Journal of Alloys and Compounds 275–277 (1998) 21–26

A novel class of luminescent polymers obtained by the sol–gel approach

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Abstract

A series of amorphous Eu^{3+}-doped hybrid organic/inorganic materials prepared by the sol–gel process is presented. The host matrix of the so-called ureasils is a silica network to which oligopolyoxyethylene chains are grafted by means of urea bonds. Trivalent europium is present as a triflate salt, $Eu(CF_3SO_3)_3$. Four different compositions of salt have been considered: n=184, 92, 55 and 37, where n represents the number of (OCH_2CH_2) polymer repeat units per ion group of $Eu(CF_3SO_3)_3$. Infrared spectroscopic studies suggest that the doped ureasils contain both free and coordinated triflate ions. The lowest decomposition temperature (about 250°C) occurs with composition n=92. This composition also exhibits the highest conductivity at room temperature (approximately $10^{-5}\ \Omega^{-1}\ cm^{-1}$). The photoluminescence spectra of these materials present a series of narrow lines assigned to $^5D_0 \rightarrow {}^7F_{0,1,2,3,4}$ transitions. The high emission intensity observed is a promising property for application of the ureasils in technological luminescent devices.

Keywords: Europium triflate; Sol–gel; X-ray diffraction; DSC; FTIR; Luminescence

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1. Introduction

The incorporation of inorganic ions into silica gels and glasses is of the utmost interest for a variety of technological applications including optical devices, such as fiber amplifiers, phosphors and solid-state lasers [1–4]. The sol–gel process is potentially attractive for synthesizing these materials as it offers the possibility of controlling the micro- and macrostructure of the host matrix. The silica network provides good mechanical resistance, an extraordinary thermal stability and leads to entirely amorphous systems. While interest continues in the conventional inorganic sol-gel materials, hybrid organic/inorganic materials are currently being subjected to more intense development [5–7].

In this paper we describe the properties of a series of luminescent and ion-conducting ormosils prepared by doping a silica network containing oligopolyoxyethylene chains with europium triflate, $Eu(CF_3SO_3)_3$. The incorporation of luminescent cations in these hybrid organic/inorganic hosts can provide relevant insights into their conformation and local dynamics. Such studies have been reported for complexes of rare-earth salts and poly(oxyethylene) (POE) [8–12] or poly(oxypropylene) (POP) [9,13]. Moreover, the observed narrow band luminescent emission may open new prospects for technological applications of these materials.

2. Experimental

Europium triflate, $Eu(CF_3SO_3)_3$, was synthesized using a procedure described previously [14]. The materials described contain short highly solvating (CH_2CH_2O) units grafted onto a silica network by means of urea bridges [15] and are classed as ureasils (ureasilicates). The bond between the alkoxysilane precursor and the oligopolyoxyethylene segment is formed by the reaction of amine with isocyanates which leads to the formation of urea bonds. The terminal amino groups of a doubly functional amine (chemically α,ω-diaminepoly(oxyethylene-co-oxypropylene)) were reacted with 3-isocyanatepropyltriethoxysilane (ICPTES). The diamine used in this study, the general formula of which is given in Scheme 1, is commercially designated as Jeffamine ED-2001® (with $a+c$=2.5 and b=40.5). The Eu(III)-doped ureasils will be

