] and the additivity principle suggested by Otvos and Stevenson [11] was used to calculate the molecular cross-section of BaO. The relative multiplier gain was calculated by assuming inverse proportionality to the square root of the mass of the vaporizing species [12]. Temperature measurement was made with a Leeds and Northrup disappearing-filament optical pyrometer, of which the error was determined to be ±5 K by comparison with the melting points of silver and platinum metals and EMF values of a Pt–Pt 13% Rh thermocouple. Observation was made through an orifice of the Knudsen cell.

3. Results and discussion

3.1. Ionization efficiency curves

BaO was identified as the predominant vapor species over the two-phase mixture of $CeO_2 + BaCeO_3$. The ionization efficiency curve of BaO^+ over $BaCeO_3 + CeO_2$ is shown in Fig. 1, where the ion intensity of BaO^+ gas species was normalized with that at 14 eV. By the linear extrapolation of the ionization efficiency curves in this figure, the appearance energy of BaO^+ was determined to be 6.5 ± 0.2 eV, which is in excellent agreement with the ionization energy of BaO^+ (6.5 eV [2,13]), indicating a simple ionization of gas species. In order to avoid fragmentation of gas species and also to provide a sufficiently high ion current, an ionization electron energy of 14 eV was chosen for the measurements in this study. The ion intensity used for the calculation of the vapor pressure of BaO(g) was obtained by converting the ion intensity at 14 eV to the corresponding value at 9.5 eV (3.0 eV higher than the appearance energy), according to the ionization efficiency curve shown in Fig. 1, in order to determine the precise vapor pressure. The absolute value of the vapor pressure of BaO(g) was determined by comparing the intensity of BaO^+ thus obtained with that of Ag^+ at 12.6 eV (3.0 eV higher than the appearance energy of Ag^+).

3.2. Vapor pressure over the two-phase mixture of CeO_2 and $BaCeO_3$

The partial vapor pressure of BaO(g) was only measured and that of Ba(g) could not be measured over $CeO_2 + BaCeO_3$ in this study, probably due to the vapor

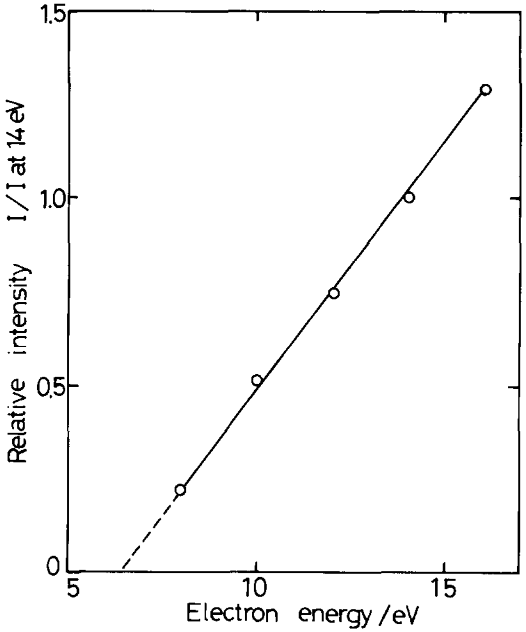

Fig. 1. Ionization efficiency curve of BaO^+ over the two-phase mixture of $CeO_2 + BaCeO_3$.

pressure of Ba(g) being too low compared to the detection limit of our mass spectrometer, as was the case for the two-phase mixture of $ZrO_2 + BaZrO_3$ [8]. The partial vapor pressure of BaO(g) over $CeO_2 + BaCeO_3$ obtained in this study is shown in Fig. 2 together with that over $ZrO_2 + BaZrO_3$ previously reported by the present author and co-workers [8] for comparison. The equation for the partial vapor pressure of BaO(g) obtained from a least squares treatment is given in Table 1 together with those over the two-phase mixtures of $ZrO_2 + BaZrO_3$ [8]. As seen in Fig. 2 the vapor pressure of BaO(g) over $CeO_2 + BaCeO_3$ obtained in this study is higher than that over $ZrO_2 + BaZrO_3$.

