



Optical properties of sol-gel materials doped with ethyl 2-(7-hydroxy-2-oxo-2H-chromen-4-yl) acetate

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ABSTRACT

Transparent sol-gel glassy monoliths doped with coumarin molecules [ethyl 2-(7-hydroxy-2-oxo-2H-chromen-4-yl) acetate] displaying a strong blue luminescence are characterized by optical spectroscopy, X-Ray diffraction, SEM and TG/FT-IR spectroscopy. The UV/Vis, luminescence and excitation spectra of the doped sol-gel materials and of ethanol solutions of coumarin are discussed. The coumarin optical spectra are used as a probe for incorporation in the gel structure.

1. Introduction

Coumarins and their complexes with metal ions have been studied extensively because of their optical properties and biological activities. Some lanthanide complexes have application as planar waveguide amplifiers, plastic lasers or light-emitting diodes [1-4]. The physiological, anticoagulant, spasmolytic, bacteriostatic and antitumor activities of coumarins and their complexes are also important for pharmacy and medicine [5,6].

Recently we described the preparation and characterization of SiO₂ gels, doped with Sm(III) ions and 3-(3-(4-(dimethylamino)phenyl)propenoyl)-2H-chromen-2-one (K2) or ethyl 2-(7-hydroxy-2-oxo-2H-chromen-4-yl)acetate (K4) for a first time [7,8]. We demonstrated that the Sm(III) ions form complexes [Sm(K4)₂(H₂O)₄]_x(NO₃)₃ or [Sm(K2)₂(H₂O)₂]_x(NO₃)₃ in the gels containing K2 or K4. This suggestion was supported by IR and UV/Vis spectroscopy. Some questions concerning the change of optical spectra due to the gel formation, the chemical composition, thermal stability of coumarin doped gels, however, remained open.

This paper is a continuation of our recent studies of embedded organic molecules in gel glasses, using sol-gel technology [7,8]. Now we describe in details the optical properties of silica gels and ethanol solutions doped with K4 using UV/Vis, excitation and luminescence spectroscopy in order to understand the luminescence/excitation properties of such materials and to use the optical spectra as a probe for coumarin incorporation in the gel structure.

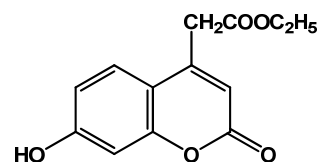
2. Experimental

2.1. Instrumentation

UV/Vis spectra were recorded using a standard Thermo Spectronic "Unicam UV 500" UV/Vis spectrophotometer between 200 and 800 nm at room temperature. Luminescence and excitation spectra were recorded with Varian "Cary Eclipse" fluorescence spectrophotometer. Scanning electron microscope investigations (SEM) were performed on a standard JEOL 5510 microscope. The samples were investigated by X-ray diffraction using a standard powder diffractometer Philips PW 1050. TG/FT-IR investigations were performed with a NETZSCH TG 209 F1 IRIS and FT-IR spectrometer Bruker TENSOR 27™ unit.

2.2. Synthesis

The coumarin, used as a doping compound (K4,) is synthesized by the described in the literature methods [9]. The strong $n \rightarrow \pi^*$ electronic transition at about 327 nm (C=O group) makes this molecule a promising candidate for UV/Vis excitation. The chemical structure of the coumarin (Ethyl 2-(7-hydroxy-2-oxo-2H-chromen-4-yl) acetate (K4)) molecule used in our study is shown Scheme 1.



Scheme 1

The preparation of K4 doped silica gels follows our recently described sol-gel procedure [7,8]. Tetraethoxysilane (TEOS) (98 %) and absolute EtOH (99.8 %) are mixed together in a 1:1 molar ratio. After homogenization of the mixture distilled H₂O

in a 1:4 molar ratio and 0.23 M HCl were added for the hydrolysis. This process takes place at $\text{pH} \approx 2$ for two hours at room temperature. To start the gelation we needed $\text{pH} = 6-7$, so a mixture of 0.14 M NH_3 in a 1:4 molar ratio $\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}$ was used to alkalize the solution. Using the described procedure, transparent non-doped gels, as well as monoliths containing 0.75×10^{-4} mol/L K4 were prepared.

