



Synthesis, structure and luminescence properties of Ho³⁺-doped La₂Zr₂O₇ nanoparticles



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ABSTRACT

(La_{1-x}Ho_x)₂Zr₂O₇ ($x = 0, 0.025, 0.05, 0.075, 0.1$) nanoparticles have been successfully synthesized by a facile chemical co-precipitation and calcination method, and were characterized by X-ray diffraction, scanning electron microscopy and photoluminescence spectroscopy. (La_{1-x}Ho_x)₂Zr₂O₇ nanoparticles calcined at 900 °C for 5 h in air exhibit a single phase of defect fluorite-type structure and have a particle size of about 50 nm. The emission bands centered at 542 nm and 553 nm are identified as the ⁵F₄, ⁵S₂ → ⁵I₈ transitions. The emission intensity increases with the increase of the Ho³⁺ ion content, and reaches the maximum for the (La_{0.95}Ho_{0.05})₂Zr₂O₇ nanoparticles, and then decreases with further increasing Ho³⁺ ion content.

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1. Introduction

In last several decades, A₂B₂O₇-type ternary oxides, in which the A-site is trivalent lanthanides or actinides, and the B-site is typically tetravalent metal elements such as Zr, Ti, Ce, Hf or Sn, have received much attention in scientific community [1]. These compounds exhibit a face-centered cubic crystal structure with the space group Fm3m (No. 225) or Fd3m (No. 227). Due to the wide range of chemical compositions and interesting physical and chemical properties, A₂B₂O₇-type oxides have emerged as prospective materials for different applications such as high-temperature ceramic thermal barrier coating materials, photocatalysts, fast ion conductors, host materials for radioactive waste and luminescence centers [2–8]. Luminescence activation by rare-earth-ion doping can give effective emission of different colors from the same materials. Ho³⁺ ion is one of the most popular candidates for such activation on account of its favorable energy levels [9–11]. An enormous amount of effort has been made on the development of rare-earth activated luminescent materials due to their practical and potential applications, such as temperature sensors, three-dimensional color displays, solid-state lasers, optical communication systems and

luminescent probes [12–17]. In the present work, Ho³⁺-doped La₂Zr₂O₇ nanoparticles were synthesized by a facile chemical co-precipitation and calcination method, and their microstructure and photoluminescence properties were investigated.

2. Experimental section

(La_{1-x}Ho_x)₂Zr₂O₇ ($x = 0, 0.025, 0.05, 0.075, 0.1$) nanoparticles were prepared by a facile chemical co-precipitation and calcination method using La₂O₃, Ho₂O₃ and ZrOCl₂·8H₂O powders as raw materials. All the powders used in the experiments were purchased from commercial sources with analytical grade. La₂O₃ and Ho₂O₃ powders were calcined at 900 °C for 2 h in an electric furnace before use. ZrOCl₂·8H₂O was dissolved in distilled water, while the proper amounts of La₂O₃ and Ho₂O₃ were dissolved in dilute nitric acid. These solutions were mixed, stirred vigorously and filtered, and then the solution was slowly added into excessive dilute ammonium hydrate solution under stirring for co-precipitation. The precipitates were washed with distilled water several times to remove Cl⁻ completely, which was tested by the AgNO₃ aqueous solution. Then the precipitates were washed twice in anhydrous ethanol. The remains were dried at 100 °C over night in an oven and calcined at different temperatures for 5 h in air atmosphere.

The crystal structure of the as-prepared Ho³⁺-doped La₂Zr₂O₇ nanoparticles was characterized using an X-ray diffractometer (Rigaku D/max-γB, Japan) with Cu Kα radiation. Diffraction data were recorded in a 2θ range from 10° to 65° at a scanning rate of 4°/

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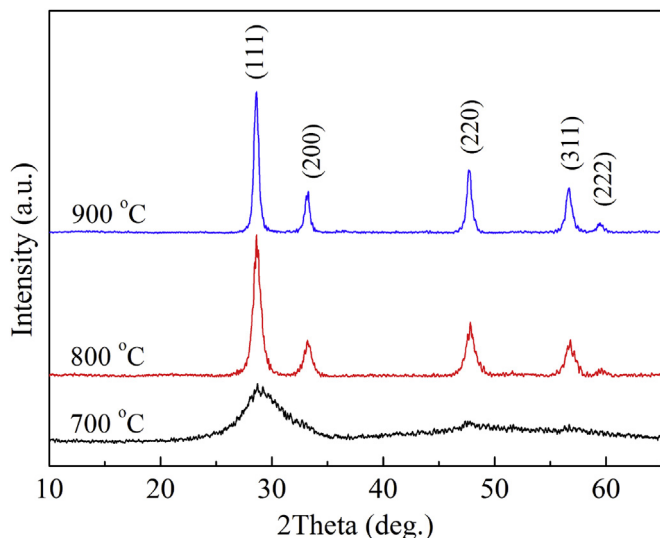


