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Luminescent properties of silica and zirconia xerogels doped with europium(III) salts and europium(III) cryptate incorporating 3, 3′-biisoquinoline-2, 2′-dioxide

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Abstract

Eu^{+3} cryptate with 3, 3′-biisoquinoline-2, 2′-dioxide unit was incorporated into glass films consisting of zirconia dioxide and into hybrid ormosil films. The absorption and the emission intensities of the europium complex were compared to the intensity of the non-complexed europium ion in the films. The transition probabilities of the complex are increased as a result of the mixing of the europium orbitals with the ligand orbitals. The emission is additionally increased as the non-radiative relaxation is diminished by the cage effect. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

It has been shown that sol–gel method can be used for the preparation of solid-state tunable lasers by incorporating laser dyes into porous glasses [1–4]. Chemical and biological sensors can also be formed by the sol–gel method when appropriate reagents are introduced into glass [5–7]. Also semiconductor nanocrystals in transparent glass films have recently received attention due to their excellent electronic properties and promising applications in non-linear optics and optical switching [8–11].

Recently, several studies have been performed on trivalent rare-earth ions doped in such gel matrices as SiO_2 and ZrO_2 via the sol–gel process [13]. Inorganic rare-earth salts, chloride or nitrate were used. Only a weak emission can be observed from rare-earth ions doped in SiO_2 and ZrO_2 prepared at moderate temperature [14] due to non-radiative relaxation which originated from an interaction of the water residue with the hydroxyl ions. It has been shown that organic complex of rare earths doped in SiO_2 gel had higher fluorescence properties with respect to comparable inorganic salts [15–18]. The implication of this finding is that rare-earth organic complexes doped in sol–gel hosts are good candidates for phosphors, active waveguides, optical sensors and markers of biological molecules.

In this context, it was of interest to study the incorporation of Eu(III) cryptate within the

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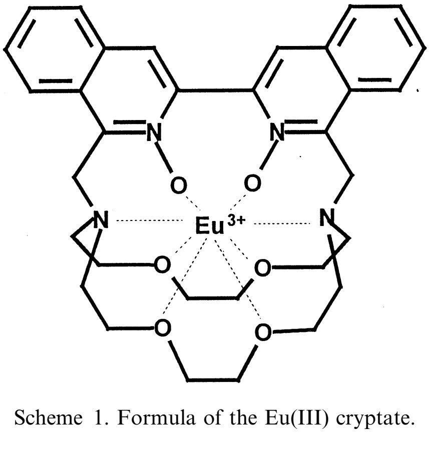
zirconia xerogel glass which is especially photochemically stable.

Earlier works on luminescent lanthanide macrocyclic and macropolycyclic complexes indicated that the most efficient ligands were those incorporating 3, 3′-biisoquinoline-2, 2′-dioxide unit as sensitiser for the lanthanide emission [19–25]. Among diverse structures, one was the most promising, having excellent quantum yield for emission, good luminescence lifetime in the range of 0.6 ms, and good stability in aqueous media. Its formula is shown in Scheme 1.

Very recently several articles dealing with the luminescence of xerogels doped with Eu(III) and Tb(III) complexes have been published [15,25,27,28].

In the present Letter, two zirconia films doped with Eu(III) cryptate were prepared, one of them as a hybrid material obtained by cross-condensation of zirconia tetrapropoxide and 3-glycidoxypropyltrimethoxysilane (glymo). The hybrid matrix incorporating silica and organic part was expected to bring two advantages: to bind water via oxirane ring opening, and to provide organic hydrophobic environment advantageous to repel the remnant water molecules from the proximity of the Eu(III) cryptate. The expectation was to enhance the luminescence performance. The Eu(III) ion was also prepared in a zirconia film for comparison.



Scheme 1. Formula of the Eu(III) cryptate.

