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# Up-conversion luminescent properties of $La_{(0.80-x)}VO_4:Yb_x, Er_{0.20}$ phosphors

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ABSTRACT

$Yb^{3+}$, $Er^{3+}$ co-doped $LaVO_4$ phosphors were synthesized by solid state reaction method. $Yb^{3+}$ concentrations were changed from 0.01 to 0.20 mol for the fixed $Er^{3+}$ concentration at 0.2 mol. The crystalline structure of samples was investigated by X-ray diffraction (XRD). The composition was investigated by X-ray photoelectron spectroscopy (XPS) analysis. The surface morphology was observed by scanning electron microscope (SEM). The red and green up-conversion emissions were observed in $Yb^{3+}$, $Er^{3+}$ co-doped $LaVO_4$ phosphors under the excitation of 980 nm laser diode. Several emissions in green and red regions of the spectrum were observed near 525 nm, 553 nm and 659 nm radiated by $^2H_{11/2} \rightarrow {}^4I_{15/2}$, $^4S_{3/2} \rightarrow {}^4I_{15/2}$, and $^4F_{3/2} \rightarrow {}^4I_{15/2}$ transitions, respectively.

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## 1. Introduction

The vanadate group materials have been one of the most outstanding materials for short wavelength photoelectric device [1], host materials of laser and phosphor [2–4], solar cell [5] and thin film phosphors [6]. Among the vanadate group materials, $LaVO_4$ has been investigated for ages. Crystalline structure of $LaVO_4$ generally has two kind of polymorphs, tetragonal phase (zircon structure) and monoclinic phase (monazite structure). $LaVO_4$ has monazite structure at atmospheric pressure and zircon structure at high pressure [4,7]. Lanthanoids show a strong tendency towards monazite structured orthovanadates on account of the higher oxygen coordination number of 9 compared with 8 of the zircon type, when increasing ionic radius. $LaVO_4$ has monazite structure at atmospheric pressure because $La^{3+}$ has the largest ion radius of all lanthanoids. Monazite structure is the thermodynamically stable state of $LaVO_4$, whereas the other orthovanadates normally adopt the zircon structure. But m-$LaVO_4$ is not a suitable host for luminescent activators compared with other orthovanadates due to its structural characteristics [8,9]. Because, the bonding angles of t-$LaVO_4$ are much greater than m-$LaVO_4$. Consequently, the effective energy transfer in t-$LaVO_4$ can appear. The structural transformation of $LaVO_4$ from monoclinic to tetragonal structure can lead to a remarkable increase in emission properties [10].

Up-conversion phosphors emitting the visible spectrum, coupled with an infrared rays (IR) excitation light source, offer substantially potential benefits in nano-materials, ultrafine powders, volumetric displays, temperature sensors, photo dynamic therapy and biological imaging agents [11–15], compared with other solid-state lighting such as down-converted phosphors. Up-conversion luminescence is a unique process and does not occur in nature. Up-conversion luminescence is based on the absorption of two or more low-energy (longer wavelength, typically IR) photons by a crystal followed by the emission of a single higher-energy shorter wavelength photon [16,17]. This energy transfer is most often accomplished using combination of lanthanoids as dopants on ceramic phosphors.

The up-converted emission properties of the rare earth doped materials have been investigated for practical applications. $Yb^{3+}$ and $Er^{3+}$ ions have been used as dopants for red and green emitting up-conversion materials. $Er^{3+}$ is one of the most studied rare-earth ions for red and green emitting operation based on up-conversion luminescence [18–20]. Normally, the up-conversion luminescence materials with lower phonon energy can lead to higher up-conversion efficiency. To improve the up-conversion luminescence

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efficiency of $Er^{3+}$ ions, $Yb^{3+}$ ions have been co-doped. $Yb^{3+}$ ions act as a sensitizer absorbing a light in 900–1000 nm region and transfer the energy to the emitting centers with long-lived excited states. They are excellent sensitizers that absorb the pump light and transfer absorbed energy to activators. Also, they have simple energy state with just two manifolds, the ground state $^2F_{7/2}$ and excited state $^2F_{5/2}$, which are separated by approximately 10,000 $cm^{-1}$ [18–20].

