

## Europium Incorporated in Silica Matrix Obtained by Sol-Gel: Luminescent Materials

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In this work we report some aspects of the chemistry involved in the preparation of modified silicon oxide by the sol-gel process. Europium III compounds were used as luminescent probe. An organic-inorganic hybrid was obtained by hydrolysis of tetraethylorthosilicate (TEOS) and 3-aminopropyltriethoxysilane (APTS). The Eu III compounds were added in different ways. In the first, silica was prepared in the presence of Eu III, and in the second, Eu III was added on the silica surface. These materials were studied by luminescence, infrared spectroscopy and thermogravimetric analysis. The results obtained for the hybrid material show different behavior for Eu III emission, which could be excited by the antenna effect and the influence of the surrounding in the luminescence quenching. The thermogravimetric data present different mass loss in samples to range temperature 50 - 150 °C. Thermogravimetric and infrared spectra showed that inorganic polymers incorporated the organic part.

**Keywords:** *sol-gel, luminescence, surface modified, silica*

### 1. Introduction

The modification of the oxide surface by organic molecules has attracted attention due to its wide possibility of applications<sup>1-3</sup>. The modified silica gel has been used to support ions and molecules<sup>4-7</sup> with potential application in luminescent devices, catalysis and sensors. The technological importance of the sol-gel method is based on its simplicity, which involves fundamental chemistry concept<sup>8</sup>. By the so-called sol-gel method a great variety of molecules and/or ions can be suitably attached to an inorganic network. Silicon alkoxides and derived organically modified matrixes have been the main precursors used for lanthanide containing materials<sup>9,10</sup>. In addition, the luminescent properties of the lanthanides ion may be enhanced by intramolecular energy transfer from moieties attached to the central ion, the so-called "antenna effect"<sup>11</sup>.

The physical and chemical properties of the rare earths in silica glass present particular interest, but the difficulty in the incorporation of high concentrations of rare earths at-

tached covalently to the silicon network is still a challenge. The sol-gel method has been used to prepare materials in the form of powders, films, fibers and monolith, which are based on different metals<sup>12</sup>. The intrinsic characteristics of the method, that are to work at room temperature and the ability to mix different chemicals at the molecular level<sup>13</sup>, make this method well adapted to prepare organic containing materials. The interest in the incorporation of luminescent species encompasses a wide variety applications such as in lasers, chemical sensors and waveguides<sup>14,15</sup>.

The rare earths are used as probes in the sol-gel method due to their sensibility to changes in the surroundings. The Europium III ion is utilized to monitor the synthesis of glass by the sol-gel method<sup>16</sup> and there is a great interest in modifying the surroundings of the ions in order to reduce the loss in energy of the excited states via non-radiative mechanism<sup>17</sup>.

In this work, silica was prepared with its surface modified by sol-gel method and studied through the incorporation of Europium III compounds in two different ways. In

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the first one, the  $\text{EuCl}_3$  and  $\text{Eu}(\text{bpy})\text{Cl}_3$  were incorporated in a solution containing tetraethylorthosilicate (TEOS) and 3-aminopropyltriethoxysilane (APTS). In the second the solid silica modified was obtained firstly and then the Eu species were incorporated on silica surface. The same systems were also studied in the absence of the modifier agent for comparison purposes. These materials were studied by luminescence, infrared spectroscopies and thermogravimetric analysis.

## 2. Experimental

The europium chloride ( $\text{EuCl}_3$ ) was prepared from europium oxide ( $\text{Eu}_2\text{O}_3$ , purchased Aldrich 99.99%), the oxide was dissolved in  $\text{HCl}$  6.0 M. The  $\text{Eu}(\text{bpy})\text{Cl}_3$  compound was prepared as described in literature<sup>18</sup>.

All the synthesis were carried out by the sol-gel method in two different ways:

### Method 1

The silica was prepared in ethanol solvent in the following tetraethylorthosilicate (TEOS): 3-aminopropyltriethoxysilane (APTS): distilled water ( $\text{H}_2\text{O}$ ) in the molar ratio 3:1:7. The acetic acid was used as catalyst. The Eu III compounds were added in the sol (TEOS:APTS: $\text{H}_2\text{O}$ ) under stirring at room temperature. Ethanol was evaporated at  $\sim 25^\circ\text{C}$  producing a white solid. The powder was dried at  $50^\circ\text{C}$  overnight.

