2007 International Nuclear Atlantic Conference - INAC 2007
Santos, SP, Brazil, September 30 to October 5, 2007
ASSOCIAÇÃO BRASILEIRA DE ENERGIA NUCLEAR - ABEN
ISBN: 978-85-99141-02-1

SPECTROSCOPIC PROPERTIES OF THE $UO_2(ACAC)_2.(H_2O)_n$:Eu^{3+} (ACAC=ACETYLACETONATE ION)

Maria Claudia F.C. Felinto[1], José Eduardo M. Sá Luiz[1], Fábio T. Nakagawa[1]
Hermi F. Brito[2], Ercules E. S. Teotonio[3]

[1] Instituto de Pesquisas Energéticas e Nucleares (IPEN / CNEN - SP)
Av. Professor Lineu Prestes 2242
05508-000 São Paulo, SP
mfelinto@ipen.br
jemsluiz@ipen.br

[2] Instituto de Química da Universidade de São Paulo (IQ/ USP - SP)
Av. Professor Lineu Prestes 748
05508-000 São Paulo, SP
hefbrito@iq.usp.br

[3] Universidade Federal de Goiás – Campus de Catalão (UFG - GO)
Av. Dr. Lamartine P. de Avelar, 1120
CEP: 75704-020 – Catalão – GO
ercteot@gmail.com

ABSTRACT

The uranyl ion possesses some properties, which makes it a potential component for a solar energy conversion system or biological application. It absorbs light in the shorter wavelength range of the solar spectrum, producing a relatively long-lived excited state. The excited state of uranyl ion has fluorescence peak at 520 nm, a property that makes it relatively convenient to investigate its reaction. The redox potential of the excited uranyl ion makes a powerful oxidizing agent. This may be of potential use in the photogeneration of oxygen, which is of great importance for the photocleavage of water. In this work, it is described the synthesis, characterization and spectroscopic study of the matrix $UO_2(ACAC)_2.(H_2O)_n.(x\%mol)\ Eu^{3+}$ (where x= 1, 3, 5 and 10). The compounds obtained were characterized by elementary analyses for determine the U^{6+} and Eu^{3+} concentrations, infrared spectra, thermal analyses, absorption in the UV-VIS range and luminescence spectra. The mainly bands in infrared spectra of the β-diketone observed in this work are ν_s C=O in 1540 cm^{-1}, ν_{ass} C=O in 1540 cm^{-1} and ν_s C=C in 1577 cm^{-1}. In the emission spectra, transitions of the triplet $^3\Pi_u \rightarrow {}^1\Sigma_g+$ was observed. The spectra of the uranyl matrix present behavior superimposed to doped 5% and 10% ones. The emission spectra of matrix doped with 1 and 3% showed a band shift to red region of spectrum light.

1. INTRODUCTION

Rising prices and sporadic shortages of fossil fuels in the 1970's provide the impetus for the present worldwide effort to develop alternative sources of energy. The exploitation of solar energy is an especially attractive option, since this resource is abundant, environmentally clean and embargo proof. This search for renewable sources of energy has led to an increasing interest in photochemical cells because of their possible role as transducers of solar to electrical energy. The photoeffects in electrochemical systems were first observed by Becquerel[1] in his investigation on the solar illumination on metal electrodes in 1839. Later it was observed by Moser[2] and Rigollot[3] that the sensitivity of silver/silver halide and copper/copper oxide electrode could be increased by coating them with a dye stuff.

Thompson[4] and Stora[5] reported that pure metal electrodes were also sensitive to light when coated with a dye or immersed in a dye solution. The result of the first 100 years had been reviewed by Copeland and co-workers[6]. A summary of the properties of photoelectrochemical (PEC) cells described in the literature up to 1965 was compiled by Kuwana[7] and later work has been reviewed by Archer[8].In that context, one approach that has been studied by several groups is the photosensitization of high-energy band GAP semiconductors. Due to the fact that the energy required to promote an electron of valence band to conduction band been high, the absorption process is now made by a sensitization specie, who transfer electrons to the semiconductor, splitting them emission and absorption processes, allowing a bigger advantage of solar spectrum.

Uranyl ion presents a great potential as luminescent material, applied in laser technology, luminescent probes, solar energy conversion cells, etc. Luminescence of UO_2^{2+} and lanthanide ions is pointed out between optical properties of this ions, because of their unique characteristics, like long lived excited state and narrow emission bands in the UV-VIS region. Luminescent properties of this ion are strongly influenced by chemical environment that surrounds it. Europium ion has been studied due to the fact that their complexes present monochromatic red emission. Their spectrum presents bands from the intraconfigurational transitions $^5D_0 \rightarrow {}^7F_J$ (where J = 0, 1, 2, 3, 4, 5 e 6), been the $^5D_0 \rightarrow {}^7F_5$ and $^5D_0 \rightarrow {}^7F_6$ rarely observed.

