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Fluorescence Properties of Hexavalent Uranium in Solids

M. K. Bhide*, V.Natarajan and S.V.Godbole

Radiochemistry Division, Bhabha Atomic Research Centre, Mumbai, India.

The luminescence of hexavalent uranium in several uranium compounds was investigated as early as in 1852, by Stokes and later in 1896 by Becquerel leading to discovery of radioactivity[1,2]. The spectroscopy of U(VI) compounds[3], in particular that of uranyl with the intense green emission had drawn greater attention of scientific community due it's use in mineral exploration and in probing the uranium contamination of soil, and subsoil waters. Amongst the first half of the actinide series U, Am and Cm are known to have good luminescence yield. Of these, Uranyl moiety of U(VI) ion is more stable and has a better luminescence efficiency. Uranyl fluorescence is attributed to electronic transitions from first excited level of triplet $^3\prod_u$ to $^1\sum_g^1$ ground state and the vibrational levels associated with ground state. The vibrational frequency of O=U=O stretching in ground state is typically in the range 750-900cm^{-1}. Uranyl exists as a free ion in aqueous solutions having pH< 2 and forms complexes at higher pH by interacting with ligands. The uranium speciation studies in complexes involving hydroxide, carbonate and humic substances in aqueous solution mimicking the natural systems has played distinctive role in understanding the migration behavior of uranium through subsoil/surface water around the nuclear waste disposal and uranium mining sites [4].

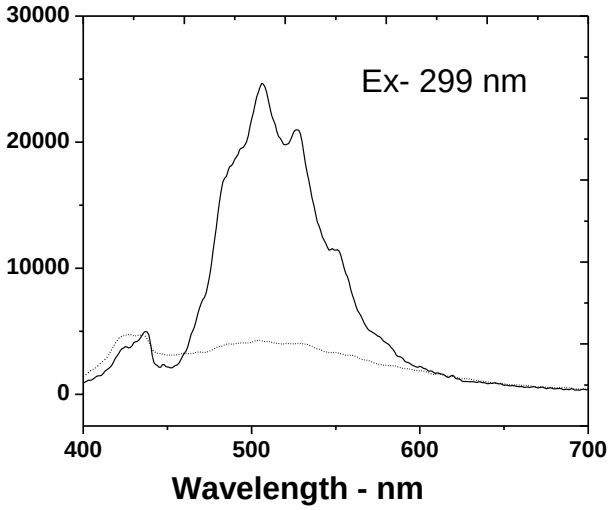

Fig. 1 –A : PL of Blank and U doped SSR- $SrMoO_4$ (500 ^{0}C annealed)

In majority of uranium salts and minerals U(VI) exists as UO_2^{2+} which is always has near linear O-U-O bonding and is coordinated in the equatorial plane by 4, 5 or 6 ligands in solids. Uranium-ligand interaction influences the electronic structure and the nature of bonding in complexes leading to significant changes in emission characteristics and lifetime. 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. 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. The green emission of UO_6^{6-} was reported by Hair et al [5] in a group of oxides with general formula $A_2BB'O_6$ (A=Ca,Sr,Ba; B=Mg, Zn, Cd and B′=Te,W) and that of UO_4^{2-} in the red region was reported by Lam et al[6] in AWO_4/$AMoO_4$, (A=Ca, Sr or Ba) compounds. The structural information about coordination of U-O bonds can be obtained from X-ray/neutron diffraction data and the bond lengths can be determined using IR spectra. The compilation of axial(primary) and equatorial (secondary) oxygen distances in various uranium complexes by Veal et al. [7] had indicated the shortest (~1.7 Å) and longest (~ 2.5 Å) distance of U-O bond in UO_2F_2, UO_2CO_3 and $NaUO_3(C_2H_3O_2)$ compound to be closer to that of free uranyl group. In $UO_2(NO_3)_2.6H_2O$, $K_3UO_2F_5$, $UO_2(OH)_2$, axial U-O distances were reported to be of the order of 1.75 -1.85 Å . The primary bond lengths (~ 1.9-1.96 Å) in metal uranates like $MgUO_4$, $CaUO_4$, Na_2UO_4 etc. increased with concomitant decrease in secondary bond lengths leading to a distorted octahedral structure. The luminescence observed in these compounds was attributed to uranyl emission resulting from $[(UO_2)O_2]^{2-}$ type of species. While, in Cr_2UO_6 and Ca_2UO_6 complexes bonding was reported to be symmetrical with six equivalent (2.08 Å) U-O bonds resulting in an octahedral UO_6 structure and the green emission observed in these complexes was due to UO_6^{6-} species.

