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# Structure and Photoluminescence Characterization of $LaPO_4:Sm^{3+}$ Nanowires Prepared by Hydrothermal Method

Pham Thi Thanh Hien, Duong Thi Mai Huong*,
Nguyen Ngoc Long, Le Van Vu, Hoang Manh Ha

*Faculty of Physics, VNU University of Science, 334 Nguyen Trai, Thanh Xuan, Hanoi, Vietnam*

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**Abstract:** $LaPO_4$ nanowires doped with 1, 2,…8 mol% $Sm^{3+}$ were prepared by a hydrothermal method. The samples were characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD), photoluminescence (PL), photoluminescence excitation (PLE), and absorption (ABS) spectroscopy. It was discovered that the PL and PLE of $Sm^{3+}$ ions resulted from the radiative intra-configurational f-f transitions. The photoluminescence spectra shows 4 peaks at 560 nm, 596 nm, 642 nm and 701 nm which were assigned to different transitions from the $^4G\ (4)_{5/2}$ excited state to the $^6H_J$ with J = 5/2; 7/2; 9/2; 11/2 ground states of $Sm^{3+}$ ion. The intensity of PL related to $Sm^{3+}$ ion reached to a maximum when the Sm doping content was 2 mol%. Diffuse reflective spectra measured at room temperature of the $Sm^{3+}$ doped $LaPO_4$ exhibited absorption peaks at 343, 362, 374, 401, 415, 439, 460 and 477 nm which were observed in PLE spectra as well.

*Keywords*: Hydrothermal method, samarium doped lanthanum orthophosphate, nanowires.

## 1. Introduction

In recent years, rare earth phosphate compound has received a lot of research attention because of its potential applications as a luminescent material in many fileds. For instance, lanthanum orthophosphate ($LaPO_4$) has been used in sensors, fluorescent lamp, display, lasers [1, 2]. In addition, rare-earth phosphate has high melting point and large specific surface areas than conventional phosphate material [3]. $LaPO_4$ crystallizes in two possible structures: hexagonal and monoclinic, depending on synthesis method and technological conditions [4, 5]. Some previous work indicates that the samples prepared at a low temperature crystallize in a hexagonal structure [6], and the material changes in structure to monoclinic phase when temperature rises. In this report, it was found that the structural phase transformation of $LaPO_4$ occured not only when the temperature changed but also when the pH value of precursor solution changed.

* Corresponding author. Tel.: 84-988648823
Email: maihuongk12@gmail.com

In the current article, $LaPO_4$ nanowires doped with $Sm^{3+}$ ions were prepared by hydrothermal technique. The structural and optical properties of the nanowires have been investigated in detail.

## 2. Experimental

### *2.1. Sample preparation*

$LaPO_4:Sm^{3+}$ were prepared by hydrothermal method from $La(NO_3)_3$, $Sm(NO_3)_3$ solution, and ammonium dihydrogen phosphate $NH_4H_2PO_4$. To prepare $NH_4H_2PO_4$ solution, 30 mg of $NH_4H_2PO_4$ was dissolved in 60 mL of double distilled water under constant stirring for 15 mins. In a typical synthesis, stoichiometric amounts of $La(NO_3)_3$ and $Sm(NO_3)_3$ aqueous solutions were mixed, under stirring for 30 mins. In next step, an appropriate amount of $NH_4H_2PO_4$ solution was added into the mixed nitrate solution, receiving 90 mL of opalescent solution. The final pH value controlled by $NH_4OH$ solution (2 M). The molar ratio of Sm:La was 0, 1, 2, …8 mol%. After thorough stirring, the milky colloidal solution was transferred to a 120 mL Teflon-lined autoclave, heated at 120-220°C for 6 h, and then cooled to room temperature naturally. The obtained precipitate was centrifuged and washed with fresh water, ethanol many times to remove chemicals possibly remaining in the final products. Last products were dried in air at 60°C for 6 hours, obtaining white fine powders.

