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The effects of preparation conditions on the structural and up-conversion properties of $NaYF_4:Yb^{3+}$, Er^{3+} nano powders

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ABSTRACT

The $NaYF_4:Yb^{3+}$, Er^{3+} powders were prepared by a co-precipitation method. The relationship between the phase ratio of cubic to hexagonal phase and the emission intensity ratio of red to green was investigated. This concluded that the cubic phase dominantly contributed to the red emission, while the green emission was mainly ascribed to the hexagonal phase. The effects of Al^{3+} doping on UC emission were investigated first. The red emission intensity of the cubic phase was drastically enhanced when 10 mol% Al was added.

1. Introduction

$NaYF_4$ has been widely recognized as one of the efficient host materials for the up-conversion (UC) phosphors doped by the rare-earth (RE) ions. Among the RE ions, the Er^{3+} ion is suitable to convert infrared (IR) to the visible light through the UC process due to its proper electronic energy level scheme. The co-doping of the Yb^{3+} ion (a sensitizer) with the Er^{3+} ion can remarkably enhance the UC efficiency from infrared to visible lights due to the efficient energy transfer from Yb^{3+} to Er^{3+} [1,2]. UC phosphors can be applied to various fields such as solid-state lasers [3] and biological labeling [4,5].

The crystal structure of $NaYF_4$ has two polymorphic forms, viz. cubic (α-phase, $Fm\bar{3}m$, $Z = 4$) and hexagonal (β-phase, $P\bar{6}$, $Z = 1$) form, depending on the synthesis conditions and methods. In the cubic structure, the Na and Y atoms randomly distribute in the cationic sub-lattices with the same amount, while in the hexagonal structure there are three different cation sites: a nine-coordinated position by Y^{3+}; another randomly nine-coordinated one by 1/2 Na^+ and 1/2 Y^{3+}; a six-fold coordinated one by Na^+ and vacancies [6,7].

Photoluminescence (PL) spectra of $NaYF_4:Yb^{3+}$, Er^{3+} under IR excitation exhibit both green emissions (522 and 542 nm) and a red one (652 nm) through UC process, which are assigned to $^2H_{11/2} \rightarrow {}^4I_{15/2}$, $^4S_{3/2} \rightarrow {}^4I_{15/2}$, and $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transitions of the Er^3 ions, respectively. Under 980 nm excitation, the excited energy of the Yb^{3+} ion ($^2F_{5/2}$) is transferred to the Er^{3+} ion, resulting in $^4I_{11/2} \rightarrow {}^4F_{7/2}$ of the Er^{3+} ion. Then the excited electrons at the $^4F_{7/2}$ level are non-radiatively relaxed to the $^2H_{11/2}$, $^4S_{3/2}$, and $^4F_{9/2}$ levels. Subsequently they are transferred to $^4I_{15/2}$ ground level, leading to the green and red emissions [1,2,8–12].

The luminescent properties of $NaYF_4:Yb^{3+}$, Er^{3+} depend on various parameters such as the precursor concentration, the particle shape, morphologies, reactants, and synthesis techniques. It is known that $NaYF_4$ powders can be synthesized by various chemical methods such as hydrothermal [1,13], solvothermal [2,8,10,14], co-precipitation [4,15–17], and so on [7,11,12,18–20]. For examples, α-$NaYF_4$ spherical nanocrystals (NCs) with multicolor UC emissions were synthesized by a co-precipitation [17] and a liquid–solid-solution (LSS) technique [20], while β-$NaYF_4$ nanorods were obtained via hydrothermal and solvothermal methods [2,8]. Monodisperse cubic and hexagonal $NaReF_4$ (Re = Pr to Lu) NCs were fabricated via the decomposition of RE $(CF_3COO)_3$ [16]. The dynamic process for the phase formation and the nano-sized particles has been widely studied in the previous works, nevertheless a correlation between the synthesized phases and the luminescence are not clearly verified.