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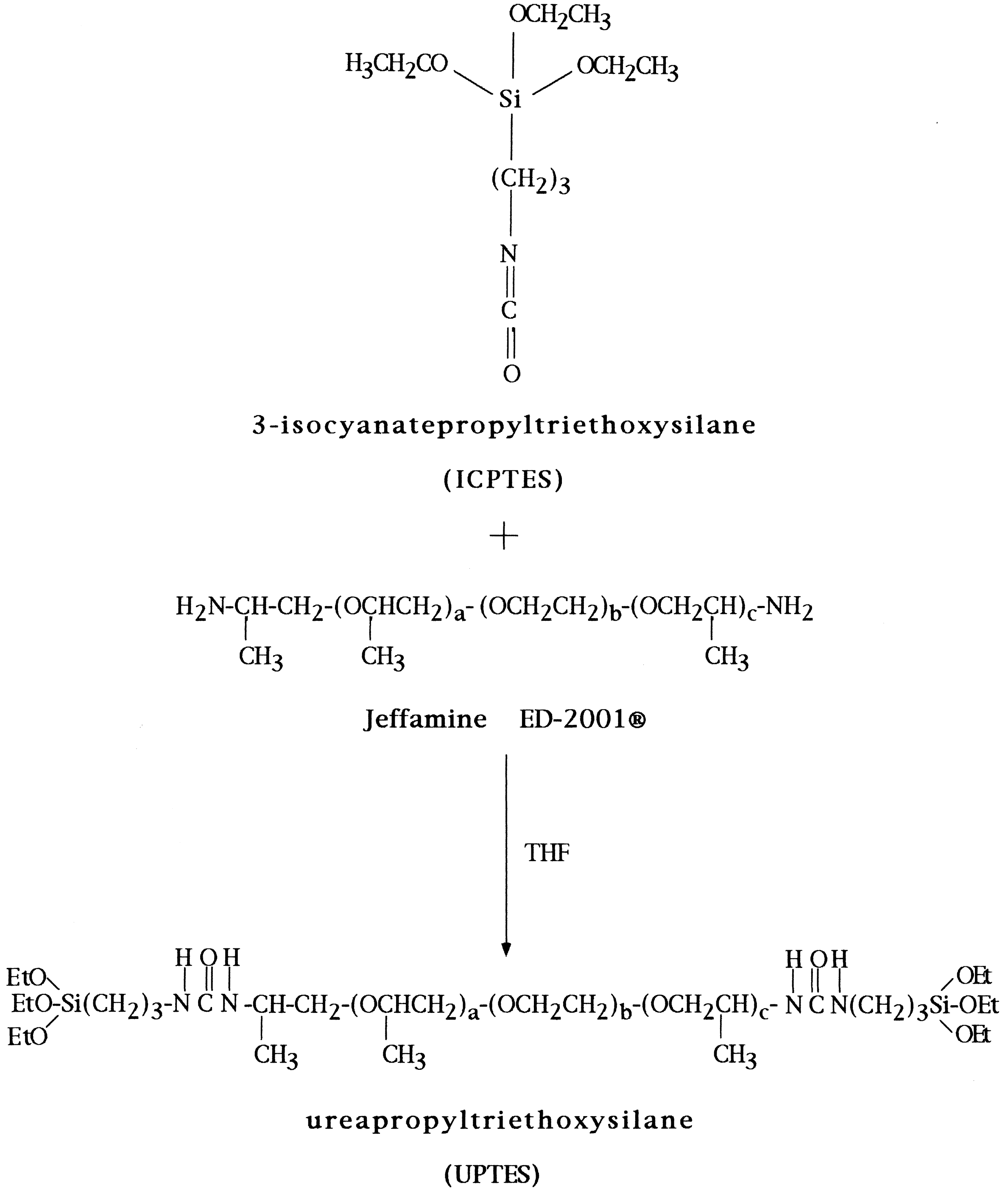
PII: S0925-8388(98)00266-7



Scheme 1. Synthesis of the ureasil precursor (ureapropyltriethoxysilane, UPTES).

identified by the designation $U(2000)_nEu(CF_3SO_3)_3$, where U originates from the word ‘urea’, 2000 indirectly indicates the length of the oxyethylene chains and n=O/Eu represents the ratio of (OCH_2CH_2) monomer units per $Eu(CF_3SO_3)_3$ ion group. Materials with n=37, 55, 92, 184 and ∞ have been prepared.

