The influence of matrix on the formation of picolinic acid: Eu^{3+} complex

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It has been extensively researched and reported in the early 60s, that the organic complexes of rare earth ions can display lasing properties, strong luminescence and energy transfer in the liquid phase [1, 2]. However, most organic complexes are synthesized in organic solutions, which limits their application due to the poor optical and thermal stability of the solution, as well as inconvenience in handling. Recently, it has been shown that the luminescent properties of the centred rare earth ions in organic complexes are highly sensitive to the chemical surroundings [3], due to which the topic is being researched with renewed interest.

The sol-gel method using organically modified SiO_2 xerogels, which was developed in the 90s, provides a practical prospect for the development of the composite luminescent materials with good properties. These composites can overcome the deficiencies of poor optical and thermal stability of organic and polymer solutions. SiO_2 xerogels and glasses exhibit excellent optical properties and can be a good surrounding for many luminescent activators. Therefore, it is possible for many organic complexes to be synthesized in SiO_2 xerogels and glasses, to prepare efficient, intensive organic-inorganic composite luminescence materials [4]. However, using the traditional sol-gel technique, it is difficult to dope organic complexes homogeneously into SiO_2 xerogels due to decomposition problems. For example, the pH value of the SiO_2 precursors must be adjusted within the acidic region, at about 3−3.5, which is in contradiction with the alkaline conditions needed for synthesizing organic complexes [5]. In order to overcome the difficulty, we developed a new *in-situ* method for synthesizing organic complexes, which are nanogeneously dispersed in SiO_2 xerogels and synthesized in the formation of the xerogels [5, 6]. In this paper, we have synthesized the picolinic acid: Eu^{3+} complex in SiO_2 xerogels through the new *in-situ* synthesis technology, and have compared it with the complex synthesized in the solution using high resolution fluorescence spectroscopy.

Eu_2O_3 (99.9%) was dissolved in distilled water by adding an appropriate amount of HCl solution. Then the picolinic acid solution and $EuCl_3$ solution were mixed with picolinic acid: $Eu^{3+} = 3: 1$ under vigorous stirring. The pH was adjusted to a certain value with diluted aqueous ammonia (final 4−6). A transparent colourless crystalline product appears in the mixture. After being filtered, cleaned and dried, the product was subjected to high resolution luminescence spectroscopy.

The sol-gel solution used to prepare the silica xerogel consisted of 1 mol tetraethyloxysilane (TEOS), 4 mol ethanol and 4 mol distilled water. A small amount of HCl was added to the solution to promote hydrolysis. Picolinic acid was added with an appropriate proportion of Eu^{3+} and the pH was controlled (pH $\sim$ 3). After being mixed for 1 h at room temperature under vigorous stirring, the solution was placed in a sealed container at 40 °C. The mixture became viscous and gelatinized within a few days. The wet gels were dried slowly at 40 °C to prevent cracking. The dried gels were then heat treated at 100 °C for 24 h. The N_2 laser excited high resolution emission spectra were measured with a Spex-1403 monochromator and boxcar.

The picolinic acid: Eu^{3+} complex synthesized in the solution and silica xerogels were analysed using differential thermal analysis (DTA), IR spectroscopy, ultraviolet spectroscopy and fluorescence spectroscopy [6].

The electron configuration of the Eu^{3+} ion used as a conformational probe is f^6. The first sub-stable state is $^5D_0$ and the ground state is ^7f_J (J = 0−6). Among these transitions, the $^5D_0 \rightarrow \, ^7F_2$ transition is the hypersensitive electronic dipole transition which is greatly affected by the co-ordination environment, while the $^5D_0 \rightarrow \, ^7F_1$ transition is the magnetic dipole transition which is much less sensitive to the co-ordination environment. The ratio of the relative intensity of the two transitions determines the local symmetry of the Eu^{3+} ion. The $^5D_0 \rightarrow \, ^7F_0$ transition does not split in the co-ordination field, so the number of the bands in the emission spectra due to the $^5D_0 \rightarrow \, ^7F_0$ transition depends on the types of Eu^{3+} ion site. Fig. 1 gives the high resolution emission spectra (showing the $^5D_0 \rightarrow \, ^7F_0$ transition) of the picolinic acid: Eu^{3+} complex synthesized in the solution. The split of the band due to the $^5D_0 \rightarrow \, ^7F_0$ transition shows that there are two types of Eu^{3+} ion site in the complex, site I ($\sim$17 268 cm^{-1}) and site II ($\sim$17 242 cm^{-1}), during the temperature variation from 11 K to 298 K. At 11 K, Eu^{3+} ion site II is dominant, as evidenced by the larger intensity of the band at about 17 242 cm^{-1} in comparison to that of the band at about 17 268 cm^{-1}. When the temperature increases to 298 K, the band at 17 268 cm^{-1} (site I) shifts to
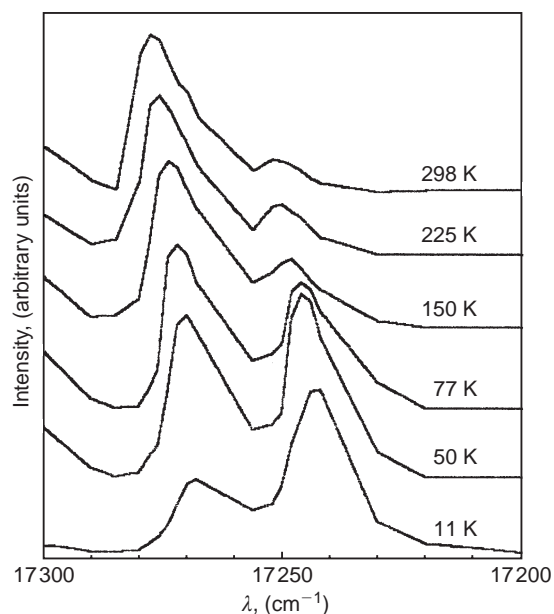
Figure 1 The N_2 laser excited high resolution fluorescence spectra (measured at different temperatures) of the picolinic acid: Eu^{3+} complex synthesized in the solution showing the $^5D_0 \rightarrow {}^7F_0$ transition ($17\,300$ cm^{-1}–$17\,200$ cm^{-1}).