3. Results and discussion

3.1. Chemical composition and thermal stability

The prepared silica gels were investigated by thermogravimetry with Fourier transforming infrared spectroscopy (TG/FT-IR). The monoliths show only H_2O and traces from $\text{C}_2\text{H}_5\text{OH}$ in the releasing gases from 40-50 °C up to 120-180 °C. Typical results from the TG/FTIR observations are shown on Figure 1. NO_x traces (300-400 °C) come from the ammonia catalyst. The detection of NO_x gases from silica gels using TG/FTIR spectroscopy is discussed in ref. [10]. The TG/FT-IR analysis confirmed the chemical purity of the as prepared gels. It is shown on Figure 1 that the prepared monoliths are chemical stable below 40-50 °C. The optical transparency of the obtained monoliths decreases due to crack formation at higher temperature. In addition, the coumarin molecules incorporated in the silica gels are stable up to 50-60 °C.

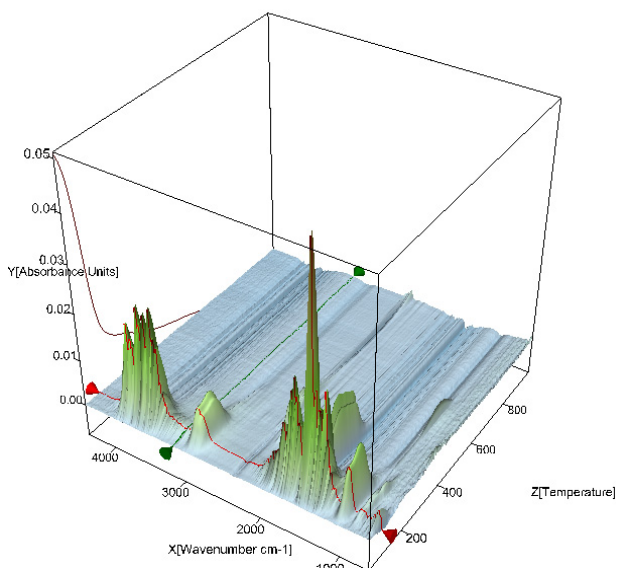


Figure 1. TG/FT-IR observations of a monolith without coumarin doping.

All the samples studied are X-ray amorphous, the monoliths prepared are transparent and colourless. The results are proved by SEM investigations (Figure 2), displaying a flat, crack-free surface.

3.2. Optical properties of coumarin in silica gels and ethanol solutions

On Figure 3 and Figure 4 are presented UV/Vis, excitation/luminescence spectra of K4 in EtOH solution and gels, respectively. There are significant differences in the spectra of coumarin in gels and the doping ethanol solution, which give an indication for the incorporation of the coumarin molecules in the silica gel network and/or complex formation between silicium and coumarin during gelation. The coumarin luminescence presented on Figure 3 and Figure 4 can be used for energy transfer to Eu(III) or Ho(III) ions because of their $f-f$ absorption transitions at 395 nm and 480 nm.

All the glassy samples and ethanol solutions of K4 are excited with $\lambda_{\text{ex}} = 327$ nm which corresponds to the absorption

maxima of $n \rightarrow \pi^*$ transition due to the C=O group in K4 molecules and have a strong luminescence with two maxima: at about 400 nm (25000 cm^{-1}) and 480 nm (20833 cm^{-1}). The relative intensity of the 480 nm maximum is higher in gels, compared to the relative intensity of the long-wavelength shoulder of the K4-ethanol solution.

