

## SUPPORTING INFORMATION

### Synthesis and Feasibility Studies of Doping U at Ti Site of $Y_2Ti_2O_7$ as a Radioactive Waste Immobilization Matrix

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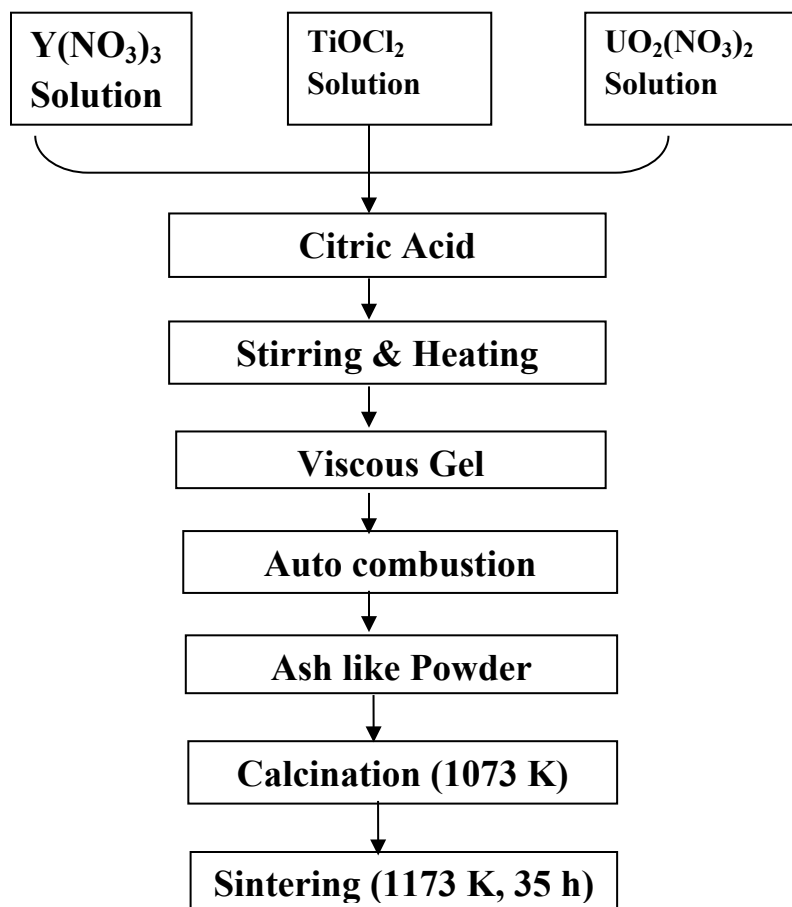


Fig. S1 Flow sheet used for synthesizing the compounds.