Figure 2 The N_2 laser excited high resolution fluorescence spectra (measured at different temperatures) of the picolinic acid: Eu^{3+} complex synthesized in the solution showing the $^5D_0 \rightarrow {}^7F_J$ transition, $J = 0, 1, 2$ ($17\,300$ cm^{-1}–$15\,900$ cm^{-1}).

$17\,278$ cm^{-1} and the band at $17\,242$ cm^{-1} (site II) shifts to $17\,252$ cm^{-1}. Furthermore, the intensity of the band corresponding to site I surpasses that corresponding to site II and becomes dominant at 298 K. The results show that the Eu^{3+} ion site in the pure complex is affected greatly by the temperature.

When irradiated by the laser at 337.1 nm, the Eu^{3+} ion is raised from the ground state to the excited state $^5D_0$. The two types of Eu^{3+} ion site make their $^5D_0$ excited states at different energy levels, which results in the overlap of the emission bands in the high resolution emission spectra. The splitting numbers of Eu^{3+} ion site I due to the $^5D_0 \rightarrow {}^7F_J$ (J = 0, 1, 2) transitions are 1, 3, 5, respectively. According to the splitting numbers of the Eu^{3+} ion's $^5D_0 \rightarrow {}^7F_J$ (J = 0, 1, 2) transitions calculated by group theory and the Judd–Ofelt method [7], the possible moieties of Eu^{3+} ion site I are C_s or C_2. Shown in Fig. 2, in the emission spectra at 11 K, there are four peaks corresponding to the $^5D_0 \rightarrow {}^7F_1$ transition, while the maximum number of peaks permitted due to splitting is 3. This implies that there are two kinds of Eu^{3+} ion site and an overlap of some of the bands results in the appearance of 4 peaks. At 298 K, the number of Eu^{3+} ion site II decreases greatly in the complex. There are three split peaks of the $^5D_0 \rightarrow {}^7F_1$ transition, corresponding to the peaks in the emission spectra of Eu^{3+} ion site I. The bands of Eu^{3+} ion site II in the spectra vanish. Hence, it can be concluded that, Eu^{3+} ion site II only exists at low temperature and disappears at high temperature (above room temperature). The splitting numbers of Eu^{3+} ion site IIs types of transitions are also 1, 3, 5, respectively. The possible moiety of Eu^{3+} ion site II is C_1, for site II this corresponds to the lower wave numbers in the emission spectra [7]. The $^5D_0$ energy level of site I is higher than that of site II. When irradiated by the laser at 337.1 nm, site I and site II
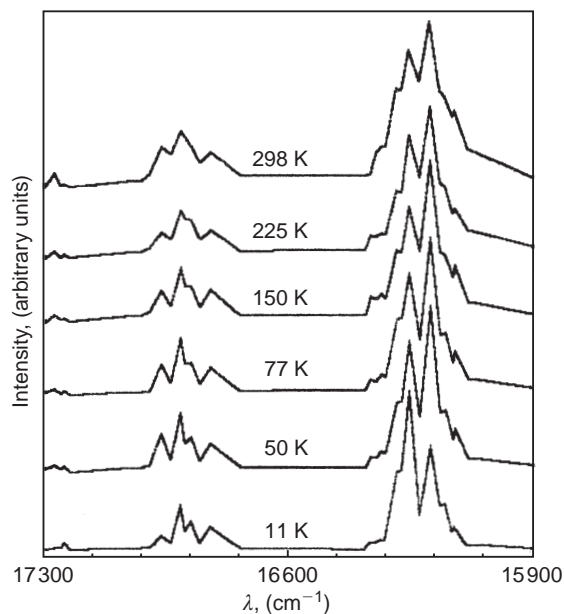
are possibly excited simultaneously, or site I is excited first and then transfers the energy to site II. The problem will be studied in further research.