2.1. Step 1: synthesis of the ureasil precursor, ureapropyltriethoxysilane (UPTES)

Jeffamine ED-2001® (2.5 g; Fluka), previously dried under vacuum at 90°C for several days, was dissolved with stirring in 10 ml of tetrahydrofuran (Riedel de Häen). A volume of 0.625 ml of ICPTES (ABCR) was added to this solution in a fume cupboard. The flask was sealed and the solution stirred overnight. It was concluded by infrared monitoring of the strong band at 2277 cm^{-1}, assigned to the stretching vibration of the $\equiv Si-(CH_2)_3-NCO$ group, that this duration is necessary for the completion of the reaction.

2.2. Step 2: synthesis of the ureasils

The preparation of one representative material ($U2000_{92}Eu(CF_3SO_3)_3$) is described. A mass of 1.645 g of $Eu(CF_3SO_3)_3$ was dissolved in 0.582 ml of ethanol (Merck) and 67.5 ml of distilled water (molar proportion 1 ICPES:4 CH_3CH_2OH:1.5 H_2O). This solution was added to the solution prepared in Step 1. The mixture was stirred in a sealed flask for 30 min and then cast into a Teflon® mould and left in a fume cupboard for 24 h. The mould was covered with Parafilm® perforated with a syringe needle in order to ensure the slow evaporation of the solvents. After a few hours gelation occurred and the mould was transferred to an oven at 40°C for a period of 7 days. The sample was then aged at about 80°C for 3 weeks to form a transparent, fairly rigid and brittle elastomeric monolithic film with a yellowish coloration.

2.3. X-ray diffraction

Diffractograms were recorded using a PW1729 Philips X-ray generator and a PW 1840 Philips diffractometer. Powdered samples were exposed to the Cu $K\alpha_1$ radiation at room temperature in the 2θ range between 10 and 50°.

2.4. Differential scanning calorimetry

The samples were studied between −40 and 300°C at a heating rate of 5°C min^{-1} under a flowing argon atmosphere using a Mettler TC11 controller with a DSC20 oven.

2.5. A.c. impedance

Bulk conductivities of samples were obtained using the complex impedance technique (Schlumberger Solartron 1250 frequency response analyzer and 1286 electrochemical interface) between 25 and 100°C [14].

2.6. FTIR spectroscopy

Mid-infrared spectra were acquired at room temperature using a Unicam FT-IR system over the range 4000–400 cm^{-1} by averaging 60 scans at a maximum resolution of 4 cm^{-1}. The samples, previously vacuum dried at 90°C, were analyzed by dispersing them in KBr (Merck) by the pressed-disc technique.

2.7. Photoluminescence spectroscopy

Photoluminescence spectra were recorded between 10 and 300 K with a resolution of about 0.05 nm. The luminescence was excited by a Kratos LH 15 IN/l S 1000-W xenon arc lamp and was recorded using a 0.25-m Kratos GM-252 monochromator and a 1-m 1704 SPEX Czerny-Turner spectrometer coupled to an RCA C31034 photomultiplier [9].

3. Results

3.1. Powder X-ray diffraction

The X-ray patterns of the undoped and doped ureasils and of the salt are depicted in Fig. 1. The length and regularity of the oxyethylene chains in the undoped ureasil explain its semi-crystalline nature as the peaks observed at 23.1, 19.0 and 35.7° are characteristic of crystalline POE. These peaks disappear completely for compositions $n=37$, 55 and 92, indicating that $Eu(CF_3SO_3)_3$ induces long-range disorder. No free salt is detected in any of the diffraction patterns.

