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Influence of $\text{Er}^{3+}/\text{Yb}^{3+}$ Concentration Ratio on the Down-conversion and Up-conversion Luminescence and Lifetime in $\text{GdVO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ Microcrystals

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Abstract:

In this paper, we studied the effects of $\text{Er}^{3+}/\text{Yb}^{3+}$ concentration ratio on structural, morphological and luminescence properties of $\text{GdVO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ green phosphors prepared by a high-temperature solid state method. The samples with different concentrations (between 0.5 to 2 mol%) of dopant Er^{3+} emitting ions and different concentrations (between 5 to 20 mol%) of sensitizer ions (Yb^{3+}) were studied. The phosphors were characterized by the X-ray diffraction (XRD), scanning electron microscopy (SEM) and photoluminescence spectroscopy. For all samples, XRD diffraction patterns confirmed a formation of a pure GdVO_4 phase, while the SEM showed that the materials are comprised of chunks of deformed particles with an average diameter ranging from approximately 2 μm to 8 μm . Both, down-conversion and up-conversion emission spectra of $\text{GdVO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ samples, under near UV and IR excitations, exhibit two strong emission bands in the green spectral region at 525 nm and 552 nm wavelengths corresponding to $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ and $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ electronic transitions of Er^{3+} ions. The intensity of the green emission was changed by changing the $\text{Er}^{3+}/\text{Yb}^{3+}$ concentration ratio. This dual-mode luminescence makes these materials ideal as green phosphors for a wide variety of applications in the fields of bioanalysis and biomedical.

Keywords: Solid state synthesis, Luminescence, Up-conversion, Vanadates, Rare-earths

1. Introduction

The rare earth (RE)-based inorganic phosphors are a significant group of materials which are commonly used in the production of displays, infrared detectors, biolabels, security markers, temperature sensors, lasers, amplifiers in optical communication, solar cells, etc. [1-3]. Most inorganic phosphors are two-component systems, consisting of a host crystal matrix containing luminescent ionic centers (activators). Note that in that system, the host matrix plays a crucial role, affecting the energy levels of the dopant atoms and thus determining the absorption and emission wavelengths of the phosphor [4].

The RE elements (specifically, the fifteen lanthanides plus scandium and yttrium) possess unique electronic, magnetic and optical properties due to the special electronic structure from their characteristic incompletely filled 4f shell. The incomplete 4f shell in RE

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ions results in large numbers of well-defined luminescence emission lines. Due to these properties, RE elements have been considered as the most important and promising activators for phosphors due to their emission characteristics in ultraviolet and visible region [5, 6].

It is well known that the optical properties of luminescent materials depend strongly on both the host material and the electronic structure and concentration of the RE ions [7, 8]. Among various host materials, the vanadates are widely studied as a kind of new phosphor hosts for RE³⁺ incorporation. Tetragonal zircon-type GdVO₄ has been the subject of interest over the last few years due to their properties: high thermal conductivity, high absorption and emission cross-sections. The GdVO₄ is a promising host for successfully and uniformly incorporating of varying the RE³⁺ concentration in a wide range without reducing emission efficiency [9-12]. The single-doped GdVO₄ phosphor emit down-conversion (DC) emission, through the process of converting high-energy photons into low-energy ones, while double-doped (or co-doped) GdVO₄ phosphor, in addition to the DC emission, also emit up-conversion (UC) transforming near-infrared excitation (980 nm) into visible light [13]. Very often a co-dopant called a sensitizer (Yb³⁺, Ce³⁺, Li⁺, etc.) is employed for higher efficiency. In co-doped materials, especially those doped with Er³⁺, the Yb³⁺ ion is an ideal co-dopant for up-conversion [14-17].

