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Vaporization behavior of $SrPuO_3$

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Abstract

The vaporization behavior of $SrPuO_3$ was investigated by mass-spectrometry with the Pt Knudsen-cell in the temperature range 1433–1913 K. The vapor species of Sr(g) and PuO(g) were identified and $SrPuO_3$ was suggested to decompose into Sr(g), PuO_2(s) and O_2(g). The standard molar enthalpy of formation of $SrPuO_3$ was determined from the vapor pressures of Sr(g) and PuO(g) by using the free energy function and heat content of $SrPuO_3$(s) estimated by the authors. Furthermore, the measurement was also carried out in the graphite Knudsen-cell in order to investigate the effect of oxygen potential on the vaporization behavior of $SrPuO_3$. © 1997 Elsevier Science B.V.

1. Introduction

A multicomponent perovskite-type oxide with the composition of ABO_3 is usually found as a gray phase in the irradiated oxide fuels [1]. Here A represents fission-produced elements such as barium, strontium and cesium, whereas B denotes zirconium, molybdenum and rare earth metals produced by fission or uranium and plutonium. The composition of this phase largely depends on the temperature gradient in the fuel, burnup, oxygen potential and so on. The thermodynamic properties of such compounds are essential for the understanding of fuel behavior under both steady-state and transient conditions. Few experimental data, however, have been reported for the relevant plutonium compounds, especially at high temperatures.

In the present study, the vaporization behavior of $SrPuO_3$ was investigated by mass-spectrometry in the temperature range 1433–1913 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 $SrPuO_3$ and (4) determine the standard molar enthalpy of formation of $SrPuO_3$ by using the heat content and free energy function of $SrPuO_3$. In addition, the effect of oxygen potential on the vaporization of $SrPuO_3$ was investigated.

2. Experimental

Two kinds of samples for the vapor pressure measurements were obtained by heating the mixtures of PuO_2 and $SrCO_3$ powders. The characteristics of PuO_2 powder were described in an earlier paper [2]. The PuO_2 powder was calcined at 773 K for 7.2 ks in dry air before mixing. The powder of $SrCO_3$ with purity of 99.999% was supplied by Rare Metallic Co., Japan. The powders of PuO_2 and $SrCO_3$ were mixed in an agate mortar with an atomic ratio Sr/Pu of 0.498 and compacted into disks, which were reacted at 1660 K for 4.5 ks in an Ar gas stream. The weight loss measured during heating corresponded well to the amount of CO gas caused by the reaction of PuO_2 and $SrCO_3$. Two phases, $SrPuO_3$ and PuO_2 were identified in the products by X-ray diffraction analysis. A nearly single-phase sample was also prepared by heating the mixture of $SrPuO_3$ and PuO_2 with a ratio of 1.03 in a similar way as the two-phase sample. The nearly single-phase sample was used in the measurements for investigating the effect of the oxygen potential as described below.

The vapor pressures were measured with a quadrupole mass-spectrometer equipped with a Knudsen-cell contained in a Ta holder. The details of the apparatus used in

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the present study were described in an earlier paper [3]. The Knudsen-cell made of Pt was used in order to avoid chemical interaction between the samples and the cell according to many mass-spectrometric studies in the strontium oxide–platinum system [4–7]. In addition to the Pt cell, the graphite cell was also applied to investigate the effect of oxygen potential on the vaporization behavior of $SrPuO_3$. The absolute pressure was calculated by comparing the ion currents of vapor species with that of Ag used as an internal standard. The values of atomic ionization cross-section σ_A of Ag, Sr, Pu and O were taken from the table by Mann [8] and the molecular ionization cross-section of PuO was calculated by using the equation: $\sigma_M = 0.75\Sigma\sigma_A$ [9]. The relative multiplier gain was calculated by assuming the inverse proportionality to the square root of the mass of the vaporized species. The temperature was measured by two sets of W/Re 3-25 thermocouples inserted into the upper and lower position of a Ta holder and calibrated by the melting point of Pd.

3. Results and discussion

3.1. Ionization efficiency curves

As predominant vapor species over the two-phase sample, Sr(g) and PuO(g) were identified but SrO(g) was not detected. Ionization efficiency curves of Sr^+ and PuO^+ are shown in Fig. 1, where the ion intensities of each gaseous species are arbitrary. It can be seen from Fig. 1 that the ion intensities of Sr^+ and PuO^+ have already been saturated at 10 eV. In order to avoid the fragmentation of the vapor species PuO^+, an ionization electron energy of 10 eV was chosen for the measurements of all gaseous species in this study.