2. Experimental section

2.1. Materials

Zirconium *n*-propoxide (70% solution in 1-propanol, Fluka) was used as received without further purification, *n*-propanol of analytical grade (Riedel-de Haen), glacial acetic acid (analytical grade, Frutarom, Israel), glymo (analytical grade, Aldrich), 2-methoxyethanol of analytical grade (Fluka) and triply distilled water were used for solution preparations.

Chemglass CGQ-0640-01 (USA) quartz slides were used as substrates for the film deposition.

The europium cryptate was prepared according to the literature [19] using europium trifluoromethanesulfonate.

2.2. Sample preparation

2.2.1. Preparation of zirconia stock solution (S)

First, zirconium *n*-propoxide (10 ml) was diluted in 20 ml of *n*-propanol and stirred for 15 min, then 3 ml of glacial acetic acid was added and stirred further for 15 min. The solution was hydrolysed with 3.3 ml of acetic acid–water solution (1:1) and stirred for 30 min, filtered and stored in a refrigerator up to 4 days, the final stock solution was obtained by diluting the concentrate solution with *n*-propanol to 72.6 ml. Eight ml of this stock solution contains 0.00248 mole of ZrO_2.

2.2.2. Preparation of zirconia film doped with Eu_2O_3 – (1)

Eight ml of the stock solution, being precursor of 0.00248 ZrO_2 was mixed with 0.01 g of europium oxide (0.0114 mole per mole ZrO_2), 0.5 ml of nitric acid (conc.) and 4 ml of 2-methoxyethanol. The film was obtained by a dip-coating technique, with a withdrawal speed of the quartz substrate of 20 cm/min, and was dried at 40°C for 1 h and heated at 100°C for 1 h.

2.2.3. Preparation of zirconia film (for a reference) – (2)

The stock solution (8 ml) and 2-methoxyethanol (4 ml) were mixed and used for dip-coating pure zirconia film which was dried and heated as above.

2.2.4. Preparation of zirconia film doped with Eu cryptate – (3)

The stock solution (8 ml), 0.02 g of europium cryptate (0.0091 mole per mole ZrO_2) and 2-methoxyethanol (4 ml) were mixed together. The film was obtained and heated as above.

2.2.5. Preparation of zirconia-ormosil film with glymo and doped with Eu cryptate – (4)

1.2 ml of glymo was added to solution (3) and was stirred for 2 h. The film was obtained and treated as film (3). The molar concentration of Eu oxide and Eu complex in the film was 0.01 ± 0.001. The thickness of the film was 250 ± 20 nm.

2.3. Measurements: UV–vis spectroscopy

Absorption spectra were measured on a Milton–Roy Spectronic M-3000 diode array spectrophotometer.

Fluorescence spectra were measured on a JASCO FP770 spectrofluorimeter.

3. Results and discussion

Absorption spectra of pure zirconia film and film doped with Eu_2O_3 were very similar. These films were transparent in the range of 350–700 nm, and zirconia doped with Eu_2O_3 showed a broad and weak band around 350 nm. The samples with Eu(III) cryptate show an intense band at 269 nm belonging to the charge transfer of Eu(III) cryptate complex (Fig. 1).

It should be noted that the charge transfer in Eu oxide is positioned in the same spectral range; however, its intensity is negligible compared with the complex prepared with the same concentration of Eu. Both Eu(III) cryptates in zirconia and in zirconia–glymo contain a band with a maximum at 350 nm characteristic of the heterocyclic ligand absorbance. The intensity in both cases is the same within the experimental error. Therefore, there is no evident influence of glymo on the electronic spectra of the cryptate. Fig. 2 presents the excitation and emission spectra of the complex in zirconia–glymo (2a) and zirconia thin films (2b) excited at 350 and 269 nm. The emission spectra consist of several bands at 590 nm ($^5D_0 \rightarrow {}^7F_1$), 617 nm ($^5D_0 \rightarrow {}^7F_2$) (the most intense), 647 nm ($^5D_0 \rightarrow {}^7F_3$) and 684 nm ($^5D_0 \rightarrow {}^7F_4$). For the most intense band there is practically no visible difference in relative intensities for zirconia cryptate and zirconia–glymo-cryptate. Fig. 3 presents the emission of quartz, zirconia oxide on quartz and zirconia oxide doped with Eu oxide, excited at 350 nm. Figs. 2 and 3 were drawn using different sensitivities. The intensities of Fig. 3 must be divided by 39.4 in order to have the same scale as Fig. 2. Hence, it is clear that the emission of Eu oxide in zirconia heated at 100°C is negligible compared to the complex.