The Er³⁺ ion is the most popular as well as one of the most efficient ions for up-conversion because the ⁴I_{9/2} and ⁴I_{11/2} levels of Er³⁺ can be conveniently populated by commercial low-cost high-power laser diodes. However, the corresponding transitions are relatively weak under the pumping with 980 nm diode laser [18, 19]. The Yb³⁺ ions have the appropriate feature as excellent sensitizers since the simple energy structure with only two states, the ²F_{7/2} ground state and the ²F_{5/2} excited state, which are separated by about 10 000 cm⁻¹, and a very high absorption cross-section at about 980 nm radiation in the near-infrared (NIR) region (where high-power laser diodes work) and can efficiently transfer the excitation energy to Er³⁺ ions [20, 21]. The phosphors activated by Er³⁺ ions have been extensively investigated in the field of their application.

In this paper, we investigated the effects of dopant concentration ratio Er³⁺/Yb³⁺ on the down-conversion and up-conversion luminescence and lifetime in GdVO₄:Er³⁺/Yb³⁺ microcrystals prepared by solid state reaction.

2. Experimental

2.1. Sample preparation

All chemicals [gadolinium (III) oxide, Gd₂O₃ (Alfa Aesar, 99.9%), erbium (III) oxide, Er₂O₃ (Alfa Aesar, 99.99%), ytterbium (III) oxide, Yb₂O₃ (Alfa Aesar, 99.9%) ammonium-vanadium oxide, NH₄VO₃, (99.0%, Alfa Aesar), sodium-hydroxide, and NaOH (99%, Moss Hemos)] are used without any purification. During a typical synthesis process [22], stoichiometric amounts of Gd₂O₃, Er₂O₃, and Yb₂O₃ were homogeneously mixed by dry grinding with NH₄VO₃ (weighted in slight excess over the stoichiometry), and the mixture was then heated for 1 h in open crucibles at 800°C. In order to complete the reaction, the product was removed from the furnace, cooled to room temperature, finely ground, and reheated at 1100°C for 3 h. The powder was homogeneously grounded and washed three times with 2-M solutions of NaOH, water, and methanol. In the final stage, the powder was calcinated at 1150°C for 90 minutes for the crystallinity improvement of material and the removal of ligands attached to the particle surface during washing stage. The aim of this work has been to see the influence of Er³⁺/Yb³⁺ concentration ratio on the down-conversion and up-conversion luminescence and lifetime in GdVO₄:Er³⁺/Yb³⁺ microcrystals, so we have prepared three series of samples under identical experimental conditions. Series 1 for contains samples with 2mol% Er³⁺, and different x-mol% (x = 5; 10; 15; 20) sensitizer (Yb³⁺) concentration, Series 2 contains samples with different x-mol% (x = 1; 1.5; 2) Er³⁺ and 5

mol% and Yb^{3+} , while Series 3 contains samples with different x-mol% ($x = 1; 1.5; 2$) Er^{3+} and 20 mol% and Yb^{3+} .

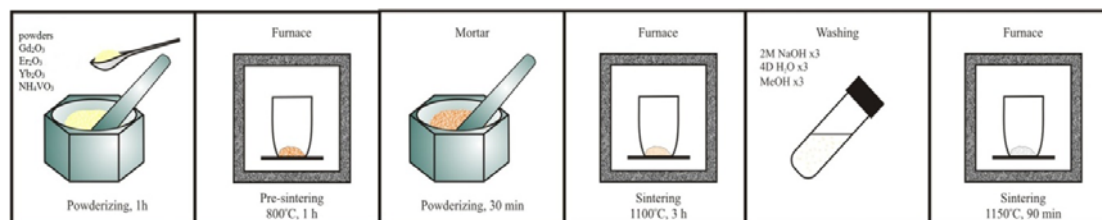


Fig. 1. Schematic illustration of synthesis procedure for $\text{Er}^{3+}/\text{Yb}^{3+}$ -doped GdVO_4 samples by solid state method

