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Ceramics International 38 (2012) 6907–6910

CERAMICS INTERNATIONAL

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Short communication

Phase formation evolution and upconversion luminescence properties of LaOF:Yb^{3+}/Er^{3+} prepared via a two-step reaction

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Received 4 April 2012; received in revised form 28 April 2012; accepted 2 May 2012
Available online 11 May 2012

Abstract

Rhombohedral and tetragonal LaOF and LaOF:Yb^{3+}/Er^{3+} have been successfully prepared via a two-step reaction, which includes a facile hydrothermal method and the following heat treatment of the as-prepared LaF_3 precursor. The phase formation evolution from LaF_3 to LaOF with different phase structures was characterized by X-ray diffraction (XRD). The upconversion (UC) luminescence properties of rhombohedral LaOF:Yb^{3+}/Er^{3+} have been investigated by the pumping power dependent UC emission spectra. Strong green and weak red UC emissions centered at 533 (544) and 669 nm were observed, respectively. The two-photon process was confirmed to be responsible for both the green and red UC emissions.

Keywords: B. X-ray methods; C. Optical properties

1. Introduction

Rare-earth metal (III) oxyhalides *Ln*O*X* (*Ln*=Sc, Y, La-Lu; *X*=*F*, Cl, Br) are considered to be a series of outstanding hosts for exploring new optical materials. Therefore, photoluminescence (PL) and upconversion (UC) luminescence properties of different activator ions doped *Ln*O*X*-type compounds have aroused widely attention in these years [1–3]. Among them, LaOF-based materials are of particular interest because of their excellent structural compatibility, good physical and chemical stability and low phonon energy [4,5]. Presently, many preparation strategies have been developed to synthesize LaOF, such as conventional high temperature solid-state reaction [4], mechanochemical grinding method [5], sol–gel method [6], hydrothermal method [7], and the thermolysis methods of trifluoroacetate precursors [8], and so on. Recently, Lin's group reported a novel synthetic route on the preparation of LaOF:Eu^{3+} under mild conditions via a facile hydrothermal method followed a heat treatment of their bastnaesite-type precursor ($LaCO_3F$) [9]. However, synthesizing LaOF-based optical materials by a facile method is still a challenge.

Accordingly in this communication, a simple two-step reaction compared to the reported $LaCO_3F$ precursor method has been developed to obtain LaOF, which includes a facile hydrothermal method and the following heat treatment of the as-prepared LaF_3 precursor. The phase formation evolution from LaF_3 to LaOF with different phase structures was characterized by X-ray diffraction (XRD). We have also successfully prepared Yb^{3+}/Er^{3+} codoped LaOF phosphors, and the UC luminescence properties and mechanism have also been discussed.

2. Experimental

The starting materials include $La(NO_3)_3 \cdot 6H_2O$ (99.995%), NaF (99.5%), PVP (99.5%), Er_2O_3 (99.995%), Yb_2O_3 (99.995%) and HNO_3 (10 mol/L). All chemicals were used directly without further purification. Er_2O_3 and Yb_2O_3 were dissolved in HNO_3 to obtain transparent solution and evaporated at 80 °C in order to remove an excessive HNO_3, and then dissolved by some amount of deionized water to

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http://dx.doi.org/10.1016/j.ceramint.2012.05.005

form 0.1 mol/L $Er(NO_3)_3$ and 0.1 mol/L $Yb(NO_3)_3$ stock solution. 0.5 mol/L $La(NO_3)_3$ and 1 mol/L NaF solutions were also prepared in advance. In a typical synthesis procedure, firstly, 0.5 g PVP was dissolved in deionized water (10 ml). Then, 6 ml 0.5 mol/L $La(NO_3)_3$, a certain amount of $Er(NO_3)_3$ and $Yb(NO_3)_3$ according to the stoichiometric amount were all introduced into the PVP solution. After vigorously stirring for 30 min, 9 ml 1 mol/L NaF was added dropwise into the mixture for another 30 min stirring. The obtained mixture was transferred into a Teflon bottle (30 mL), held in a stainless steel autoclave, sealed, and maintained at 170 °C for 20 h. As the autoclave was cooled to room temperature naturally, the precipitate was separated by centrifugation (6500 rpm), washed with deionized water and ethanol in sequence. The precipitate was dried in oven at 80 °C for 24 h, and the LaF_3 precursor was obtained. Finally, the precursor was calcined in air at 100, 300, 500, 700, 800, 900 and 1000 °C for 3 h or 6 h. The phases were examined by using X-ray diffraction (XRD) on a SHIMADZU model XRD-6000 X-ray powder diffractometer (Cu Kα radiation), 40 kV, 30 mA and a scanning speed $6.0°(2\theta)\mathrm{min}^{-1}$. The UC spectra were recorded on a JOBIN YVON FL3–21 spectrofluorometer and an external power-controllable 980 nm semiconductor laser (Beijing Viasho Technology Company, China) was used as the excitation source. All the measurements were performed at room temperature.

