

# Oxidation state determination of uranium in various uranium oxides: Photoacoustic spectroscopy complimented by photoluminescence studies



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## HIGHLIGHTS

- Oxidation state of uranium by PAS.
- Fluorination of uranium oxides is explored.
- PAS techniques is complimented by PL.

## ARTICLE INFO

### Article history:

Received 9 September 2014  
Received in revised form 2 December 2014  
Accepted 2 December 2014  
Available online 10 December 2014

### Keywords:

Uranium  
Photo-acoustic  
Photoluminescence  
Actinides  
Oxidation state

## ABSTRACT

Photoacoustic spectroscopy (PAS) has been utilized for the determination of U(IV). Initial experiments were carried out for determination of U(IV) in uranium tetra fluoride, and were further extended to the determination of U(IV) in uranium oxide samples having various O/M ratios like  $\text{UO}_{2.00}$ ,  $\text{UO}_{2.17}$ ,  $\text{U}_3\text{O}_8$ , and  $\text{U}_3\text{O}_7$ . All these oxides, since dark gray/black in color, were having featureless spectra in the visible region, hence solid state reaction of uranium oxide with ammonium bi-fluoride was utilized for the formation of U(IV) and U(VI) oxyfluorides, having narrow well resolved spectra, prior to estimation by Photoacoustic spectroscopy technique. The strong absorption for U(IV) complex at 630 nm was monitored using a He–Ne laser resulting in good sensitivity for determination of U(IV). It was observed that fluorinated uranium dioxide ( $\text{UO}_2$ ) is having spectra similar to U(IV); fluorinated uranium trioxide ( $\text{UO}_3$ ) is having spectra of uranyl only whereas Triuranium octoxide ( $\text{U}_3\text{O}_8$ ) spectra consist of both U(IV) and uranyl component. This was further supported by photoluminescence studies.

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## Introduction

Uranium compounds have attracted growing attention from researchers within the last couple of decades. These materials are interesting not only from a technological point of view as the constituents of the nuclear fuel cycle, but also from a scientific point of view since their electronic structures and their macroscopic properties are strongly affected by the partially localized nature of the 5f-electrons. Thus, uranium compounds belong to a class of materials with properties intermediate to those characteristic of localized systems and itinerant systems [1]. Earlier radioactive properties of the actinide compounds have been a limiting factor for more extensive studies of these materials. An additional point of interest particularly concerning the uranium oxides is the connection between their electronic structures, the physical properties

of the material and the geometric arrangement of the atoms i.e., the presence of the inequivalent crystallographic sites occupied by chemically identical atoms. The 5f electrons in actinides and relatively more close-lying  $5f^{n-1}6d$  configurations are more strongly affected by a crystal field than the corresponding state of lanthanides. Whenever the states arising from these configurations are excited, the relaxation is predominantly through non-radiative processes. This makes the actinide solids attractive candidates for Photoacoustic spectral investigations.

In general externally excited solid can relax to thermal equilibrium by emission of either photons (radiative processes) or phonons (nonradiative processes). Highly sophisticated spectroscopic techniques to detect and analyze emitted photons have been well established. Since Photoacoustic (PA) signals are produced only by the absorbed light actually converted to heat in the sample. PA spectroscopy is applicable to the study of nonradioactive processes [2].

Conventional absorption spectroscopy is based on excitation by electromagnetic radiation with intensity  $I_0$  and the measurement

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of reflected or transmitted light intensity  $I$ . Thus, the absorbencies derived indirectly from transmittance or reflectance, whereas in PAS pressure waves are detected which are generated directly by the absorbed energy [3].

