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Preparation and luminescence properties of sol-gel hybrid materials incorporated with europium complexes

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Microporous silica gel has been prepared by the sol-gel method utilizing the hydrolysis and polycondensation of tetraethylorthosilicate (TEOS). The gel has been doped with the luminescent ternary europium complex $Eu(TTA)_3{\cdot}phen$: where HTTA = 1-(2-thenoyl)-3,3,3-trifluoracetone and phen = 1,10-phenanthroline. By contrast to the weak f-f electron absorption bands of Eu^{3+}, the complex organic ligand exhibits intense near ultraviolet absorption. Energy transfer from the ligand to Eu^{3+} enables the production of efficient, sharp visible luminescence from this material. Utilizing the polymerization of methyl methacrylate or ethyl methacrylate, the inorganic/polymer hybrid materials containing $Eu(TTA)_3{\cdot}phen$ have also been obtained. SEM micrographs show uniformly dispersed particles in the nanometre range. The characteristic luminescence spectral features of europium ions are present in the emission spectra of the hybrid material doped with $Eu(TTA)_3{\cdot}phen$. *© 2000 Kluwer Academic Publishers*

1. Introduction

The sol-gel method has been shown to be a suitable approach for the preparation of novel luminescent materials [1–5]. Photoactive lanthanide-organic coordinated compounds, such as europium and terbium chelates with organic ligands, exhibit intense narrow band emissions via an energy transfer from the ligands to the metal ions under near UV excitation [6]. Recently, some papers have reported the luminescence behavior of Eu^{3+} and Tb^{3+} complexes with 1,10-phenanthroline [7], β-diketones [8], aromatic carboxylic acids [9], and heterocylic ligands [10] in sol-gel derived host materials. Unfortunately, the dopant concentrations of complexes in a silica matrix must be low, and it is difficult to obtain transparent and uniform material. Besides this, the pure inorganic matrix has some disadvantages such as poor mechanical properties that restrict its practical applications.

The incorporation of a polymer into the silica gel matrix forms an inorganic/polymeric hybrid material [11–14], which can modify the mechanical properties. High luminescence intensity has been reported for the complexes $Eu(TTA)_3{\cdot}xL$ (where L = DBSO and PTSO sulfoxides, and derivatives of 15C5 and 18C6 macrocyclics) [15]. In the present work, $Eu(TTA)_3{\cdot}phen$ was incorporated into poly(methyl methacrylate) (PMMA) and poly(ethyl methacrylate) (PEMA) matrices, and the corresponding hybrid materials SiO_2/PXMA: $Eu(TTA)_3{\cdot}phen$ (X = M or E) were also synthesized, so that the compositional, luminescence and thermal properties could be investigated. The ultimate aim is the development of display devices, since the hybrid matrix possesses superior thermal and mechanical properties for incorporation of luminescent europium complexes.

2. Experimental

Methyl methacrylate (MMA) was previously treated with dilute sodium hydroxide solution in order to remove impurities that might hinder polymerization. DMF solutions of $Eu(TTA)_3{\cdot}phen$ (2.0 cm^3) were mixed with MMA (5.3 cm^3), with dopant concentrations (in wt. %) of 0.05, 0.1, 0.5, 1.0, 2.0 and 5.0. Then benzoyl peroxide (BPO) (ca. 0.003 g), as the initiator for the preparation, was added into the mixed solution. The mixture was placed in water bath at 353–363 K for 15 to 30 min. After the pre-polymerization of the monomers, the mixture became viscous, and was placed into a mold or poured along microscope glass slides. The polymerization process was completed in an oven at 323 K for 24 h. Analogous preparations were employed for ethyl methacrylate (EMA).

Microporous silica gel was prepared by the sol-gel method utilizing the hydrolysis and polycondensation processes of TEOS [16]. On formation, the silica xerogel was immersed in a DMF solution of MMA containing $Eu(TTA)_3{\cdot}phen$. The polymerization was first performed at 358 K for 30 min, then at 323 K for 24 h, and finally at 358 K for 1 h to obtain the silica/polymer hybrid material containing Eu(TTA)$_3$·phen.

