pH 值对 NaYW₂O₈:Ln³⁺微米晶形成及上/下转换荧光的影响

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摘要：用水热法合成了 NaYW₂O₈:Ln³⁺(Ln=Yb/Er and Eu)微米晶,并研究了 pH 值对微米晶组成、形貌和荧光性质的影响。通过调节微米晶的形貌和结构对微米晶的上转换荧光进行了调控。在 NaYW₂O₈:Eu³⁺微米晶的激发光谱中,Eu³⁺-O² 电荷迁移带和 W⁶⁺-O²⁻跃迁与 Eu³⁺离子的 f-f 激发峰的比值随着微米晶的形貌和结构的不同发生改变。

Effect of pH Value on Synthesis of NaYW₂O₈:Ln³⁺ Microcrystals with Tunable up/down Conversion Luminescence

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Abstract: Tetragonal phase NaYW₂O₈:Ln³⁺ (Ln=Yb/Er and Eu) microcrystals were synthesized using a hydrothermal method and a subsequent calcination treatment. The effect of pH value of the reaction solutions on the phase composition, morphologies, and luminescence properties of NaYW₂O₈:Ln³⁺ microcrystals was investigated. Upconversion luminescence tuning of NaYW₂O₈:Er³⁺/Yb³⁺ under 980 nm excitation was achieved by adjusting the crystal structure and morphology of samples. The upconversion luminescence mechanism was also investigated. In the excitation spectra monitored at 618 nm of NaYW₂O₈:Eu³⁺, the intensity ratio of the charge transfer bands of the Eu³⁺-O²⁻ and W⁶⁺-O²⁻ transitions to the f-f shell transitions of Eu³⁺ ions changed with the structure and morphology of the sample. Under 254 and 396 nm excitation, the $^5D_0{\rightarrow}^7F_1$, $^5D_0{\rightarrow}^7F_2$, $^5D_0{\rightarrow}^7F_3$, and $^5D_0{\rightarrow}^7F_4$ emissions were observed. For the sample prepared at pH=12, the $^5D_0{\rightarrow}^7F_1$ emission was split into two sub-bands.

Key words: Ln³⁺; microcrystals; hydrothermal method; luminescence

Physical and chemical studies on the nanometer scale have experienced an enormous development since the 1990s and have led to the appearance of the new interdisciplinary fields of "nanoscience and nanotechnology"[1]. In these fields, the fabrication of nanostructures with designable well-confined morpho- logy and size has sparked considerable interest in exploring new nanomaterials not only for their unique physical properties but also for their potential applications in developing novel phosphors and building mini optoelectronic devices[2-7].

　　Trivalent rare earth (RE) ions are well known for

their unique spectroscopic and magnetic properties which make them important in technological, medical, and biological research areas[8-20]. In particular, the ability to manipulate color output of micro/nanocrystals doped with RE ions is important for their applications as light emitting displays, lasers, and optoelectronic devices to multiplexed biological labeling[21]. So far, RE-doped microcrystals have been proposed to be a promising new class of biological fluorescent labels as possible alternatives to organic fluorophores[22-24].

The host material is an important factor to obtain high efficient up/down conversion emissions[25-27]. Among the candidates of host materials for RE ions, $NaYW_2O_8$ has been an attractive material as laser hosts, which possesses suitable hardness, high chemical durability, and favorable physical properties. Especially, the concentration quenching effect hardly occurs in $NaYW_2O_8$ doped with RE ions because the polarization of oxygen ions in the polyhedron can be induced by the adjacent high-covalent tungsten[28-29].

Herein, tetragonal phase $NaYW_2O_8$:Ln^{3+} (Ln=Yb/Er and Eu) microcrystals were synthesized using a hydrothermal method and a subsequent calcination treatment. The up/down luminescence tuning of $NaYW_2O_8$:Ln^{3+} was achieved by adjusting the crystal structure and morphology of the samples. The effect of pH value on the phase compositions, morphologies, and luminescence properties of $NaYW_2O_8$:Ln^{3+} microcrystals was investigated in detail.

