Synthesis and Optical Characterization of Samarium Doped Lanthanum Orthophosphate Nanowires

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LaPO₄ nanowires doped with 0, 1, 2, 3, 4 and 5 mol% Sm³⁺ were prepared by co-precipitation technique. These nanowires were studied by X-ray diffraction (XRD), transmission electron microscopy (TEM), photoluminescence (PL), photoluminescence excitation (PLE) spectra and energy-dispersive X-ray spectra (EDS). The PL spectra exhibited 4 groups of emission peaks, which are assigned to the transitions from the excited state ⁴G_{5/2} to the ground states ⁶H_J with $J = 5/2; 7/2; 9/2$ and $11/2$ of Sm³⁺ ions. The intensity of PL related to Sm³⁺ ion reached to a maximum when the Sm doping content was 2 mol%. The PLE spectra show 8 peaks, which are attributed to the absorption transitions from the ⁶H_{5/2} ground state to the ⁴K_{15/2}, ⁴D_{3/2}, ⁶P_{7/2}, ⁴F_{7/2}, ⁶P_{5/2}, ⁴G_{9/2}, ⁴I_{13/2} and ⁴I_{11/2} excited states. [doi:10.2320/matertrans.MA201526]

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1. Introduction

In recent years, rare-earth phosphates have proved to be very useful host lattices for luminescence, and have found widespread applications in various kinds of display devices. For instance, lanthanum orthophosphate (LaPO₄) has been used in lasers, fluorescent lamps, displays and sensors. In particular, LaPO₄ is known as a promising host material for lanthanide ions to fabricate phosphors. Doping with different rare earth ions (Eu³⁺, Tb³⁺, Ce³⁺, Pr³⁺, etc.) allows to synthesize the phosphors emitting in a broad range of colours.¹⁻⁷⁾ To the best of our knowledge, most of previous works have been focused on the Eu³⁺-, Tb³⁺-, Ce³⁺-doped LaPO₄;^{1-3,6)} only a few works were devoted to the doping LaPO₄ with Sm³⁺ ions.⁷⁾ In Ref. 7) the LaPO₄:Eu³⁺,Sm³⁺ nanorods were synthesized by hydrothermal method and possessed a pure monoclinic structure.

In this article, hexagonal LaPO₄ nanowires doped with Sm³⁺ ions were prepared by co-precipitation technique. The structure, the PL and PLE properties of LaPO₄:Sm³⁺ nanowires have been investigated in detail.

2. Experimental Procedure

Undoped and Sm³⁺-doped LaPO₄ nanowires were prepared by co-precipitation method from lanthanum oxide La₂O₃, samarium oxide Sm₂O₃ and ammonium dihydrogen phosphate NH₄H₂PO₄ as precursors. The lanthanum nitrate La(NO₃)₃ and samarium nitrate Sm(NO₃)₃ solution were obtained by dissolving La₂O₃ and Sm₂O₃, respectively, in nitric acid HNO₃ (30%) solution under heating with agitation for 15 min. To prepare NH₄H₂PO₄ solution, 30 mg of NH₄H₂PO₄ was dissolved in 60 mL of double distilled water under constant stirring for 15 min. In a typical synthesis, stoichiometric amounts of La(NO₃)₃ and Sm(NO₃)₃ aqueous solutions were mixed. The molar ratio of Sm : La was 0, 1, 2, 3, 4 and 5 mol%. Then appropriate amounts of NH₄H₂PO₄ solution were added into the mixed nitrate solution under

stirring for 3 h at room temperature. The resulting precipitate was filtered off and washed many times in water and ethanol to remove chemicals possibly remaining in the final products. The last products were dried in air at 65°C for 6 h, obtaining white fine powders.

The synthesized nanowires were studied by X-ray diffractometer SIEMENS D5005, Bruker with CuK_{α1} irradiation ($\lambda = 1.54056 \text{ \AA}$), transmission electron microscope JEOL JEM 1010, spectrofluorometer Fluorolog FL 3-22 Jobin-Yvon-Spex and X-ray spectrometer OXFORD ISIS 300 attached to the JEOL-JSM5410 LV scanning electron microscope.

3. Results and Discussion

TEM images of the 2% Sm³⁺-doped LaPO₄ samples are illustrated in Fig. 1. It can be seen clearly that the LaPO₄ samples are composed of nanowires which are 7–8 nm in diameter and about several hundred nm in length.

