The preparation and luminescence of Eu(III) activated o-phenanthroline containing Gd(III) succinate phosphors

Wen-Lian Li, Gui Yu and Xu Zhao
Changchun Institute of Physics, Academia Sinica, 1-Yan An Street, Changchun 130021 (China)

Abstract

The preparation and luminescent properties of Eu(III) activated complex phosphors of Gd(III) with succinic acid (SA) and o-phenanthroline(phen), $(Gd_{1-x}Eu_x)_2SA_3phen_2$, were investigated. From the infrared spectra, X-ray diffraction patterns and fluorescent excitation and emission spectra, it was demonstrated that the phosphors may possess chain structure. The precipitate phosphors show an intense red emission under ultraviolet excitation, and the emission intensities were kept a constant when $x = 0.01$–1. The effects of the precipitation, the activator content on the emission in the complex system, and the energy transfer from the Gd chelate cages to Eu(III) ions are also discussed.

1. Introduction

The fluorescent properties of a number of solid complexes of lanthanide ion [Ln(III)] with β-dichetone [1, 2] or the aromatic carboxylic acids [3–5] have been investigated extensively. Ln(III) complexes are important luminescent materials for many industries, for example, fluorescent paint, interior displays, *etc.* [6]. However, complex luminescent materials in which the ligands are alkyl chain dicarboxylic acids were given little attention [7]. We have been interested in the effects of Ln(III) with inert electron structure on the luminescence properties of Eu(III) or Tb(III) in their β-dichetonate [8, 9] and aromatic carboxylate [10], and studied the enhancement effects of Y(III), La(III), Gd(III) and Lu(III) ions on Eu(III) or Tb(III) luminescence in the solution systems.

In this paper we will continue the studies, but luminescent materials are solid precipitate complexes rather than the solution complexes. The general formula of the solid complex phosphors is:

$$(Gd_{1-x}Eu_x)_2SA_3phen_2 \quad (x = 0.01\text{–}1)$$
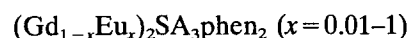
Here SA = succinic acid, phen = phenanthroline. The luminescence materials are precipitate complexes; the preparation method is simple differing from other inorganic phosphors, such as, YVO_4:Eu, $Y_3Al_5O_{12}$:Tb, *etc.* [11, 12]. In these phosphor systems, we will show that because of the intermediate role of Gd(III), the energy transfer to Eu(III), complete at fairly low Eu content, gives a great advantage for complex phosphors since the price of these are dominated by Eu content.

2. Experimental details

2.1. Methods of preparation of the complex phosphors

Europium and gadolinium chloride stock solutions were prepared by the methods described in ref. 8; the concentrations of the Eu(III) and Gd(III) stock solutions were 10^{-1} and 5×10^{-1} M, respectively. The stock solution (1.5 M) of SA was prepared by dissolving the SA-to-water solution of NaOH (SA/NaOH = 1/2), and the stock solution of phen was prepared by dissolving phen to 95% ethanol; the concentration of phen stock solution was 0.5 M. The reagents were analytical grade without further purification before use. Prototype reactions for the precipitation of $(Gd, Eu)_2SA_3phen_2$ complexes are shown in the following.

A mixture of an aqueous $(Gd, Eu)Cl_3$ solution and phen ethanol solution was slowly added in the sodium succinate solution at 75 °C, thus, a white crystalline precipitate was obtained and then separated by filtration, washed with deionized water, and thereafter dried at 90 °C for 5–10 h.

2.2. Apparatus

Fluorescence excitation and emission spectra were measured on a Hitachi MPF-4 spectrophotometer. The pH value of the solutions was determined on a PHS-255 pH meter. Phase identification of the powder sample

was achieved using a D/MAX-rA X-ray diffractometer employing CuKα radiation and operating at 40 kV and 15 mA. The infrared (IR) spectra of the samples in KBr pellet were recorded in the region of 4000–400 cm^{-1} with a Fourier transform IR spectrometer (Nicolt mode 7199B).