### Method 2

All the synthesis were carried out in ethanolic medium. 1,5 mL of the 0,02 mol/L stock solution of  $\text{EuCl}_3$  and  $\text{Eu}(\text{bpy})\text{Cl}_3$  were reacted with 500 mg of silica powder or functionalized silica<sup>21</sup> under stirring. The solid was washed with ethanol and dried at  $50^\circ\text{C}$ .

The luminescence data were obtained with a Spex Fluorolog II spectrofluorometer at room temperature. Samples were placed in a capillary tube (I.D. = 1.0 mm). The emission was collected at  $22.5^\circ$  (front face) from the excitation beam. Luminescence lifetime measurements were performed with a Spex 1934D model phosphorimeter. IR absorption spectra of the samples in KBr pallets were taken on a Perkin-Elmer spectrometer. Thermogravimetric analyses were carried out (Thermal Analyst 2100 - TA Instruments SDT 2960 - Simultaneous DTA - TGA) in air, with a heating rate of  $10^\circ\text{C}/\text{min}$  from 25 to  $900^\circ\text{C}$ .

## 3. Results and discussion

The presence of the organic groups in the silica was confirmed through thermogravimetric analysis and IR spectra.

The properties of the silica/water system may be summarized as follows: i) the physic-sorbed water can be eliminated and surface silanol (Si-O-H) groups condensate, with this process starting at about  $170^\circ\text{C}$ ; ii) dehydration is com-

pletely reversible up to about  $400^\circ\text{C}$  and decomposition of organic residues occurs up to  $400^\circ\text{C}$ ; iii) above  $400^\circ\text{C}$ , the dehydration process is irreversible<sup>19</sup>. The first decrease in mass, which took place in a temperature range from 50 to  $150^\circ\text{C}$ , was attributed to water molecules absorbed on the silica surface. In the range from 250 to  $650^\circ\text{C}$ , we attribute the mass decrease to decomposition of the organic part (amino propyl groups). We can observe that the samples prepared without the modifier agent APTS present a larger amount of absorbed water. Comparing the samples that contain the agent APTS, we noticed that the amount of water absorbed is smaller than the samples obtained by the method 2. This can be an indicative that the presence of the europium compounds in the preparation of the silica affects the condensation degree, affecting the amount of absorbed

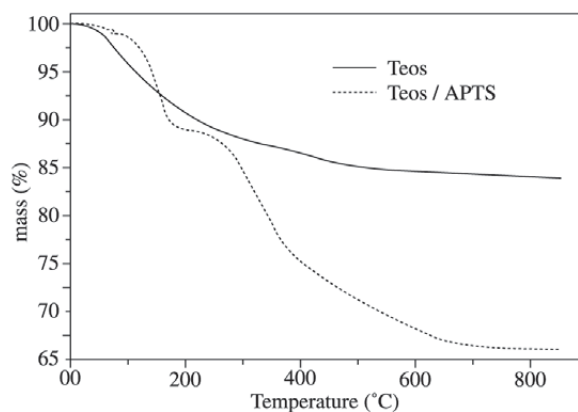


Figure 1. Thermogravimetric curve for samples used as control.

Table 1. Percentage loss of mass of the samples obtained by TGA analyses.

Samples	Temperature Range	
	50 to 150 °C (% mass)	250 to 650 °C (% mass)
<i>Method 1</i>		
TEOSEuCl <sub>3</sub>	8.70	-
TEOSEu(bpy)Cl <sub>3</sub>	10.00	-
TEOSAPTSEuCl <sub>3</sub>	6.50	17.00
TEOSAPTSEu(bpy)Cl <sub>3</sub>	6.90	22.20
<i>Method 2</i>		
TEOSEuCl <sub>3</sub>	13.50	-
TEOSEu(bpy)Cl <sub>3</sub>	8.82	-
TEOSAPTSEuCl <sub>3</sub>	2.94	33.33
TEOSAPTSEu(bpy)Cl <sub>3</sub>	3.13	32.26

water absorbed in the silica. In Fig. 1 we present TGA for sample used as control, prepared only TEOS and TEOS/APTS.

