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Luminescent properties of Lu_2SiO_5: Eu^{3+} derived from the in-situ sol-gel assembly of hybrid precursors

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Firstly Using rare earth coordination polymers with salicylic acid as precursors for the luminescent species and polyvinyl alcohol (PVA) as dispersing media, novel multicomponent hybrid precursor was assembled with an in-situ sol-gel technology and then Lu_2SiO_5 doped with Eu^{3+} was prepared. Both X-ray diffraction and scanning electronic microscope show that these materials have particle size of 100 ~ 200 nm and the luminescent spectrum exhibits strong red emission at 612 nm.

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1. Introduction

Inorganic luminescent materials have practical applications in almost any device involving the artificial production of light [1]. Cathode ray tubes, lamps and X-ray detectors are well-known examples [2]. Among the host lattices for luminescent materials, specially the ones used in lamps, silicate compounds have been extensively investigated [3] because of their stability, visible light transparency, and relative easy preparation. Materials containing lanthanide ions have been used as phosphors and laser materials because of their sharp, intensely luminescent f-f electronic transitions. The last two decades witnessed a rapidly growing interest in lutetium-based compounds and materials. Since its discovery by Melcher and Schweitzer in 1992 [4], Lutetium oxyorthosilicate Lu_2SiO_5 (LSO) has attracted a great deal of attention and has been recognized as one of the best scintillating materials. Recently, many research groups have undertaken investigations of Lu_2SiO_5 doped with Ce^{3} + which is particularly well suited for positron emission tomography (PET), a nuclear medical imaging technique [5]. However, to our best knowledge, reports on the synthesis and luminescence of materials with trivalent Europium ions doped in Lu_2SiO_5 are scarce. The luminescence of Eu^{3+} is particularly interesting because the major emission band is centered near 612 nm (red), which is one of the three primary colors (red, blue, and green) from which a wide spectrum of colors, including white, can be generated by appropriate mixing. For this reason, Eu^{3+} has been thoroughly investigated as luminescent activator in many host lattices [6, 7]. Traditional synthesis methods for luminescent silicate materials doped with rare earth ions were mainly focused on the solid state reaction or simple soft chemical technology such as chemical coprecipitation, sol-gel and colloidal reactions, etc [8-10]. Jagannathan et al. [11] employed some organic polymers to serve both as a fuel and a dispersing medium for nanocrystal formation, which can limit the agglomeration of particles effectively.

In this paper, we firstly select rare earth coordination polymers of salicylic acid (HSal) $[Lu(Sal)_3]_n$ and $[Eu(Sal)_3]_n$ as the precursors of corresponding rare earth oxides (Lu_2O_3 and Eu_2O_3) for their infinite chain-like polymeric structure similar to organic polymer template. Organic polymer, i.e. polyvinyl alcohol (PVA); was used as dispersing medium template and the polybasic hybrid polymeric precursors were assembled with other functional components such as tetraoxy silicate TEOS for the precursor of silicate network, urea for a fuel and rare earth nitrate for rare earth oxide. On the basis of this, the polybasic hybrid polymeric precursors were assembled and the materials Lu_2SiO_5: Eu^{3+} was synthesized by the thermolysis of 1100 °C for assembling the polybasic hybrid precursors. Photoluminescence properties of Lu_2SiO_5 doped with Eu^{3+} are discussed in detail.

2. Experimental

2.1 Synthesis of Lu_2SiO_5: Eu^{3+}

The starting materials Lu_2O_3 and Eu_2O_3 were dissolved in diluted HNO_3. The synthesis of Lu_2SiO_5: Eu^{3+} by rare earth salicylate coordination polymers—PVA precursors was described in the following: Excess salicylic acid (5.0 mmol) was dissolved into 95% ethanol solution (10 ml) and its pH value was adjusted to be about 7.0 with ammonia solution. Then mixed solutions of rare earth nitrates $Lu(NO_3)_3$ and $Eu(NO_3)_3$ with different molar ratio were added and mixed homogenously. The solutions of urea (10 ml), PVA (10 ml) and stoimetric TEOS were added into the above solutions and heated under 60 °C by dipping diluted HNO_3 until the pH value becomes acidity. After that, the heating temperature was increased to 100 °C to evaporate the solvent until the solution becomes viscous to form the gel, dried and the precursors were achieved finally. The scheme of for the synthesis can be shown as below:

$$Lu(NO_3)_3 + Eu(NO_3)_3 + HSAl + NH_3{\cdot}H_2O$$
$$\longrightarrow [RE(Sal)_3]_n \text{ coordination polymer}$$
$$+ TEOS + PVA + NH_2\text{-}CO\text{-}NH_2 + NH_3{\cdot}H_2O$$
$$\longrightarrow Lu_2SiO_5\text{: }Eu^{3+} + CO_2\uparrow + H_2O\uparrow + NH_3\uparrow + NO_2\uparrow$$

2.2 Physical measurements of Lu_2SiO_5: Eu^{3+}

The materials particle was characterized by means of X-ray powder diffraction (XRD, Bruke, D8-Advance, CuKα target with a working voltage of 40KV and a current of 40 mA) and scanning electronic microscope (SEM, Philps XL-30). Excitation spectra were determined with Perkin-Elmer LS-55 model fluorophotometer (excitation wavelength = 564 nm, scan rate = 1000 nm/s, excitation slit width = 10 nm, emission slit width = 5 nm). In order to avoid the influence of multiple frequencies, we recorded the excitation spectra in the two regions 200 nm – 290 nm and 320 – 550 nm, respectively.

3. Results and discussion

X-Ray diffraction (XRD) performed on the powders obtained clearly demonstrates that a pure LSO phase is obtained (Fig. 1). These first results confirm that the sol-gel process allows the preparation of pure LSO. It has also been observed that doping LSO with Eu^{3+} (1 mol %) does not affect the structure of the material and the LSO phase is maintained with efficient substitution of Lu^{3+}. The average crystallite size was estimated from the full width at half maximum of the diffraction peak by the Sherrer equation [12, 13].

$$D_{hkl} = k\lambda/[\beta(2\theta)\cos\theta]] \qquad (1)$$

Where $\beta(2\theta)$ is the width of the pure diffraction profile in radians, k is the constant, 0.89, λ is the wavelength of the X-rays (0.154056 nm), θ is the diffraction angle, and D_{hkl} is the average diameter of the crystallite. From the estimated data, it can be found that the nanometer RE_2SiO_5: Eu^{3+} materials are in the range of 100 – 200 nm size. The nanometer sizes were relatively larger for the thermolysis temperature was 1100°C.

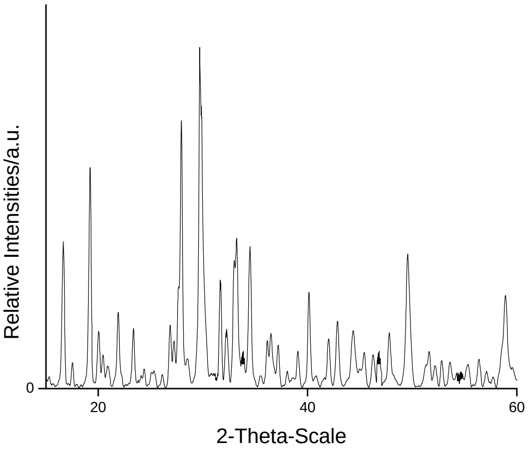

Fig. 1. XRD of nanometer of Lu_2SiO_5: 5%Eu^{3+}.

The morphology of the powders has been studied by scanning electron microscopy (SEM), typical images can be found in Fig. 2. The size distribution of these particles is very uniform, which can be seen as direct consequence of the use of the sol-gel process.

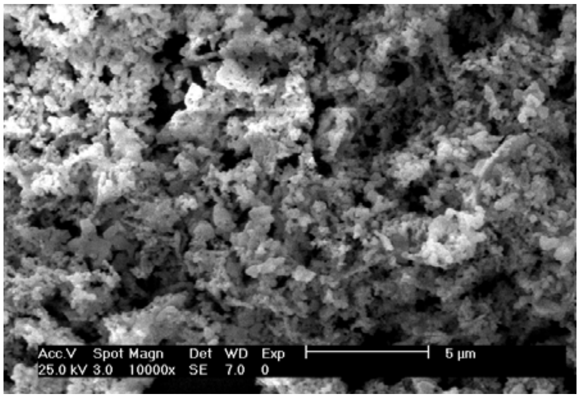

Fig. 2. SEM of Lu_2SiO_5: 5%Eu^{3+}.

The excitation spectra of Lu_2SiO_5 incorporating Eu3+ ions are shown in Fig. 3, which is taken at an emission wavelength of 612 nm. The excitation bands consist of a broad band and a small peak in the short ultraviolet region within the range between 200 nm to 280 nm and several broad bands in the longer wavelength region at the range of 350-550 nm which would be attributed to intraconfigurational 4f→4f transitions from the ground $^7F_0$ level. While the strong wide band centered at 240 nm originates from transitions to the charge transfer state (CTS) due to europium-oxygen interactions. The small peak at 210 nm is corresponding to the host absorption (HB). This excitation spectrum indicates that for the 4f-4f transitions, the most intense one corresponds to the electric dipole transition $^7F_0\rightarrow{}^5L_6$, while the magnetic dipole transitions $^7F_1\rightarrow{}^5D_2$ and $^7F_0\rightarrow{}^5D_1$ are weaker. Which is consistent with a noncentrosymmetric site provided by the monoclinic symmetry of the ligand arrangement. The radiative transitions within the [Xe] $4f^6$ configuration of Eu^{3+} are partiy forbidden and consist mainly of weak magnetic dipole (MD) and induced electric dipole (ED) transitions.