XRD analysis of the synthesized LaPO₄ nanowires showed that the samples exhibited a pure hexagonal structure (Fig. 2). All the diffraction peaks were in good agreement with the standard data JCPDS 04-0635. The lattice parameters calculated from XRD patterns are $a = b = 7.08 \text{ \AA}$, $c = 6.52 \text{ \AA}$.

Figure 3 shows EDS spectra of the LaPO₄ nanowires undoped and doped with 5% Sm³⁺. The undoped LaPO₄ nanowires mainly consist of the following elements: lanthanum (La), phosphorus (P) and oxygen (O). The 5% Sm³⁺-doped LaPO₄ nanowires exhibit some peaks related to samarium (Sm) element, indicating the penetration of Sm³⁺ ions into the host lattice.

The room temperature PL spectra of LaPO₄ nanowires undoped and doped with 1, 2, 3, 4 and 5% Sm³⁺ excited by 402 nm wavelength are represented in Fig. 4. The undoped nanowires do not exhibit the groups of emission peaks in the wavelength range from 525 to 750 nm. The Sm³⁺-doped LaPO₄ nanowires show 4 groups of emission peaks at 560, 596, 645 and 705 nm. Figure 4 and its inset indicate that the intensity of PL spectra related to Sm³⁺ ion reaches to a maximum when the Sm doping content is 2 mol%, which is

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Fig. 1 (a) Low magnified and (b) high magnified TEM images of the LaPO_4 doped with 2% Sm^{3+} .

Fig. 2 XRD patterns of the LaPO_4 nanowires doped with different Sm^{3+} contents.

Fig. 4 PL spectra of LaPO_4 nanowires doped with different Sm^{3+} contents. The inset shows the intensity of 596 and 560 nm peaks as a function of Sm concentration.

Fig. 3 EDS spectra of the LaPO_4 nanowires (a) undoped and (b) doped with 5% Sm^{3+} .

in good agreement with Ref. 7). However, PL intensity decreases with further increasing the doping concentration. It is well known that, in general, when the concentration of an activator is higher than an appropriate value, the luminescence of the phosphor is usually lowered. This effect is called concentration quenching. The origin of this effect is known to be one of the following:⁸⁾

- (1) Excitation energy is lost from the emitting state due to cross-relaxation between the activators.
- (2) Excitation migration due to the resonance between the activators is increased with increasing the concentration, so that the energy reaches remote quenching centers or the surface states acting as quenching centers.

- (3) The activator ions are paired or coagulated and are changed to a quenching center.

The decrease of luminescence intensity in our Sm^{3+} -doped LaPO_4 samples at the Sm^{3+} ion concentrations higher than 2 mol% can be attributed to the concentration quenching effect due to the pairing or coagulation of the Sm^{3+} ions. The groups of peaks at 560, 596, 645 and 705 nm are assigned to the transitions from the excited state $^4G_{5/2}$ to the ground states 6H_J with $J = 5/2; 7/2; 9/2$ and $11/2$ of Sm^{3+} ions,⁹⁾ respectively.

It is worth noting that all the emission line groups have the same excitation spectra. Typical PLE spectrum monitored at 596 nm emission line of 2% Sm^{3+} -doped LaPO_4 nanowires

Fig. 5 PLE spectrum monitored at 596 nm emission line of LaPO_4 nanowires doped with 2% Sm^{3+} .

is depicted in Fig. 5. The excitation lines located around 345, 362, 374, 402, 415, 439, 463 and 475 nm are attributed to the absorption transitions from the $^6H_{5/2}$ ground state to the $^4K_{15/2}$, $^4D_{3/2}$, $^6P_{7/2}$, $^4F_{7/2}$, $^6P_{5/2}$, $^4G_{9/2}$, $^4I_{13/2}$ and $^4I_{11/2}$ excited states,⁹⁾ respectively.

4. Conclusion

The Sm^{3+} -doped LaPO_4 nanowires were prepared by co-precipitation technique. The XRD analysis showed that the nanowires exhibited a pure hexagonal structure. The intensity of PL spectra related to Sm^{3+} ions reached to a maximum

when the Sm doping content was 2 mol%. The PL and PLE spectra originate from the optical transitions between the ground and excited states within Sm^{3+} ions in the LaPO_4 host lattice.

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