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Oxidation state of uranium: an XPS study of alkali and alkaline earth uranates

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Abstract

X-ray photoelectron spectroscopy (XPS) studies are performed on some mixed oxides of uranium with alkali and alkaline earth metals (Na, Li, Rb, Tl, Sr, Ba) to investigate the presence of multiple valence states of uranium in these compounds. Photoelectron peak positions, peak widths and satellite positions were measured to identify the chemical states. The analysis of the shake up satellites and the deconvolution of the principal peaks are used to quantify the chemical states. The domination of U(V) chemical state is inferred in $Na_2U_3O_9$ and $Sr_2U_3O_{10}$. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Extensive crystallographic and thermodynamic data are available in the literature on uranium oxides and also alkali and alkaline earth uranates, because of their possible formation during fuel–coolant or fuel–fission products interactions in fast reactors [1]. The lower valent uranates, where the overall oxidation state of uranium is less than VI, are particularly important since these are more likely to be formed depending upon the local oxygen potential. Recently, a number of new lower valent uranates such as $Na_2U_3O_9$, $Sr_2U_3O_9$, $Ba_2U_3O_9$, $Rb_2U_4O_{11}$ and $Tl_2U_4O_{11}$ have been reported [2–4]. Also fluorite type solid solutions have been reported for the first time in Li–U–O and Na–U–O systems with the compositions $A_yU_{1-y}O_{2+x}$ ($A = $ Li or Na, $y = 0$–0.2) [5].

Due to the multivalent character of uranium, which can exist in U(IV), U(V) and U(VI) states apart from the rather unstable U(III) state, it is difficult to fix or identify the valence state of uranium in these compounds. Thus, $Rb_2U_4O_{11}$ can be represented as $Rb_2U_4^{V}O_{11}$ or $Rb_2U_2^{IV}U_2^{VI}O_{11}$. Similarly, $Na_2U_3O_9$ can be represented as $Na_2U_2^{V}U^{VI}O_9$ or $Na_2U^{IV}U_2^{VI}O_9$. This problem could not be resolved by chemical methods involving dissolution, precipitation or titration since U(V) disproportionates to U(IV) and U(VI). Reactions of uranium oxides with ammonium sulphate in the solid state at 523 K were found to give mixtures of U(IV) and U(VI) sulphates; this led to the conclusion of presence of U(IV) and U(VI) oxidation states for $UO_{2.17}$, U_4O_9, U_3O_7 and U_3O_8 [6]. This of course assumes no change of valence state of uranium during the reaction.

Among various solid state methods, X-ray and neutron diffraction could not definitely establish the oxidation state of uranium in U_4O_9, U_3O_7 and U_3O_8. Lattice parameter variations in fluorite type solid solutions, $A_yU_{1-y}O_{2+x}$ ($A = $ Li, Na, Ba, Y) have been explained assuming U^{IV} and U^{V} valence states using simple ionic model [5,7]. Computation of effective magnetic moments per uranium atom under the three categories L–S coupling, ‘Spin-only’ and ‘J–J Coupling’ for comparing with the measured values were not found to be in agreement [6]. The oxidation state of uranium in $Y_yU_{1-y}O_{2+x}$ solid solution was

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Table 1
Methods of preparation of uranium compounds and their crystallographic data

Compound	Crystal system	Lattice parameters (nm)			Method of preparation				
		a	*b*	*c*	Starting materials	Atmosphere	Temperature (K)	h	Reference
UO_2	Cubic	0.547	–	–	UO_{2+x}	Ar/H_2	1073	8	[15]
$Na_2U_{12}O_{27}$	Cubic	0.5433	–	–	$Na_2U_2O_7 + 10UO_2$	Ar	1473	7	[5]
$Li_2U_{15}O_{33}$	Cubic	0.5418	–	–	$Li_2U_2O_7 + 13UO_2$	Ar	1473	7	[5]
$RbUO_3$	Cubic	0.4323	–	–	$Rb_2UO_4 + UO_2$	Ar	1273	8	[16]
$Rb_2U_4O_{11}$	Tetragonal	0.9738	–	1.9922	$Rb_2U_2O_7 + 2UO_2$	Ar	1473	7	[2]
$Tl_2U_4O_{11}$	Tetragonal	0.9741	–	1.9905	$Tl_2U_2O_7 + 2UO_2$	Ar	973	8	[3]
$Na_2U_3O_9$	Orthorhombic	1.5289	1.1285	0.7173	$Na_2U_2O_7 + UO_2$	Ar	1473	8	[2]
$Sr_2U_3O_9$	Hexagonal	0.3937	–	1.8628	$Sr_2U_3O_{11}$	Ar/H_2	1073	2	[4]
$Sr_2U_3O_{10}$	Hexagonal	0.3921	–	1.8529	$Sr_2U_3O_9$	Air	573	2	[a]
$Ba_2U_3O_9$	Hexagonal	0.8079	–	1.9512	$Ba_2U_3O_{11}$	Ar/H_2	1073	2	[4]
$Rb_2U_4O_{13}$	Hexagonal	1.4339	–	1.4311	$3Rb_2CO_3 + 4U_3O_8$	Air	1073	8	[16]

[a] S.K. Sali, S. Sampath, V. Venugopal, unpublished results.

discussed by means of magnetic susceptibility measurement from 4.2 K to room temperature [8]. Substitution of Y^{III} for U^{IV} in UO_2 proved to show magnetic dilution effect with simultaneous oxidation of U^{IV} to U^{V}.

