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YVO₄:RE (RE = Eu, Tm, and Yb/Er) nanoparticles synthesized by the microwave-assisted hydrothermal method for photoluminescence application

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ABSTRACT: Here, an experimental study is presented on the YVO4:RE (RE = Eu, Tm, and Yb/Er) nanoparticles synthesized by means of the microwave-assisted hydrothermal method. Different characterization techniques (X-ray diffraction, Raman and ultraviolet-visible spectroscopy, field emission scanning electron microscopy, transmission electron microscopy, and photoluminescence emissions) have been employed to examine the structural, optical, as well as its morphology and photoluminescent properties. The as-synthetized samples present different emission colors due to RE³⁺ ions, as well as nanosized spherical morphology because of synthesis method. These materials can be considered efficient materials for optical devices.





1. Introduction

Photoluminescent (PL) materials with high quantum efficiency present practical applications in many research areas, such as optoelectronics, medicine, biolabels, physics, among others (Ferreira *et al.*, 2018; Panayiotakis *et al.*, 1996; Shen *et al.*, 2010). Consequently, several inorganic matrices are studied, in which its PL property was deeply explored due to its host lattice composition, structure, morphology as well as doping and others crystal modifications (Li *et al.*, 2021). Ideally, these materials may present well-defined characteristics such as size, optical properties, and a wide range of emission colors (Liu *et al.*, 2016).

Moreover, visible-emitting phosphors can be achieved by doping different kinds of rare earth (RE) ions into lanthanide orthovanadates. The orthovanadate absorbs in the ultraviolet region of matrix electromagnetic spectrum due to ligand-metal charge transfer (LMCT) from the 2p orbital in O²⁻ to the 3d orbital in vanadate. The YVO₄ nanoparticles, as an example, are an ideal transparent host lattice for PL activators and present low toxicity in biological medium (Rivera-Enríquez and Fernández-Osorio, 2021). YVO₄ also presents relative low phonon energy, excellent thermal, mechanical, and chemical stability and high optical performance. Furthermore, the D_{2d} local point symmetry of the eight-coordinated Y^{3+} ion in the tetragonal crystal structure (space group D_{4h}) is an ideal doping site for RE³⁺ ions (Liu *et al.*, 2015). For instance, controlled fabrication of YVO4:Eu3+ nanoparticles and nanowires were achieved by microwave assisted chemical synthesis (Huong et al., 2016).

Several works related the doping of RE^{3+} ions into different types of inorganic matrices (Pinatti et al., 2015; 2016; 2019a; 2019b; Yang et al., 2018). The RE emissions arise from the 4f-4f or 5d-4f transitions from the UV to near-IR range of electromagnetic spectrum. Also, upconverting (UC) materials are an unprecedented technology which consists of absorption of two or more lower-energy photons and subsequently emission of one higher-energy photon. This strategy is specially used for solar energy materials, bioimaging, among other applications. Materials composed of Yb³⁺/Er³⁺ as activator ions can be efficiently excited using NIR (nearinfrared) laser radiation to generate visible emission. For example, photostable and small YVO₄:Yb/Er

upconversion nanoparticles in water were obtained and presented intense upconversion emission (Alkahtani *et al.*, 2021). However, many of these materials present poor luminescence efficiency and/or complicated synthesis procedure, which results in no defined or irregular sizes particles (Ji *et al.*, 2021; Kshetri *et al.*, 2018; Sousa Filho *et al.*, 2019; Woźny *et al.*, 2019).

Accordingly, in this work, we report the synthesis of YVO_4 :RE (RE = Eu, Tm, and Yb/Er) nanoparticles by the microwave-assisted hydrothermal (MAH) method. These nanoparticles were structurally characterized and potentially studied in terms of its PL properties. In addition, the structure, vibrational frequency and morphology are compared to rationalize the structure, morphology, and PL emissions.

2. Experimental

2.1 Synthesis

One mmol of NH₄VO₃ (99%, Sigma-Aldrich) was dissolved in 40 mL of distilled water at room temperature under magnetic stirring until the reagent was completely dissolved. Additionally, 2 mmol of $Y(NO_3)_3 \cdot 4H_2O$ (99.999%, Sigma-Aldrich) was dissolved in 40 mL of distilled water at room temperature. $RE(NO_3)_3$ (RE = Eu, Tm, Yb, and Er) solutions were prepared by dissolving RE_2O_3 in aqueous hot solution of HNO₃ and evaporating the excess of acid. Stoichiometric volume of RE solutions were mixed together with the Y solution. The amount of 5 mol% of Eu³⁺, and Tm³⁺; and 5 mol%Yb³⁺/2 mol%Er³⁺ were chosen due to previous works related to maximum PL emission intensity achieved. After complete dissolution of the reactants, the V solution was mixed with the Y solution to obtain YVO₄ and with the Y/RE solution to obtain YVO₄:RE nanoparticles. Subsequently, the mixture was stirred for 10 min, and, thereafter, it was transferred to the MAH system at 160 °C for 32 min, as it was the ideal conditions for many materials obtained by this methodology. The precipitates formed were collected at room temperature, washed with distilled water until the pH was neutralized, and dried in a conventional furnace at 60 °C for 12 h. Figure 1 shows a representation of the synthesis procedure herein described.



Figure 1. Schematic representation of synthesis procedure of the nanoparticles.

2.2 Characterizations

The nanoparticles were structurally characterized by X-ray diffraction (XRD) patterns using a D/Max-2000PC diffractometer Rigaku (Japan) with Cu Ka radiation ($\lambda = 1.5406$ Å) in the 2 θ range from 10° to 80° in the normal routine, with a scanning velocity of 2° min⁻¹. This unit cell was modelled using the visualization for electronic and structural analysis (VESTA) program (Momma and Izumi, 2008; 2011), version 3. Micro-Raman spectroscopy was conducted on a Horiba Jobin-Yvon (Japan) spectrometer chargecoupled device detector and argon-ion laser (Melles Griot, United States) operating at 532 nm with a maximum power of 200 mW. The ultraviolet-visible spectrophotometry (UV-vis) spectra were taken using a spectrophotometer (model Cary 5G) (Varian, USA) in diffuse-reflectance mode. Morphological analysis of the particles was recorded via field-emission scanning electron microscopy (FE-SEM) using a Carl Zeiss microscope (model Supra 35) operated at an accelerating voltage of 30 kV and a working distance of 3.7 mm. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) analysis was performed using a Jeol JEM-2100F with a field-emission gun (FEG) operating at 200 kV. For the micrographs, the samples (approximately 1 mg) were dispersed in 3 mL of distilled water and kept 15 min in the ultrasound bath. Then, one drop of the suspension was deposited on a silicon wafer, dried at room temperature and finally attached to a sample stub using carbon tape for FE-SEM analysis; and one drop of the suspension was deposited on the cupper grid and dried at room temperature for TEM analysis. Photoluminescence (PL) measurements were performed by two distinct equipment. In the first one, the samples were excited by a 355 nm laser (Cobolt/Zouk) focused on a 20 µm spot, 50 µW of power. The backscattered luminescence was dispersed by a 20 cm spectrometer with the signal detected by a charged coupled device

detector (Andor technologies). In the second one, the PL spectra were carried out with 325 nm excitation source of a krypton ion laser (Coherent Innova) and 200 mW laser output, at monochromator Thermal Jarrel-Ash Monospec and a Hamamatsu R446 photomultiplier. All measurements were performed at room temperature.

3. Results and discussion

3.1 X-ray diffraction patterns

Figure 2 shows the XRD patterns of YVO₄:RE, and all the diffraction peaks can be readily indexed to the pure tetragonal YVO₄ phase (PDF No. 17-0341) (Rivera-Enríquez and Fernández-Osorio, 2021; Yu *et al.*, 2002). The intense and sharp peaks confirm the samples are pure and present high crystallinity, as well as structural long-range order. Also, Y³⁺ site is an ideal environment with a D_{2d} point symmetry for RE emitter. So, effectively Y-by-RE substitution occurs in the host lattice because RE³⁺ and Y³⁺ have similar ionic radius, as widely reported by many works (Matos *et al.*, 2016; Rivera-Enríquez and Fernández-Osorio, 2021). This substitution was not perceived on the XRD patterns due to the limitation of detection of the XRD instrument.

A representation of the unit cell for the orthorhombic YVO_4 :RE nanoparticles are presented in Fig. 3. This unit cell was modelled using the lattice parameters and atomic positions, as well as the possible RE-by-Y substitution. The Y/RE coordination environment is a distorted dodecahedral $[YO_8]/[REO_8]$ clusters, while V is a distorted tetrahedral $[VO_4]$ cluster.



Figure 2. X-ray diffraction patterns of the YVO₄:RE nanoparticles.



Figure 3. Unit cell representation of YVO_4 :RE nanoparticles. Gray, blue, and yellow balls are Y/RE, V and O atoms, respectively.

3.2 Raman spectroscopy

Figure 4 shows the room temperature Raman spectra of YVO_4 :RE nanoparticles excited by a green laser. Experimentally, seven active Raman modes were observed at 155, 260, 367, 482, 796, 820, and 874 cm⁻¹ for the YVO_4 , YVO_4 :5Eu, and YVO_4 :5Tm samples. For the YVO_4 :5Yb/2Er, six active Raman modes were

observed at 328, 402, 638, 796, 818, and 871 cm⁻¹. Also, the YVO₄:5Yb/2Er nanoparticle present a broad PL emission, as observed in the Raman spectra, due to the Yb/Er ions. These results confirm the structural short-range order of all samples (Jayaraman *et al.*, 1987).



Figure 4. Raman spectra of the (a) YVO_4 :RE (RE = Eu and Tm), and (b) YVO_4 :5Yb/2Er nanoparticles.

3.3 UV-vis spectroscopy

Figure 5 illustrates the UV-vis diffuse reflectance spectra of the YVO₄:RE nanoparticles in the range of 275–750 nm. The samples showed absorption in the ultraviolet region at approximately 450 nm. The absorption is a result of electronic transition between the valence band (VB) formed predominantly by O 2p state, and the conduction band (CB) composed mainly by V 3d states (Yang *et al.*, 2018). Also, the YVO₄:5Tm sample present the ${}^{3}H_{6} \rightarrow {}^{3}F_{3}$ transition, and the YVO₄:5Yb/2Er present the ${}^{4}I_{15/2} \rightarrow {}^{2}H_{J}$ (J = 11/2 and 9/2) transitions.

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Figure 5. The UV-vis diffuse reflectance spectra of the YVO₄:RE nanoparticles.

The band gap energy (E_{gap}) values were calculated using the relation of the Kubelka-Munk and Wood Tauc function, as previously reported (Pinatti et al., 2019a), and it was obtained by linear extrapolation of the UVvis curve in the $[F(R_{\infty})hv]^n$ versus hv graph. $F(R_{\infty})$ is the Kubelka–Munk function, hv is the photon energy, and nis a constant related to the type of electronic transition of a semiconductor (n = 0.5 for direct allowed, n = 2 for indirect allowed, n = 1.5 for direct forbidden, and n = 3for indirect forbidden). The theoretical calculation predicts a direct allowed transition for YVO₄. Thus, the E_{gap} values obtained were 3.54, 3.41, 3.46, and 3.39 eV for the YVO₄, YVO₄:5Eu, YVO₄:5Tm, and YVO₄:5Yb/2Er samples, respectively (Fig. 6). These results show that the E_{gap} values decrease due to insertion of the RE ions, indicating that the degree of order-disorder at electronic level were affected due to Yby-RE substitution. This behavior was previously observed in other RE doped materials and is attributed mainly by the contribution of 4fⁿ electrons of RE³⁺ ions either to the VB or CB, which can increase the covalent bonding of V–O and reduce the E_{gap} . This happens because the energy level of RE3+ ions matches the energy level of VO43-, contributing to an effective energy transfer from the VO4³⁻ to the excited states of RE³⁺ ions (Yang *et al.*, 2018).



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Figure 6. Band gap energy (E_{gap}) for the YVO₄:RE nanoparticles.

3.4 Field-emission scanning electron microscopy and TEM

The detailed morphology and particle size of YVO_4 nanoparticles were assessed by FE-SEM, and the nanostructures were further characterized by TEM and HRTEM. Field emission scanning electron microscopy micrographs of the YVO_4 nanoparticles are shown in Fig. 7a and b. It is clearly seen spherical nanoparticles which exhibit a high degree of homogeneity in the shape and size. As shown in Fig. 7a and b, the particles present smooth surface, well-defined shape, and are mainly aggregated with a monodisperse size distribution.

Figure 7c shows the TEM image of YVO₄ nanoparticles. It was mainly observed spherical-like particles of sizes ranging from 20 to 50 nm. Most of them have perfect circular morphology, while other present small deformations. Figure 7d shows the HRTEM image of YVO₄ nanoparticles. The YVO₄ nanoparticles presented a single crystalline nature and the lattice spacing was calculated to be 0.363 nm between two adjacent lattice fringes, which could be indexed to 200 planes of zircon-type YVO₄. This is in agreement with the XRD results (Shen et al., 2010). Moreover, the other YVO4:RE samples also showed similar morphology and as single-crystalline and this can be attributed to the similar preparative conditions and the low dopant concentration of $\overline{RE^{3+}}$ ions (data not shown).

These results confirm that nanosized YVO_4 of spherical morphology can be obtained by the MAH method at short reactional time and low temperature. Moreover, this morphology, as well as the size, are effectively acquired without the use of surfactants, templates, organic solvents, or adjustment of pH value of the medium, which is usually required to obtain homogeneous and nanosized particles.





Figure 7. (a, b) FE-SEM images, (c) TEM image, and (d) HRTEM image of YVO₄ nanoparticles.

3.5 Photoluminescence spectroscopy

Figure 8 shows the PL emission spectra at room temperature of YVO₄:RE nanoparticles under the excitation wavelength of 355 nm. Figure 8a shows the PL emission spectra of YVO₄:RE (RE = Tm, and Yb/Er) nanoparticles, presenting an intense band at 540 nm due to VO₄³⁻ clusters (Jin *et al.*, 2011), and the YVO₄:5Tm nanoparticles also present the ³H₄ \rightarrow ³H₆ transition at 806 nm. Particularly, the YVO₄:Eu nanoparticles present intense ⁵D₁ \rightarrow ⁷F_J (J = 1 and 2) and ⁵D₀ \rightarrow ⁷F_J (J = 1–4) transitions, which arises due to the efficient energy transfer from VO₄³⁻ clusters to the Eu³⁺ ions (see Fig. 8b) (Matos *et al.*, 2016; Pinatti *et al.*, 2019a; Saltarelli *et al.*, 2014).





Figure 8. Photoluminescent emission spectra of (a) YVO_4 :RE (RE = Tm and Yb/Er), and (b) YVO_4 :5Eu nanoparticles.

Figure 9 shows the PL emission spectra at room temperature of YVO₄:RE nanoparticles under the excitation wavelength of 325 nm, as well as the CIE chromatic diagram. Figure 9a shows the PL emission spectra of the YVO₄:5Eu nanoparticles, which presents characteristic Eu³⁺ peaks at 543, 564, 595, 622, 655, and 705 nm ascribed to the ${}^{5}D_{1} \rightarrow {}^{7}F_{J}$ (J = 1 and 2), and ${}^{5}D_{0} \rightarrow {}^{7}F_{J}$ (J = 1–4) transitions, respectively (Almeida *et* al., 2021; Pinatti et al., 2015). Figure 9b shows the PL emission spectra of the YVO₄:5Tm nanoparticles, which present characteristic Tm³⁺ peaks at 480, 548, 650, and 795 nm related to the ${}^{1}D_{2} \rightarrow {}^{3}F_{I}$ (J = 4 and 5), ${}^{1}G_{4} \rightarrow {}^{3}F_{4}$, and ${}^{3}H_{4} \rightarrow {}^{3}H_{6}$ transitions, respectively (Pinatti *et al.*, 2019a). Figure 9c shows the PL emission spectra of the YVO₄:5Yb/2Er nanoparticles, which present characteristic Er³⁺ peaks at 530, 555, and 671 nm attributed to the ${}^{2}H_{11/2} \rightarrow {}^{4}I_{15/2}$, ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$, and ${}^{4}F_{9/2} \rightarrow {}^{4}I_{15/2}$ transitions, respectively (Alkahtani *et al.*, 2021; Mahata et al., 2015; Sun et al., 2006; Woźny et al., 2018; Zhang et al., 2010). Figure 9d shows the CIE chromatic diagram and the respective positions of x, and y coordinates of the YVO_4 :RE (RE = Eu, Tm, and Yb/Er) nanoparticles obtained through the PL emission spectra. The (x;y) chromatic coordinates positions are listed in Tab. 1. The YVO4:5Eu, YVO4:5Tm, and YVO₄:5Yb/2Er nanoparticles present intense emitting color in the red, blue, and green region of the diagram, respectively. These results confirm the pureness and brightness of the samples and can be considered as optimum materials for optical devices.

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Figure 9. Photoluminescent emission spectra of (a) YVO₄:5Eu, (b) YVO₄:5Tm, (c) YVO₄:5Yb/2Er nanoparticles, and (d) CIE chromatic diagram.

Table 1. Chromatic coordinates values obtained by the PL emission spectra of the YVO₄:RE nanoparticles.

Samples	Chromatic coordinates	
	Х	У
YVO4:5Eu	0.65	0.34
YVO4:5Tm	0.36	0.29
YVO4:5Yb/2Er	0.33	0.53

Figure 10 shows a schematic energy level diagram and a proposed energy transfer mechanism for the YVO₄:RE nanoparticles. For the YVO₄:5Eu nanoparticles, it is observed that, under excitation at 325 nm, electrons are excited from VB into the charge transfer state (CTS) of the VO₄³⁻ clusters. Then, the excitation energy is transferred from the VO₄³⁻ group to the ⁵D₄ level of Eu³⁺ cations. Afterwards, Eu³⁺ cations in the populated ⁵D₄ level undergo multiphonon relaxation to the ⁵D₁ level that radiatively decay to the ⁷F_J (J = 1 and 2) levels; and to the ⁵D₀ level that radiatively decay

to the ${}^{7}F_{J}$ (J = 1–4) levels. For the YVO₄:5Tm nanoparticles, the excitation energy is transferred from the VO_4^{3-} group to the ${}^{3}P_2$ level of Tm^{3+} cations. Then, Tm^{3+} cations in the populated ${}^{3}P_{2}$ level undergo multiphonon relaxation to the ${}^{1}D_{2}$ level that radiatively decay to the ${}^{7}F_{4}$ and ${}^{3}H_{4}$ levels; and to the ${}^{1}G_{4}$ level that radiatively decay to the ${}^{7}F_{4}$ and ${}^{3}H_{6}$ levels. Finally, for the YVO₄:5Yb/2Er nanoparticles, the excitation energy is transferred from the VO_4^{3-} group to the ${}^4F_{7/2}$ level of Er^{3+} cations. Then, Er^{3+} cations in the populated ${}^{4}F_{7/2}$ level undergo multiphonon relaxation to the ${}^{2}H_{11/2}$ and ${}^{4}S_{3/2}$ levels that radiatively decay to the ${}^{4}I_{15/2}$ level; and to the ${}^{4}F_{9/2}$ level that radiatively decay to the ${}^{4}I_{15/2}$ level. Alternatively, according to the energy conservation law, a two-photon process can occur and populate the green and red UC emissions of Er³⁺ ions. The successive energy transfers are: ${}^{4}I_{15/2}$ (Er³⁺) + ${}^{2}F_{5/2}$ (Yb³⁺) $\rightarrow {}^{4}I_{11/2}$ $(\text{Er}^{3+}) + {}^{2}\text{F}_{7/2}(\text{Yb}^{3+}) \text{ and } {}^{4}\text{I}_{11/2}(\text{Er}^{3+}) + {}^{2}\text{F}_{5/2}(\text{Yb}^{3+}) \rightarrow {}^{4}\text{F}_{7/2}$ $(Er^{3+}) + {}^{2}F_{7/2}(Yb^{3+})$ excite Er^{3+} ions to the ${}^{4}F_{7/2}$ state. Er^{3+}

ions at the ${}^{2}H_{11/2}/{}^{4}S_{3/2}$ states, arising from the nonradiative relaxation (NR) process of the ${}^{4}F_{7/2}$ state, radiatively decay to the ${}^{4}I_{15/2}$ state, resulting the green UC emissions. The ${}^{4}F_{9/2}$ red emitting state is populated

by the process: ${}^{4}I_{13/2}(Er^{3+}) + {}^{2}F_{5/2}(Yb^{3+}) \rightarrow {}^{4}F_{9/2}(Er^{3+}) + {}^{2}F_{7/2}(Yb^{3+})$, where the ${}^{4}I_{13/2}$ state is populated by NR process of the ${}^{4}I_{11/2}$ state (Ji *et al.*, 2021).



Figure 10. Schematic energy level diagram and a proposed energy transfer mechanism for the YVO₄:RE nanoparticles. Solid arrows = radiative transition, dashed arrows = energy transfer, and dotted arrows = nonradiative transition.

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4. Conclusions

In summary, we reported the efficient synthesis of YVO₄:RE nanoparticles by the microwave-assisted hydrothermal method. Long-range order was confirmed by XRD patterns, which showed sharp and well-defined peaks with no segregated materials. Vibrational Raman modes observed represent a signature of the structural organization in the short-range. The UV-vis spectra indicate that the band gap value decreases due to RE doping attesting structural order-disorder of the materials. The FE-SEM, TEM, and HRTEM images prove that the materials are spherical and in the nanoscale size. Photoluminescent emission spectra present transitions in the red, blue, and green regions, attesting these materials as good phosphors in the visible region. Also, the YVO4:5Yb/2Er is a good candidate as promising material for UC phosphor.

Authors' contribution

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Data availability statement

The data will be available upon request.

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References

Alkahtani, M.; Alfahd, A.; Alsofyani, N.; Almuqhim, A. A.; Qassem, H.; Alshehri, A. A.; Almughen, F. A.; Hemmer, P. Photostable and small YVO₄:Yb,Er upconversion nanoparticles in water. *Nanomaterials* **2021**, *11* (6), 1535. https://doi.org/10.3390/nano11061535

Almeida, P. B.; Pinatti, I. M.; Oliveira, R. C.; Teixeira, M. M.; Santos, C. C.; Machado, T. R.;Longo, E.; Rosa, I. L. V. Structural, morphological and photoluminescence properties of β -Ag₂MoO₄ doped with Eu³⁺. *Chem. Pap.* **2021**, *75*, 1869– 1882. https://doi.org/10.1007/s11696-020-01489-4

Ferreira, N. H.; Furtado, R. A.; Ribeiro, A. B.; Oliveira, P. F.; Ozelin, S. D.; Souza, L. D. R.; Rinaldi Neto, F.; Miura, B. A.; Magalhães, G. M.; Nassar, E. J.; Tavares, D. C. Europium(III)-doped yttrium vanadate nanoparticles reduce the toxicity of cisplatin. *J. Inorg. Biochem.* **2018**, 182,9–17. https://doi.org/10.1016/j.jinorgbio.2018.01.014

Huong, T. T.; Vinh, L. T.; Phuong, H. T.; Khuyen, H. T.; Anh, T. K.; Tu, V. D.; Minh, L. Q. Controlled fabrication of the strong emission YVO₄:Eu³⁺ nanoparticles and nanowires by microwave assisted chemical synthesis. *J. Lumin.* **2016**, *173*, 89–93. https://doi.org/10.1016/j.jlumin.2016.01.003

Jayaraman, A.; Kourouklis, G. A.; Espinosa, G. P.; Cooper, A. S.; Van Uitert, L. G. A high-pressure Raman study of yttrium vanadate (YVO₄) and the pressure-induced transition from the zircon-type to the scheelite-type structure. *J. Phys. Chem. Solids* **1987**, *48* (8), 755–759. https://doi.org/10.1016/0022-3697(87)90072-2

Ji, H.; Tang, J.; Tang, X.; Yang, Z.; Zhang, H.; Qian, Y. Enhanced upconversion emissions of NaNbO₃:Er³⁺/Yb³⁺ nanocrystals via Mg²⁺ ions doping. *Mater. Lett.* **2021**, *302*, 130348. https://doi.org/10.1016/j.matlet.2021.130348

Jin, Y.; Li, C.; Xu, Z.; Cheng, Z.; Wang, W.; Li, G.; Lin, J. Microwave-assisted hydrothermal synthesis and multicolor tuning luminescence of $YP_xV_{1-x}O_4$:Ln³⁺ (Ln = Eu, Dy, Sm) nanoparticles. *Mater. Chem. Phys.* **2011**, *129* (1–2), 418–423. https://doi.org/10.1016/j.matchemphys.2011.04.035

Kshetri, Y. K.; Regmi, C.; Kim, H.-S.; Lee, S. W.; Kim, T. H. Microwave hydrothermal synthesis and upconversion properties of Yb^{3+}/Er^{3+} doped YVO_4 nanoparticles. *Nanotechnology* **2018**, *29* (20), 204004. https://doi.org/10.1088/1361-6528/aab2bf

Li, K.; Chen, T.; Mao, H.; Chen, Y.; Wang, J. Preparation and Upconversion Emission Investigation of the $YVO_4:Yb^{3+}:Er^{3+}$ Nanomaterials and Their Coupling with the Au Nanoparticles. *J. Electron. Mater.* **2021**, 50,1189–1195. https://doi.org/10.1007/s11664-020-08636-3

Liu, Y.; Xiong, H.; Zhang, N.; Leng, Z.; Li, R.; Gan, S. Microwave synthesis and luminescent properties of YVO_4 :Ln³⁺ (Ln = Eu, Dy and Sm) phosphors with different morphologies. *J. Alloys Compd.* **2015**, *653*, 126–134. https://doi.org/10.1016/j.jallcom.2015.09.015

Liu, Y.; Yang, C.; Xiong, H.; Zhang, N.; Leng, Z.; Li, R.;Gan, S. Surfactant assisted synthesis of the YVO₄: Ln³⁺ (Ln = Eu, Dy, Sm) phosphors and shape-dependent luminescence properties. *Colloids Surf. A Physicochem. Eng. Asp.* **2016**, *502*, 139–146. https://doi.org/10.1016/j.colsurfa.2016.05.006

Mahata, M. K.; Kumar, K.; Rai, V. K. $Er^{3+}-Yb^{3+}$ doped vanadate nanocrystals: A highly sensitive thermographic phosphor and its optical nanoheater behavior. *Sens. Actuators B Chem.* **2015**, *209*, 775–780. https://doi.org/10.1016/j.snb.2014.12.039

Matos, M. G; Rocha, L. A.; Nassar, E. J.; Verelst, M. Influence of Bi^{3+} ions on the excitation wavelength of the $YVO_4:Eu^{3+}$ matrix. *Opt. Mater.* **2016**, *62*, 12–18. https://doi.org/10.1016/j.optmat.2016.09.035

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Momma, K.; Izumi, F. *VESTA*: a three-dimensional visualization system for electronic and structural analysis. *J. Appl. Cryst.* **2008**, *41*, 653–658. https://doi.org/10.1107/S0021889808012016

Momma, K.; Izumi, F. VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data. *J. Appl. Cryst.* **2011**, *44*, 1272–1276. https://doi.org/10.1107/S0021889811038970

Panayiotakis, G.; Cavouras, D.; Kandarakis, I.; Nomicos, C. A study of X-ray luminescence and spectral compatibility of europium-activated yttrium-vanadate (YVO₄: Eu) screens for medical imaging applications. *Appl. Phys. A* **1996**, *62*, 483–486. https://doi.org/10.1007/BF01567121

Pinatti, I. M.; Nogueira, I. C.; Pereira, W. S.; Pereira, P. F. S.; Gonçalves, R. F.; Varela, J. A.; Longo, E.; Rosa, I. L. V. Structural and photoluminescence properties of Eu^{3+} doped α -Ag₂WO₄ synthesized by the green coprecipitation methodology. *Dalton Trans.* **2015**, *44* (40),17673–17685. https://doi.org/10.1039/C5DT01997D

Pinatti, I. M.; Mazzo, T. M.; Gonçalves, R. F.; Varela, J. A.; Longo, E.; Rosa, I. L. V. CaTiO₃ and Ca_{1-3x}Sm_xTiO₃: Photoluminescence and morphology as a result of Hydrothermal Microwave Methodology. *Ceram. Int.* **2016**, *42* (1) (Part B), 1352–1360. https://doi.org/10.1016/j.ceramint.2015.09.074