In this study, $La_{(0.80-x)}VO_4$:$Yb_x^{3+}$, $Er_{0.20}^{3+}$ ($x$ = 0.01, 0.05, 0.10, 0.15 and 0.20) phosphors were synthesized by solid state reaction to investigate its crystalline and optical properties as a function of $Yb^{3+}$ concentration.

## 2. Experimental details

$La_{(0.80-x)}VO_4$:$Yb_x^{3+}$, $Er_{0.20}^{3+}$ ($x$ = 0.01, 0.05, 0.10, 0.15 and 0.20) samples were synthesized by a solid state reaction. The raw materials $La_2O_3$ (99.99%, Aldrich), $V_2O_5$ (99.6+%, Aldrich), $Er_2O_3$ (99.9%, Aldrich) and $Yb_2O_3$ (99.9%, Aldrich) were weighted, mixed with ethanol in plastic container and ball milled with zirconia balls for 12 h. After milling, the mixed materials were dried in oven at 40 °C for 24 h. The dried materials were pulverized in an agate mortar and sintered at 900 °C for 5 h in air. In this experiment, the $Er^{3+}$ concentration was fixed at 0.20 mol to investigate the effects of $Yb^{3+}$ concentrations ranging from 0.01 to 0.20 mol. The structural characteristics of the samples were analyzed by X-ray diffraction (XRD: Rigaku, Ultima IV) with Cu-K$\alpha_1$ radiation. X-ray photoelectron spectroscopic (XPS) measurements were carried out with a XPS spectrometer (ESCALAB250), using MgK$\alpha$ as the X-ray source. Binding energy calibration was based on C1s (284.6 eV). The surface morphology of the powders was observed by field emission scanning electron microscope (FE-SEM: HITACHI, S-4200) operated at 15 kV. The up-conversion emission spectra were recorded by the spectrometer (HR4000, Ocean Optics) at room temperature. The excitation source for up-conversion luminescence was 980 nm semiconductor laser (TCLDM9, Thorlabs).

## 3. Results and discussion

### *3.1. Crystal structure and surface morphology characterizations*

The XRD patterns of $La_{(0.80-x)}VO_4$:$Yb_x^{3+}$, $Er_{0.20}^{3+}$ ($x$ = 0.01, 0.05, 0.1, 0.15 and 0.2) powder phosphors are shown in Fig. 1. Several diffraction peaks are observed which are in good agreement with the results of International Center for Diffraction Data (ICDD) 50-0367 for $LaVO_4$. However, the XRD patterns of the samples also revealed the small amount of impurity peaks of $ErVO_4$ (ICDD 17-0199) at higher $Yb^{3+}$ ion concentrations. This might be due to the several reactions occurring during the phase formation process, including the sintering temperature, time and atmosphere [21]. The polycrystalline phase of $La_{(0.80-x)}VO_4$:$Yb_x^{3+}$, $Er_{0.20}^{3+}$ powder samples with (1 2 0), (2 0 0), (0 1 2) and (0 2 0) peaks was measured. The (1 2 0) plane was the preferred orientation of $LaVO_4$ powders, and the characteristic peaks for the monoclinic $LaVO_4$ host lattice were observed. The revealed impurity peaks of $ErVO_4$ showed a polycrystalline phase with (2 0 0), (1 1 2), (1 0 1) and (3 1 2) peaks. The (2 0 0) plane was the preferred orientation of $ErVO_4$ powders and observed tetragonal phase. When $Yb^{3+}$ concentrations were 0.01 mol, the intensity of $LaVO_4$ main peak (27.76°) was highest. The monoclinic phase was produced for the sample with the $Yb^{3+}$ concentrations under 0.05 mol. Increasing $Yb^{3+}$ concentrations, intensity of $ErVO_4$ peaks (18.76 °, 24.96°, 33.52 °, 49.6 °) and rate of tetragonal phase were increased. For the samples of $Yb^{3+}$ concentrations over 0.05 mol, the monoclinic and tetragonal phases were coexisted. When substitute $Yb^{3+}$ for $La^{3+}$, oxygen coordination number changed from 9 to 8. Change of oxygen coordination number was caused by difference of ion radius of $Yb^{3+}$ (0.086 nm) and $La^{3+}$ (0.106 nm) ions. As a result, this change occurred increase of tetragonal phase. Little difference of ion radius between $Yb^{3+}$ (0.086 nm) and $Er^{3+}$ (0.088 nm) makes easily overlap each other. So Intensity of $ErVO_4$ peaks were increasing [8,9]. Also, the full width at half maximum (FWHM) of the XRD peak was smallest at $Yb^{3+}$ 0.15 mol. By using the FWHM and Scherrer's formula, the crystallite size can be calculated. Scherrer's formula is $D = K\lambda/\beta\cos\theta$, where $D$ is crystallite size, $K$ is instrument constant (0.94), $\lambda$ is the wavelength of X-ray, $\beta$ is the full width at half maximum and $\theta$ is the angle of diffraction [9,22]. The result of using Scherrer's formula automatically calculated by PDXL program, the crystallite size of the samples were obtained about 121–2753 nm.

