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Development of two series of solid complexes with intense characteristic fluorescence

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In this study, $Eu_{1-x}RE_x$(TLA)phen(RE=Gd, Y; x=0,0.1,0.2,0.3,0.4,0.5,0.6,0.7,0.8) were obtained by the trimellitic acid, 1,10-phennanthroline and mixed rare earth chloride of $EuCl_3$ and $GdCl_3$ or YCl_3 in CH_3CH_2OH solution. These complexes were characterized by FT-IR, TG-DTG and SEM. The FT-IR spectra showed that the oxygen atoms of carboxylate and the nitrogen atoms with RE^{3+}, and these complexes have similar structure. The TG-DTG analysis showed that these complexes are thermally stable. The fluorescence properties of these complexes were also studied. The results indicate that the complexes can emit intense characteristic fluorescence from europium ion. The experimental results showed that the fluorescence intensities of europium complexes were enhanced after doping Gd^{3+} or Y^{3+}. And the intensity of fluorescence is the best when Eu^{3+}:Gd^{3+}=0.4:0.6 or Eu^{3+}:Y^{3+}=0.8:0.2. Furthermore, among these rare earth ions, Gd^{3+} is better than Y^{3+} in sensitizing the fluorescence of Eu^{3+}.

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1. Introduction

The rare earth complexes have become excellent luminescence materials, this is related to lanthanide ions' peculiar characteristics, and has potential use in laser, photoluminescence and electroluminescence [1-3]. The rare-earth complexes with aromatic carboxylic acids are a kind of good luminous materials because of the good light-emitting singleness, high luminous intensity and high quantum efficiency. In recent years, more and more attention was paid to the fluorescence properties of these complexes [4-7]. Zhao G.H. and Gao J.Z. *et al.* in Northwest Normal University in China have done a lot of work in this field. The research showed that addition of the non-fluorescent rare-earth ions can enhance the fluorescence intensity of rare-earth complexes.

With aromatic carboxylic acid as the ligands, the triplet state energy level of carboxylic acids is more suitable for the lowest emission energy level $^5D_0$ of europium ion. The trimellitic acid, which has a variety of forms of coordination, is a good performance of the organic ligand. A lot of researches about the complexes of europium with trimellitic acid have been reported [8], but the study of europium-lanthanum or europium-yttrium complexes with trimellitic acid and 1,10-phenanthroline is seldom reported.

This work studies the fluorescence enhancement of europium(Ш) with trimellitic acid and 1,10-phenanthroline doped with Gd^{3+} and Y^{3+}. And the complexes were characterized by FTIR, TG-DTG and SEM.

2. Experimental

2.1 Materials and characterization

The solutions of lanthanide ions (0.1 mol/L) were prepared from the corresponding oxides (99.99% in purity, rare earth from the Baotou research institute of rare earths) by dissolving these in hot hydrochloric acid, evaporating these to syrup and diluting with anhydrous ethanol to a desired volume. The solution of trimellitic acid (0.1 mol/L) was prepared from the corresponding 1,2,4-benzenetricarboxylic anhydride (>99% in purity) by dissolution in denionized distilled water. The solution of 1,10-phenanthroline (0.1 mol/L) was obtained by dissolving 1,10-phenanthroline in anhydrous ethanol.

FT-IR spectra of the prepared complexes were obtained between 4000~300 cm^{-1} on a KBr pellet using Nicolet AVATAR370 FT-IR spectrometer. Thermal-gravimetric analysis was performed on Perkin Elmer Pyris 6. The programmed heating range was from room temperature to 800℃, with a heating rate of 10℃/min under a nitrogen atmosphere. The morphology of phosphor powder was examined on FEI Sirion 200. Fluorescence spectrum of the complexes was characterized by Shimadzu RF5301-PC.

2.2 Complex synthesis

To a 250 mL three necked bottle, the solutions were added in the following order: lanthanide ion solutions, trimellitic acid solution, 1,10-phenanthroline solution. After being stirred at 80℃ water bath for 3-4h, the mixed solution was added with sodium hydroxide solution to adjust the pH value to about 6-7. Then the solution was violently stirred at 80℃ water bath for 1-2h. Many solid precipitates were deposited at the bottom of the reactor after stopping stirring for a few minutes, then filtered and washed with anhydrous ethanol. Finally, a pink solid powder was obtained.

