# Heat capacity measurements and XPS studies on uranium–lanthanum mixed oxides

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### ABSTRACT

Heat capacity measurements were carried out on $(U_{1-y}La_y)O_{2\pm x}$ ($y$ = 0.2, 0.4, 0.6, and 0.8) using differential scanning calorimeter (DSC) in the temperature range 298–800 K. Enthalpy increment measurements were carried out on the above solid solutions using high temperature drop calorimetry in the temperature range 800–1800 K. Chemical states of U and La in the solid solutions of mixed oxides were determined using X-ray photoelectron spectroscopy (XPS). Oxygen to metal ratios of $(U_{1-y}La_y)O_{2\pm x}$ were estimated from the ratios of different chemical states of U present in the sample. Anomalous increase in the heat capacity is observed for $(U_{1-y}La_y)O_{2\pm x}$ ($y$ = 0.4, 0.6 and 0.8) with onset temperatures in the range of 1000–1200 K. The anomalous increase in the heat capacity is attributed to certain thermal excitation process, namely, Frenkel pair defect of oxygen. The heat capacity value of $(U_{1-y}La_y)O_{2\pm x}$ ($y$ = 0.2, 0.4, 0.6, and 0.8) at 298 K are 65.3, 64.1, 57.7, 51.9 J K$^{-1}$ mol$^{-1}$, respectively. From the XPS investigations, it was observed that the O/M ratios at the surface are higher than that in the bulk. In uranium rich mixed oxide samples, the surface O/M ratios are greater than 2 whereas that in La rich mixed oxides, they are less than 2, though the bulk O/M in all the samples are less than 2.

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## 1. Introduction

High temperature heat capacity of the fuel under irradiation is one of the important properties for evaluating the fuel temperature profile during normal operation and the evaluation of fuel temperature under accident conditions. Uranium–plutonium mixed oxides are used as fast reactor fuels. Rare earth fission products (La to Gd) have significant fission yields on fast fission of $^{235}$U, $^{238}$U and $^{239}$Pu [1]. These trivalent rare earth oxides form extensive solid solutions with $UO_2$ [2]. Hence high temperature heat capacity data of uranium–rare earth mixed oxides are important to predict the fuel behavior during irradiation. Heat capacity of uranium–rare earth mixed oxides has been determined by various authors [3–16]. Anomalous increase in the heat capacity with temperature was reported by various authors [3–11] whereas certain authors [12–16] reported no anomalous increase in the heat capacity. Earlier [11], we have measured the heat capacity of $(U_{1-y}Gd_y)O_{2\pm x}$ ($y$ = 0.1, 0.2, and 0.5) by DSC in the temperature range 298–800 K. Considerable anomalous increase in the heat capacity was observed

for $(U_{1-y}Gd_y)O_{2\pm x}$ with $y$ = 0.1–0.5. To investigate whether similar anomalous increase in the heat capacity with temperature could be observed in case of $(U_{1-y}La_y)O_{2\pm x}$, heat capacity measurements on $(U_{1-y}La_y)O_{2\pm x}$ ($y$ = 0.2, 0.4, 0.6, and 0.8) were carried out in this study. These solid solutions were prepared by combustion synthesis and characterized by XRD, HPLC and ICP-AES. The preparation, characterization, solubility studies and thermal expansion measurements by high temperature XRD were reported in our previous publication [17]. In the present investigation, heat capacity of $(U_{1-y}La_y)O_{2\pm x}$ ($y$ = 0.2, 0.4, 0.6, and 0.8) were measured by DSC in the temperature range 298–800 K, and their high temperature enthalpy increment measurements in the temperature range 800–1800 K by using drop calorimeter. The chemical states of U and La in their mixed oxide solid solutions have not been studied, previously. In this paper, a detailed analysis of the chemical states of U and La in $(U_{1-y}La_y)O_{2\pm x}$ obtained from XPS is presented. As the depth of the information is limited to few nanometers from the surface of the sample, the oxygen to metal ratio obtained from the XPS results is applicable only to few atomic layers from the surface.

## 2. Experimental

### 2.1. Sample preparation and characterization

Sample preparation by combustion synthesis and characterization by XRD, impurity analysis by ICP-MS, etc. of $(U_{1-y}La_y)O_{2\pm x}$ ($y$ = 0.2, 0.4, 0.6, and 0.8) have

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been discussed in detail in our previous publication [17]. The O/M ratios of the solid solutions were determined by spectrophotometric technique [11] as described below.