### *2.2. Characterization*

The surface morphology of the samples was observed by using a JEOL JEM 1010 transmission electron microscope (TEM). Crystal structure of the powders was analyzed by X-ray diffraction (XRD) using an X-ray diffractometer SIEMENS D5005, Bruker with Cu $K\alpha_1$ ($\lambda$ = 1.54056 Å) irradiation. The composition of the samples was determined by an energy-dispersive X-ray spectrometer (EDS) OXFORD ISIS 300 attached to the JEOL-JSM5410LV scanning electron microscope. The PL and the PLE spectra of the samples were carried out on a spectrofluorometer Fluorolog FL 3-22 Jobin-Yvon-Spex with a 450W xenon lamp as an excitation source. All the spectra have been measured at room temperature. Diffuse reflection spectroscopy measurements were carried out on a UV-VIS-NIR Cary-5000 spectrophotometer. The spectra were recorded at room temperature in the wave length region of 200-900 nm. Absorption spectra of the samples were obtained from the diffuse reflectance data by using the Kubelka-Munk function [7]:

$$F(R) = \frac{(1-R)^2}{2R} = \frac{K}{S}$$

where *R, K* and *S* are the reflection, the absorption and the scattering coefficient, respectively.

## 3. Results and discussion

### *3.1. Morphology and Crystal Structure*

Fig. 1 shows TEM image of the $LaPO_4$ sample prepared 220 °C for 6 h. It can be seen clearly from TEM that the $LaPO_4$ sample are composed of nanowires which are about 2.5 µm

in length and 7-20 nm in diameter. XRD analysis of the synthesized $LaPO_4$ nanowires indicated that the samples hydrothermally prepared at low temperatures (120, 140 $^oC$) exhibited a pure hexagonal structure (JCPDS 04-0635) (lines a, b in Fig. 2). The lattice parameters calculated for the hexagonal phase from the XRD patterns are $a = 7.05 \pm 0.01$ Å, $c = 6.45 \pm 0.01$ Å. When the hydrothermal temperature was increased to 160, 170 $^oC$, apart from the XRD peaks of hexagonal phase, some peaks of monoclinic phase could be seen.

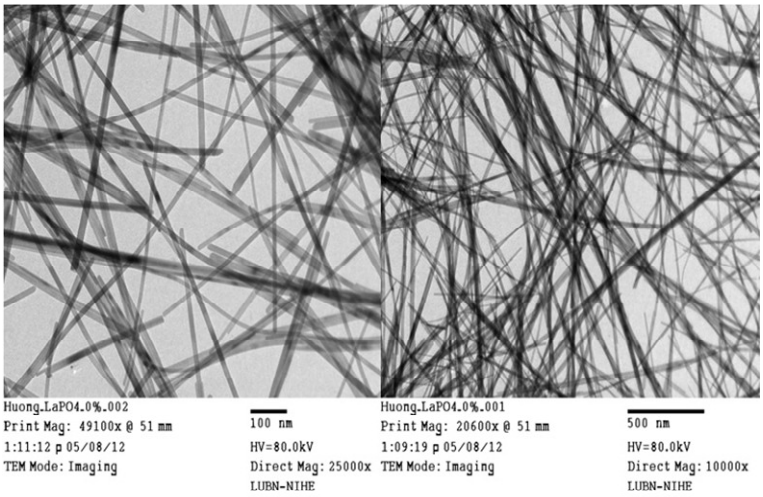


Fig. 1. TEM image of $LaPO_4$ nanowires synthesized at 220$^o$C for 6 h.

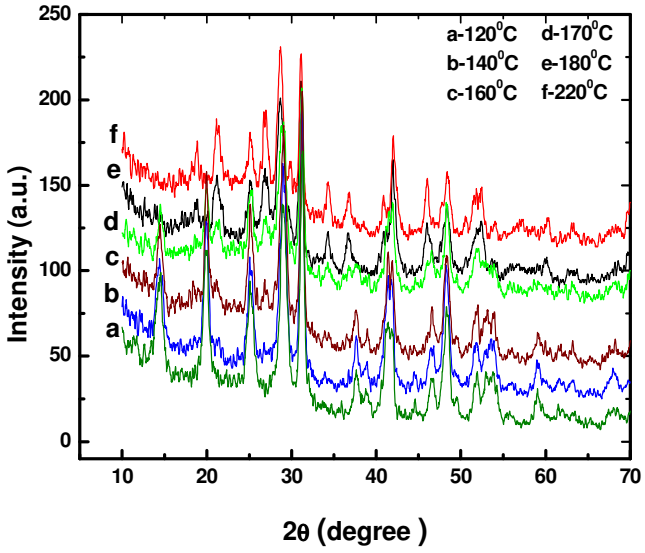


Fig. 2. XRD patterns of $LaPO_4$ nanowires prepared at hydrothermal temperatures of 120 – 220$^o$C for 6 h.