* Corresponding author: Email:bhidemak@yahoo.com
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We in radiochemistry have carried out spectroscopic characterization of number of U (VI) doped alkaline earth molybdates, sulphates and borate matrices using PL, TSL and EPR techniques. PL investigations of these compounds have helped in identification of $UO_2^{2+}/UO_6^{6-}/UO_4^{2-}$ species in these hosts. Stabilization of these species was governed by synthesis conditions and structure of the host. In molybdates, Photoluminescence (PL) of U^{6+} (1 M%) doped $SrMoO_4$ (SrM) and $BaMoO_4$ (BaM) was investigated. SrM samples were prepared using two different routes viz. solid state reaction(SSR) and precipitation reaction(PR) using $Sr(NO_3)_2$ and $(NH_4)_6Mo_7O_{24}$ as the starting materials. $SrMoO_4$ could be stabilized in scheelite phase on annealing at 500 and 700 ^{0}C . PL spectra of 500 ^{0}C annealed SSR and PR samples respectively had shown characteristic emission of UO_2^{2+} (green) (Fig.1-A) and UO_4^{2-} (red) – (Fig.2A). The uranyl emission consisted of vibronic bands at 489,507,527 and 551 nm . The stretching frequency obtained from separations of these band was around ν_1= 720 cm^{-1}. In uranate signal vibronic structure was absent. On annealing at 700 ^{0}C, a new signal at 658 nm typical of UO_4^{2-} emission appeared with diminishing of UO_2^{2+} signal in SSR sample (Fig.1-B), whereas, intensity of UO_4^{2-} signal decreased in PR sample (Fg.2-B).

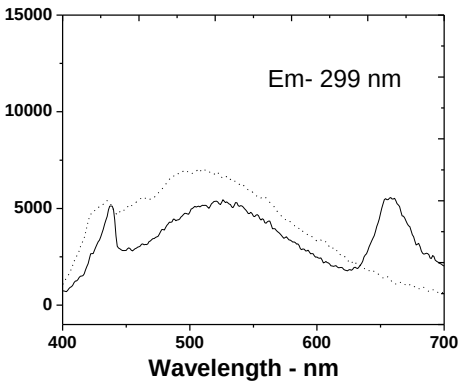

Fig. 1-b : PL of Blank and U doped SSR-$SrMoO_4$ (700 ^{0}C annealed)

Uranium emission could be monitored using any of the peaks at 261, 299 and 326 nm present in the excitation spectra. The decay profile of (UO_2^{2+}) emission at 507 nm could fitted using bi-exponential components having lifetime of 59 μs and 16 μs . The decay of UO_4^{2-} emission at 658 nm in SSR and PR samples had shown life times of 15 μs and 5 μs respectively. The reduced life times observed in uranate are possibly due to lowering of uranium site symmetry under tetrahedral co-ordination. The results uranate emission in $SrMoO_4$ are in analogy with those reported for uranate ion in Ca, Sr and Ba Molybdates by Lam et al [7]. In U^{6+} doped $BaMoO_4$, PL of 400 ^{0}C annealed samples did not show any distinctive signal of (UO_4^{2-}) and only characteristic features of (UO_2^{2+}) emission were observed at room temperature. PL intensity of uranyl emission monitored at different U^{6+} (0.3, 0.6 and 1 M %) concentrations in $BaMoO_4$ indicated optimum signal intensity for 0.6 M% of uranium (Fig.3). The decay of uranyl emission at 519 nm suggested presence of uranium at two different sites in the host having lifetime of τ_1= 10 μs and τ_2= 50 μs. PL intensity of uranyl emission decreased significantly in 700 ^{0}C annealed sample and was accompanied by appearance of a broad and weak signal around 675 nm which probably can be due to formation of (UO_4^{2-}). These emission features were absent SrM and BaM blank samples.

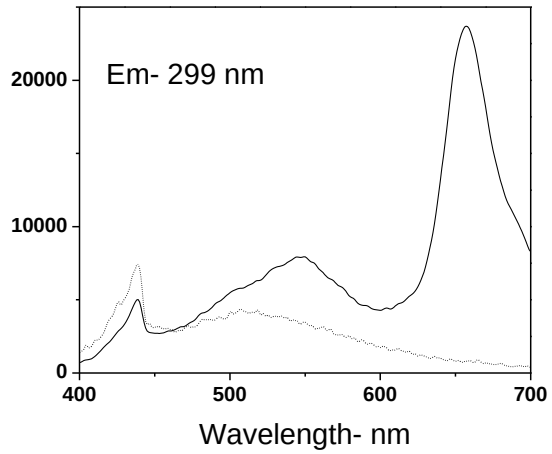

Fig. 2 –A: PL of Blank and U doped PR- $SrMoO_4$ (500 ^{0}C annealed)

In sulphates, emission typical of (UO_2^{2+}) was reported by Seshagiri et al [8] in $CaSO_4$ host and depending on heat treatment, part of the UO_2^{2+} could be transformed into UO_4^{2-} having emission in the orange-red region. However, in $BaSO_4$ irrespective of heat treatment only green emission of UO_2^{2+} was observed. The emission signal observed at room temperature was broadened due to overlapping vibronic bands (Fig. 4) and could be resolved by de-convolution into emission bands corresponding to 498, 516, 534, 554 and 575 nm.

