Artigo

Photoluminescence and Structural Analysis of $\text{Er}^{3+}/\text{Yb}^{3+}/\text{Tm}^{3+}$ Triply Doped Gd_2O_3

Durante, L. P. B.; Rocha, L. A.; Machado, W. S.; Martelli, P. B.; Schiavon, M. A.; Manzani, D.; Pecoraro, E.; Ribeiro, S. J. L.; Ferrari, J. L.*

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Fotoluminescência e Análise Estrutural do Gd_2O_3 Triplamente Dopado com Er^{3+} , Yb^{3+} e Tm^{3+}

Abstract: Spectroscopic and structural properties of $\text{Er}^{3+}:\text{Yb}^{3+}:\text{Tm}^{3+}$ triply doped Gd_2O_3 nanocrystals were investigated. The effect of heat treatment at 800, 900, 1000 and 1100 °C for 4h, on the luminescence and the energy upconversion emissions (excited at 980nm) in the visible and near infrared spectral regions was discussed. The doping process with RE^{3+} was effective on Gd_2O_3 cubic phase, and structural parameters were determined for this phase. The morphology of the particles did not present significant differences on shape and size, demonstrating the reproducibility of the synthesis methods. Infrared to visible upconversion as well as infrared emissions at 1550nm were detected, suggesting that energy transfer processes from Yb^{3+} to Er^{3+} are predominant in $\text{Gd}_2\text{O}_3:\text{Yb}^{3+}:\text{Er}^{3+}:\text{Tm}^{3+}$ samples. The results pointed out the potential of $\text{Gd}_2\text{O}_3:\text{Yb}^{3+}:\text{Er}^{3+}:\text{Tm}^{3+}$ as a material for solar concentrators and optical telecom C-band (1550nm) applications.

Keywords: PEG; up-conversion; $\text{Er}^{3+}:\text{Tm}^{3+}:\text{Yb}^{3+}$; Gd_2O_3 ; infrared emission.

Resumo

Propriedades espectroscópicas e estruturais dos nanocristais de Gd_2O_3 triplamente dopados com $\text{Er}^{3+}:\text{Yb}^{3+}:\text{Tm}^{3+}$ foram investigadas. Os materiais foram tratados termicamente a 800, 900, 1000 e 1100 °C por 4h, e o efeito do tratamento térmico na luminescência foi discutido. O processo de dopagem com TR^{3+} foi efetivo na fase cúbica de Gd_2O_3 , e os parâmetros estruturais foram determinados para esta fase. A morfologia das partículas não apresentou diferença na forma e tamanho, demonstrando a reprodutibilidade do método de síntese. A luminescência nas regiões do visível e infravermelho foi estudada excitando as amostras em 980 nm. Os materiais apresentam intensa *upconversion* no visível e emissão no infravermelho em 1550 nm, e as emissões do Er^{3+} são favorecidas nos materiais, concluindo que nos materiais dopados com $\text{Er}^{3+}:\text{Yb}^{3+}:\text{Tm}^{3+}$ a transferência entre Yb^{3+} e Er^{3+} ocorre preferencialmente. Os materiais devido à absorção nas regiões do UV e IV podem ser aplicados em concentradores solares, e em aplicações de telecomunicações ópticas na banda C, em 1550nm.

Palavras-chave: *up-conversion*; $\text{Er}^{3+}:\text{Tm}^{3+}:\text{Yb}^{3+}$; Gd_2O_3 ; emissão infravermelha.

* Universidade Federal de São João Del Rei, Grupo de Pesquisa em Química de Materiais, Departamento de Ciências Naturais, Campus Dom Bosco, CEP 36301-160, São João Del Rei-MG, Brazil.

ferrari@ufsj.edu.br, jeffersonferrari@gmail.com

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Photoluminescence and Structural Analysis of $\text{Er}^{3+}/\text{Yb}^{3+}/\text{Tm}^{3+}$ Triply Doped Gd_2O_3

Lorena P. B. Durante,^a Leonardo A. Rocha,^a Wagner S. Machado,^a Patrícia B. Martelli,^b Marco A. Schiavon,^a Danilo Manzani,^c Edison Pecoraro,^c Sidney José L. Ribeiro,^c Jefferson L. Ferrari^{a,*}

^a Universidade Federal de São João Del Rei, Grupo de Pesquisa em Química de Materiais (GPQM), Departamento de Ciências Naturais, Campus Dom Bosco, CEP 36301-160, São João Del Rei-MG, Brazil.

^b Universidade Federal de São João Del Rei, Departamento de Ciências Naturais, Campus Dom Bosco, CEP 36301-160, São João Del Rei-MG, Brazil

^c Universidade Estadual de Londrina, Departamento de Química, Rodovia Celso Garcia Cid, Km 380, Campus Universitário, CEP 86057-970, Londrina-MG, Brazil.

^d Universidade Estadual Paulista, Laboratório de Materiais, Fotônicos (LAMF), Institute of Chemistry, P.O. Box 355, CEP 14800-970, Araraquara-SP, Brazil.

