ELSEVIER

Thermochimica Acta 297 (1997) 169–175

thermochimica acta

Thermal and X-ray studies on mixed metal oxalates – $(NH_4)Ln^{III}U^{IV}(C_2O_4)_4 \cdot 8H_2O$ (Ln = La, Ce, Pr, Nd Tb)

K.D. Singh Mudher, K. Krishnan, A.K. Chadha, V. Venugopal*

Fuel Chemistry Division, Bhabha Atomic Research Centre, Bombay 400 085, India

Received 6 June 1995; received in revised form 13 May 1996; accepted 2 January 1997

Abstract

Five mixed metal oxalates of lanthanides and uranium of the formula $(NH_4)Ln^{III}U^{IV}(C_2O_4)_4 \cdot 8H_2O$ were prepared and characterised by chemical, infrared spectroscopy, X-ray diffraction and thermal methods. The X-ray powder diffraction data of all the compounds were indexed on an orthorhombic unit cell. Thermal decomposition of the compounds proceeded with the loss of water molecules below 475 K followed by decomposition in the temperature range of 625 to 655 K to give $Ln_2O_2CO_3$ and UO_{2+x} as intermediate products. The intermediate products reacted above 975 K to form solid solutions of mixed oxides having a fluorite structure. Activation energy values were derived for the dehydration of lanthanum and terbium compounds. Lattice parameters of the fluorite phases of the mixed oxides formed by heating the compounds in air, argon and N_2/H_2 have been determined. © 1997 Elsevier Science B.V.

Keywords: Lanthanides; Mixed oxalates; Thermal; Uranium(IV); X-ray diffraction

1. Introduction

The partial replacement of K^+ ions in aqueous solution of $K_4U(C_2O_4)_4$ by bivalent or trivalent ions led to the formation of mixed metal compounds with composition $K_2MU(C_2O_4)_4 \cdot 8H_2O$ [1], where $M = Ca^{2+}$ or Cd^{2+} and $KLnU(C_2O_4)_4 \cdot 8H_2O$ [2], where $Ln = La^{3+}$, Ce^{3+}, Pr^{3+}, Nd^{3+} or Tb^{3+}. On heating to 1075 K in air, $K_2MU(C_2O_4)_4 \cdot 8H_2O$ compounds gave new mixed oxide phases having perovskite-related cubic structure [1,3], whereas KLnU $(C_2O_4)_4 \cdot 8H_2O$ at the same temperature formed $K_2U_2O_7$ and mixed oxides solid solution $(Ln,U)O_{2\pm x}$ [2]. As a part of the systematic studies on the mixed metal compounds of uranium, the present paper deals with the preparation, infrared spectroscopy, X-ray powder diffraction and thermal studies of $(NH_4)LnU(C_2O_4)_4 \cdot 8H_2O$, where $Ln = La^{3+}$, Ce^{3+}, Pr^{3+}, Nd^{3+} or Tb^{3+}.

2. Experimental

2.1. Preparation

The five ammonium oxalate compounds of lanthanides(III) and uranium(IV) were prepared from the respective lanthanide chloride (99.9% purity) and $(NH_4)_4U(C_2O_4)_4 \cdot 6H_2O$. $(NH_4)_4U(C_2O_4)_4 \cdot 6H_2O$ was crystallised by dissolving uranium(IV) oxalate in aqueous solution of ammonium oxalate followed by the addition of acetone [4]. About 0.1 M solution of

---

*Corresponding author. Fax: 00 91 01 22 5560750.

PII S0040-6031(97)00068-3

lanthanide chloride and 0.01 M solution of $(NH_4)_4U(C_2O_4)_4{\cdot}6H_2O$ in dilute hydrochloric acid were mixed in the required stoichiometric proportions and allowed to stand for 3–4 h. The solid compounds which get precipitated were filtered off, washed with absolute alcohol and dried in air.