3.3. *Thermodynamic quantities*

3.3.1. *Enthalpies of vaporization over $CeO_2 + BaCeO_3$*

From the identification of the predominant vapor species of BaO(g) over $CeO_2 + BaCeO_3$, the vaporization reaction can be expressed as

$$BaCeO_3(s) = BaO(g) + CeO_2(s) \tag{1}$$

The second law enthalpy of vaporization of reaction (1) for the median temperature of the measurements is obtained directly from the slope of the logarithmic plot of the vapor pressure of BaO(g) versus inverse temperature and is then converted to the value at standard conditions by using the change in heat content (i.e. enthalpy increment $\Delta(H_{T_m} - H_{298})$ where T_m is the median temperature) for

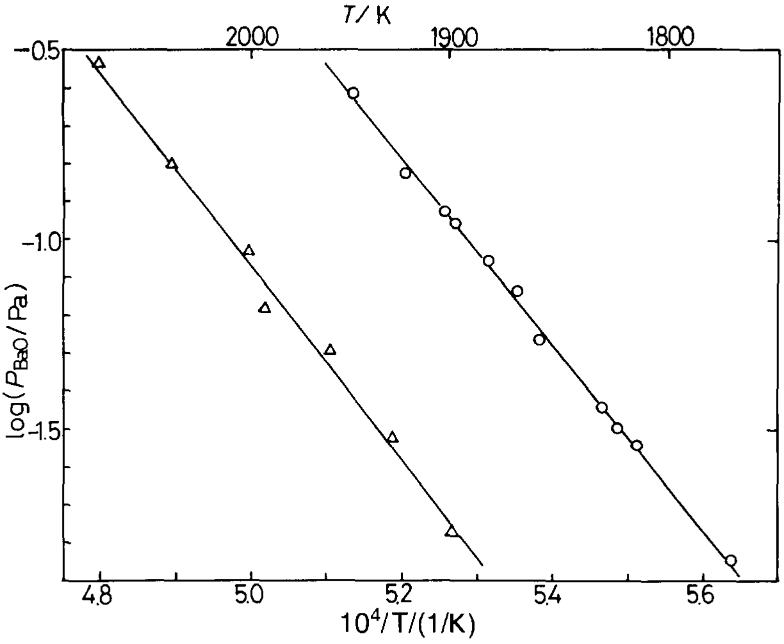

Fig. 2. Vapor pressure of BaO(g) over the two-phase mixture of $CeO_2 + BaCeO_3$. —○—, $CeO_2 +$ $BaCeO_3$ in this study; —△—, $ZrO_2 + BaZrO_3$ in our previous study [8].

Table 1
Equations for partial vapor pressures [a]

System	BaO(g) A	BaO(g) B	Temp. range/ K	Reference
$CeO_2 + BaCeO_3$	24.54 ± 0.12	11.97 ± 0.22	1774-1947	This study
$ZrO_2 + BaZrO_3$	25.64 ± 0.70	11.75 ± 0.94	1899-2085	[8]

[a] $\log(P/\mathrm{Pa}) = -(A \times 10^3)/T + B$.

reaction (1). The third law enthalpy is taken as the averaged value of the standard enthalpy derived from each individual experimental data point with the relation

$$-(R \ln P_{BaO} + \Delta\mathrm{fef})T = \Delta_f H^{\ominus}_{298} \quad (2)$$

where Δfef is the change in the free energy function for reaction (1). The heat content and the free energy function of $BaCeO_3$(s) used for the calculation were taken from the table recently reported by Saha et al. [4] using high temperature differential calorimetry. The second and the third law enthalpies of reaction (1) are summarized in Table 2 and the third law enthalpies for the reaction (1) derived from each data point are given in Table 3. As seen in Tables 2 and 3 the second law

Table 2
Enthalpy and entropy of vaporization

Samples	Gas species	T_{med}/ K	$\Delta_{\mathrm{V}}H_{T_{\mathrm{m}}}$ (2nd)/ (kJ mol^{-1})	$\Delta_{\mathrm{V}}S_{T_{\mathrm{m}}}$ (2nd)/ (J K^{-1} mol^{-1})	$\Delta_{\mathrm{V}}H^{\ominus}_{298}$ (2nd)/ (kJ mol^{-1})	$\Delta_{\mathrm{V}}H^{\ominus}_{298}$ (3rd)/ (kJ mol^{-1})	Reference
$CeO_2 + BaCeO_3$	BaO(g)	1861	469.9 ± 2.4	133.4 ± 4.2	497.5 ± 2.4 [a]	499.3 ± 0.7 [a]	This study
$ZrO_2 + BaZrO_3$	BaO(g)	1992	491.0 ± 13.5	129.0 ± 18.0	514.8 ± 13.5 [b]	515.4 ± 0.8 [b]	[8]
					512.6 ± 13.5 [c]	523.6 ± 0.9 [c]	[8]