3 Results and discussion

3.1 FT-IR Spectra of the complexes

The FT-IR spectra showed that two series of solid complexes $Eu_{1-x}RE_x$(TLA)phen(RE=Gd, Y; x=0,0.1,0.2,0.3,0.4,0.5,0.6,0.7,0.8) have similar structure. The FT-IR spectra of the Eu(TLA)phen, $Eu_{0.4}Gd_{0.6}$(TLA)phen and $Eu_{0.8}Y_{0.2}$(TLA)phen are shown in Fig. 1.

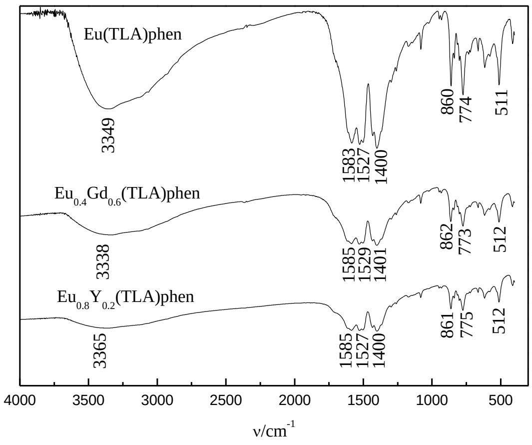

Fig. 1. The FT-IR spectra of Eu(TLA)phen, $Eu_{0.4}Gd_{0.6}$(TLA)phen and $Eu_{0.8}Y_{0.2}$(TLA)phen.

In the first ligand trimellitic sodium, the absorption band associated with $\upsilon_{as(coo-)}$ appears at 1569 cm^{-1}, $\upsilon_{s(coo-)}$ appears at 1379 cm^{-1}[9]. The value of $\Delta n[\upsilon_{as(coo-)}-\upsilon_{s(coo-)}]$ is 190 cm^{-1}. As shown in IR spectra, a shift of $\upsilon_{as(coo-)}$ frequency in the complexes of Eu(TLA)phen, $Eu_{0.4}Gd_{0.6}$(TLA)phen and $Eu_{0.8}Y_{0.2}$(TLA)phen, which toward lower wave number, appear at 1527 cm^{-1}, 1529 cm^{-1} and 1527 cm^{-1}. And a shift of $\upsilon_{s(coo-)}$ frequency in the complexes of Eu(TLA)phen, $Eu_{0.4}Gd_{0.6}$(TLA)phen and $Eu_{0.8}Y_{0.2}$(TLA)phen, which toward higher wave number, appear at 1400 cm^{-1}, 1401 cm^{-1} and 1400 cm^{-1}. What's more, the value of $\Delta n[\upsilon_{as(coo-)}-\upsilon_{s(coo-)}]$ in these complexes is lower than that of $\Delta n[\upsilon_{as(coo-)}-\upsilon_{s(coo-)}]$ in trimellitic sodium.

This showed that trimellitic acid bonded with RE^{3+} ions by one oxygen atom in carboxyl group which coordinate as a chelate bidentate group or a bidentate-bridge group. In addition, the absorption bands of 860 cm^{-1} and 774 cm^{-1}, 862 cm^{-1} and 773 cm^{-1}, 861 cm^{-1} and 775 cm^{-1} correspond to C-H plane bending vibration of 1,2,4-substituted benzene ring in the first ligand trimellitic acid.

In the second ligand phenanthroline, the absorption band, which associated with the C=N stretching vibration, C=C stretching vibration and C-H plane bending vibration, appear at 1588 cm^{-1}, 1622 cm^{-1}, 852cm^{-1} and 739 cm^{-1} [10]. As shown in IR spectra, the C=C stretching vibration and C-H plane bending vibration of phenanthroline are essentially absent. A shift of the C=N stretching vibration in the complexes of Eu(TLA)phen, $Eu_{0.4}Gd_{0.6}$(TLA)phen and $Eu_{0.8}Y_{0.2}$(TLA)phen, which toward lower wave number, appear at 1583 cm^{-1}, 1585 cm^{-1} and 1585 cm^{-1}. This showed that the nitrogen atoms of phen coordinate with RE^{3+}.