For the samples synthesized at hydrothermal temperatures of 180, 200 and 220°C, XRD analysis clearly indicates that the $LaPO_4$ samples possess monoclinic crystal structure. The lattice parameters calculated from XRD patterns for the monoclinic phase are $a$ = 6.84 ± 0.01 Å, $b$ = 7.09 ± 0.01 Å, $c$ = 6.50 ± 0.01 Å, $\beta$ = 103.6°. They are in good agreement with the standard data JCPDS 32-0493.

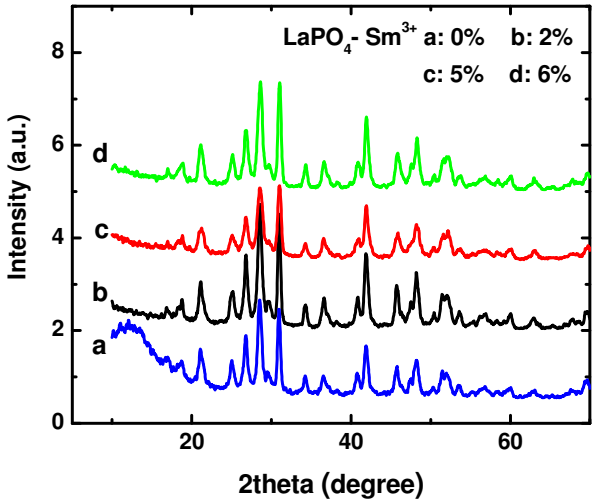


Fig. 3. XRD patterns of $LaPO_4$:$Sm^{3+}$ (0, 2, 5, and 6 mol%) nanowires prepared at 220 °C for 6 h.

Typical XRD patterns of $LaPO_4$ nanowires doped with 0, 2, 5 and 6 mol% $Sm^{3+}$ prepared at 220 °C for 6h are shown in Fig. 3. All the peaks in the XRD patterns clearly indicate that the undoped and $Sm^{3+}$-doped $LaPO_4$ samples possess monoclinic crystal structure. No other diffraction peaks are detected except for the $LaPO_4$ related peaks. All the diffraction peaks are in good agreement with the standard data JCPDS 04-0635.

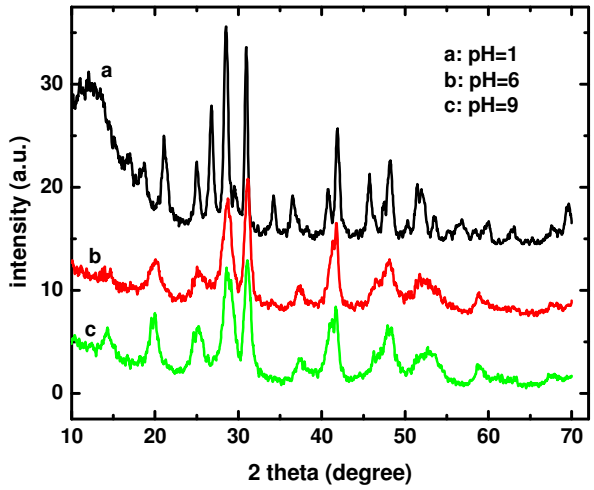


Fig. 4. XRD patterns of the undoped $LaPO_4$ nanowires prepared at pH = 1, 6, and 9.

Fig. 4 shows typical XRD patterns of undoped $LaPO_4$ nanowries prepared at different pH condition. As can be seen from the figure, the structure changes from monoclinic to hexagonal when the solution pH value increases from 1 to 9. All the XRD peaks of the sample prepared at pH = 1 clearly indicate that the undoped $LaPO_4$ samples possess monoclinic crystal structure. When pH value increases up to 9 the samples exhibit hexagonal crystal structure.