[a] Calculated with the assessed values of BaO(g) [14], $CeO_2(s)$ [15] and $BaCeO_3(s)$ [4]. [b] Calculated with the assessed values in Ref. [14]. [c] Calculated with the assessed values in Ref. [15].

Table 3
Third law enthalpies of vaporization for reaction (1)

Temp./ K	$-R \ln K_{\mathrm{P}}$/ (J K^{-1} mol^{-1})	−fef/ (J K^{-1} mol^{-1})	$\Delta_{\mathrm{V}}H^{\ominus}_{298}$/ (kJ mol^{-1})
1774	232.8	149.9	498.7
1815	227.7	149.6	499.2
1823	226.9	149.5	499.5
1830	226.1	149.5	499.6
1858	223.0	149.2	500.3
1868	219.7	149.2	498.3
1881	218.4	149.1	498.7
1897	216.5	148.9	499.0
1903	216.1	148.9	499.4
1922	214.5	148.7	500.3
1947	209.5	148.5	498.7
			Av. 499.3 ± 0.7

enthalpies of vaporization for reaction (1) are in good agreement with the third law values, showing the reliability of our vapor pressure measurements.

3.3.2. Standard molar enthalpy and Gibbs energy of formation

The combination of the second and the third law enthalpies of vaporization for reaction (1), 497.5 ± 2.4 and 499.3 ± 0.7 kJ mol^{-1} in Table 2 with the enthalpies of formation of BaO(g) [14] and CeO_2 [15] yields the standard molar enthalpy of formation of $BaCeO_3(s)$, $\Delta_{\mathrm{f}}H^{\ominus}_{298}(BaCeO_3(s)) = -1713.8 \pm 2.4$ and -1715.6 ± 0.7 kJ mol^{-1}, respectively. The standard molar enthalpies of formation of other ternary barium oxide such as $BaCeO_3$ [9], $BaZrO_3$ [8], Ba_2ZrO_4 [8], $BaMoO_3$ [16], $BaMoO_4$ [17], $BaTiO_3$ [15] and Ba_2TiO_4 [15], $BaUO_3$ [9], $BaThO_3$ [9] and $BaPuO_3$ [9] previously determined are summarized in Table 4. The standard molar enthalpies of formation of these oxides calculated on the basis of Aronson's semiempirical equation [18] by the present author in this study and also by Aronson himself [18] are given in Table 4 for comparison. It is seen in the table that the standard molar

Table 4
Standard molar enthalpies of formation

Compound	$\Delta_f H^\ominus_{298}$(exp.)/ (kJ mol^{-1})	$\Delta_f H^\ominus_{298}$(calc.)/ (kJ mol^{-1})
$BaCeO_3$	−1716 [a] −1689 [9]	−1749 [b]
$BaZrO_3$	−1747 [8]	−1749 [18]
Ba_2ZrO_4	−2269 [8]	−2384 [b]
$BaMoO_3$	−1258 [16]	−1397 [b]
$BaTiO_3$	−1660 [15]	−1643 [18]
Ba_2TiO_4	−2243 [15]	−2286 [18]
$BaMoO_4$	−1546 [17]	−1772 [b]
$BaUO_3$	−1695 [20]	−1743 [b]
$BaThO_3$	−1800 [c]	−1846 [b]
$BaPuO_3$	−1689 [c]	−1722 [b]

[a] Experimental value (third-law value) in this study. [b] Calculated in this study on the basis of Aronson's equation. [c] Calculated by the present author from the data in Ref. [20].

enthalpies of formation of the ternary barium oxides determined experimentally are in fairly good agreement with those calculated from Aronson's equation within 50 kJ mol^{-1} except for $BaCeO_3$ [9], $BaMoO_3$ [16] and $BaMoO_4$ [17], indicating the value of the standard molar enthalpy of formation of $BaCeO_3$ determined in this study is more reliable than the previous one [9]. It is noted that among the ternary perovskite oxides, the stability of $BaThO_3$ is seen to be largest and those of $BaUO_3$ and $BaPuO_3$ seem to be similar to that of $BaTiO_3$ according to the sequence of the standard molar enthalpy of formation in Table 4, but the contradictory experimental evidence that these three oxides were difficult to prepare free of other second phase compounds has been reported [9,21,22].