Thermal analysis was carried out using a Seiko SSC/5200 Thermogravimetric Analyzer. Infra-red absorption spectra were measured on a Bomen MB420 FTIR spectrometer using the KBr pellet technique or a ZnSe ATR accessory. The excitation and emission spectra were recorded at room temperature using a SLM 4800C Spectrofluorometer equipped with a xenon lamp as the excitation source. UV-visible absorption spectra were measured by a Shimadzu Spectrometer at a resolution of 1 nm. The morphologies of the surface of the blend specimens were observed in a Jeol JSM 820 scanning electron microscope (SEM).

3. Results and discussion

Scanning electron micrographs of the hybrid material containing 0.5 wt% Eu(TTA)$_3$·phen showed homogeneous dispersion of the Eu complex, with the sizes of the micropores of the interpenetrating polymeric network structure being between 50–100 nm. Fig. 1 shows the micrograph of this concentration of dopant ion in a 20 wt% silica and 80% wt% PMMA matrix. Comparison of the TG-DTA curves of Eu(TTA)$_3$·phen, PMMA: Eu(TTA)$_3$·phen (Fig. 2a) and PMMA/SiO$_2$:Eu(TTA)$_3$·phen (Fig. 2b) shows that the temperature for 5% loss in mass of the material, due to decomposition, increases in the order 451 K, 478 K and 590 K. This indicates that the silica gel/polymer hybrid matrix exhibits greater thermal stability than that of pure complex or pure polymer matrix. The silica gel/PMMA hybrid material thus provides a stable structural host matrix for the Eu(TTA)$_3$·phen complex, and is a promising candidate for practical applications.

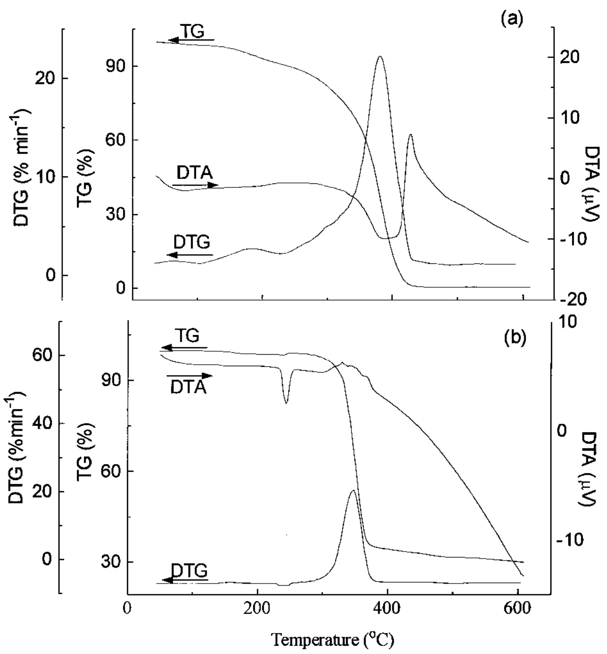

Figure 2 TG/DTG/DTA curves of 0.5 wt% Eu(TTA)$_3$·phen in (a) PMMA and (b) SiO$_2$/PMMA.

Further characterisation of the Eu(TTA)$_3$·phen complex and the sol-gel materials was carried out by FTIR spectrometry. Strong bands near 1600 cm^{-1} due to >C=O stretching and aromatic C-C stretching, respectively, have been reported in the IR spectra of Eu(TTA)$_3$·2H$_2$O [15] and Eu(phen)$_2$Cl$_3$·2H$_2$O [7]. Several bands occur in the IR spectrum of the Eu(TTA)$_3$·phen complex in this region, with the strongest being at 1598 cm^{-1} (Fig. 3a). The IR spectrum also shows that the neat complex is anhydrous. The strongest bands in the IR spectrum of the silica gel matrix (Fig. 3b) are due to the Si-O-Si stretch TO and LO modes, at 1080 cm^{-1} and 1215 cm^{-1}, respectively. Other bands are observed near 464 cm^{-1} (Si-O-Si bending), 801 cm^{-1} (O-Si-O bending), and 960 cm^{-1} (asym.