The vibronic frequency of O=U=O stretching ν_1= 670 cm^{-1} was found to be lower than that obtained in UO_2SO_4 solid samples [9]. This could result due to stronger interaction between U(VI) and equatorial ligands leading to weaker U=O apical bonding in $BaSO_4$. Characteristic decay time of uranyl was found

to be of the order of 45 μs suggesting single occupancy of uranium in $BaSO_4$.

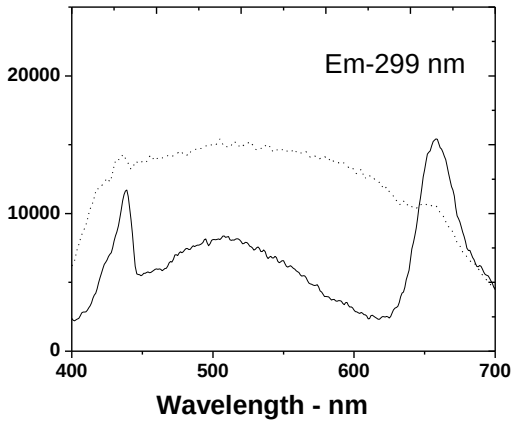

Fig. 2-B : PL of Blank and U doped PR- $SrMoO_4$ (700 ^{0}C annealed)

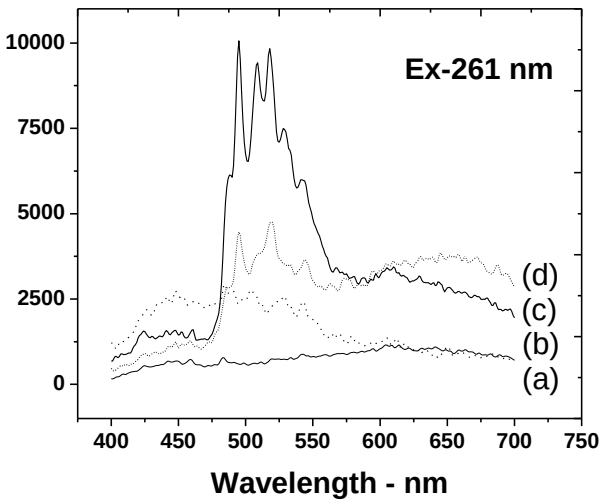

Fig.3 : Variation of UO_2^{2+} intensity with Concentration - (a)0.0, (b)0.3, (c)0.6, (d)1 M %.

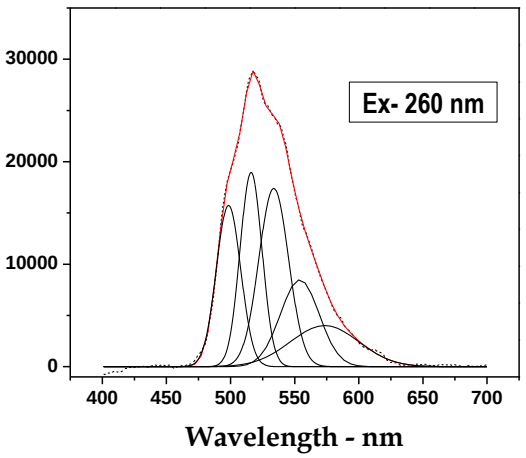

Fig. 4 *: Uranyl emission in $BaSO_4$*

In borates, the observation of zp line at 499 nm along with vibronic structure having stretching frequency ν_1 = 790 cm^{-1} suggested stabilization of UO_2^{2+} in YBO_3. The decay profile of intense emission could be fitted using bi-exponential components, which suggested presence of uranium at two different sites with lifetime τ_1= 40 μs for major fraction and τ_2= 275 μs for minor fraction. The time resolved emission of sample recorded at different delay times (0.3 and 1.8 ms) were identical indicating their origin to be from the same species. This suggested higher defect concentration around the site corresponding to shorter life time and smaller defect concentration around other site corresponding to higher life time [10]. PL investigations of sodium borosilicate glasses containing uranium oxide and (uranium oxide + thorium oxide) had shown a broad emission in the green region around 538 nm without any vibronic structure. This was attributed to stabilization of octahedral uranate UO_6^{6-} in borosilicate glass[11]. The decrease in PL intensity and lifetime observed in U^{6+}, Th^{4+} co-doped glasses was attributed to enhanced nonradiative losses resulting from increase in defect concentration around uranate ion.

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