In Table 1 we present the percentage mass loss for the other samples.

Infrared spectra showed absorption bands due to asymmetric and symmetric vibrational modes of the methyl groups in 2957 and 2859  $\text{cm}^{-1}$  and deformation C-H in 1409  $\text{cm}^{-1}$ <sup>17,20</sup>. The decrease in the band in 956  $\text{cm}^{-1}$  ascribed to the deformation Si-OH<sup>13</sup> in the samples which contain propyl groups, showed that the -OH groups were substituted by propyl groups<sup>21</sup>.

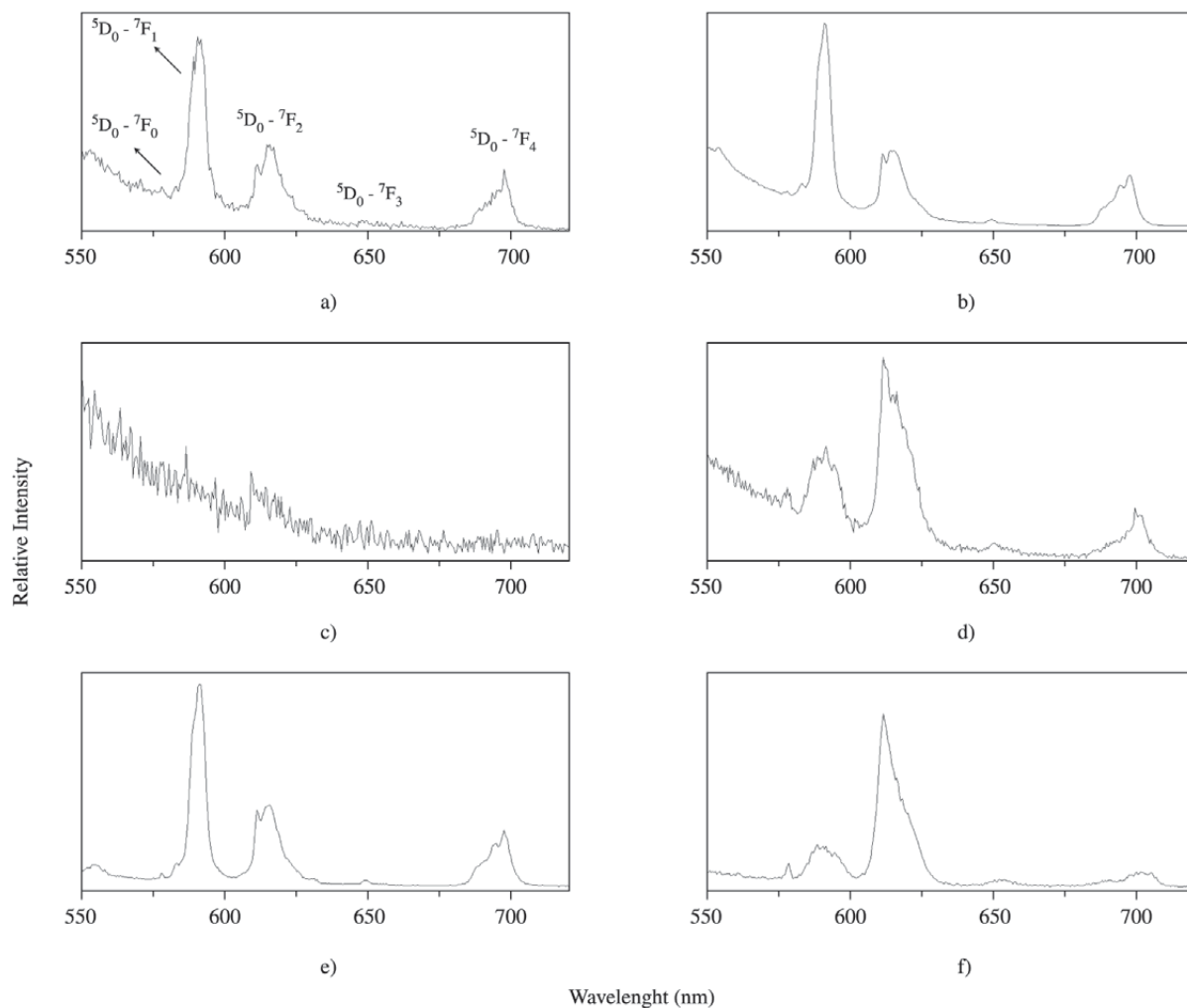
Control samples were prepared from TEOS and TEOS-APTS, hence silica particles (TEOS) and modified