The search for a sensitizer for europium is very important because it presents low intensity absorption bands. Specifically, we can point out the energy transfer studies of Kropp[9], where he shows that there are energy transfer in a short-range of UO_2^{2+} to the Eu^{3+} in aqueous solution of perchlorate, suggesting a strong influence of oligomeric hidroxo complex, probably containing OH^- bridges between UO_2^{2+} and Eu^{3+} ion. Energy transfer from UO_2^{2+} group to $^5D_0$ Eu^{3+} level was also observed in phosphate glasses [10].

Recently, Suib and co-workers[11] investigates the energy transfer process in zeolites matrix. They show that efficiency of energy transfer process could be controlled by preparation method and by structural chain of zeolites in particular. Sheng Dai and co-workers investigates interfacial photochemical reactions in doped uranyl ions in sol-gel matrix and ethanolic solution. As a extension of their studies, the same authors studies energy transfer between UO_2^{2+} and Eu^{3+} in sol-gel glasses[12]. Seregina and co-workers also studied energy transfer between UO_2^{2+} and Eu^{3+} in $POCl_3.SnCl_4$ solution[13].

β-diketones ligands are excelent chelates for transition metal, rare earths and actinide ions, where the 1,3-dicarbonyl group presents a efficient coordination site. The first rare earths complexes with β-diketones were the acetylacetonate, reported by Urbain in the end of XIX century. The major of rare earths β-diketones complexes are obtained in form of hydrated tris-complexes. However, anydrous complexes with formula Sc(β-diketones)$_3$ are usually synthesized when substitutions groups in β-diketones are relatively large, like t-butyl group. The tris(acetylacetonate) complexes can also been obtained under controlled conditions, using anydrous solvents and low coordinated ability anion. Figure 1 show the β-diketone acetylacetonate (ACAC)

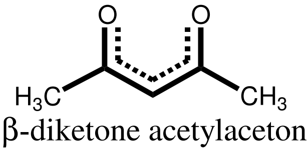

Figure 1 - β-diketone acetylacetonate (ACAC)

2. EXPERIMENTAL SECTION

2.1 Synthesis

Synthesis of hydrated rare-earths β-diketones (ACAC) was made dissolving about 0.03 mol of ACAC in 50ml of ethanol (~50°C) until pH = 7.0. Subsequently it was added to the solution 0.01 mol of $EuCl_3.6H_2O$ dissolved in 50ml of water. After this, pH of the solution drop to 3 and more solution of ammonium hydroxide was required to pH of the solution reach 6.5. The solution was submitted to agitation under 2 hours, until it form a characteristic oil of Eu - β-diketones. The yellow precipitated obtained was recrystallized in ethanol and kept under vacuum at room temperature. The complexes of uranyl β-diketones (UO_2-ACAC) was obtained in a similar way to the procedure used in the rare-earths complexes synthesis, and after, the mixture of solutions of neutralized β-diketones with the base and respective uranyl nitrate occurred formation of a red precipitated, the complex in form of a fine powder.

2.2 Characterization

The Scanning Electron Microscopy (SEM) provides information about the morphology of he materials, and was obtained in a scanning electron microscope Philips model XR-30; the infrared spectra of the samples were used to provide information about the nature of the coordination of the ACAC ligand to the UO_2^{2+} ion. These spectra were recorded in the range from 4000 to 400 cm^{-1} in KBr pellets by using a Bomen model MB102 FTIR spectrophotometer; the excitation spectra of the complexes in the solid state were obtained in the spectral range of 250-475 nm by monitoring the intensity of the $^3\Pi_u \rightarrow {}^1\Sigma_g+$ transitions at ~530 and 495 nm, while the emission spectra were obtained in the range of 420 to 720 nm with excitation monitored at $^3\Pi_u \rightarrow {}^1\Sigma_g+$ at the maximal in the excitation spectra. This luminescence instrument was fully controlled by a DM3000F spectroscopic program and computer, and the spectral intensities were automatically corrected for the photomultiplier response.

3. RESULTS AND DISCUSSION

The scanning electronic microscopy shows material with crystaline composition and agglomerated particles in majority smaller then 5 µm. It was observed that these agglomerated are formed by particles that presents homogeneous morphology and a hygroscopic behaviour is also observed.

