

Density functional theory calculations of structural, electronic and optical properties of LaPO₄:Eu



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ABSTRACT

Monoclinic LaPO₄ and LaPO₄:Eu have been prepared by the hydrothermal method. The phase composition, UV–Vis absorption spectrum, excitation and emission spectra of as-obtained products were measured. Theoretical calculations of the structural, electronic and optical properties of LaPO₄ and LaPO₄:Eu were also carried out. The results indicated that the lattice parameters, energy gap and optical properties were in good agreement with the experimental results. The impurity energy levels induced by the 4f states of Eu expanded the absorption edge and decreased the band gap. The charge transfer energy of O(2p)–Eu(4f) calculated was about 4.41 eV, which was close to the value achieved in excitation spectrum (4.5 eV).

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1. Introduction

As functional inorganic materials, lanthanide orthophosphates are widely applied to fluorescent lamp, biomedicine, catalysts and proton conductors [1–4]. Recent years, considerable attention has been paid to its synthesis methods, raw material selection and photoluminescence property [5–8]. However, there are still some challenges such as the energy transfer, the occupation of doping ions and the luminescence mechanism.

Nowadays, theoretical calculations have become a useful method to study electronic structure [9], spectral properties [10], crystallographic evolution [11], reaction mechanism [12] and morphology [13]. Also, the calculated results require experimental data to confirm or revise.

In this paper, we present a work based on the experimental and theoretical study on LaPO₄:Eu. We prepared the LaPO₄ and LaPO₄:Eu powder under the hydrothermal conditions. The products are characterized by the X-rays diffraction microscopy (XRD), photoluminescence spectroscopy (PL) and ultraviolet visible absorption analysis (UV–Vis). The structural, electronic and optical properties of LaPO₄ and LaPO₄:Eu are calculated. The comparison between the experimental and calculated results is also been discussed.

2. Experimental section

2.1. Material preparation

The monoclinic LaPO₄:Eu were prepared by the hydrothermal method with lanthanum nitrate (La(NO₃)₃;99.99%), europium oxide (Eu₂O₃;99.99%), diammonium phosphate ((NH₄)₂HPO₄;99.99%) and nitric acid (HNO₃;68%) as starting materials. Firstly, 1.25 × 10^{−2} mmol Eu₂O₃ were dissolved into 68% HNO₃. 4.75 mmol La(NO₃)₃ and 5 mmol (NH₄)₂HPO₄ were dissolved in 30 ml deionized water, respectively, and then mixed together by dropwise. The obtained suspension was adjusted to pH = 9–10 by adding HNO₃ solution and poured into the Teflon-lined autoclave. The Teflon-lined autoclave was sealed and heated at 180 °C for 12 h. The product was washed by deionized water for several times and dried in vacuum oven at 80 °C. Pure LaPO₄ was prepared in the same way without adding Eu₂O₃.

2.2. Characterization

The phase compositions were identified by the X-ray diffraction method (XRD, Model D8 Advance, BRUKER/AXS). The excitation and emission spectra were obtained by Fluorolog-3P photoluminescence spectroscopy (Jobin Yvon Inc.). The absorption spectrum of the sample was measured by Hitachi U-4100 UV–VIS–NIR spectrophotometer.

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2.3. Computation method

Calculations of the structural, electronic and optical properties of LaPO_4 and $\text{LaPO}_4:\text{Eu}$ were performed by the CASTEP module of the Materials Studio package. Exchange and correlation effects were treated within the Perdew–Burke–Ernzerhof (PBE) function of the generalized gradient approximation (GGA). The plane-wave cutoff energy was set at 340 eV; the Monkhorst-Pack scheme k-points grid sampling for the Brillouin zone was performed with a $3 \times 3 \times 5$ mesh; norm-conserving pseudopotentials were carried out for all chemical elements; BFGS algorithm was chosen. The convergence parameters were as follows: total energy tolerance -1×10^{-5} eV/atom, maximum force tolerance 0.01 eV/Å, maximal stress 0.02 GPa and maximal displacement 5×10^{-4} Å, SCF tolerance 2×10^{-6} eV/atom [14]. The electron–ion interaction ($2s^2 2p^4$ for O and $3s^2 3p^3$ for P, $5d^1 6s^2$ for La and $4f^7 5s^2 5p^6 6s^2$ for Eu) were described.

3. Results and discussion

3.1. Structure, absorption and luminescence spectra

The XRD patterns of LaPO_4 , $\text{LaPO}_4:\text{Eu}$ and the standard data for the monoclinic LaPO_4 is shown in Fig. 1. According to the diffraction peaks, two samples measured can be readily indexed to the monoclinic monazite-type phase of LaPO_4 with the lattice parameters of $a = 6.84$, $b = 7.07$, $c = 6.45$ Å and $\beta = 103.85^\circ$. No additional peaks can be noted due to the Eu doping, indicating that Eu ions might have been uniformly diffused into the LaPO_4 lattice. However, the diffraction peaks at $2\theta = 26.914^\circ$ and 31.206° of $\text{LaPO}_4:\text{Eu}$ show a little shift toward the larger angle in comparing with those of pure LaPO_4 , which might result from the size of the Eu^{3+} (1.12 Å) is smaller than La^{3+} (1.216 Å) in the ninefold coordination of monoclinic structure [15].

