

Thermodynamic properties

HEAT CAPACITY MEASUREMENT OF $U_{1-y}La_yO_2$ ($y = 0.044, 0.090, 0.142$) FROM 300 TO 1500 K

T. MATSUI*, Y. ARITA, K. NAITO

*Department of Nuclear Engineering, Faculty of Engineering, Nagoya University,
Furo-cho, Chikusa-ku, Nagoya 464-01 (Japan)*

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Heat capacities of $U_{1-y}La_yO_2$ were measured by means of direct heating pulse calorimetry in the temperature range from 300 to 1500 K. An anomalous increase in the heat capacity curve of each sample was observed similarly to the case of $U_{1-y}Gd_yO_2$, found recently in our laboratory. As the lanthanum content of $U_{1-y}La_yO_2$ increased, the onset temperature of an anomalous increase in the heat capacity decreased and the excess heat capacity increased. The enthalpy of activation (ΔH_f) and the entropy of activation (ΔS_f) of the thermally excited process, which cause the excess heat capacity were obtained to be 2.14, 1.63 and 1.50 eV and 39.4, 34.2 and 31.8 $J \cdot K^{-1} \cdot mol^{-1}$ for $U_{0.956}La_{0.044}O_2$, $U_{0.910}La_{0.090}O_2$ and $U_{0.858}La_{0.142}O_2$, respectively. The values at zero La content extrapolated by using the data of ΔH_f and ΔS_f for $U_{1-y}La_yO_2$ were in good agreement with the experimental values of undoped UO_2 so far reported, similarly to the case of Gd-doped UO_2 . The electrical conductivities of $U_{1-y}La_yO_2$ ($y = 0.044$ and 0.142) were also measured as a function temperature. No anomaly was seen in the electrical conductivity curve. It may be concluded that the excess heat capacity originates from the predominant contribution of the formation of oxygen clusters and from the small contribution of the formation of electron-hole pairs.

Introduction

A small amount of aliovalent cations such as Ti, Nb, La, etc., was added to UO_2 to improve mechanical properties and irradiation behaviour.¹ Lanthanum is also one of the typical fission products with high yield. The electrical conductivity and the non-stoichiometric composition of $U_{1-y}La_yO_{2 \pm x}$ ($y = 0.01$ and 0.05) have been measured by the present authors as functions of temperature and oxygen partial pressure to discuss the defect structure.²

*Author for correspondence.

The heat capacities of gadolinia-doped UO_2 ($U_{1-y}Gd_yO_{2.0}$, $y = 0.044, 0.073, 0.101, 0.142$) have been recently measured from room temperature to 1500 K in the author's laboratory,^{3,4} and an anomalous increase in the heat capacity of each sample was first observed at high temperature from about 700 for $y = 0.142$ to 1200 K for $y = 0.044$. The anomalous increase in the heat capacity of UO_2 was interpreted as due to the Frenkel pairs of oxygen by several investigators^{5,6} and reviewed by one of the present authors.⁷ The heat capacity of $U_{1-y}La_yO_2$ has not been measured yet.

In the present study, the heat capacity of $U_{1-y}La_yO_2$ ($y = 0.044, 0.090$ and 0.142) and the electrical conductivity ($y = 0.044$ and 0.142) were measured from 300 to 1500 K by means of direct heating pulse calorimetry to discuss the origin of excess heat capacity of $U_{1-y}La_yO_2$ in comparison with the data for $U_{1-y}Gd_yO_2$ and undoped UO_2 .

Experimental

The mixture of La_2O_3 and UO_2 powder was shaped into a cylindrical rod of about 6 mm in diameter and 60 mm in length, using an evacuated rubber press with a hydrostatic pressure of about 400 MPa. The cylindrical rod was sintered and homogenized at 1673 K for 5 days in a purified Ar gas flow and then at 1323 K for 2 days in a hydrogen gas stream. This sintering and homogenizing process was repeated several times. X-ray diffraction analysis indicated that each sample rod was a single phase.

The heat capacity and the electrical conductivity were measured simultaneously by a direct heating pulse calorimeter, whose details have been given elsewhere.⁸ In this calorimeter, the temperature of the sample rod was varied from room temperature to 1500 K by an external heater, and a current pulse was supplied to both the sample rod and the double cylindrical molybdenum shields simultaneously so as to obtain the same small temperature rise. The electric potential drop, the current and the temperature rise of the sample rod were measured to obtain the heat capacity and the electrical conductivity.

