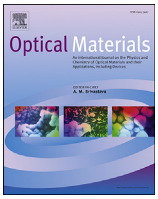
Optical Materials 66 (2017) 589–594

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat



Synthesis and distinct up-converting behaviors of Er^{3+}, Yb^{3+} doped LaOF and $LaO_{0.65}F_{1.7}$ phosphors

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ARTICLE INFO

Article history:
Received 16 November 2016
Received in revised form
14 February 2017
Accepted 27 February 2017

Keywords:
Oxyfluorides
X-ray diffraction
Phosphors
Up-conversion

ABSTRACT

Optical materials composed of tetragonal $La_{1-x-y}Er_xYb_yO_{0.65}F_{1.7}$ ($x = 0.005–0.1$, $y = 0–0.1$) and from tetragonal and trigonal $La_{0.99}Er_{0.005}Yb_{0.01}OF$ were prepared via a solid-state reaction using an excess of NH_4F flux at 950 or 1050 °C for 2 h. X-ray diffraction patterns of $La_{1-x-y}Er_xYb_yO_{0.65}F_{1.7}$ and $La_{0.99}Er_{0.005}Yb_{0.01}OF$ were obtained using different molar ratios of the NH_4F: $La(Er,Yb)O_{3/2}$. The effective spectral conversion properties of Er^{3+}-Yb^{3+} ions in non-stoichiometric $LaO_{0.65}F_{1.7}$ host lattices were monitored upon excitation of the samples using a 980 nm diode-laser. By selecting appropriate Er^{3+} and/or Yb^{3+} concentrations in the $LaO_{0.65}F_{1.7}$ matrix, up-conversion emission at desired wavelengths in the green to red region of the spectrum was obtained. Furthermore, the mechanism of up-conversion in the non-stoichiometric $LaO_{0.65}F_{1.7}$ phosphors was described with the help of an energy-level schematic. Up-converted emission spectra and the dependence of the emission intensity on pump power in the $La_{1-x-y}Er_xYb_yO_{0.65}F_{1.7}$ phosphors were also investigated.

1. Introduction

Up-converting phosphors, which upon excitation, produce high energies from low input energies by means of anti- Stokes processes, have been widely studied. Today, up-converting phosphors are applied in various devices such as three-dimensional displays, up-conversion-enhanced solar cells, optical temperature sensors, non-destructive optical memory, and biosensors [1–6]. Fluoride (or chloride) host-materials, in contrast to oxyfluoride (chloride) compounds, provide relatively low non-radiative relaxation rates due to low phonon energies. However, oxyfluoride (chloride) host-materials have several merits including chemical stability, and low toxicity, and they can be synthesized by convenient methods [7–13]. In a previous study, the spectral up-converting properties of Er^{3+}-Yb^{3+} doped stoichiometric YOF and non-stoichiometric $Y_6O_5F_8$ vernier structures, as spectral-converting luminescent host materials, were elucidated under 980 nm diode laser excitation [13]. When rare-earth ions such as Er^{3+} and Yb^{3+} were substituted in a non-stoichiometric $Y_6O_5F_8$ host lattice, improved spectral converting properties were observed owing to the low non-radiative relaxation due to the strong formation of a metastable energy level [13,14].

Fig. 1 shows the structures of tetragonal stoichiometric LaOF and non-stoichiometric $LaO_{0.65}F_{1.7}$ oxyfluorides. The stoichiometric LaOF structure comprises alternating layers of $(YO)^{n+}$ cations and $F(1)^{n-}$ anions along to the *c*-axis arranged in a tetragonal crystal lattice structure (*P*4/*nmm* space group); the La^{3+} sites are coordinated by four O^{2-} and three or four F^- anions. In contrast, for the non-stoichiometric $LaO_{0.65}F_{1.7}$ lattice, the anion-excess phase has the following structural formula:

$$La(F(1)_{0.86}V_{0.14})(F(2)_{0.35}O_{0.65})(F(3)_{0.49})$$

Anion F(1) atom associated with vacancies, the partial substitution of F atoms for O atoms, and F-interstitials generated from the stoichiometric LaOF structure are associated to non-stoichiometric $LaO_{0.65}F_{1.7}$. The host structure $LaO_{0.65}F_{1.7}$ contains a single La^{3+} site with nine or ten-fold coordination by oxygen and fluorine atoms [15,16]. In this paper, Er^{3+}-Yb^{3+} substituted lanthanum-oxyfluoride compounds, which contain LaOF and $LaO_{0.65}F_{1.7}$ structures, were prepared using a simple solid-state thermal process in air with NH_4F flux. The spectral converting luminescence properties of Er^{3+}-Yb^{3+} doped lanthanum-oxyfluoride phosphors were investigated. Using these up-converting luminescence materials, emission