3. Results and discussion

The photoluminescence intensities of Eu(III) emission of the complexes under 365 nm excitation reached 90% of that of commercial YVO_4:Eu at $x = 0.01–1.0$ in formula $(Gd_{1-x}Eu_x)_2SA_3phen_2$ complexes. It was found that the relative fluorescence intensities of Eu(III) ion in the complexes depend considerably on the pH value during the precipitate reactions. When pH < 4 no luminescent precipitates were obtained; maximum fluorescent intensities for the precipitates were achieved when the pH of the reaction solutions were kept at 6–7. However, when pH = 4–5 the precipitates showed weak fluorescence intensities. The results were explained on the basis of two different dissociation constants ($pK_{a1} = 4.21$ and $pK_{a2} = 5.64$) [13]. That is, succinate ions have been known to form $^-OOC(CH_2)_2COO^-$ at pH 6; only one of the carboxylic groups dissociated and could coordinate with Ln(III) (Ln ≡ Gd or Eu) ions at pH 4–5. Thus an unsaturated chelate sphere may be formed in the latter; this was penetrated by small water molecules which lost excited energies of $^5D_0$ from the Eu(III) ions by O–H vibrations. However, two carboxylic groups on the two sides of the dicarboxylic acid were coordinated simultaneously with Ln(III) (Ln ≡ Gd or Eu) ions when pH = 6–7. The difference between the emission intensities of the precipitates obtained at the different pH values was presumably attributed to the different crystalline structure, as shown in Fig. 1 in which X-ray diffraction patterns of the two precipitates prepared at pH 4.5 and pH 6.5 for complexes are illustrated.
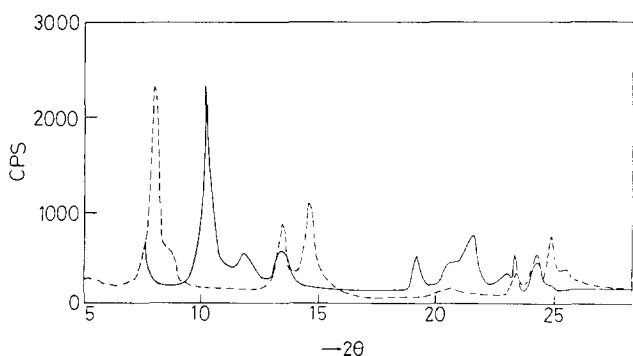
The molar ratio of (Gd, Eu)/SA/phen was 2/3/2 when used in the reactions. When phen was not added to the reaction solutions, the emission intensities of fluorescence for the precipitates were very weak for $(Gd_{0.0}Eu_{1.0})_2SA_3 \cdot H_2O$ ($Eu_2SA_3 \cdot H_2O$) and almost not obtained for $(Gd_{1-x}Eu_x)_2SA_3phen_2$ (0.01 ≤ x < 1.0). Figure 2 indicates the dependence of Eu content on the emission intensities of the red fluorescence for complex phosphors. It is seen from Fig. 2 that the relative intensities of the emissions of the phosphors are kept almost constant at 0.01 ≤ x < 1.0, and were slowly decreased with decreasing Eu content. Thus we can say that highly efficient phosphors were obtained with content which is much lower than the hitherto known simple Eu complex phosphors. On the other hand, the cost of dicarboxylic acid as chelating agent is much lower than that of fluorinated β-dichetone which has been known to produce chelates with highly efficient Eu fluorescence, such as Eu–TTA–phen (TTA = thenoyltrifluoroacetone) [14]. Moreover, the Eu–TTA–phen · complex is relatively unstable with time in the presence of atmospheric moisture, presumably due to hydrolysis and even the synergic agent (phen) complexes decompose on standing for long periods [15, 16]. It was also found that when the Eu was partly replaced by Gd in the Eu–TTA–phen solid complexes, the Eu-fluorescence was obviously reduced, which differs from the solution complexes of the systems [8].