Because of the capability of X-ray photoelectron spectroscopy (XPS) to give a direct picture of the electronic structure and chemical state of a material nondestructively, the technique has been employed to probe the chemical states of U in the oxides. XPS along with X-ray absorption fine structure (EXAFS), Infrared (IR), Raman and electron spin resonance (ESR) have been used to ascertain the oxidation state of uranium. In the case of U_3O_8, the results led to the formulation of $U^{IV}U_2^{VI}O_8$ [9]. An extensive review on U binary oxides and mixed oxides has been done by Veal and Lam [10], where U 4f level chemical shift has been observed and correlated with the formal valence state of U. These studies not only gave an identification of the mixed chemical states present in the compounds but also details of the valence-band electronic structure of the U–O chemical bond. Because of the closeness of binding energy for U 4f lines for U(IV), U(VI) (App. 1.0 eV [10]), sometimes it is difficult to investigate and identify U(V) states whose binding energy is expected in between. Thus, valence-band related spectral features are probed for analyzing the mixed valence states of U. The presence of U(V) in mixed oxides was detected by Keller and Jorgensen [11] using shake up and shake off satellites of U 4f photoelectron peaks. The analysis of shake up satellites in the core level photoelectron spectra of uranium oxides has been used to infer the presence of U^{IV} and U^{VI} in U_3O_8 and U_2O_5 [12]. Still, XPS studies in this field are relatively less abundant. Recently, some applied research on oxidation of UO_2 by alpha radiolysis of water [13] and formation of U_3O_8 on a UO_2 disk in the presence of a gamma field [14] has been done by deconvoluting the U $4f_{7/2}$ peak into U^{IV} and U^{VI} contributions.

In this paper a detailed XPS analysis of mixed oxides M–U–O (M = Na, Li, Rb, Tl, Sr, Ba, which were earlier

Table 2
Theoretically computed percentage atom ratios for combinations of different oxidation states of uranium in the compounds under study

Compound	O/U	Formula 1	Uranium (%)			Formula 2	Uranium (%)		
			U^{IV}	U^{V}	U^{VI}		U^{IV}	U^{V}	U^{VI}
UO_2	2.00	$U^{IV}O_2$	100	–	–	–	–	–	–
$Na_2U_{12}O_{27}$	2.167	$Na_2U_8^{IV}U_4^{V}O_{27}$	67	33	–	$Na_2U_{10}^{IV}U_2^{VI}O_{27}$	83	–	17
$Li_2U_{15}O_{33}$	2.133	$Li_2U_{11}^{IV}U_4^{V}O_{33}$	73	27	–	$Li_2U_{13}^{IV}U_2^{VI}O_{33}$	87	–	13
$RbUO_3$	2.5	$RbU^{V}O_3$	–	100	–	$RbU_{0.5}^{IV}U_{0.5}^{VI}O_3$	50	–	50
$Rb_2U_4O_{11}$	2.5	$Rb_2U^{V}O_{11}$	–	100	–	$Rb_2U_2^{IV}U_2^{VI}O_{11}$	50	–	50
$Tl_2U_4O_{11}$	2.5	$Tl_2U_4^{V}O_{11}$	–	100	–	$Tl_2U_2^{IV}U_2^{VI}O_{11}$	50	–	50
$Sr_2U_3O_9$	2.33	$Sr_2U^{IV}U_2^{V}O_9$	33	67	–	$Sr_2U_2^{IV}U^{VI}O_9$	67	–	33
$Ba_2U_3O_9$	2.33	$Ba_2U^{IV}U_2^{V}O_9$	33	67	–	$Ba_2U_2^{IV}U^{VI}O_9$	67	–	33
$Sr_2U_3O_{10}$	2.66	$Sr_2U^{IV}U_2^{VI}O_{10}$	33	–	67	$Sr_2U_2^{V}U^{VI}O_{10}$	–	67	33
$Na_2U_3O_9$	2.66	$Na_2U^{IV}U_2^{VI}O_9$	33	–	67	$Na_2U_2^{V}U^{VI}O_9$	–	67	33
$Rb_2U_4O_{13}$	3.0	$Rb_2U_4^{VI}O_{13}$	–	–	100	–	–	–	–

prepared and well characterised) are presented. Peak positions, peak widths (FWHM) and satellite features are probed and compared with standard spectroscopic data to quantify the mixed states present in the oxides.

