Vaporization Behavior of BaPuO₃

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Vaporization behavior of BaPuO₃ was investigated by high-temperature mass spectrometry with a Pt Knudsen cell in the temperature range from 1,673 to 1,873 K. The vapor species of Ba(g) and PuO(g) were identified over BaPuO₃ with the second phase of PuO₂. It was suggested from the experimental results that the decomposition of BaPuO₃ was expressed as the following equation;

\[ \text{BaPuO}_3(s) = \text{PuO}_2(s) + \text{BaO}(g) \]

\[ 2\text{BaO}(g) \rightarrow 2\text{Ba}(g) + \text{O}_2(g) \]

The second- and third-law standard molar enthalpies of formation of BaPuO₃ were evaluated to be −1,661 and −1,173 kJ mol⁻¹, respectively, which almost agreed with the calculated values previously reported.

1. Introduction

A multicomponent perovskite-type oxide with the composition of ABO₃ is usually found as a gray phase in the irradiated oxide fuels.³ Here "A" represents fission-produced elements such as barium, strontium, and cesium, whereas "B" denotes zirconium, molybdenum, and rare earth metals produced by fission, uranium and plutonium. The composition of this phase largely depends on temperature gradient in the fuel, burnup, oxygen potential, and so on. The thermodynamic properties of such compounds are, therefore, essential for the understanding of fuel behavior under both steady-state and transient conditions. Thermo-chemical properties of these ternary barium oxides⁴⁻⁵ at high temperature have been widely investigated. Few experimental data have, however, been reported for the relevant plutonium compounds, due to experimental difficulties. Recently, the present authors have clarified the vaporization behavior and the thermodynamic quantities of SrPuO₃.⁶

In this study, the vaporization behavior of BaPuO₃ was investigated by mass spectrometry in the temperature range of 1,673–1,873 K in order to (1) identify the vapor species, (2) determine the vapor pressures as a function of temperature, (3) calculate the enthalpy of vaporization/decomposition of BaPuO₃, and (4) determine the standard molar enthalpy of formation of BaPuO₃ by using the heat content and free energy function of BaPuO₃ estimated by the authors.

2. Experimental

The two-phase sample of BaPuO₃ + PuO₂ for the vapor pressure measurements was prepared by heating the mixtures of PuO₂ and BaCO₃ powders. The characteristics of PuO₂ powder were described in an earlier paper⁷ and it was calcined at 773 K for 7.2 ks in dry air before mixing. The BaCO₃ powder with purity of 99.999% was supplied by Rare Metallic Co., Ltd., Japan. The powders were mixed in an agate mortar with an atomic Ba/Pu ratio of 0.5 and compacted into disks, then heated at 1,660 K for 4.5 ks in Ar gas stream. Two phases, orthorhombic-BaPuO₃ and cubic-PuO₂ were identified in the product by X-ray diffraction analysis. The present X-ray diffraction pattern showed that BaPuO₃ was slightly distorted from the cubic perovskite structure as indicated by the neutron diffraction analysis.⁸

The vapor pressures were measured with a quadrupole mass spectrometer (ANELVA Co., Ltd.) equipped with a Knudsen-cell contained in a Ta holder. The details of the apparatus used in the present study were described in an earlier paper.⁹ The Pt Knudsen-cell was used in order to avoid chemical interaction between the sample and cell according to many mass-spectrometric studies in the barium oxide–platinum system.⁵,⁶,¹¹ Indeed no evidence of other phases was

![Graph](image)

**Fig. 1.** Temperature dependence of the vapor pressures of Ba(g) and PuO(g) over the two-phase sample of BaPuO₃ + PuO₂

**Table 1.** Equations for Vapor Pressures* over BaPuO₃ + PuO₂

<table>
<thead>
<tr>
<th>Vapor species</th>
<th>A</th>
<th>B</th>
<th>Temp. range (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba(g)</td>
<td>24.89±0.39</td>
<td>13.42±0.22</td>
<td>1673–1873</td>
</tr>
<tr>
<td>PuO(g)</td>
<td>23.81±1.36</td>
<td>11.70±0.75</td>
<td>1573–1873</td>
</tr>
</tbody>
</table>