As mentioned above, in our (Gd, Eu)$_2SA_3phen_2$ system the Ln(III) ion coordinates via three carboxylic groups of three succinates situated on one side of the dicarboxylates, that is, there will be six oxygen atoms around the Ln(III) ions; this is similar to Ln(III)–β-dichetone–phen [17]. However, Ln(III) ions prefer 7 or 8 (or 9) oxygen atoms in their coordinating sphere [18]. Since the aliphatic saturated hydrocarbon is attached by two carboxylic groups and has no unsaturated bond or aromatic ring, it has a weak ability to absorb
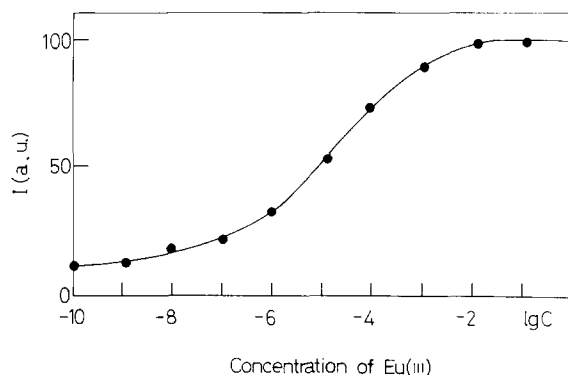

−2θ

Fig. 1. X-ray diffraction patterns of the precipitates prepared at pH 4.5 (‐ ‐ ‐) and pH 6 (——) for $Eu_2SA_3phen_2$ systems.

Concentration of Eu(ııı)

Fig. 2. The dependence of relative emission intensities of luminescence for the complex phosphors $(Gd_{1-x}Eu_x)_2SA_2phen_2$ (lg x = −10–0) on Eu content.

UV light energy at 200–400 nm. Phen has been known to be a bidentate heterocyclic ligand and the lowest triplet state is situated at 22,213 cm^{-1} [19]. Thus, the two nitrogen atoms from each of the phen molecules could coordinate with the Ln(III) (Gd or Eu) ions, as described for the Eu–TTA–phen system [17]. Therefore, many chelate cages around the Ln(III) ions were probably formed by six oxygen atoms and two nitrogen atoms; the chelate cages should be a large conjugated system to increase the rigidity of the chelate. Therefore, if the neutral ligand, phen, is not added to the (Gd, Eu)–succinic acid complexes, the red Eu emission would not be observed. The chelate cage as the chain element in the $(Gd_{1-x}Eu_x)_2SA_3phen_2$ molecule is shown schematically as:
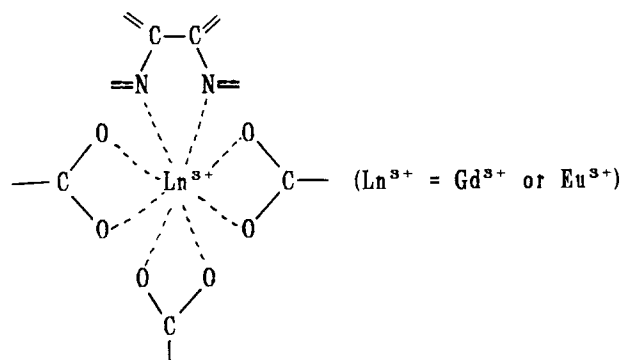
Now referring to Fig. 2, it can be seen that even when the Eu content was reduced to 0.01 molar fraction, high red emissions still remained constant, and that the emission intensities of the Eu fluorescence decreased with decreasing Eu content for the $(Gd_{1-x}Eu_x)_2SA_3phen_2$ complex phosphors. It indicates that there would be an intramolecular energy transfer from Gd–chelate cages to Eu–chelate cages in the complex molecule. The phen ligands act as both neutral bidentate ligand and an energy donor for the Ln(III) ions (Ln ≡ Gd or Eu). However, since the excited level, $^6P_{3/2}$ (32,000 cm^{-1}), of the Gd(III) ion is higher than the lowest excited triplet state (22,300 cm^{-1}) of the phen, the energy absorbed by $\pi^* \leftarrow \pi$ in the nitrogen heterocyclic ring could not be transferred to the Gd(III) ions but only to the Eu(III) ions. However, the Eu content is below the 0.01 molar fraction, and the red emission intensities slowly decrease with decreasing Eu content (see Fig. 2). It illustrates that the number of "luminescence centres" (energy acceptors) is decreased. The dependence on Eu content of the relative emission intensity of luminescence in the $(Gd_{1-x}Eu_x)_2SA_3phen_2$ system differs from other inorganic crystalline phosphors [20].