In this paper, the effects of the phase ratio (α- to β-phase) on the UC emission properties were investigated. NCs were prepared by a co-precipitation method. Their phases and shapes were controlled by various parameters such the annealing temperatures and the composition of the mixture. Furthermore the effects of Al^{3+} substitution for Y^{3+} on the luminescence were also investigated.

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2. Experiment

The $NaYF_4$:Yb^{3+}, Er^{3+} powders were prepared by a co-precipitation method using NaF and EDTA as a precipitator and a lanthanide metal chelator, respectively. Sodium fluoride (NaF, 99.99%), ethylenediaminetetraacetic acid (EDTA, 99.995%), yttrium chloride (YCl_3, 99.99%), erbium chloride ($ErCl_3$, 99.9%), and ytterbium chloride ($YbCl_3$, 99.9%) were used as starting materials. To prepare the precursors from the mixture of NaF:EDTA:Ln^{3+} = 12:1:1 (a molar ratio), 2.1 g NaF (0.05 mol) was dissolved in deionized water (80 ml) by sonicating for 1 h. The complex of lanthanides and EDTA was prepared by stirring the dissolved mixture of 16 ml of 0.2 M YCl_3, 3.4 ml of 0.2 M $YbCl_3$, 0.6 ml of 0.2 M $ErCl_3$, and 20 ml of 0.2 M EDTA solutions for 1 h at the room temperature, and then was injected into the NaF solution quickly. The precipitation reaction occurred immediately, and the product was stirred for 1 h at the room temperature. Precipitates collected by centrifugation were filtered, washed by deionized water and ethanol repeatedly, and dried under vacuum at 80 °C for 12 h. The white powders were annealed at the different temperatures for 5 h under 5% H_2 (95% N_2) atmosphere in an electric tube furnace. The particle size and morphology were observed by a field-emission scanning electron microscope (FESEM, JEOL, JSM-6500F). X-ray diffractometer (XRD, Rigaku, Miniflex II) using CuKα radiation (λ = 1.5406 Å) was used to determine the crystal structure. The scanning angle and speed were 10–70° and 5°/s, respectively. UC luminescent spectra were measured by PL system (PSI, Darsa-5000) with an external 200 mW IR laser diode (λ: 980 nm, Sancity laser).

3. Results and discussion

$NaYF_4$:Yb^{3+}, Er^{3+} precursors, which were prepared from the mixture of NaF:EDTA:Ln^{3+} = 12:1:1, were annealed at the different annealing temperatures, and the XRD patterns are shown in Fig. 1. XRD of precursors exhibits a single α-phase (cubic), which lasted up to 300 °C. With increasing the annealing temperature the α-phase is drastically transformed to the β-phase (hexagonal) with the minor α-phase at 400–500 °C. At the higher temperature of 600–700 °C α-phase preferably increases rather than β-phase, leading to the α-phase dominant powders at 700 °C. However, this α-phase is partly transformed to the β-phase again by elevating the temperature up to 800 °C, resulting in the coexistence of the both phases.

It is reported that the α → β transition is exothermic, whereas β → α is endothermic, indicating that the β-phase is a thermodynamically stable one [17,19]. The precursor of $NaYF_4$ prepared by a co-precipitation method, for instance, consisted of the α-phase, and then the annealing process at the high temperature caused the transition to β-phase. This phenomenon is attributed to the ordered-disordered arrangement of the cations [17]. On the other hand, it is also suggested that the β-phase is unstable above 700 °C [10,15,17,18]. The phase transitions in this experiment are very complicated, and so partly coincide with those in the previous works or not [4], because the phase formation is hypersensitive to the synthesis method in each work. In this work, the powders size gradually developed with the increase in the annealing temperature as shown in Fig. 2. At 300 °C the cubical particles with size of about 100 nm are uniformly distributed, whereas the increase in the temperature up to 500 °C enlarges the particle size gradually, showing the non-uniform distribution. Above 600 °C the particles begin to agglomerate and abruptly grow into about several tens micrometer in size, while the spherical shape does not last any longer. Consequently, it can be speculated that the phase transition is affected by the particle size as well as the temperature. However, it is not easy to explain the exact mechanism for the repeated phase transitions occurred at various temperatures.