* ferrari@ufsj.edu.br, jeffersonferrari@gmail.com

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1. Introduction
2. Experimental
3. Results and Discussion
4. Conclusions

1. Introduction

The interest of optoelectronics industries on materials containing rare earth ions (RE^{3+}) have constantly grown, mainly aiming for its particular narrow emission and excitation bands with long lifetimes (ms), originated from intraconfigurational $f-f$ electronic transitions.^{1,2} Based on such features, RE^{3+} are used in nanotechnology in a wide range of applications in photonics and biophotonics, such as optical amplifiers,³ luminescent markers,⁴ contrast agents⁵ and

photovoltaics.⁶

RE^{3+} , including Yb^{3+} , Er^{3+} , Tm^{3+} , can show non-linear optical effects called energy upconversion, when through multi-photons absorption of wavelengths in the near infrared (NIR) and energy transfer processes, NIR photons are converted in photoluminescence in the visible spectral region (VSR).^{7,8} To improve the NIR to VSR conversion, sensitizers are used to increase the absorption cross-section in the NIR, once most of the RE^{3+} VSR emitters show low absorption cross-section at NIR. One of the best in this sense is Yb^{3+} , which yields

significant improvement when paired with multiple or single RE^{3+} , such as $\text{Yb}^{3+}:\text{Er}^{3+}:\text{Tm}^{3+}$, $\text{Er}^{3+}:\text{Yb}^{3+}$ and $\text{Tm}^{3+}:\text{Yb}^{3+}$, resulting in photoluminescence in VSR (470, 550 and 660 nm, *i.e.*, blue, green and red).⁹ Er^{3+} emissions rise from $^2\text{H}_{11/2}$, $^4\text{S}_{3/2}$ and $^4\text{F}_{9/2}$ to $^4\text{I}_{15/2}$ energy levels, emitting at 525, 545 and 657 nm respectively.¹⁰ Tm^{3+} also can present emission at blue region, assigned to the transition $^1\text{G}_4 \rightarrow ^3\text{H}_6$ at 472 nm.⁹

Previous reports have presented Gd_2O_3 as a proper host regarding RE^{3+} photoluminescence, since it shows low phonons energy as well as photothermal and photochemical stability.^{8,11-16} For instance, Gd_2O_3 nanotubes triply doped with $\text{Er}^{3+}:\text{Tm}^{3+}:\text{Yb}^{3+}$ shows white emission by means of energy upconversion processes for Yb^{3+} concentration of 10%.¹⁴ The similarity of ionic radii between Gd^{3+} and RE^{3+} is a key point for successful incorporation of RE^{3+} into this oxide host.¹⁵ However, crystalline solids, as Gd_2O_3 , may present several structural defects intrinsically connected to its synthesis, or by the replacement of one of the atoms by other, as in the case of dopants as RE^{3+} , which can induce structural microstrains.¹⁵ One way to prospect into microstrains behavior of crystalline solids from XRD data is to apply Williamson-Hall method.¹⁷ Microstrains caused by atoms vacancies contributes for deactivation of the excited state of RE^{3+} and reduces its emissions intensities. Vidya *et al.* (2015), reported microstrains (between 7.123 and 6.5×10^{-3}) for Eu^{3+} -doped Gd_2O_3 heat treated at 600°C .¹⁸ They reduced the microstrains by controlling the heat treatment temperature.¹⁵

This work reports on the synthesis assisted by polyethylene glycol (PEG) and structural and luminescence characterization of Gd_2O_3 nanocrystals triply doped (GNTD) with Er^{3+} , Yb^{3+} and Tm^{3+} . The effect of heat treatments on the photoluminescence of the RE^{3+} in the visible and near infrared will be discussed by means of the energy transfer processes from Yb^{3+} to $\text{Er}^{3+}/\text{Tm}^{3+}$.

2. Experimental

$\text{Er}^{3+}:\text{Yb}^{3+}:\text{Tm}^{3+}$ triply doped Gd_2O_3 powder shape samples were prepared by using polyethylene glycol (PEG) precursor, as described elsewhere.¹⁶ RE^{3+} concentrations were taken as 0.2 mol% for Er^{3+} , 0.5 mol% for Tm^{3+} and 1.2 mol% for Yb^{3+} , regarding to Gd^{3+} concentration. To obtain water soluble salts of RE^{3+} , rare earth oxides were dissolved in concentrated HCl 12M at 100°C under stirring (500 rpm). The respective aqueous solutions were titrated with EDTA 0.01 mol.L^{-1} to derive the correspondent RE^{3+} concentrations. For the synthesis process, a mass of PEG corresponding to 10 times the molar concentration of RE^{3+} [$\text{Er}^{3+} + \text{Gd}^{3+} + \text{Yb}^{3+} + \text{Tm}^{3+}$], was dissolved in deionized water and transferred to a 50mL beaker containing the RE^{3+} solutions, which are added previously at the stoichiometric ratios. The solution was kept at 60°C under magnetic stirring until the formation of a viscous liquid, designated hereinafter as precursor solution. Four identical precursor solutions were prepared and each one was submitted to a different heat treatment: 800, 900, 1000 and 1100°C for 4h, under air atmosphere and allowed to cool down to room temperature, yielding on 4 white powder samples.

