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Letter

Color-tunable and white-light emitting lanthanide complexes based on $(Ce_xEu_yTb_{1-x-y})_2(BDC)_3(H_2O)_4$

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ABSTRACT

Ce^{3+}, Eu^{3+} and Tb^{3+} complexes were synthesized through facile and mild approaches with terephthalic acid (H_2BDC) as the ligand. Their chemical compositions were determined as $(Ce_xEu_yTb_{1-x-y})_2(BDC)_3(H_2O)_4$ by elemental analysis (EA), Fourier transform infrared (FTIR) spectra and X-ray diffraction (XRD) measurements. Fluorescent properties of the as-synthesized complexes were investigated by changing the molar ratio of Ce^{3+}, Tb^{3+} and Eu^{3+} ions, and the optimized ratio of 3.0:2.0:0.15 for Ce^{3+}:Tb^{3+}:Eu^{3+} in the complex was determined for white-light emission. Tuning on the emitting color was realized by adjusting the ratio among lanthanide ions, indicating the energy transfer process inside the complex. It was found that Tb^{3+} could sensitize the fluorescence of Eu^{3+} while its own fluorescence was quenched by the latter ion, and concentration quenching of Ce^{3+} was also observed. Fairly good thermal stability and oxidation resistance of the as-synthesized complexes were also demonstrated.

1. Introduction

In recent years, white-light emitting materials have attracted much research interests due to their extensive applications in various areas such as panel display, imaging, illumination and so on [1–3]. Currently, the most commonly employed white-light emitting fluorescent materials were the inorganic salt and/or oxide doped with rare earth or transition metal ions [4–7], while white-light emission from organic molecules have also been reported [8–11]. Besides these materials, lanthanide complexes, composed of lanthanide ions and organic ligands by coordination bonds or hydrogen-bonds, and π–π interactions as one kind of coordination polymers [12], have been applied in various fields such as displays, illumination, biomedicine, agriculture and military [13–15] due to their features including the high quantum efficiency and brightness, good color purity, and long fluorescence lifetime.

In comparison with other traditional white-light emitting materials, lanthanide complexes have some unique advantages. Theoretically, the choices on organic ligands of lanthanide complexes could be unlimited due to the numerous diversities of organic molecules and capabilities of lanthanide complexes in the fields of bio markers, small molecule detection, and gas separation could also be realized by changing the ligands. On the other hand, their inorganic salt/oxide counterparts have relatively simpler structures and thereby the possibility for significant performance improvement was low and capabilities such as the bio markers mentioned above were also not available.

It was suggested that the white-light emission spectra from the materials were preferred to be composed of various narrow-band emission in cases where the color purity of red, green and blue (RGB) emission was also required, respectively beside the need for white-light [16]. Due to the well-known "Antenna effect", lanthanide complexes emitted the characteristic line spectra according to the specific transition of each lanthanide ion, while the traditional white-light emitting materials especially the organic molecules could only obtain broad-band emission [16,17]. Up to now, the white-light emitting lanthanide complexes have been rarely reported, to the best of our knowledge [18,19].

Herein, we reported the synthesis and characterization of white-light emitting lanthanide complexes based on Ce^{3+}, Eu^{3+} and Tb^{3+} with H_2BDC as the organic ligand. Color-tuning on the emission from the lanthanide terephthalate complexes was demonstrated and the energy transfer mechanism involved was discussed.

2. Experimental

2.1. Materials and methods

The commercially available terbium(III) nitrate pentahydrate (99.99%), europium(III) nitrate hexahydrate (99.99%), cerium(III) nitrate hexahydrate (99.99%) and H_2BDC (99%) were used as received, without further purification.

The FTIR spectra were measured with a Nicolet Thermo Scientific Nicolet iS10 spectrometer. Absorption bands then were labeled as follows: strong (s), medium (m), and weak (w). Photoluminescence (PL) spectra were obtained with an Hitachi F4500 spectrophotometer and powder X-ray diffraction (PXRD) data were recorded by a PANalyticalr X'Pert PRO diffractometer at 40 kV, 25 mA for Cu Kα (λ = 1.541 Å).

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Thermo gravimetric analysis (TGA) was carried out in a N_2 atmosphere at a scan speed of 10 °C/min on a Netzsch TG209 F3 system, and EA was carried out on a Thermo Finnigan Flash EA1112 system.