2.2. Instruments and measurements

X-ray diffraction (XRD) patterns were measured using a Rigaku Smart Lab diffractometer in a 2θ range from 10° to 100° and were counted at $0.7^\circ/\text{min}$ in 0.02° steps. Microstructural characterization was performed on a JEOL JSM-6610LV scanning electron microscope (SEM). All DC photoluminescence measurements were performed at room temperature using a Fluorolog-3 spectrofluorometer (model FL3-221, Horiba Jobin Yvon), which uses a 450-W xenon lamp as an excitation source ($\lambda_{\text{exc}} = 320 \text{ nm}$) and xenon–mercury pulsed lamp for time-resolved emission measurements. The signal was detected with a fast TBX-04 detector. UC emission spectra were measured on an AvaSpec-2048 Fiber-Optic Spectrometer upon excitation with 980-nm radiation (MDLH 980 3w).

3. Results and discussion

3.1. X-ray diffraction analysis (XRD)

Typical X-ray diffraction patterns of all three series of $\text{Er}^{3+}/\text{Yb}^{3+}$ -doped GdVO_4 samples are shown in Fig. 2 (a) and Fig. 2 (b). All patterns clearly show the presence of a single tetragonal zircon-type phase of GdVO_4 (space group $I4_1/\text{amd}$, JCPDS card no. 17-0260). The absence of impurity phases compared to the reflection positions of bulk GdVO_4 indicate that the dopant ions (Er^{3+} and Yb^{3+}) are successfully and uniformly incorporated into the GdVO_4 host lattice.

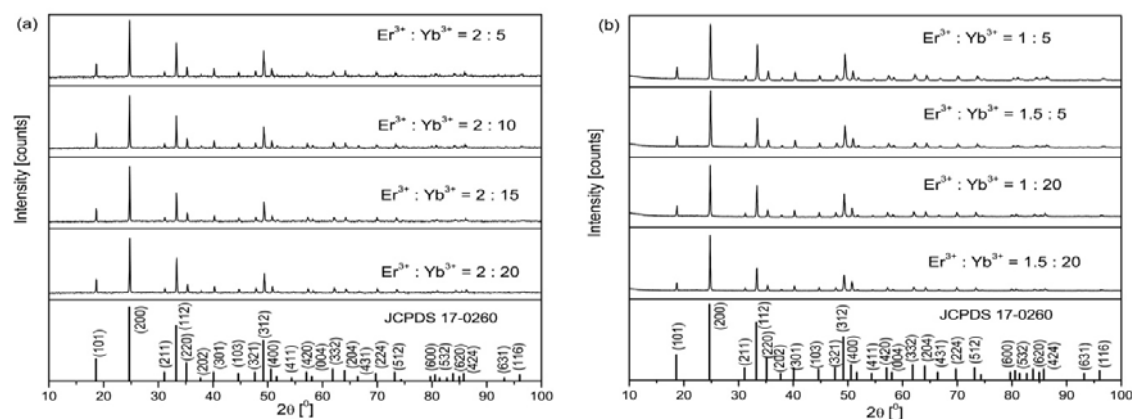


Fig. 2. XRD patterns for: (a) Series 1 and (b) Series 2 and Series 3 of $\text{Er}^{3+}/\text{Yb}^{3+}$ -doped GdVO_4 microcrystals prepared by the solid state method. Vertical bars denote the standard data for a tetragonal zircon structure of a bulk GdVO_4 (JCPDS, card No. 17-0260).

3.2. Scanning electron microscopy (SEM)

SEM technique is applied to characterize the micro-morphologies of prepared samples. The Fig. 3 shows SEM images of the microstructure of prepared $\text{Er}^{3+}/\text{Yb}^{3+}$ -doped GdVO_4 microcrystals at two different magnifications. The material is comprised of chunks of irregular spherical (deformed) particles with an average diameter ranging from approximately 2 μm to 8 μm . Various doping concentrations of Er^{3+} and Yb^{3+} have no effect on the crystal structure of GdVO_4 .

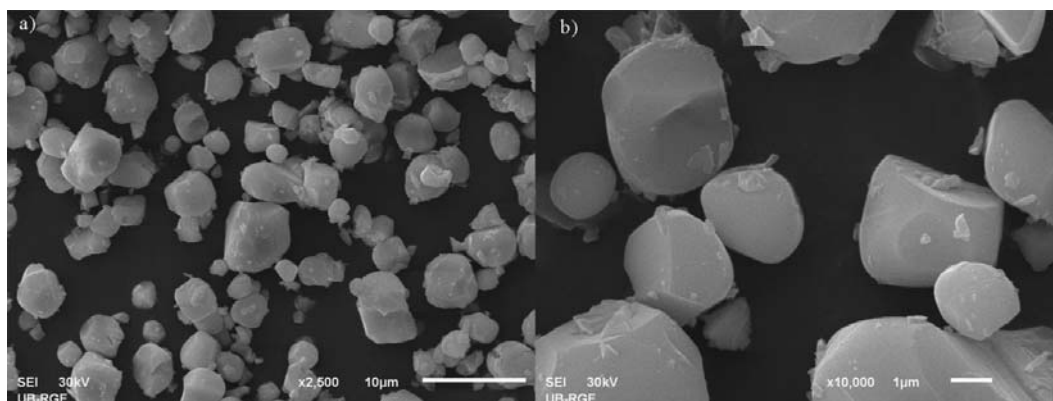


Fig. 3. Representative SEM images of $\text{Er}^{3+}/\text{Yb}^{3+}$ -doped GdVO_4 microcrystals at two different magnifications.

3.3. Luminescence properties

3.3.1. Influence of the $\text{Er}^{3+}/\text{Yb}^{3+}$ concentration ratio on the DC luminescence

Fig. 4 shows DC emission spectra for Series 1 and 2 of $\text{Er}^{3+}/\text{Yb}^{3+}$ -doped GdVO_4 microcrystals recorded under 320 nm excitation. Two emission bands in the green spectral were observed at 525 nm and 552 nm wavelengths corresponding to $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ and $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ electronic transitions of Er^{3+} ions. In order to see Yb^{3+} concentration effects on an intensity of green DC emission, the samples with constant Er^{3+} concentration (2mol%) and variable Yb^{3+} concentration (5-20mol%) (Series 1) were studied and obtained spectra are presented in Fig. 4 (a). As can be seen, the magnitude of both green DC emissions decreases with increasing Yb^{3+} concentration and reaches a maximum value for the sample with 2:5 ($\text{Er}^{3+}:\text{Yb}^{3+}$) molar ratio doped- GdVO_4 microcrystals.