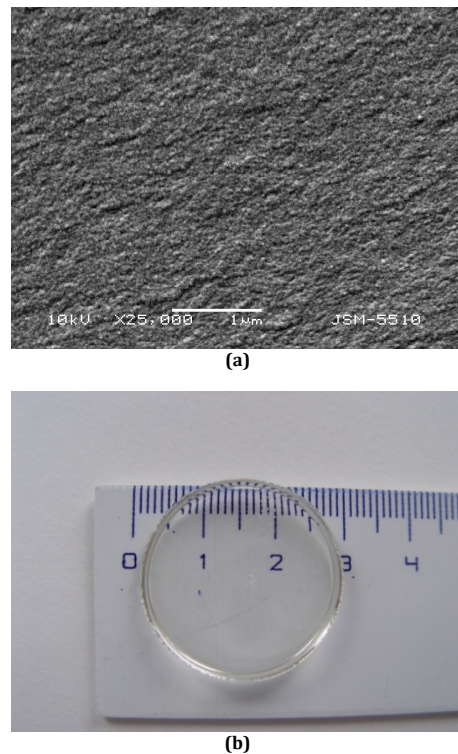


Figure 2. Scanning electron microscope (SEM) results of the surface of a non-doped gel (a) and a typical photograph from a gel (b).

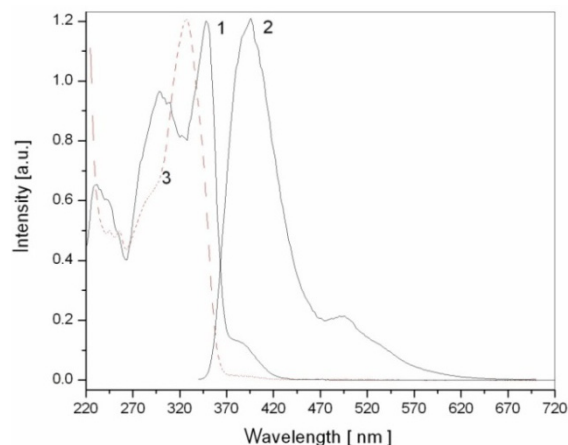


Figure 3. Excitation (395 nm monitoring)/luminescence spectra (327 nm excitation) of a 1×10^{-4} mol/L K4 ethanol solution. The absorption spectrum (3) is given for comparison. Line 1-excitation spectrum, line 2-luminescence spectrum.

The excitation spectra of K4 in gels and in ethanol solutions, however, display significant differences. It is evident that the excitation spectrum of gels (GK4) follows the absorption spectrum, while the spectrum of K4 in ethanol solution displays two maxima at 300 nm and 347 nm. It could be concluded from the optical spectra that the site symmetry of the coumarin activator increases as a result of incorporation in the silica gels. A possible explanation for the experimentally detected change of the optical spectra could be the formation of silicium-coumarin complexes during gelation.

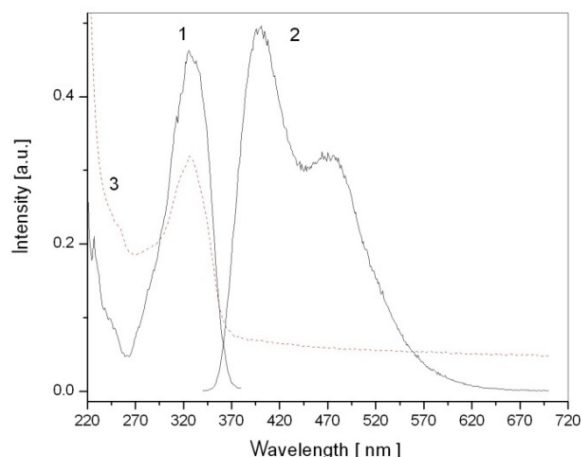


Figure 4. Excitation (395 nm monitoring) / luminescence spectra (327 nm excitation) of K4 in silica gels. The concentration of K4 in the gels is 0.75×10^{-4} mol/L. The absorption spectrum (line 3) is given for comparison. Line 1 – excitation spectrum, line 2 – luminescence spectrum.

The molar extinction coefficients ϵ of K4 in solution and in sol-gel monolith at 327 nm are calculated according to Beer's law: $\epsilon_{\text{solution}} = 12050$ L/mol.cm; $\epsilon_{\text{gel}} = 13209$ L/mol.cm. The calculated values are close to the molar extinction coefficient of 7-methoxycoumarin-4-acetic acidis $\epsilon = 11820$ L/mol.cm, defined in methanol at 324 nm [11]. This compound has a chemical structure similar to K4.