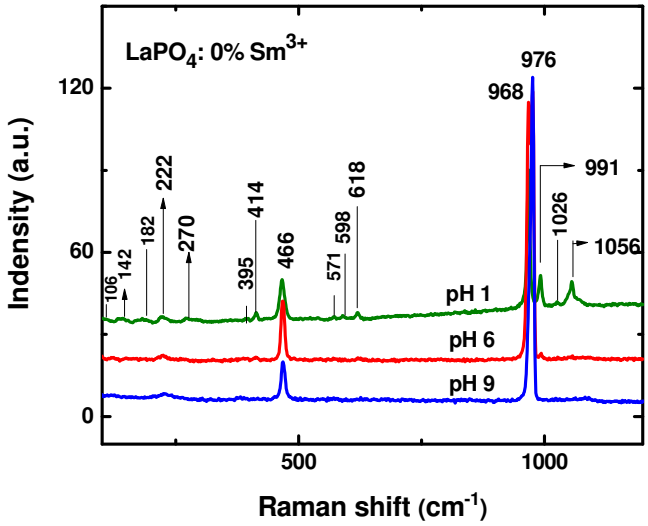


Fig. 5. Room temperature Raman spectra of $LaPO_4$ nanopowders prepared at pH = 1, 6, and 9.

In addition to XRD, TEM techniques, Raman scattering spectroscopy is becoming a powerful technique for the characterization of materials. Our Raman measurements were performed at room temperature in the wavenumber range from 100 to 1200 $cm^{-1}$. The Raman spectra of the undoped $LaPO_4$ nanowires prepared at pH = 1, 6, and 9 are depicted in Fig. 5 and 6. As can be seen from the figure, the Raman spectrum of the $LaPO_4$ nanowires fabricated at pH = 1 with monoclinic structure exhibits fine structure consisted of several scattering line groups: the first group: 106, 142, 182, 222 and 270 $cm^{-1}$ in the range of 100-300 $cm^{-1}$, the second group: 395, 414 and 466 $cm^{-1}$ in the range of 375-500 $cm^{-1}$; the third group: 571, 598 and 618 $cm^{-1}$ in the range of 525-625 $cm^{-1}$; the fourth group: 968 and 976 $cm^{-1}$ in the range of 950-980 $cm^{-1}$; and the fifth group: 991, 1026 and 1056 $cm^{-1}$ in the range of 990-1075 $cm^{-1}$. Whereas the Raman spectrum of the $LaPO_4$ nanowires fabricated at pH = 9 with hexagonal crystal structure shows the first group: 227 $cm^{-1}$; the second group: 381, 466 $cm^{-1}$; the third group: 571 $cm^{-1}$; the fourth group: 976 $cm^{-1}$. The observed lines of Raman spectra of $LaPO_4$ nanowires are assigned to the lattice vibrations and typical vibrational bands of the $(PO_4)^{3-}$ tetrahedron [8].

Representative EDS spectra of the $LaPO_4$ powder are shown in Fig. 7. The EDS spectrum of the undoped sample confirms the presence of lanthanum (La), phosphorus (P) and oxygen (O). The spectrum of the $LaPO_4$ sample doped with 5 mol% $Sm^{3+}$ exhibits the peaks related to La, P, O, and the peaks of $Sm^{3+}$. It can be noted that the weak peak ralated to natri (Na) and aluminum (Al) in the EDS spectra is the residual not totally removed during washing, the peak related to carbon (C) comes from the carbon tapes used for sticking samples.

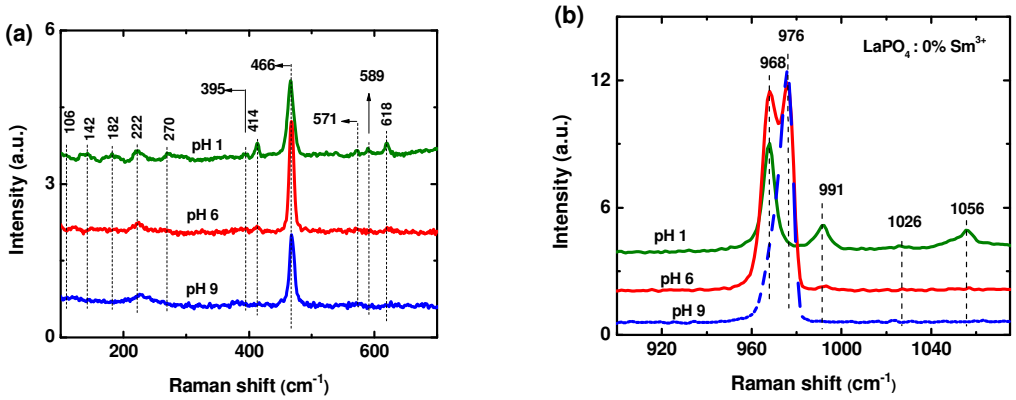


Fig. 6. Room temperature Raman spectra of the $LaPO_4$ nanopowers prepared at pH = 1, 6, and 9 in various wavenumber region (a) from 100 $cm^{-1}$ to 700 $cm^{-1}$ and (b) from 900 $cm^{-1}$ to 1080 $cm^{-1}$.