The absorption band associated with the O-H stretching vibration appear at 3349 cm^{-1}, 3338 cm^{-1} and 3365cm^{-1} due to physically absorbed water in air exist in all powders. Moreover, there are stretching vibration of RE-O at around 511 cm^{-1}, 512 cm^{-1} and 512 cm^{-1}. These results suggest that the RE^{3+} and the complex monomer are really conjunct t

3.2 TG-DTG Curve of the complexes

The thermal analyses of complex patterns are similar. It showed that these complexes have a similar decomposition mechanism. TG-DTG results of the Eu(TLA)phen, $Eu_{0.4}Gd_{0.6}$(TLA)phen and $Eu_{0.8}Y_{0.2}$(TLA)phen are given in Fig. 2.

The TG-DTG curve of Eu(TLA)phen indicated that the complex was decomposed from 30 to 763℃. And the largest weight loss rates of decomposition temperatures are 103℃, 271℃, 565℃ and 612℃. The first decomposition temperature ranges of 30~189℃. The corresponding rate of weight loss in TG curve is 5.38% (theatrically 5.41%), which means the loss of 1.7 water molecular. This result indicates that there is crystalline water in the complex, which is in agreement with the result of FT-IR. The second decomposition temperature is from 189 to 763°C, and it can seen that the obvious weight loss due to the decomposition of the ligands. The rate of weight loss in TG line is 35.33% (theatrically 34.93%), which is corresponding to the loss of one phenanthroline, one carbon molecular and 0.5 oxygen molecular. The final products were determined to be $Eu_4O(C_8H_3O_5)_2$.

The other complexs have a similar decomposition mechanism. The actual decomposition temperatures of these complexes are more than 185℃. The results showed that these complexes are thermally stable.

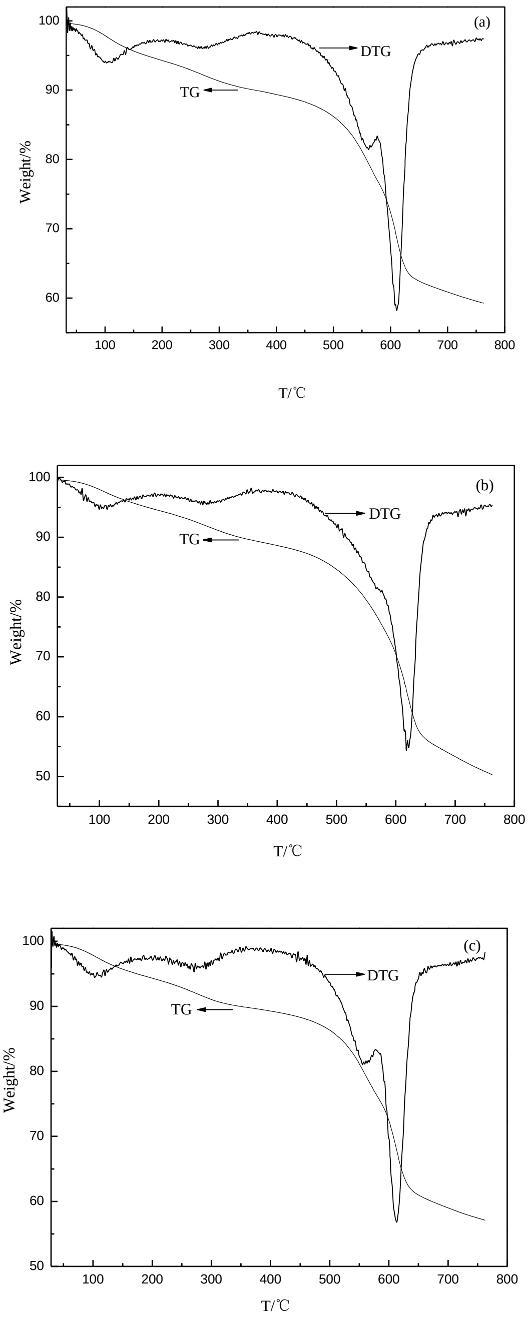

Fig. 2. The TG-DTG curve of Eu(TLA)phen, $Eu_{0.4}Gd_{0.6}$(TLA)phen and $Eu_{0.8}Y_{0.2}$(TLA)phen. (a) Eu(TLA)phen ; (b) $Eu_{0.4}Gd_{0.6}$(TLA)phen ; (c) $Eu_{0.8}Y_{0.2}$(TLA)phen.