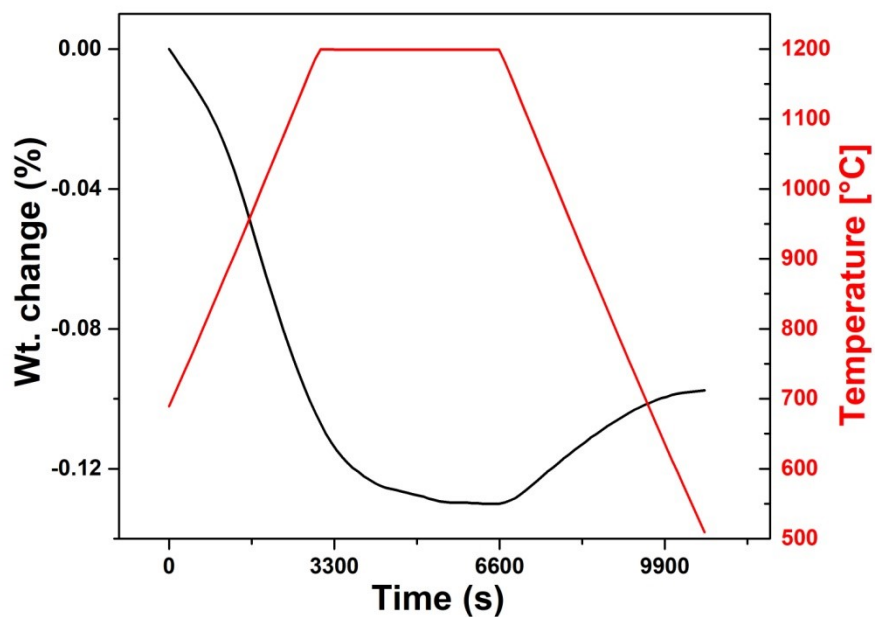


Fig. S2 Thermogram of YUT3 sample recorded in air

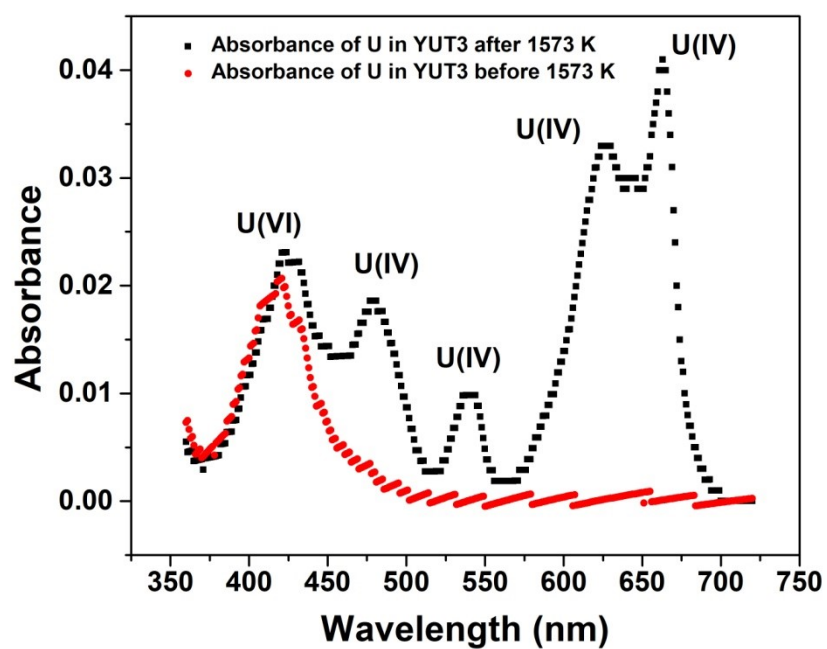


Fig. S3 Absorbance spectra of YUT3 sample before and after high temperature treatment