2.2. Preparation of lanthanide complexes

The $Eu_2(NO_3)_3{\cdot}6H_2O$, $Ce_2(NO_3)_3{\cdot}6H_2O$ and $Tb_2(NO_3)_3{\cdot}5H_2O$ water solutions were mixed in appropriate ratio to obtain the 0.1 M water solutions. H_2BDC was mixed with NaOH (twice molar amount of H_2BDC) to produce 0.1 M Na_2BDC water solution. The prepared solutions with the corresponding molar ratio (M^{3+}:BDC^{2-} = 2:3) were mixed and stirred in water bath at 60 °C for 1 h. After the cooling down of the mixtures to room temperature, the precipitates were washed with deionized water for 3 times and dried at 60 °C for 12 h in a vacuum oven to yield white powder (yield: 90%), which were stable in air and insoluble in water and common organic solvents such as ethanol, acetone, tetrahydrofuran, 1,2-dichloroethane and DMF. The emission from the as-synthesized lanthanide complexes was observed under the excitation of a 315 nm UV lamp. As the contrast, complexes containing only one kind of lanthanide ion were also synthesized and pure bright purple, green, and red emitting color of the Ce^{3+}, Tb^{3+} and Eu^{3+} ions under the UV lamp was observed, respectively.

3. Results and discussion

The FTIR spectra of all the complexes with various concentrations of Ce^{3+}, Eu^{3+} and Tb^{3+} were similar, in which the absorption bands at (cm^{-1}): 3454 (s), 1609 (w), 1684 (m), 1537 (s), 1507 (s), 1417 (s), 1312 (w), 1156 (w), 1100 (w), 1020 (w), 884 (w), 826 (w), 760 (m), 751 (m) and 510 (m) could be observed. The broad band centered at 3454 cm^{-1} (ν_{O-H}) was attributed to coordinated waters among which hydrogen bonds exist [20]. The $\nu_{C=O}$ stretching mode of BDC shifted to lower wave numbers 1609 cm^{-1} in comparison with that of the free BDC molecule (1679 cm^{-1}), indicating that ligation of BDC molecules by the carbonyl groups [20]. The absence of absorptions at 1690–1730 cm^{-1} indicated the complete deprotonation of carboxyl groups in products. The strong absorption bands at 1417 and 1537 cm^{-1} could be ascribed to the carbonyl groups of BDC, suggesting the carboxyl group to be bridge coordination mainly. PXRD patterns of all the complexes synthesized with various Ce^{3+}, Eu^{3+} and Tb^{3+} ratios were consistent with previous reports [19], indicating that the lanthanide complexes were isostructural, and the chemical compositions were determined as $(Ce_xEu_yTb_{1-x-y})_2(BDC)_3(H_2O)_4$, which were also confirmed by the results of EA. High agreement between the experimental and calculated data were found from the EA results (Experiment/Calculated) for $Ce_2(BDC)_3(H_2O)_4$: C, 33.45/33.96; H, 2.26/2.59; for $Tb_2(BDC)_3(H_2O)_4$: C, 32.38/32.65; H, 2.17/2.27; and for $Eu_2(BDC)_3(H_2O)_4$: C, 32.77/33.18; H, 2.22/2.30.

The thermal properties of the as-synthesized lanthanide complexes were investigated by the TGA experiment in which a weight loss of four coordinated water molecules at about 120 °C could be observed in all cases. For convenient calculation, the weight losses (Experiment/Calculated) of the three complexes containing only one kind of lanthanide ion, $Tb_2(BDC)_3(H_2O)_4$, $Eu_2(BDC)_3(H_2O)_4$ and $Ce_2(BDC)_3(H_2O)_4$ which were used as the reference samples, were compared and found to be 7.79%/8.16%, 8.34%/8.29% and 8.84%/8.49%, respectively. The decomposition temperature of the complexes was found to be above 400 °C, indicating a good thermal stability of these complexes. The PXRD patterns of $(Ce_{0.583}Eu_{0.029}Tb_{0.388})_2(BDC)_3(H_2O)_4$ before and after thermal treatment at 250 °C for 1 h in an air atmosphere were shown in Fig. 1, from which the intact crystal structure after heat treatment in air could be found and fairly good oxidation resistance of the complexes could be claimed.