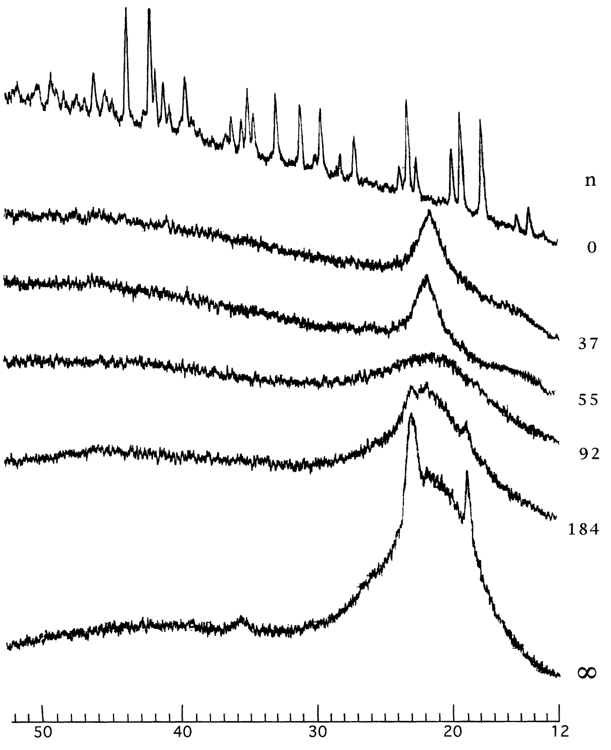


Fig. 1. X-ray diffraction patterns for the europium(III)-doped and undoped ureasils $U(2000)_nEu(CF_3SO_3)_3$.

3.2. Thermal studies

The DSC traces of the $U(2000)_nEu(CF_3SO_3)_3$ materials are shown in Fig. 2. The presence of two melting peaks (centered at 26 and 47°C) instead of one in the thermogram of the undoped ureasil may be associated with reorganization of the partially fused oxyethylene chains or with the fusion of polymer hedrites with different structures. The broad peak centered at about 90°C observed in the DSC traces of the ureasils with compositions $n=37$, 55 and 92 is often assigned to the evaporation of water and ethanol. The DSC results suggest that there is some short-range order but the materials are clearly largely amorphous. No glass transition temperatures are detected within the range of temperatures studied. Thermal decomposition of the samples is evident in some thermograms, at temperatures ranging from 250 to 310°C depending on the salt content. The highest decomposition temperature (320°C) was registered with the undoped ureasil, indicating that the salt causes a destabilization of the host matrix.

3.3. A.c. impedance

The Arrhenius conductivity plot of the $U(2000)_nEu(CF_3SO_3)_3$ polymer materials illustrated in Fig. 3 demonstrates that the total ionic conductivity of the doped ureasils varies little with salt concentration. Composition $n=92$ exhibits the highest conductivity at room temperature (approximately 10^{-5} Ω^{-1} cm^{-1} at 30°C).

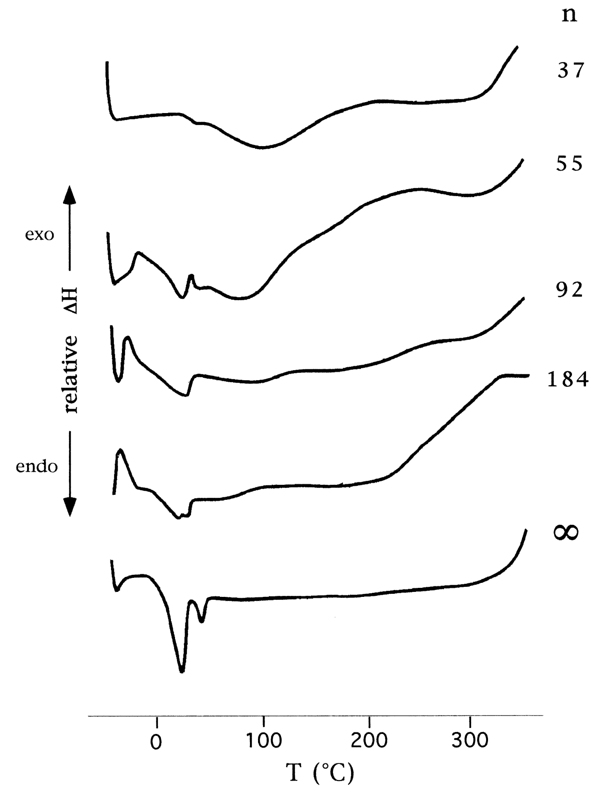


Fig. 2. DSC traces for the europium(III)-doped and undoped ureasils $U(2000)_nEu(CF_3SO_3)_3$ (first heating cycle).