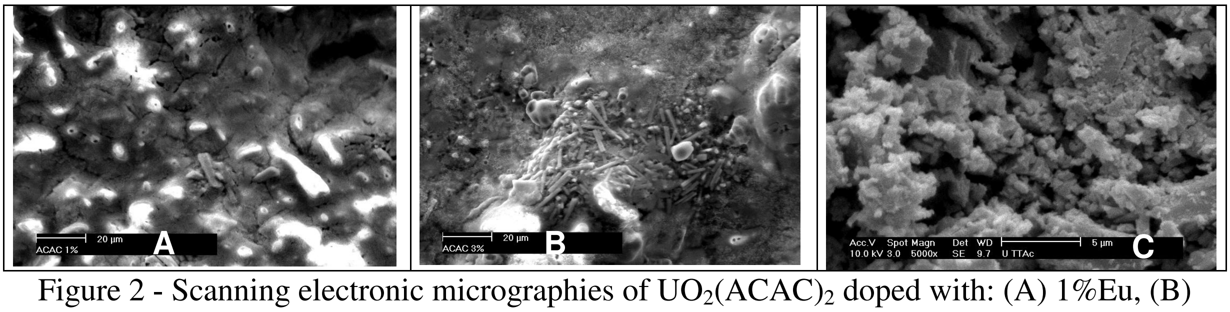

Figure 2 - Scanning electronic micrographies of $UO_2(ACAC)_2$ doped with: (A) 1%Eu, (B) 3% Eu and (C) 5% Eu, with increase of 5000X.

Vibrational spectra in the infrared region give helpful information about nature of carbonyl groups of β-diketones linked to metallic ions in coordination compounds. The main band involved in the studies of β-diketones-ion interaction are those associated to stretching frequencies ν_s(C=O) (~1600 cm^{-1}), ν_{ass}(C=O) (~1400 cm^{-1}), ν_s(C=C) (1531 cm^{-1}) and ν(O-M^{n+}) (~ 450 cm^{-1}). The behaviour of vibrational modes ν(C=O) and ν(C=C) was intensively studied by Holtzclaw and Collman, who suggested that the double link character C=C in chelated ring of the β-diketones is relatively weak and that the absorption frequency of carbonyl group is related to: electronic density relative of σ link, the are usually controlled by substituted groups linked to the carbons of carbonyl group; the mass of substituted groups linked to carbonylic group; and the interaction with orbitals of metallic ion.

From the analyses of the spectrum, it was observed bands in the region of 3400 cm^{-1} attributed to stretching ν O-H of coordination water. Bands attributed to angular deformation of water δH-O-H are convoluted with the ν_s C=O of β-diketones. Bands attributed to UO_2^{2+} group (ν U=O stretching) are observed in the region of 825 (ν_sU=O) and 943 cm^{-1} (ν_{ass} U=O) for all doped percentages used in this work. The main bands referent to β-diketones observed in this work are ν_s C=O in 1620 cm^{-1} convoluted with the bands of angular deformation of water, ν_{ass} C=O in 1385 cm^{-1}, ν_s C=C observed in 1532 cm^{-1} e finally ν M-O who is observed in two convoluted bands, with maxima in 455 cm^{-1} and 462 cm^{-1}, showing two M-O sizes.

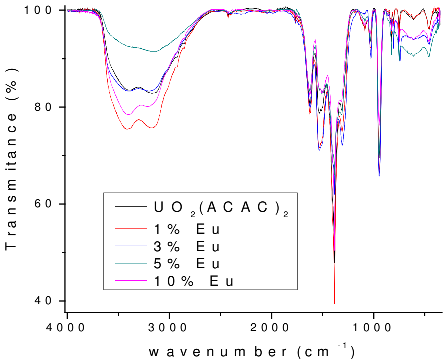

Figura 3 – IR spectra of $UO_2(ACAC)_2$:n%Eu

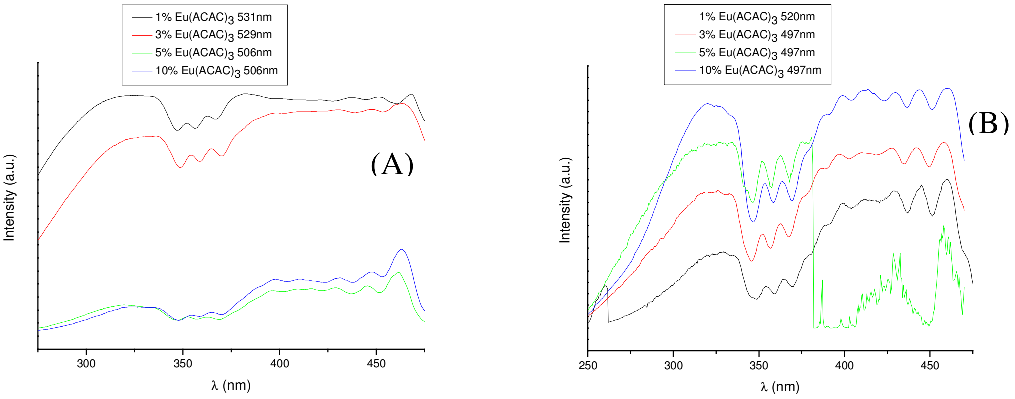

Figure 4 – Excitation spectra of $UO_2(ACAC)_2$:n%Eu at (A) room temperature and (B) 77 K

Excitation spectra show large bands attributed to organic part of the ACAC and uranyl ions. Intraconfigurational transitions of europium ion are not observed in the obtained spectrum.

