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Specific heats of ternary oxides in the Li–U(VI)–O System

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ABSTRACT

Seven ternary oxides; Li_4UO_5, Li_2UO_4, $Li_{22}U_{18}O_{65}$, $Li_2U_{1.75}O_{6.25}$, $Li_2U_2O_7$, $Li_2U_3O_{10}$ and $Li_2U_6O_{19}$ in the system Li–U(VI)–O were prepared by solid-state reaction route and characterized by X-ray diffraction method. Specific heats of these compounds were measured by differential scanning calorimetry in the temperature range from 300 to 860 K. The specific heats show a decreasing trend with increase in UO_3(s) content in these lithium uranates. However, the specific heat per gram atom shows an increasing trend with decrease in number of oxygen atoms in the formula unit.

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1. Introduction

Spent nuclear fuels are usually voloxidised by heating in oxygen or air at 773–973 K to disintegrate the fuel rods into fine powders as well as to remove tritium from it before dissolution in nitric acid [1]. For the spent fuel from liquid metal-cooled fast breeder reactor, it has been reported that this process needs higher temperatures of more than 1123 K and results into large amount of insoluble residue which holds large amount of plutonium [2]. Thus, it is advisable to use a fused salt for digesting the spent fuels [1]. The feasibility of this process has been studied by many researchers [3–5]. Avogadro and De Plano [6] and Toussaint and Avogadro [7] have explored the reaction of UO_2 in molten alkali metal nitrates and found that compounds of types $Na_{2-x}MeU_2O_7$ (Me = Li, K, Cs) are formed at 723–773 K. Similarly, Fujino [8] has studied the reaction of lithium and sodium nitrates and carbonates with uranium to find out the minimum amounts of alkali metal salts required to form uranates as well as their reactivity. In this context, it is important to know the thermodynamic stabilities of various alkali metal uranates.

Considering the Li–U–O system, several lithium uranates have been prepared and their structural and spectroscopic properties have been investigated by many authors [9–14]. However, the thermal and thermodynamic data on such compounds is scarce. Hauck [10] has investigated a number of lithium based uranates and tungstates within the system $Li_2O–UO_3–WO_3$ in which the valency of the uranium is (VI) and observed that uranium can have seven or eight fold coordination with usual uranyl bonds which are strong. The system $Li_2O–UO_3$ was also investigated by Prins and Cordfunke [13] and phase boundaries were determined more accurately. Cordfunke et al. [15] measured enthalpies of solution of Li_2UO_4, $Li_2U_3O_{10}$ and Li_4UO_5 in aqueous sulfuric acid calorimetrically and by combining this information with the enthalpies of solution of Li_2SO_4 and UO_3 in the same solvent could obtain standard enthalpies of formation of Li_2UO_4, $Li_2U_3O_{10}$ and Li_4UO_5. As a systematic study, the system Li–U–O has been explored in this study, in particular the lithium uranates with uranium in hexavalent state. We have synthesized Li_4UO_5, Li_2UO_4, $Li_{22}U_{18}O_{65}$, $Li_2U_{1.75}O_{6.25}$, $Li_2U_2O_7$, $Li_2U_3O_{10}$ and $Li_2U_6O_{19}$ compounds and measured their specific heats by differential scanning calorimetry (DSC).

2. Experimental

2.1. *Preparation of lithium uranates*

Lithium uranates with uranium in hexavalent state were prepared by solid-state reaction route. Seven stoichiometric compounds namely Li_4UO_5, Li_2UO_4, $Li_{22}U_{18}O_{65}$, $Li_2U_{1.75}O_{6.25}$, $Li_2U_2O_7$, $Li_2U_3O_{10}$ and $Li_2U_6O_{19}$ were prepared by the reaction of Li_2CO_3 with U_3O_8 at elevated temperatures. Li_2CO_3 and U_3O_8 were weighed accurately in the stoichiometric proportion keeping Li/U atomic ratio fixed for each compound, mixed and ground thoroughly in an agate mortar. The fine powdered mixture so obtained is pelletized to a cylindrical shape of 10 mm diameter. For the preparation of $Li_2U_{1.75}O_{6.25}$, $Li_2U_2O_7$, $Li_2U_3O_{10}$ and $Li_2U_6O_{19}$, the pellets were heated to 1073 K for 24 h using resistance heating furnace in an alumina boat in oxygen atmosphere for 24 h. The pellets turned orange in color indicating the formation of uranates. The pellets were reground, pelletized and heated again at 1073 K for 24 h. However,

