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# Probing local coordination and oxidation state of uranium in $ThO_2$: U nanostructured

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## ABSTRACT

Uranium doped thorium oxide nanoparticle (UDT) was synthesized using citric acid assisted combustion method. The concentration of uranium was varied from 0.5 to 5.0 mol % to investigate the effect of doping concentration on its optical properties. The synthesised UDT powder were characterized systematically using X-ray diffraction (XRD), transmission electron microscopy (TEM) and selected area electron diffraction (SAED) respectively for phase purity, morphology and crystallinity. Pertaining to nuclear industry, UDT is an important material and investigating the local structure of uranium in UDT is interesting as well as challenging because of complexity involved in synthesis of such ceramic powder. We have used time resolved photoluminescence spectroscopy (TRPLS) to probe the local coordination and oxidation state of uranium in UDT. Based on PL emission spectroscopy it was confirmed that uranium stabilizes as $UO_2^{2+}$ ion in UDT. Lifetime spectroscopy shows that uranyl ion is not homogenously distributed in UDT lattice; rather it has two different chemical environments. Effect of concentration on PL behaviour shows that, concentration quenching takes place beyond 2.0 mol %; and based on critical distance calculation multipolar interaction was found to be responsible for such non-radiative quenching. As far as application in luminescence industry is concerned PL measurement shows that UDT gives intense green emission under UV excitation.

## 1. Introduction

Thorium dioxide is an interesting host material for investigating luminescence of lanthanide ion due its desirable property such as its low highest phonon energy (~450 $cm^{-1}$) [1,2] which minimizes the losses due to non-radiative decay and also the ionic radius of $Th^{4+}$ is 0.104 nm which highly favours the substitution of all of the rare earths ion. The phonon energy indeed is one of the most crucial parameter to be considered for developing highly efficient luminescent materials. Not only $ThO_2$ meets the requirement of low phonon energy, but it is also highly stable both chemically as well as mechanically which is very important for practical use in optoelectronic industry [3,4]. Recently we have extensively explored $ThO_2$ for studying the optical properties of lanthanide ion such as Eu, Sm, Tb, Dy, Nd, Ho, Yb etc. using photoluminescence and photoacoustic spectroscopy [3–6].

Actinide elements exhibit various interesting electronic and nuclear properties because they have partially filled 5f- orbitals. Unlike lanthanide ion, actinides (mainly early series) exhibit variable oxidation state. This together with its radioactive nature arise the possibility of stabilization of some unusual oxidation state of actinide ion particularly in solid matrices.

Compared to lanthanide ion, the larger spin–orbit coupling (due to more number of electrons) and significantly large crystal-field in actinides decrease the gap between energy level of excited states [7]. As a result there is a ladder like pathway for de-excitation via non-radiative transition. Consequently actinide ions are less fluorescing than lanthanide ion. In that context solid matrix with low phonon energy play a very important role.

As far as applications are concerned luminesce of both lanthanides as well as actinide in various inorganic hosts is explored in laser and non-linear optics. The fact that in case of actinide ion; the first $5f^n \rightarrow 5f^{n-1}6\,d^1$ transition occurs at lower energy, excitation of f-electron to this broad and intense band is quiet easy [8]. Among actinides uranium has very rich and complicated chemistry. Its outer shell configuration is $5f^3 6d7s^2$ which allows the element to have oxidation states +2, +3, +4, +5, and +6. Each oxidation state offer some interesting properties and interesting application.

There are lot of application pertaining to $U^{3+}$ doped single

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crystal such as for optical amplification in lasers, radars and telecommunication system [9–12] due to a 2.5 mm emission. Uranyl doped silicate glasses are used for luminescent solar concentrator [13].

Also because it has six valence electrons similar to that of Cr, Mo, and W, it has the ability to form high coordination complex, and this property has been used extensively for catalysis such as in Fischer–Tropsch synthesis, dehydrogenation and oxidation [14,15]. As far as solid state lighting is concerned $U^{6+}$ doped SrO has been reported to be used as a potential green light emitting phosphors [16].

Host play an important role in stabilization of uranium in various oxidation states. Uranium stabilizes as $U^{3+}$ in variety of single crystal such as $LaBr_3$ [17], $CsCdCl_3$ [18], $PbCl_2$ [19], $SrCl_2$ [20]. Similarly $U^{4+}$ also get's stabilized in large number of single crystals such as $KPb_2Cl_5$, $Cs_2GeF_6$, $LiYF_4$ [21–23] etc. Oxidation state of +5 is also reported for uranium in CaO [24]. Lots of reports also exist where uranium stabilizes as $U^{6+}$ [13,16,25–27].

In fact in some of our recent work on this peculiar actinide ion, we have found an interesting behaviour; uranium stabilizes as octahedral uranate ion in $SrZrO_3$ whereas in $Sr_2SiO_4$, it stabilizes as uranyl ion [26,27].

Hexavalent Uranium depending on the synthesis conditions and thermal treatment can have different molecular species such as tetrahedral uranate ($UO_4^{2-}$), hexagonal uranate ($UO_6^{6-}$) or uranyl ($UO_2^{2+}$) species. The stabilization of U(VI) in the octahedral ($UO_6^{6-}$)/ tetrahedral ($UO_4^{2-}$) uranates is reported in solids only, whereas $UO_2^{2+}$ moiety is stable both in solutions and solids.