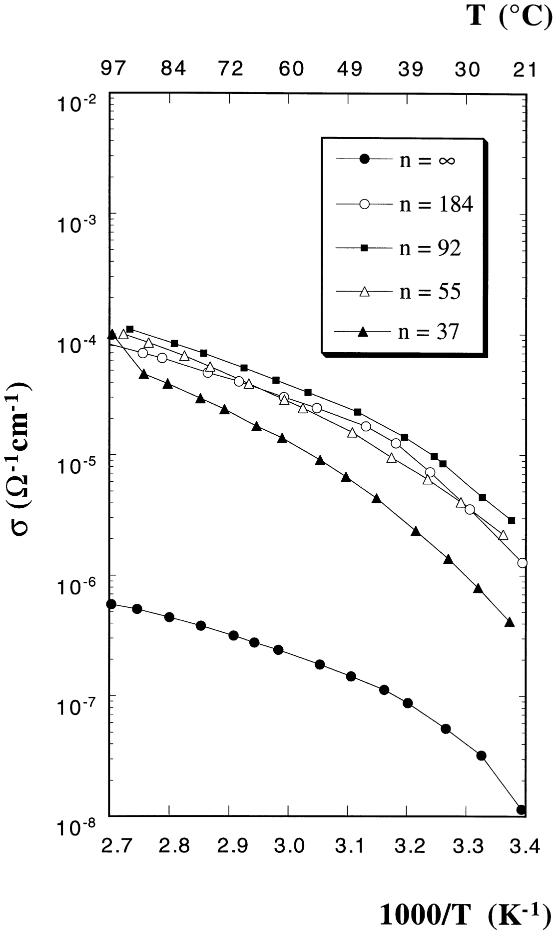


Fig. 3. Arrhenius conductivity plot of the europium(III)-doped and undoped ureasils $U(2000)_nEu(CF_3SO_3)_3$.

3.4. FTIR spectroscopy

The infrared spectra of the Jeffamine ED-2001®, of the undoped ureasil and of the europium(III)-doped ureasils at 300 K in the spectral region ranging from 1400 to 800 cm^{-1} are presented in Fig. 4. Dramatic differences are observed between the infrared spectrum of the Jeffamine ED-2001® and that of U(2000). The most marked effect is in the shift of the strongest bands of the diamine situated at 1116 cm^{-1} (attributed to C–O stretching vibrations) and 1147 cm^{-1} (attributed to C–O stretching and CH_2 rocking vibrations) downward to 1108 cm^{-1} and to a shoulder at approximately 1145 cm^{-1}, respectively, in the spectrum of U(2000). Also, the medium-intensity bands at 1344 cm^{-1} (assigned to the wagging of the CH_2 groups of the (CH_2CH_2O) units of the diamine) and at 1060 cm^{-1} (assigned to CH_2 rocking and to C–C and C–O stretching