2. Experiments

All the compounds selected for XPS study were prepared by the solid-state route, heating the mixtures of oxides or carbonate in the appropriate ratios in different atmospheres. The characterisation of the compounds was carried out by X-ray powder diffraction (XRD) using Cu K_α radiation. Heating was carried out until the required compound was exclusively identified. Table 1 gives the methods of preparations of the various compounds along with the crystallographic data of the compounds. Starting materials $Na_2U_2O_7$ and $Li_2U_2O_7$ were obtained by heating the analytical grade carbonates with U_3O_8, in 3:2 molar ratios, in dry air at 1073 K for 10–12 h, till the products were exclusively identified. $Tl_2U_2O_7$ was similarly obtained by heating at 973 K. Uranium oxide with $O/U = 2.00$ was obtained by reduction of nuclear grade UO_{2+x} in Ar gas with 7 v/v% hydrogen at 1073 K. $Sr_2U_3O_{11}$ and $Ba_2U_3O_{11}$ were also prepared by intimate mixing of carbonates of strontium and barium with U_3O_8 in appropriate ratios and heating in air at 1173 K for 20–30 h. Table 2 gives the compounds under study, their O/U ratios and two possible representations in terms of uranium oxidation states and their corresponding uranium percentages.

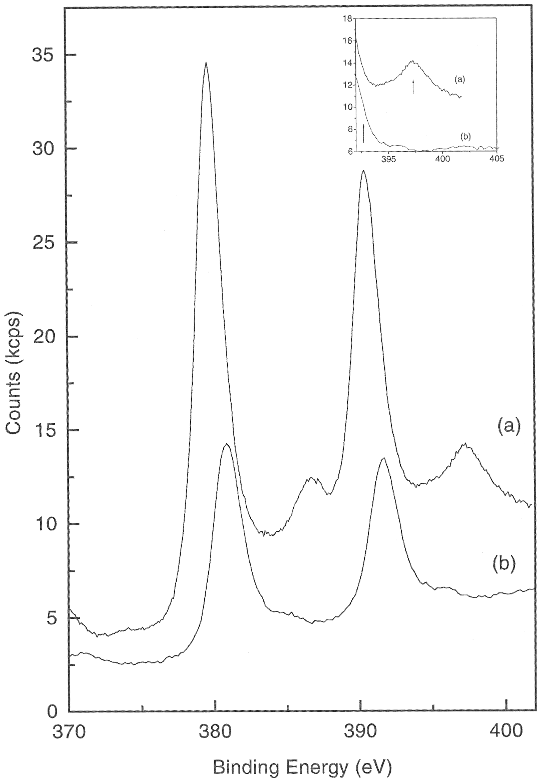

Fig. 1. XPS of U 4f in (a) UO_2 and (b) $Rb_2U_4O_{13}$. The inset of the figure shows the details of the satellites of the U $4f_{5/2}$ photoelectron peaks.

Table 3
U $4f_{7/2}$ photoelectron peak parameters for standard U(IV) and U(VI) chemical states

Oxide	Uranium oxidation state	BE of $4f_{7/2}$ (eV)	FWHM of $4f_{7/2}$ (eV)	Satellite of $4f_{5/2}$ (eV)
UO_2	(IV)	379.9	2.2	6.8
$Rb_2U_4O_{13}$	(VI)	381.1	2.5	4.4

The XPS system used for this study was a VG ESCALAB MK200X, with 150 mm hemispherical analyser. The spectra were collected using Al K_α X-ray source and with 20 eV pass energy of the analyser. The data acquisition and processing were carried out using Eclipse software. The instrument was earlier calibrated with Au $4f_{7/2}$ line at 84.0 eV with 1.6 eV FWHM [17] for the specimen of Au film on Si substrate [18].

UO_2 is highly oxidisable in atmosphere [19]. So a piece of freshly prepared UO_2 was broken in an Ar atmosphere and the cleaved surface was loaded immediately for XPS analysis. The powders of uranates were individually further ground in a mortar and a few milligram of the sample was uniformly spread over indium foil and pressed. The foil was attached to a stainless steel stub for mounting to the *X*–*Y*–*Z* translator of the XPS system. In order to check on the charging effect, the background In $3d_{5/2}$ at 443.8 eV and C1s signal (very weak) at 284.6 eV were also monitored for each spectra and suitable corrections were employed.

Table 4
U 4f peak analysis in $RbUO_3$, $Tl_2U_4O_{11}$, $Sr_2U_3O_9$ and $Ba_2U_3O_9$

Oxide		BE of $4f_{7/2}$ (eV)	FWHM (eV)	Area (%)	Satellite of $4f_{5/2}$ (eV)
$RbUO_3$	[a]	380.7	3.4		3.5, 10.2
	U(VI)	381.2	2.5	61	
	U(IV)	379.6	2.2	39	
$Tl_2U_4O_{11}$	[a]	380.6	3.4		9.0
	U(VI)	381.3	2.6	46	
	U(IV)	379.9	2.2	54	
$Sr_2U_3O_9$	[a]	380.5	3.2		7.5
	U(VI)	381.3	2.4	55	
	U(IV)	379.9	2.2	45	
$Ba_2U_3O_9$	[a]	380.7	3.2		7.5
	U(VI)	381.5	2.5	48	
	U(IV)	380.0	2.2	52	

[a] As observed and other data pertain to deconvoluted peaks.