Results and discussion

The heat capacities measured on $U_{0.956}La_{0.044}O_2$, $U_{0.910}La_{0.090}O_2$ and $U_{0.858}La_{0.142}O_2$ are shown in Figs 1, 2 and 3, respectively. In Fig. 1, the reference data of UO_2 and $U_{0.956}Gd_{0.044}O_2$ measured in our laboratory^{3,4} and $U_{0.956}Gd_{0.044}O_2$ recently reported by MILLS et al.⁹ are also shown for comparison. As seen in Fig. 1, an anomalous increase in the heat capacity curve of $U_{0.956}La_{0.044}O_2$ similar to that of $U_{0.956}Gd_{0.044}O_2$ is observed above 1200 K. Below 1200 K the baseline heat capacity of $U_{0.956}La_{0.044}O_2$ is nearly equal to

those of $U_{0.956}Gd_{0.044}O_2$ and UO_2 . The equation for the heat capacity of $U_{0.956}La_{0.044}O_2$ is determined by the least-squares method as:

$$C_p / J K^{-1} mol^{-1} = 36.295 + 2.1627 \cdot 10^{-2} (T/K) + 3.7635 \cdot 10^4 (T/K)^{-1} - 1.5823 \cdot 10^7 (T/K)^{-2} + 2.4178 \cdot 10^9 (T/K)^{-3}, \quad (300 < T/K < 1200). \quad (1)$$

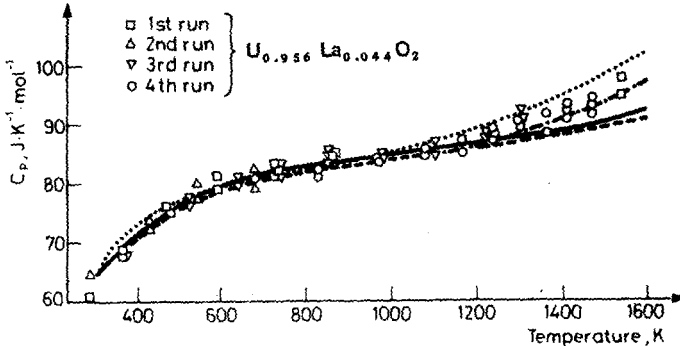


Fig. 1. Heat capacity of $U_{0.956}La_{0.044}O_2$ — UO_2^4 , - - - $U_{0.956}Gd_{0.044}O_2^4$, ···· $U_{0.956}Gd_{0.044}O_2^9$, — baseline heat capacity of $U_{0.956}La_{0.044}O_2$

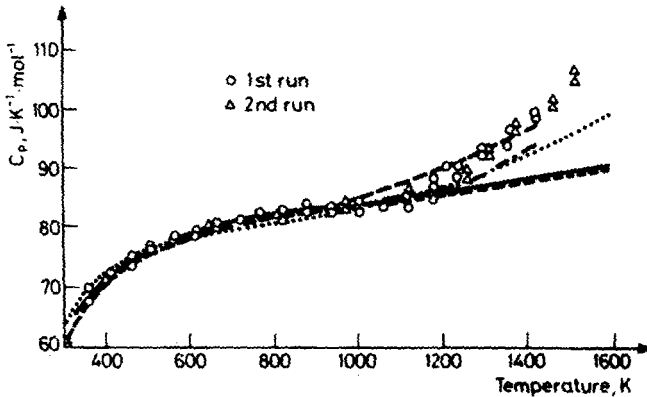


Fig. 2. Heat capacity of $U_{0.910}La_{0.090}O_2$ — UO_2^4 and baseline heat capacity of $U_{0.910}La_{0.090}O_2$, - - - $U_{0.899}Gd_{0.101}O_2^4$, ···· $U_{0.927}Gd_{0.073}O_2^4$, ···· $U_{0.927}Gd_{0.073}O_2^9$, - - - $0.931 UO_2 + 0.092 LaO_{1.5}$