3.2. Vapor pressures

The results of vapor pressure measurements over the two-phase $SrPuO_3 + PuO_2$ sample were described here. Unfortunately there is no reference on the $SrO–PuO_2$ pseudobinary system. But it was expected from the $SrO–ZrO_2$ phase diagram [10], indicating the existence of the complex oxide of $SrZrO_3$, with the same perovskite-type structure as $SrPuO_3$ that only two phases, i.e., $SrPuO_3 + PuO_2$, existed under the vaporization condition in this study. Temperature dependencies of the vapor pressures of Sr(g) and PuO(g) are shown in the Fig. 2. The equations for the partial pressures of Sr(g) and PuO(g) obtained from the least squares treatment are given in Table 1. Since the partial pressure of Sr(g) was much higher than that of PuO(g) as seen in the figure, the decomposition of $SrPuO_3$ was assumed in the Pt cell with the following manner:

$$2SrPuO_3(s) = 2PuO_2(s) + 2Sr(g) + O_2(g), \qquad (1)$$

$$2PuO_2(s) = 2PuO(g) + O_2(g). \qquad (2)$$

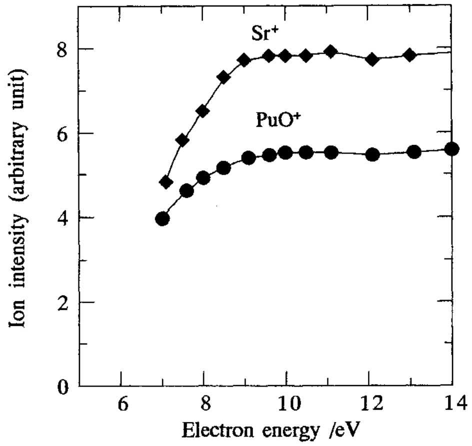

Fig. 1. Ionization efficiency curves for Sr^+ and PuO^+ ions.

The lattice parameter of $SrPuO_3$ did not change significantly before and after the mass-spectrometric measurement as listed in Table 2. Furthermore, the results of vapor pressure measurements on both heating and cooling processes agreed with each other. Therefore, it was considered that the chemical formula of sample almost kept unchanged during the measurement.

3.3. Thermodynamic quantities

3.3.1. Enthalpies of vaporization

The enthalpy of vaporization/decomposition was calculated by the second and third law treatments. The second law enthalpy of vaporization for Eq. (1) for the median temperature of the measurements was directly obtained from the slope of the logarithmic plot of the vapor pressure of Sr(g) and O_2(g) versus the reciprocal temperature,

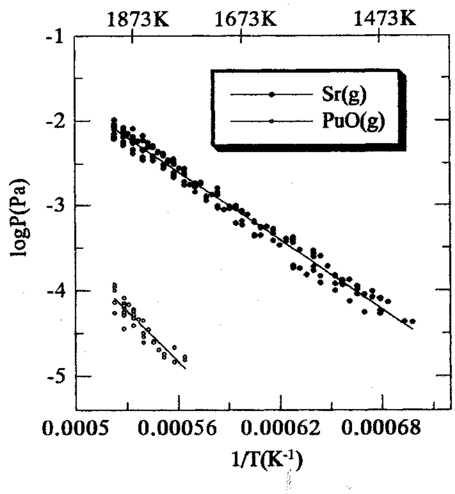

Fig. 2. Temperature dependence of vapor pressures over $SrPuO_3 + PuO_2$ in the Pt cell

Table 1
Equations for vapor pressures [a]

Sample	Sr(g)		PuO(g)		O_2(g)		Temp. range (K)
	A	*B*	*A*	*B*	*A*	*B*	
$SrPuO_3 + PuO_2$	13.55 ± 0.15	4.997 ± 0.09	19.83 ± 1.35	6.273 ± 0.73	60.38	27.65	1433–1913

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

Table 2
Lattice parameter of $SrPuO_3$ before and after the mass-spectrometric measurement

Samples		Lattice parameter (nm)			Unit cell volume (nm^3)
		a	*b*	*c*	*V*
$SrPuO_3 + PuO_2$	before	0.59911 ± 0.00088	0.42752 ± 0.00061	0.61243 ± 0.00111	0.15686 ± 0.000429
	after	0.59893 ± 0.00088	0.42741 ± 0.00062	0.61237 ± 0.00112	0.15676 ± 0.000432

where the pressure of $O_2(g)$ was calculated from that of PuO(g) in Eq. (2) as also shown in Table 1. 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: median temperature) for Eq. (1).