Normally uranium luminescence is observed in green and red for solid. Kroger [28] ascribed the green emission to uranyl groups and the red emission to uranate groups. However, Runciman [29] ascribed, the green emission of CaO:U and $Ca_2MgWO_6$:U to uranate ($UO_6^{6-}$) group.

Both $UO_2^{2+}$ and octahedral $UO_6^{6-}$ give emission in the green region, but $UO_2^{2+}$ emission can be distinguished from that of the latter on the basis of its characteristic vibronic structure exhibiting set of equidistant lines, while characteristic emission of ($UO_4^{2-}$) species was reported to be in the red region.

There is no report in literature where speciation and coordination behaviour of uranium doped thoria (UDT) is studies. In view of importance attached to UDT in nuclear industry as the futuristic fuel, it is an important step towards understating the photophysical characteristics of uranium in thorium dioxide.

We have prepared $U_xTh_{1-x}O_2$ (x = 0.005, 0.01, 0.02, 0.05) using gel-combustion route and investigated its optical spectroscopy using time resolved fluorescence spectroscopy (TRFS) to identify the valence state and nature of uranium species present in UDT. We have also explored the effect of uranium concentration on its luminescence properties.

## 2. Experimental

UDT nanoparticles were synthesized by citric acid assisted combustion method [30]. In a combustion reaction, thorium nitrate gel containing appropriate amounts of uranium [in the form of $UO_2(NO_3)_2$] was mixed with citric solution in a molar ratio of 1:1. This solution was dried under IR lamp and heated at 500 °C to give nanocrystalline powders of $Th_{1-x}U_xO_2$ (x = 0.005, 0.01, 0.02, 0.05).

## 3. Instrumentation

Powders XRD of the samples were carried out using RIGAKU Miniflex-600 diffractometer operating in the Bragg–Brentano focussing geometry. Cu–Ka radiation (l = 1.5406 Å) has been used as X-ray source. The instrument was operated at 40 kV voltage and 15 mA current. The XRD pattern has been taken with a scan rate of 1°/min.

To obtain the crystallite size from X-ray line broadening, we applied Scherrer's formula ($t = 0.9\lambda/B\cos\theta$), where t is the diameter of the crystallite, λ is the wavelength (for Cu–$K_\alpha$, λ = 1.5418 Å) and $B = \sqrt{(B_M^2 - B_S^2)}$ ($B_M$ is the full width at half maximum of the sample and $B_S$ is that of a standard grain size of around 2 μm). The standard used was silicon (~100 micron) and was so chosen such that the sample and standard have reflections at nearly similar 2θ values. PL data were recorded on an Edinburgh CD-920 unit equipped with Xe flash lamp with 10–100 Hz frequency as the excitation source. The data acquisition and analysis were done by F-900 software provided by Edinburgh Analytical Instruments, UK. Time resolved emission studies (TRES) were carried out on an Edinburgh F-900 unit equipped with M 300 monochromator.

## 4. Results and discussion

### 4.1. Structural analysis: PXRD

Powder XRD pattern of varied concentration of UDT sample is shown in Fig. 1. All the pattern matches well with the reported XRD of thoria (ICDD No. 7,80,685). They possess fluorite cubic geometry with space group Fm3m. Sharp peaks in the patterns indicate that all the sample are well crystallized having lattice parameter of ~5.595 °A, which are in close agreement to the one reported for bulk $ThO_2$. The products doped with uranium exhibit similar patterns as compared with undoped $ThO_2$ sample. From these patterns it can also be concluded in all the UDT samples, uranium is properly doped in thoria lattice and has not distorted the crystal structure of parent compound. All the diffraction peaks are properly labelled and they closely resemble that of ICDD pattern 7,80.685. The diffraction peaks are broadened which confirms the sizes of UDT particles are in nanoregime. The strongest peak (2θ = 27.56°), was used to calculate the average crystallite size (t) of the UDT samples, which was found to be~ 12 nm for all the samples.

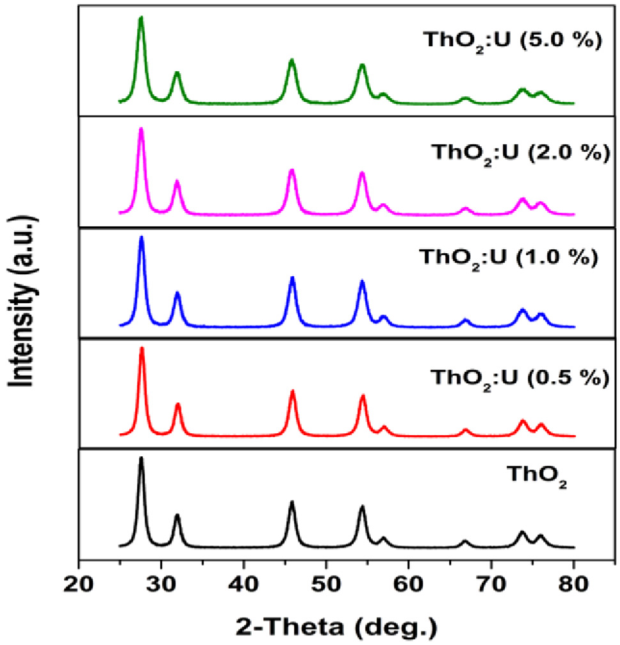

**Fig. 1.** XRD pattern of pure $ThO_2$ and $Th_xU_{1-x}O_2$ (x = 0.005, 0.01, 0.02 and 0.05).