2.2. *Chemical analysis*

The chemical composition of the compounds was established by elemental analysis of lanthanides, uranium, carbon, nitrogen and hydrogen. The lanthanides and uranium were determined following the method reported earlier [2]. The carbon content in the compound was determined by oxidation to CO_2 at 1475 K and measuring the thermal conductivity in a LECO carbon analyser. Nitrogen and hydrogen were determined by inert gas fusion techniques, using LECO determinators.

2.3. *Instrumental analysis*

The infrared (IR) spectra were recorded on a Pye Unicam IR spectrophotometer with the sample dispersed in nujol mulls and pressed in KBr discs. Thermogravimetry (TG) and differential thermal analysis (DTA) curves were recorded upto 1175 K using a ULVAC thermoanalyser. Preheated Al_2O_3 as a reference material for DTA and platinum crucibles as containers were used for measurements. X-ray diffraction patterns were recorded on a DIANO diffractometer using Cu Kα ($\lambda = 1.54178$ Å) radiation and a graphite monochromator. The density of the compounds were determined pyknometrically using carbon tetrachloride as solvent.

3. Results and discussion

The results of the chemical analysis given in Table 1 are in agreement with the expected values for the molecular composition of the compounds as $(NH_4)Ln^{III}U^{IV}(C_2O_4)_4{\cdot}8H_2O$.

The IR spectra recorded for all the compounds in the range of 4000–400 cm^{-1} showed absorption bands in the same region indicating their structural similarity. A typical spectrum of $(NH_4)TbU(C_2O_4)_4{\cdot}8H_2O$ (Fig. 1) shows characteristic absorption bands in the region of 3300–3050 cm^{-1} due to ammonium ions and bands at 1310 and 810 cm^{-1} due to oxalate groups [5]. The absorption band at 1630 cm^{-1} due to oxalate group overlaps with the H-O-H bending mode of water molecules. Besides the absorption band at 1630 cm^{-1}, the absorption band for O-H stretch around 3600 cm^{-1} confirm the presence of water molecules in the compounds. The absorption band around 480 cm^{-1} corresponds to metal-oxygen bond in the structure.

The X-ray powder data for all the five compounds were indexed on orthorhombic unit cells. The similarity in the least squares refined crystal data presented in Table 2 show that cerium, praseodymium, neodymium and terbium compounds are isostructural. However, the lanthanum compound could be indexed on a unit cell with different cell parameters. The indexed X-ray data for the lanthanum and terbium compounds are given in Table 3.

The TG and DTA curves recorded at the heating rate of 6 K min^{-1} in flowing air showed that all the compounds lose water molecules below 475 K. The lanthanum compounds lose all the eight water molecules in a single step, whereas cerium, praseodymium, neodymium and terbium compounds lose six water

Table 1
Results of chemical analysis (weight %) of $(NH_4)LnU(C_2O_4)_4{\cdot}8H_2O$

Ln	Hydrogen		Carbon		Nitrogen		Lanthanide		Uranium	
	A	B	A	B	A	B	A	B	A	B
La	2.07	2.24	11.19	10.78	1.53	1. 57	15.37	15.59	26.94	26.71
Ce	2.18	2.24	10.80	10.76	1.49	1. 57	15.45	15.71	25.68	26.68
Pr	2.29	2.24	10.95	10.75	1.45	1. 57	15.43	15.78	26.07	26.65
Nd	2.15	2.23	10.80	10.71	1.48	1. 56	15.78	16.09	25.84	26.56
Tb	2.16	2.20	10.78	10.54	1.45	1. 54	17.25	17.45	27.58	26.13

A = determined experimentally and B = calculated from molecular formula.