3. Results and discussions

The chemical shift in the U $4f_{7/2}$ peak position is directly related to the oxidation state of uranium. Its binding energy decreases as the oxidation state is decreased from (VI) to (IV). However, uranium (V) and uranium (VI) oxidation states exist as UO_2^+ and UO_2^{2+} instead of a mere uranium ions [20]. As a consequence of this oxygen bonding, the chemical shift between (V) and (VI) states should differ only marginally in the BE scale.

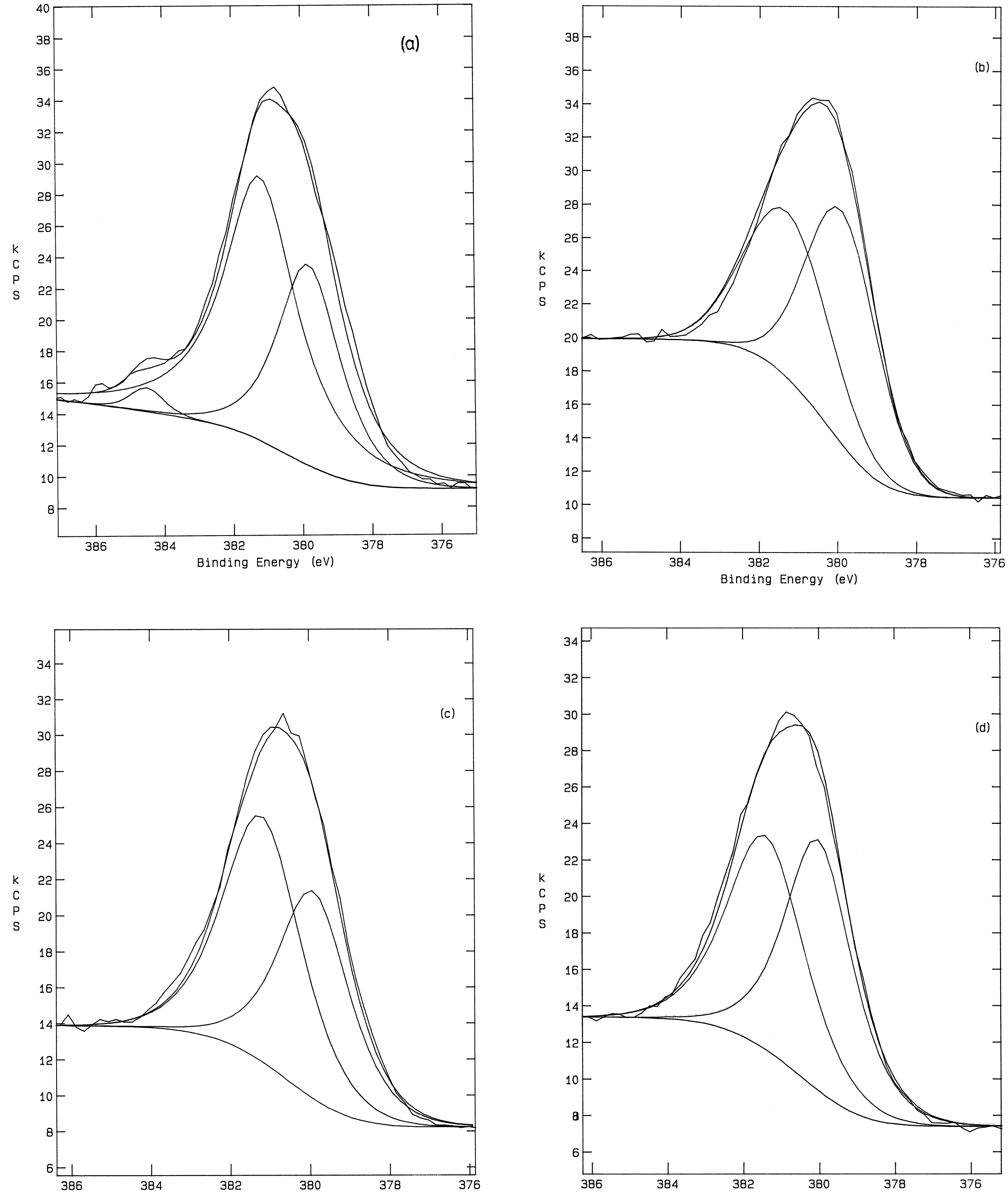

Fig. 2. Deconvolution of the U $4f_{7/2}$ photoelectron peaks from (a) $RbUO_3$, (b) $Tl_2U_4O_{11}$, (c) $Sr_2U_3O_9$ and (d) $Ba_2U_3O_9$ into U(IV) and U(VI) valence states.