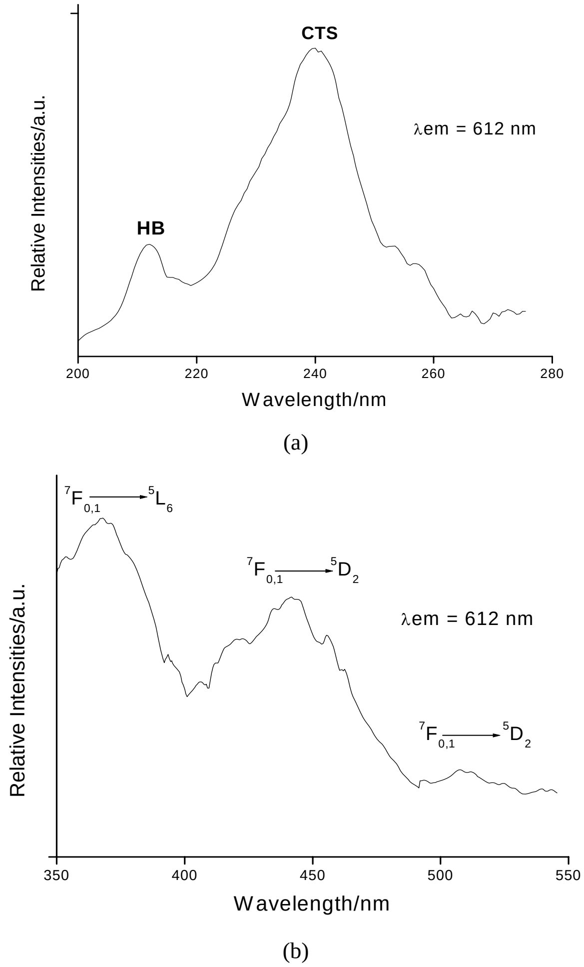

Fig. 3. Excitation spectra of Lu_2SiO_5: 5%Eu^{3+} in the range of 200-280 nm (a) and in the range of 350-550 nm (b).

Fig. 4 shows the emission spectrum of Lu_2SiO_5: Eu^{3+}, which is measured by an excitation wavelength of 240 nm. The emission transitions of Eu^{3+} ions clearly indicate sharp emission bands due to the inner shell transitions from the excited level to the lower levels: $^5D_0 \rightarrow {}^7F_j$. The emission spectrum consist of several bands at 587 nm ($^5D_0 \rightarrow {}^7F_0$), 596 nm ($^5D_0 \rightarrow {}^7F_0$), 612 nm ($^5D_0 \rightarrow {}^7F_2$) and 660 nm ($^5D_0 \rightarrow {}^7F_3$). The strongest red emission comes from Eu^{3+} center can be assigned to the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition working using a forced electric dipole transition mechanism. When the Eu3+ is located at a low-symmetry local site (without an inversion center), the $^5D_0 \rightarrow {}^7F_2$ electric dipole transition will be permitted and the luminescence intensity will be much stronger than that of the $^5D_0 \rightarrow {}^7F_1$ transitions. This is actually the case for Eu^{3+} in the Lu_2SiO_5 host lattice. While the minor emission components in the orange region around 596 nm due to the $^5D_0 \rightarrow {}^7F_1$ magnetic dipole transition are structurally independent. Due to weaker interaction Eu^{3+} and O^{2-} ions in Lu_2SiO_5 doped with Eu^{3+}, no little level split can be caused by the crystal field and no obvious split of Eu^{3+} emission bands has been observed.

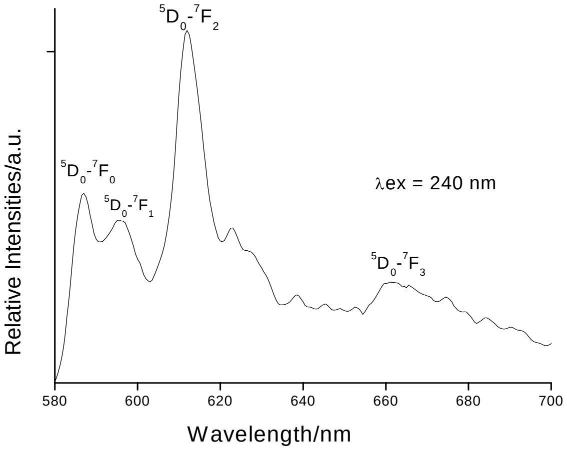

Fig. 4. Emission spectrum of Lu_2SiO_5: 5%Eu^{3+}.

4. Conclusion

The preparation of Lu_2SiO_5 doped with Eu^{3+} luminescent materials using a gel-polymer pyrolysis appears to be a more feasible method for the large scale production. The materials sizes for these phosphors were determined in the range of 100–200 nm with XRD and SEM. The luminescent materials of Lu_2SiO_5: Eu^{3+} exhibit the characteristic red fluorescence of Eu^{3+} ion at 612 nm, which indicates that the Eu^{3+} occupies the sites without an inversion center. Lu_2SiO_5: Eu^{3+} materials can be expected to have some potential applications in red phosphors for lighting and display.

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