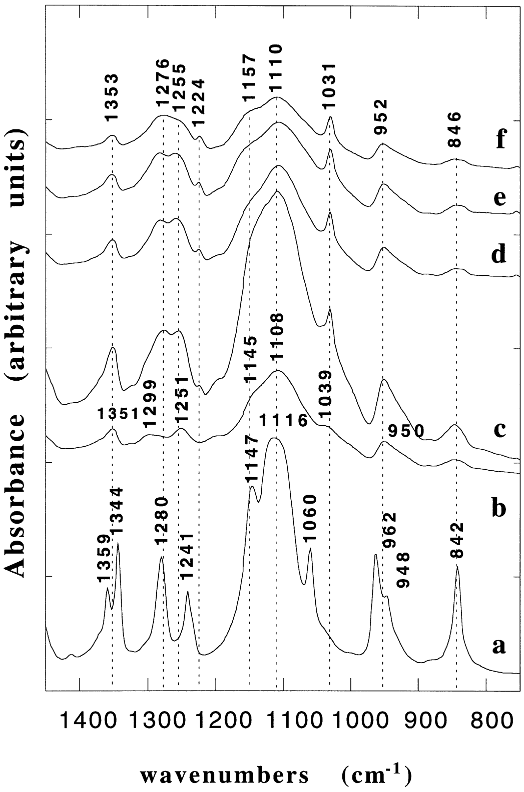


Fig. 4. Infrared spectra of the Jeffamine ED-2001 (a) and of the europium(III)-doped and undoped ureasils U(2000)$_n$Eu(CF$_3$SO$_3$)$_3$ at 300 K ((b)=∞, (c) n=184, (d) n=92, (e) n=55 and (f) n=37).

vibrations) are reduced to weak bands at 1351 and 1039 cm^{-1}, respectively, in the spectrum of the undoped ureasil. These modifications, among others, are similar to those reported by several authors upon melting of crystalline high molecular weight poly(ethylene glycol) [16,17] and allow us to conclude that by grafting the Jeffamine ED-2001® into the silica network the oligopolyoxyethylene chains of the diamine become less ordered.

The coordination of the europium(III) triflate in the ureasils may be analysed considering the assignment proposed by Bernson et al. [12,13] for the $\nu_a(SO_3)$, $\nu_s(SO_3)$, $\nu_s(CF_3)$ and $\nu_a(CF_3)$ bands of the free and coordinated triflate ion. Two bands suggest the free nature of the triflate ion in these materials: the strong band at 1031 cm^{-1}, assigned to the symmetric stretching vibration of the SO$_3$ group, and the band situated at 1224 cm^{-1}, attributed to the CF$_3$ symmetric stretching vibration. Both bands are observed for all compositions and remain unshifted. However the band at about 1271 cm^{-1}, associated with the asymmetric stretching vibrations of the SO$_3$ group in the free triflate ion, is absent in all the spectra. Instead two bands are detected at 1276 and 1259 cm^{-1}. They are tentatively assigned to the two components which result from the lifting of the degeneracy of the $\nu_a(SO_3)$ mode upon coordination of the triflate ion. These results reveal that the samples analysed contain both free and coordinated triflate.

3.5. Photoluminescence spectroscopy

Fig. 5 shows the Eu^{3+} emission lines at 10 K (λ_{exc}= 375 nm) for the doped ureasils. These lines were assigned to transitions between the first excited state $^5D_0$ and the $^7F_{0-4}$ levels of the fundamental septet. Luminescence from higher excited states such $^5D_1$ is not observed, indicating very efficient non-radiative relaxation to $^5D_0$. The observed transitions are mainly of an electric dipole (ED) nature, except the $^5D_0 \to {}^7F_1$ line which has a predominant magnetic dipole (MD) contribution. The presence of the $^5D_0 \to {}^7F_0$ transition, prohibited by the free ion ED/MD selection rules, and the full J-degeneracy splitting observed for the $^7F_{1-4}$ levels (3, 5, 7 and 9 Stark components, respectively) indicates a low symmetry local environment for the Eu^{3+} cations in these materials. As the temperature increases from 10 to 300 K, although no variations were detected in the number of Stark levels, the line intensity is generally reduced by approximately one order of magnitude. The emission spectra of these hybrid organic/inorganic materials show a wide blue-green broad band associated with the host emission (not represented in Fig. 5 but similar to the spectrum of the undoped ureasil – see insert of Fig. 5). A detailed characterization of the nature of this band is under progress. Similar results have been obtained with various excitation wavelengths used and for different europium concentrations.

4. Conclusion

This exploratory study introduces a series of interesting Eu^{3+}-based hybrid organic/inorganic materials, classed as ureasils. They are prepared by the sol–gel technique and obtained as amorphous transparent monoliths, thermally stable up to 250°C, intensely luminescent and exhibiting a ionic conductivity of about $10^{-5}\ \Omega^{-1}\ cm^{-1}$ at 30°C.