Furthermore, the same oxidation state, of (VI) for example, the U $4f_{7/2}$ peak position in different compounds may differ as dictated by the crystal structure, the influence of which is due to the nearest neighbouring ions.

In addition to the peak position the full width at half maximum (FWHM) of a peak is related to the life time of the excited state which has a direct bearing on the chemical environment or bonding. In a crystal lattice, the neighbouring ions influence the width of the photo peak by such interaction. However, when two photo peaks lying very close-by overlap, it gives an apparent feeling of a single peak with broad FWHM. The composite peak could be resolved by suitable deconvolution procedures and using photo peak position and FWHM values for the respective oxidation states taken from similar standard compounds.

When a core-level electron is expelled by photo absorption, an electrostatic potential is experienced by the valence electrons. They get excited to higher empty orbitals or get knocked off to the continuum almost at the same time. This is called as shake-up or shake-off peaks, respectively. The core-electron kinetic energy is decreased by that extent. Hence, there appears a BE peak (called satellites) at slightly (a few eV) higher than the normal BE. Thus, satellite peaks carry the valence band informations and are a good probe to identify chemical state and understand the chemical interaction. This is applicable for both the U $4f_{7/2}$ and U $4f_{5/2}$ peaks. The spin–orbit interaction separates these two levels by 10.85 eV, and hence the satellites of $4f_{7/2}$ which generally appear in this energy range buried in the intense $4f_{5/2}$ peak or may appear as shoulder. So the satellites for $4f_{5/2}$ are considered for spectral interpretation in the present work.

In the process of oxidation, valence-band redistribution takes place which is reflected in the satellite position. It is possible that more than one oxidation state is present in a compound and that more than one satellite peak associated with each core-level peak could be present. The basis of identifying the oxidation state of uranium in different mixed oxide in the present study centers around the above mentioned three parameters namely peak position, peak width and satellite position.

The uranium 4f photoelectron spectra in oxides exhibit a satellite structure of low intensity when compared to the spectra of transition metal compounds. This complicates the proper identification of the peak positions of the satellites in an already complicated system like mixed oxides. Pireaux et al. [12] have reported satellites for U(IV) at 5.8, 8.2 and 16 eV higher binding energy than 4f photo peak position. In the case of U(IV), the 5.8 and 16 eV satellites of $4f_{7/2}$ should be clearly seen. In the case of U(VI), the satellites are at 3.7 and 10.6 eV away from the principal peaks. Usually the FWHM of $4f_{5/2}$ is higher than that of $4f_{7/2}$ because of merging of 10.6 eV satellite. Nevertheless, the satellite positions are likely to vary significantly depending upon the crystal structures, the presence of alkali metal ions, etc.

In this work, UO_2 and $Rb_2U_4O_{13}$ are considered as standard reference material for (IV) and (VI) uranium oxidation states, respectively. Typical XPS spectra of UO_2 and $Rb_2U_4O_{13}$, with satellites marked by arrows are given in Fig. 1. The characteristic binding energy, FWHM and satellite position are given in Table 3.