An anomalous increase in the heat capacity of $U_{0.910}La_{0.090}O_2$ is also seen above 1100 K in Fig. 2. In the figure, the heat capacity of $U_{0.899}Gd_{0.101}O_2^4$, $U_{0.927}Gd_{0.073}O_2^4$,⁹ and UO_2^4 are also shown for comparison. The heat capacity of $U_{0.910}La_{0.090}O_2$ falls between those of $U_{0.899}Gd_{0.101}O_2$ and $U_{0.927}Gd_{0.073}O_2$. The equation for the heat capacity of $U_{0.910}La_{0.090}O_2$ is given by the least-squares method as:

$$C_p / J K^{-1} \text{ mol}^{-1} = 55.267 + 1.6340 \cdot 10^{-2} (T/K) + 2.0499 \cdot 10^4 (T/K)^{-1} - 8.1166 \cdot 10^6 (T/K)^{-2} + 6.2934 \cdot 10^8 (T/K)^{-3}, \quad (300 < T/K < 1100). \quad (2)$$

Similarly, as seen in Fig. 3, an anomalous increase in the heat capacity of $U_{0.858}La_{0.142}O_2$ is seen above 1000 K, though the excess heat capacity is smaller than that of $U_{0.858}Gd_{0.142}O_2$ measured in our laboratory.⁴ The equation for the

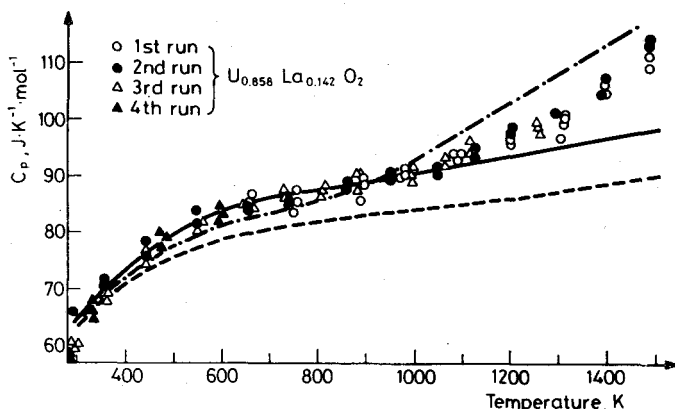


Fig. 3. Heat capacity of $U_{0.858}La_{0.142}O_2$ — baseline heat capacity of $U_{0.858}La_{0.142}O_2$.
 - - - UO_2 ,⁴ - · - $U_{0.858}Gd_{0.142}O_2$ ⁴

heat capacity of $U_{0.858}La_{0.142}O_2$ is given by the least-squares method as:

$$C_p / J K^{-1} \text{ mol}^{-1} = 43.548 + 2.3102 \cdot 10^{-2} (T/K) + 3.7635 \cdot 10^4 (T/K)^{-1} - 1.5823 \cdot 10^7 (T/K)^{-2} + 1.6582 \cdot 10^9 (T/K)^{-3}, \quad (300 < T/K < 1000). \quad (3)$$

The excess heat capacity was evaluated by subtracting the smoothed base line of heat capacity, where the smoothed base line was determined from a least-squares fitting for the data in the lower temperature region. Assuming the presence of the contribution of a thermally activated process due to the mechanism of the formation of Frenkel pair of oxygen to the excess heat capacity, similarly to the case of Gd-doped UO_2 , the excess heat capacity ΔC can be expressed as:^{4,6}

$$\Delta C = (\Delta H_f)^2 / (\sqrt{2} RT^2 \exp(\Delta S_f / 2R) \exp(-\Delta H_f / 2RT)) \quad (4)$$

where ΔS_f and ΔH_f are the entropy and enthalpy of formation per Frenkel pair, respectively. The results of $U_{1-y}La_yO_2$ ($y = 0.044, 0.090$ and 0.142) obtained in this study are summarized in Table 1 and shown in Figs 4 and 5 together with those