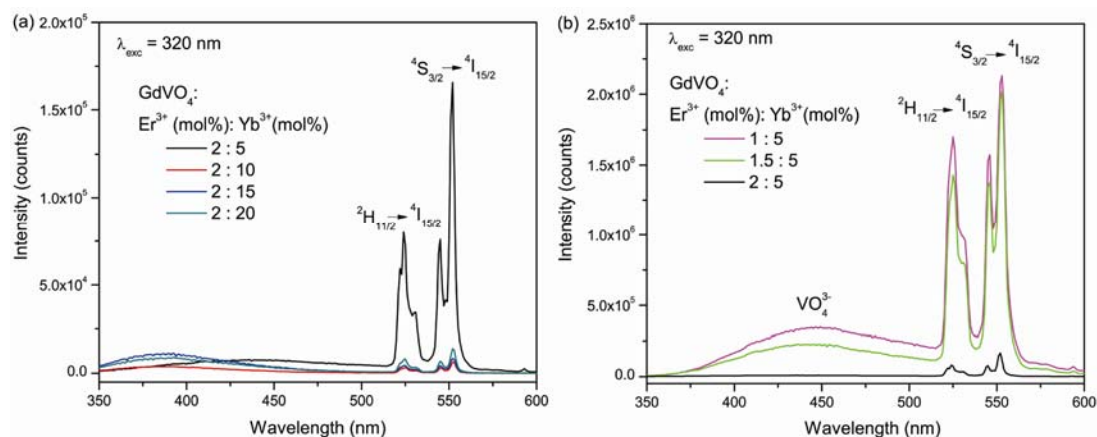


Fig. 4. Down-conversion emission spectra of: a) Series 1 and b) Series 2 of $\text{Er}^{3+}/\text{Yb}^{3+}$ -doped GdVO_4 microcrystals recorded under 320 nm excitation.

In order to see the Er^{3+} concentration effects on an intensity of green emission, two new samples with lower concentrations of Er^{3+} (1mol% and 1.5mol%) and constant concentration of Yb^{3+} (5mol%) were studied and obtained spectra are presented in Fig. 4 (b) (Series 2). As it can be seen, in this case, the intensities of green emission increase for lower Er^{3+} and reaches a maximum value for 1:5 ($\text{Er}^{3+}:\text{Yb}^{3+}$) molar ratio doped- GdVO_4 microcrystals. After this comparison, it can be concluded from Fig. 4, that the most intensive green emission under 320nm excitation wavelength, has been recorded for 1mol% Er^{3+} :5mol% Yb^{3+} -doped GdVO_4 sample. The emission intensity was ten times larger than the intensity for 2mol% Er^{3+} :5mol% Yb^{3+} -doped GdVO_4 .

3.3.2. Influence of the $\text{Er}^{3+}/\text{Yb}^{3+}$ concentration ratio on the UC luminescence

Fig. 5 presents the room-temperature UC emission spectra of the $\text{GdVO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ microcrystals for Series 1 and 3. Their emission spectra were measured upon excitation with 980 nm radiation under identical conditions for comparing the UC emission intensities.

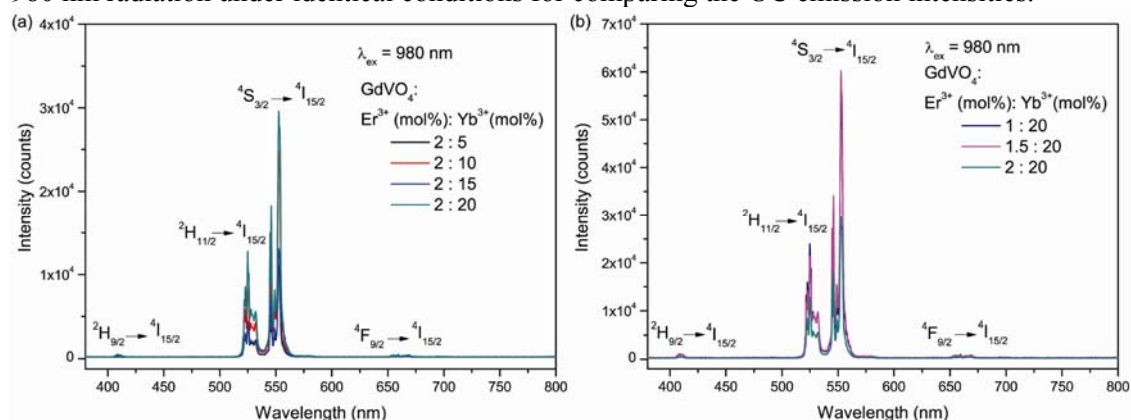


Fig. 5. Up-conversion emission spectra of a) Series 1 and b) Series 3 of $\text{Er}^{3+}/\text{Yb}^{3+}$ -doped GdVO_4 microcrystals recorded under 980 nm excitation.