It is well known that there is concentration quenching in RE-activated inorganic phosphors. This is due to quenching the cluster of 3 or 4 Ln(III) (Ln ≡ Eu, Tb,

etc.) as the luminescence centre. However, "concentration quenching" was not observed, which perhaps supports our mode on the chain molecule structure.

Table 1 illustrates some IR spectrum data of $x = 0.01$, 0.1 and 1 in the $(Gd_{1-x}Eu_x)_2SA_3phen_2$ system. Under Table 1 we note that the asymmetric stretching vibration, $[\nu_{as}(COO)]$ and symmetric stretching vibration $[\nu_s(COO)]$ bands were only a little moved in the molar region of $x = 0.01–1$. The bands at 1588–1591 cm^{-1} and at 1423–1435 cm^{-1} are assignable to the stretching vibrations of $\nu_{as}(COO)$ and $\nu_s(COO)$, respectively (see Table 1), and the vibration bands replaced the two characteristic bands of carboxylic acid, $\nu_{OH}(35,000\,cm^{-1})$ and $\nu_{C=O}(2500–3000\,cm^{-1})$ [21]. So it was suggested that the coordinate bond was formed between $-COO^-$ groups and Ln(III) (Ln ≡ Gd or/and Eu) ions in these compounds, and the structure of the compounds at $x = 0.01–1$ in $(Gd_{1-x}Eu_x)_2SA_3phen_2$ complex phosphors was similar, which is evident by the analyses of X-ray diffraction patterns (see Fig. 3). It is seen from Fig. 3 that the diffraction lines have similar intensities at the same diffraction angle for $Gd_2SA_3phen_2$ ($x = 0$), $(Gd_{0.9}Eu_{0.1})_2SA_3phen_2$ ($x = 0.1$) and $(Gd_0Eu_1)_2SA_3phen_2$ ($x = 1$) in $(Gd_{1-x}Eu_x)_2SA_3phen_2$ systems.

Figure 4 shows the excitation and emission spectra of the luminescence of the $(Gd_{0.99}Eu_{0.01})_2SA_3phen_2$ and $(Gd_0Eu_1)_2SA_3phen_2$ phosphors. The emission peaks of 595 nm, 615 nm and 695 nm are assignable to the electron transitions between $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_4$, the excitation bands caused by electron transition between $\pi^* \leftarrow \pi$ of the complexes which is a wide band. This indicates that the Eu(III) emissions are caused by the energy transfer from chelating rings formed by the nitrogen heterocyclic ligand (phen) and the three carboxylic groups in the complex system. Therefore, from the IR spectra, X-ray diffraction patterns and fluorescence excitation and emission spectra, it is presumed that the $(Gd_{1-x}Eu_x)_2SA_3phen_2$ compounds should possess a chain structure, as illustrated in Fig. 5, in which Gd(III) and Eu(III) ions seem to be distributed randomly at the chelating cages attached to the alkyl chain. It would appear that the molecular rigidity of the chelate could be increased if the complex has a chain structure. The highly efficient luminescence at low Eu content was attributed to intramolecular

TABLE 1. Some IR spectrum data of $(Gd_{1-x}Eu_x)_2SA_3phen_2$ ($x = 0.01$, 0.1 and 1.0)