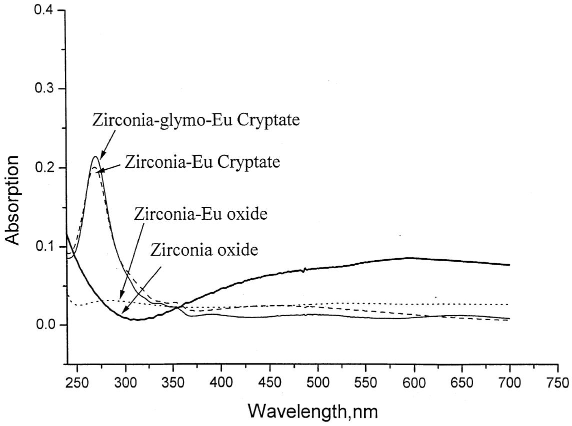


Fig. 1. Absorption spectra of zirconia and zirconia–glymo thin films doped with Eu_2O_3 and Eu(III) cryptate.

Table 1 summarises the absorption and the emission intensities obtained under excitation of 269 and 350 nm. It should be noted, however, that because of the very low absorption of samples not containing complexes the number of zirconia oxide and zirconia doped with Eu oxide is insignificant. These features indicated the absence of efficient excitation of inorganic lanthanide materials, due to the absence of sensitising ligands.

Zirconia films were doped with organic Eu(III) complex that has been selected on the basis of the best luminescence efficiency among the family of cryptates incorporating 3, 3′-biisoquinoline-2, 2′-dioxide. This complex, with the combination of

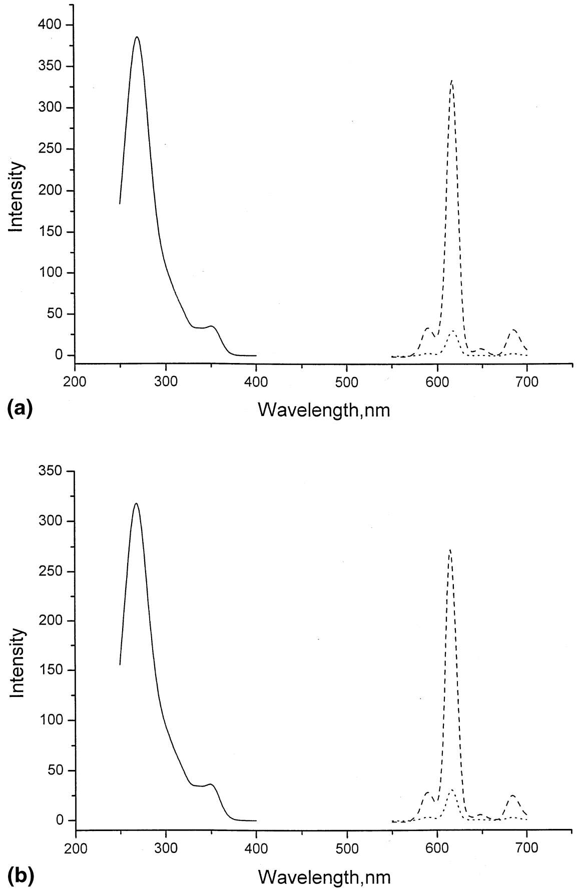


Fig. 2. (a) Excitation (617 nm) and emission spectra (excited at 269 and 350 nm) of Zr–glymo film doped with Eu(III) cryptate; (——) excitation spectra; (- - -) exc. at 269 nm; (···) exc. at 350 nm. (b) Excitation (617 nm) and emission spectra (excited at 269 and 350 nm) zirconia film doped with Eu(III) cryptate; (——) excitation spectra; (- - -) exc. at 269 nm; (···) exc. at 350 nm.