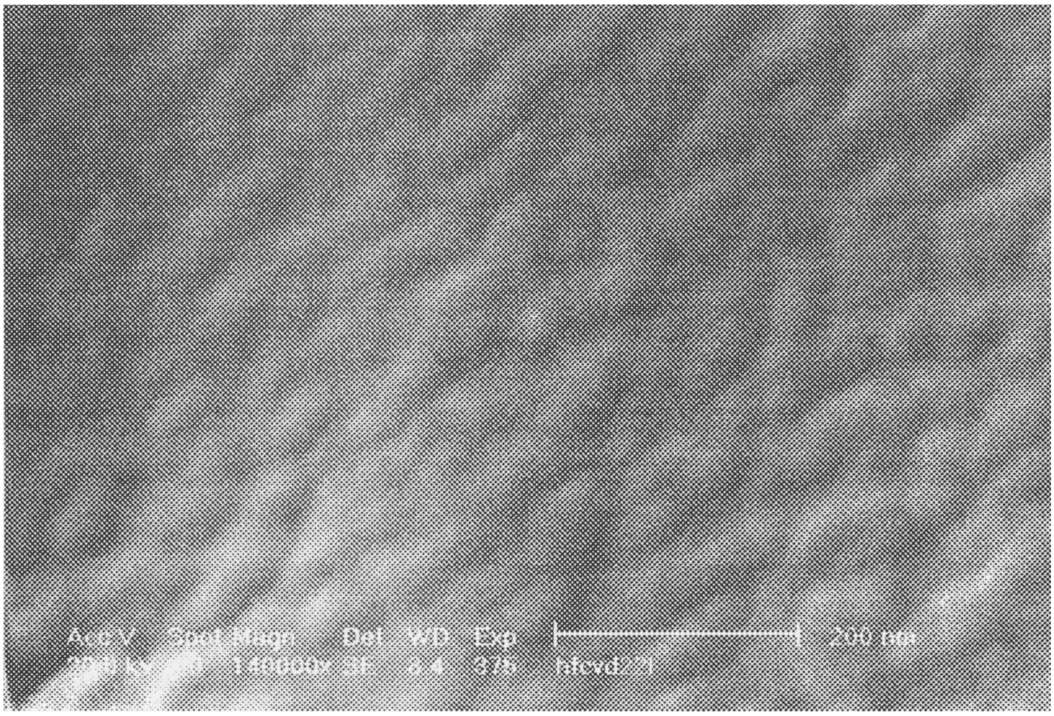

Figure 1 SEM micrograph of 0.5 wt% Eu(TTA)$_3$·phen in SiO$_2$/PMMA.