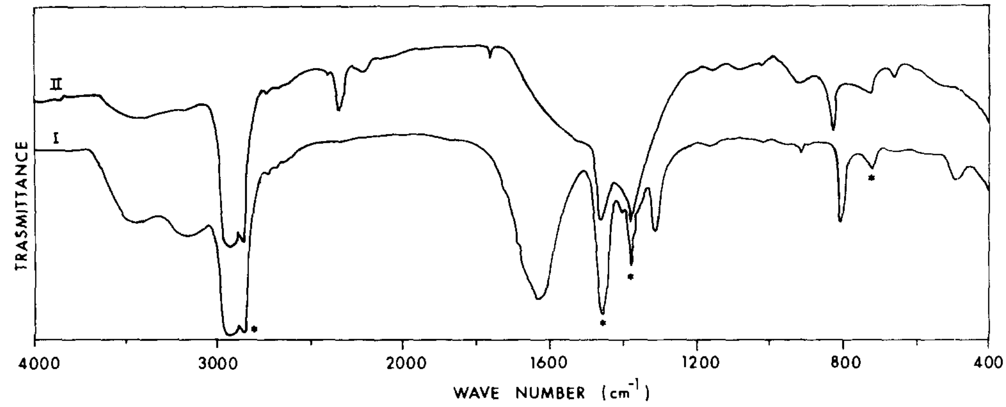

Fig. 1. IR spectra of $(NH_4)TbU(C_2O_4)_4{\cdot}8H_2O$ (spectrum-I), and its intermediate products at 655 K (spectrum-II). Absorption bands from nujol are indicated in an asterisk.

Table 2
Crystal data of $(NH_4)LnU(C_2O_4)_4{\cdot}8H_2O$

Ln	a(Å)	b(Å)	c(Å)	ρ_{obs}.g.cm^{-3}	Z
La	13.865(9)	9.761(9)	8.716(8)	2.42	2
Ce	8.895(6)	17.845(10)	16.066(9)	2.28	4
Pr	8.901(8)	17.733(11)	16.074(10)	2.29	4
Nd	8.846(7)	17.743(12)	16.044(9)	2.31	4
Tb	8.775(5)	17.494(11)	15.963(9)	2.41	4

The numbers in parentheses represent estimated standard deviations.

Table 3
X-ray diffraction data of $(NH_4)LaU(C_2O_4)_4{\cdot}8H_2O$ and $(NH_4)TbU(C_2O_4)_4{\cdot}8H_2O$ (λ = 1.54178 A)

$(NH_4)LaU(C_2O_4)_4{\cdot}8H_2O$				$(NH_4)TbU(C_2O_4)_4{\cdot}8H_2O$			
hkl	d_{obs}.	d_{calc}.	I/I$_o$	hkl	d_{obs}.	d_{calc}.	I/I$_o$
010	9.815	9.761	65	100	7.985	7.982	100
011	6.506	6.501	55	120	6.202	6.196	70
210	5.644	5.652	100	102	5.940	5.905	20
201	5.415	5.426	25	022		5.896	
020	4.885	4.881	15	122	4.898	4.894	55
021	4.266	4.258	20	040	4.377	4.377	10
202	3.691	3.690	10	004	3.990	3.991	20
022	3.248	3.250	25	024	3.642	3.661	15
003	2.906	2.906	15	104		3.633	
420	2.818	2.825	15	142	3.515	3.515	20
014	2.127	2.127	15	124	3.353	3.355	15
621	2.031	2.031	10	240	3.097	3.098	15
				204	2.953	2.952	10
				044		2.948	
				242	2.888	2.888	20
				160	2.767	2.767	15
				322	2.620	2.621	10
				262	2.324	2.323	10
				046	2.272	2.273	10
				400	2.195	2.194	15

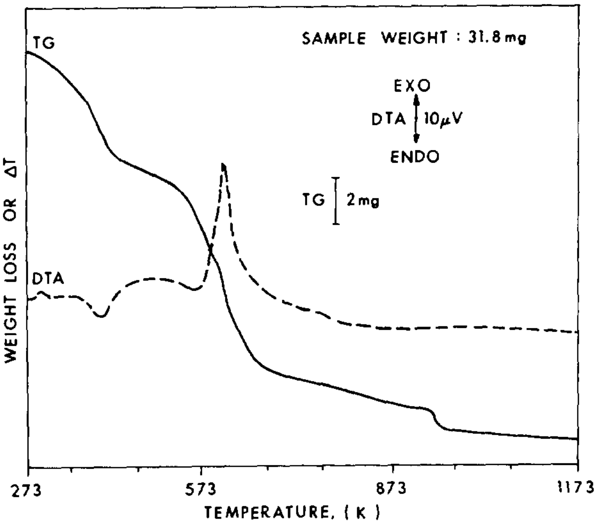

Fig. 2. TG and DTA curves of $(NH_4)LaU(C_2O_4)_4{\cdot}8H_2O$ in air.

molecules in the first step followed by the loss of later two water molecules in the second step. The TG and DTA curves of the lanthanum compound and terbium compound are shown in Figs. 2 and 3, respectively. The TG and DTA curves of cerium, praseodymium and neodymium compounds were similar to those of terbium compound. The observed weight loss of the water molecules in the compounds is compared with the expected weight loss in Table 4.