* log(P/Pa) = -(A×10^3)/T - B

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observed by X-ray diffraction analysis of the sample after the mass-spectrometric measurement. The effusion orifice in the Knudsen cell had a diameter of 0.5 mm. As predominant vapor species, Ba(g) and BaO(g) were identified. Ionization efficiency curves of Ba and BaO showed that the ion intensities became maximum at 9 eV and 20 eV, respectively. In order to avoid the fragmentation of BaO*, an ionization electron energy of 9 eV was chosen for the measurements of all gaseous species in this study. The absolute pressure of Ba(g) was calculated by a modified integral method and derived from the following equation:

\[ P_{\text{Ba}}(T) = \frac{\Delta W}{a \Delta T} \times \frac{I_{\text{Ba}^+}(T) / T^2 \Delta T(T)}{\sum I_{\text{Ba}^+}(T) / T^2 \Delta T(T) + I_{\text{BaO}^+}(\text{imag}) / T^2 \Delta T(T)} \times \sqrt{\frac{2 \pi R T}{M_{\text{Ba}}}}. \]  

(1)

where \( \Delta W \) is the weight difference of the sample before and after the measurement, \( a \) the cross section of effusion orifice, \( \Delta T(T) \) the time interval of temperature \( T \), \( I_{\text{Ba}^+} \) the ion current of Ba, \( R \) the gas constant, \( M_{\text{Ba}} \) the mass number of gas species, and \( I_{\text{BaO}^+}(\text{imag}) \) the imaginary ion current of BaO, which was equivalent to \( I_{\text{BaO}^+} \) and calculated by the following equation:

\[ I_{\text{BaO}^+}(\text{imag}) = \frac{\sigma_{\text{BaO}} T_{\text{BaO}} M_{\text{BaO}}}{\sigma_{\text{Ba}} M_{\text{Ba}}} I_{\text{Ba}^+}. \]  

(2)

In this study, the efficiency of electron multiplier, \( \gamma \), was corrected for the mass dependence by a factor of the reciprocal of square root of the mass number and the atomic ionization cross sections, \( \sigma \), of Ba and O were taken from the table by Mann and the effective relative cross section of BaO was estimated from the ionization efficiency curve of BaO using the following relationship:

\[ \sigma_{\text{BaO}} = 0.75 \sigma_{\text{Ba}^+} + 0.25 \sigma_{\text{O}^+} \left( \frac{I_{\text{Ba}^+}(9 \text{ eV})}{I_{\text{Ba}^+}(20 \text{ eV})} \right). \]  

(3)

where the coefficient 0.75 is recommended to provide more practical results for the ionization cross sections of polyatomic molecules than the additivity rule by Otvos and Stevenson. The partial pressure of BaO(g) was calculated by using the equation:

\[ P_{\text{BaO}}(T) = \frac{I_{\text{BaO}^+} \sigma_{\text{BaO}} M_{\text{BaO}}}{I_{\text{Ba}^+} \sigma_{\text{Ba}} M_{\text{Ba}}} P_{\text{Ba}}(T). \]  

(4)

Clausing correction was not made as assumed that the effect of orifice-channel length was negligible. Since the sample consisted of porous lumps the sample surface/orifice area ratio was big enough to assure the prevalence of equilibrium condition. Temperature was measured by two sets of W/Re 3–25 thermocouple inserted into the upper and lower position of a Ta holder and calibrated by the melting point of Pd.

<table>
<thead>
<tr>
<th>Investigator</th>
<th>Lattice parameter (nm)</th>
<th>Unit cell volume (nm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Christoph et al.</td>
<td>0.6193 (1) 0.8744 (1) 0.6219 (1) 0.3368</td>
<td></td>
</tr>
<tr>
<td>This work</td>
<td>0.6198 (9) 0.8739 (12) 0.6209 (7) 0.3363 (8)</td>
<td></td>
</tr>
</tbody>
</table>

* By neutron powder diffraction.