1　Experimental

Analytical grade $Ln(NO_3)_3 \cdot 6H_2O$ (Ln=Y, Yb, Er, and Eu), Na_2WO_4, Polyvinylpyrrolidone (PVP, 55 kDa), NaOH, HNO_3, and ethanol, were obtained from Beijing Chemical Reagents, China. All of the reagents and solvents were used as received without further purification. Deionized water was used throughout.

In a typical synthesis, 1 mmol $Ln(NO_3)_3$ and 0.62 g PVP were dissolved in 20 mL distilled water. After vigorous stirring and bath ultrasonication for 30 min, 4 mL Na_2WO_4 (0.5 mol·L^{-1}) aqueous solution was added dropwise into the Ln $(NO_3)_3$-PVP aqueous

solution, and the pH value was adjusted to a specific value using a HNO_3 or NaOH (1 mol·L^{-1}) solution. Subsequently, the mixed solution was transferred to a 50 mL Teflon-lined autoclave, and heated at 180 ℃ for 24 h. The systems were then allowed to cool to room temperature. The resultant products were collected by centrifugation, washed with distilled water, and dried at 80 ℃. Then, the final products were annealed at 500~700 ℃ for 2 h in air.

The crystal structure was determined by a Rigaku (Japan) D/MAX-rA X-ray diffraction meter equipped with graphite monochromatized Cu $K\alpha$ radiation (λ=0.154 187 nm). The size and morphology of the final products were investigated by scanning electron microscope (SEM, Hitachi, S-4800). The DC luminescence spectra were recorded with a Hitachi F-4600 fluorescence spectrophotometer at room temperature. The upconversion luminescence spectra were recorded using a Hitachi F-4600 fluorescence spectrophotometer with an adjustable laser (980 nm, Beijing Hi-Tech Optoelectronic Co., China) as the excitation source with a fiber-optic accessory.

2　Results and discussion

2.1　Crystal structure and morphology of $NaYW_2O_8$ and $NaYW_2O_8$:Ln^{3+}

Fig.1 shows the XRD patterns of the samples prepared at different pH values of the reaction
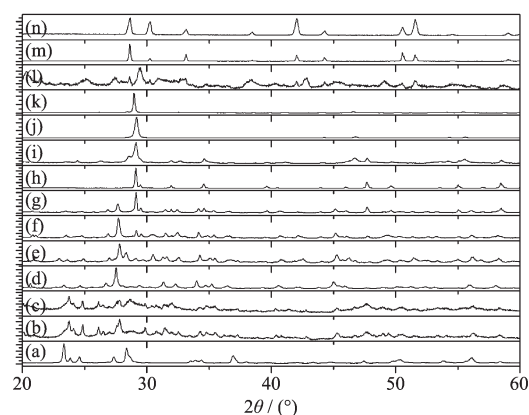

