



Extensive studies of host lattices and activators in lanthanide phosphors based on efficient synthesis



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ABSTRACT

Uniform and dispersive NaLa(MoO₄)_{2-x}(WO₄)_x (abbreviated as NLMW): Eu³⁺/Tb³⁺ (5 mol%) microspheres were successfully synthesized at low temperature (393 K). The incorporation of Bi³⁺ or Mn²⁺ into CaMoO₄: Eu³⁺ with tetragonal crystalline phase has also been studied. The structure, morphology, and luminescent properties of these powder samples were examined by means of X-ray diffraction (abbreviated as XRD), scanning electron microscopy (abbreviated as SEM), and fluorescent spectrophotometry, respectively. SEM images substantiated that these phosphors have uniform sphere-shaped morphologies. The samples exhibited the characteristic emission of Eu³⁺(⁵D₀ → ⁷F_J)/Tb³⁺(⁵D₄ → ⁷F_J) under ultraviolet excitation. Effects of the ratio of MoO₄/WO₄ on the luminescence behavior were investigated in detail. The MoO₄/WO₄ ratio was optimized as 1/1. The international commission on illumination (abbreviated CIE for its French name) chromaticity coordinates of NLMW: Eu³⁺ and NLMW: Tb³⁺ indicate the emissions were located in the red and green region, which will be beneficial for the potential device fabrication. Encapsulation of Bi³⁺ and Mn²⁺ both can effectively sensitize europium (III) ions, generating stronger red emissions (⁵D₀ → ⁷F_J).

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1. Introduction

Recently, rare-earth-doped optical materials have attracted great interests due to their excellent luminescence and potential applications in bio-labels, solid-state lasers and display devices [1–10]. Many approaches including the molten salts, hydrothermal (solvo-thermal), sol-gel treatment and template-direction have been explored [11–14]. However, the significant disadvantages, such as time-consuming, tedious processing, high cost and low yields, have restricted the practical application of these approaches. Therefore, developing a facile and template-free route still remains a real challenge.

Microwave irradiation can promote the nucleation and growth

stage of nanocrystals, while ultrasound irradiation can effectively enhance chemical reactivity and improve the powder particle morphology and dispersion properties [15,16]. In particular, the supersonic and microwave co-assistance (abbreviated as SMC) route calls for low reaction temperature and short time periods for the preparation process [17]. Therefore, it is anticipated that we could connect the two technologies simultaneously to synthesize the targeted materials.

Double alkaline rare-earth molybdate-tungstates A Ln(MO₄)₂ (A = alkali metal ions; Ln = trivalent rare earth ions, M = Mo, W) are good hosts for the encapsulation of lanthanide ions [18–20]. The tetrahedral ionic radius for Mo⁶⁺ (0.41 Å) and W⁶⁺ (0.42 Å) was analogous and the replacement and combination of the two species have been reported [21–25]. In this work, a series of terbium/europium ions-activated NaLa(MoO₄)_{2-x}(WO₄)_x phosphors with uniform sphere-shaped morphologies have been synthesized by a facile SMC process. The crystal structure and luminescent spectra of these phosphors with different ratio of MoO₄/WO₄ were investigated. In addition, Bi³⁺ and Mn²⁺ ions have been proven to be good

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sensitizers for Eu^{3+} in various host materials. We introduced Bi^{3+} and Mn^{2+} into CaMoO_4 : 0.05Eu^{3+} by this ultrasound-microwave co-irradiations method without any surfactant or template. The structures and morphologies of the CaMoO_4 products and photoluminescence properties of $\text{Eu}^{3+}/\text{Bi}^{3+}$ and $\text{Eu}^{3+}/\text{Mn}^{2+}$ co-doped CaMoO_4 phosphors were explored.