the sensitising ligand and 4,13-diaza-18-crown-6, was found to encapsulate Eu(III) cation efficiently, thus hiding it from the influence of external environment, in particular water molecules and to increase the transition probabilities as a result of mixing of the ligand orbitals with the orbitals of europium. We have shown previously that Eu(III) is an excellent indicator of site symmetry and chemical bonding in glasses and biological molecules. Our findings were based on the fact that Eu(III) incorporated in low-symmetry sites exhibits enhanced f–f radiative transition probabilities. The hypersensitive transitions such as $^5D_0 \rightarrow {}^7F_0$ and $^5F_0 \rightarrow {}^5D_2$ (440 nm) are especially sensitive to the chemical bond formed between Eu(III) and its surrounding ligands. The removal of degeneracy in low-symmetry sites of electronic levels having $J > 0$ is also observed. In addition, the non-radiative transition probabilities of Eu(III) in aqueous solutions are increased by the OH vibrations due to electron–phonon coupling. The inhomogeneous broadening is typical for ions in glasses prepared from the melt [12,26].

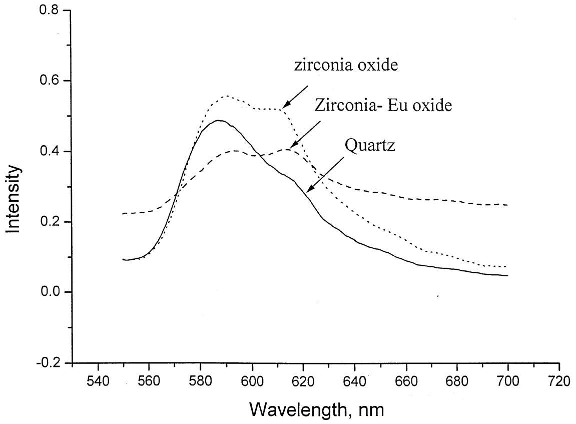


Fig. 3. Emission spectra of quartz, zirconia oxide film and zirconia doped with Eu_2O_3 excited at 350 nm.

It is important to mention that the presence of OH oscillators leads to the quenching of fluorescence by non-radiative multiphonon decay. Therefore, this complex turned out to be the best for this study.

As seen above, the excitation spectrum displays two distinct bands with the maxima at 350 nm of relatively weak intensity, and at 269 nm with high intensity. There are two emission spectra for this thin film; one of low intensity when the excitation was performed at 350 nm and the second of high intensity with the excitation at 269 nm. This is consistent with the expectation that excitation at maximum of absorbance leads to high population of the singlet excited state, therefore, radiationless process of energy transfer from the singlet state via triplet state to the level $^5D_0$ of the Eu(III) is efficient.

The excitation and emission spectra for the Eu(III) cryptate in zirconia and Zr–glymo-cryptate presented in Fig. 3 are very similar. This indicates

Table 1
Compositions and properties of zirconia and zirconia–glymo films doped with Eu oxide and Eu cryptate

Films	Absorbance		exc. 269/em. 617 nm		exc. 350/em. 617 nm	
	269 nm D_1	350 nm D_2	Luminescence intensity (L_1)	RI L_1/D_1	Luminescence intensity (L_2)	RI L_2/D_2
ZrO_2–Eu_2O_3	0.031	0.023	2.89	93.2	0.4	17.39
ZrO_2	0.041	0.0197	3.85	93.9	0.46	23.35
ZrO_2–EuCpt	0.201	0.0289	10,728	53,373	1198	41,453
ZrO_2–glymo–EuCpt	0.214	0.0231	13,168	61,532	1175	50,866

that the hybrid Zr–Si films do not change the microenvironment around the Eu(III) cryptate too much. Although the water chemical binding by epoxy groups may lead to remarkable reduction of residual water in organic/inorganic network, there are still hydroxyl groups on organic chains of the initial glymo substrate that potentially may quench the luminescence to some degree. On the other hand, architecture of the cryptate provides the eight heteroatoms for the co-ordination sphere of the Eu(III), thus the cation is well hidden from the external environment.