3.3 SEM Images of the complexes

Fig. 3 is a typical SEM images of the Eu(TLA)phen, $Eu_{0.4}Gd_{0.6}$(TLA)phen and $Eu_{0.8}Y_{0.2}$(TLA)phen.

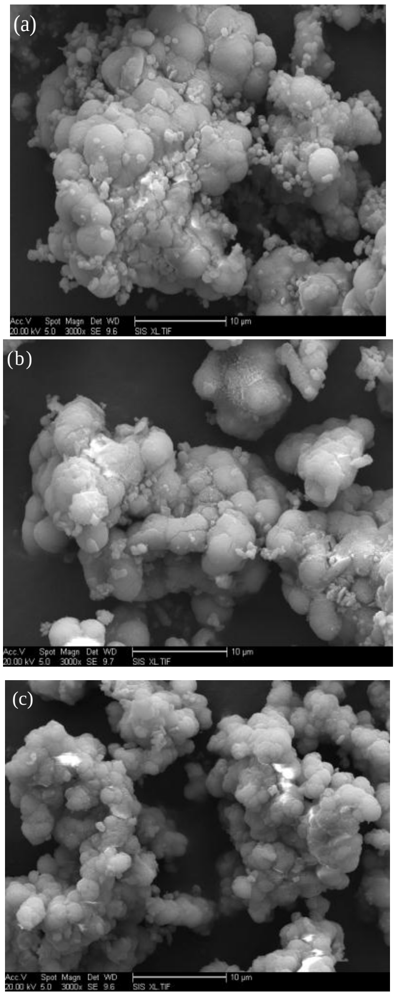

Fig. 3. SEM images of Eu(TLA)phen, $Eu_{0.4}Gd_{0.6}$(TLA)phen and $Eu_{0.8}Y_{0.2}$(TLA)phen. (a) Eu(TLA)phen; (b) $Eu_{0.4}Gd_{0.6}$(TLA)phen; (c) $Eu_{0.8}Y_{0.2}$(TLA)phen.

From Fig. 3(a), it can be seen that big particles adsorb small particles which are linked each other. The shape of the powder is closed to be spherical and agglomerate. From Fig. 3(b) and (c), it can be seen that there is a smaller grain size and a better uniformity compared to the former.

3.4 Fluorescene properties of the complexes

Fig. 4 presents the emission spectrum of complexes when excited at 276 nm. The emission spectrum of complexes indicated that the complexes can emit intense characteristic fluorescence from europium ion, the emission peak centered at 579 nm ($^5D_0 \rightarrow ^7F_0$), 592nm($^5D_0 \rightarrow ^7F_1$), 617 nm($^5D_0 \rightarrow ^7F_2$), 652 nm($^5D_0 \rightarrow ^7F_3$), 695nm($^5D_0 \rightarrow ^7F_4$). Compared to the Eu(TLA)phen, the fluorescence intensity of the $Eu_{0.4}Gd_{0.6}$(TLA)phen and $Eu_{0.8}Y_{0.2}$(TLA)phen were greater especially in $^5D_0 \rightarrow ^7F_2$ due to the sensitization of the lanthanum ions. And the intensity of fluorescence is the best when Eu^{3+}:Gd^{3+}=0.4:0.6 or Eu^{3+}:Y^{3+}=0.8:0.2. Among these rare earth ions, Gd^{3+} is better than Y^{3+} in sensitizing the fluorescence of Eu^{3+}.