Uranium oxides with highly oxidized uranium states contain inequivalent O–U bonds. Uranium dioxide ( $\text{UO}_2$ ) (black–brown color), however, has a simple cubic  $\text{CaF}_2$  crystal structure and is ideally an insulator but is in reality a semiconductor [4]. The increase of the oxygen content and the oxidation states from  $\text{UO}_2$  to Triuranium octoxide ( $\text{U}_3\text{O}_8$ ) and uranium trioxide ( $\text{UO}_3$ ) results in a decrease of conductivity in the uranium oxides [5]. The formal valency of uranium in  $\text{UO}_2$  is tetravalent (U(IV)) with  $\text{Oh}^5$  symmetry around the uranium ion. The lattice structure has identical O sites and has a O–U bond length of  $\sim 2.37 \text{ \AA}$  [6]. In contrast to  $\text{UO}_2$ , the crystal structure is more complicated in the case of the mixed-valency oxide  $\text{U}_3\text{O}_8$  (dark-green color) which contains both U(IV) and U(VI) in a 1:2 ratio. In the orthorhombic crystal structure of  $\text{U}_3\text{O}_8$ , which is an insulator, there are two inequivalent atomic positions for uranium and four different positions for oxygen within the distorted octahedron so that the following uranium–oxygen bonds are formed:  $\text{U}_I\text{–O}_{II} = 2.07 \text{ \AA}$ ,  $\text{U}_I\text{–O}_{IV} = 2.18 \text{ \AA}$ ,  $\text{U}_{II}\text{–O}_{III} = 3 \times 2.07 \text{ \AA}$  and  $\text{U}_{II}\text{–O}_I = 2.21 \text{ \AA}$  [6]. On the contrary, orthorhombic  $\gamma\text{-UO}_3$ , (orange–yellow color) has a formal U valency of U(VI), and two types of U–O distances are known: short axial oxygen uranyl bonds ( $\sim 1.79 \text{ \AA}$ ) and longer, planar, equatorial bonds ( $\sim 2.30 \text{ \AA}$ ) [6,7]. Investigation of oxides of uranium by X-ray absorption and emission spectroscopies, extended X-ray absorption fine structure (EXAFS) and Fourier transformed infrared (FTIR) were reported [8–10]. Also a large number of reports are available in the literature regarding the absorption data of uranium in various oxidation states. Gruen and Fred [11] in one of their earliest works have given a detailed account of the absorption spectra of tetravalent uranium ions in different fluoride matrices. Conway [12] has reported on absorption spectrum of  $\text{UF}_4$  in calcium fluoride matrix and energy levels of Uranium (V). Carnall et al. [13] and Hodul [14] in their respective papers have also showed the absorption and PAS spectra of tetravalent uranium ions in different fluoride matrix. Uranium in 4+ oxidation state strongly absorbs in the region 600–650 nm. Similarly, pentavalent uranium absorption in  $\alpha$  and  $\beta$   $\text{UF}_5$  has also been reported in the literature by Hecht et al. [15] where the absorption maxima is observed in the near-IR region at 900–1100 nm. Kimura et al. [16] have investigated the speciation study of uranium in aqueous solutions and in precipitates by Photoacoustic spectroscopy. Schrepp et al. [17] has used PAS technique for detection of U(IV) and U(VI) in aqueous solution.

Triuranium octoxide,  $\text{U}_3\text{O}_8$ , in particular is one of the most important compounds in the uranium–oxygen system because of its usability either as a starting material for various kinds of reactions or as a standard for determining O/U ratio of uranium oxides [18]. Understanding the exact stoichiometry and the oxidation states of uranium in this complicated U–O systems is very important in view of increasing use of urania based fuels in nuclear reactors. This is understandable because of the fact that the stoichiometry and oxidation states dictate the interaction behavior of materials with structural materials [19]. For having stoichiometric  $\text{U}_3\text{O}_8$  as the standard for compositional analyses in the U–O systems, the heating condition of 800–850 °C in air has been often recommended [20]. However, several other reports state that, the stoichiometric  $\text{U}_3\text{O}_8$  could only be prepared by heating at 600 °C which was supported by several experimental results on equilibrium oxygen pressure of the  $\text{U}_3\text{O}_8$  phase [21].