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

$$-\left(R \ln P_{\mathrm{Sr}} P_{\mathrm{O}_2}^{1/2} + \Delta \mathrm{fef}\right) T = \Delta_{\mathrm{v}} H^{0_{298}}, \tag{3}$$

where Δfef is the change of the free energy function for Eq. (1).

The heat content and the free energy function of $SrPuO_3$ are necessary for the determination of the second and third law enthalpies of vaporization for Eq. (1). Since there have been no experimental data and assessed values for $SrPuO_3(s)$, the heat content and the free energy function were estimated in a manner generally adopted [11]. Namely, the heat capacity and the entropy S^0_{298} of $SrPuO_3(s)$ were assumed to be the sum of those of SrO(s) and $PuO_2(s)$ plus the difference between those of $SrZrO_3(s)$ and the sum of those of SrO(s) and $ZrO_2(s)$, since $SrZrO_3(s)$ and $SrPuO_3(s)$ possess almost the same crystal structure. All the necessary thermodynamic data of Sr(g), PuO(g), $PuO_2(s)$, $SrZrO_3(s)$ and so on were taken from Cordfunke and Konings' [12]. The thermodynamic quantities assessed by the present authors are listed in Table 3 and the second and third law enthalpies for Eq. (1) obtained are summarized in Table 4. It is seen in Table 4 that the agreement between the second and the third law enthalpies for Eq. (1) seems to be good, indicating the reasonable thermodynamic values of

Table 3
Thermodynamic quantities of $SrPuO_3(s)$

Temp. (K)	C_p ($J\,K^{-1}\,mol^{-1}$)	$H^0_T - H^0_{298}$ ($kJ\,mol^{-1}$)	S^0_T ($J\,K^{-1}\,mol^{-1}$)	$-(G^0_T - H^0_{298})/T$ ($J\,K^{-1}\,mol^{-1}$)
1400	153.374	148.995	313.285	206.859
1500	150.446	170.290	327.900	214.374
1600	152.481	185.437	337.676	221.777
1700	156.538	200.809	346.994	228.872
1800	166.966	216.986	356.238	235.691
1900	177.383	234.203	365.544	242.280

Table 4
Enthalpy of vaporization for Eq. (1)

Samples	Gas species	T_{med} (K)	$\Delta_v H_{T_m}$ (2nd) ($kJ\,mol^{-1}$)	$\Delta_v H^0_{298}$ (2nd) ($kJ\,mol^{-1}$)	$\Delta_v H^0_{298}$ (3rd) ($kJ\,mol^{-1}$)	$\Delta_f H^0_{298}$ (2nd) ($kJ\,mol^{-1}$)	$\Delta_f H^0_{298}$ (3rd) ($kJ\,mol^{-1}$)
$SrPuO_3 + PuO_2$	Sr(g)	1673	259.4 ± 2.8	857.8 ± 2.8	833.0 ± 3.5	−1752 ± 2.8	−1728 ± 3.5
	$1/2O_2(g)$	1673	578.1				

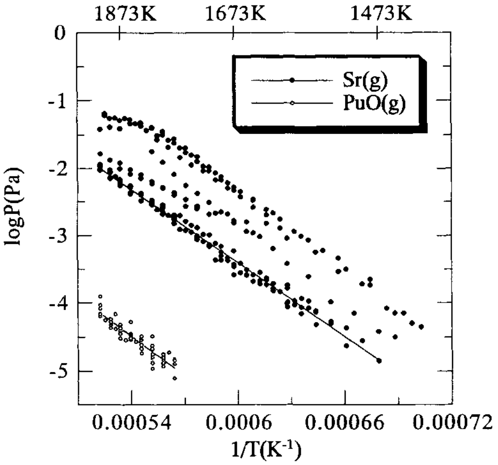

Fig. 3. Temperature dependence of vapor pressures over the single-phase $SrPuO_3$ in the Pt cell.

$SrPuO_3(s)$ in Table 3 and the reliability of our vapor pressure measurements.