Thermogravimetric analysis (TG) and differential thermal analysis (DTA) of the precursor solution were performed by using a DTG-60H (SHIMADZU) under synthetic air atmosphere and heating rate of $10^\circ\text{C}/\text{min}$. XRD analysis for heat-treated samples were performed by a Shimadzu diffractometer using $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$), graphite monochromator, scan step of 0.02 degrees and 2θ angle interval from 10° to 80° . Scherrer's equation was used to estimate the crystallite grain sizes. UV/Vis diffuse reflectance was performed using an Agilent Cary 5000 spectrometer between 200-800nm. Experimental band gap were calculated by Kubelka-Munk method. The particles morphologies were analyzed through scanning electron microscopy (SEM - Hitachi TM-3000 electron microscope).

Photoluminescence were performed at room temperature, by using a Spectra Pro 300i spectrometer, coupled with a photomultiplier detector for visible range and an InGaAs detector for near infrared region. Energy upconversion spectra were collected from 400 to 800 nm and from 1400 to 2000 nm. Samples were excited at 980nm through a fiber CW diode laser.

3. Results and Discussion

In order to establish and understand the steps of triply doped Gd_2O_3 synthesis, the viscous precursor solution was submitted to TG/DTA analyses, from room temperature (25°C) up to 1000°C. The resulting thermograms are shown in Figure 1.

Figure 1. TG/DTA analysis for viscous precursor solution containing Gd^{3+} , Er^{3+} , Yb^{3+} and Tm^{3+} obtained via PEG precursor

TG curve shows three main events represented by AB, BC and CD steps at 100, 400 and 550 °C, respectively. AB step correspond to free solvent (water) elimination, which yields close to 30% of the total mass. BC step correspond to the thermal decomposition of the organic compounds, *i.e.*, PEG and shows a mass loss higher than AB, once PEG molecule presents higher molecular mass than water. CD step is attributed to the elimination of hydration water. The endothermic events in DTA curve at 65 (AB) and 380°C (BC) corroborate the results seen in TG analysis. Moreover, exothermic events at 410 and 498 °C can be assigned to the formation of Gd_2O_3 cubic phase.¹⁹

Figure 2 shows the XRD diffractograms for samples heat-treated at 800, 900, 1000 and

1100°C. The most intense peak reflections are at 28.6, 33.1, 47.5 and 56.4°, assigned to (222), (400), (440) and (622) crystal planes, respectively. Such group of reflections corresponds to Gd_2O_3 in a cubic structure, according to JCPDF card number 00-012-0797. That corroborates with the thermal analysis results arguments, specifically that represented by the peak close to 410°C (TG curve), which was associated to the formation of Gd_2O_3 cubic phase. The synthesis of such phase is due to the high concentration of Gd^{3+} in the precursor solution. Moreover, the doping process was feasible because all doping ions (Yb^{3+} , Tm^{3+} and Er^{3+}), present similar charge, coordination number and ionic radii regarding to Gd^{3+} in such crystalline structure.²⁰

Figure 2. XRD diffractograms for samples heat-treated at 800, 900, 1000 and 1100 °C

Scherrer's method was used to determine the crystallite size for the heat-treated samples²¹. Equation 1 represent the Scherrer equation, where D is the crystallite size, K is the shape factor ($K = 0.89$ for spherical particles), λ is the X-ray wavelength ($\text{CuK}\alpha = 1.5418\text{\AA}$) and θ is the full width at half maximum for the highest intense diffraction peak. By using the values obtained from

$$\varepsilon_{hkl} = \frac{K\lambda}{\beta_f \cos \theta} \quad \text{Eq. 1}$$

$$\delta = \frac{1}{D^2} \quad \text{Eq. 2}$$

$$\beta_{hkl} \cos \theta = \frac{K\lambda}{D} + 4\varepsilon \sin \theta \quad \text{Eq. 3}$$

Scherrer's equation, the dislocation density (δ) could be inferred using the Equation 2.¹⁸ Williamson-Hall method (Equation 3) was used to define the strain values, ε , from the linear slope of plotting $4\varepsilon \sin \theta$ (x axis) as function of $\beta_{hkl} \cos \theta$ (y axis), as presented in Figure 3. All values for structural parameters are shown in Table 1.

Figure 3. Williamson-Hall plot for $\text{Gd}_2\text{O}_3:\text{Er}^{3+}:\text{Yb}^{3+}:\text{Tm}^{3+}$ heat-treated samples at (a) 800, (b) 900, (c) 1000 and (d) 1100 °C for 4h

Table 1. Structural parameters for $\text{Gd}_2\text{O}_3:\text{Er}^{3+}:\text{Yb}^{3+}:\text{Tm}^{3+}$ based on the 28.6° (222) reflection peak.