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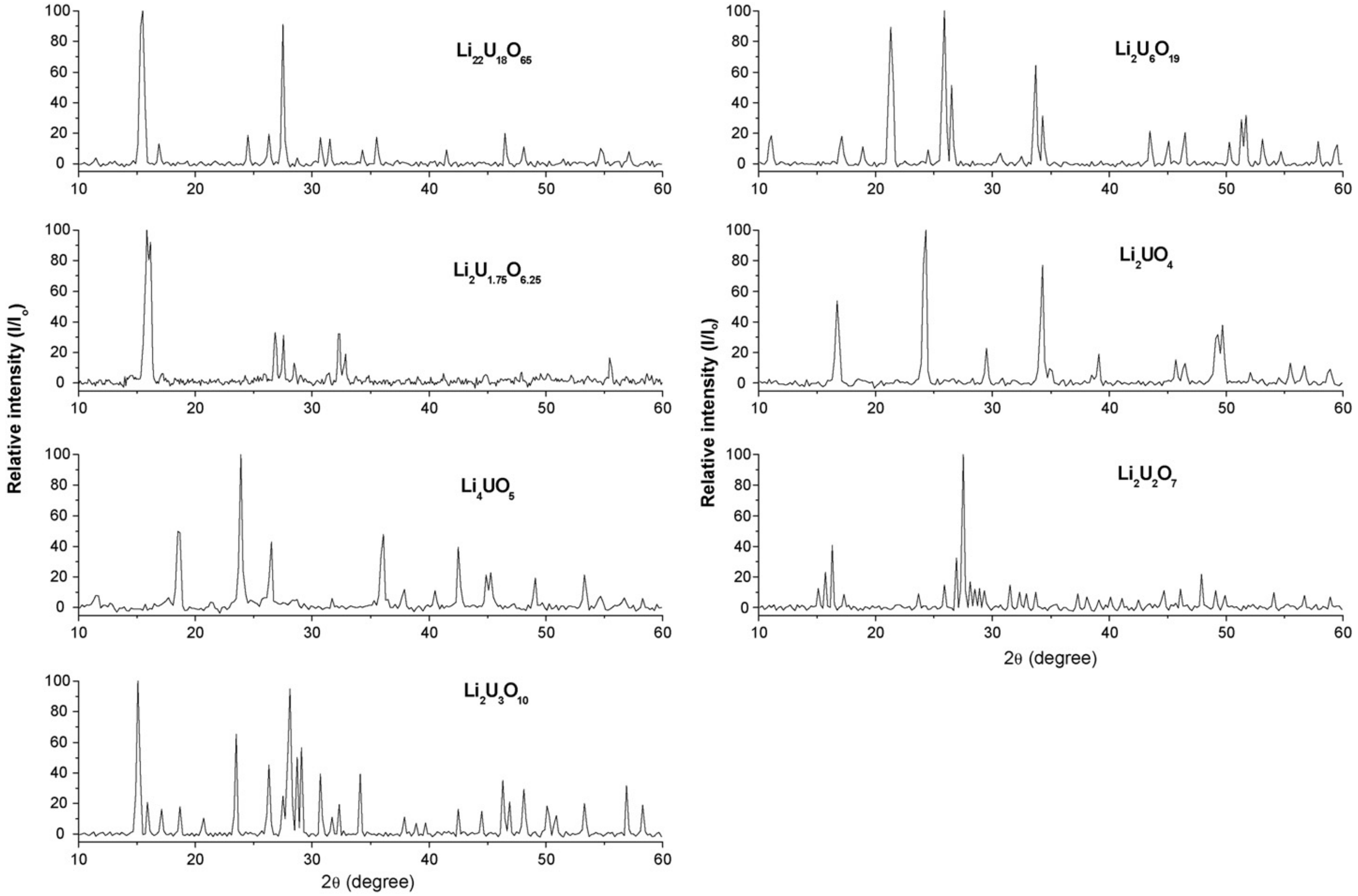

Fig. 1. X-ray diffraction patterns of lithium uranates.

the preparation of uranates viz. Li_2UO_4, Li_4UO_5 and $Li_{22}U_{18}O_{65}$ required careful heat treatment of the pellets. For the preparation of these compounds an alternate heat treatment procedure was adopted. The pellets were first heated at 923 K for 5 h, cooled, reground, pelletized again and heat treated in oxygen atmosphere for 5 h at 923 K. The pellets were finally heat treated to 1073 K for 48 h. All the compounds were characterized by power X-ray diffraction method using a STOE X-ray diffractometer (theta–theta geometry) using a graphite monochromator. The XRD patterns were recorded with 2θ range of 20–60° using monochromatized Cu-Kα_1 ($\lambda = 1.5406$ Å) radiation. The formation of the various phases was established from the comparison of their XRD patterns with the JCPDS (Joint Committee on Powder Diffraction Standards) files [16].