3.3.2. Standard molar enthalpy of formation

The combination of the third law enthalpy of vaporization for Eq. (1); 833.0 ± 3.5 kJ mol^{-1}, which is generally regarded as more reliable than the second-law value, with the enthalpies of formation of Sr(g) and $PuO_2(s)$ yields the standard molar enthalpy of formation of $SrPuO_3(s)$, $\Delta_f H^0_{298}(SrPuO_3,s) = -1728 \pm 3.5$ kJ mol^{-1}. On the other hand, the second-law value was obtained to be -1752 ± 2.8 kJ mol^{-1}.

3.4. Effect of oxygen potential

In order to investigate the effect of oxygen potential on the vaporization behavior of $SrPuO_3$, the mass-spectrometric measurement was carried out by use of the graphite Knudsen-cell besides the Pt cell. In this case, samples with a nearly single-phase of $SrPuO_3$ were adopted to avoid chemical interaction between PuO_2 and the graphite Knudsen-cell.

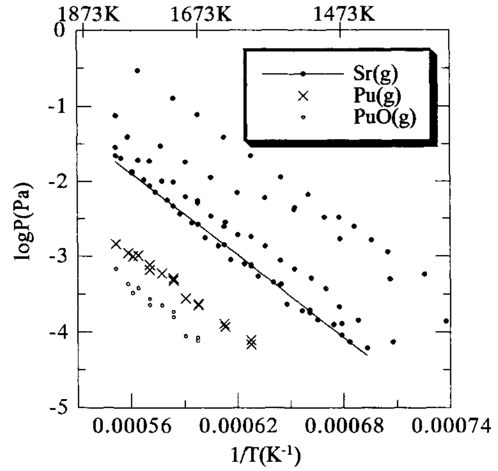

Fig. 4. Temperature dependence of vapor pressures over the single-phase $SrPuO_3$ in the graphite cell.

Figs. 3 and 4 show the temperature dependencies of the vapor pressures over the single-phase $SrPuO_3$ in the Pt and graphite cells, respectively. The vapor species of Pu(g) was also identified besides Sr(g) and PuO(g) in case of the graphite cell. A large variation of vapor pressures of Sr(g) was observed before they settled down the location indicated by the linear lines in these cases but the partial pressure of Sr(g) in the graphite cell was about 6 times higher than that in the Pt cell. Although some compositional change of the sample was suggested from the results mentioned above, it was considered that the increase of partial pressure of Sr(g) would be caused by the lowering of oxygen potential with the following equation:

$$2C(s) + O_2(g) = 2CO(g). \qquad (4)$$

On the other hand, the vapor species of Pu(g) and PuO(g) represented in Fig. 4 were not detected at the beginning of the mass-spectrometric measurement. Therefore they would be caused by the reaction product of the sample and the graphite Knudsen-cell such as Pu oxycarbide [13]. Therefore, it was impossible to determine the exact oxygen potential in this case since the partial pressure CO(g) could not be measured and the partial pressure of PuO(g) observed would not correspond to Eq. (2).

Partial pressures of PuO(g) over the single-phase $SrPuO_3$ were measured in the Pt cell as shown in Fig. 3. The enthalpy of vaporization/decomposition was calculated by the same manner described above by using the linear lines indicated in Fig. 3. However, the agreement between the second and the third law enthalpies for Eq. (1) was not good, where these enthalpies were 948.7 ± 3.4 and 837.4 ± 7.9 kJ mol^{-1}, respectively. As one of the reasons of this disagreement, the use of inadequate thermodynamic quantities was suggested since some deviation from the stoichiometric composition of PuO_2 occurred during the measurement in the case of nearly-single phase sample.

4. Conclusion

The vaporization behavior of $SrPuO_3$ was investigated by mass spectrometry by use of the Pt and graphite Knudsen-cells. In this study the following results were found.

(1) Decomposition of $SrPuO_3(s)$ into Sr(g), $PuO_2(s)$ and $O_2(g)$ was suggested from the vapor pressures of Sr(g) and PuO(g) over $SrPuO_3 + PuO_2$.

(2) The standard molar enthalpy of formation of $SrPuO_3(s)$ was determined to be -1728 ± 40 kJ mol^{-1} in consideration of the uncertainties in the vapor pressure

measurements and the heat content and the free energy function of $SrPuO_3(s)$ assessed in this study.

(3) It was found that the partial pressures of Sr(g) over $SrPuO_3(s)$ in the graphite cell were much higher than those in the Pt cell due to the lower oxygen potential in the former system.

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