silica particles (TEOS/APTS), which were used as standard were obtained. The results for all the samples have been compared to these particles to understand its compartment. The infrared spectra present differences in the wavenumber 956, 1600 and 2939  $\text{cm}^{-1}$ , ascribed to Si-OH, NH<sub>2</sub> and CH, respectively<sup>22</sup>. The vibrational mode at 1600  $\text{cm}^{-1}$  appears in all samples that contain aminopropyl groups.

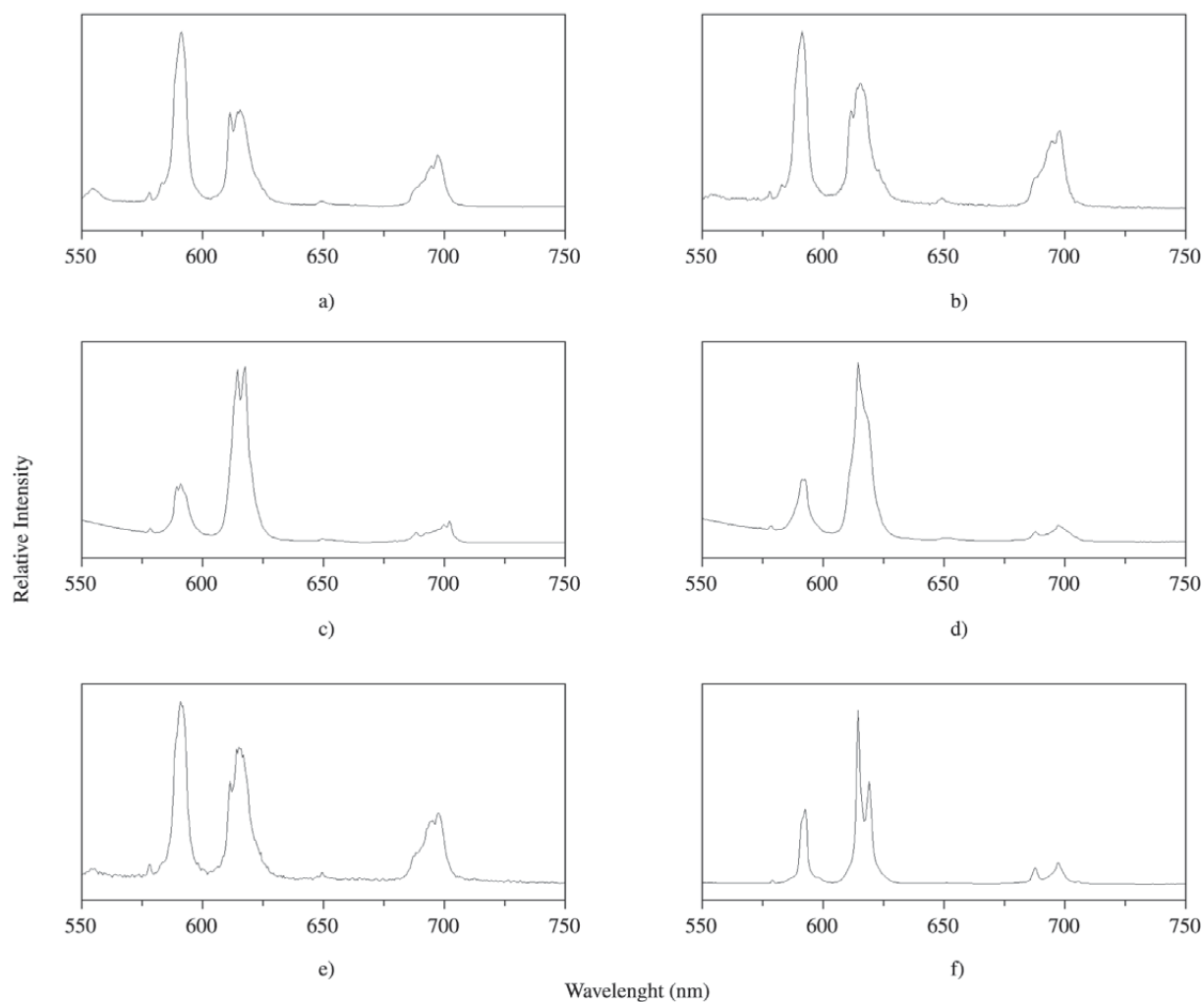
Figures 1 and 2 show emission spectra of Eu III ion, when excited at 393 nm (<sup>5</sup>L<sub>6</sub> level of Eu III and ligand band).