Temperature (°C)	Crystallite size (nm)	Stacking fault (222) (10^{-4})	Strain (10^{-3})
800	31.22	10.30	0.93
900	47.62	4.41	0.76
1000	50.69	3.89	0.27
1100	48.27	4.29	-1.10

Crystallite sizes varied from 31 and 51nm, which are consistent with values found in the literature for cubic Gd_2O_3 heat-treated at these temperatures.¹⁶ As expected, the dislocation density decreases as the annealing temperature increases, indicating a reduction of structural defects. The small change on the linear slope in the Williamson-Hall curves demonstrates that the heating temperature induces internal structural

forces. The increasing in heat treatment temperature leads to a decreasing on the strain, resulting even in negative values, *i.e.*, the higher the temperature, the lower the strain. For instance, at 1000°C the cubic phase of Gd_2O_3 present lowest positive strain, while at 1100°C the negative value can be assigned to the structure be nearby a phase transition (from cubic to monoclinic), which will come to happens at 1200°C.¹⁵ The

results presented on Table 1 are smaller than that reported for Gd_2O_3 nanocrystals prepared at 600°C ¹⁸. That supports the calculations, which show that the increasing on the heat-treatment temperature results in higher crystallinity, which in turn, favors low strain.

In order to evaluate if the increasing on the heat treatment temperature could induces variations on the morphology of $\text{Gd}_2\text{O}_3:\text{Er}^{3+}:\text{Yb}^{3+}:\text{Tm}^{3+}$ particles, scanning electron microscopy was performed and the

results are shown in Figure 4. The micrographs show uniformly particles size distribution at the nanoscale. Gd_2O_3 triply doped particles present slightly elongated spherical morphology, which is associated with the sintering process between adjacent particles, resulting in an agglomerate of particles²². Neither size nor morphology seems to be affected by the difference in 300°C among the lowest and the highest temperatures of the heat-treatment.

Figure 4. Micrographs of $\text{Gd}_2\text{O}_3:\text{Er}^{3+}:\text{Yb}^{3+}:\text{Tm}^{3+}$ heat-treated at (a) 800, (b) 900, (c) 1000 and (d) 1100°C for 4h

Diffuse reflectance analysis from UV to visible range was performed in order to calculate the electronic band gap for each sample heat-treated at different temperature. The spectra in Figure 5 show

that the samples present consistent reflection over the region from 350 to 800nm . They show also a strong absorption band from 200 to 230nm , associated with the electronic transitions from valence to

conduction bands of the oxide host. On the other hand, the low intensity band at 275nm is assigns to electronic transitions involving extrinsic states, such as surface defects,

faulty states or impurities, and may also be associated with the $f-f$ transition $^8S_{7/2} \rightarrow ^6I_J$ from Gd^{3+} .²³

Figure 5. Diffuse reflectance spectra for $Gd_2O_3:Er^{3+}:Yb^{3+}:Tm^{3+}$ heat-treated at different temperatures (as indicate for each spectrum)

The relative diffuse reflectance (R_∞) corresponds to the ratio between the scattered and the reflected radiation flux (FR). It arises from the interaction of the incident radiation flux (FI) with the structure and composition of the samples, since scattering depends on the polarizability and

spatial distribution of the atoms. Equation 4 represents the ratio for R_∞ . Usually, relative diffuse reflectance is presented in terms of light absorption and scattering coefficients by Kubelka-Munk function, as shown by Equation 5:²⁴

$$R_\infty = \frac{FR}{FI} \quad \text{Eq. 4}$$

$$F(R_\infty) = \frac{K}{S} = \frac{(1 - R_\infty)^2}{2R_\infty} \quad \text{Eq. 5}$$

where, R_∞ is the relative diffuse reflectance for each wavelength, K is the absorption coefficient and S is the light scattering

coefficient. Band gaps are estimated by applying Kubelka-Munk function to the relative diffuse reflectance spectra as

function of the absorption energy. Moreover, indirect energy band gap can be assessed from the slope of the linear adjust of $[F(R_\infty)hv]^2$ versus hv .²⁵ Figure 6 shows the Kubelka-Munk plots with the respective calculated band gaps. The results (between 5.16 and

5.18 eV) for $Gd_2O_3:Er^{3+}:Yb^{3+}:Tm^{3+}$ samples are similar to the results reported for Gd_2O_3 cubic phase, suggesting that doping did not affect at all the electronic energy levels structure of the host.²⁶

Figure 6. Kubelka-Munk plots based on the diffuse reflectance spectra for $Gd_2O_3:Er^{3+}:Yb^{3+}:Tm^{3+}$ heat-treated at (a) 800, (b) 900, (c) 1000 and (d) 1100 °C

The emission spectra from upconversion process (UCP) for $Gd_2O_3:Er^{3+}:Yb^{3+}:Tm^{3+}$ heat-treated samples are shown in Figure 7. As for the current samples, Yb^{3+} act as sensitizer for Tm^{3+} and Er^{3+} , once these ions do not present significant absorption cross section for 980nm, which is the best wavelength to

induces UCP in such system.²⁷ In Figure 7, the emission bands related to Er^{3+} are those in the green region, ranging from 510 to 575nm and assigned to $^2H_{11/2} \rightarrow ^4I_{15/2}$ and $^4S_{3/2} \rightarrow ^4I_{15/2}$ transitions, and those in the red region, centered at 658nm and assigned to $^4F_{9/2} \rightarrow ^4I_{15/2}$ transition.