When the luminescence intensity is compared for the excitation at 350 nm for zirconia- and zirconia–glymo-doped Eu(III) complex, a little difference is observed for the most intense emission band at 617 nm (Table 1). The same comparison, when excitation is at 269 nm, shows that the hybrid material Zr–Si has better performance in Eu(III) luminescence. Therefore, it seems reasonable to say that cross-linking the zirconia gel with glymo has some advantage to get better material. In this way, it was possible to obtain highly luminescent materials based on Eu(III) cryptate, whose potential may still be enhanced by the addition of co-ligands complementing the co-ordination sphere of the Eu(III) cation in order to exclude fully the residual water in the first co-ordination sphere. An alternative can be envisioned by adding additional photoactive ligands that will not only complement the co-ordination sphere of the Eu(III), but will act synergistically to streamline the collected light to Eu(III) (antenna, and co-fluorescence effect). In the future, the luminescence lifetimes and the quantum yields of emission will shed more light on the interpretation of luminescence features of these new materials. Work in this direction is in progress.

An additional feature requires attention: it is well known [26] that the ratio between the hypersensitive transition picking at 617 nm ($^5D_0 \rightarrow {}^7F_2$) to the magnetic dipole transition picking 590 nm ($^5D_0 \rightarrow {}^7F_1$) reflects the site symmetry at which europium is situated. By comparing these ratios in Eu cryptate–zirconia films to Eu oxide in zirconia film (Figs. 2 and 3, Table 2) we conclude that the symmetry at which the Eu is situated is much lower in the cryptate complex than in Eu ion surrounded by water molecules. Table 2 collects the following data: absorbance (D), luminescence intensity (L) and relative intensity (RI) defined as L/D. It can be noted that the best luminescence for cryptate was observed in the zirconia–glymo film.

The Eu oxide as well as the complexes in zirconia film were heated to 100°C.

Table 2
Wavelength and emission intensities of Eu-doped zirconia films excited at 350 nm

Films	Total emission wavelength (nm) types of transitions and intensities				The ratio between transition intensities
	590 $^5D_0 \rightarrow {}^7F_4$	617 $^5D_0 \rightarrow {}^7F_1$	647 $^5D_0 \rightarrow {}^7F_2$	684 $^5D_0 \rightarrow {}^7F_3$	617 nm/590 nm
ZrO_2–Eu_2O_3	0.396	0.401	0.285	255	1.016
ZrO_2	0.556	0.461	0.192	0.088	0.829
ZrO_2–EuCpt	176	1198	45.48	157.33	6.807
ZrO_2–glymo–EuCpt	148	1175	46.97	137.79	7.939

At this temperature Eu does not lose water when incorporated into zirconia in the form of its inorganic salt; however, it is clear that water was completely removed in the complexes. During the heating of zirconia with inorganic Eu salt to about 800°C water is completely removed (the high temperature cannot be applied to Eu cryptate) and this results in inversion of the intensities of 617–590 nm emission intensities similarly to the complexes.

4. Conclusions

The incorporation of the Eu(III) cryptate complexes into zirconia films results in a dramatic increase of the emission intensity as well as in the increase of the absorbance intensity of Eu complex. The cross-linking the sol–gels with 'glymo' resulted in binding the water molecules, thus diminishing the number of OH oscillators quenching the luminescence. The dramatic increase of Eu(III) cryptate embedded in the mixed Si–Zr sol–gel matrix will be the subject for further studies to rationalise the origin of this remarkable luminescence enhancement.

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