Even though  $\text{U}_3\text{O}_8$  has been extensively studied since the time of Manhattan project, the determination of exact stoichiometry of this compound has eluded a number of techniques. PAS technique has earlier been utilized to study  $\text{UO}_2$  and  $\text{U}_3\text{O}_8$  systems where in the authors have used free ion energy level diagram for

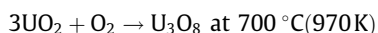
interpretation of the data [22]. In those reports it was observed that, the stoichiometry had almost no influence on the structure of the spectrum which was broad and featureless. Thus concluding that, direct speciation of these systems as such is not feasible by PA technique.

The main problem in the analysis of U–O systems is the fact that these oxides are dark in color and the spectra are featureless. Though U(IV) has well resolved bands in the visible region due to f–f transition, in case of  $\text{UO}_2$ , the strong charge transfer band between U(IV) and  $\text{O}_2$  overlaps the f–f transition, making it unsuitable for investigation as such. Moreover, the very broad and intense spectrum of  $\text{UO}_2$  masks the spectrum of  $\text{UO}_3$ , thus making the direct assay of  $\text{UO}_3$  very difficult in the presence of bulk  $\text{UO}_2$ . The present paper deals with our work where in we have tried to overcome the above said limitation by a simple solid state fluorination reaction. A solid state reaction was planned between ammonium bi-fluoride (ABF) and three U–O systems namely  $\text{UO}_2$ ,  $\text{UO}_3$  and  $\text{U}_3\text{O}_8$ . This result in the formation of the respective fluorides where the charge transfer bands are shifted to UV/Visible region, well separated from the f–f transitions which further can be analyzed with ease. Understanding spectroscopy of uranium is very important because it is a radioactive material and can cause hazard to environment and as well to personnel. It is difficult to handle these materials in normal laboratory conditions without any specific protection. The authors have made great efforts on operating these dangerous experiments. These results could be useful in the nuclear industry, particularly within the field of chemical quality control. This is the first report where PAS has been used as an analytical technique to understand the oxidation state of various uranium compounds. PAS technique was utilized to study the reaction between ABF and U–O systems as well as an analytical tool for determination of U(IV) and uranyl ion (U(VI)) in the fluorinated uranium oxides samples.

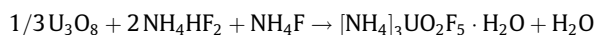
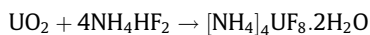
## Experimental

### Sample preparation

High purity  $\text{UO}_2$  and  $\text{U}_3\text{O}_8$  are used in the synthesis of their fluorinated counter parts. Their origin is



Ammonium bifluoride ( $\text{NH}_4\text{HF}_2$ , also known as ammonium hydrogen fluoride) has been shown to fluorinate uranium dioxide ( $\text{UO}_2$ ), and has been used successfully in the preparation of both tetravalent uranium fluoride salts and ammonium uranium fluoride double salts [23,24].



The compound form as can be observed using Thermogravimetric analysis (TGA)/differential thermal analysis (DTA) and X-ray diffraction (XRD) analysis is  $(\text{NH}_4)_4\text{UF}_8 \cdot 2\text{H}_2\text{O}$  and  $(\text{NH}_4)_3\text{UO}_2\text{F}_5 \cdot \text{H}_2\text{O}$  [25–28].

The crystal structure of potassium uranyl fluoride has been reported by Zachariassen [29]. In  $\text{K}_3\text{UO}_2\text{F}_5$ , the  $\text{UO}_2\text{F}_5^{3-}$  group is a pentagonal bipyramid with U–O distance =  $1.76 \pm 0.03 \text{ \AA}$  and the U–F distance =  $2.24 \pm 0.02 \text{ \AA}$ . Since ammonium uranyl fluoride has been reported as isostructural [30] with potassium salt, it may be stated that in  $(\text{NH}_4)_3\text{UO}_2\text{F}_5$  crystals, the  $\text{UO}_2\text{F}_5^{3-}$  group is also pentagonal bipyramid.

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