Table 3. Thermodynamic Quantities of BaPuO₃(α) Evaluated in the Present Study

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>( G_f ) (kJ mol⁻¹)</th>
<th>( H_{\text{f298}} ) (kJ mol⁻¹)</th>
<th>( S_f ) (J K⁻¹ mol⁻¹)</th>
<th>( -\Delta_f^\circ H_{\text{f298}} / T ) (kJ K⁻¹ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1600</td>
<td>163.61</td>
<td>181.227</td>
<td>365.66</td>
<td>265.398</td>
</tr>
<tr>
<td>1700</td>
<td>163.947</td>
<td>197.682</td>
<td>378.637</td>
<td>262.351</td>
</tr>
<tr>
<td>1800</td>
<td>157.864</td>
<td>213.772</td>
<td>387.835</td>
<td>269.072</td>
</tr>
<tr>
<td>1900</td>
<td>151.747</td>
<td>229.254</td>
<td>396.206</td>
<td>275.546</td>
</tr>
</tbody>
</table>

3. Results and Discussion

3.1 Vapor pressures

Temperature dependences of the vapor pressures of Ba(g) and BaO(g) over the two-phase sample of BaPuO₃ + PuO₂ are shown in Fig. 1. The equations for the partial pressures of Ba(g) and BaO(g) obtained from the least squares treatment are given in Table 1. Since the partial pressures of BaO(g) was much higher than that of Pu-bearing vapor species, the decomposition of BaPuO₃ could be expressed with the following manner;

\[ \text{BaPuO}_3(\alpha) = \text{PuO}_2(\alpha) + \text{BaO}(g). \]  

(5)

And the partial pressure of Ba(g) in Fig. 1 was considered to be derived from the following equation (6);

\[ 2\text{BaO}(g) = 2\text{Ba}(g) + \text{O}_2(g). \]  

(6)

The lattice parameter of BaPuO₃ after the mass-spectrometric measurement is listed in Table 2 together with the value given by Christoph et al. who used the neutron powder diffraction method. The similar lattice parameters in Table 2 indicate that the chemical formula of the present sample does not largely deviate from the stoichiometric composition.

3.2 Thermodynamic quantities

3.2.1 Enthalpies of vaporization

The enthalpy of vaporization/decomposition was calculated by the second- and third-law treatments. The second law enthalpy of vaporization for the reaction (5) at the medium temperature was directly obtained from the slope of the logarithmic plot of the vapor pressure of BaO(g) versus the reciprocal temperature. Then it was converted to the value at standard state by using the change of the heat content (i.e., enthalpy increment \( \Delta(H_{T_m} - H_{298}) \), \( T_m \); medium temperature) for the reaction (5).

The third law enthalpy was taken as the averaged value of the standard enthalpy derived from each individual experimental data point with the relation;

\[ \Delta_{f} H_{298} = \Delta_{f} H_{298} + \Delta \ln(P) / T. \]  

(7)

where \( \Delta \ln(P) / T \) is the change of the free energy function for the reaction (5).

The heat content and the free energy function of BaPuO₃ are necessary for the determination of the second and third law enthalpies of vaporization at standard state. Since there have been no experimental data
and assessed values for BaPuO$_3$(s), the heat content and the free energy function were estimated in a manner generally adopted.\textsuperscript{6,10} Namely, the heat capacity and the entropy of BaPuO$_3$(s) were assumed to be the sum of those of BaO(s) and PuO$_2$(s) plus the difference between those of BaZrO$_3$(s) and the sum of those of BaO(s) and ZrO$_2$(s). All the necessary thermodynamic data of BaO(g), PuO$_2$(s), 3aZrO$_2$(s), and so on were taken from Cordfunke and Konings' reference.\textsuperscript{10} The thermodynamic quantities assessed by the present authors are listed in Table 3 and the second- and third-law enthalpies for the reaction (5) are summarized in Table 4. It is seen in Table 4 that the agreement between the second- and third-law enthalpies for the reaction (5) seems to be good, indicating the reasonable thermodynamic values of BaPuO$_3$(s) in Table 3 and the reliability of the present vapor pressure measurements.

### 3.2.2 Standard molar enthalpy of formation

The combination of the third-law enthalpy of vaporization for the reaction (5), which is generally regarded as more reliable than the second-law value, with the enthalpies of formation of BaO(g) and PuO$_2$(s) yields the standard molar enthalpy of formation of BaPuO$_3$(s), $\Delta H^\circ_{fBaPuO_3}(s)$, evaluated as $-1,673$ kJ mol$^{-1}$.

### Acknowledgements

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### References


### Keywords: