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Preparation and Luminescence Properties of Europium(III) and Tungstate Co-doped in Silicate Materials *via* The Sol-Gel Method

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In the preparation of this precursor tetraethylortho silicate (TEOS), sodium tungstate, ethyl alcohol and HCl were mixed and then heated at different temperatures for 3 h, leading to a luminescent compound. TG-DTA and IR show the stable and network structure of luminescence material. The three-dimension fluorescence spectra, excitation and emission spectra were used to characterize the luminescence properties of Eu^{3+} doped silica materials. The results indicate that the luminescence materials were excited by $^7F_0 \rightarrow {}^5L_6$ transition of Eu^{3+} at 393 nn and the bands in the emission spectrum are corresponding to the $^5D_0 \rightarrow {}^7F_J$ (J = 0, 1, 2) transitions of europium ion. The strongest band is the electronic dipole transition and the material in green lights. Furthermore, we found that WO_4^{2-} absorbed most of the energy and transferred to rare earth ion Eu^{3+} effectively. The effect of WO_4^{2-} on the glass network and neighbouring configuration of Eu^{3+} is discussed based on the optical spectra. The f-f transitions of the materials were interpreted by energy level of the luminescence materials. In this paper, we have also investigated the influence of tungstate content and annealing temperature in europium doped silicate materials on luminescence properties. Finally, the doped agent WO_4^{2-} sensitized the luminescence intensity of rare earth Eu^{3+} more than 6 times when doped quantity is up to 3.26 %.

Key Words: Sol-gel, Europium(III), Tungstate, Silicate materials, Luminescent properties.

INTRODUCTION

The research on inorganic luminescent materials containing trivalent rare earth ions (RE^{3+}) has increased considerably in recent years[1-4]. In many cases, rare earth phosphors noticeably improved the performance of the devices. Glass host material is a very important factor for developing rare-earth-doped optical devices. RE-doped glasses, therefore, play an important role for optical applications such as glass lasers, lamps and optical fiber amplifiers and also hold promise for photochemical hole-burning memory, flat-panel display, *etc*. Up to now, silicon dioxide glasses are

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more suitable for practical applications due to their high chemical durabilities and thermal stabilities[5]. Europium ion has great advantages on luminescence properties in rare earth ions, because it has non-degenerate ground and emitting states and the hypersensitive $^6D_0 \rightarrow ^7F_2$ red transition. The sol-gel method provides a convenient method for synthesizing the novel luminescence materials, due to the low temperature conditions, low cost and versatility of sol-gel processing[6-9]. However the key problems associated with the phosphors are photodecomposition and luminescence quenching. So it is of great interest to explore alternative co-doped ions for applications in optical sources. Therefore, in this paper, the Eu^{3+} ion and Na_2WO_4 doped silicate glasses were prepared by the sol-gel method and the influence of tungstate content and annealing temperature on luminescence properties were investigated.

EXPERIMENTAL

Preparation of Eu^{3+} and tungstate doped SiO_2 materials: The materials were prepared by sol-gel method. The starting materials were tetraethylorthosilicate (TEOS), tungstate sodium, Eu_2O_3 (99.99 %), ethyl alcohol and HCl (0.10 mol/L). The Na_2WO_4 solution was dissolved in deionized water. $EuCl_3$ were obtained by dissolve Eu_2O_3 in HCl and deionized water. The TEOS was first hydrolyzed at room temperature with a mixed solution of H_2O, C_2H_5OH and HCl. Then Na_2WO_4 and $EuCl_3$ were added to this solution under stirring for 0.5 h. The adding proportions of the materials are shown in Table-1.

TABLE-1
PROPORTION OF THE SOLUTION IN RARE EARTH DOPED SiO_2 MATERIALS

No.	1	2	3	4	5	6	7	8	9
TEOS (mL)	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
0.1 mol/L $EuCl_3$ (mL)	0.5	0.0	0.5	0.5	0.5	0.5	0.5	0.5	0.5
CH_3CH_2OH (mL)	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
0.1 mol/L HCl (mL)	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
0.1 mol/L Na_2WO_4 (mL)	0.0	0.5	0.2	0.6	1.0	1.4	1.8	2.2	2.6
Redistilled water (mL)	4.5	4.5	4.3	3.9	3.5	3.1	2.7	2.3	1.9

The gels were annealed at 25, 200, 400, 600, 800 ºC for 3 h, respectively. Sample 1 is with Eu^{3+} ion only, while sample 2 is with WO_4^{2-} only and sample 3 is co-doped with Eu^{3+} ion and WO_4^{2-}. The other samples are for investigate the effect of the WO_4^{2-} to the luminescence properties of the samples.

Thermogravimetry (TG) and differential thermal analysis (DTA) curves were obtained with a comprehensive hot analyzer (ZRY-1P), using platinum crucibles with 2.1 mg of the materials, under a continuous nitrogen flow(40 mL/min), at a heating rate of 10 ºC/min. The IR absorption spectra of materials were measured with a Nicolet fourier transform spectrophotometer (Model PE-M1730) using the KBr pellet technique, scan 32 times. The XRD patterns from 10º to 90º (2θ) were recorded on a X-ray diffractometer (D8-ADVANCE model) with CuKα (40 KV and 40 mA) for the materials. The emission and excitation spectra of the materials were obtained on a F-4500 fluorescence spectrophotometer with 5.0 nm excitation and emission slit and a 150 W xenon lamp as an excitation source (scan speed 240 nm/min). All measurements were performed at room temperature.

RESULTS AND DISCUSSION

In order to investigate the effect of annealing temperature to the structure of the materials, the results of thermogravimetry (TG) and differential thermal analysis (DTA) were as shown in Fig. 1. The TG curve shows that the weight lost of 51.9 %, in the temperature interval from 25 to 180 ºC, was associated with water loss and the decomposition of the organic constituents, correspondingly the DTA curve showed obvious endothermic band peak at the same temperature range. The weight lost during 180 to 500 ºC, is related to the loss of hydroxyl groups and coordination water. In the temperature interval from 500 to 800 ºC no weight loss was observed (Fig. 1), therefore, the precursor was stable above 500 ºC.

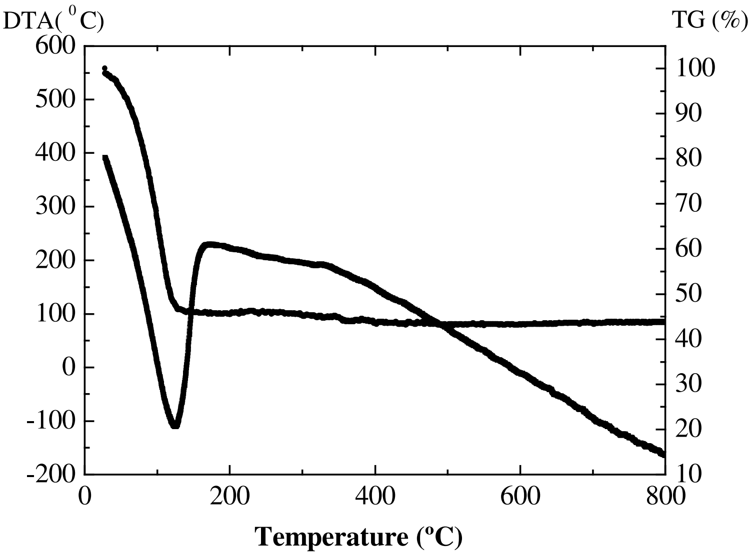

Fig. 1. TG-DTA curves of the materials in nitrogen atmosphere

Fig. 2 shows IR spectra of Eu^{3+} doped SiO_2 gel and glass annealed at 800 ºC for 3 h. It is concluded that all vibration of Si-O-Si and O-Si-O exist in the materials at 1080 and 467 cm^{-1}, indicating that Si-O-Si and O-Si-O are the main structures and do not vary with doping of the tungstate sodium. The band at 832 cm^{-1} is corresponding to the bending vibration of Na_2WO_4. These results suggest that doping Na_2WO_4 doesn't destroy the net structure of SiO_2. XRD patterns indicate that the materials were in amorphous phase.

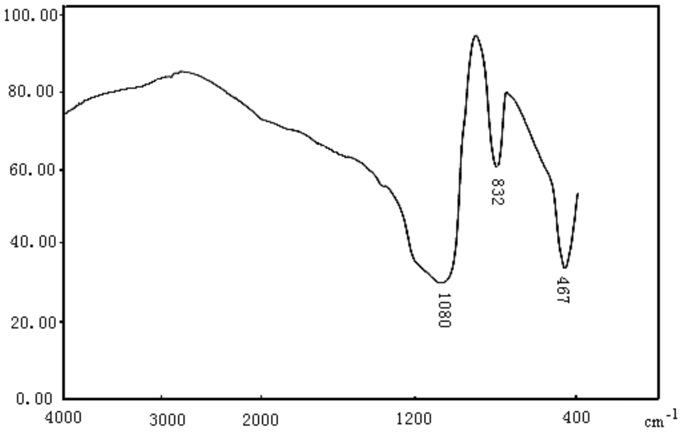

Fig. 2. IR spectrum of the material

Luminescence properties of the materials: Fig. 3 shows the three-dimension fluorescence spectrum of Eu^{3+} doped SiO_2 materials. It is clear to find that there are two strong points which indicate to WO_4^{2-} and Eu^{3+} excitation band (Fig. 3).

Fig. 4 shows the three-dimension fluorescence spectrum of Eu^{3+} and Na_2WO_4 co-doped SiO_2 materials. From the comparison, it is found that the characteristic transition of Eu^{3+} at 612 nm strengthen remarkably. It means the co-doped material WO_4^{2-} sensitized the luminescence intensity of rare earth ion europium.

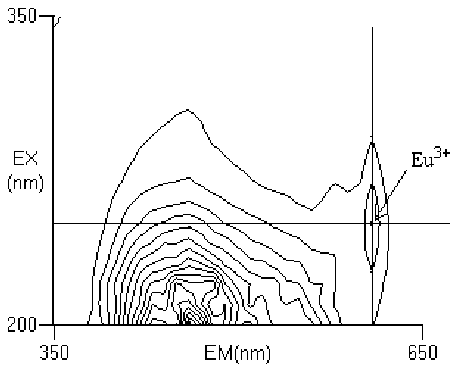

Fig. 3. Three-dimension fluorescence spectrum of Eu^{3+} doped sample

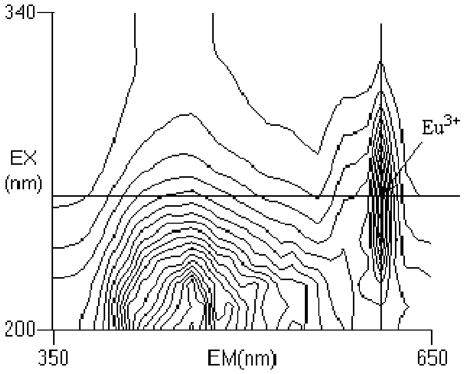

Fig. 4. Three-dimension fluorescence spectrum of Eu^{3+} and Na_2WO_4 co-doped material

Fig. 5 shows the excitation spectrum of Eu^{3+} and Na_2WO_4 co-doped SiO_2 materials under emission of 612 nm, where the excitation band has a broad band in the short ultraviolet region is corresponding to O→W charge transfer state (Table-2). The f-f transitions within $4f^6$ configuration in longer spectral region, with $^7F_0 \rightarrow {}^5L_6$ as the most prominent group, the sharp lines consistent with the $^7F_J \rightarrow {}^5D_J$ (J = 0, 2 and J' = 0-7) transition of Eu^{3+} ion is shown exactly in Table-2. The O→W charge transfer

TABLE-2
TRANSITION ENERGY AND INTENSITY OF THE MATERIALS OBSERVED IN THE EXCITATION SPECTRA

Transition	Wavelength (nm)	Intensity (arb. unit)
$O \rightarrow W$	278	1325.0
$O \rightarrow {}^5L_3$	317	478.1
${}^7F_0 \rightarrow {}^5D_4$	360	291.0
${}^7F_0 \rightarrow {}^5L_7,{}^5G_2$	380	608.2
${}^7F_0 \rightarrow {}^5L_6$	393	1398.0
${}^7F_0 \rightarrow {}^5D_3$	412	243.0
${}^7F_0 \rightarrow {}^5D_2$	463	1038.0
${}^7F_0 \rightarrow {}^5D_1$	530	534.2
${}^7F_2 \rightarrow {}^5D_{1m}$	555	491.3
${}^7F_0 \rightarrow {}^5D_{0m}$	581	827.6

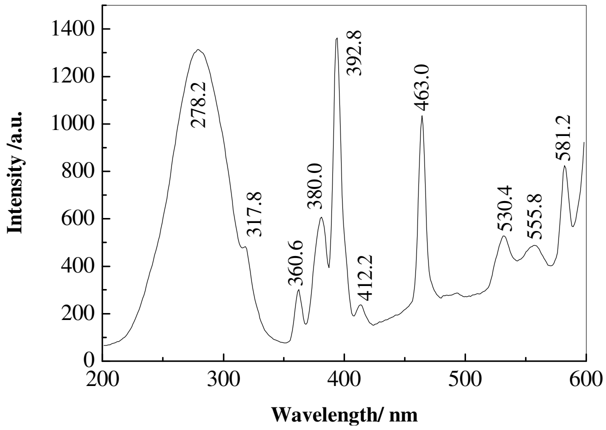

Fig. 5. Excitation spectrum of the materials monitored at 612 nm at room temperature

band has a half width of 60 nm and a maximum at 278 nm. However, O-Eu^{3+} charge transfer state is overlap with O-W charge transfer state observed around 260 nm. From the broad strong band at 278 nm it is found that the great quantity of energy get to the O-W charge transfer state, therefore, doping Na_2WO_4 influence the luminescence intensity of the luminescence materials remarkably.

The emission spectra obtained by excitation into the ${}^7F_0 \rightarrow {}^5L_6$ transition of Eu^{3+} ion at 393 nm are composed of ${}^5D_0 \rightarrow {}^7F_J$ (J = 0, 1, 2, 3, 4) emission lines of Eu^{3+} ion. However, the emission spectrum is dominated by the ${}^5D_0 \rightarrow {}^7F_2$ (612 nm) electric-dipole transition accompanied by the presence of ${}^5D_0 \rightarrow {}^7F_0$ transition at 577 nm, indicating that most of the Eu^{3+} ions are located at sites without inversion symmetry. All the other bands at 588, 651 and 701 nm are corresponding to the characteristic transition of ${}^5D_0 \rightarrow {}^7F_1$, ${}^5D_0 \rightarrow {}^7F_3$ and ${}^5D_0 \rightarrow {}^7F_4$, respectively. The electric-dipole transition ${}^5D_0 \rightarrow {}^7F_2$ (612 nm) is stronger than magnetic-dipole transition ${}^5D_0 \rightarrow {}^7F_1$ (588 nm), which is indicating that Eu^{3+} ions are located at sites without inversion symmetry, again. Based on the number of bands corresponding to the $^5D_0 \rightarrow {}^7F_0$ transition observed around 577 nm (Fig. 6) the presence of only one peak suggests the existence of one local site symmetry for the Eu^{3+} ion chemical environment. When Eu^{3+} and Na_2WO_4 co-doped SiO_2 material is irradiated with ultraviolet light, the material has a red luminescence were observed clearly. All the transition observed in the luminescence spectrum start from the $^5D_0$ level, which is populated by radiationless deactivation of the $^5L_6$ level. The most intense transition is the hypersensitive transition $^5D_0 \rightarrow {}^7F_2$ transition at 612 nm. A careful analysis of the emission spectrum in Fig. 7(b and c)

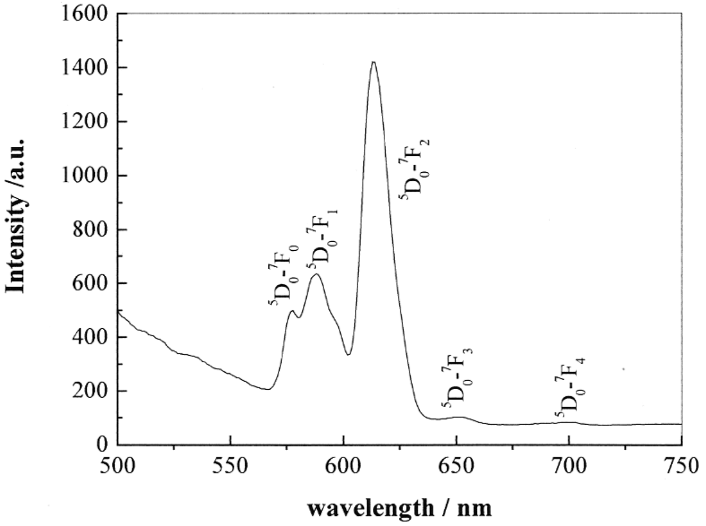

Fig. 6. Emission spectrum of the materials excitation monitored at 393 nm at room temperature

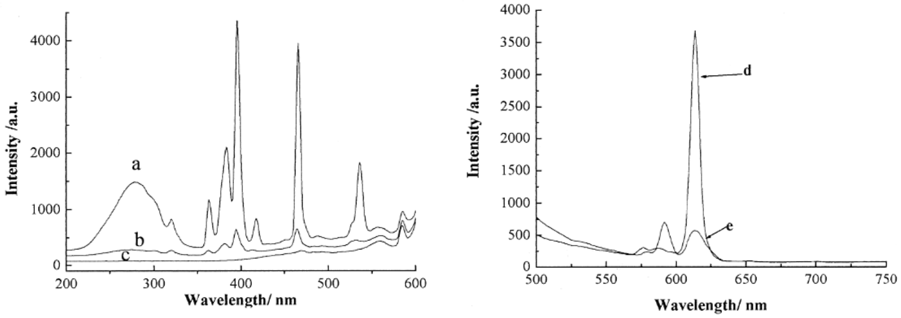

Fig. 7. Excitation and emission spectra of the luminescence materials monitored at λ_{em} = 612 nm and λ_{ex} = 393 nm, respectively, (a) and (d) Eu^{3+} and W co-doped materials (b) and (e) only Eu^{3+} doped materials (c) only W doped materials

reveals the absence of the broad band assigned to the O-W charge transfer state at 278 nm in Fig. 7(c). From the Fig. 7(a and b) indicate that doping WO_4^{2-} sensitized the transition of rare earth Eu^{3+} ion dramatically. The luminescence spectrum in Fig. 7 also displays the most intense emission band assigned to the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition. From the comparison of Fig. 7 d and e, the luminescence intensity of $^5D_0 \rightarrow {}^7F_2$ transition at 612 nm increase more than 6 times. It is reveal the sensitive effect of WO_4^{2-} to Eu^{3+} ion, again.

It is important to study the influence of the tungstate anion on the europium luminescence behaviour by energy absorption and transfer between the W^{6+} to $^5D_0$ emitting level. In order to interpret the Na_2WO_4 effects on the luminescence behaviour, the energy level was obtained as shown in Fig. 8. From the excitation spectrum (Table-2), it is find that there is a broad band of O-W and O-Eu^{3+} ligand to metal charge transfer state, which indicate partly energy transfer to W^{6+} ion, considering that the energy transfer from O-W charge transfer state to 4f state of Eu^{3+} ion. The energy level indicate the non-radiative process between the emitting state of W^{6+} and emitting state of Eu^{3+} ion, at the excitation of 393 nm.Then the energy transfer from the higher emitting level to the first emitting level ($^5D_0$) in resonance relaxation process. This indicates that the tungstate group transfers energy efficiently for the rare earth ion.