All UC emission spectra contain two strong green emissions centered at 525 nm and 552 nm wavelengths corresponding to $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ and $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ transitions, and two weak emissions, violet emission at about 410 nm and red emission at about 660 nm wavelengths corresponding to $^2\text{H}_{9/2} \rightarrow ^4\text{I}_{15/2}$ and $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ transitions, respectively [23].

In order to see Yb^{3+} concentration effects on the intensity of green UC emission, the samples from Series 1 were studied and obtained spectra are presented in Fig. 5 (a). As can be seen, the magnitude of both green UC emissions increases with increasing Yb^{3+} concentration and reaches a maximum value for a sample with 2:20 ($\text{Er}^{3+}:\text{Yb}^{3+}$) molar ratio doped- GdVO_4 microcrystals. The $^2\text{H}_{9/2} \rightarrow ^4\text{I}_{15/2}$ and $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ emissions are very weak and they are not dependent on changing the Yb^{3+} concentration. In order to see Er^{3+} concentration effects on an intensity of green emission, two new samples with lower concentrations of Er^{3+} (1mol% and 1.5mol%) and constant concentration of Yb^{3+} (20mol%) were studied and obtained spectra are presented in Fig. 5 (b) (Series 3). As it can be seen, in this case, the intensities of green emission firstly increase with Er^{3+} concentration and reaches a maximum value for 1.5mol%, while a further increase in Er^{3+} concentration results in a decrease of the green emission intensities. After this comparison, it can be concluded that the most intensive UC green emission has been obtained for 1.5mol% Er^{3+} :20mol% Yb^{3+} -doped GdVO_4 sample. This value is about 2 times more than the value for the intensity for 2mol% Er^{3+} :20mol% Yb^{3+} -doped

GdVO₄. Here, the effect of Er³⁺ and Yb³⁺ concentration on the intensity ratio of the green to

red emission ratio was not studied because the red emission was very weak and no dependent on changing the Er³⁺ or Yb³⁺ concentration. For example, this intensity ratio for the 1.5mol%Er³⁺:20mol%Yb³⁺-doped GdVO₄ sample is about 120. It suggests that obtained material has very higher color purity of the green upconversion emission. This value is about 3 times higher than value reported by Mahalingam et. al [24] for the similar system, Er³⁺/Yb³⁺-doped GdVO₄ nanocrystals. Also, it should be emphasized that in the sesquioxide (Y₂O₃) nanocrystals, Er³⁺/Yb³⁺ co-doping displayed an enhancement in the intensity of the red emission at 660 nm, i.e. reduction the green/red emission and lower color purity.

3.3.3. Influence of the Er³⁺/Yb³⁺ concentration ratio on the emission lifetime

The fluorescence decay curves and calculated lifetimes for all three Series the Er³⁺/Yb³⁺-doped GdVO₄ microcrystals recorded for the ⁴S_{3/2} → ⁴I_{15/2} transition (552 nm) at room temperature are shown in Fig. 6. It was found that all these curves, as well as all the other measured decay curves in this study, exhibit single exponential behavior. The calculated values of a lifetime for the ⁴S_{3/2} → ⁴I_{15/2} transition recorded under 980 nm excitation are written into Fig. 6 (a) and 6 (b). The values of a lifetime at wavelengths of 552 nm (⁴S_{3/2} → ⁴I_{15/2}) are about 100μs.