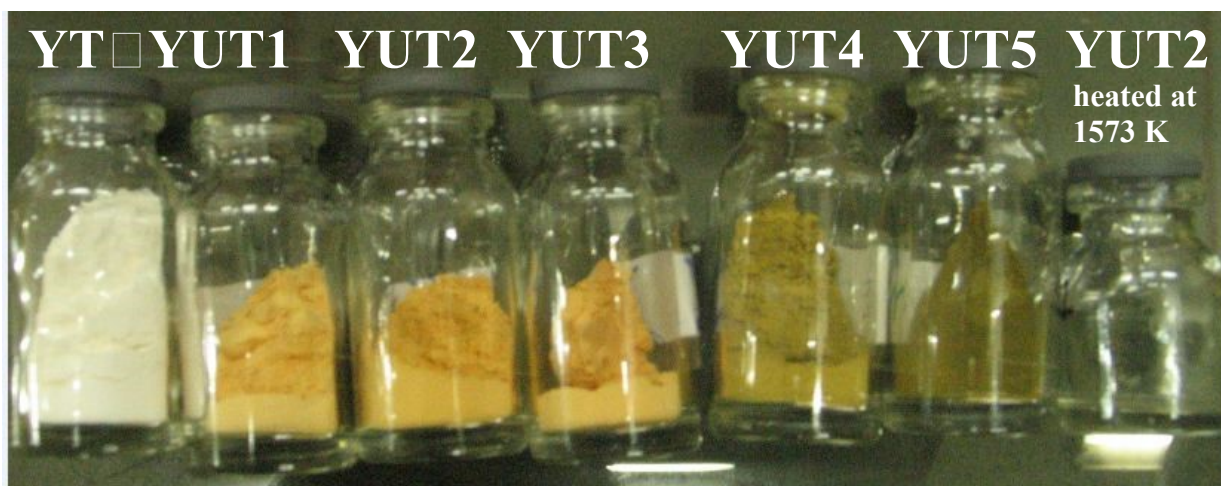


Fig. S4 Color of the samples heated at 1173 K and YUT2 heated at 1573 K