From the analysis of emission spectra, it is observed a characteristic band group of the matrix of hexavalent uranium, with sharpness lines, showing transitions of uranyl ion triplet state to singlet $^3\Pi_u \rightarrow {}^1\Sigma_g+$. Bands centered in approximately 486.2, 507.2, 530, 554.2 and 580 nm are shifted to high-energy region in doped matrix with 1 and 3% of $Eu(ACAC)_3$, respectively in 501, 534.8, 556.2, 580 and 618.6 (shift to the blue). This fact agrees with restructuraction of matrix with these two compositions.

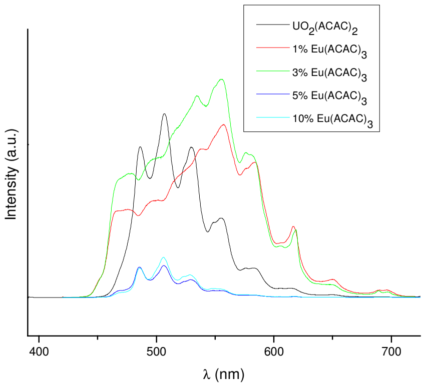

Figure 5 – Emission Spectra of $UO_2(ACAC)_2$:n%Eu at room temperature

4. CONCLUSIONS

The micrographies show material with crystalline composition and agglomerated size in majority smaller then 5 μm, and presents homogeneous morphology. IR data shows coordination of the β-diketones to the metallic center, with two distinct link size. The emission spectra showed characteristic fluorescence bands of uranyl ion, attributed to transition $^3\Pi_u \rightarrow {}^1\Sigma_g+$ of matrix. The emission spectra of the materials with 1 and 3% show band shifting to the blue region when compared to the other ones.

5. ACKNOWLEDGEMENTS

The authors acknowledge to Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq)/ Rede de Nanotecnologia Molecular e Interfaces(RENAMI) and Instituto do Milênio de Materiais Compostos II (IMMC2) and Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) for financial support. They also acknowledge IPEN`s Laboratoriy of MEV.

REFERENCES

1. C. Becquerel, *C.R. Acad. Sci, Paris,* **v.9,** pp.14 (1839).
2. J. Moser, *Mh. Chem.,* **v.8,** pp.373 (1887).
3. H. Rigollot, *C.R. Acad. Sci. Paris,* **v.116,** pp.878 (1893).
4. G. E. Thompson, *Phys. Rev.,* **v.5,** pp.43 (1915).
5. C. Stora, *J. Chim. Phys.,* **v.34,** pp.536 (1937).
6. A.W. Copeland, O.D. Black and A.B. Garett, *Chem. Rev.,* **v.31,** pp.177 (1942).
7. T. Kuwana, *Electroanal. Chem.,* **v.1,** pp.197- (1966)
8. M. D. Archer, *J. Appl. Electrochem.* **v.5,** pp.17- (1975).
9. J. Kropp, Energy Transfer in Solution between UO_2^{2+} and Eu^{3+}. *J. Chem. Phys.* **v.46**, n.3, p.843-847 (1967)
10. D.B. Joshi, A.G.I. Daloi and T.R.Bangior, Intermolecular energy tranfer from UO_2^{2+} to Eu^{3+} in solutions. *J. Lumin.*, **v.10**(4), p261 (1975)
11. S.L Suib and K.A. Carrado, Zeolite Photochemistry: Energy Transfer Between Rare-Earth and Actinide Íons in Zeolites. *Inorg. Chem.*, **v.24**(2), p.200 (1985)
12. S. Dai, W. Xu, S.H. Metcalf and L.M. Toth, Energy Transfer Between UO_2^{2+} and Eu^{3+} in Sol-Gel Glasses: A Spectroscopy Investigation. *Chem. Phys. Lett***.**, **v.262**, p315 (1996)
13. E.A. Seregina, A.A.Seregin and G.V. Tekhanoo, Energy Transfer Between UO_2^{2+} and Eu^{3+} in $POCl_3$-$SnCl_4$ Solutions. *J. Alloys Comp.*, **v.341**, p.283-287 (2002)