



Effective fabrication of lanthanide activated phosphors and photoluminescence studies



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ABSTRACT

Reactions under hydrothermal conditions between lanthanide ions and different loading hosts (phosphates, vanadates and molybdates) lead to a group of rare earth-based solid state materials. As for the cases of phosphates and vanadates, a novel self-sacrificing template route with ultrasonic assisted hydrothermal treatments has been utilized. The emission intensities of building blocks derived from yttrium ($\text{YPO}_4:\text{Eu}^{3+}$ and $\text{YVO}_4:\text{Eu}^{3+}$) were significantly stronger than their counterparts ($\text{GdPO}_4:\text{Eu}^{3+}$ and $\text{GdVO}_4:\text{Eu}^{3+}$). Ultrasonic irradiation of reaction solution ahead of hydrothermal treatments would also improve their red luminescence. In the case of molybdates, red/green emissive phosphors ($\text{BaMoO}_4:\text{Eu}^{3+}$ and $\text{BaMoO}_4:\text{Tb}^{3+}$) were achieved in the presence of polyaspartic acid as the template. Their structures and photophysical features have been investigated in detail.

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1. Introduction

In recent years, directed synthesis has received considerable interests due to its control on the size, structure, morphology of the synthetic materials [1–3]. Corresponding template-oriented growth through hard approaches usually requires drastic conditions and complicated operations. Hence, current improvement on soft solution chemistry may offer a facile and low-cost way for the assembly of advanced functional materials with desired properties. Among the emerging general strategies, hydrothermal reactions assisted by soft templates have been widely employed during the process of crystal growth and formation [4–6]. Especially the newly-emerging self-sacrificing template method spontaneously used the reactant precursor as a oriented attachment template in the hydrothermal treatment, which avoided the removal steps of

the template and replaced the interaction between the precursor and template [7–13]. As a result, the combination of solvothermal process and specific building blocks would exert significant effects on the features of inorganic hosts and solubility of the reacted materials under enhanced pressure and temperature.

In view of the materials sources, lanthanide elements have aroused significant attention due to their importance in the fabrication of phosphors, lasers, scintillators and display devices [14–16]. It has been accepted that phosphates, vanadates and molybdates are frequently used in luminescence fields and these lanthanide activated phosphors have potential application in terms of their effective energy absorption in VUV region, long excited states and excellent chromaticity [17–19]. Here a family of europium (III)-doped LnPO_4 and LnVO_4 ($\text{Ln} = \text{Y, Gd}$) has been synthesized by ultrasonic assisted hydrothermal process with the aid of a sacrificial template such as LnOHCO_3 . In addition, the efficient preparation of lanthanide incorporated molybdates has been realized based on the effective building units like polyaspartic acid. To our knowledge, such polymeric soft template has never been applied for the design of $\text{BaMoO}_4:\text{Eu}^{3+}/\text{Tb}^{3+}$. This hydrothermal process is quite simple and easy to handle with a few variable

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parameters such as lanthanide species, supersonic irradiation and temperature.

2. Experimental procedures

2.1. Chemicals and materials

The lanthanide oxides Y_2O_3 , Gd_2O_3 , Eu_2O_3 and Tb_4O_7 were purchased from Aladdin Chemistry Co. Ltd. Lanthanide nitrates were obtained by dissolving lanthanide oxides into nitric acid. Urea [$CO(NH_2)_2$], $NH_4H_2PO_4$, NH_4VO_3 , HNO_3 , HCl , $Ba(NO_3)_2$ and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, were provided by the Shanghai Chemical Reagent Company. All the starting materials were used as received without further purification.

2.2. Preparation of Eu^{3+} -doped $LnOHCO_3$ ($Ln = Y, Gd$) precursors

0.19 mmol $LnNO_3$ ($Ln = Y, Gd$) and 0.01 mmol Eu were dissolved into deionized water, 0.2 mmol Urea was dispersed into the above solution with stirring. Ten minutes later, the mixture was transferred into a 50 mL Teflon-lined autoclaves. The autoclaves were sealed and maintained at 120 °C for 12 h. Then the autoclaves cooled naturally to room temperature, and the precipitates were washed with deionized water and ethanol several times, finally dried at 80 °C for 24 h in the air.

2.3. Preparation of Eu^{3+} -doped $LnPO_4$ and $LnVO_4$ ($Ln = Y, Gd$) products

The as-prepared sample was dispersed into deionized water by ultrasonic treatment for half an hour. 4 mmol $NH_4H_2PO_4$ (or NH_4VO_3) was added to deionized water with pH value adjusted to 1–2 by 2 mol/L HCl solution. The above two solutions were mixed through magnetic stirring. After several minutes, the mixture was transferred into a three-necked flask and installed into the reactor, and the supersonic power was set as 300 W with a reverse duty cycle of 2 s for 1 h. After the reactor was cooled to room temperature, the Eu^{3+} -doped $LnPO_4$ (or $LnVO_4$) ($Ln = Y, Gd$) precursors were transferred into autoclaves and maintained at 180 °C for 24 h. Finally, the solid products were achieved through centrifugation, washing and drying. To further compare the luminescent properties, the Eu^{3+} -doped $LnPO_4$ (or $LnVO_4$) ($Ln = Y, Gd$) precursors were prepared by the ultrasound irradiation solely and the Eu^{3+} -doped $LnPO_4$ (or $LnVO_4$) ($Ln = Y, Gd$) samples were achieved by the hydrothermal route without ultrasound process.