The excitation spectra of the samples containing the compound Eu(bpy)Cl<sub>3</sub> present a new broad band with maximum at about 310 nm. This maximum can be attributed to absorption maxima of ligand bpy.

In the samples that do not contain the modified agent



**Figure 2.** Emission spectra for the samples prepared by the first one a)  $\text{TEOS EuCl}_3$ ,  $\lambda_{\text{exc}} = 393$  nm; b)  $\text{TEOS Eu(bpy)Cl}_3$ ,  $\lambda_{\text{exc}} = 393$  nm; c)  $\text{TEOS APTSEuCl}_3$ ,  $\lambda_{\text{exc}} = 393$  nm; d)  $\text{TEOS APTSEu(bpy)Cl}_3$ ,  $\lambda_{\text{exc}} = 393$  nm; e)  $\text{TEOS Eu(bpy)Cl}_3$ ,  $\lambda_{\text{exc}} = 320$  nm; f)  $\text{TEOS APTSEu(bpy)Cl}_3$ ,  $\lambda_{\text{exc}} = 311$  nm.



**Figure 3.** Emission spectra for the samples prepared by the second one a)  $\text{TEOSEuCl}_3$ ,  $\lambda_{\text{exc}} = 393$  nm; b)  $\text{TEOSEu}(\text{bpy})\text{Cl}_3$ ,  $\lambda_{\text{exc}} = 393$  nm; c)  $\text{TEOSAPTSEuCl}_3$ ,  $\lambda_{\text{exc}} = 393$  nm; d)  $\text{TEOSAPTSEu}(\text{bpy})\text{Cl}_3$ ,  $\lambda_{\text{exc}} = 393$  nm; e)  $\text{TEOSEu}(\text{bpy})\text{Cl}_3$ ,  $\lambda_{\text{exc}} = 317$  nm; f)  $\text{TEOSAPTSEu}(\text{bpy})\text{Cl}_3$ ,  $\lambda_{\text{exc}} = 309$  nm.

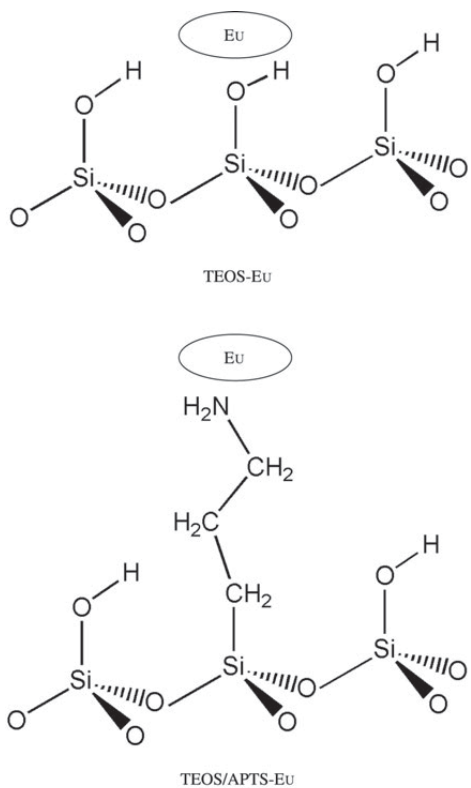
(APTS), the emission spectra showed that the relative intensity between the transition magnetic dipole  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$  (~591 nm) and the electric dipole  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  (~612 nm) suggests a local symmetry for the Eu III ion with inversion center<sup>23</sup>. A water-like environment for the Eu III ions was observed for these systems<sup>24</sup>, showing that Eu III ions can be located in porous silica. This behavior was not observed for the samples containing the modifier agent APTS, there is the probability that Eu III compounds are coordinated in the nitrogen atom of the amino propyl groups, indicating a longer distance of Eu III ion from the silica surface, as shown in Scheme 1. This behavior was observed by us in functionalized commercial silica gel containing imidazole propyl<sup>4</sup>.