Acknowledgements

The financial support provided by JNICT (contract number PBIC/CTM/1965/95) is gratefully acknowledged. The authors are indebted to Professor F. Lencart for enlightening discussions and also wish to thank Mr. Tito Azevedo, of the Geology Department of the University of Trás-os-Montes e Alto Douro, for the X-ray diffraction measurements, and R.A. Sá Ferreira, of the Physics Department of the University of Aveiro, for her help in the photoluminescence studies.

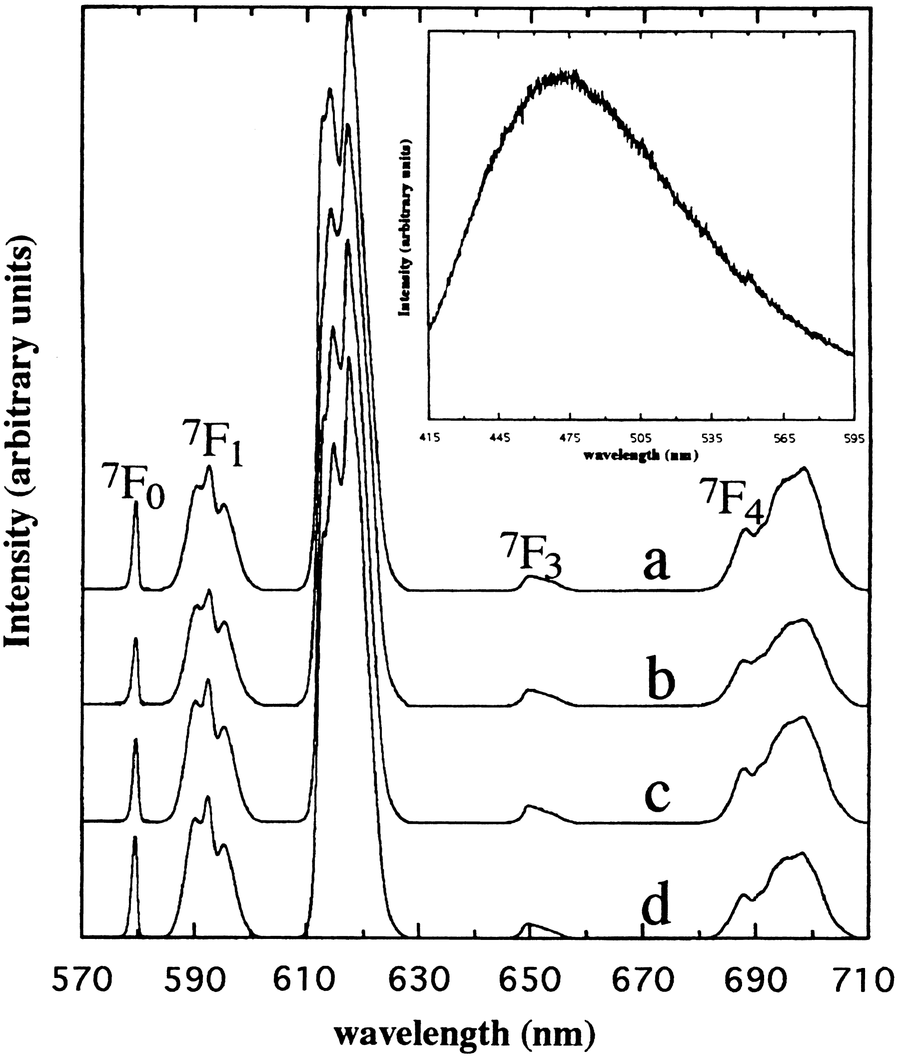


Fig. 5. Emission spectra (λ_{exc}=375 nm) for the europium(III)-doped ureasils U(2000)$_n$Eu(CF$_3$SO$_3$)$_3$ ((a) n=184; (b) n=92; (c) n=55; and (d) n=37) at 10 K. Intensities are proportional to the photon flux and normalized to the most intense peak in each spectrum. Insert shows the undoped ureasil (λ_{exc}=350 nm) emission spectrum at 10 K.

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