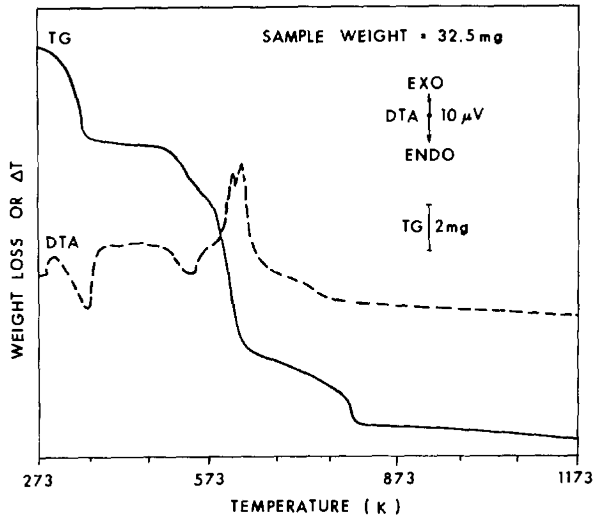

Fig. 3. TG and DTA curves of $(NH_4)TbU(C_2O_4)_4{\cdot}8H_2O$ in air.

Further heating of the compounds after removal of water in air led to the decomposition of the ammonium and oxalate groups in the temperature range of 575 to 655 K which was accompanied by one DTA exothermic peak for the lanthanum compound and two exothermic peaks for other four compounds. The weight losses calculated for the decomposition show the formation of dioxymonocarbonates $Ln_2O_2CO_3$ and UO_{2+x} as intermediates (Table 4). X-ray diffraction patterns of the compounds heated isothermally at 655 K showed a diffused pattern corresponding to UO_{2+x}. No X-ray pattern could be observed for the dioxymonocarbonates, even though the compounds were heated for 40 h. The intermediate compounds when reacted with dilute acid gave effervescence showing the presence of carbonate. The IR spectra of these intermediates were similar and in agreement with the IR spectra of dioxymonocarbonates of lanthanides reported by Turcotle et al. [6] in the range of 1800–700 cm^{-1}. The IR spectrum of 655 K heated intermediate products of terbium compound is included in Fig. 1 (spectrum-II). The absorption band at 830 cm^{-1} in the spectrum further support the presence of carbonate [5] in the product. However, the principal carbonate peak centered around 1450 cm^{-1} is obscured by the nujol peaks in the region. The conversion of oxalate compounds to oxycarbonates has also been reported during the thermal decomposition of europium oxalate [7,8] and plutonium oxalate [9]. The absorption band at 2300 cm^{-1} as shown in Fig. 2-(II), has also been observed in the IR spectra of the decomposition products of europium oxalate and plutonium oxalate, thus confirming the formation of carbonate as intermediate.

On further heating beyond 975 K, the intermediate products $Ln_2O_2CO_3$ and UO_{2+x} react together to form solid solutions of the mixed oxide $(Ln,U)O_{2\pm x}$ of fluorite structure, as seen in X-ray diffraction patterns. The observed loss of about 5 wt% at 975 K is in close agreement with the formation of mixed oxides $(Ln,U)O_2$ (Table 4). Lanthanides oxides and uranium oxide are reported to form mixed oxide solid solutions in different composition range with varying oxygen stoichiometry [10]. In the present study, no attempt was made to determine the oxygen stoichiometry. The decomposition scheme for $(NH_4)TbU(C_2O_4)_4{\cdot}8H_2O$ as one of the cases is shown below:

Table 4
Thermogravimetric data on $(NH_4)LnU(C_2O_4)_4{\cdot}8H_2O$

Ln	Percentage weight loss							
	I		II		III		IV	
	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc. *
La			16.04 +	16.16	48.74	48.94	55.31	54.10
Ce	12.18	12.11	16.51	16.14	49.32	48.87	54.08	54.03
Pr	12.13	12.09	15.97	16.13	47.65	48.83	53.18	53.98
Nd	12.65	12.05	17.10	16.09	47.88	48.65	53.29	53.78
Tb	12.25	11.86	16.61	15.81	46.76	47.86	53.29	52.91
Products	$(NH_4)LnU(C_2O_4)_4{\cdot}2H_2O$		$(NH_4)LnU(C_2O_4)_4$		$Ln_2CO_3 + UO_{2+x}$		$(Ln,U)O_{2+x}$	

+ Observed weight loss in single step.
* Weight loss calculated for $(Ln,U)O_2$.

$$(NH_4)TbU(C_2O_4)_4 \cdot 8H_2O \underset{-6H_2O}{\overset{425K}{\longrightarrow}} (NH_4)TbU(C_2O_4)_4 \cdot 2H_2O \quad (I)$$

$$(NH_4)TbU(C_2O_4)_4 \cdot 2H_2O \underset{-2H_2O}{\overset{500K}{\longrightarrow}} (NH_4)TbU(C_2O_4)_4 \quad (II)$$

$$(NH_4)TbU(C_2O_4)_4 \overset{575-655\,K}{\longrightarrow} 1/2Tb_2O_2CO_3 + UO_{2+x} \quad (III)$$

$$1/2Tb_2O_2CO_3 + UO_{2+x} \overset{>975\,K}{\longrightarrow} (Tb,U)O_{2\pm x} \quad (IV)$$

The decomposition of cerium, praseodymium and neodymium compounds follow similar pattern. However, for lanthanum compound, steps I and II merge into a single step.

Activation energy of the dehydration of $(NH_4)LaU(C_2O_4)_4{\cdot}8H_2O$ and $(NH_4)TbU(C_2O_4)_4{\cdot}8H_2O$ were evaluated from the isothermal TG data. Isothermal runs were carried out at 316, 328 and 338 K for the lanthanum compound and at 328, 333 and 338 K for the first step and at 498, 503, 508 and 513 K for the second step of dehydration for the terbium compound. On analysis of the kinetic data the dehydration of $(NH_4)LaU(C_2O_4)_4{\cdot}8H_2O$ showed linearity of $-\ln(1-\alpha)$ with time plot for 'α' in the range of 0.10 to 0.85, 'α' is the fraction decomposed at time 't'. The equation $g(\alpha) = -\ln(1-\alpha) = kt$ represent the nucleation and growth mechanism of unimolecular reaction suggested by Mampel [11]. In the case of $(NH_4)TbU(C_2O_4)_4{\cdot}8H_2O$, the dehydration step where six water molecules are removed followed the function, $g(\alpha) = \alpha$ for the 'α' ranging between 0.08 to 0.90 and $g(\alpha) = -\ln(1-\alpha)$ vs. 't' for the second step of dehydration in the 'α' range of 0.15 to 0.85. This suggests that for the first step, the mechanism is phase boundary controlled for unidirectional process whereas for the second step the mechanism is nucleation and growth controlled. The Arrhenius plots of $-\ln k$ with $1/T$(K) are given in Fig. 5Fig. 6Fig. 7. The activation energy values were found to be 25.8 kJ/mole for the dehydration of lanthanum compound and 72.8 kJ/mole and 130.8 kJ/mole for the first and second step of dehydration of the terbium compound.