The  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  emission electric dipole transition is particularly dependent upon the local symmetry<sup>25,26</sup>, but the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$  emission is allowed by magnetic dipole considerations and is indifferent to the local symmetry, the ratio of  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2 / {}^5\text{D}_0 \rightarrow {}^7\text{F}_1$  emission intensity gave us valuable information about environment changes around the Eu III ion. The high value obtained to the samples containing the agent APTS indicated that Eu III is situated at low symmetry sites.

The Eu III emission could be excited by the antenna effect through the bpy molecules, where the ligand absorbs and transfers energy for the ion, a dissociation phenomena is observed for the bpy complex.

The lifetimes for the samples prepared by method one

showed values close to the ion in aqueous solution (100 to 120  $\mu\text{s}$ ), but when Eu III ion is excited by energy transfer from ligand the lifetime increase. In the second method of preparation of the samples the lifetime revealed that the presence of the modifier excludes water molecules from the lan-



**Scheme 1.** Schematic representation of the silica particles (TEOS) and modified silica particles (TEOS/APTS) with Eu III compounds.

thanide surrounding. In Table 2 we present the lifetime for the samples excited in  $^5L_6$  level of Eu III ion and ligand band and their respective quantum efficiency.

Luminescence quantum efficiency, relation between number photons emissive and photons absorbed, was calculated as described by T. Jin *et al.*<sup>10</sup>. Luminescence quantum efficiency of the samples obtained in method 2 and which contain modifying agent (APTS) are higher than in method 1. This enhancement can be mainly due to the decrease of the loss of non-radiative energy. This loss occurs mainly by vibration modes of the water molecules present on the silica surface (Scheme 1). In the samples with APTS the Eu III compounds are distant from the silica surface. Another fact observed is that the excitation by ligand enhances the luminescence quantum efficiency, mainly in the sample TEOSAPTSEu(bpy)Cl<sub>3</sub>. In the Eu(bpy)Cl<sub>3</sub> complex the lower quantum efficiency is due to the presence of water molecules coordinated in the Eu III ion.

#### 4. Conclusion

We conclude that functionalized silica with APTS is an important support for Eu<sup>3+</sup> compound. The modifier agent APTS can be controlled by the sol-gel method and the amount of Eu<sup>3+</sup> ion too.

We observed that the antenna effect is very important to amplify the luminescence of Eu<sup>3+</sup> ion. Quantum efficiency do not depend only on ligand, but mainly on the Eu III neighbor.

The second methodology utilized for incorporation of the Eu III compounds presented better results in relation to Eu luminescence, because when Eu ion was incorporated an exchange between ion and water molecules occurred and they were adsorbed in silica surface attenuating the vibrational losses.

**Table 2.** Lifetime of the samples and quantum efficiency.

Samples	Lifetime ( $\mu\text{s}$ ) $^5L_6 \rightarrow ^7F_2$	Lifetime ( $\mu\text{s}$ ) Ligand band $\rightarrow ^7F_2$	Quantum efficiency $\phi_1$ (%)	Quantum efficiency $\phi_2$ (%)
Eu(bpy)Cl <sub>3</sub>	180	270	4	4
<i>Method 1</i>				
TEOSEuCl <sub>3</sub>	120	-	1	-
TEOSEu(bpy)Cl <sub>3</sub>	110	170	1	3
TEOSAPTSEuCl <sub>3</sub>	< 100	-	-	-
TEOSAPTSEu(bpy)Cl <sub>3</sub>	< 100	550	-	18
<i>Method 2</i>				
TEOSEuCl <sub>3</sub>	120	-	1	-
TEOSEu(bpy)Cl <sub>3</sub>	120	180	1	2
TEOSAPTSEuCl <sub>3</sub>	610	-	17	-
TEOSAPTSEu(bpy)Cl <sub>3</sub>	1020	2300	28	49