Pinatti, I. M.; Fern, G. R.; Longo, E.; Ireland, T. G.; Pereira, P. F. S.; Rosa, I. L.V.; Silver, J. Luminescence properties of α -Ag₂WO₄ nanorods co-doped with Li⁺ and Eu³⁺ cations and their effects on its structure. *J. Lumin.* **2019a**, *206*, 442–454. https://doi.org/10.1016/j.jlumin.2018.10.104

Pinatti, I. M.; Pereira, P. F. S.; Assis, M.; Longo, E.; Rosa, I. L. V. Rare earth doped silver tungstate for photoluminescent applications. *J. Alloys Compd.* **2019b**, *771*, 433–447. https://doi.org/10.1016/j.jallcom.2018.08.302

Rivera-Enríquez, C. E.; Fernández-Osorio, A. L. Synthesis of YVO₄:Eu³⁺ nanophosphors by the chemical coprecipitation method at room temperature. *J. Lumin.* **2021**, *236*, 118110. https://doi.org/10.1016/j.jlumin.2021.118110

Saltarelli, M.; Matos, M. G.; Faria, E. H.; Ciuffi, K. J.; Rocha, L. A.; Nassar, E. J. Preparation of YVO_4 :Eu³⁺ at low temperature by the hydrolytic sol–gel methodology. *J. Sol-Gel Sci. Technol.* **2014**, *73*, 283–292. https://doi.org/10.1007/s10971-014-3525-z

Shen, J.; Sun, L. D.; Zhu, J. D.; Wei, L. H.; Sun, H. F.; Yan, C. H. Biocompatible bright YVO₄:Eu nanoparticles as versatile optical bioprobes. *Adv. Funct. Mater.* **2010**, *20* (21), 3708–3714. https://doi.org/10.1002/adfm.201001264

Sousa Filho, P. C.; Alain, J.; Leménager, G.; Larquet, E.; Fick, J.; Serra, O. A.; Gacoin, T. Colloidal Rare Earth

Vanadate Single Crystalline Particles as Ratiometric Luminescent Thermometers. *J. Phys. Chem. C* **2019**, *123* (4), 2441–2450. https://doi.org/10.1021/acs.jpcc.8b12251

Sun, Y.; Liu, H.; Wang, X.; Kong, X.; Zhang, H. Optical spectroscopy and visible upconversion studies of YVO₄:Er³⁺ nanocrystals synthesized by a hydrothermal process. *Chem. Mater.* **2006**, *18*, 2726–2732. https://doi.org/10.1021/cm051971m

Woźny, P.; Szczeszak, A.; Lis, S. Effect of various surfactants on changes in the emission color chromaticity in upconversion YVO₄: Yb³⁺, Er³⁺ nanoparticles. *Opt. Mater.* **2018**, 76, 400–406. https://doi.org/10.1016/j.optmat.2018.01.009

Woźny, P.; Runowski, M.; Lis, S. Emission color tuning and phase transition determination based on high-pressure upconversion luminescence in YVO_4 : Yb^{3+} , Er^{3+} nanoparticles. *J. Lumin.* **2019**, *209*, 321–327. https://doi.org/10.1016/j.jlumin.2019.02.008

Yang, L.; Peng, S.; Zhao, M.; Yu, L. New synthetic strategies for luminescent YVO_4 : Ln^{3+} (Ln = Pr, Sm, Eu, Tb, Dy, Ho, Er) with mesoporous cell-like nanostructure . *Opt. Mater. Express* **2018**, *8*, 3805–3819. https://doi.org/10.1364/OME.8.003805

Yu, M.; Lin, J.; Wang, Z.; Fu, J.; Wang, S.; Zhang, H. J.; Han, Y. C. Fabrication, patterning, and optical properties of nanocrystalline YVO₄:A (A = Eu³⁺, Dy³⁺, Sm³⁺, Er³⁺) phosphor films via sol-gel soft lithography. *Chem. Mater.* **2002**, *14*, 2224–2231. https://doi.org/10.1021/cm011663y

Zhang, Y.-m.; Li, Y.-h; Li, P.; Hong, G.-y.; Yu, Y.n. Preparation and upconversion luminescence of $YVO_4:Er_{3+}$, Yb_{3+} . *Int. J. Miner. Metall. Mater.* **2010**, *17*, 225–228. https://doi.org/10.1007/s12613-010-0218-7