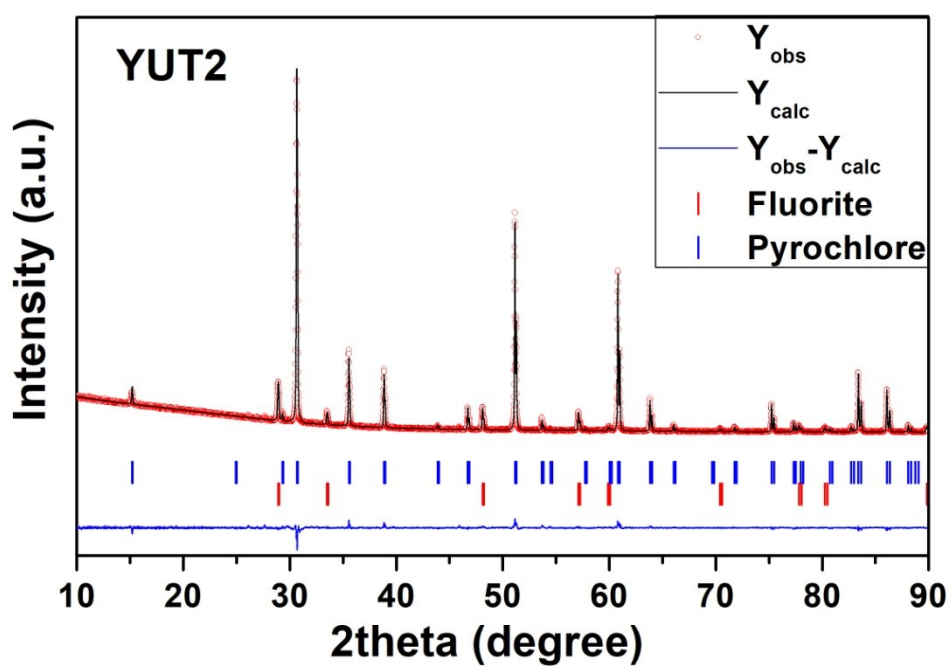
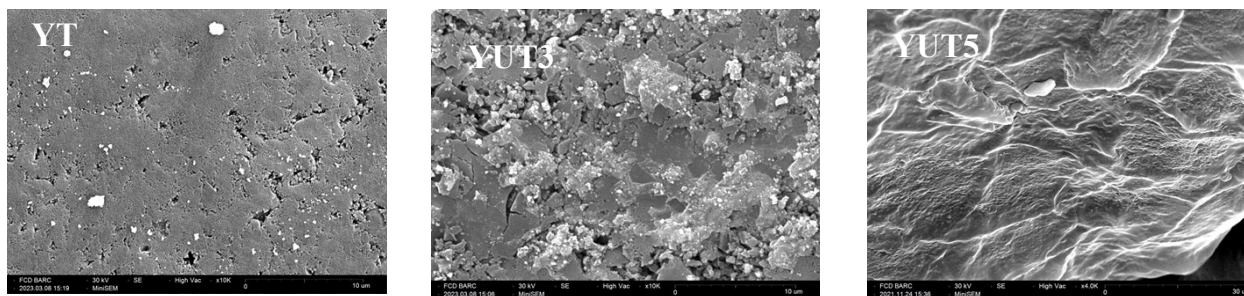
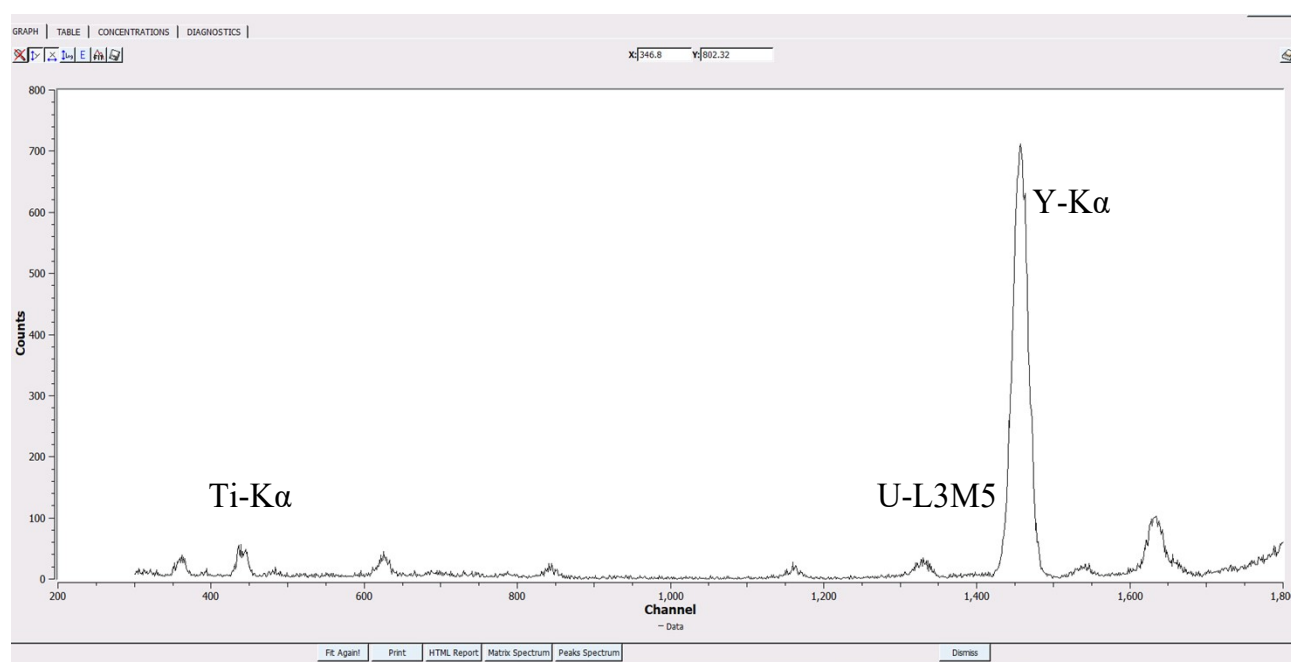