Fig. 1. XRD patterns of $(\text{La}_{0.9}\text{Ho}_{0.1})_2\text{Zr}_2\text{O}_7$ nanoparticles calcined at various temperatures for 5 h in air.

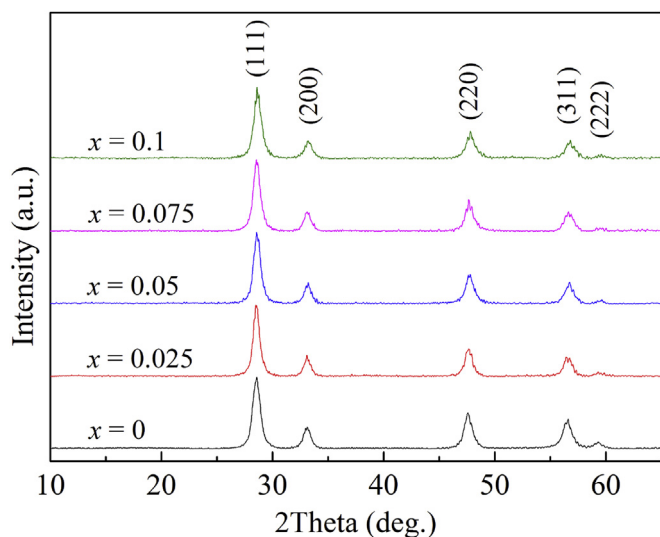


Fig. 2. XRD patterns of $(\text{La}_{1-x}\text{Ho}_x)_2\text{Zr}_2\text{O}_7$ nanoparticles calcined at 900 °C for 5 h in air.

min. The morphology of Ho^{3+} -doped $\text{La}_2\text{Zr}_2\text{O}_7$ nanoparticles was observed using a field-emission scanning electron microscope (FEI Helios Nanolab600i, USA). The photoluminescence measurements were performed at room temperature using a fluorescence spectrophotometer (Hitachi F-4600, Japan).

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of $(\text{La}_{0.9}\text{Ho}_{0.1})_2\text{Zr}_2\text{O}_7$ nanoparticles calcined at various temperatures for 5 h in air. It is obvious that $(\text{La}_{0.9}\text{Ho}_{0.1})_2\text{Zr}_2\text{O}_7$ nanoparticles calcined at 700 °C are primarily amorphous, which can be evidenced by the broad diffraction peak at 2θ value of about 29°. With the increase of the calcination temperature, the intensity of the diffraction peaks becomes stronger, indicating a better crystallization. The XRD patterns of $(\text{La}_{0.9}\text{Ho}_{0.1})_2\text{Zr}_2\text{O}_7$ nanoparticles calcined at 800 °C and 900 °C are similar and exhibit a single phase of defect fluorite-type structure, which suggests that $(\text{La}_{0.9}\text{Ho}_{0.1})_2\text{Zr}_2\text{O}_7$ nanoparticles

crystallize completely at 900 °C. The diffraction peaks are indexed on the basis of defect fluorite-type structure with $Fm\bar{3}m$ space group. Miller indices, hkl , corresponding to each peak are shown in Fig. 1.