Under the excitation by the UV lamp, the PL spectra of complexes with various lanthanide ions concentrations were systematically investigated and close to white-light emission was observed in some cases. In the PL spectra of the complexes containing only one kind of lanthanide ion, $Tb_2(BDC)_3(H_2O)_4$, $Eu_2(BDC)_3(H_2O)_4$ and $Ce_2(BDC)_3(H_2O)_4$, only the characteristic emission bands of each lanthanide ion were found without the broad-band emission of ligands, indicating the pure light colors and efficient energy transfer from the lowest triplet state of the ligands to excited states of the lanthanide ions [21–24]. The PL intensity of Tb^{3+} was found to be the highest among the three kinds of ions, followed by Eu^{3+} and Ce^{3+} (the weakest), indicating the best match between the $^5D_4$ energy level of Tb^{3+} and the lowest triplet state of the ligands. Thus, color tuning and white-light emissions were possible by adjusting the ion concentrations before the synthesis reaction. For white-light emission, the optimized ratio of Ce^{3+}:Tb^{3+}:Eu^{3+} in the complex was determined to be 3.0:2.0:0.15. Color tuning on the emission light was realized by adjusting the ion concentrations continuously around the optimized ratio.

As shown in Fig. 2, the PL spectra of the complexes with molar ratios of Ce^{3+}:Tb^{3+}:Eu^{3+} as 3.0:*x*:0.15, where *x* varied from 0 to 3.0 were obtained together with the images of emitting colors at each composition. The strong emission lines centered at 490, 545

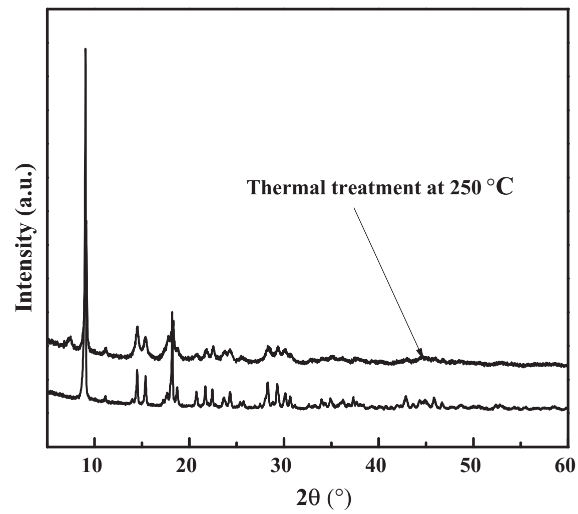

Fig. 1. PXRD patterns of $(Ce_{0.583}Eu_{0.029}Tb_{0.388})_2(BDC)_3(H_2O)_4$ before and after thermal treatment at 250 °C.

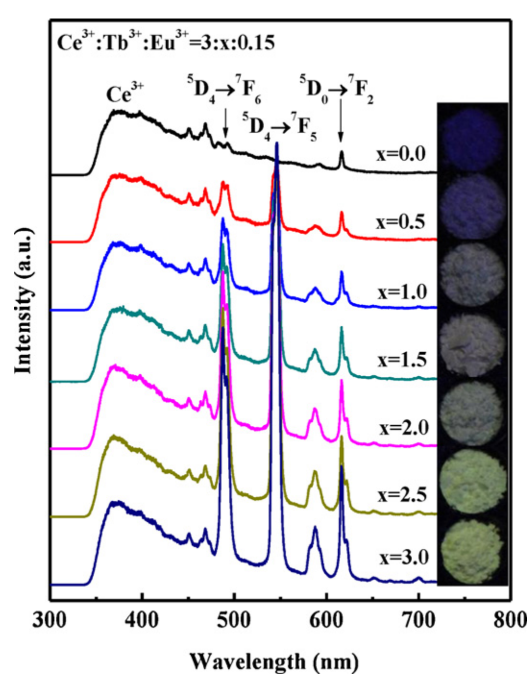

Fig. 2. Dependence of PL profiles and colors on Tb^{3+} concentrations.