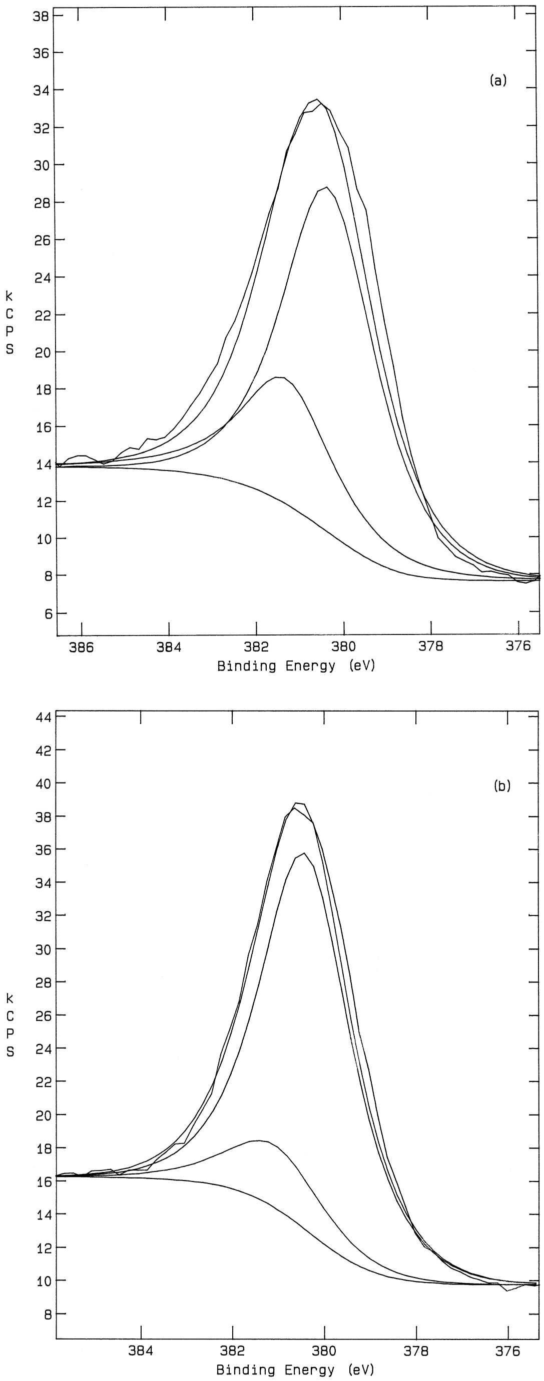

Fig. 3. Deconvolution of the U $4f_{7/2}$ photoelectron peaks into U(V) and U(VI) from (a) $Na_2U_3O_9$ and (b) $Sr_2U_3O_{10}$.

Table 5
U 4f photoelectron peak analysis of $Na_2U_3O_9$ and $Sr_2U_3O_{10}$, $Na_2U_{12}O_{27}$, $Li_2U_{15}O_{33}$ and $Rb_2U_4O_{11}$

Oxide		BE of $4f_{7/2}$ (eV)	FWHM (eV)	satellite of $4f_{5/2}$ (eV)	area (%)
$Na_2U_3O_9$	[a]	380.3	3.0	8.5	
	U(VI)	381.4	2.5		30
	U(V)	380.4	2.5		70
$Sr_2U_3O_{10}$	[a]	380.5	2.8	8.5	
	U(VI)	381.1	2.5		16
	U(V)	380.4	2.4		84
$Na_2U_{12}O_{27}$	[a]	380.1	3.0	7.7	
	U(V)	380.4	2.4		30
	U(IV)	379.7	2.3		70
$Li_2U_{15}O_{33}$	[a]	380.1	2.8	7.7	
	U(V)	380.5	2.5		35
	U(IV)	379.8	2.3		65
$Rb_2U_4O_{11}$	[a]	380.7	3.7	7.6	
	U(VI)	381.2	2.6		50
	U(V)	380.4	2.6		26
	U(IV)	379.7	2.5		24

[a] As observed and other data pertain to deconvoluted peaks.

Binding energy values available in the literature for U $4f_{7/2}$ in UO_2 ranged from 379.2 to 380.9 eV and that for UO_3 was 380.7 to 381.9 eV [10]. The separation in BE between (IV) and (VI) was 1.2 eV. FWHM of $4f_{7/2}$ in pure (IV) and (VI) uranium compounds was < 3.0 eV but definitely broader than in metallic U which was 1.8 eV obtained from the same instrument. In this work, the satellite of (IV) was observed at 6.8 eV higher than the BE of $4f_{5/2}$ while that was 4.4 eV in U(VI). These data were comparable to those observed by Pireaux et al. [12].

The oxides $RbUO_3$, $Rb_2U_4O_{11}$ and $Tl_2U_2O_{11}$, having O/U ratio of 2.5, are grouped together as either 100% uranium (V) or a 1:1 mixture of U(IV) and U(VI) (Table 2). The $4f_{7/2}$ peak has a large FWHM (> 3.4 eV) suggesting the presence of multiple valence states corresponding to (IV) and (VI) of U and rules out the presence of U(V) single valence state. The origin of the of (IV) and (VI) chemical states in these compounds is shown in Table 2 by modified chemical formulation. The compounds $Sr_2U_3O_9$ and $Ba_2U_3O_9$ although have O/U ratio of 2.33 also showed the FWHM of 3.2 eV which again pointed to the presence of IV and VI states of U. In Table 4, the peak position FWHM and satellite position for the corresponding compounds are shown. These peaks were resolved by standard deconvolution procedures as shown in Fig. 2. In the deconvoluted spectra the top most curves refer to the raw and fitted composite curve. The resolved components are shown underneath these curves. The levels for the resolved individual peaks can be identified by their peak positions corresponding to binding energy of U(IV) and U(VI) as given in the Table 4. The compound $Rb_2U_4O_{11}$ showed the U $4f_{7/2}$ peak at 380.7 eV with a peak width of 3.7 eV. The deconvolution of U $4f_{7/2}$ in $Rb_2U_4O_{11}$ into U^{+4} and U^{+6} resulted in a FWHM of U^{+6} (3.0 eV) higher than the standard U^{+6} (2.5 eV) FWHM. Hence, the presence of the U(V) was also suspected in this compound and the probable deconvolution and composition is shown later.