2. Experimental

La_2O_3 (99.99%) and Eu_2O_3 (99.99%) were supplied by Aladdin Chemistry Co. Ltd. $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (A.R.), $\text{Na}_2\text{WO}_4 \cdot \text{H}_2\text{O}$ (A.R.), $\text{NH}_3 \cdot \text{H}_2\text{O}$ (A.R.) $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and HNO_3 (A.R.) were purchased from Shanghai chemical reagent company. All the above chemicals were used without further purification. The supersonic assisted microwave reactor was commercially available and produced by Nanjing Xianou technology company, China. X-ray diffraction patterns were taken with a Bruker D8 Advance X-Ray Diffractometer operating at 40 kV and 40 mA. ($\text{CuK}\alpha$ radiation, $\lambda = 1.5418 \text{ \AA}$). The 2-theta angular range is between 10 and 80° . Data were collected with a step size of 0.03° and a counting time of 1s/step. The morphologies and particle sizes of the microstructures were determined on a JSM-6360LV scanning electron microscope (SEM). The samples were spread on conductive copper adhesive tabs and examined at 1 kV after Pt sputter coating for 15 s before observation. Fluorescence spectra were measured in a Hitachi F-4500 at room temperature. Dynamic light scattering (DLS) experiments were carried out with a Malvern Mastersizer-2000. Inductively coupled plasma mass spectrometry (abbreviated as ICP-MS) was carried out on an Agilent7500a (Agilent, USA). The samples were digested in a Mars 5 microwave reaction system (CEM Corporation, USA). The thiocyanate spectrometric method was performed on a Shimadzu UV-2550 machine.

In a typical SMC synthesis of $\text{NaLa}(\text{MoO}_4)(\text{WO}_4)$: Eu^{3+} (5 mol%): rare earth oxides were dissolved in dilute HNO_3 to form the rare earth nitrates. $\text{La}(\text{NO}_3)_3$ ($1 \times 10^{-3} \text{ mol}$) and $\text{Eu}(\text{NO}_3)_3$ ($5 \times 10^{-5} \text{ mol}$) were dissolved in deionized water, then $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ ($1.5 \times 10^{-4} \text{ mol}$) and $\text{Na}_2\text{WO}_4 \cdot \text{H}_2\text{O}$ ($1 \times 10^{-3} \text{ mol}$) were added. pH value was adjusted to 8.0 by aqueous ammonia. After additional agitation for 10 min, the as-obtained white colloidal precipitate was transferred into a program-controlled sonochemistry-assisted microwave reactor with the microwave power set as 300 W and operated at 120°C . Supersonic power was 200 W with the reverse duty cycle 2s. All the reaction time was fixed as 2 h. Finally, the products were retrieved by centrifugation, washing with ethanol and distilled water several times, then dried at 80°C in vacuum. The other $\text{NaLa}(\text{MoO}_4)_{2-x}(\text{WO}_4)_x$: $\text{Eu}^{3+}/\text{Tb}^{3+}$ (5 mol%) phosphors were prepared in a similar procedure. For comparison, the bulk NLMW($x = 1$): $\text{Eu}^{3+}/\text{Tb}^{3+}$ (5 mol%) was obtained by a direct solid-state reaction technique. La_2O_3 (99.99%), Eu_2O_3 (99.99%), Tb_4O_7 (99.99%), $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (A.R.), WO_3 (A.R.) and Na_2CO_3 (A.R.) were used as the starting materials and were weighed in corresponding stoichiometric ratio. The mixtures were first mixed and ground in an agate mortar for 15 min and then pre-calcination at 600°C for 1 h. Finally, the prepared samples were sintered at 1200°C for 3 h.

As for the synthesis of $\text{Ca}_{0.95-x}\text{Eu}_{0.05}\text{Bi}_x\text{MoO}_4$ ($0 \leq x \leq 0.1$), $\text{Ca}(\text{NO}_3)_2$ (0.1 mol/L), $\text{Bi}(\text{NO}_3)_3$ (0.01 mol/L) and $\text{Eu}(\text{NO}_3)_3$ (0.01 mol/L) solution were mixed together. Subsequently, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (0.1 mol/L) was added. After the pH value was adjusted to 7.0 with aqueous ammonia, the mixture was transferred to a supersonic assisted microwave reactor (power: 200 W) with a reverse duty cycle of 2 s, the temperature was maintained at 80°C for 1 h. Actually, we also tried to use pH 8.0 as the previous samples, unexpected impurities were always found in the crystalline phases

after at least three parallel experiments. Accordingly, we fixed the reaction pH value to 7.0. Here we have to mention that the preparation temperature for $\text{NaLa}(\text{MoO}_4)_{2-x}(\text{WO}_4)_x$ was 120°C and no effective crystalline phase could be formed under this temperature. The above mixture was centrifuged to collect the bottom product and sequentially washed with distilled water and absolute ethyl alcohol several times. Finally, the material was dried at 60°C in the air for further characterization. The stoichiometric raw materials $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Eu}(\text{NO}_3)_3$, $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ with the formula of $\text{Ca}_{0.95-x}\text{Eu}_{0.05}\text{Mn}_y\text{MoO}_4$ ($0 \leq y \leq 0.15$) were used to prepare $\text{Eu}^{3+}/\text{Mn}^{2+}$ co-doped CaMoO_4 phosphors by the similar synthetic method.