3. Results and discussion

Fig. 1 shows the XRD patterns of a series of LaF_3 samples obtained by hydrothermal method after heat-treatment at different temperature, 100 °C, 300 °C, 500 °C and 700 °C, for the same time of 3 h. As shown in Fig. 1, all the powder samples obtained below 700 °C are of hexagonal structure of LaF_3 according to Powder Diffraction File PDF 84–0943, which means that the phase structure of LaF_3 keeps stable in a wide temperature range. However, some impurity phase of $LaF_{1.7}O_{0.65}$ appears when the heat-treatment temperature increases to 700 °C, as shown in Fig. 1d. It is believed that O_2 in the air plays an important role in the phase transformation. When the reaction temperature reaches 700 °C, there will be enough thermodynamics force in the reaction of $LaF_3+O_2\rightarrow LaF_{1.7}O_{0.65}$. As also demonstrated in our experimental section, PVP is a hydrophilic surfactant and its pyrrolidone groups can coordinate with lanthanide ions [10]. On the basis of the introduction of PVP, the as-prepared LaF_3 should have small particle size and monodisperse morphology free of agglomeration, so that there are very large contact surface with O_2 to induce the phase formation of oxyfluorides.

It is reported that there are three forms of LaOF phases, which include cubic, tetragonal, and rhombohedral phase, respectively [9]. In the calcined temperature controlled experiment, tetragonal LaOF (space group P4/nmn and a = 4.091, c = 5.836), has been firstly prepared at 800 °C for 3 h owing to the O_2 oxidation effect of LaF_3 precursor, as shown in Fig. 2. With increasing temperature to 900 °C, rhombohedral phase LaOF (space group R-3 m and $a=4.052$, $c=20.211$) has been further obtained. When the temperature increased to 1000 °C, the main diffraction peaks keep in accordance with rhombohedral phase LaOF according to Powder Diffraction File PDF 89–5166. However, some impurity phase originated from La_2O_3 can also be found, which should be in relation with the decomposition of LaOF in high temperature.

To further validate the phase transformation of rhombohedral LaOF and tetragonal LaOF obtained in 800–900 °C for different heating time, Fig. 3 shows the XRD patterns of LaOF obtained at 800 °C/3 h, 800 °C/6 h, and 900 °C/3 h, respectively. The rhombohedral LaOF (JCPDS No. 89-5166) and tetragonal LaOF (JCPDS No.

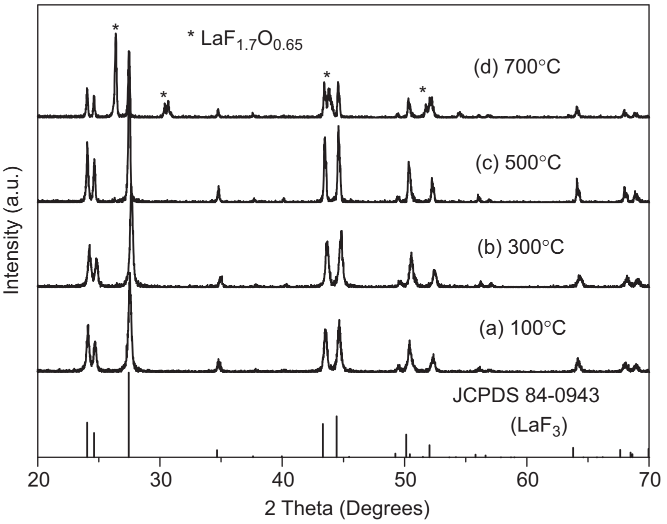

Fig. 1. The XRD patterns of LaF_3 obtained by hydrothermal after heat-treatment at different temperature, (a) 100 °C, (b) 300 °C, (c) 500 °C, (d) 700 °C and the hexagonal LaF_3 (JCPDS No. 84–0943) is also shown as a reference.