Fig.1　XRD patterns of $NaYW_2O_8$ prepared at different pH values (before annealing) the pH value for (a), (b), (c), (d), (e), (f), (g), (h), (i), (j), (k), (l), (m) and (n) is 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13 and 14, respectively
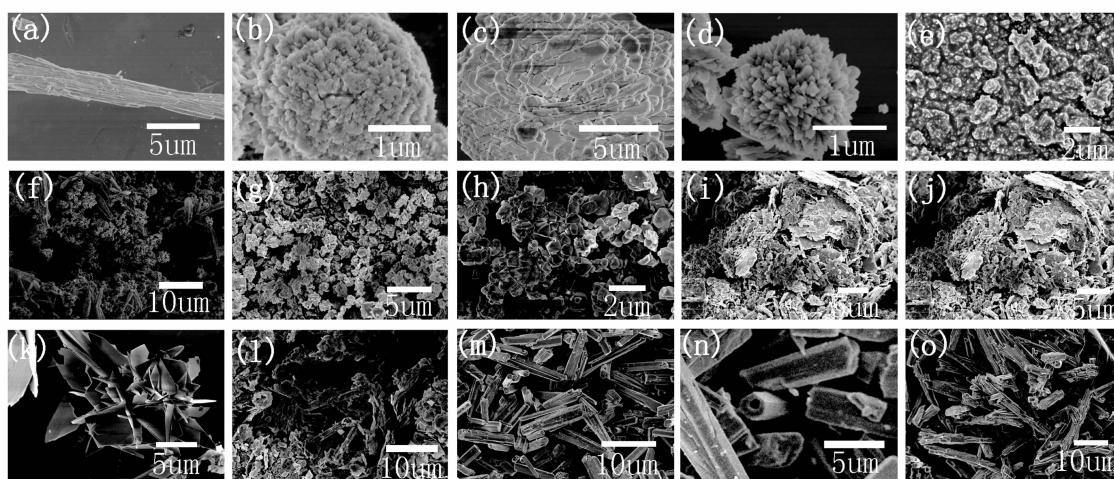
Fig.2　SEM images of NaYW₂O₈ prepared at different pH values (before annealing) the pH value for (a), (b), (c), (d), (e), (f), (g), (h), (i), (j), (k), (l), (m, n) and (o) are 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13 and 14, respectively

solutions. When the pH values were 7~11, tetragonal phase NaYW₂O₈ (PDF: 82-2369) microcrystals were synthesized. When the pH value was 13 or 14, hexagonal phase Y(OH)₃ (PDF: 24-1422) can be obtained. The corresponding SEM images of the samples prepared with 1 mmol of Y(NO₃)₃ aqueous solution and 2 mmol of Na₂WO₄ aqueous solution as raw materials at different pH values are shown in Fig.2.

Fig.3 shows the XRD patterns of samples after annealing at 700 ℃ for 2 h. When the pH values are 7~11, these patterns are in agreement with the tetragonal phase NaYW₂O₈. When the pH values are 12~14, Y₂O₃ nanotubes were synthesized.

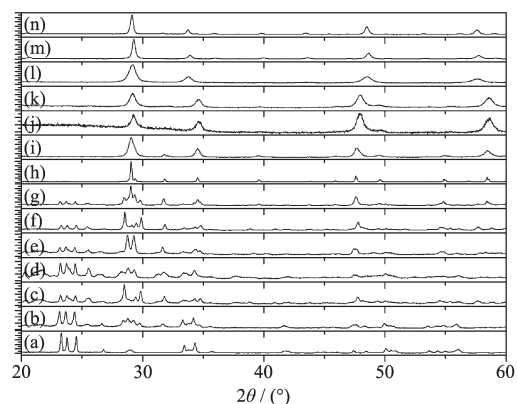The corresponding SEM images of samples after annealing at 700 ℃ are shown in Fig.4. The

Fig.3　XRD patterns of NaYW₂O₈ prepared at different pH values (after annealing at 700 ℃ for 2 h) ,the pH value for (a), (b), (c), (d), (e), (f), (g), (h), (i), (j), (k), (l), (m) and (n) is 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13 and 14, respectively