From the crystallographic point of view, the perovskite structure ABX_3 occurs only within the range $0.75 < t < 1.00$, where t is the Goldschmidt tolerance factor [23]: $t = (R_A + R_X)/[\sqrt{2}(R_B + R_X)]$, where R_A, R_B and R_X are ionic radii of cation A in twelvefold coordination, cation B in sixfold coordination and anion, respectively. In addition to this useful parameter t, the correlation of two other parameters with t, i.e. the size of ionic radius of cation B and the molar enthalpy of formation of the perovskite oxides from the constituent binary oxides (ΔH) has been proposed for the barium perovskite oxides (A is Ba and X is O) by Morss and co-workers [9,20], although the sequence of ΔH summarized by them is not in accordance with that of t for the cases where B is Mo and Ce. In this study the values of ΔH were calculated from the values of $\Delta_f H^\ominus_{298}$ given in Table 4 and are summarized in Table 5. It is seen in Table 5 that the molar enthalpy of formation ΔH in this study decreases in the order of decreasing tolerance factor and of increasing ionic radius of cation B, indicating the reliability of our present experimental value for $\Delta_f H^\ominus_{298}(BaCeO_3(s))$ and the value of $\Delta_f H^\ominus_{298}(BaMoO_3(s))$ [16]. The marginal stability of $BaThO_3$ and $BaUO_3$ is clearly shown in Table 5, which is in good accord with the difficulty of preparing the single-phase compound.

Table 5
Structural and thermodynamic parameters for $BaMO_3$

Compound	$R_M/(10^{-1}$ nm) [a]	t [b]	$\Delta H/(\mathrm{kJ\ mol^{-1}})$ [c]	Reference
$BaTiO_3$	0.61	0.97	−162	This study
			−163	[20]
$BaMoO_3$	0.65	0.95	−116	This study
			−92	[20]
$BaZrO_3$	0.72	0.92	−96	This study
			−126	[20]
$BaPuO_3$	0.86	0.860	(−80) [d]	[20]
$BaCeO_3$	0.87	0.856	−74	This study [e]
			−52	[20]
$BaUO_3$	0.89	0.849	−57	[20]
$BaThO_3$	0.94	0.831	(−20) [d]	[20]

[a] Ionic radii of M^{4+} in sixfold coordination from Shannon [24]. [b] Goldschmidt tolerance factor [20]. [c] ΔH from the constituent binary oxides. [d] Estimated values by Morss [20]. [e] Calculated by the present author from previous data in Ref. [16].

The standard molar Gibbs energy of formation ($\Delta_f G^{\circ}_T$) can be calculated from the relation

$$\Delta_f G^{\circ}_T = \Delta_f H^{\circ}_{298} + T\Delta \mathrm{fef} \qquad (3)$$

The temperature dependences of $\Delta_f G^{\circ}_T$ of $BaMO_3$ (M is Ce, Zr) and Ba_2ZrO_4 calculated from Eq. (3) in this study are summarized in Table 6 together with those of $BaMO_3$ (M is Ti, Mo), Ba_2TiO_4 and $BaMO_4$ (M is Mo, U). The thermodynamic quantities including $\Delta_f G^{\circ}_T$ and $\Delta_f H^{\circ}_T$ are given as a function of temperature for $BaCeO_3$(s), $BaZrO_4$(s) and Ba_2ZrO_4(s) in Tables 7, 8 and 9, respectively.