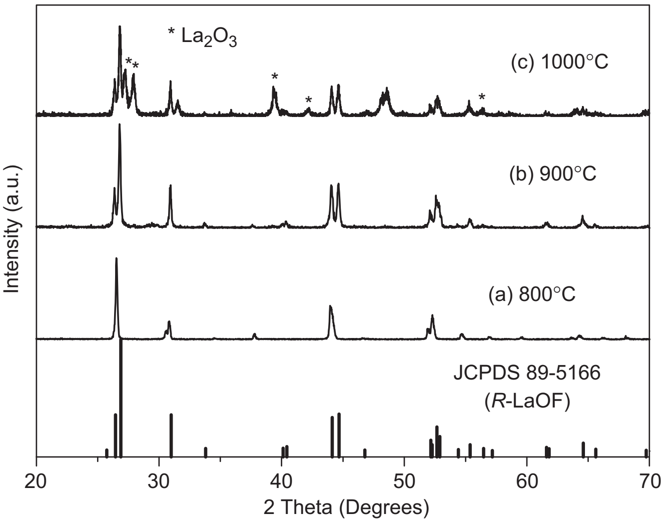

Fig. 2. The XRD patterns of LaOF obtained at different calcined temperature above 800 °C, (a) 800 °C, (b) 900 °C, (c) 1000 °C and the rhombohedral LaOF (JCPDS No. 89-5166) is also shown as references.

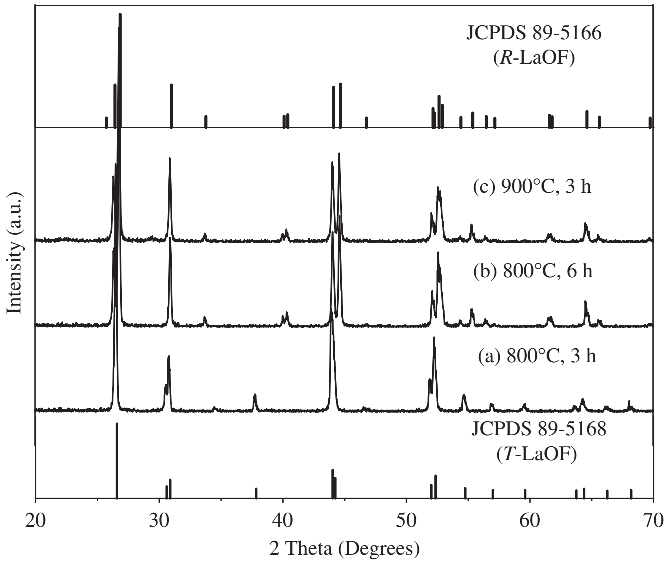

Fig. 3. The XRD patterns of LaOF obtained at different calcined temperature and time, (a) 800 °C/3 h, (b) 800 °C/6 h, (c) 900 °C/3 h and the rhombohedral LaOF (JCPDS No. 89-5166) and tetragonal LaOF (JCPDS No. 89-5168) are shown as references.

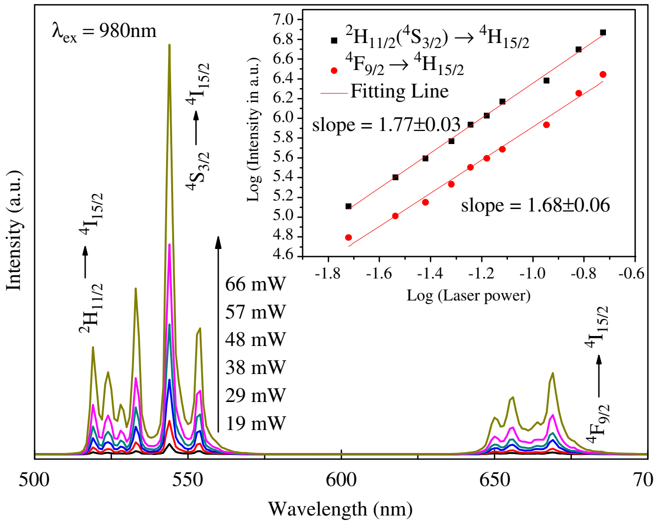

Fig. 4. 980 nm LD power dependent upconversion emission spectra for the sample R-LaOF:0.2Yb^{3+},0.05Er^{3+} obtained at 900 °C, and the inset shows the depenence of upconversion emission intensities on pumping power for $^2H_{11/2}(^4S_{3/2})\rightarrow 4I_{15/2}$ and $^4F_{9/2}\rightarrow ^4I_{15/2}$ transitions of Er^{3+}.