2.2. Specific heat measurements

Specific heat measurements were carried out using a heat flux type differential scanning calorimeter (DSC 131, SETARAM Instrumentation, France). Temperature calibration for the calorimeter was carried out using the phase transition temperatures of NIST reference materials (indium: $T_{fus} = 429.748$ K; tin: $T_{fus} = 505.078$ K; lead: $T_{fus} = 600.600$ K; mercury: $T_{fus} = 234.316$ K; potassium nitrate: $T_{trs} = 400.850$ K; silver sulfate; $T_{trs} = 703.150$ K). Heat calibration of the calorimeter was carried out using the transition heats of the above-mentioned materials. For specific heat measurements, in the first run, two empty aluminum crucibles of identical masses (10^{-4} dm^3 capacity) with covering lid kept in the sample and reference cells and the heat flow versus temperature were measured in the temperature range from 300 to 860 K at a heating rate of 5 K min^{-1} with high purity argon as the carrier gas with a flow rate of 2 dm^3 h^{-1}. In the second run, the heat flow versus temperature were measured by loading NIST synthetic sapphire (SRM-720) in the powder form (~200 mg) in the sample cell keeping the reference cell empty. In the third run, heat flow versus temperature were measured by loading the actual experimental sample (~200 mg) in the powder form into the sample cell and keeping the reference cell empty. Identical conditions were maintained in all the three sets of experiments. The specific heat of the sample under investigation can be calculated by a simple comparison of the heat flow rates into the sample and into the calibration substance as illustrated in the literature [17]. The expression used for the calculation of specific heat of the sample is given as:

$$C_p^o(T)_{\text{Sample}} = \left\{ \left(\frac{\text{HF}_{\text{Sample}} - \text{HF}_{\text{Blank}}}{\text{HF}_{\text{Ref}} - \text{HF}_{\text{Blank}}} \right) \right\} \times \left(\frac{M_{\text{Ref}}}{M_{\text{Sample}}} \right) \times C_p^o(T)_{\text{Ref}}, \qquad (1)$$

where HF_{blank}, HF_{Ref} and $\text{HF}_{\text{sample}}$ represent heat flow during first, second and third runs, respectively. $C_p^o(T)_{\text{Sample}}$ and $C_p^o(T)_{\text{Ref}}$ represent the specific heats of sample and reference material, where as M_{Sample} and M_{Ref} represent the masses of sample and reference, respectively. The specific heat of nuclear grade ThO_2 and NIST standard molybdenum were measured in the temperature range from 300 to 860 K in order to check the accuracy of the measurement. The values were found to be within ±2 per cent compared to the literature values [18].

Table 1
The values of lattice parameters of lithium uranates.

Compound	Crystal system	Unit cell parameters (a, b, c in Å and β in °)	
		This study	Literature [16]
$Li_{22}U_{18}O_{65}$	Orthorhombic	a = 20.371	a = 20.37
		b = 11.713	b = 11.73
		c = 11.430	c = 11.42
$Li_2U_{1.75}O_{6.25}$	*Monoclinic	a = 6.725	–
		b = 18.826	–
		c = 6.989	–
		β = 119.99	–
Li_4UO_5	Tetragonal	a = 6.718	a = 6.725
		c = 4.446	c = 4.451
$Li_2U_3O_{10}$	Monoclinic	a = 6.806	a = 6.805
		b = 19.052	b = 19.067
		c = 7.225	c = 7.250
		β = 121.13	β = 121.12
Li_2UO_4	Orthorhombic	a = 6.046	a = 6.06
		b = 5.116	b = 5.13
		c = 10.559	c = 10.51
$Li_2U_2O_7$	*Monoclinic	a = 6.775	–
		b = 18.948	–
		c = 7.086	–
		β = 120.81	–

* The crystal system is not reported in the literature.