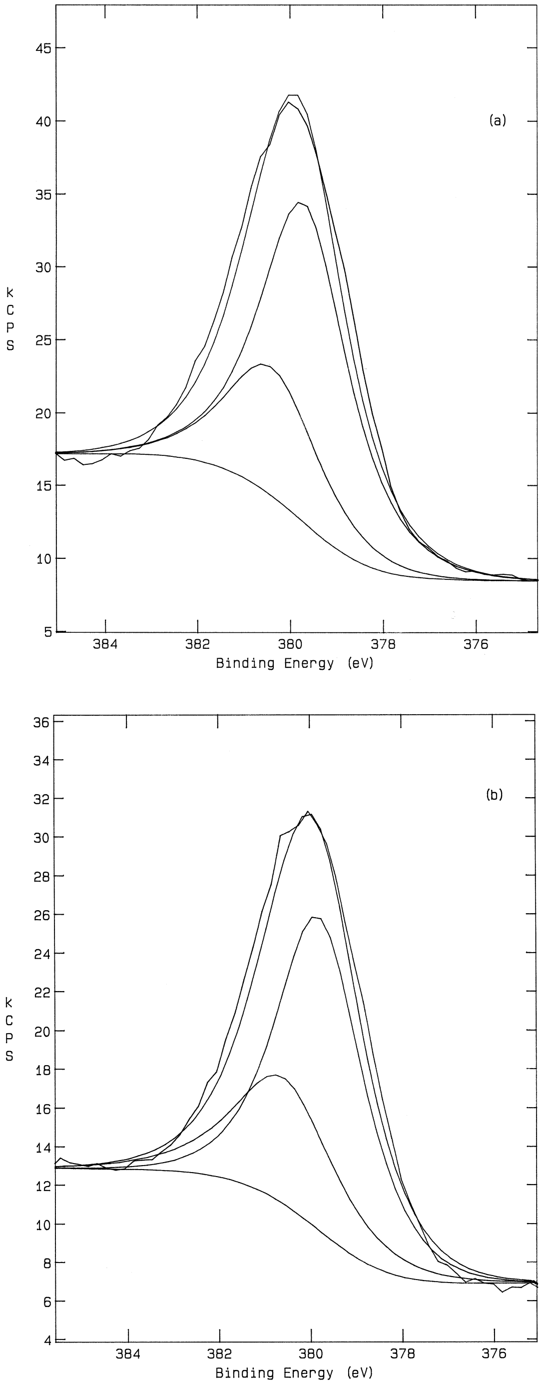

Fig. 4. Deconvolution of the U $4f_{7/2}$ photoelectron peaks into U(IV) and U(V) from (a) $Na_2U_{12}O_{27}$ and (b) $Li_2U_{15}O_{33}$.

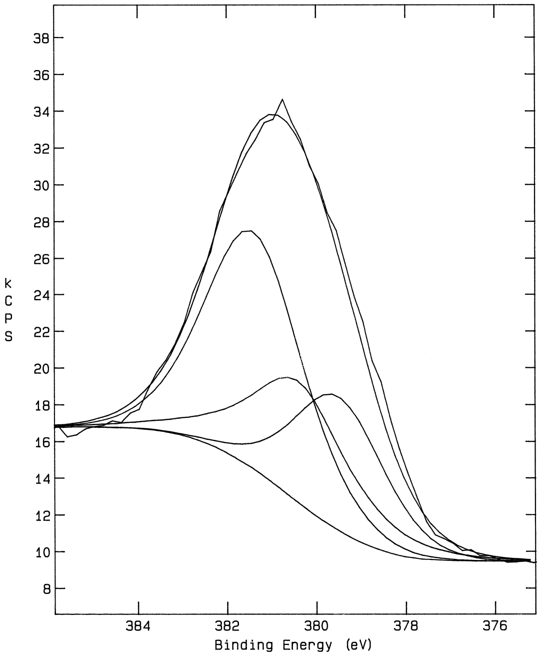

Fig. 5. Deconvolution of the U $4f_{7/2}$ photoelectron peaks into U(IV), U(V) and U(VI) from $Rb_2U_4O_{11}$.

$Na_2U_3O_9$ and $Sr_2U_3O_{10}$ have orthorhombic and hexagonal structures, respectively. The FWHM of U $4f_{7/2}$ was 3.0 and 2.8 eV, respectively, suggesting the domination of one oxidation state, which could be (V) with (VI) in an expected ratio of 67 and 33%. The other possibility namely (IV) and (VI) with area ratio of 33% and 67% is less likely because of low FWHM. The deconvolution of the peak into U(V) and U(VI) is shown in Fig. 3 and the corresponding peak parameters are shown in Table 5. From the deconvolutions it is clear that, these compounds are dominated by U(V) and so the convoluted peak showed the position of the U(V) state. The deconvolution thus gave the peak position of U(V) to be 380.4 eV with FWHM 2.4 eV.