2.4. Preparation of Eu/Tb doped $BaMoO_4$ samples

0.1 g polysuccinimide (PSI) was dissolved in 2 or 3 mmol $NaOH$ solution with stirring, then 1.0 mmol MoO_4^{2-} solution was added into above transparent solution. 10 min later, the mixed solution of 0.95 mmol $Ba(NO_3)_2$ and 0.05 mmol Lanthanide nitrates ($Eu(NO_3)_3$ or $Tb(NO_3)_3$) was slowly added to above mixture, and maintained stirring for half an hour. The precursor was transferred into a 50 mL Teflon-lined autoclave with the reaction temperature of 100–180 °C for 10 h. After the autoclave was cooled to room temperature naturally, the $BaMoO_4: Eu^{3+}/Tb^{3+}$ powders were separated by centrifugation and washed with deionized water and ethanol several times, and then dried at 60 °C in the air for further characterization.

2.5. Preparation of cellulose $BaMoO_4: Ln^{3+}$ hydrogels

Microcrystalline cellulose (2.5 g) was dispersed into 100 ml of 1.5 M $NaOH/0.65$ M urea aqueous solution and then stirred for

10 min. The cellulose slurry was held at -5 °C for about 4 h and then thawed with intermittent stirring at $0-4$ °C to obtain a transparent solution. Epichlorohydrin (12 mg), as a cross-linking agent, and $BaMoO_4: Ln^{3+}$ (11 mg) were added to the cellulose solution, and the mixture was stirred for 0.5 h to yield a homogeneous solution. After reaction at 60 °C for 3 h, cellulose hydrogels were obtained.

2.6. Characterization

The supersonic assisted microwave reactor was commercially available and produced by Nanjing Xianou technology company, China. The X-ray diffraction (XRD) were measured by a Bruker D8 Advance X-Ray Diffractometer with $Cu K\alpha$ radiation ($\lambda = 1.54$ Å). Luminescent spectra were measured by a Hitachi F-4500 equipped with a xenon lamp at room temperature. Overall quantum yields were collected at room temperature based on an integrating sphere (Edinburgh FLS 920 spectrometer). The excitation light entered the sphere by the optical fiber. When the specific excitation wavelength was selected, the quantum yields were calculated automatically by the computer software.

3. Results and discussion

3.1. Structural analysis

The crystal structures of europium doped $YOHCO_3$, YPO_4 and YVO_4 were investigated by the X-ray diffraction measurements. Their XRD patterns of these samples were given in Fig. 1. The diffraction peaks of $YOHCO_3: Eu^{3+}$ powder prepared by hydrothermal method can be indexed to the $YOHCO_3$ phase (PDF # 30–1444). Moreover, all the peaks of $YPO_4: Eu^{3+}$ powder were found to agree well with the tetragonal YPO_4 (PDF # 11–0254) with space group $I4_1/a$ and cell parameters of $a = 6.904$ Å, $b = 6.904$ Å, $c = 6.035$ Å. The XRD patterns of as-synthesized $YVO_4: Eu^{3+}$ sample were consistent with YVO_4 (PDF # 17–0341) which revealed the tetragonal space group $I4_1/a$ and cell parameters of $a = 7.119$ Å, $b = 7.119$ Å and $c = 6.290$ Å. The diffraction peaks of $YPO_4: Eu^{3+}$ and $YVO_4: Eu^{3+}$ samples are sharp and narrow. No other crystalline forms could be found.

The XRD curves of $GdOHCO_3: Eu^{3+}$, $GdPO_4: Eu^{3+}$ and $GdVO_4: Eu^{3+}$ powders were also studied in detail. As provided in Fig. 2, the

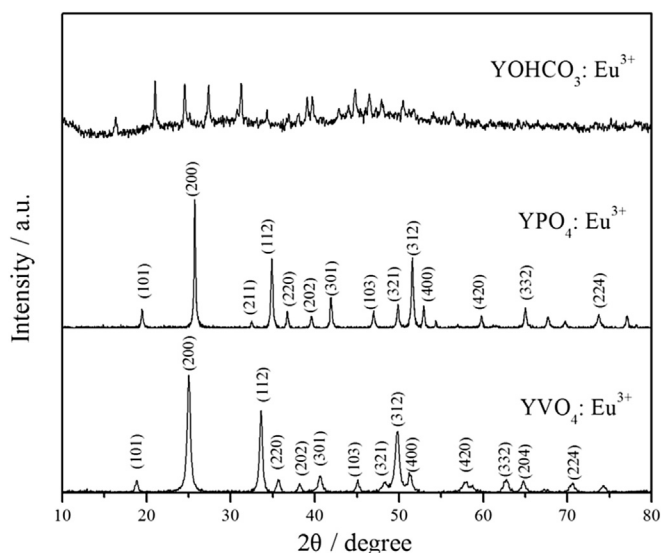


Fig. 1. XRD patterns for as-synthesized Eu^{3+} -doped $YOHCO_3$, YPO_4 and YVO_4 samples.

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