Figure 7. Upconversion emission spectra ($\lambda_{\text{exc}} = 980\text{nm}$) for $\text{Gd}_2\text{O}_3:\text{Er}^{3+}:\text{Yb}^{3+}:\text{Tm}^{3+}$ heat-treated at 800, 900, 1000 and 1100 °C for 4h

The emission in the red region also could be assigned to ${}^1\text{G}_4 \rightarrow {}^3\text{F}_4$ Tm^{3+} transition⁹, but the absence of the Tm^{3+} emissions at blue region (${}^1\text{G}_4 \rightarrow {}^3\text{H}_6$) indicates that the energy has been redirected to Er^{3+} , which has major (and probably the only) contribution to emissions at 658nm. This assumption is based on the fact that the spectra for $\text{Yb}^{3+}:\text{Tm}^{3+}:\text{Er}^{3+}$ triply doped Gd_2O_3 are very similar to those of Er^{3+} -doped or $\text{Er}^{3+}:\text{Yb}^{3+}$ Gd_2O_3 co-doped emission spectra.¹²

Zheng, et al.¹⁴, showed that intense emission of Tm^{3+} can be detected for this system, when Yb^{3+} concentration is about 10 mol%. That leads to conclude that Yb^{3+} concentration used in the present work (1.2mol%) is not enough to sensitize Tm^{3+} in Gd_2O_3 . Previous study on upconversion emission by co-doping $\text{Er}^{3+}:\text{Tm}^{3+}$ chalcogenide glasses ($70\text{GeS}_2-10\text{In}_2\text{S}_3-20\text{CsBr}$)²⁹, reports that Tm^{3+} (${}^3\text{H}_4 \rightarrow {}^3\text{H}_4$) also can sensitize Er^{3+} (${}^4\text{I}_{15/2} \rightarrow {}^4\text{I}_{9/2}$) by energy transfer process, once both energy levels are close to resonance, and this could contribute to reduce Tm^{3+} photoluminescence, as observed in the present work.

Regarding to its intrinsic mechanisms, UPC has two predominant pathways: (i) excited state absorption (ESA) and (ii) energy transfer upconversion (ETU). Figure 8 depicts a proposed mechanism for such processes in $\text{Gd}_2\text{O}_3:\text{Er}^{3+}:\text{Yb}^{3+}:\text{Tm}^{3+}$. Co-doping with Yb^{3+} ions turns ETU the mandatory mechanism. In addition, ETU is two orders of magnitude greater than the ESA process²⁸. The most probable mechanism corresponds to Yb^{3+} efficiently absorbing photons at 980nm and transferring its energy to Er^{3+} through the resonant energy levels ${}^2\text{F}_{5/2}$ (Yb^{3+}) and ${}^4\text{I}_{11/2}$ (Er^{3+}), respectively. Then, a second 980nm photon promotes the excited electron from ${}^4\text{I}_{11/2}$ level to higher energy levels of Er^{3+} . Still, after non-radiative processes to lower energy levels, radiative decays take place from ${}^2\text{H}_{11/2}$, ${}^4\text{S}_{3/2}$ and ${}^4\text{F}_{9/2}$ energy levels of Er^{3+} , correspond to emissions at 524, 545 and 657nm, respectively. Similar energy transfer between Yb^{3+} and Er^{3+} ions also can occur from ${}^2\text{F}_{5/2}$ (Yb^{3+}) and ${}^2\text{H}_{9/2}$ or ${}^4\text{F}_{7/2}$ (Er^{3+}) energy levels⁹. Besides Yb^{3+} energy transfer to Er^{3+} , it can also play a similar mechanism with Tm^{3+} , when ${}^2\text{F}_{5/2}$ excited energy level of Yb^{3+}

transfer its energy to Tm^{3+} levels ($^3\text{H}_5$, $^3\text{F}_2$, $^3\text{F}_3$ and $^3\text{H}_5$). After that, through non-radiative processes, the electrons population decay to intermediated energy levels and, from there, a second 980nm photon can be absorbed and

electrons will be promoted to $\text{Tm}^{3+} ^1\text{G}_4$ level. Usually, $\text{Tm}^{3+} ^1\text{G}_4$ energy level undergo radiative decay process, resulting in emissions at blue ($^1\text{G}_4 \rightarrow ^3\text{H}_6$) and red region ($^1\text{G}_4 \rightarrow ^3\text{F}_4$).²⁹

Figure 8. Upconversion mechanism proposed for $\text{Gd}_2\text{O}_3:\text{Er}^{3+}:\text{Yb}^{3+}:\text{Tm}^{3+}$. The curved arrows show the possible energy transfer pathways from Yb^{3+} to Er^{3+} and Tm^{3+}