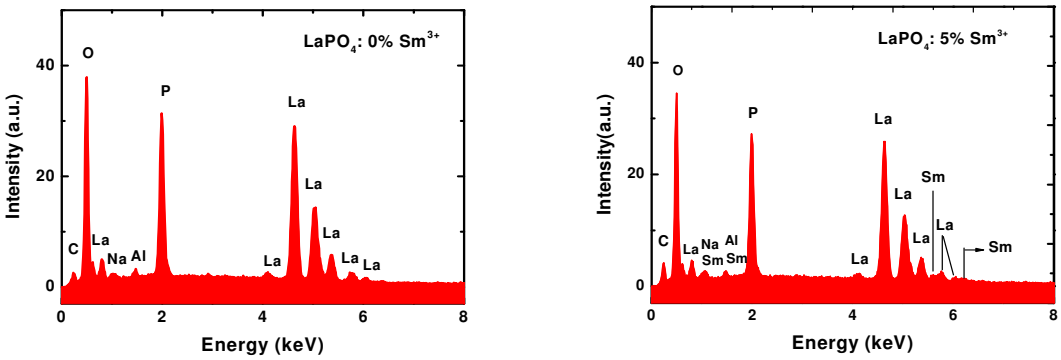


Fig. 7. The EDS spectra of $LaPO_4$ and $LaPO_4$:$Sm^{3+}$ (5 mol%) nanowires prepared at 220 $^oC$ for 6 h.

### *3.2. Optical properties*

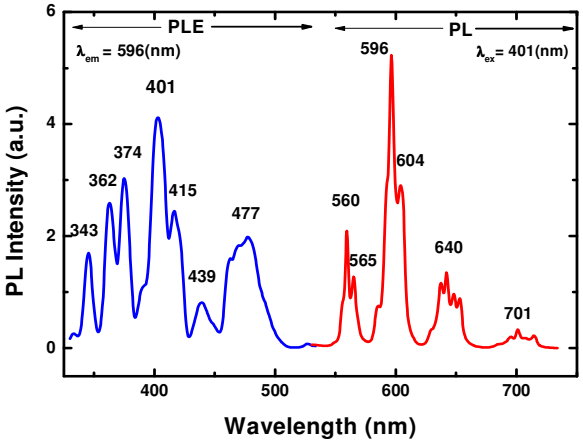


Fig. 8. Typical PL and PLE spectra of $LaPO_4$:$Sm^{3+}$ (2 mol %) nanowires.

The room temperature PLE spectrum monitored at 596 nm and the PL spectrum under excitation wavelength of 401 nm of the $LaPO_4$ nanowires doped with 2 mol% $Sm^{3+}$ are shown in Fig. 8. As seen below, the lines in the two spectra are interpreted as the absorptive and radiative intra-configurational f-f transitions in the $Sm^{3+}$ ions.

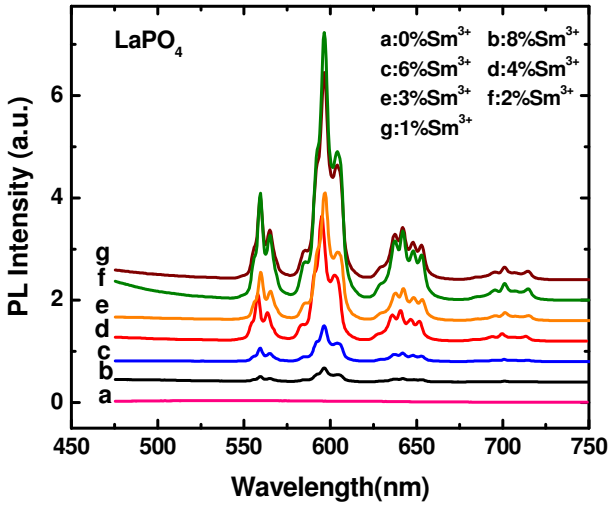


Fig. 9. PL spectra of $LaPO_4$: $Sm^{3+}$ (0, 1, 2, 3, 4, 6, 8 mol%) under 401 nm excitation wavelength.