Fig. 2 presents the XRD patterns of $(\text{La}_{1-x}\text{Ho}_x)_2\text{Zr}_2\text{O}_7$ nanoparticles calcined at 900 °C for 5 h in air. It can be observed that $(\text{La}_{1-x}\text{Ho}_x)_2\text{Zr}_2\text{O}_7$ nanoparticles show a single phase of defect fluorite-type structure, and have wide diffraction peaks because of fine $(\text{La}_{1-x}\text{Ho}_x)_2\text{Zr}_2\text{O}_7$ nanoparticles. Additionally, no other possible impure phases such as La_2O_3 , Ho_2O_3 , and ZrO_2 are detected. Fig. 3 gives the typical SEM images of $(\text{La}_{0.95}\text{Ho}_{0.05})_2\text{Zr}_2\text{O}_7$ nanoparticles calcined at different temperatures for 5 h in air. From SEM observations, $(\text{La}_{0.95}\text{Ho}_{0.05})_2\text{Zr}_2\text{O}_7$ nanoparticles calcined at different temperatures have similar morphology characteristics: either spheroidal or spherical, relative uniform particle size and a certain extent agglomeration. The average particle size of $(\text{La}_{1-x}\text{Ho}_x)_2\text{Zr}_2\text{O}_7$ nanoparticles calcined at 900 °C is about 50 nm, obtained from the SEM images by averaging 50 particles.

Fig. 4 displays the typical excitation spectra of $(\text{La}_{1-x}\text{Ho}_x)_2\text{Zr}_2\text{O}_7$ nanoparticles calcined at 900 °C for 5 h in air, measured at 544 nm and 554 nm. It is clearly seen from Fig. 4(a) and (b) that the spectral shape is very similar under different emission wavelengths, and the spectra consist of eight excitation peaks centered at about 362 nm, 386 nm, 419 nm, 449 nm, 456 nm, 464 nm, 473 nm and 485 nm, respectively. Compared with the energy levels of the Ho^{3+} ion [18], these eight excitation peaks come from the direct excitation from the ground state to the excited state of the Ho^{3+} ion, corresponding to the $4f$ transition from $^5\text{I}_8$ to $^3\text{H}_6$, $^5\text{G}_4$, $^5\text{G}_5$, $^5\text{F}_1$, $^5\text{G}_6$, $^3\text{K}_8$, $^5\text{F}_2$ and $^5\text{F}_3$ of the Ho^{3+} ion, respectively. The intensity of these peaks increases with the increase of the Ho^{3+} ion content from $x = 0$ to $x = 0.05$, and then decreases with further increasing the Ho^{3+} ion content from $x = 0.05$ to $x = 0.1$.

Fig. 5 shows the emission spectra of $(\text{La}_{1-x}\text{Ho}_x)_2\text{Zr}_2\text{O}_7$ nanoparticles calcined at 900 °C for 5 h in air. Three main emission bands centered at about 542 nm, 553 nm and 591 nm can be observed under the excitation wavelength of 363 nm, while there are two main emission bands centered at about 542 nm and 553 nm under the excitation wavelength of 460 nm. Compared with the energy levels of the Ho^{3+} ion [18], the emission bands centered at 542 nm and 553 nm are identified as the $^5\text{F}_4$, $^5\text{S}_2 \rightarrow ^5\text{I}_8$ transitions, which are the transitions from the excited state to the ground state of the Ho^{3+} ion. However, the emission band centered at 591 nm can be assigned to the $^5\text{G}_6 \rightarrow ^5\text{I}_7$ transition of the Ho^{3+} ion between two different excited states. Obviously, the Ho^{3+} ion content has a great influence on the emission intensity. The emission intensity of $\text{La}_2\text{Zr}_2\text{O}_7$ nanoparticles without Ho^{3+} ion is quite weak. With the increase of the Ho^{3+} ion content x , the emission intensity increases from $x = 0$ to $x = 0.05$, and reaches the maximum at $x = 0.05$, and then decreases from $x = 0.05$ to $x = 0.1$. When $\text{La}_2\text{Zr}_2\text{O}_7$ nanoparticles doped with Ho^{3+} ion are excited, the emission intensity rapidly increases. Meanwhile, the fluorescence quenching has more and more influence on the emission intensity with the increase of the Ho^{3+} ion content, and it will lead to the decrease of the emission intensity. Thus, these two processes are competing, which result in the change of the emission intensity.

4. Conclusions

$(\text{La}_{1-x}\text{Ho}_x)_2\text{Zr}_2\text{O}_7$ ($x = 0, 0.025, 0.05, 0.075, 0.1$) nanoparticles with a particle size of about 50 nm were synthesized by the chemical co-precipitation and calcination method, and exhibit a single phase of defect fluorite-type structure. The emission bands centered at 542 nm and 553 nm are identified as the $^5\text{F}_4$, $^5\text{S}_2 \rightarrow ^5\text{I}_8$ transitions. The emission intensity increases with the increase of the Ho^{3+} ion content, and reaches the maximum for the

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