RE^{3+} spectral features, such as emission intensity, bandwidth and even transition probabilities are driven by the ligand electrostatic field distribution (crystal field symmetry - CFS) around the ion. Such influence is summarized by the selection rules for $f-f$ transitions, which can be disrupted by removing the field symmetry, *i.e.*, when a crystal structure turns to amorphous. In the case of the present work it is the opposite, *i.e.*, the structure goes from amorphous to cubic phase. Further, especially for UCP, energy transfer rates (ETR) between resonant energy levels of close ions, also play a crucial role on the spectral features, once ETR depends on the energy levels wavefunctions coupling, which in turn, is influenced by CFS. The effect of both mechanisms in the present work is shown in Figure 9, which come up with the results for the ratio (G/R) between

integrated areas of emission bands from UCP, in the green (510-575nm) and the red (658nm) regions of the visible spectra. From Figure 9(a), G/R exhibit a linear increasing as the heat-treatment temperature get higher, which could be explained by the emergence of the selection rules and $\text{Yb}^{3+} \rightarrow \text{Er}^{3+}$ ETR on UCP, when the structural transition from amorphous to cubic takes place over the rising of the temperature. G/R ratio develops by the reduction on the intensity of 658nm band emission, as shown in Figure 7, which leads to a change in color perception from UCP net emissions. The chromaticity diagram presented in Figure 9(b) depicts such change. The CIE plotting shows that the increase on G/R shifts the color coordinates from orange to green. Besides the application suggested earlier for $\text{Gd}_2\text{O}_3:\text{Er}^{3+}:\text{Yb}^{3+}:\text{Tm}^{3+}$ in the areas of solar energy and telecom, such feature could

be used as a steady value luminescent microthermometer for calibration, mapping or monitoring industrial processes that operates in the range of the $\text{Gd}_2\text{O}_3:\text{Er}^{3+}:\text{Yb}^{3+}:\text{Tm}^{3+}$ phase transition. The

temperature of the process would be recorded permanently on the structure of $\text{Gd}_2\text{O}_3:\text{Er}^{3+}:\text{Yb}^{3+}:\text{Tm}^{3+}$, and could be read by means of G/R calculation.

Figure 9. (a) Ratio of emissions Green/Red (G/R) and (b) CIE plotting for $\text{Gd}_2\text{O}_3:\text{Er}^{3+}:\text{Yb}^{3+}:\text{Tm}^{3+}$ heat-treated at 800, 900, 1000 and 1100°C for 4h

In addition, Figure 10 shows the near infrared emission spectra, which show an emission band centered at 1537nm, assigned to $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ transition from Er^{3+} . This emission was detect concomitant to those from UCP, and shows the possibilities for GNTD as a unique compound, which could find application in fields as solar

concentrators, steady value luminescent microthermometer, as well as optical amplifiers, operating in the third telecommunication window.²⁹ It was observed that, the higher the heat-treatment temperature, the more intense is the emission band at NIR region, in the same way for UCP emissions.

Figure 10. Near infrared emission spectra of the $\text{Gd}_2\text{O}_3:\text{Er}^{3+}:\text{Tm}^{3+}:\text{Yb}^{3+}$ heat-treated at different temperatures ($\lambda_{\text{exc}} = 980 \text{ nm}$, 100 mW)

Tm³⁺ doped compounds usually show infrared emission centered close to 1800nm, assigned to the transition ³F₄→³H₆. However, such was not observed for the triply doped Gd₂O₃ obtained in this work. It can indicate that i) the energy transfer between Yb³⁺ and Er³⁺ is more efficient than that between Yb³⁺ and Tm³⁺, or ii) Tm³⁺ are transferring energy to Er³⁺, as proposed in the mechanism depicted in Figure 8. This behavior is similar to that reported by Guo *et al.*, 2004³⁰, where the same emission is missing in Gd₂O₃:Er³⁺:Tm³⁺:Yb³⁺ prepared by sol-gel process and heat-treated at 900 °C.

4. Conclusions

By using PEG assisted synthesis, it was possible to obtain Er³⁺:Yb³⁺:Tm³⁺ triply doped Gd₂O₃ nanocrystals. XRD analyses confirm the efficiency of doping and heat-treatment processes by obtain Gd₂O₃ single phase. The typical morphology corresponds to clusters of particles agglomerates, probably due the sintering process. Diffuse reflectance analysis applying Kubelka-Munk method shows that doping does not influence significantly the electronic band gap, with values between 5.16 and 5.18eV. Gd₂O₃:Er³⁺:Tm³⁺:Yb³⁺ present luminescence at visible and NIR regions when excited at 980nm, and such luminescence shows to be dependent on heat-treatment temperature. The ratio between green and red UCP emission (G/R) showed linear dependence regarding the heat-treatment temperature, *i.e.*, the higher the last, the higher the first, shifting the chromaticity from orange to yellow coordinates. The samples also present intense emission centered at 1500nm, favored by increasing the heat-treatment temperature. The energy transfer from Yb³⁺ shows more efficiently to Er³⁺ than for Tm³⁺, and Tm³⁺ may also be contributing to Er³⁺ photoluminescence, once its typical blue emission (¹G₄→³H₆) is missing. The results in the present work for Gd₂O₃:Er³⁺:Tm³⁺:Yb³⁺ demonstrated partially its potential for photonics applications, such as solar

concentrators, steady value luminescent microthermometer, as well as optical amplifiers at 1500 nm.