The TG and DTA curves recorded in flowing argon gas showed endotherm in DTA during the decomposi-

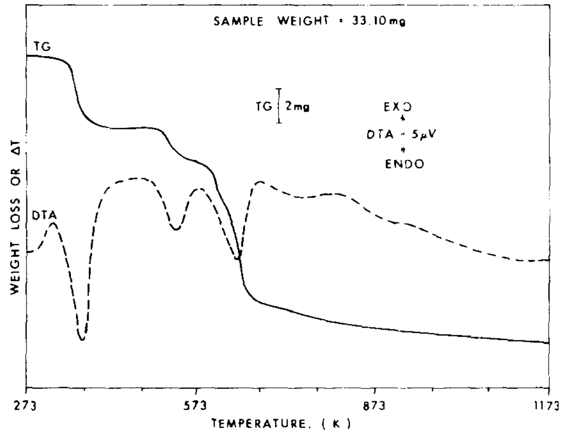

Fig. 4. TG and DTA curves of $(NH_4)TbU(C_2O_4)_4{\cdot}8H_2O$ in argon.

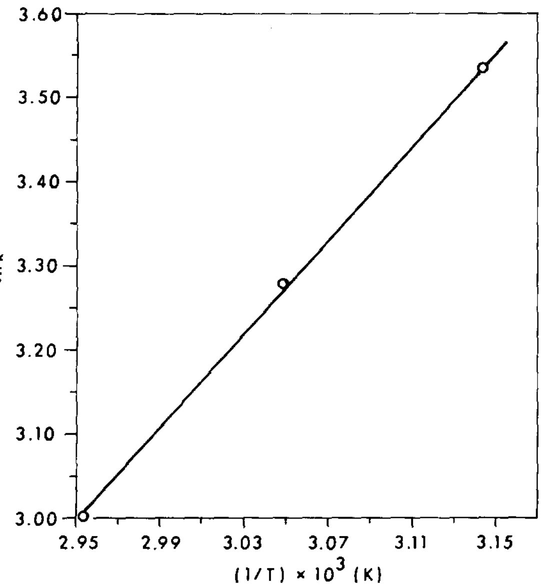

Fig. 5. Arrhenius plot of $-\ln k$ vs $1/T$(K) for the dehydration of $(NH_4)LaU(C_2O_4)_4{\cdot}8H_2O$.

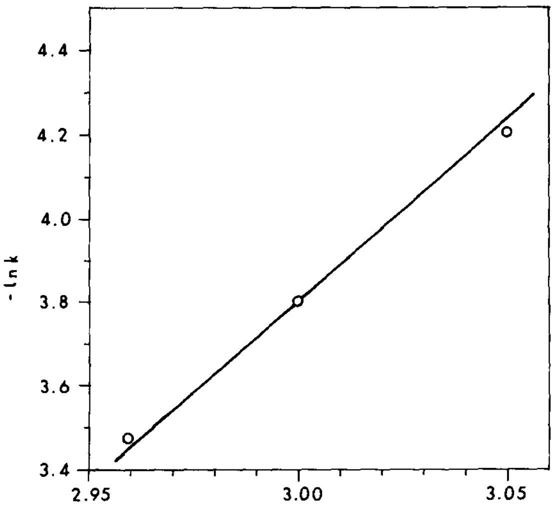

Fig. 6. Arrhenius plot of $-\ln k$ vs $1/T$(K) for the first step dehydration of $(NH_4)Tb(C_2O_4)_4{\cdot}8H_2O$.

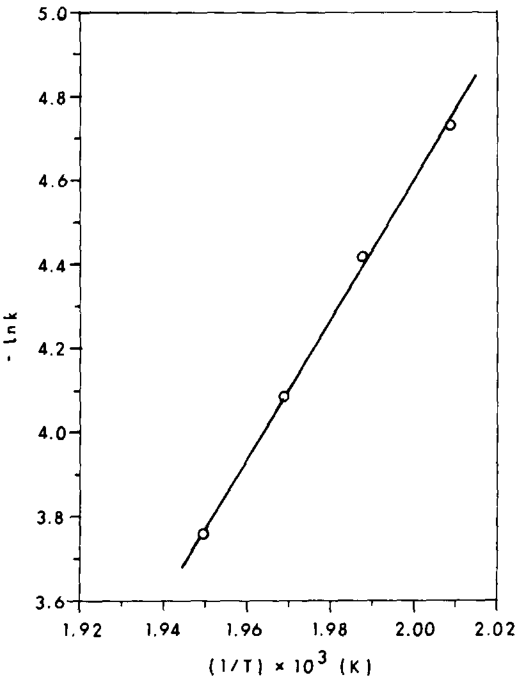

Fig. 7. Arrhenius plot of $-\ln k$ vs $1/T$(K) for the second step dehydration of $(NH_4)TbU(C_2O_4)_4{\cdot}8H_2O$.