Following the discussion in our previous contributions, we calculated the oscillator strengths of the coumarin absorption transitions f [12,13] from the absorption spectra of K4 incorporated in silica gels and ethanol solutions. The results are summarized in Table 1, they show that the oscillator strengths are changed as a result of incorporation of the coumarin molecules in the silica gel. The results in Table 1 strongly suggest that the chemical and/or geometrical environment of the coumarin activator changes as a result of gelation of the silica sol.

Table 1. Results from Gaussian analysis of UV-Vis absorption spectra: x_c – peak position, A – integrated absorbance, f – oscillator strength.

No	Transition	GK4 gel 0.75×10^{-4} mol/L K4		
		x_c [cm ⁻¹]	A [cm ⁻²]	f
1	$n \rightarrow \pi^*$ (C=O)	29038 ± 63	55 ± 10	0.00315 ± 0.0004
2	$n \rightarrow \pi^*$ (C=O)	30216 ± 103	25 ± 10	0.0014 ± 0.0004
3	$n \rightarrow \pi^*$ (C=O)	30636 ± 28	652 ± 11	0.0374 ± 0.0005
4	$n \rightarrow \pi^*$ (C=O)	33571 ± 100	189 ± 4	0.0108 ± 0.0002
1x10 ⁻⁴ mol/L K4 ethanol solution				
1	$n \rightarrow \pi^*$ (C=O)	28890 ± 22	478 ± 52	0.02065 ± 0.002
2	$n \rightarrow \pi^*$ (C=O)	30019 ± 19	1044 ± 184	0.0451 ± 0.008
3	$n \rightarrow \pi^*$ (C=O)	31291 ± 89	1451 ± 149	0.0627 ± 0.006
4	$n \rightarrow \pi^*$ (C=O)	33571 ± 20	2734 ± 19	0.11 ± 0.0008

In order to quantitatively evaluate the diffuse reflectance from the gels, the absorption spectra are compared with the spectra of an ideal transmitting liquid and solid substance to solutions containing K4 and polished zirconia single crystals.

The absorbance A at 630 nm, far away from the coumarin absorption peaks, is presented in Table 2 together with sample thickness d and absorption coefficient α . It can be seen that both doped and non-doped gels display an increase of the diffuse reflectance compared to the absorption coefficient of solutions and polished cubic zirconia single crystals, which is independent from the wavelength [14]. Thus, the diffuse reflectance increase comes from micrometer-scaled imperfections from the gel surface. The diffuse reflectance could be diminished by polishing; it is difficult, however, to polish sol-gel glasses because of their low mechanical strength.

Table 2. Optical properties of gels, solutions and polished zirconia single crystals. A – Absorbance at 630 nm, sample thickness d and absorption coefficient α .

Sample	Composition	d [cm]	A (630 nm)	α [cm ⁻¹]
GK4	SiO ₂ : K4	0.25	0.1	0.40
G30	SiO ₂	0.25	0.1	0.40
K4	EtOH : K4	1	0.02	0.02
YSZ:Ho	Zr _{0.78} Y _{0.21} Ho _{0.01} O _{1.90}	0.16	0.015	0.09

4. Conclusion

The preparation of new hybrid sol-gel materials with a strong UV-absorption and blue luminescence at room temperature is reported. The peaks in the optical spectra of the gels come from C=O $n \rightarrow \pi^*$ transitions in the coumarin molecule. The optical spectra from doped gels and coumarin ethanol solution are changed after the coumarin incorporation in the gels, which gives an indication for effective doping during sol-gel process and interactions between the coumarin molecule and the silica network. The coumarin luminescence presented in this contribution can be used for an energy transfer to Ho(III) and Eu(III) ions incorporated in silica gels. Another potential application of the sol-gel materials prepared could be in the field of advanced security inks due to the blue coumarin emission.

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