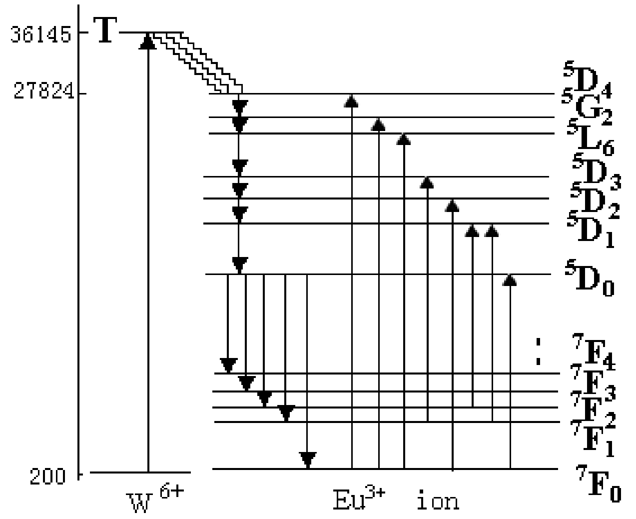

Fig. 8. Schematic diagram of the ground ($^7F_0$), emitting (^5D_J) and charge transfer state for the Eu^{3+} and Na_2WO_4 co-doped luminescence materials

Concentration effect on the luminescence intensity: In order to examine the doped concentration of Na_2WO_4 effect on the luminescence intensity, seven different amounts (sample 3-9), from 0.2 to 2.6 mL (volume) of Na_2WO_4 were introduced to the matrix. The luminescence intensity of different concentration tungstate sodium was shown in Fig. 9. As expected, the luminescence intensity decreased with increasing the doped concentration. However, the luminescence intensity of the gels doped with 1.6 mL shows a nearly highest value, indicating that optimal doped concentration is no more than 3.26 %, under the chosen experimental conditions.

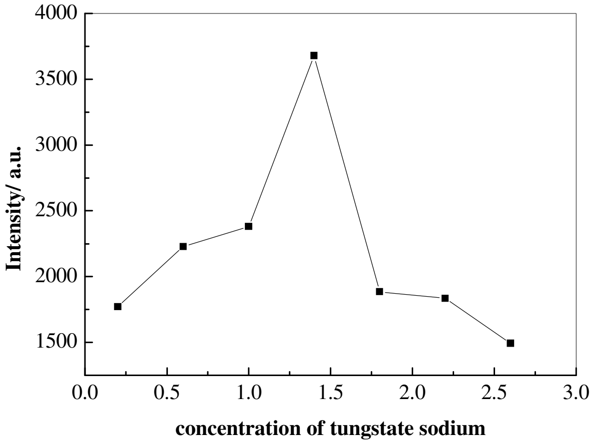

Fig. 9. Schematic diagram of luminescence intensity with Na_2WO_4 in different concentration

Temperature effect on the luminescence intensity: The temperature effect on magnetic dipole $^5D_0\rightarrow{}^7F_1$ transition and electric dipole $^5D_0\rightarrow{}^7F_2$ transition are shown in Fig. 10. The radiative rate of the $^5D_0\rightarrow{}^7F_1$ transition allowed by magnetic dipole, is almost independent of the environment around the europium ion. With the increasing of temperature changed imperceptibly. Consequently, it can be regarded as a standard transition to determine the radiative rates. However, the $^5D_0\rightarrow{}^7F_2$ hypersensitive transition increased remarkably with the increasing temperature indicating that water and organic constituents quenched the electric dipole transition strongly.

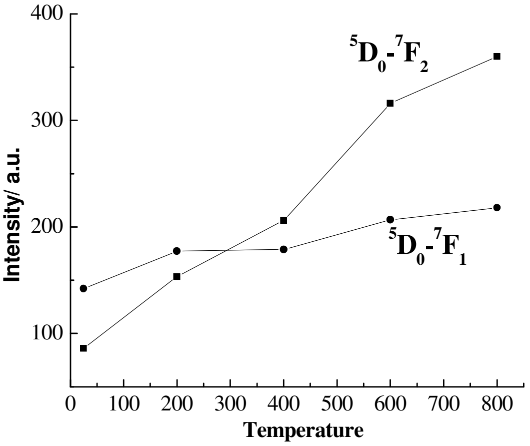

Fig. 10. Relation of luminescence intensity and annealing temperature

Conclusion

Europium ion and sodium tungstate co-doped silica materials were prepared *via* the sol-gel method. The material in stable structure is obtained and tungstate sensitized the luminescence intensity of Eu^{3+} ion more than 6 times when doped in 3.26 %.

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