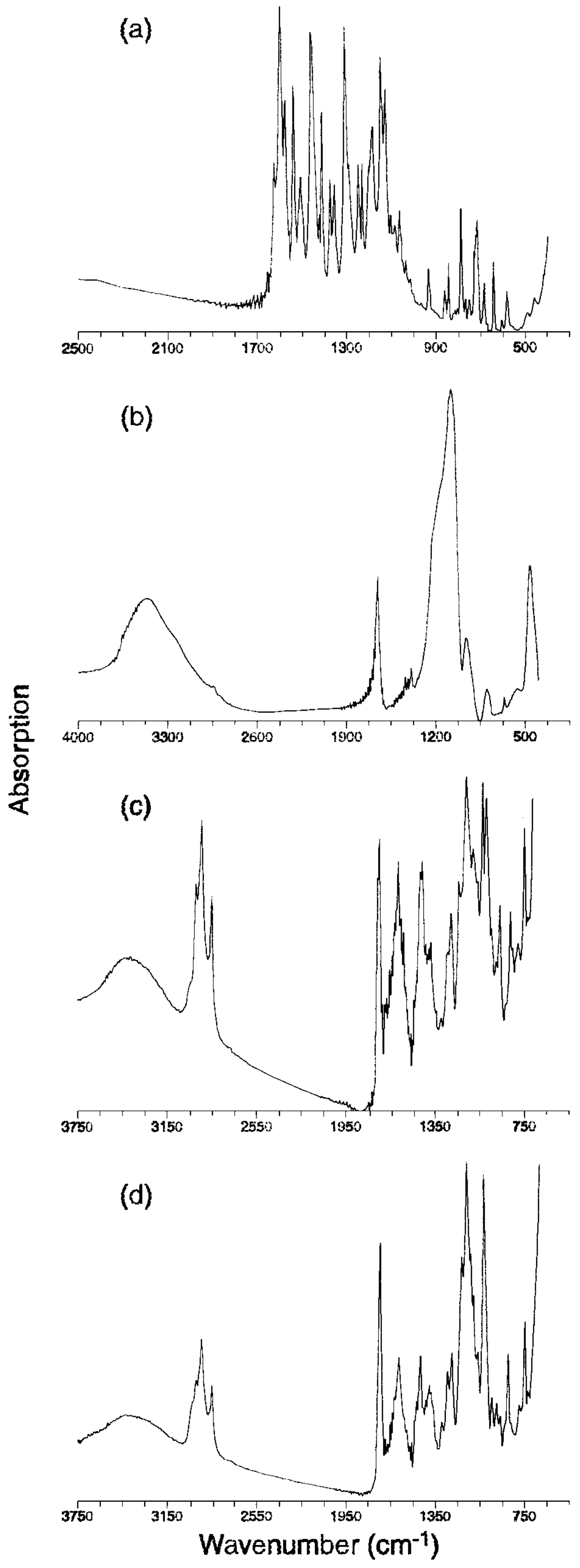

Figure 3 Infrared absorption spectrum of pure complex and FTIR-ATR spectra of sol-gel materials: (a) nujol mull transmission spectrum of Eu(TTA)$_3$·phen complex; ATR spectra of (b) 0.5 wt% Eu(TTA)$_3$·phen in SiO$_2$; (c) 2.0 wt% Eu(TTA)$_3$·phen in PMMA; (d) 5 wt% Eu(TTA)$_3$·phen in PEMA. The drying temperatures were 373 K for (b) and 298 K for (c) and (d). Note the changes in wavenumber scale.

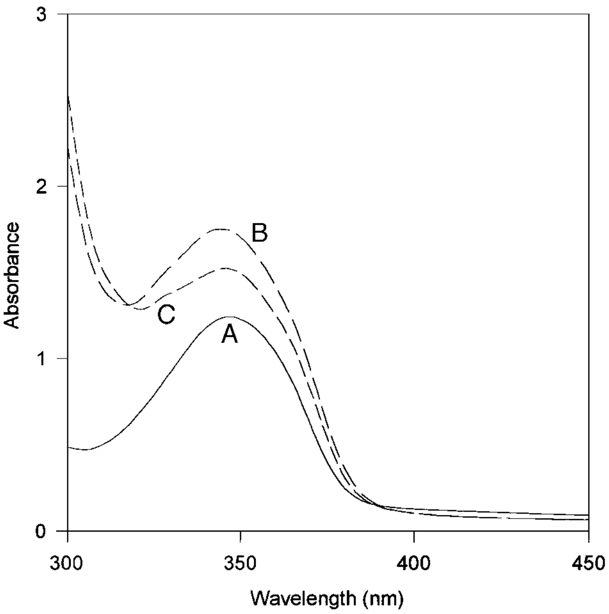

Figure 4 Ultraviolet absorption spectra of Eu(TTA)$_3$·phen: (A) 2×10^{-5}M ethanolic solution; 0.5 wt% in (B) PMMA and (C) PEMA.

O-Si-O stretching). In addition, bands due to the bending and stretching modes of water molecules are prominent at 1657 cm^{-1} and 3430 cm^{-1}. Most of these bands are broad so that the wavenumbers for samples dried at room-temperature, 353 K and 373 K were similar. From the change in band intensities, however, it was estimated that only about 20% of water was lost from the silica gel on heating samples previously dried in a desiccator up to 373 K. The most distinct feature in the IR spectra of the PXMA hybrid materials (Fig. 3c,d) is the peak near 1730 cm^{-1} due to >C=O stretching. Comparison of the peak intensities at 1730 cm^{-1} and 1080 cm^{-1} enabled estimates to be made of the composition of the hybrid materials.