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References

- ¹ GSchneider Jr., K. A.; Cappellen, J. (Eds), *Two hundred Years of Rare Earths*, Rare Earth Information Center, IPRT: North-Holland, 1987. [[link](#)]
- ² Serra, O. A.; Lima, J. F.; de Sousa Filho, P. C. A luz e as Terras Raras. *Revista Virtual de Química* **2015**, *7*, 242. [[CrossRef](#)]
- ³ Aquino, F. T.; Pereira, R. R.; Ferrari, J. L.; Ribeiro, S. J. L.; Ferrier, A.; Goldner, P.; Gonçalves, R. R. Unusual broadening of the NIR luminescence of Er³⁺-doped Nb₂O₅ nanocrystals embedded in silica host: Preparation and their structural and spectroscopic study for photonics applications, *Materials Chemistry and Physics* **2014**, *147*, 751. [[CrossRef](#)]
- ⁴ Bacigalupo, M. A.; Meroni, G.; Secundo, F.; Scalera, C.; Quici, S. Antibodies conjugated with new highly luminescent Eu³⁺ and Tb³⁺ chelates as markers for time resolved immunoassays. Application to simultaneous determination of clenbuterol and free cortisol in horse urine. *Talanta* **2009**, *80*, 954. [[CrossRef](#)]
- ⁵ Yan, B.; Sheng, C.; Guo, L. Lanthanide (Eu³⁺, Tb³⁺, Gd³⁺) hybrid system with functionalized diethylenetriamine pentaacetic acid: coordination bonding assembly, luminescence and MRI contrast agent

- property. *Inorganic Chemistry Communications* **2012**, *18*, 43. [CrossRef]
- ⁶ Wild, J.; Meijerink, A.; Rath, J. K.; Van Sark, W. G. J. H. M.; Schropp, R. E. I. Upconverter solar cells: materials and applications. *Energy & Environmental Science* **2011**, *4*, 4835. [CrossRef]
- ⁷ Ledemi, Y.; El Amraoui, M.; Ferrari, J. L.; Fortin, P.-L.; Ribeiro, S. J. L.; Messaddeq, Y. Infrared to Visible Up-Conversion Emission in $\text{Er}^{3+}/\text{Yb}^{3+}$ Codoped Fluoro-Phosphate Glass-Ceramics. *Journal of American Ceramic Society*. **2013**, *96*, 825. [CrossRef]
- ⁸ Singh, S. K.; Kumar, K.; Rai, S. B. $\text{Er}^{3+}/\text{Yb}^{3+}$ codoped Gd_2O_3 nano-phosphor for optical thermometry. *Sensors and Actuators A: Physical* **2009**, *149*, 16. [CrossRef]
- ⁹ Zhang, c.; Ma, P.; Li, C.; Li, G.; Huang, S.; Yang, D.; Shang, M.; Kang, X.; Lin, J. Controllable and white upconversion luminescence in $\text{BaYF}_5:\text{Ln}^{3+}$ ($\text{Ln} = \text{Yb}, \text{Er}, \text{Tm}$) nanocrystals. *Journal of Materials chemistry* **2011**, *21*, 717. [CrossRef]
- ¹⁰ Ferrari, J. L.; Lima, K. O.; Maia, L. J. Q.; Ribeiro, S. J. L.; Gomes, A. S. L.; Gonçalves, R. R. Broadband NIR Emission in Sol-Gel Er^{3+} -Activated SiO_2 - Ta_2O_5 Glass Ceramic Planar and Channel Waveguides for Optical Application. *Journal of Nanoscience and Nanotechnology*. **2011**, *11*, 2540. [CrossRef]
- ¹¹ Ferrari, J. L.; Parreira, R. L. T.; Pires, A. M.; Lima, S. A. M.; Davolos, M. R. A route to obtain $\text{Gd}_2\text{O}_3:\text{Nd}^{3+}$ with different particle size. *Materials Chemistry and Physics* **2011**, *127*, 40. [CrossRef]
- ¹² Rocha, L. A.; Ribeiro, S. J. L.; Pereira, A. C.; Schiavon, M. A.; Ferrari, J. L. Up-conversion and infrared emission of $\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped SiO_2 - Gd_2O_3 obtained by the sol-gel process. *Processing and application of Ceramics* **2015**, *9*, 23. [CrossRef]
- ¹³ Hai-Yong, C.; Chun-Yuan, H.; Chun-Xiao, G.; Jia-Hua, Z.; Shi-Yong, G.; Hong-Liang, L.; Yan-Guang, N.; Dong-Mei, L.; Shi-Hai, K.; Guang-Tian, Z. Structural Transition of $\text{Gd}_2\text{O}_3:\text{Eu}$ Induced by High Pressure. *Chinese Physics Letters* **2007**, *24*, 158. [CrossRef]
- ¹⁴ Zheng, K.; Zhang, D.; Zhao, D.; Liu, N. Bright white upconversion emission from Yb^{3+} , Er^{3+} and Tm^{3+} -codoped Gd_2O_3 nanotubes. *Physical Chemistry Chemical Physics* **2010**, *12*, 7620. [CrossRef]
- ¹⁵ Rocha, L. A.; Schiavon, M. A.; Ribeiro, S. J. L.; Ferrari, J. L. Eu^{3+} -doped SiO_2 - Gd_2O_3 prepared by the sol-gel process: Structural and optical properties. *Journal Sol-Gel Science and Technology* **2015**, *76*, 260. [CrossRef]
- ¹⁶ Durante, L. P. B.; Rocha, L. A.; dos Santos, D. P.; Coelho, F. O.; Schiavon, M. A.; Ribeiro, S. J. L.; Ferrari, J. L. Synthesis, characterization and evaluation of scintillation properties of Eu^{3+} -doped Gd_2O_3 obtained using PEG as precursor. *Journal of Alloys and Compounds* **2015**, *648*, 467. [CrossRef]
- ¹⁷ Mote, V. D.; Purushotham, Y.; Dole, B. N. Williamson-Hall analysis in estimation of lattice strain in nanometer-sized ZnO particles. *Journal of Theoretical and Applied Physics* **2012**, *6*, 1. [CrossRef]
- ¹⁸ Vidya, Y. S.; Anantharaju, K. S.; Nagabhushana, H.; Sharma, S. C. Euphorbia tirucalli mediated green synthesis of rose like morphology of $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ red phosphor: Structural, photoluminescence and photocatalytic studies. *Journal of Alloys and Compounds* **2015**, *619*, 760. [CrossRef]
- ¹⁹ Morales Ramírez, A. J.; García Murillo, A.; Carrillo Romo, F. J.; García Hernández, M.; Jaramillo Vigueras, D.; Chaderyron, G.; Boyer, D. Properties of $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$, Tb^{3+} nanopowders obtained by sol-gel process. *Materials Research Bulletin* **2010**, *45*, 40. [CrossRef]
- ²⁰ Shannon, R. D. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica Section A* **1976**, *32*, 751. [CrossRef]
- ²¹ Patterson, A. L. The Scherrer Formula for X-Ray Particle Size Determination, *Physical Review* **1939**, *56*, 978. [CrossRef]
- ²² Li, J.; Li, J.-G.; Li, J.; Liu, S.; Li, X.; Sun, X. Sakka, Y. Photoluminescent properties of new up-conversion phosphors of Yb/Tm co-doped $(\text{Gd}_{1-x}\text{Lu}_x)_3\text{Al}_5\text{O}_{12}$ ($x = 0.1-0.5$) garnet

