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Red-emitting LaOF:Eu^{3+} phosphors: Synthesis, structure and their Judd–Ofelt analysis for LED applications

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ABSTRACT

In the present study, we have synthesized a series of $La_{1-x}Eu_xOF$ ($0.01 \leq x \leq 0.09$) phosphors by the conventional solid-state reaction route at relatively low temperature (500 °C) and shorter duration of 2 h. The compounds were crystallized in the rhombohedral structure with the space group R-3m (No. 166). Upon UV excitation (254 nm), the photoluminescence spectra exhibit characteristic luminescence $^5D_0 \rightarrow {}^7F_J$ ($J = 1, 2, 3$, and 4) intra-4f shell Eu^{3+} ion transitions. An intense red emission peak at 610 nm was observed due to electric dipole ($^5D_0 \rightarrow {}^7F_2$) transition. Judd–Ofelt theory was employed to evaluate various radiative parameters such as radiative emission rates, lifetime, branching and asymmetry ratios. CIE color coordinates confirmed the red emission of the phosphors. The luminescent results reveal that LaOF:Eu^{3+} phosphor can be used as potential candidate for developing red component in white LED applications.

1. Introduction

In the recent years, rare earth ion-doped inorganic materials have attracted considerable interest because of its excellent luminescent properties [1]. It has been considered that the host matrix plays a significant role on the luminescent properties of the rare-earth ion [2]. Among various materials, lanthanum oxyfluoride (LaOF) has been drawn much attention due to their high chemical stability, low phonon energy and lasing characteristics [3,4]. The lanthanum oxyfluoride compounds have been used for a long time as hosts for various activators, such as Yb^{3+}, Er^{3+}, Eu^{3+}, Ce^{3+}, Pr^{3+} [5–9]. It is generally accepted that trivalent europium ions (Eu^{3+}) in phosphor materials have been widely used as an activator, which exhibit red luminescence under UV excitation due to $^5D_0 \rightarrow {}^7F_2$ transition [10]. Eu^{3+} provides a favorable situation for substitution in La^{3+} sites with suitable isostructural replacement. Trivalent europium ions exhibit narrow band emissions, large Stokes shifts and long lifetimes [11].

Various synthesis methods have been reported to prepare LaOF materials such as hydrothermal, sol–gel, chemical vapor deposition, stearic acid and combustion methods [12–16]. However, most of these methods cannot be applied economically on large scale due to their complicated synthesis route, high reaction temperature, long reaction time, less yield and difficult to control stoichiometric compositions.

In this paper, we report the synthesis of $La_{1-x}Eu_xOF$ ($0.01 \leq x \leq 0.09$) phosphors by the facile solid-state method at 500 °C for 2 h. The crystallographic structural parameters, functional groups, morphology were analyzed by powder X-ray diffraction (PXRD), fourier transform infrared (FTIR) spectroscopy and field emission scanning electron microscopy (FESEM), respectively. Electron paramagnetic resonance (EPR) and UV–vis absorption spectroscopy were also studied. The influence of Eu^{3+} concentration on the photoluminescence properties of LaOF phosphors was reported in detail. Further, the Judd–Ofelt intensity parameters, radiative emission rates, lifetime, branching and asymmetry ratios were calculated from the luminescence data.

2. Experimental

2.1. Materials

Analytical reagent grade La_2O_3, Eu_2O_3 and NH_4F were procured from Sigma–Aldrich and used as precursors for the synthesis of LaOF:Eu^{3+} phosphors. Before weighing, La_2O_3 and Eu_2O_3 were

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calcined at 800 °C for 6 h to remove moisture from the starting materials.

2.2. Synthesis of LaOF:Eu^{3+} phosphors

A series of $La_{1-x}Eu_xOF$ ($0.01 \leq x \leq 0.09$) phosphors were synthesized using the conventional solid-state reaction route. The required amount of La_2O_3, Eu_2O_3 and NH_4F (20% excess) were ground thoroughly in an agate mortar with pestle. The mixed powder was transferred into porcelain crucible, calcined at 500 °C for 2 h (ambient atmosphere) and cooled down to room temperature. The chemical reaction for the synthesis of $La_{1-x}Eu_xOF$ phosphors are represented as follows:

$$(1-x)\,La_2O_3 + xEu_2O_3 + 2NH_4F \rightarrow 2La_{1-x}Eu_xOF + 2\ NH_3 + H_2O \qquad (1)$$

2.3. Characterization

Powder X-ray diffraction (PXRD) of the phosphors were performed on PANalytical X'Pert Pro Powder diffractometer using Cu Kα radiation ($\lambda = 1.5418$ Å) with a nickel filter. Rietveld refinement data were collected at a scan rate of 1°/min with a 0.02° step size for 2θ from 10° to 80°. FullProf suite—2000 programme were used to estimate the structural parameters using Rietveld refinement method. The surface morphology was examined using FEI Quanta 200 scanning electron microscope. FTIR spectra were recorded using Perkin Elmer Frontier Spectrometer in the wave number range of 300–4000 cm^{-1}. The data was collected at room temperature using pellet method with transmission mode and KBr as a reference. The 13 mm diameter thin pellet was made by mixing the sample with dried KBr powder. UV–vis absorption spectra have been recorded for solid powders on PerkinElmer Lambda 750 spectrophotometer with deuterium and tungsten halogen light sources and double holographic grating monochromators using $BaSO_4$ as a background or standard reference. Electron paramagnetic resonance (EPR) were performed using Bruker X-band ESR spectrometer and DPPH (2,2-diphenyl-1-picrylhydrazyl) was used as a field marker. The photoluminescence (PL) studies have been carried out using a Jobin Yvon spectrofluorometer (Fluorolog-3, Horiba) equipped with a 450 W xenon lamp as the excitation source. All the measurements were performed at room temperature.