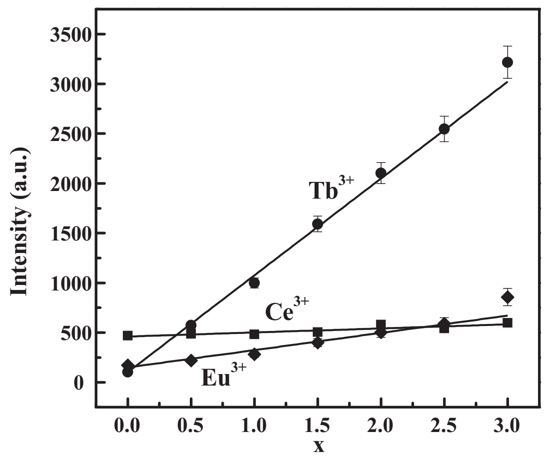

Fig. 3. Dependence of PL intensity of lanthanide ions on Tb^{3+} concentrations.

and 616 nm could be ascribed to the transitions $^5D_4 \rightarrow {}^7F_6$ and $^5D_4 \rightarrow {}^7F_5$ of Tb^{3+}, and $^5D_0 \rightarrow {}^7F_2$ of Eu^{3+}, respectively. The peak at about 590 nm resulted from the superposition of the transition of $^5D_4 \rightarrow {}^7F_4$ of Tb^{3+} and $^5D_0 \rightarrow {}^7F_1$ of Eu^{3+}. There might be some splits in the emission lines, which were due to the splitting of crystal field caused by lanthanide ions with different coordination environments [25,26]. The purple broad-band emission could be ascribed to the $^2D_{3/2} \rightarrow {}^2F_{5/2}$ and $^2D_{3/2} \rightarrow {}^2F_{7/2}$ transitions of Ce^{3+}. At a low concentration and temperature, the two peaks in the spectra of Ce^{3+} were caused by transitions from the lowest 5d level to the two spin-orbit split ground states, $^2F_{5/2}$ and $^2F_{7/2}$. However, with the increase on the Ce^{3+} concentration, the emission bands broadened due to the energy transfer among the Ce^{3+} ions which was much more prominent at higher temperature [27–31].

The dependence of PL intensities of Ce^{3+}, Eu^{3+} and Tb^{3+} on the Tb^{3+} concentration was shown in Fig. 3, in which the peak PL intensities of each ion were recorded. The intensity of green emission by Tb^{3+} enhanced with the increase on Tb^{3+} concentration. Meanwhile, the intensity of red emission by Eu^{3+} enhanced also, indicating an energy transfer from Tb^{3+} to Eu^{3+} in the complexes. Almost no change on the intensity of purple emission by Ce^{3+} was observed, indicating that there was no energy transfer between Ce^{3+} and Tb^{3+} or Eu^{3+}, which simplified the design on tuning the emission colors.

As shown in Fig. 4, the PL spectra of the complexes with molar ratios of Ce^{3+}:Tb^{3+}:Eu^{3+} as 3.0:2.0:x, where x varied from 0.03 to 0.24, together with the images of emitting colors at each composition were obtained. The dependence of PL intensities of three ions on the Eu^{3+} concentration was shown in Fig. 5. Good agreement with the above theory was observed, from which an enhanced red emission, decreased green emission and almost unchanged purple emission were predicted with the increase of the Eu^{3+} concentration. The decrease of green emission was caused by the reduction of Tb^{3+} concentrations and quenching by the increasing Eu^{3+} concentration.

As shown in Fig. 6, the energy transfer mechanism was concluded based on the above results. Due to the effective energy transfers between ligands and ions, there was only non-radiative transition in BDC [21,22]. The energy transfer from Tb^{3+} to Eu^{3+} was observed, while energy transfer between Ce^{3+} and Tb^{3+} or Eu^{3+} might not happen.

Thus, the tuning on the emission colors by changing the lanthanide ions concentrations could be explained and predicted based on the energy transfer mechanism shown in Fig. 6. Photographs of emission colors evolution with the Tb^{3+} and Eu^{3+} concentrations were shown in Figs. 2 and 4. In case that the