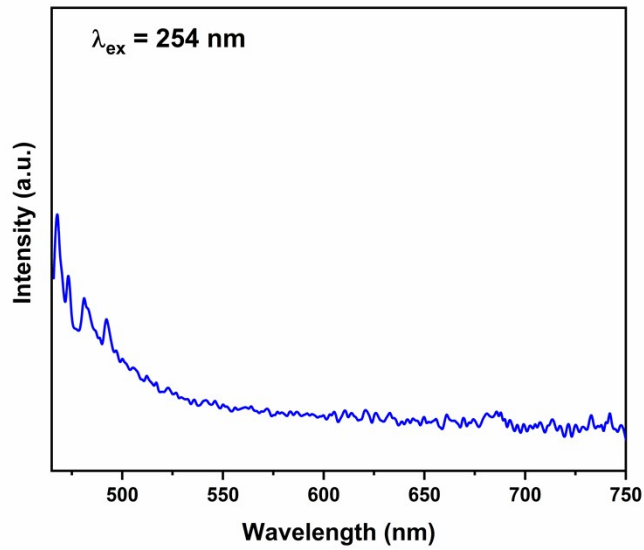
Fig. S5 Rietveld refined XRD pattern of YUT2 heated at 1573 K for 4 h in air.



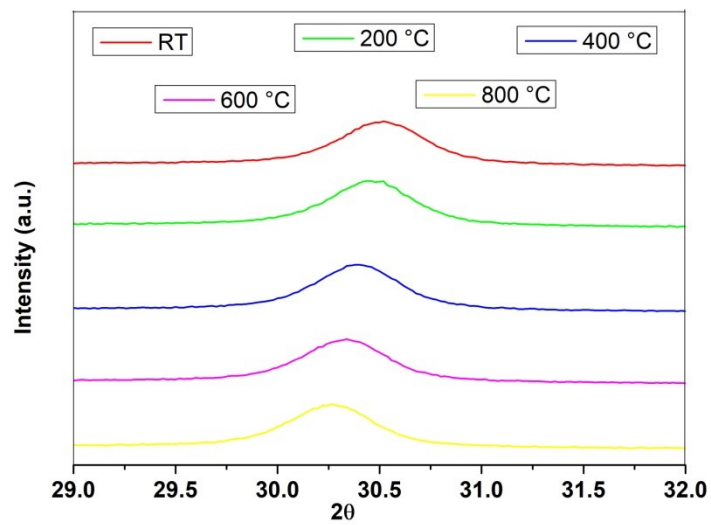
**Fig. S6 Scanning Electron Micrographs of YT, YUT3 and YUT5.**



**Fig. S7 Sample TXRF Spectrum observed for YUT1**



**Fig. S8** Luminescence spectrum of YUT4 sample heated at 1573 K for 4h.



**Fig. S9** High Temperature XRD pattern of YUT3 showing positive thermal expansion coefficient.

**Supplementary Table S1. Stoichiometric amounts of reagents used for the synthesis for YUT's.**

Sample	Amount in mL		
	TiOCl <sub>2</sub> (4.18 M)	UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> (2.91 M)	Y(NO <sub>3</sub> ) <sub>3</sub> (1.23 M)
YT	21.08	-	10.09
YTU1	20.58	0.21	9.65
YTU2	20.33	0.32	9.44
YTU3	20.09	0.42	9.23
YTU4	19.19	0.81	8.43
YTU5	18.37	1.16	7.68

**Supplementary Table S2. Calculated r<sub>A</sub>/r<sub>B</sub> ratio of nominal compositions prepared**

Sr. No.	Nominal Composition	Calculated r <sub>A</sub> /r <sub>B</sub> ratio
1.	Y <sub>2</sub> Ti <sub>2</sub> O <sub>7</sub>	1.684
2.	Y <sub>2</sub> Ti <sub>1.95</sub> U <sub>0.05</sub> O <sub>7+δ</sub>	1.675
3.	Y <sub>2</sub> Ti <sub>1.925</sub> U <sub>0.075</sub> O <sub>7+δ</sub>	1.673
4.	Y <sub>2</sub> Ti <sub>1.90</sub> U <sub>0.10</sub> O <sub>7+δ</sub>	1.667
5.	Y <sub>2</sub> Ti <sub>1.80</sub> U <sub>0.20</sub> O <sub>7+δ</sub>	1.650
6.	Y <sub>2</sub> Ti <sub>1.70</sub> U <sub>0.30</sub> O <sub>7+δ</sub>	1.633

**Supplementary Table S3. % Phase(s) and composition of the different samples heated at 1573 K**

Sample	Nominal Composition Y <sub>2</sub> (Ti <sub>2-x</sub> U <sub>x</sub> )O <sub>7</sub>	Phases (%)			Phase composition
		Pyrochlore (Y <sub>2</sub> Ti <sub>2</sub> O <sub>7</sub> )	Fluorite (U <sub>0.58</sub> Y <sub>0.42</sub> O <sub>2</sub> )	Brannerite (Y,U)Ti <sub>2</sub> O <sub>6</sub>	
YT	X=0	100	-	-	Y <sub>2</sub> Ti <sub>2</sub> O <sub>7</sub>
YUT1	X=0.05	95	5	-	Y <sub>2</sub> Ti <sub>1.95</sub> U <sub>0.05</sub> O <sub>7+δ</sub>
YUT2	X=0.07	88	12	-	Y <sub>2</sub> Ti <sub>1.93</sub> U <sub>0.07</sub> O <sub>7+δ</sub>
YUT3	X=0.10	79	21	-	(Y <sub>2</sub> Ti <sub>1.90</sub> U <sub>0.10</sub> O <sub>7+δ</sub> )
YUT4	X=0.20	66	30	4	0.79 (Y <sub>1.95</sub> Ti <sub>1.92</sub> U <sub>0.13</sub> O <sub>7+δ</sub> ) + 0.21 (Y <sub>0.7</sub> U <sub>0.3</sub> O <sub>2-γ</sub> )