Fig.4　SEM images of NaYW₂O₈ prepared at different pH values (after annealing at 700 ℃ for 2 h), the pH value for (a), (b), (c), (d), (e), (f), (g), (h), (i), (j), (k), (l), (m, n) and (o) is 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13 and 14, respectively
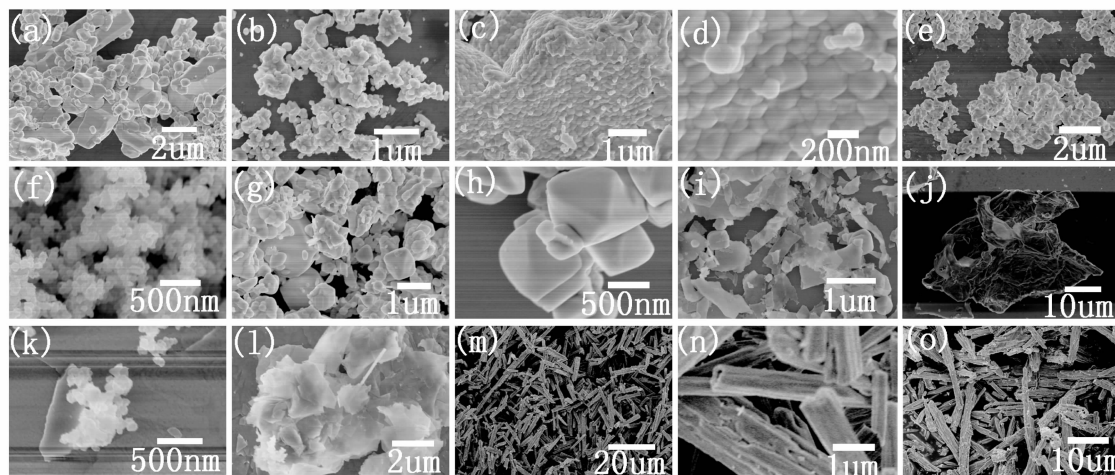
morphologies of the final products are related to hydrothermal crystallization and ripening process[30]. The fastest crystal growth will occur in the direction perpendicular to the face with the highest surface energy. When the pH value is decreased/increased over the critical pH value, the nucleation and growth behavior is out of the kinetic control due to the existence of H⁻ and OH⁻ ions[31]. Therefore, the $NaYW_2O_8$ with different morphologies were obtained by tuning the pH value of the reaction solutions. It is worth noting that the crystal structure and morphology of $NaYW_2O_8$:Ln^{3+} (Ln=Eu, Er^{3+}, and Yb) have not obvious change after doping with Ln^{3+} ions.

2.2　Green upconversion luminescence of $NaYW_2O_8$:Yb^{3+}/Er^{3+}

Fig.5 shows the upconversion luminescence spectra of $NaYW_2O_8$:Yb^{3+}/Er^{3+} and Y_2O_3:Yb^{3+}/Er^{3+} prepared at different pH values after annealing at 700 ℃ for 2 h. The spectral peaks correspond to the following transitions: $^2H_{11/2} \rightarrow ^4I_{15/2}$ (~532 nm), $^4S_{3/2} \rightarrow ^4I_{15/2}$ (~553 nm), and $^4F_{9/2} \rightarrow ^4I_{15/2}$ (~659 nm). The relative intensity of $^4F_{9/2} \rightarrow ^4I_{15/2}$ to $^2H_{11/2}/^4S_{3/2} \rightarrow ^4I_{15/2}$ changed with the crystal structure and morphology of samples. For the samples prepared at pH=8 and 9, the $^2H_{11/2} \rightarrow ^4I_{15/2}$ emission is the strongest. For the samples prepared at pH=13 and 14, the $^4S_{3/2} \rightarrow ^4I_{15/2}$ emission is the strongest.

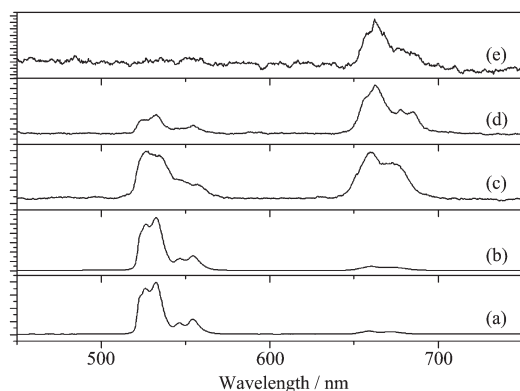To understand the number of photons involved in populating the $^2H_{11/2}/^4S_{3/2}$ and $^4F_{9/2}$ states, the pumping power dependences of the fluorescent intensities for $NaYW_2O_8$:Yb^{3+}/Er^{3+} (pH=9) have been investigated. Although the population of the $^4F_{9/2}$ comes from a two-photon process, the value of n for red emission ($^4F_{9/2} \rightarrow ^4I_{15/2}$) is 0.97 in the $NaYW_2O_8$:Yb^{3+}/Er^{3+} (pH=9) micro-crystals. Pollnau et al. attribute this phenomenon to the "saturation process" due to the competition between linear decay and upconversion processes for the depletion of the intermediate excited states[32,33]. According to their report, the value of n for a two-phonon process is ~2 when the linear decay of the intermediate state is dominant mechanism, while n is 1 when the upconversion is the dominant in the Yb^{3+}/Er^{3+} codoped systems. The value of n for green emission bands was determined to be 1.29, indicating a two-photon process.