solid solutions. *Journal of Alloys and Compounds* **2014**, 582, 623. [[CrossRef](#)]

²³ Dhanajaya, N.; Nagabhushana, H.; Nagabhushana, B. M.; Rudraswamy, B.; Sharma, S. C.; Sunitha, D. V.; Shivakumara, C.; Chakradhar, R. P. S. Effect of different fuels on structural, thermo and photoluminescent properties of Gd₂O₃ nanoparticles. *Spectrochimica Acta Part A: Molecular Spectroscopy* **2012**, 96, 532. [[CrossRef](#)]

²⁴ Wedlandt, W.; Hecht, H. G. *Reflectance Spectroscopy*, Wiley Interscience: New York, 1966.

²⁵ Patterson, E. M.; Shelden, C. E.; Stockton, B. H. Kubelka-Munk optical properties of a barium sulfate white reflectance standard. *Applied Optics* **1977**, 16, 729. [[CrossRef](#)]

²⁶ Adachi, G.-Y.; Imanaka, N. The Binary Rare Earth Oxides. *Chemical Reviews* **1998**, 98, 1479. [[CrossRef](#)]

²⁷ Camargo, A. S. S.; Nunes, L. A. O.; Silva, J. F.; Costa, A. C. F. M.; Barros, B. S.; Silva, J. E.

C.; de Sá, G. F.; Alves Jr, S. Efficient green and red upconversion emissions in Er³⁺/Yb³⁺ co-doped ZnAl₂O₄ phosphor obtained by combustion reaction. *Journal of Physics: Condensed Matter* **2007**, 19, 246209. [[CrossRef](#)]

²⁸ Auzel, F. Upconversion and anti-stokes processes with f and d ions in solids, *Chemical Reviews* **2004**, 104, 139. [[CrossRef](#)]

²⁹ Shen, C.; Zhang, Q.; Xu, Y.; Chen, D.; Zeng, H.; Chen, G. Effects of the Tm³⁺ Ion Codoping on the Upconversion Luminescence of Er³⁺ Ion-Doped Chalcohalide, *Glasses Journal of the American Ceramic Society* **2009**, 92, 3122. [[Link](#)]

³⁰ Guo, H.; Dong, N.; Yin, M.; Zhang, W.; Lou, L.; Xia, S. Visible Upconversion in Rare Earth Ion-Doped Gd₂O₃ Nanocrystals, *Journal of Physical Chemistry B* **2004**, 108, 19205. [[CrossRef](#)]