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## References

1. Leyden, E.D.; Luttrell, G.H. *Analyt. Chem.*, v. 47, n. 9, p. 1612, 1975.
2. Gushikem, Y.; Moreira, J.C. *J. Coll. Inter. Sci.*, v. 107, n. 1, p. 70, 1985.
3. Iamamoto, Y.; Ciuffi, K.J.; Sacco, H.C.; Prado, C.M.C.; Morais, M. de Nascimento, O.R. *J. Mol. Catal.*, v. 88, p. 167, 1994.
4. Serra, O.A.; Nassar, E.J.; Zapparolli, G.; Rosa, I.L.V. *J. Alloys Comp.*, v. 207/208, p. 454, 1994.
5. Nassar, E.J.; Serra, O.A.; Rosa, I.L.V. *J. Alloys Comp.*, v. 250, p. 380, 1997.
6. Serra, O.A.; Nassar, E.J.; Rosa, I.L.V. *J. Lumin.*, v. 72-74, p. 263, 1997.
7. Nassar, E.J.; Serra, O.A.; Calefi, P.S.; Manso, C.M.C.P.; Neri, C.R. *Materials Research*, v. 4, n. 1, p. 18, 2001.
8. Buckley, A.M.; Greenblatt, M. *J. Chem. Educ.*, v. 71, n. 7, p. 599, 1994.
9. Serra, O.A.; Nassar, E.J.; Calefi, P.S.; Neri, C.R. *Proceeding of the First International Conference on Inorganic Material 1998*, Versailles, França.
10. Jin, T.; Inoue, S.; Machida, K.; Adachi, G. *J. Alloys Comp.*, v. 265, p. 234, 1998.
11. Sabbatini, N.; Guardigli, M.; Manet, I.; Ungaro, R.; Casnati, A.; Ziessel, R.; Uldich, G.; Asfari, Z.; Lehn, J.-M. *Pure & Appl. Chem.*, v. 67, p. 135, 1995.
12. Silva, M.A.; Oliveira, D.C.; Papacidero, A.T.; Mello, C.; Nassar, E.J.; Ciuffi, K.J.; Sacco, H.C. *J. Sol-Gel Scie. Tech.*, v. 26 (1/2/3), p. 329, 2003.
13. Guodong, Q.; Minquan, W.; Mang, W.; Xiaping, F.; Zhaglian, H. *J. Lumin.*, v. 75, p. 63, 1997.
14. Ciuffi, K.J.; Lima, O.J.; Sacco, H.C.; Nassar, E.J. *J. Non-Cryst. Solids*, v. 304, p. 126, 2002.
15. Nassar, E.J.; Gonçalves, R.R.; Ferrari, M.; Messaddeq, Y.; Ribeiro, S.J.L. *J. Alloys Comp.*, v. 344, p. 221, 2002.
16. Apedreje, B.T.; Costa, V.C.A.; Moa, K.L. *Chem. Mater.*, v. 9, p. 2592, 1997.
17. Yan, B.; Zhang, H.; Wang, S.; Ni, J. *J. Photochem. Photobiol. A: Chem.*, v. 112, p.231, 1998.
18. Hart, F.A.; Laming, F.P. *J. Inorg. Nucl. Chem.*, v. 27, p. 1725, 1965.
19. Hench, L.L.; West, J.K. *Chem. Rev.*, v. 90, n. 1, p. 33, 1990.
20. Haruvy, T.; Gilath, I.; Maniewickz, M.; Eisenberg, N. *Chem. Mater.*, v. 9, p. 2604, 1997.
21. Nassar, E.J.; Neri, C.R.; Calefi, P.S.; Serra, O.A. *J. Non-Cryst. Solids*, v. 247, p. 124, 1999.
22. Chiang, C.-H.; Ishida, H.; Koenig, J.L. *J. Coll. Inter. Scie.*, v. 74, n. 2, p. 396, 1980.
23. Ribeiro, S.J.L.; Hiratsuka, R.S.; Massabini, A.M.G.; Davolos, M.R.; Santilli, C.V.; Pulcinelli, S.H. *J. Non-Cryst. Solids*, v. 147/148, p. 162, 1992.
24. Habemchuss, A.; Spedding, F.H. *J. Chem. Phys.*, v. 73, p. 442, 1980.
25. Blasse, G. *Adv. Inorg. Chem.*, v. 35, p. 319, 1990.
26. Reisfeld, R. *Structure Bonding*, v. 13, p. 53, 1973.