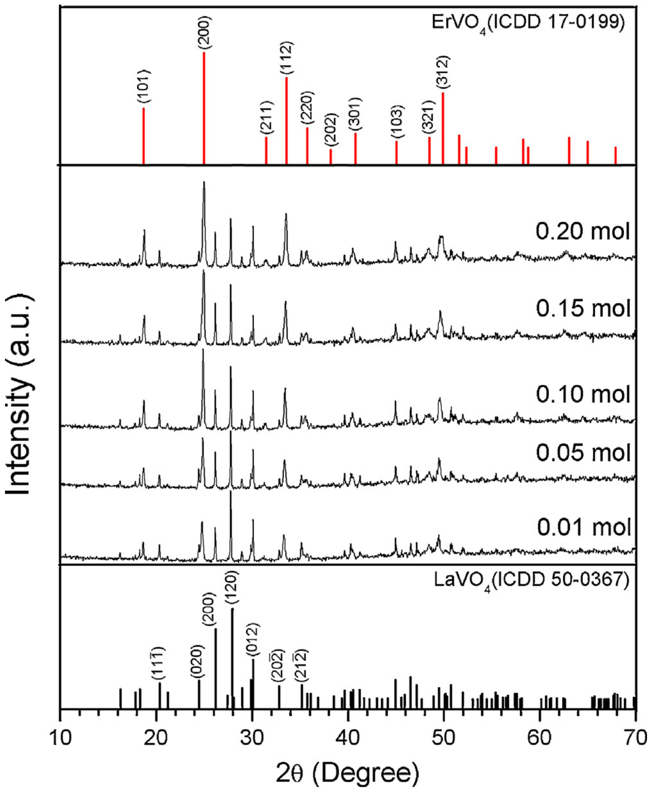

**Fig. 1.** XRD patterns of $La_{(0.80-x)}VO_4$:$Yb_x$, $Er_{0.20}$ powders. Standard patterns of ICDD 50-0367 and 17-0199 are presented.

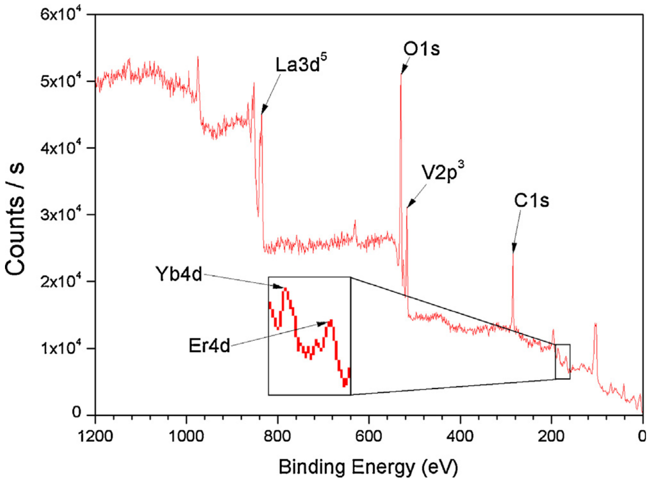

**Fig. 2.** XPS spectra of $La_{0.65}VO_4$:$Yb_{0.15}$, $Er_{0.20}$ sample.

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