No.	Sample	as(COO) (cm^{-1})	s(COO) (cm^{-1})
1	$(Gd_{0.99}Eu_{0.01})_2SA_3phen_2$	1591	1423
2	$(Gd_{0.90}Eu_{0.10})_2SA_3phen_2$	1593	1427
3	(Eu_2SA_3phen) $(Gd_{0.00}Eu_{1.00})_2SA_3phen_2$	1588	1435
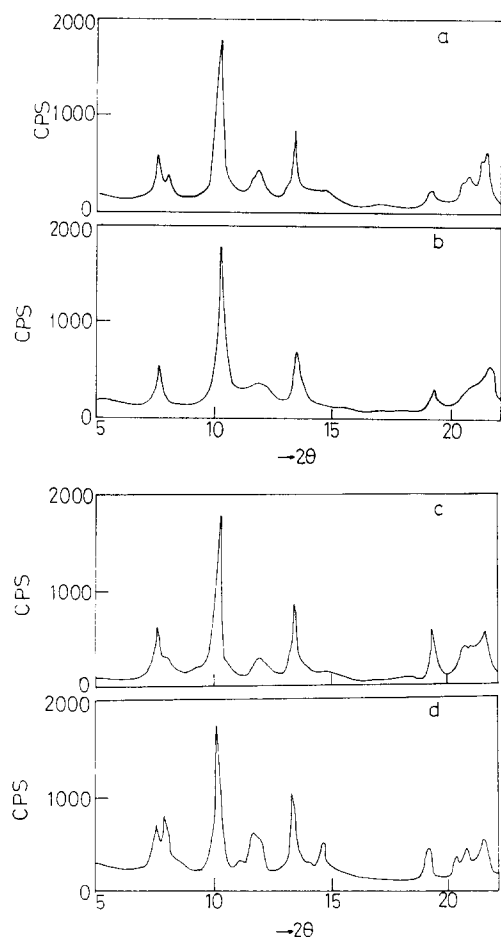
Fig. 3. X-ray diffraction patterns of $(Gd_{0.70}Eu_{0.30})_2SA_3phen_2$ (a), $(Gd_{0.90}Eu_{0.10})_2SA_3phen_2$ (b), $(Gd_{0.99}Eu_{0.01})_2SA_3phen_2$ (c) and $(Gd_{1.00}Eu_{0.00})_2SA_3phen_2$ (d).
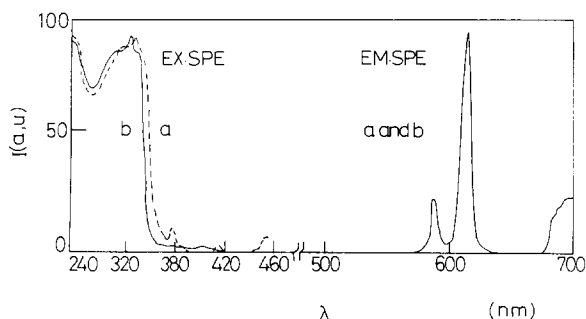

Fig. 4. The excitation and emission spectra of the fluorescence for $(Gd_{0.99}Eu_{0.01})_2SA_3phen_2$ (b) and $Eu_2SA_3phen_2$ (a) complex phosphors.

energy transfer from Gd-chelating cage to Eu(III) although the Eu(III) ions were also directly excited by the energy absorbed by the phen ligand. The transfer would be through the alkyl chain in the complex molecule; this will be the subject of further investigation.
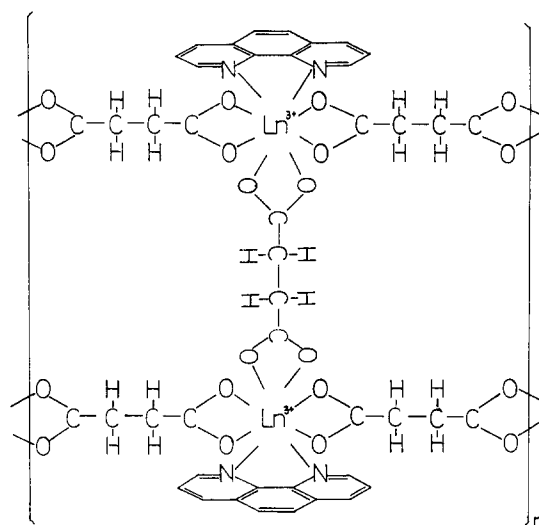

Fig. 5. Schematic representation of the chain structure of the $(Gd, Eu)_2SA_3phen_2$ solid complex phosphors. $Ln^{3+}:Gd^{3+}$ or Eu^{3+}.

4. Summary

In the studies presented, we have obtained excellent complex phosphors which are much cheaper than simple Eu complex fluorescent materials. Our data indicate that the new complex phosphors have a chain structure. The involvement of Gd(III) in the energy transfer will open up new possibilities for the development of new luminescent materials.

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