The solid solutions $Na_2U_{12}O_{27}$ and $Li_2U_{15}O_{33}$ belong to the group with well defined structure similar to UO_2. Such compounds may exhibit (IV) and (V) oxidation state of U in the percent area ratio 67/33 and 73/27 for Na and Li oxides. The (IV)/(VI) combination is another possibility with area contribution 83/17 and 87/13 for Na and Li cases. Because of the lower FHHM of U $4f_{7/2}$ peak as shown in Table 5, the combination of IV and V is more probable. Assuming the U(V) position (380.4 eV) and FWHM (2.4 eV) as obtained in the previous deconvolution, the composition of the compounds are shown in Table 5. The deconvoluted spectra are shown in Fig. 4. The deconvoluted spectra exhibited (IV) and (V) oxidation state of U in the percent area ratio 70/30 and 65/35 for the Na and Li compounds.

The deconvolution of $Rb_2U_4O_{11}$ into U(VI) and U(IV) left the FWHM of U(VI) to be 3.0 eV which probably required further deconvolution. So the peak was deconvoluted into IV, V and VI components keeping U(V) peak position to be 380.4 eV. The deconvolution of $Rb_2U_4O_{11}$ is shown in Fig. 5 where the compound was observed to be dominated by U(VI) (50%) and the presence of U(V) (26%) was also observed in this compound.

Shake up satellites of mixed oxides give a valence band picture of the compounds. Satellites appear mostly due to the transitions from U–O bonding band to the empty states above the Fermi level as explained in case of U-oxides [12]. In mixed oxides some change in the valence band is expected which is reflected in the satellite positions as shown in Fig. 6. Satellites for U(IV) and U(VI) standard match well with the literature value. The compounds like $Sr_2U_3O_{10}$ and $Na_2U_3O_9$ which are dominated by U(V) states showed the satellites at 8.5 eV. In Tables 4 and 5 the satellite positions for all the compounds are shown along with possible mixtures of the U chemical states. The compounds $Na_2U_{12}O_{27}$ and $Li_2U_{15}O_{33}$, although dominated by U(IV) state showed the satellite shifted to 7.7 eV in presence of U(V) state. In $RbUO_3$, the domination of

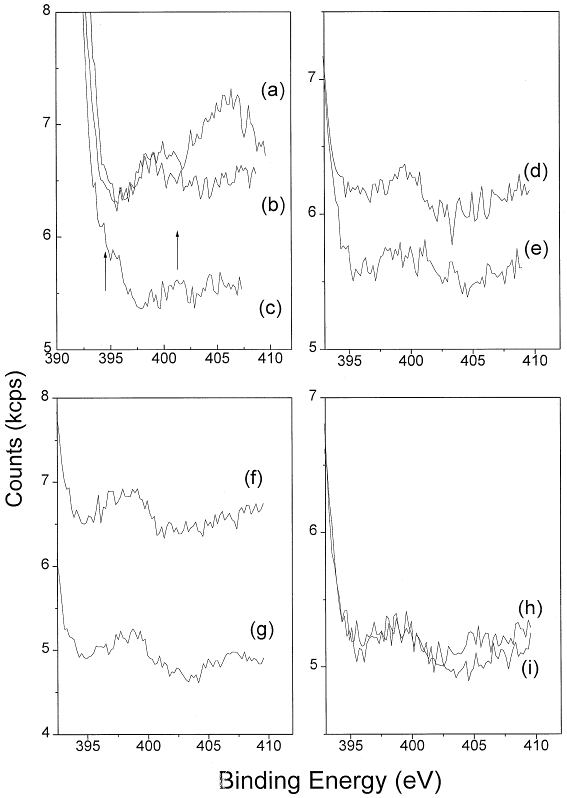

Fig. 6. Shake up satellites of (a) $Tl_2U_4O_{11}$, (b) $Rb_2U_4O_{11}$, (c) $RbUO_3$, (d) $Sr_2U_3O_{10}$, (e) $Na_2U_3O_9$, (f) $Na_2U_{12}O_{27}$, (g) $Li_2U_{15}O_{33}$, (h) $Ba_2U_3O_9$ and (i) $Ba_2U_3O_9$.

U(VI) over U(IV) was confirmed by the satellite at 3.5 eV where as in $Sr_2U_3O_9$ and $Ba_2U_3O_9$, the satellite positions were seen at 7.5 eV reflecting characteristic valence band. $Rb_2U_4O_{11}$ although dominated by U(VI) did not show any satellite at 3.5 eV maybe because of the presence of U(V) which contributes to form different valence band. Detailed analysis of the position of the satellites indicates that U(V) satellite is likely to be at 8.5 eV above the main peak.

4. Conclusions

Uranium is present in multiple valence states in most of the mixed oxides keeping their signature in peak width, peak position and satellite position. The satellites of the main peak reflect the valence band and conduction band.

The peak position of U(IV) $4f_{7/2}$ peak in different compounds investigated in the present work was at 379.82 ± 0.13 eV with an FWHM 2.23 ± 0.05 eV. Similarly U(VI) and U(V) peaks had shown consistent $4f_{7/2}$ peak values at 381.3 ± 0.13 eV (FWHM 2.5 ± 0.06 eV) and 380.42 ± 0.05 (FWHM 2.45 ± 0.05), respectively. In addition the peak area values also substantiated the formula proposed in Table 2.

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