Table 6
Standard molar Gibbs energy of formation: $\Delta_f G^{\circ} = A + B(T/\mathrm{K})$

Compound	$\Delta_f G^{\circ}/(\mathrm{kJ\ mol^{-1}})$		Temp. range/K	Reference
	A	B		
$BaCeO_3$	−1717.4 ± 0.9	0.30833 ± 0.00020	298.15–1800	This study [a]
$BaZrO_3$	−1747.9 ± 0.4	0.28380 ± 0.00008	298.15–2000	This study [a]
Ba_2ZrO_4	−2270.5 ± 0.8	0.36078 ± 0.00015	298.15–2000	This study [a]
$BaTiO_3$	−1658.3 ± 0.3	0.28792 ± 0.00007	298.15–1700	Barin [15] [b]
Ba_2TiO_4	−2243.5 ± 0.6	0.36629 ± 0.00010	298.15–2133	Barin [15] [b]
$BaUO_4$	−1994.8 ± 0.3	0.34762 ± 0.00012	298.15–1100	Barin [15] [b]
$BaMoO_3$	−1256.1	0.2922	1192–1360	[16]
$BaMoO_4$	−1554.8	0.3623	1192–1690	This study [c]

[a] Calculated from vapor pressure data measured by the present author. [b] Calculated by the present author from the table by Barin [15]. [c] Calculated from the Gibbs free energy change for the oxidation of $BaMoO_3$ to $BaMoO_4$ [19] and $\Delta_f G(BaMoO_3(s))$ reported by Dash et al. [16].

Table 7
Thermodynamic quantities of $BaCeO_3(s)$

T/K	C_p/ (J K mol^{-1})	$(H_T^\circ - H_{298}^\circ)$/ (kJ mol^{-1})	S_T°/ (J K^{-1} mol^{-1})	$(-(G_T^\circ - H_{298}^\circ)/T)$/ (J K^{-1} mol^{-1})	$\Delta_f H_T^\circ$/ (kJ mol^{-1})	$\Delta_f G_T$/ (kJ mol^{-1})
298	111.13	0	131.80	131.80	−1715.600	−1623.855
300	111.32	0.206	132.48	131.80	−1715.558	−1623.286
400	118.52	11.740	165.62	136.20	−1713.023	−1592.689
500	122.55	23.808	192.53	144.91	−1710.869	−1562.433
600	125.33	36.209	215.13	154.78	−1709.519	−1532.205
700	127.53	48.856	234.62	164.83	−1707.050	−1502.025
800	129.41	61.705	251.78	174.64	−1704.930	−1471.904
900	131.11	74.732	267.12	184.08	−1702.665	−1441.824
1000	132.70	87.923	281.01	193.09	−1700.333	−1411.773
1100	134.21	101.269	293.73	201.67	−1714.380	−1380.530
1200	135.67	114.763	305.47	209.84	−1711.935	−1348.928
1300	137.09	128.401	316.39	217.62	−1709.271	−1317.352
1400	138.49	142.181	326.60	225.64	−1706.448	−1286.646
1500	139.88	156.099	336.20	232.14	−1703.485	−1254.315
1600	141.24	170.155	345.28	238.93	−1700.385	−1222.862
1700	142.59	184.347	353.88	245.44	−1697.146	−1191.456
1800	143.94	198.674	362.07	251.69	−1693.771	−1160.094
1900	145.28	213.135	369.89	257.71	−1690.263	−1131.593
2000	146.62	227.730	377.38	263.52	−1686.621	−1100.760