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http://dx.doi.org/10.1016/j.optmat.2017.02.057
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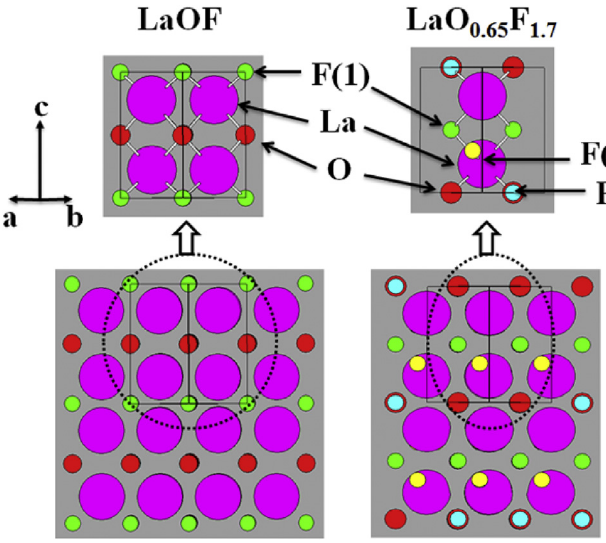

Fig. 1. Structures of tetragonal LaOF and $LaO_{0.65}F_{1.7}$ host lattices.

in the desired wavelength region spanning green, yellow, orange, and red light was achieved. The mechanisms of up-conversion are proposed on the basis of the energy-level diagram of the Er^{3+} and Yb^{3+} ions. Intense up-conversion emission spectra were observed and the dependence of the emission intensity of $La_{1\text{-}x\text{-}y}Er_xYb_yO_{0.65}F_{1.7}$ ($x = 0.01$, $y = 0.05$, $x = 0.05$, $y = 0.05$, $x = 0.1$, $y = 0.1$) phosphors on the excitation power was investigated.

2. Experimental

Samples of $La_{1\text{-}x\text{-}y}Er_xYb_yO_{0.65}F_{1.7}$ ($x = 0.005–0.1$, $y = 0–0.1$) with $La_{0.99}Er_{0.005}Yb_{0.01}OF$ were prepared by heating the appropriate amounts of La_2O_3 (Alfa 99.9%), Er_2O_3 (Alfa 99.9%), Yb_2O_3 (Alfa 99.9%) and NH_4F (Alfa 99%) at 950 or 1050 °C for 2 h in air [13,14,17]. Phase identification was established using a Shimadzu XRD-6000 powder diffractometer (Cu-$K\alpha$ radiation) and the unit cell parameters were determined by using the Rietveld refinement program Rietica. UV spectroscopy to measure the excitation and emission spectra of the phosphor materials were done using spectrofluorometers (Sinco Fluoromate FS-2) at room temperature. Up-conversion emission spectra were monitored with an Ocean spectrometer using 980 nm diode lasers at room temperature.