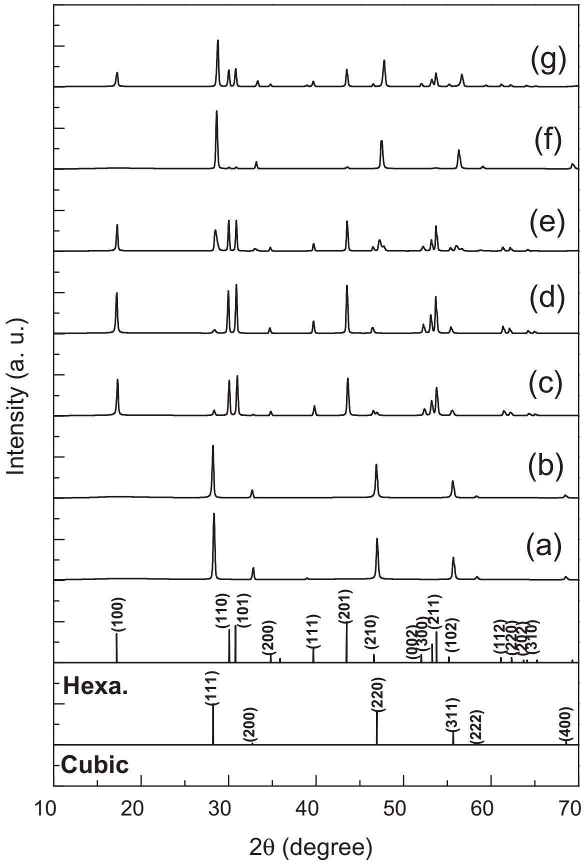

Fig. 1. XRD patterns of $NaYF_4$:Yb^{3+},Er^{3+} powders annealed at different temperatures: (a) precursor, (b) 300 °C, (c) 400 °C, (d) 500 °C, (e) 600 °C, (f) 700 °C, and (g) 800 °C.

Fig. 3 (a) shows the UC emission spectra under IR (980 nm) excitation corresponding to the samples in Fig. 1. The precursor did not show any luminescence, but the annealing process promoted the luminescence of $NaYF_4$:Yb^{3+}, Er^{3+} powders. The UC spectra consist of green (522 and 542 nm) and red (652 nm) emissions, showing the dependence of the intensities on the annealing temperatures. In addition to them, insignificantly weak peaks at 408 nm assigned to the $^2H_{9/2} \rightarrow {}^4I_{15/2}$ are also observed. These spectra generate from the energy-transfer up-conversion (ETU) process between Yb^{3+} and Er^{3+}. At 300 °C the red emission is much stronger than the green one. The increased annealing temperatures of 400–500 °C make the red emission weaken, whereas the green one significantly increase. With increasing the temperature up to 600 °C the strongest green and red emissions appear simultaneously. At 700 °C the strong red emission intensity stayed unchanged, but the green one rapidly dropped, and then the red emission also decreased at 800 °C. This luminescent evolution is closely connected with the phase ratio ($R_p = I_\alpha/(I_\alpha + I_\beta)$), where I_α and I_β are the XRD intensity of α-phase (1 1 1) at 28.23° and β-phase (2 0 1) at 43.45°, respectively. Fig. 3 (b) shows the relationship between R_p and the emission intensity ratio of red to green ($R_e = I_R/(I_G + I_R)$), where I_G and I_R represent the emission intensity at 542 and 652 nm, respectively. This figure apparently shows the relationship between R_e and R_p, revealing that the variation of R_e is just proportional to that of R_p. From this result it is concluded that the α-phase dominantly contributes to the red emission, while the green emission is mainly ascribed to the β-phase. However, the sample annealed at 500 °C showed a weaker green emission than that at 600 °C, even though