The maximum absorption peak of Eu(TTA)$_3$·phen in ethanolic solution (λ_{max}) is at 350 nm, and λ_{max} of Eu(TTA)$_3$·phen in silica gel/PMMA is at 346 nm. The corresponding wavelengths for the complex dispersed in PMMA or PEMA are similar (Fig. 4). This band corresponds to an electric dipole transition within the ligand, with the ligand excited state energy being just above that of the $^5D_4$ level of Eu^{3+}. Various nonradiative pathways may populate the luminescent $^5D_0$ level of Eu^{3+} from $^5D_4$, including cross-relaxations, multiphonon emission, and transfer involving defect sites.

The 300 K excitation spectra of Eu(TTA)$_3$·phen in PMMA and in silica gel/PMMA are similar, and show a broad band between 300 nm to 420 nm, with λ_{max} near 370 nm. Fig. 5 shows the corresponding emission spectrum, with excitation into the ligand absorption band. The emission transitions centred near 582, 593, 614, 652 and 700 nm correspond to the $^5D_0 \rightarrow {}^7F_{0,1,2,3,4}$ transitions respectively. The excitation, energy transfer and luminescence intramolecular processes of Eu(TTA)$_3$·phen in silica gel/PMMA matrix are thus analogous to those of the neat Eu(TTA)$_3$·phen complex.

The emission intensity of the $^5D_0 \rightarrow {}^7F_0$ transition of Eu^{3+} was investigated, under constant excitation intensity, for various materials. The results are summarized as follows:

1. For the complex doped into the silica gel matrix (0.5 wt%), the difference in luminescence intensity for samples air dried or dried at 373 K was compa-

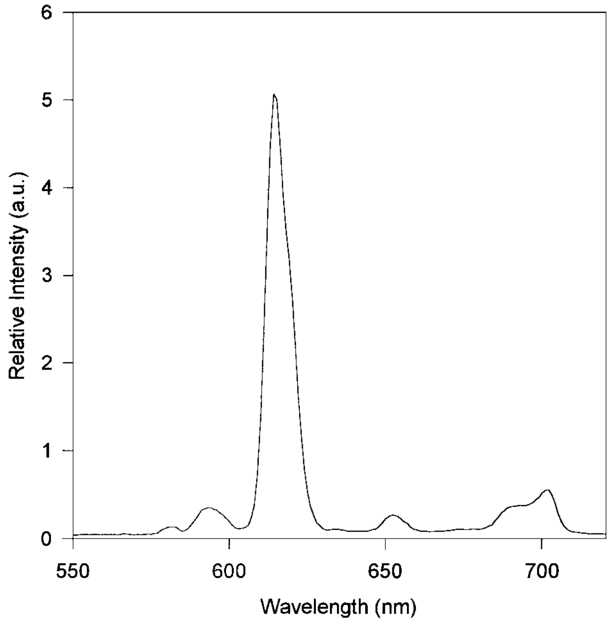

Figure 5 370-nm excited room temperature emission spectrum of 2 wt% Eu(TTA)$_3$·phen in silica gel/PMMA.

rable to the variability in measurement for the air-dried samples.

2. The luminescence intensity showed an increase, with mean slope greater than unity, with increasing Eu(TTA)$_3$·phen dopant concentrations between 0.05 to 1 wt% in the silica gel matrix.

3. The luminescence intensity of each PXMA/SiO$_2$ (50 : 50 wt%) hybrid material increased with dopant concentration, in the range studied from 0.05 to 5 wt% Eu(TTA)$_3$·phen. However, the intensity increased up to ca. 1 wt%, and then decreased in the range from 1 to 5 wt%, for the complex doped into the PEMA and PMMA polymers.

4. For both hybrid materials containing 0.5 wt% Eu(TTA)$_3$·phen, the luminescence intensities did not exhibit significant decreases, as compared with sample to sample variations, for the range of compositions from 0 to 100 wt% PXMA/SiO$_2$.

The results show that the matrix plays a minor role in determining the luminescence intensity of dilute samples of the Eu(TTA)$_3$·phen complex. Nonradiative relaxation pathways via the C-H stretching modes of PXMA, and the O-H stretch in silica gel are of less importance than the C=O and C-H modes in the complex itself. However, it is clear that depopulation of the $^5D_0$ excited state occurs at a lower dopant concentration regime in the neat polymer matrices, than in the hybrid or pure silica gel matrices. The explanation requires further investigation, but the sample homogeneity at higher dopant concentrations, and occurrence of defect sites may play important roles.

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