The $(U_{1-y}La_y)O_{2\pm x}$ samples were dissolved in concentrated phosphoric acid (2–3 mg/ml). $U^{4+}$ and $U^{6+}$ present in the sample do not change their oxidation states when dissolved in concentrated phosphoric acid whereas $U^{5+}$ is not stable in liquid state and undergoes following disproportionation reaction

$$2U^{5+} \rightarrow U^{4+} + U^{6+} \qquad (1)$$

The concentration of $U^{4+}$ was determined by measuring the absorbance at 540 nm and $U^{6+}$ by absorbance at 315 nm [11]. Assuming that the La in the solid solution is present only in +3 valence state and oxygen in −2 valence state, the O/U ratio was determined as follows.

$$\frac{O}{U} = \frac{3n_{U(VI)} + 2n_{U(IV)}}{n_{U(VI)} + n_{U(IV)}} \qquad (2)$$

where $n_{U(VI)}$ and $n_{U(IV)}$ are number of moles of U(VI) and U(IV), respectively. The O/M of $(U_{1-y}La_y)O_{2\pm x}$ is calculated as follows:

$$\frac{O}{M} = (1-y)\frac{O}{U} + 1.5y \qquad (3)$$

### 2.2. Calorimetric measurements

A heat flux type differential scanning calorimeter, model number DSC821e/700 of M/s. Mettler Toledo GmbH, Switzerland was used in this study. Temperature, heat and $\tau$-lag calibrations were carried out, as explained in our previous publication [18]. The uncertainty in the heat capacity data measured by DSC was estimated to be in the range of 2–3% based on our previous measurements on standard $ThO_2$ samples [19]. Prior to each heat capacity measurement heat rate calibration was performed, using a thin disc of sapphire supplied by M/s. Mettler Toledo GmbH. The heat capacity data of sapphire from NIST, USA was used in the calibration. Heat capacity measurements were carried out in the temperature range 298–800 K. To remove any adsorbed moisture on the sample, it was heated to 573 K before starting the experiment. In a typical measurement about 100–150 mg of sample in the form of pellet was weighed accurately and hermetically sealed in a 40 μl Al-pan. The flow rate of the purge gas (ultra high pure argon) was 50 mL min$^{-1}$. A three segment-heating program, as explained in our previous work [18], was used for heat capacity measurements. Each heat capacity measurement consisted of three runs (1) a blank run with empty pans on the sample and the reference sides, (2) a calibration run with empty pan on the reference side and a pan with sapphire (heat capacity standard) on the sample side and (3) a sample run with empty pan on the reference side and the pan with $(U_{1-y}La_y)O_{2\pm x}$ sample on the sample side.

The enthalpy increments of the samples in the temperature range 800–1800 K were determined by drop calorimetry using a multi-detector high temperature calorimeter (MHTC-96) of M/s. SETARAM. The calorimetric detector is a thermopile which comprises 28 thermocouples embedded on the inner side of an alumina tube. The sample crucible and an empty reference crucible are positioned one above the other in the calorimetric detector. The thermocouples of the thermopile detector are positioned at different levels surrounding the outer surfaces of the crucibles so that an integrated heat exchange between the two crucibles is obtained as the output signal. In the present study, a detector, made of Pt-30%Rh/Pt-10% thermocouples was employed. The detector is centered in a leak-tight alumina muffle placed in a graphite resistance furnace.

In a typical experiment, five samples of α-alumina reference (SRM 720) material and five samples of $(U_{1-y}La_y)O_{2\pm x}$, each weighing about 150–200 mg, were initially placed in the individual slots of the specimen chamber kept at ambient temperature. The α-alumina references and $(U_{1-y}La_y)O_{2\pm x}$ samples were placed in such a way that each $(U_{1-y}La_y)O_{2\pm x}$ sample was sandwiched between two α-alumina references. The furnace was gradually heated to the desired preset temperature and argon was passed through the furnace. Once the temperature of the furnace reached the measurement temperature, the samples were dropped from the specimen chamber. The samples maintained at the ambient temperature fell into the sample crucible maintained at temperature ($T$). About 20–25 min was found to be sufficient for the re-stabilization of both the temperature and the heat flow signals. The heat flow, $Q$ (in μV) was monitored as a function of time ($t$) and the peak area $\int Q\,dt$ (after subtracting the baseline) associated with each drop corresponded to the respective enthalpy increment. From the resultant heat flow signals corresponding to the α-alumina reference ($Q_R$) and the sample ($Q_S$), the enthalpy increments $(H_T - H_{298})_S$ of samples were computed using the known enthalpy increment values of α-alumina reference $(H_T - H_{298})_R$ from the literature [20] and the following expression