3. Results and discussion

The crystallographic phases of $La_{0.99}Er_{0.005}Yb_{0.01}OF$ and $La_{1\text{-}x\text{-}y}Er_xYb_yO_{0.65}F_{1.7}$ ($x = 0.005–0.1$, $x = 0–0.1$) powers obtained after the substitution of Er^{3+} and Yb^{3+} ions for La^{3+} ions in the LaOF and $LaO_{0.65}F_{1.7}$ host lattices, were identified from powder X-ray diffraction (XRD) patterns. The synthesis procedure to obtain for a single-phase of tetragonal $La_{1\text{-}x\text{-}y}Er_xYb_yO_{0.65}F_{1.7}$ phosphors was optimized by heating Y_2O_3, Er_2O_3, Yb_2O_3, and NH_4F at 1050 °C for 2 h. Tetragonal and trigonal $La_{0.99}Er_{0.005}Yb_{0.01}OF$ phosphors were obtained by heat treatment for 2 h in air at 950 and 1050 °C, respectively. Calculated XRD patterns of the trigonal LaOF (ICSD 30622, R-3mR), tetragonal LaOF (ICSD 76427, P4/nmmS), and tetragonal $LaO_{0.65}F_{1.7}$ (ICSD 40371, P4/nmmZ) structures are shown in Fig. 2(a)–(c). Fig. 2(d) and (e) show the XRD patterns of 0.5 mol% Er^{3+}- and 1 mol% Yb^{3+}-doped trigonal and tetragonal LaOF synthesized at 1050 and 950 °C with a 1:1 stoichiometric molar ratio of $La(Er,Yb)O_{3/2}$ and NH_4F. When the molar ratio of the $La(Er,Yb)O_{3/2}$ precursor to the NH_4F flux was 1:2, the $La_{0.985}Er_{0.005}Yb_{0.01}O_{0.65}F_{1.7}$ structure was formed (Fig. 2(f)). For molar ratios of $La(Er,Yb)O_{3/2}$/NH_4F flux of 1:1 and 1:2, phase-pure tetragonal LaOF and $LaO_{0.65}F_{1.7}$ were obtained at 950 and 1050 °C respectively, as seen in Fig. 2 (e) and (f). However, when the annealing temperature was 1050 °C, the trigonal LaOF phase was stabilized for 1:1 M ratio of the precursor and the flux, owing to a phase transition from the tetragonal to the trigonal LaOF structure at this relatively high temperature. As we reported earlier, the excitation and emission spectra of rare-earth Er^{3+}-Yb^{3+}, Ce^{3+}- Tb^{3+}, or Ce^{3+}-Mn^{2+} co-doped in non-stoichiometric $Y_nO_{n\text{-}1}F_{n+2}$ vernier host structures exhibited more efficient conversion properties than in stoichiometric yttrium oxyfluoride (YOF) host lattice [13,14,17]. The excitation range of non-stoichiometric $Y_nO_{n\text{-}1}F_{n+2}$ is much broader than that of stoichiometric YOF, which means that metastable energy levels are formed in view of the stronger Stark splitting; these metastable levels are essential for the realization of good up-conversion phosphors. Furthermore, phonon energies generally decrease from oxides (O) to fluorides (F) in host materials with decreased non-radiative relaxation at low phonon frequencies, thereby leading to improved conversion properties. The excitation range of Er^{3+}-Yb^{3+}-doped non-stoichiometric $LaO_{0.65}F_{1.7}$ is much broader than that of both tetragonal and trigonal Er^{3+}-Yb^{3+}-doped LaOF phases as shown in Fig. 3. Substituting a combination of Er^{3+} and Yb^{3+} ions into the $LaO_{0.65}F_{1.7}$ host structure leads to high efficiency up-conversion phosphors demonstrated by the very intense up-conversion emission shown in Figs. 3 and 4. Fig. 4 shows photographs of the up-conversion emission radiation from trigonal and

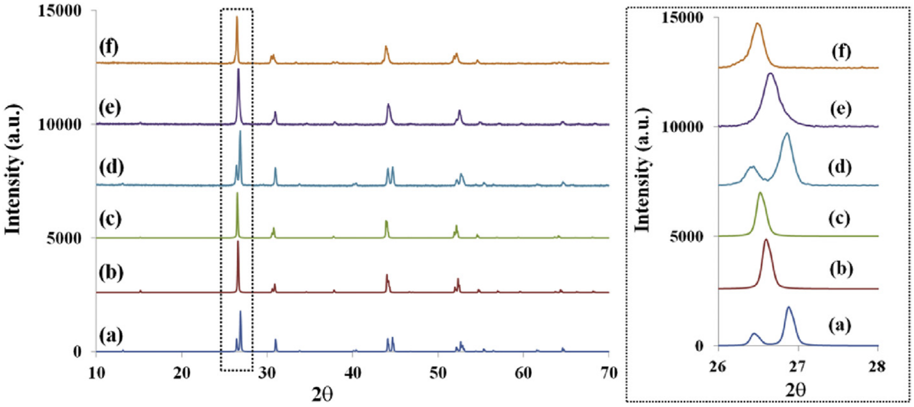

Fig. 2. The calculated XRD patterns of (a) trigonal LaOF (ICSD 30622), (b) tetragonal LaOF (ICSD 76427), (c) tetragonal $LaO_{0.65}F_{1.7}$ (ICSD 40371) and the obtained XRD patterns of 0.5 mol% and Er^{3+} and 1 mol% Yb^{3+}-doped (d) LaOF (trigonal), (e) LaOF (tetragonal) (f) $LaO_{0.65}F_{1.7}$ (tetragonal).