Table 8
Thermodynamic quantities of $BaZrO_3(s)$

T/K	C_p/ (J K mol^{-1})	$(H_T^\circ - H_{298}^\circ)$/ (kJ mol^{-1})	S_T°/ (J K^{-1} mol^{-1})	$(-(G_T^\circ - H_{298}^\circ)/T)$/ (J K^{-1} mol^{-1})	$\Delta_f H_T^\circ$/ (kJ mol^{-1})	$\Delta_f G_T$/ (kJ mol^{-1})
298	100.710	0	124.683	124.683	−1747.200	−1662.429
300	101.030	0.187	125.307	124.685	−1747.194	−1661.903
400	112.586	10.944	156.174	128.815	−1746.440	−1633.574
500	118.407	22.521	181.984	136.942	−1745.881	−1605.436
600	121.971	34.552	203.909	146.323	−1746.108	−1577.330
700	124.468	46.880	222.908	155.937	−1745.245	−1549.276
800	126.397	59.427	239.659	165.376	−1744.767	−1521.314
900	127.996	72.149	254.642	174.476	−1744.192	−1493.416
1000	129.390	85.019	268.201	183.182	−1743.638	−1465.582
1100	130.650	98.022	280.593	191.482	−1751.074	−1437.034
1200	131.819	111.146	292.012	199.390	−1754.420	−1408.279
1300	132.923	124.384	302.607	206.927	−1753.501	−1379.470
1400	133.981	137.729	312.496	214.118	−1752.544	−1350.734
1500	135.004	151.179	321.775	220.989	−1751.579	−1322.067
1600	136.001	164.729	330.520	227.564	−1750.614	−1293.465
1700	136.977	178.378	338.795	233.866	−1749.662	−1264.922
1800	137.938	192.124	346.651	239.916	−1748.734	−1236.435
1900	138.886	205.165	354.135	245.732	−1747.842	−1207.999
2000	139.824	219.901	361.282	251.332	−1746.995	−1179.608

Table 9
Thermodynamic quantities of $Ba_2ZrO_4(s)$

T/K	C_p/ (J K mol^{-1})	$(H_T^\ominus - H_{298}^\ominus)$/ (kJ mol^{-1})	$S_T^\ominus$/ (J K^{-1} mol^{-1})	$(-(G_T^\ominus - H_{298}^\ominus)/T)$/ (J K^{-1} mol^{-1})	$\Delta_f H_T^\ominus$/ (kJ mol^{-1})	$\Delta_f G_T$/ (kJ mol^{-1})
298	150.877	0	213.384	213.384	−2268.700	−2161.183
300	151.319	0.208	214.319	213.386	−2268.653	−2160.471
400	167.346	16.318	260.349	219.554	−2265.480	−2124.687
500	175.470	33.479	298.648	231.654	−2262.810	−2089.207
600	180.484	51.311	331.114	245.596	−2261.579	−2053.719
700	184.028	69.545	359.215	259.865	−2257.961	−2018.267
800	186.789	88.091	383.975	273.861	−2254.894	−1982.946
900	189.095	106.888	406.112	287.348	−2251.421	−1947.710
1000	191.119	125.901	426.142	300.241	−2247.784	−1912.573
1100	192.958	145.106	444.445	312.530	−2259.938	−1875.990
1200	194.672	164.488	461.309	324.236	−2260.026	−1839.212
1300	196.297	184.037	476.956	335.389	−2255.670	−1802.414
1400	197.857	203.745	491.560	346.028	−2251.161	−1765.721
1500	199.370	223.607	505.263	356.192	−2246.548	−1729.132
1600	200.847	243.618	518.177	365.916	−2241.850	−1692.649
1700	202.295	263.775	530.397	375.235	−2237.078	−1656.258
1800	208.544	284.076	542.000	384.180	−2232.244	−1619.962
1900	210.590	304.519	553.053	392.780	−2227.366	−1583.758
2000	212.609	325.102	563.610	401.059	−2222.452	−1547.628

4. Conclusions

The vapor pressure of BaO(g) over $CeO_2 + BaCeO_3$ was measured by mass spectrometry. From the third-law enthalpy of vaporization of BaO(g), the standard molar enthalpy of formation of $BaCeO_3(s)$ was determined to be -1716 ± 1 kJ mol^{-1}, which was closer to the calculated value on the basis of Aronson's empirical equation in this study than the previous value reported by use of solution calorimetry [9]. The relative stabilities of various barium perovskite oxides were compared by the use of Goldschmidt tolerance factor and the molar enthalpy of formation ΔH from the constituent binary oxides. The enthalpies of formation ΔH are seen to decrease in the order of decreasing tolerance factor and of increasing ionic radius of tetravalent cations, indicating the reliability of the present experimental value of $\Delta_f H_{298}^\ominus(BaCeO_3(s))$. The standard molar Gibbs energies of formation of $BaCeO_3$, $BaZrO_3$ and Ba_2ZrO_4 were determined from our experimental data. The standard enthalpies and Gibbs energies of formation of various ternary oxides containing barium were also summarized and compared.

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