In SiO_2 xerogels heated at 100 °C, there is only one peak of the $^5D_0 \rightarrow {}^7F_0$ transition, corresponding to Eu^{3+} ion site I (see Fig. 3). With an increase of the temperature, the peak shifts to the high wave numbers and the peak shape does not change significantly. It is obvious that there exists only one kind of Eu^{3+} ion site in SiO_2 xerogels which corresponds to the high wave numbers and that the Eu^{3+} ion site corresponding to the low wave numbers does not exist. The possible moieties of the Eu^{3+} ion in SiO_2 xerogels are C_s or C_2. The silica network in SiO_2 xerogels limits the free
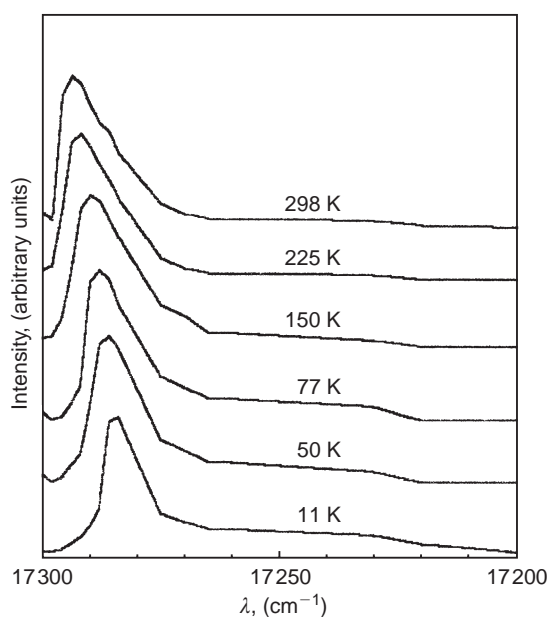

Figure 3 The N_2 laser excited high resolution fluorescence spectra (measured at different temperatures) of picolinic acid and Eu^{3+} doped SiO_2 xerogels showing the $^5D_0 \rightarrow {}^7F_0$ transition ($17\,300$ cm^{-1}–$17\,200$ cm^{-1}).
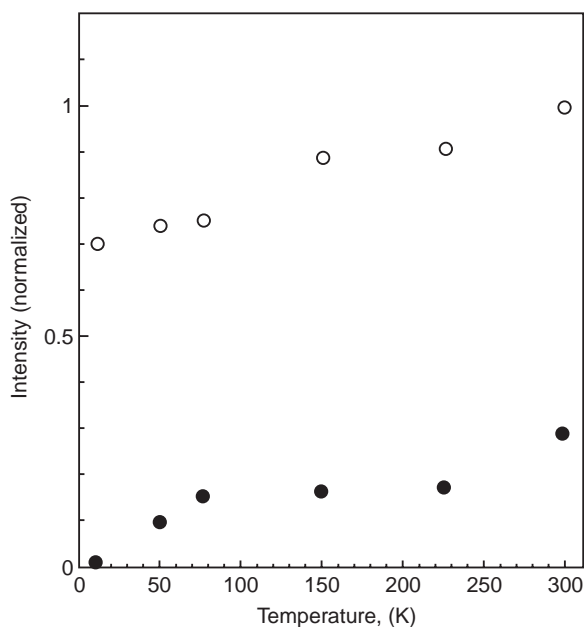
Figure 4 The temperature dependence of the relative luminescence intensity of the pure picolinic acid: Eu complex (●) and the complex synthesized in SiO_2 xerogels (○).

movement of organic molecules and makes them coordinate most densely with Eu^{3+} ions.

The temperature dependence of the relative fluorescence intensity of the picolinic acid: Eu^{3+} complex synthesized in the solution and SiO_2 xerogels is shown in Fig. 4. The intensity of the complex synthesized in the solution increases with temperature, which indicates that Eu^{3+} ion site I is more beneficial than Eu^{3+} ion site II for the luminescent properties of the complex. Furthermore, the energy transfer from Eu^{3+} ion site I to Eu^{3+} ion site II does not exist in SiO_2 xerogels. Hence, the intensity of the complex in SiO_2 xerogels is much greater than that synthesized in the solution. SiO_2 xerogels are better surroundings than solutions for the luminescence of the organic complex.

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