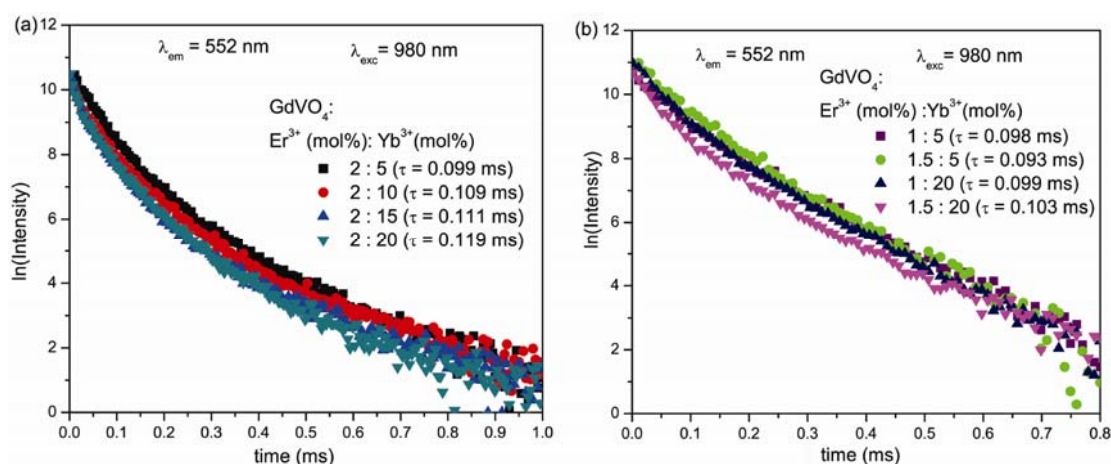


Fig. 6. a) Emission decay curves for the ⁴S_{3/2} → ⁴I_{15/2} transition (552 nm) of Er³⁺ for: a) Series 1 and b) Series 2 and Series 3 of Er³⁺/Yb³⁺-doped GdVO₄ microcrystals recorded under 980 nm excitation.

4. Conclusion

In this paper, we discuss the effect of concentration ratio Er³⁺/Yb³⁺ in Er³⁺/Yb³⁺-doped GdVO₄ microcrystals for changing and enhancing the green emission intensity in DC and UC luminescence. The intensity of the green emission was changed by changing Er³⁺/Yb³⁺ concentration ratio. Obtained results indicate that the molar ratio 1:5 and 1.5:20 (Er³⁺:Yb³⁺) could be the optimum concentration ratio for production of material with high DC and UC green emission intensity, respectively. The obtained pure green color is particularly important as the human eye possesses the maximum sensitivity in that region of the electromagnetic

spectrum and potentially making these phosphors ideal as green phosphors for a wide variety of applications in the fields of bioanalysis and biomedical.

Acknowledgments

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5. References

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Садржај: У овом раду је проучаван утицај различитих концентрационих односа $\text{Er}^{3+}/\text{Yb}^{3+}$ на структурне, морфолошке и луминесцентне особине $\text{GdVO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$, зеленог фосфора који је добијен на високој температури синтезом у чврстом стању. Испитивања су извршена на узорцима са различитим концентрацијама (између 0.5 до 2 мол%) јона Er^{3+} као емитирујућег допанта и различитим концентрација (између 5 до 20 мол%) Yb^{3+} као јона сензибилизатора. Синтетисани фосфори су окарактерисани помоћу дифракције X-зрака (XRD), скенирајуће електронске микроскопије (SEM) и фотолуминесцентне спектроскопије. Из дифракције X-зрака показано је да је добијена чиста фаза GdVO_4 , за све синтетисане узорке док је SEM показао да се материјал састоји од деформисаних сферних честица са просечним дијаметром у распону од око 2 μm до 8 μm . За екситације у блиској UV и IR области добијени емисиони спектри у „down-conversion“ и „up-conversion“ за све синтетисане $\text{GdVO}_4:\text{Er}^{3+}/\text{Yb}^{3+}$ узорке показују две јаке емисионе траке у зеленом спектралном региону на 525 nm и 552 nm таласне дужине које одговарају $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ и $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ електронским прелазима Er^{3+} јона. Са променом концентрационог односа $\text{Er}^{3+}/\text{Yb}^{3+}$ мењао се и интензитет зелене емисије. Овакав дуални мод луминесценције чини ове материјале, као зелене фосфоре, идеалним за примене у биоанализи и биомедицини.

Кључне речи: синтеза у чврстом стању, луминесценција, up-conversion, ванадати, ретке земље