2.3　Photoluminescence of $NaYW_2O_8$:Eu^{3+}

Fig.6 shows the room-temperature excitation spectra monitored at 618 nm of $NaYW_2O_8$:Eu^{3+}(5%) prepared at different pH values after annealing at 700 ℃ for 2 h. The sharp lines in Fig.6 (a~d) are associated with the direct excitation of the f-f shell transitions of Eu^{3+} ions. The most intense peak is centered at 396 nm. In Fig.6 (b~d), the broad bands extending from 200 to 300 nm are assigned to the charge transfer bands (CTBs) of the Eu^{3+}-O^{2-} and W^{6+}-O^{2-} transitions. In most cases, the spectra of the two CTB components overlap each other. The presence of

Fig.5　Upconversion luminescence spectra of $NaYW_2O_8$: Yb^{3+}/Er^{3+} prepared at different pH values (after annealing at 700 ℃ for 2 h), the pH value for (a), (b), (c), (d) and (e) is 8, 9, 11, 13 and 14, respectively
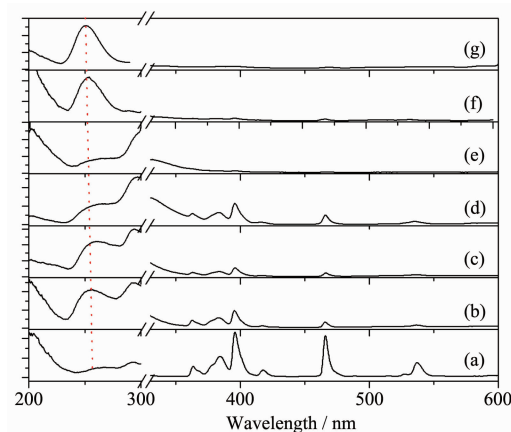
Fig.6　Excitation spectra of $NaYW_2O_8$:Eu(5%) prepared at different pH values (after annealing at 700 ℃ for 2 h), the pH value for (a), (b), (c), (d), (e), (f) and (g) is 8, 9, 10, 11, 12, 13 and 14, respectively

the excitation band of the WO$_4^{2-}$ groups in the excitation spectra of Eu^{3+} indicates that an energy transfer process occurs from the WO$_4^{2-}$ groups to Eu^{3+} ions in NaYW$_2$O$_8$:Eu^{3+}. It is noted that the intensity ratios of the CTBs to the *f-f* shell transitions of Eu^{3+} ions changed with the pH values of the reaction solutions. Especially, for the samples prepared at pH=12~14, only the CTBs were detected in the excitation spectra.