<b>YUT5</b>	X=0.30	55	42	3	0.54 ( $Y_{1.82}Ti_{2.07}U_{0.11}O_{7+\delta}$ ) + 0.46 ( $Y_{0.7}U_{0.3}O_{2-\gamma}$ )
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**Supplementary Table S4. Nominal phase composition and phases composition observed using TXRF**

Sample	Composition observed using TXRF	Nominal Compositon
<b>YUT1</b>	$Y_2Ti_{1.94\pm0.04}U_{0.06\pm0.02}$	$Y_2Ti_{1.95}U_{0.05}$
<b>YUT2</b>	$Y_2Ti_{1.85\pm0.05}U_{0.08\pm0.02}$	$Y_2Ti_{1.925}U_{0.075}$
<b>YUT3</b>	$Y_2Ti_{1.8\pm0.05}U_{0.12\pm0.02}$	$Y_2Ti_{1.9}U_{0.10}$

**Supplementary Table S5. Edge position of U L<sub>3</sub> edge obtained from XANES spectra**

Sample	Edge position (eV)	White line (eV)
YUT1	17171.8	17180.2
YUT2	17172.8	17180.4
YUT3	17173.7	17180.5
UO <sub>3</sub>	17174.6	17180.5

**Supplementary Table S6. Photoluminescence life times in  $Y_2Ti_{2-x}U_xO_{7+\delta}$  (x = 0.05, 0.075, 0.1, 0.2 and 0.3;  $\lambda_{ex}$  = 254 nm;  $\lambda_{em}$  = 500 nm).**

Sample	$\tau_1(\mu s)$	A <sub>1</sub> (%)	$\tau_2(\mu s)$	A <sub>2</sub> (%)
$Y_2Ti_{1.70}U_{0.30}O_{7+\delta}$	<b>12.24</b>	<b>22</b>	<b>109.56</b>	<b>78</b>
$Y_2Ti_{1.80}U_{0.20}O_{7+\delta}$	<b>11.32</b>	<b>8</b>	<b>106.57</b>	<b>92</b>
$Y_2Ti_{1.90}U_{0.10}O_{7+\delta}$	<b>9.92</b>	<b>7</b>	<b>118.11</b>	<b>93</b>
$Y_2Ti_{1.925}U_{0.075}O_{7+\delta}$	<b>11.28</b>	<b>14</b>	<b>121.3</b>	<b>86</b>
$Y_2Ti_{1.95}U_{0.05}O_{7+\delta}$	<b>10.13</b>	<b>7</b>	<b>121.27</b>	<b>93</b>

**XPS experimental details:** XPS experiments of the samples were carried out at X-ray Photo-Electron Spectroscopy (PES) Beamline (BL-14) of Indus-2 at RRCAT, Indore, India. The energy of Indus-2 storage ring is 2.5 GeV. For the XPS measurements of the given samples, a double-crystal Silicon monochromator and HV hemispherical electron energy analyzer (SPECS in the PHOIBOS 225) with an X-ray radiation source of energy 4360 eV were employed for recording the XPS spectra. The achievable base pressure of the analytical chamber was  $\leq 5 \times 10^{-9}$  mbar.

The XPS survey scan was taken by sweeping the binding energy from 604.2 to 0 eV with a pass energy of 150 eV [1].