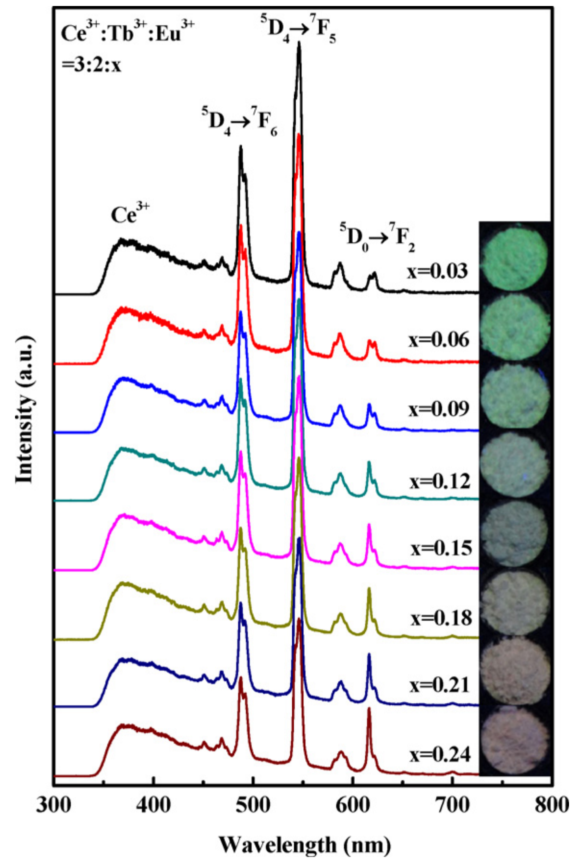

Fig. 4. Dependence of PL profiles and colors on Eu^{3+} concentrations.

Tb^{3+} concentration was taken as a variable, the colors shifted directly from purple towards yellow with increasing concentration of Tb^{3+}. It was resulted from that the increasing Tb^{3+} concentrations enhanced green and red without changing purple emission. Similarly, the colors changed from green to red with increasing Eu^{3+}, which were caused by the enhanced red and quenched green simultaneously by increasing Eu^{3+} concentrations. The same fact illustrated in these two figures showed that the colors fall in white region with the ratio of Ce^{3+}:Tb^{3+}:Eu^{3+} to be 3.0:2.0:0.15, and the composition is $(Ce_{0.583}Eu_{0.029}Tb_{0.388})_2(BDC)_3(H_2O)_4$.

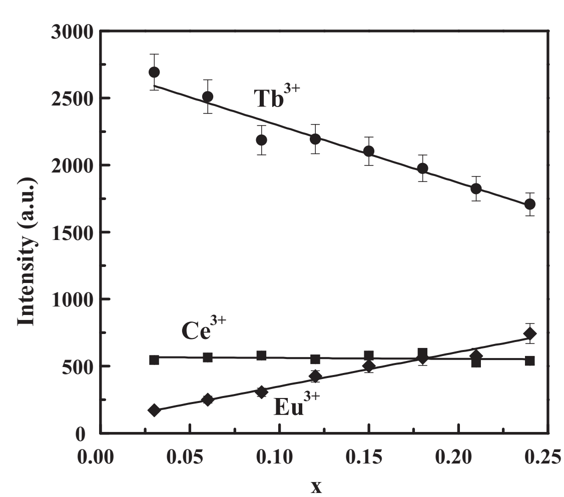

Fig. 5. Dependence of PL intensity of lanthanide ions on Eu^{3+} concentrations.

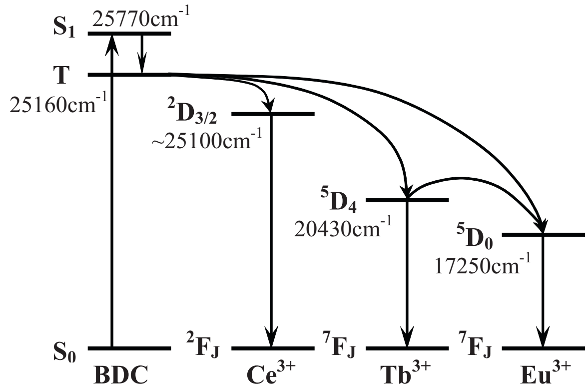

Fig. 6. Energy transfer scheme in $(Ce_xEu_yTb_{1-x-y})_2(BDC)_3(H_2O)_4$.

4. Conclusions

In summary, a serial of lanthanide terephthalate complexes with various lanthanide ions concentrations were synthesized, which showed white-light emission and good tunability on emitting colors under UV excitation. The optimized composition for white-light emission was determined to be $(Ce_{0.583}Eu_{0.029}Tb_{0.388})_2(BDC)_3(H_2O)_4$, and color tuning within or around the white region was realized and predicted by the materials compositions. Fairly good thermal stability and oxidation resistance were also observed for the complexes.

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