Fig.7 (a ~g) presents the emission spectra of NaYW$_2$O$_8$:Eu^{3+} (5%) prepared at different pH values after annealing at 700 ℃ for 2 h under 254 nm excitation. The $^5D_0{\rightarrow}^7F_1$, $^5D_0{\rightarrow}^7F_2$, and $^5D_0{\rightarrow}^7F_3$ emissions were observed. It is well known that the $^5D_0{\rightarrow}^7F_1$ line originates from magnetic dipole transition, while the $^5D_0{\rightarrow}^7F_2$ lines originate from electric dipole transition. The $^5D_0{\rightarrow}^7F_3$ transition exhibits a mixed magnetic dipole and electric dipole character. The $^5D_0{\rightarrow}^7F_4$ is electric dipole transition. It is noted that the positions of the emission peaks shift toward short wavelengths with increasing the pH values of the raw reaction solutions. Especially, when the pH value of the raw reaction solutions was 12, the $^5D_0{\rightarrow}^7F_1$ emission was split into two sub-bands, which may be explained by analyzing high resolution spectra and decay times of the luminescence. However, these measurements cannot be performed because of our experiment limitations. In addition, the emission spectra of NaYW$_2$O$_8$:Eu^{3+} under 396 nm excitation have the similar behaviors. Fig.7 (h ~l) presents the emission spectra of NaYW$_2$O$_8$:Eu^{3+}(5%) under 396 nm excitation. The $^5D_0{\rightarrow}^7F_1$, $^5D_0{\rightarrow}^7F_2$, $^5D_0{\rightarrow}^7F_3$, and $^5D_0{\rightarrow}^7F_4$ emissions were observed. It is imperative to point out that no emissions were detected for the samples prepared at pH=13 and 14.

3　Conclusions

In this study, tetragonal phase NaYW$_2$O$_8$:Yb^{3+}/Er^{3+} and NaYW$_2$O$_8$:Eu^{3+} microcrystals were synthesized using a hydrothermal method and a subsequent calcination treatment. The effect of pH value of the reaction solutions on the phase composition, morphologies, and luminescence properties of the samples was investigated. In the upconversion luminescence spectra of NaYW$_2$O$_8$:Er^{3+}/Yb^{3+} under 980 nm excitation, the relative intensity of $^4F_{9/2}{\rightarrow}^4I_{15/2}$ to $^2H_{11/2}/^4S_{3/2}{\rightarrow}^4I_{15/2}$ changed with increasing pH value. The upconversion mechanism of NaYW$_2$O$_8$:Er^{3+}/Yb^{3+} was investigated. In the excitation spectra monitored at 618 nm of NaYW$_2$O$_8$:Eu^{3+}, the intensity ratio of the charge transfer bands of the Eu^{3+}-O^{2-} and W^{6+}-O^{2-} transitions to the f-f shell transitions of Eu^{3+} ions also changed with the crystal structure and morphology of the samples. Under 254 or 396 nm excitation, the $^5D_0{\rightarrow}^7F_1$, $^5D_0{\rightarrow}^7F_2$, $^5D_0{\rightarrow}^7F_3$, and $^5D_0{\rightarrow}^7F_4$ emissions were observed. In addition, for the sample prepared at pH= 12, the $^5D_0{\rightarrow}^7F_1$ emission was split into two sub-bands.

Fig.7 Emission spectra of NaYW$_2$O$_8$:Eu(5%) prepared at different pH values (after annealing at 700 ℃ for 2 h) under (a ~g) 254 nm and (h ~l) 396 nm excitation, the pH value for (a, h), (b, i), (c, j), (d, k), (e, l), (f) and (g) is 8, 9, 10, 11, 12, 13 and 14, respectively

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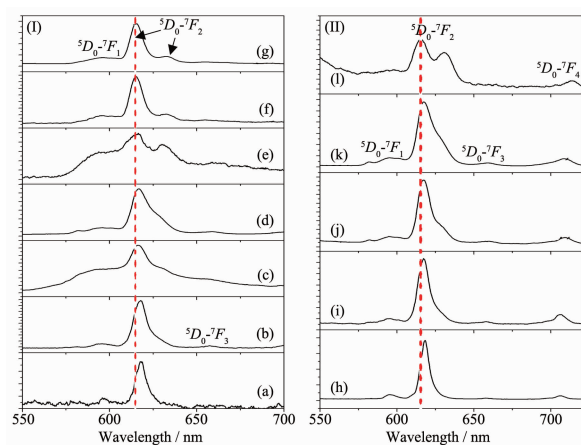[7] Wang G, Qin W, Wang L, et al. *Opt. Express*, **2008**,**16**:11907 -11914

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