**XANES Experimental details:** The measurements have been carried out at the Energy-Scanning EXAFS beamline (BL-9) at the Indus-2 Synchrotron Source (2.5 GeV, 100 mA) at Raja Ramanna Centre for Advanced Technology (RRCAT), Indore, India. The beamline operates in the energy range of 4 KeV to 25 KeV. The beamline optics consists of an Rh/Pt coated collimating meridional cylindrical mirror and the collimated beam reflected by the mirror is monochromatized by a Si (111) ( $2d=6.2709 \text{ \AA}$ ) based double crystal monochromator (DCM). The second crystal of DCM is a sagittal cylinder used for horizontal focusing while a Rh/Pt coated bendable post mirror facing down is used for vertical focusing of the beam at the sample position. Rejection of the higher harmonics content in the X-ray beam is performed by detuning the second crystal of DCM. In the present case, XAS measurements have been performed in the fluorescence mode at Ti K-edge and U L3-edge. For measurements in the fluorescence mode, the sample is placed at  $45^\circ$  to the incident X-ray beam, and a fluorescence detector is placed at right angle to the incident X-ray beam to collect the signal. One ionization chamber detector is placed prior to the sample to measure the incident flux ( $I_0$ ) and fluorescence detector measures the fluorescence intensity ( $I_f$ ). In this case the X-ray absorption co-efficient of the sample is determined by,

$$\mu = I_f / I_0$$

and the spectrum was obtained as a function of energy by scanning the monochromator over the specified range.

**Supplementary Equation 1. Expression used for calculating specific heat capacity of different compounds.**

$$C_{p(\text{sample(s)})} = \frac{C_{p(\text{sapphire})} \cdot (\Phi_{\text{sample(s)}} - \Phi_o) \cdot m_{\text{sapphire}}}{(\Phi_{\text{sapphire}} - \Phi_o) \cdot m_{\text{sample(s)}}$$



Where  $C_{p(\text{sample}(s))}$ ,  $C_{p(\text{sapphire})}$ ,  $m_{\text{sample}(s)}$ ,  $m_{\text{sapphire}}$ ,  $\Phi_{\text{sample}(s)}$ ,  $\Phi_{\text{sapphire}}$  and  $\Phi_o$  represents the specific heat capacity of sample, specific heat capacity of sapphire, mass of sample, mass of sapphire, heat flow rate for sample, heat flow rate for sapphire and the heat flow rate for blank runs respectively. For each sample, several runs were carried out.

**Details of Thermogravimetry:** Thermogravimetric measurement of single phase YUT3 sample was carried out by loading about 20 mg of sample in an alumina crucible and heated upto 1473 K in a thermo balance [ model: TGA/SDTA 851e/MT5/LF1600] at a heating rate of 10 K min<sup>-1</sup> in air. The samples were cooled in the same atmosphere and weight changes were recorded during the cooling period also.

**Details of O/U measurement using spectrophotometry:** The oxygen-to-uranium ratio (O/U) in the YUT3 sample before and after high temperature heat treatment was determined by absorbance measurement in the range of 360–720 nm using a Shimadzu UV-1700 Pharma Spec UV–visible spectrophotometer. For this analysis, about 20 mg of single phase YUT3 sample was refluxed with about 20 ml of conc. phosphoric acid. During the dissolution in the phosphoric acid medium, the valence state of uranium remains unchanged. Similar dissolution was performed on the sample heated at 1573 K for 4 h in air. The resultant solution was filtered and after proper dilution, presented for recording the absorbance spectra. A fitting of the spectra using linear combinations of absorbance spectra of U<sup>4+</sup> and U<sup>6+</sup> standard solutions reveals the fraction of U<sup>4+</sup> and U<sup>6+</sup> in the sample, which enables the determination of the O/U ratio.

## References

1. Jagannath UK, Goutam RK, Sharma J, Singh K, Dutta US, Sule R, Pradeep SC (2018) Gadkari, HAXPES beamline PES-BL14 at the Indus-2 synchrotron radiation source. J Synchrotron Rad 25:1541–1547.