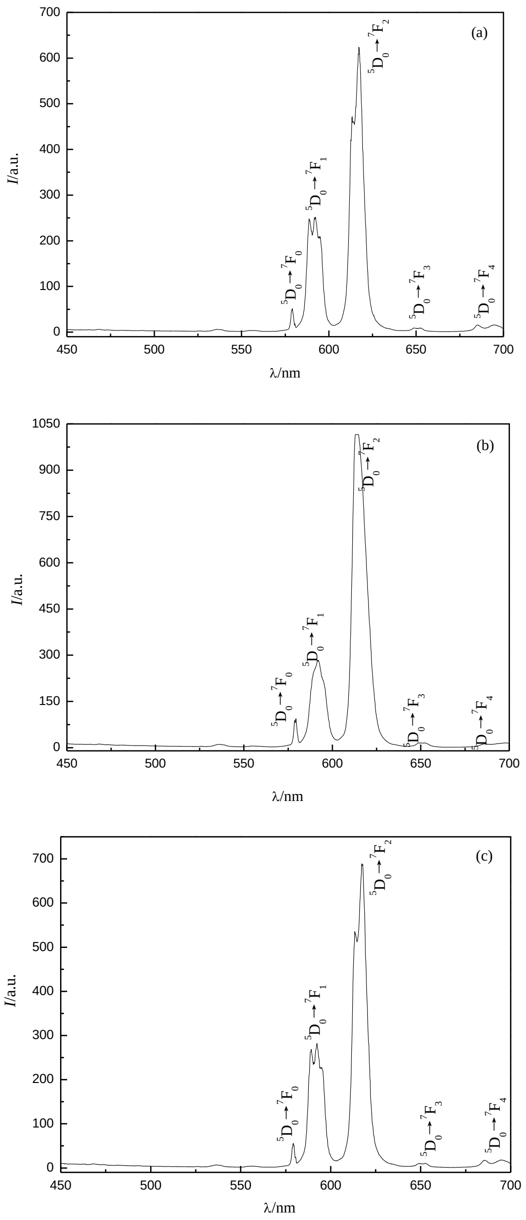

Fig. 4. The emission spectrum of Eu(TLA)phen, $Eu_{0.4}Gd_{0.6}$(TLA)phen and $Eu_{0.8}Y_{0.2}$(TLA)phen. (a) Eu(TLA)phen;(b) $Eu_{0.4}Gd_{0.6}$(TLA)phen; (c) $Eu_{0.8}Y_{0.2}$(TLA)phen.

There are two factors affected the fluorescence intensity:

(1) Matching extent of triplet state of ligands with excited state of the rare earths

The excited state energy level of Gd(Ш) and Y(Ш), which is higher than that of the excited state of Eu(Ш), due to the non-f electronic of Y(Ш) and half-filled 4f orbit of Gd(Ш). The triplet energy of ligands could not transfer to the excited state of Gd(Ш) and Y(Ш). And the energy can transfer from the triplet state to the excited state of Eu(Ш) effectively to achieve more excitation energy resulting a total luminous effect.

(2) The symmetry of complexes

If the rare earth ions are not lie in the symmetry center of the crystalline field, the exclusion of f-f transition was released. That is, the lower the symmetry of complexes is, the stronger the fluorescence intensity is. Attributed to the addition of the Gd(Ш) and Y(Ш), the symmetry of the complexes was always decreased, as a result, the fluorescence intensity was increased.

4. Conclusions

Two series of solid complexes $Eu_{1-x}RE_x$(TLA)phen(RE=Gd, Y; x=0,0.1,0.2,0.3, 0.4,0.5,0.6,0.7,0.8) were synthesized an characterized. The FT-IR spectra showed that the oxygen atoms of carboxylate and the nitrogen atoms of phen coordinate with RE^{3+}, and these complexes have similar structure. The TG-DTG analysis showed that these complexes had excellent thermal stability. The complexes containing Eu^{3+} exhibited fluorescence properties with a single strong characteristic fluorescence 617 nm. In addition, the fluorescence intensities of europium ions were sensitized by the doping elements lanthanum ions. And the intensity of fluorescence is the best when Eu^{3+}:Gd^{3+}=0.4:0.6 or Eu^{3+}:Y^{3+}=0.8:0.2. Furthermore, among these rare earth ions, Gd^{3+} is better than Y^{3+} in sensitizing the fluorescence of Eu^{3+}.

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