The determination of doped $\text{Eu}(\text{III})$ or $\text{Tb}(\text{III})$ was briefly described as follows: 0.5 g sample, 3 ml HF, 7 ml HNO_3 , 3 ml HCl and 2 ml H_2O_2 were transferred into the tetrafluorometoxil reaction vessels and microwave assisted digestion was performed. After cooling, the resultant sample was diluted with ultrapure water to final volume of 50 ml. ^{115}In (for Eu) and ^{185}Re (for Tb) were used as internal standard elements. Corresponding ICP-MS analysis results were added in Table S1. The ratios of Mo and W were also studied. After the sample has been digested, the collected solutions were added in a strong base (NaOH) and the interference ions were precipitated. Perchloric acid was added in the mixture. Tungstic acid and molybdic acid were achieved. Then hot $\text{NH}_3 \cdot \text{H}_2\text{O}$ was added. The total amounts of W and Mo can be measured by the calcination and gravimetric method. In order to determine the concentration of Mo, we added citric acid to form complex with W in the above parallel samples and the amounts of molybdenum can be obtained by the thiocyanate colorimetric approach (Table S2) [26,27].

3. Results and discussion

3.1. Phase and morphology of the products

The crystal phases of the as-prepared samples were identified by XRD. Fig. 1a shows the XRD patterns of the prepared NLMW ($x = 0, 0.5, 1.0, 1.5, 2.0$): Eu^{3+} phase as a function of doped W content. As the value of x increases, the XRD patterns were found to be similar to each other without any obvious shifting and all of the diffraction peaks can be well indexed to the tetragonal phase of $\text{NaLa}(\text{MoO}_4)_2$ (Joint Committee on Powder Diffraction Standards abbreviated as JCPDS Card No. 24-1103, unit cell parameters: $a = 5.345 \text{ \AA}$, $c = 11.790 \text{ \AA}$) [28], which can be rationalized by the similar tetrahedral ionic radius of Mo^{6+} (0.41 \AA) and W^{6+} (0.42 \AA). According to the structure data of XRD in Fig. 1b, NLMW ($x = 0, 0.5, 1.0, 1.5, 2.0$): Tb^{3+} also belongs to $\text{NaLa}(\text{MoO}_4)_2$ crystal (JCPDS Card No. 24-1103) with the lattice constants of $a = 5.345 \text{ \AA}$, $c = 11.790 \text{ \AA}$, indicating that different doping lanthanide ions rarely change the crystal lattice. No peaks of any other phases or impurities were detected. And the strong and sharp diffraction peaks indicated a high degree of crystallinity. Additionally, we also compared the results with the sample synthesized by solid state method and both of them were readily indexed as tetragonal phases (Fig. S1).

The crystal structures of the as-prepared $\text{Ca}_{0.95-x}\text{MoO}_4$: 0.05Eu^{3+} , $x\text{Bi}^{3+}/y\text{Mn}^{2+}$ ($x = 0, 0.01, 0.05$; $y = 0.03, 0.05$) products were also measured. As provided in Fig. 2, the XRD patterns of $\text{Ca}_{0.95}\text{Eu}_{0.05}\text{MoO}_4$ form a pure tetragonal crystal phase with the space group $I4_1/a$, which are in agreement with JCPDS standard card No. 29-0351 without any impurity peaks. The sharp diffraction peaks indicated that small crystals precipitated with high efficiency (80°C and 60 min) during the microwave and ultrasonic irradiations. Furthermore, when the doping concentration of Bi^{3+} increased, a new XRD peak of $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ was observed at $2\theta = 27.9^\circ$, and the crystallinity tended to decrease. As for the case

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