T. MATSUI et al.: HEAT CAPACITY MEASUREMENT OF $U_{1-y}La_yO_2$

Table 1
Enthalpy and entropy of formation of defects

Samples	ΔH_f , eV	ΔS_f , $J \cdot K^{-1} \cdot mol^{-1}$	Authors
$U_{0.956}La_{0.044}O_2$	2.14	39.4	This study (exp.)
$U_{0.910}La_{0.090}O_2$	1.63	34.2	This study (exp.)
$U_{0.858}La_{0.142}O_2$	1.50	31.8	This study (exp.)
$U_{0.956}Gd_{0.044}O_2$	2.25	43.5	INABA, NAITO et al. ⁴ (exp.)
$U_{0.927}Gd_{0.073}O_2$	1.88	40.5	INABA, NAITO et al. ⁴ (exp.)
$U_{0.899}Gd_{0.101}O_2$	1.45	26.9	INABA, NAITO et al. ⁴ (exp.)
$U_{0.858}Gd_{0.142}O_2$	1.10	25.1	INABA, NAITO et al. ⁴ (exp.)
UO_2	1.86	6.11	HYLAND, RALPH ¹² (cal. for e-h pairs)
UO_2	5.12–5.20	–4.18	HARDING et al. ¹⁰ (cal. for Frenkel defects)
UO_2	1.64–1.74	28.5–30.5	HARDING et al. ¹⁰ (cal. for e-h pairs)
UO_2	3.11	62.0	SZWARC ⁶ (exp.)

exp: experimental value from the excess heat capacity.
cal: theoretical calculation.

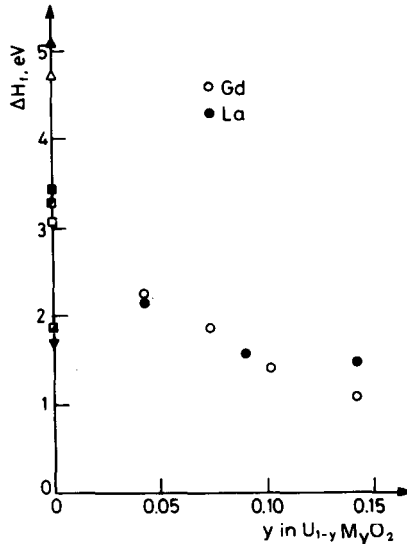


Fig. 4. Enthalpy of activation: ● present study of $U_{1-y}La_yO_2$, ○ $U_{1-y}Gd_yO_2$,⁴ ▲ theoretical value for the formation of a Frenkel pair,¹⁰ △ from neutron-scattering study,¹³ ■,¹¹ ■⁵ and □⁶ the values obtained from the excess heat capacity of UO_2 , ▣ calculated value for the formation of an electron-hole pair from the electrical conductivity and Seebeck coefficient,¹² ▼ theoretical value for the formation of an electron-hole pair¹⁰

of UO_2 ^{5,6,10-13} and $U_{1-y}Gd_yO_2$ ⁴ reported previously. As seen in these figures, lanthanum addition apparently decreases the enthalpy and the entropy of formation, and the extrapolation of the present data to zero La content yields the estimated values for undoped UO_2 : $\Delta H_f = 3.0$ eV and $\Delta S_f = 62$ J · mol⁻¹ · K⁻¹, which are in good agreement with the experimental values of undoped UO_2 so far reported,^{5,6,11} similarly to the case of Gd-doped UO_2 .⁴ The value of ΔH_f for UO_2 in Fig. 4, thus

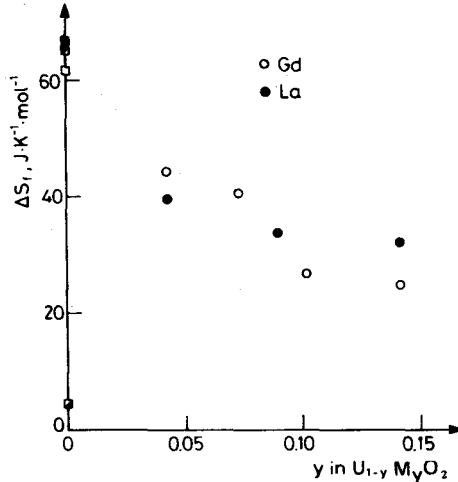


Fig. 5. Entropy of activation: ● present study of $U_{1-y}La_yO_2$, ○ $U_{1-y}Gd_yO_2$,⁴ ■⁵, ■⁶ and ■¹¹ values obtained from the excess heat capacity of UO_2 , ■ calculated value for the formation of an electron-hole pair from the electrical conductivity and Seebeck coefficient^{1,2}