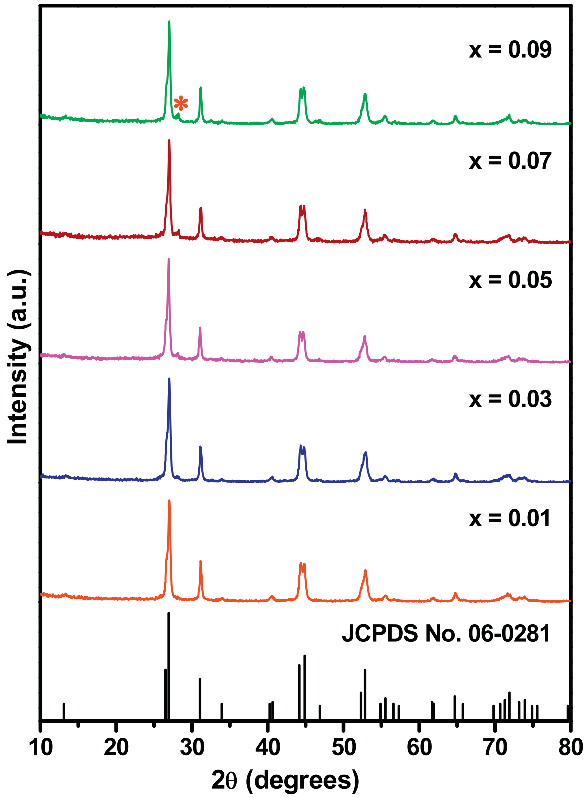

Fig. 1. Powder XRD patterns of $La_{1-x}Eu_xOF$ ($0.01 \leq x \leq 0.09$) phosphors (The asterisk represents the small Eu_2O_3 impurity).

3. Results and discussion

Fig. 1 shows the powder X-ray diffraction patterns of $La_{1-x}Eu_xOF$ ($0.01 \leq x \leq 0.09$) phosphors. All diffraction peaks could be indexed with the standard rhombohedral phase of LaOF (JCPDS No. 06-0281) with space group R-3m (No. 166), that indicates the synthesized compounds were in single crystalline phase. On increasing the substitution of Eu^{3+} ion to La^{3+} ion in LaOF matrix, we observed a small impurity of Eu_2O_3. The structural parameters were obtained from the Rietveld refinement method using PXRD data. The patterns were typically refined for lattice parameters, scale factor, backgrounds, pseudo-Voigt profile function (u, v and w), atomic coordinates and isothermal temperature factors (B_{iso}). Fig. 2 shows the observed, calculated and the difference PXRD patterns of $La_{1-x}Eu_xOF$ ((a) $x = 0.01$, (b) $x = 0.05$, and (c) $x = 0.09$). The difference between XRD pattern profiles experimentally observed and calculated data display near to zero in the intensity scale as illustrated by a line (Y_{obs}–Y_{calc}). The refined structural parameters for $La_{1-x}Eu_xOF$ ($x = 0.01$, 0.05, and 0.09) phosphor are summarized in Table 1. With the substitution of 8-coordinated Eu^{3+} ion ($r_{Eu3+} = 1.066$ Å) to La^{3+} ($r_{La3+} = 1.160$ Å) ion in LaOF matrix, we did not observe any appreciable change in the structural parameters. The crystal structure of rhombohedral LaOF was modeled through VESTA software using lattice parameters and atom positions obtained from the Rietveld refinement data (Fig. 2(d)). The La^{3+} ions or Eu^{3+} ions are coordinated by four oxide and four fluoride anions. All ions occupy the six-fold 6c Wyckoff positions and the symmetry for La^{3+} ions is C_{3v}.

Fig. 3 shows the FESEM micrographs of (a) $La_{0.99}Eu_{0.01}OF$ and (b) $La_{0.93}Eu_{0.07}OF$ phosphors. The images revealed the plate-like morphology which is agglomerated due to the solid-state reaction route. The FTIR spectra of $La_{1-x}Eu_xOF$ phosphors were measured in the wave number region of 300–4000 cm^{-1} as shown in Fig. 4. The spectra show two characteristic absorption bands around 500 and 370 cm^{-1} for all the compositions. These bands can be attributed to La–O vibrations [17]. The low intensity band at 1430 cm^{-1} was assigned to the vibrational mode of adsorbed CO_3^{2-} group from the atmosphere. The peak around 3436 cm^{-1} can be ascribed to the bending vibration of surface adsorbed water molecule.

Fig. 5 shows the UV–vis absorption spectra of $La_{1-x}Eu_xOF$ phosphors in the range of 250–800 nm. The absorption peak and edge of LaOF:Eu^{3+} are located around 260 and 330 nm, respectively. Further, we observed the small sharp peaks in 400–600 nm range which was due to the absorption of Eu^{3+} ion. The absorption peaks at 416, 465, and 536 nm were assigned to $^7F_0 \rightarrow {}^5D_3$, $^7F_0 \rightarrow {}^5D_2$, and $^7F_1 \rightarrow {}^5D_1$, respectively (inset of Fig. 5). The optical energy band gap (E_g) was estimated from these absorption spectra using Wood and Tauc relation [18]. The energy band gap for all compounds was ~4.77 eV which is close to the reported value [19,20].

The EPR spectra of $La_{1-x}Eu_xOF$ ($x = 0.01$ and 0.09) phosphors were measured at room temperature and is shown in Fig. 6. It was observed that the EPR signals consist of broad spectra in the range of 0–7000 Gauss. The g value calculated for $x = 0.01$ and 0.09 was found to be 1.78 and 1.80, respectively which suggests that there is no variation in EPR spectra with the higher Eu^{3+} ion content.