3. Results and discussion

3.1. X-ray diffraction measurements

The formation of lithium uranates were confirmed by comparing the recorded X-ray diffraction (XRD) patterns of samples with the JCPDS patterns [16] without any detectable impurities. The XRD patterns of these compounds are shown in Fig. 1. The lattice parameters were calculated by indexing the reflection lines using the program POWD [19]. For the compounds $Li_{22}U_{18}O_{65}$, Li_4UO_5, $Li_2U_3O_{10}$ and Li_2UO_4, the lattice parameters obtained in this study are listed in Table 1 and found to be in reasonable agreement with those reported in the literature [16]. However, for the compounds $Li_2U_{1.75}O_{6.25}$, $Li_2U_2O_7$ and $Li_2U_6O_{19}$, the crystal system and lattice parameters are not reported in the literature. In this study, the reflection lines of compounds $Li_2U_2O_7$ and $Li_2U_{1.75}O_{6.25}$ were indexed with the monoclinic system assuming them to be structurally isomorphous with the compounds $Na_2U_2O_7$ and $K_2U_2O_7$ having monoclinic crystal system [16]. However, for the compound $Li_2U_6O_{19}$, we could not find any isomorphous compound and hence this compound has not been indexed in this study. However, the observed interplanar spacing found in this study are in good agreement with those reported in the literature [16].

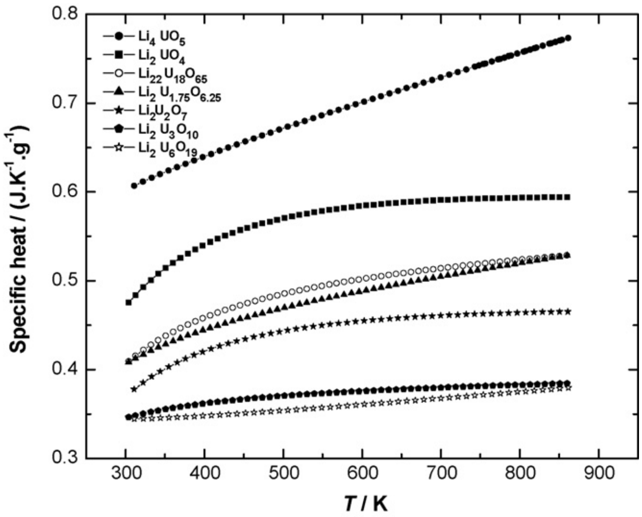

Fig. 2. Variation of specific heat as a function of temperature for lithium uranates.

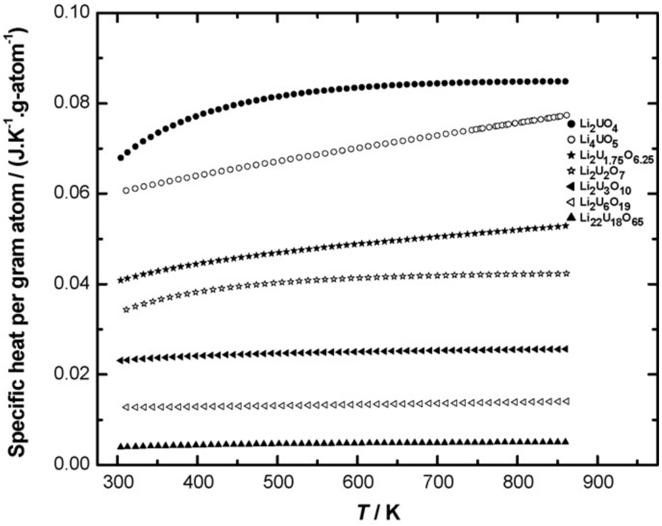

Fig. 3. Variation of specific heat per gram atom as a function of temperature for lithium uranates.

3.2. Specific heat measurements

The specific heat data obtained from DSC experiments are shown in Fig. 2 for all the lithium uranates. The accuracy of the measurements is within ±2 per cent as was found for nuclear grade ThO_2 and NIST standard molybdenum. The measured specific heats for each compound were least squares fitted as a function of temperature and the expressions are given in Eqs. (2)–(8).