$$(H_T - H_{298})_S = \frac{\int Q_S\,dt}{\int Q_R\,dt}\frac{M_S}{m_S}\frac{m_R}{M_R}(H_T - H_{298})_R \qquad (4)$$

where $M_R$ and $m_R$ are the molar mass and mass of the α-alumina reference pellet and $M_S$ and $m_S$ are the molar mass and mass of the mixed oxide sample. The mean of the five heat flow values for the standard and that for the sample were used to compute the enthalpy increment at that temperature, $T$. Further, four or five measurements were carried out for a given temperature and the mean value of the enthalpy increments from these runs at temperature, $T$ were used for fitting.
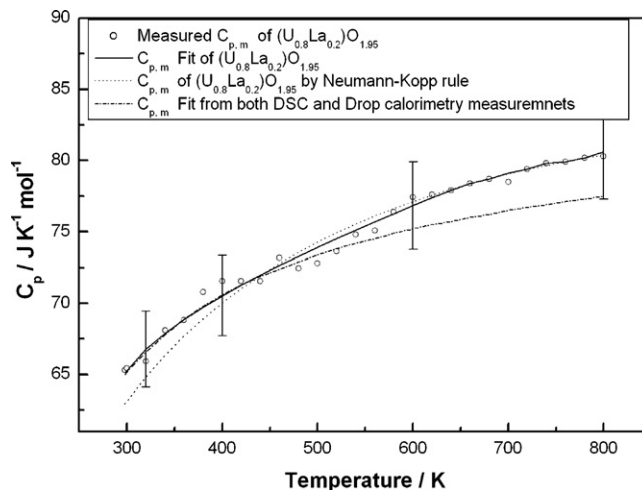


**Fig. 1.** Heat capacity data of $(U_{0.8}La_{0.2})O_{1.95}$ measured by DSC.

### 2.3. XPS studies

XPS studies were carried out using VG ESCALAB MKII system. The base vacuum of the chamber was $10^{-10}$ mbar and AlKα was used as excitation source for photoelectron emission.

## 3. Results

### 3.1. Heat capacity measurements by DSC

Heat capacity of $(U_{1-y}La_y)O_{2\pm x}$ ($y = 0.2, 0.4, 0.6,$ and $0.8$) measured by DSC are the mean of nine measurements. The measured heat capacity values of samples were least square fitted to a polynomial in temperature. The measured heat capacity data of the mixed oxides along with the fit values are shown in Figs. 1–4 and are also listed in Tables 1–4. The heat capacity data estimated by Neumann–Kopp's law using the literature heat capacity data of $La_2O_3$ [21] and $UO_2$ [22] are also given in Figs. 1–4. The corrections for non-stoichiometry in the heat capacity values were made using the method described by Mills et al. [7].

$$C_{p,m}(UO_2) = \frac{3}{3+x}C_{p,m}(UO_{2+x}) \qquad (5)$$

In our previous publication [11] on the heat capacity of $(U_{1-y}Gd_y)O_{2\pm x}$ ($y = 0.1, 0.2$ and $0.5$) considerable anomalous increase in the heat capacity was observed in the temperature range
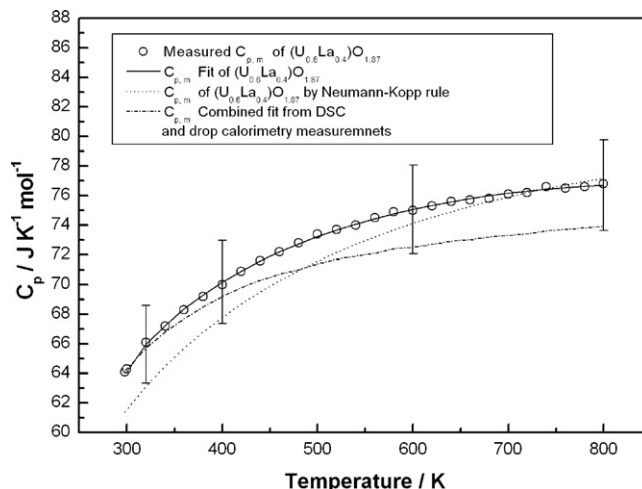


**Fig. 2.** Heat capacity data of $(U_{0.6}La_{0.4})O_{1.87}$ measured by DSC.