obtained, is higher than the enthalpy of formation of an electron-hole pair calculated theoretically by HARDING et al.,¹⁰ but lower than that of a Frenkel pair of oxygen calculated theoretically also by HARDING et al.¹⁰ In Fig. 5 the extrapolated value of ΔS_f for UO_2 obtained in this study seems to be higher than the entropy of formation of an electron-hole pair estimated from the electrical conductivity and the thermoelectric Seebeck coefficient of UO_2 by HYLAND and RALPY.¹² It is noted that the excess heat capacity due to the formation of electron-hole pair can be expressed by:

$$\Delta C = \frac{(\Delta H_f')^2}{2RT^2} \exp\left(\frac{\Delta S_f'}{2R}\right) \exp\left(\frac{-\Delta H_f'}{2RT}\right) \quad (5)$$

where $\Delta H_f'$ and $\Delta S_f'$ are the enthalpy and entropy of formation per electron-hole pair,

respectively. We can see that the value of $\Delta H'_f$ equals ΔH_f in Eq. (4) and the value of $\Delta S'_f$ is $5.8 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ higher than ΔS_f . Therefore, even if Eq. (5) is used instead of Eq. (4) for the analysis of excess heat capacity, the same conclusion can be obtained.

The electrical conductivities of $U_{1-y}La_yO_2$ ($y = 0.044$, and 0.142) were measured by us in order to find the occurrence of electron-hole pair formation and the results are shown in Fig. 6. The slight increase of the slope in the electrical conductivity curve

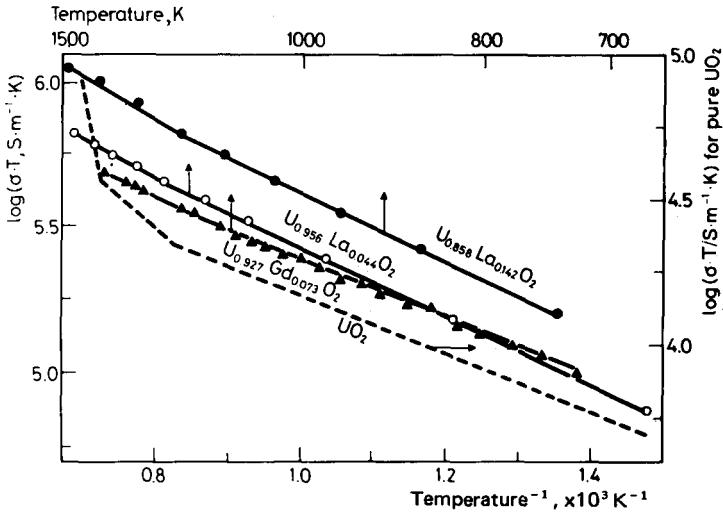


Fig. 6. Electrical conductivity of $U_{1-y}La_yO_2$ ($y = 0.044$ and 0.142) —▲— $U_{0.927}Gd_{0.073}O_2$ by MATSUI and NAITO,² — — — UO_2 by MATSUI and NAITO²

is seen at around 1200 K in both samples of $U_{0.956}La_{0.044}O_2$ and $U_{0.858}La_{0.142}O_2$ similarly to the cases of $U_{0.927}Gd_{0.073}O_2$ and UO_2 and UO_2 previously measured by the present authors.² From the facts that (1) the temperature at which the slope changes is independent of the dopant content and is close to that of UO_2 , and (2) the temperature does not coincide with the onset temperature of the anomalous increase in the heat capacity curve especially in the case of $U_{0.858}La_{0.142}O_2$, the slight increase of the slope in the conductivity curve is thought to be due to gradual transition from the extrinsic to intrinsic conduction region. It is not likely that the excess heat capacity of $U_{1-y}La_yO_2$ is due, therefore, to the formation of electron-hole pairs.

It is concluded that the anomalous increase in the heat capacity of $U_{1-y}La_yO_2$ observed at relatively low temperatures below 1200 K originates from the same

mechanism as that of $U_{1-y}Gd_yO_2$ and undoped UO_2 , and that the predominant thermal activated process as the origin of the excess heat capacity is likely to be the formation of Frenkel pairs of oxygen. By doping trivalent cations such as La^{3+} and Gd^{3+} into UO_2 , U^{5+} ions with smaller ionic radius than that of U^{4+} ions are formed from the electroneutrality condition, and then the Frenkel pairs of oxygen could be easily formed at low temperature.

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