89-5168) are also shown as references. The phase formation for tetragonal LaOF takes place and completes at 800 °C for 3 h. However, tetragonal LaOF acts as the metastable phase in the three form of LaOF compound. With prolonging heating time from 3 h to 6 h at 800 °C and increasing heating temperature from 800 °C to 900 °C, it will help to experience the tetragonal–rhombohedral phase transformation of LaOF, which means that rhombohedral LaOF will be stable from the consideration of thermodynamics factor. Therefore, the phase stable rhombohedral LaOF (R-LaOF) were selected as the host of UC luminescence properties.

Yb^{3+} ion is a good sensitizer which can greatly enhance UC efficiency through energy transfer and Er^{3+} is the most important active ion applied to UC luminescence [11,12]. Accordingly, the optimum Yb^{3+}/Er^{3+} doping concentration has been determined as 0.2/0.05 in this work. Fig. 4 shows pumping power dependent UC emission spectra of R-LaOF:0.2Yb^{3+},0.05Er^{3+} sample obtained at 900 °C/3 h, and the doping concentration is determined from other reported references. By using a 980 nm laser diode (LD) as an excitation source, it is clearly found that the UC emission spectra can be divided into two parts, the green emission lines in the range of 520–560 nm and the red emission lines of 640–680 nm, respectively. The bands in the green region are associated with the $^2H_{11/2}\rightarrow ^4I_{15/2}$ and $^4S_{3/2}\rightarrow ^4I_{15/2}$ transitions of Er^{3+} ions, respectively, while the band in the red region is associated with the $^4F_{9/2}\rightarrow ^4I_{15/2}$ transition of Er^{3+} ions [11–13]. In order to further know the UC mechanism, the inset of Fig. 4 shows the depenence of upconversion emission intensities on pumping power for $^2H_{11/2}(^4S_{3/2})\rightarrow ^4I_{15/2}$ and $^4F_{9/2}\rightarrow ^4I_{15/2}$ transitions of Er^{3+}. For the unsaturated UC process, the number of photons required to populate the upper emitting state can be described by the following relation: $I_{em}\propto(P_{pump})^n$, where I_{em} is the UC emission intensity, P_{pump} denotes the incident pump power, n is the number of photons involved in the pumping mechanism. As given in the inset, the slopes (n values) obtained were 1.77 ± 0.03 and 1.68 ± 0.06 for $^2H_{11/2}(^4S_{3/2})\rightarrow ^4I_{15/2}$ transitions and $^4F_{9/2}\rightarrow ^4I_{15/2}$ transition. These results indicate the observed UC luminescence is ascribed to the two-photon process, as reported in many references [12–14].

4. Conclusions

In summary, rhombohedral and tetragonal LaOF and LaOF:Yb^{3+}/Er^{3+} were prepared via a facile hydrothermal method followed by a heat treatment of LaF$_3$. The phase formation evolution from LaF$_3$ to LaOF with different phase structures was investigated. Heating temperature and time dependent XRD patterns indicate that rhombohedral LaOF will be stable in the process of phase transitions. The UC luminescence property of R-LaOF:Yb^{3+}/Er^{3+} has been investigated, and strong green and weak red UC emissions centered at 533 (544) and 669 nm were ascribed to $^2H_{11/2}(^4S_{3/2})\rightarrow ^4I_{15/2}$ and $^4F_{9/2}\rightarrow ^4I_{15/2}$ transitions, respectively. The two-photon process was confirmed to be responsible for both the green and red UC emissions.

Acknowledgment

This present work was supported by the National Natural Science Foundations of China (Grant no. 51002146), the Ph.D. Programs Foundation of Ministry of Education of China (Grant no. 20090022120002) and the Fundamental Research Funds for the Central Universities (2010ZY35, 2011YYL131).

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