tion of the compounds in place of exotherm observed in air around 625 K. The decomposition of oxalates is known to proceed with the evolution of CO gas which is an endothermic reaction in the inert atmosphere. In air, the oxidation of CO to CO_2 gives exothermic DTA peak during the thermal decomposition of the compounds. The TG and DTA curves of $(NH_4)TbU(C_2O_4)_4{\cdot}8H_2O$ in flowing argon are shown in Fig. 4. The end product at 1175 K showed the formation of solid solution of mixed oxides having fluorite structure.

In separate experiments, the compounds were heated for 6 to 8 h separately in a furnace in air at 1275 and 1175 K in argon and $N_2/8\%$ H_2 atmospheres. The lattice parameter of the products obtained from the X-ray diffraction data scanned at the rate of 0.5° $\min^{-1}$ are given in Table 5. The lattice parameters of fluorite phases are marginally different from those obtained from the corresponding mixed oxide phases obtained after heating $KLnU(C_2O_4)_4{\cdot}8H_2O$ [2]. The interaction of potassium ions in the later case could have some influence on the cell size of the cubic phase. The observed decrease in the values of lattice parameter of the mixed oxides (with the increase in atomic number) is in general consistent with the decrease in ionic radius for the lanthanides [12]. However, the observed lower lattice parameter value of $(U,Ce)O_{2\pm x}$ may be due to the presence of cerium in +4 state. The observed value for cerium–uranium mixed oxide is in agreement with the reported value of 5.528 Å for $(U^{4+},Ce^{4+})O_2$ [13].

Acknowledgements

The authors are thankful to Dr. H.C. Jain, Head, Fuel Chemistry Division for his keen interest in this work. The authors thank Dr. Y.S. Sayi and his group for the help in elemental analyses and Dr. M.S. Nagar for recording the infrared spectra.

References

[1] A. Chadha, N.C. Jayadevan and K.D. Singh Mudher, Thermochim. Acta, 111 (1987) 67.
[2] A.K. Chadha, K.D. Singh Mudher, K. Krishnan and N.C. Jayadevan, Thermochim. Acta, 191 (1991) 323.
[3] K.D. Singh Mudher and N.C. Jayadevan, XXI Natl. Seminar on Crystallography, Bombay, India, 1989, C-2.
[4] S.K. Awasthi, K.L. Chawla and D.M. Chackraburtty, J. Inorg. Nucl. Chem., 35 (1973) 3805.
[5] K. Nakamoto, Infrared and Raman spectra of Inorgranic and Coordination Compounds, 3rd edn., Wiley, New York, 1978.
[6] R.P. Turcotte, J.O. Sawer and I. Eyring, Inorg. Chem., 22 (1961) 39.
[7] A. Glasner, E. Levy and M. Steinberg, J. Inorg. Chem., 22 (1961) 39, 25 (1963) 1415.
[8] A. Glasner, E. Levy, M. Steinberg and W. Bodenheimer, Talanta, 11 (1964) 405.
[9] D.A. Nissen J. Therm. Analysis, 18 (1980) 99.
[10] T. Ohmichi, S. Fukushima, A. Maeda and H. Watanabe, J. Nucl. Mater., 102 (1981) 40.
[11] K.L. Mampel, Z. Phys. Chem. A., 187 (1940) 235.
[12] R.D. Shannon, Acta Crystallgr., Sec. A., 32 (1976) 751.
[13] H.P. Nawada, P.S. Ramamoorthy, K.V.G. Kutty, S. Rajagopalan, R.S. Yadav, R.V. Rao and C.K. Mathews, J. Nucl. Mater., 139 (1988) 192.