Fig. 9 shows the room temperature PL spectra under excitation wavelength of 401 nm of $LaPO_4$ nanowires doped with various concentrations of $Sm^{3+}$. The undoped samples do not emit light. The figure indicates that the PL intensity achieved its maximal value in the samples doped with 2 mol% $Sm^{3+}$. The decrease of PL intensity is observed in samples doped with $Sm^{3+}$ at the concentrations higher than 2 mol%. This is the well-known concentration quenching phenomenon.

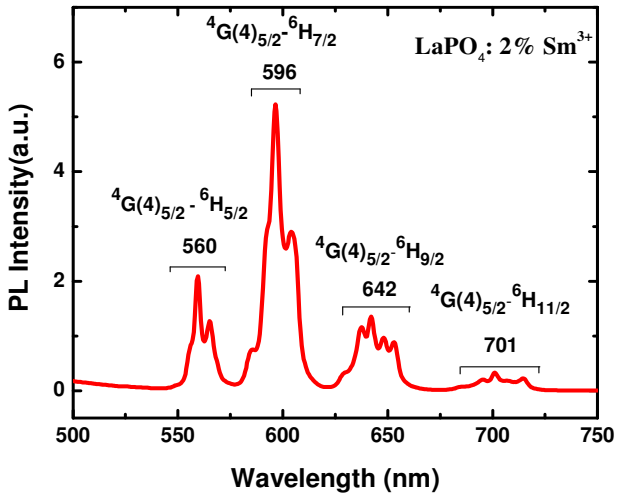


Fig. 10. PL spectrum of $LaPO_4$: $Sm^{3+}$ (2 mol%) nanowires under 403 nm excitation wavelength.

In order to interpret the origin of the emission lines, the room temperature PL spectrum under 401 nm excitation wavelength of $LaPO_4$ doped with 2 mol% of $Sm^{3+}$ is illustrated in Fig.10. The emission lines located at around 560, 596, 642 and 701 nm are attributed to the radiative transitions from the $^4G(4)_{5/2}$ exited states to the $^6H_{5/2}$, $^6H_{7/2}$, $^6H_{9/2}$, $^6H_{11/2}$ ground states, respectively. It is worth noting that all the emission line groups have the same excitation spectra, which prove that all these lines possess the same origin.

Fig. 11 represented a typical PLE spectrum monitored at 596 nm emission line of $LaPO_4:Sm^{3+}$ (2 mol%) nanowires. The groups of excitation lines located at around 343, 362, 374, 401, 415, 439, 460 and 477 nm are attributed to the absorption transitions from the $^6H_{5/2}$ ground state to the $^4H(1)_{9/2}$, $^4F(3)_{9/2}$, $^6P_{7/2}$, $^4F(3)_{7/2}$, $^4P_{5/2}$, $^4M_{17/2}$, $^4I(3)_{13/2}$ and $^4I(3)_{11/2}$ excited states, respectively.

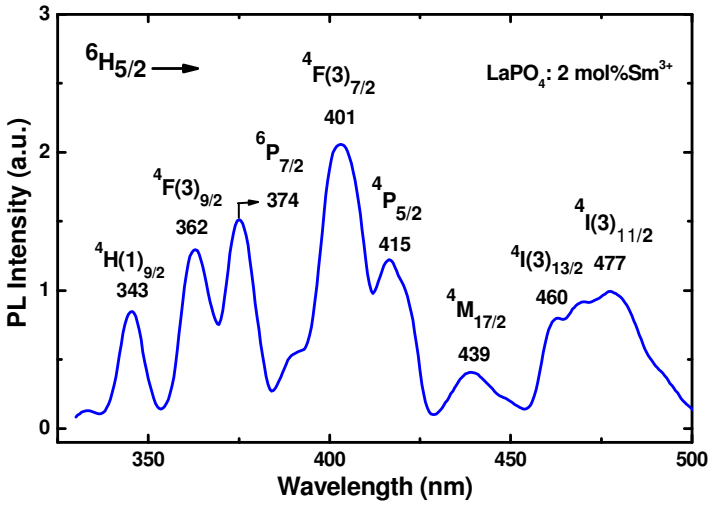


Fig. 11. PLE spectrum monitored at 596 nm of $LaPO_4:Sm^{3+}$ (2 mol%) nanowires.