$$C_p^o\left(\frac{Li_4UO_5,\,s}{J\times g^{-1}\times K^{-1}}\right) = 0.5488 + 2.6\times10^{-4}\times\left(\frac{T}{K}\right) - 2328\times\left(\frac{K}{T}\right)^2 \quad (2)$$

$$C_p^o\left(\frac{Li_2UO_4,\,s}{J\times g^{-1}\times K^{-1}}\right) = 0.6547 - 5.0\times10^{-5}\times\left(\frac{T}{K}\right) - 15262\times\left(\frac{K}{T}\right)^2 \quad (3)$$

$$C_p^o\left(\frac{Li_{22}U_{18}O_{65},\,s}{J\times g^{-1}\times K^{-1}}\right) = 0.4994 + 5.0\times10^{-5}\times\left(\frac{T}{K}\right) - 9696\times\left(\frac{K}{T}\right)^2 \quad (4)$$

$$C_p^o\left(\frac{Li_2U_{1.75}O_{6.25},\,s}{J\times g^{-1}\times K^{-1}}\right) = 0.4283 + 1.2\times10^{-4}\times\left(\frac{T}{K}\right) - 5360\times\left(\frac{K}{T}\right)^2 \quad (5)$$

$$C_p^o\left(\frac{Li_2U_2O_7,\,s}{J\times g^{-1}\times K^{-1}}\right) = 0.4966 - 2.0\times10^{-5}\times\left(\frac{T}{K}\right) - 10923\times\left(\frac{K}{T}\right)^2 \quad (6)$$

Table 2
Thermodynamic parameters for lithium uranates.

Compound	$S^o{}_m$(298.15 K) (J mol^{-1} K^{-1})	$\Delta_f H^o{}_m$(298.15 K) (kJ/mol) Ref. [20]	$\Delta_f G^o{}_m$(298.15 K) (kJ/mol)	$\Delta_{f,ox} G^o{}_m$(298.15 K) (kJ/mol)
Li_4UO_5	169	−2639	−2487	−147
Li_2UO_4	136	−1968	−1854	−219
$Li_{22}U_{18}O_{65}$	2208	–	–	–
$Li_2U_{1.75}O_{6.25}$	212	–	–	–
$Li_2U_2O_7$	238	−3214	−3023	−170
$Li_2U_3O_{10}$	340	−4437	−4171	−172
$Li_2U_6O_{19}$	646	–	–	–

$$C_p^o\left(\frac{Li_2U_3O_{10},\,s}{J \times g^{-1} \times K^{-1}}\right) = 0.3744 + 2.0 \times 10^{-5} \times \left(\frac{T}{K}\right) - 3060 \times \left(\frac{K}{T}\right)^2 \qquad (7)$$

$$C_p^o\left(\frac{Li_2U_6O_{19},\,s}{J \times g^{-1} \times K^{-1}}\right) = 0.3126 + 8.0 \times 10^{-5} \times \left(\frac{T}{K}\right) - 770 \times \left(\frac{K}{T}\right)^2 \qquad (8)$$

The specific heats of these lithium uranates are found to show a decreasing trend with increase in the UO_3 content. However, the temperature variation of specific heats of these uranates does not show any systematic trend. Hence, the specific heats of these uranates have been converted to specific heat per gram atom by dividing the specific heat in Eqs. (2)–(8) by the total number of atoms present in the respective compounds. The values thus obtained are shown in Fig. 3. It is evident from Fig. 3 that the specific heat per gram atom shows an increasing trend with decrease in number of oxygen atoms in the formula unit.

The standard molar entropy, $S^o{}_m$(298.15 K), of these hexavalent uranates are estimated using Latimer's method [20]. The enthalpy of formation, $\Delta_f H^o$(298.15 K), of Li_4UO_5, $Li_2U_2O_7$, Li_2UO_4 and $Li_2U_3O_{10}$ are reported in the literature [21]. However, for the other three hexavalent uranates the values of $\Delta_f H^o$(298.15 K) are not available in the literature.

Taking the estimated $S^o{}_m$(298.15 K) and $\Delta_f H^o{}_m$(298.15 K) of Li_4UO_5, $Li_2U_2O_7$, Li_2UO_4 and $Li_2U_3O_{10}$, the standard molar Gibbs energy of formation from the elements ($\Delta_f G^o{}_m$) and the Gibbs energy of formation ($\Delta_{f,ox} G^o{}_m$) from component oxides Li_2O(s) and UO_3(s) for these four uranates are calculated and listed in Table 2.

4. Conclusions

Specific heats for lithium hexavalent uranates were measured using differential scanning calorimetry. The specific heats show a decreasing trend with increase in UO_3(s) content in these lithium uranates. However, the specific heat per gram atom shows an increasing trend with decrease in number of oxygen atoms in the formula unit. The standard molar entropy and the standard molar enthalpy of formation of Li_4UO_5, $Li_2U_2O_7$, Li_2UO_4 and $Li_2U_3O_{10}$ were calculated from the measured data and the estimated auxiliary data.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2009.02.010.

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