The excitation and emission spectrum of $\text{LaPO}_4:\text{Eu}$ is presented in Fig. 2. In the excitation spectrum, a wide band with the maximum value of around 275 nm is associated with the charge transfer transition from O (2p) to Eu (4f), while the other narrow peaks originate from Eu 4f–f direct excitation. In the emission spectrum, ${}^5\text{D}_0\text{--}{}^7\text{F}_j$ ($j = 0, 1, 2, 3, 4$) transition of $\text{LaPO}_4:\text{Eu}$ is observed. According to the Judd–Ofelt theory, magnetic dipole transition (${}^5\text{D}_0\text{--}{}^7\text{F}_1$) is permitted; electric dipole transition (${}^5\text{D}_0\text{--}{}^7\text{F}_2$) is allowed only when Eu^{3+} occupied the site without an inversion center. Meanwhile, the intensity of ${}^5\text{D}_0\text{--}{}^7\text{F}_1$ transition is not the strongest. All these results indicate that Eu ion does not take the place of the inversion center in as-prepared $\text{LaPO}_4:\text{Eu}$ in this work [16].

Fig. 3 illustrates the UV–Vis absorption spectra of LaPO_4 and $\text{LaPO}_4:\text{Eu}$. It shows two samples have close absorption region in the range from near ultraviolet to visible light due to the few quantities of Eu doping. According to the Kubelka–Munk function, the

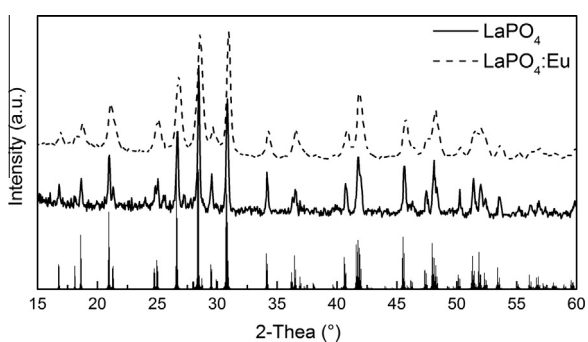


Fig. 1. XRD patterns of LaPO_4 and $\text{LaPO}_4:\text{Eu}$ and standard pattern.

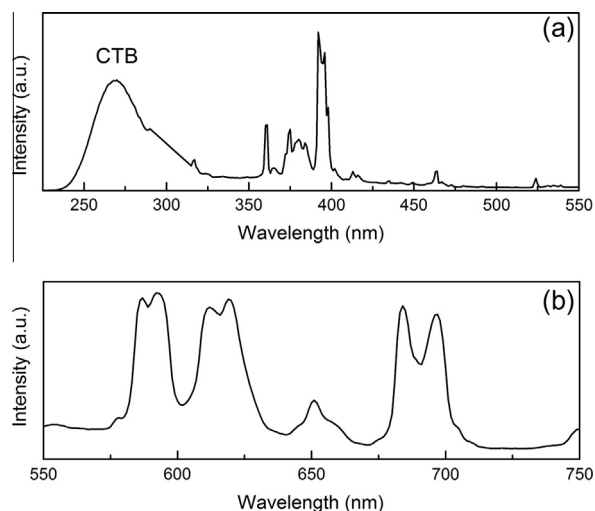


Fig. 2. Luminescence excitation spectrum and emission spectrum.

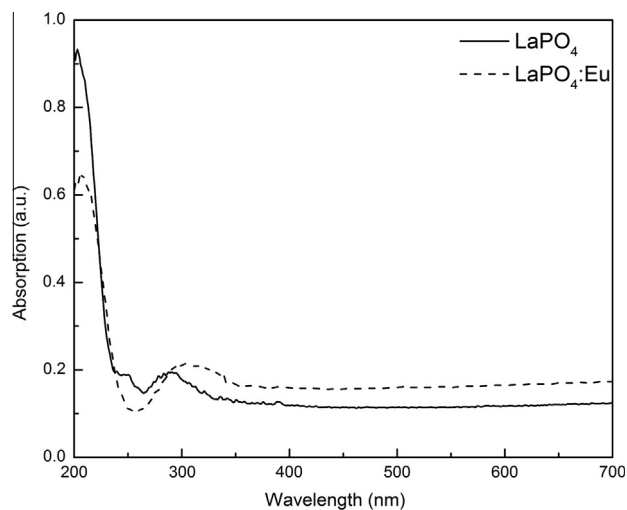


Fig. 3. UV–Vis diffused reflectance spectra of LaPO_4 and $\text{LaPO}_4:\text{Eu}$.

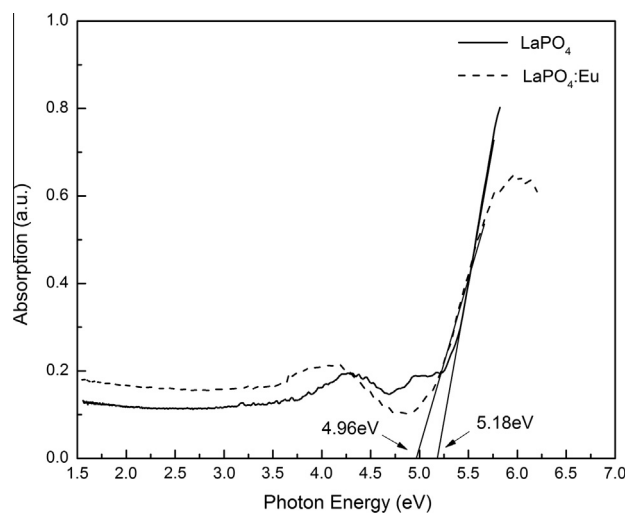


Fig. 4. UV–Vis absorption-energy curves of LaPO_4 and $\text{LaPO}_4:\text{Eu}$.

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