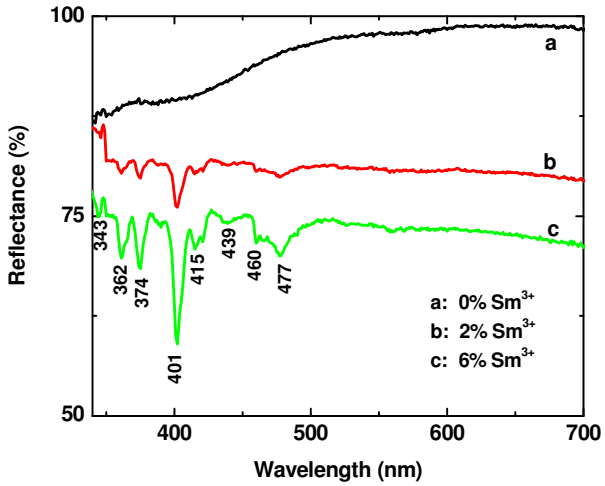


Fig. 12. Diffuse reflection spectra at room temperature of the $LaPO_4:Sm^{3+}$ (0, 2, 6 mol%) nanowires.

Fig. 12 depicts diffuse reflection spectra measured at room temperature of the undoped $LaPO_4$, 2 mol% and 6 mol% $Sm^{3+}$-doped $LaPO_4$ nanowires. Can be seen that none of the absorption lines appears in the diffuse reflection spectrum of the undoped $LaPO_4$ , while eight absorption lines located at 343, 362, 374, 401, 415, 439, 460 and 477 nm are clearly observed in the spectrum of 6 mol% $Sm^{3+}$-doped $LaPO_4$ nanowires.

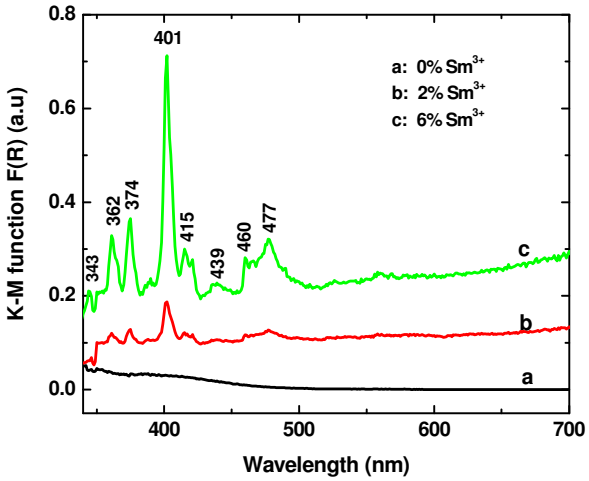


Fig. 13. Plot of Kubelka-Munk function F(R) proportional to absorption coefficient for the $LaPO_4$:$Sm^{3+}$ (0, 2, 6 mol%) nanowires.

Absorption spectra obtained from the diffuse reflectance data by using the Kubelka–Munk function F(R) for the undoped, the 2 and 6 mol% $Sm^{3+}$-doped $LaPO_4$ are shown in Fig. 13. It is interesting to note that eight mentioned above absorption lines observed in the plot of Kubelka-Munk function have appeared in the excitation spectrum and are interpreted as shown in Fig. 11.

## 4. Conclusion

The $LaPO_4$ nanowires doped $Sm^{3+}$ with concentrations from 1 to 8 mol% have been successfully synthesized by the hydrothermal method. Crystal structure of the $LaPO_4$ nanowires changes from monoclinic phase to hexagonal one when the pH value of precursor solution increases from 1 to 9. TEM images show that $LaPO_4$ nanowires have about 2.5 µm in length and 7-20 nm in diameter. The PL intensity is strongest in the $LaPO_4$ samples doped with 2 mol% $Sm^{3+}$. The PL and PLE spectra of $Sm^{3+}$ ions result from the optical intra-configurational f–f transitions. The excitation lines were observed as well in diffuse reflection spectra measured at room temperature.

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