Efficient Multicolor Tunability of Ultrasmall Ternary doped LaF₃

Nanoparticles: Energy Conversion and Magnetic Behavior

Navadeep Shrivastava,^{a,b} L. U. Khan,^{*b,c} J. M. Vargas,^d Carlos Ospina,^c J. A. Q. Coaquira,^e Giorgio Zoppellaro,^f H. F. Brito,^b Yasir Javed,^g D. K. Shukla,^h M. C. F. C. Felinto,ⁱ and S. K. Sharma,^{**a}

^aDepartment of Physics, Federal University of Maranhão, Av. dos Portugueses, 1966 – Bacanga, São Luis - MA, 65080-805, Brazil.

^bDepartment of Fundamental Chemistry, Institute of Chemistry, University of Sao Paulo, Av. Prof. Lineu Prestes, 748, 05508-000, São Paulo-SP, Brazil

^cBrazilian Nanotechnology National Laboratory (LNNano-CNPEM), Rua Giuseppe MaximoScolfaro 10000, 13083-100, Campinas-SP, Brazil.

^dConsejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Centro Atómico Bariloche, Av. Bustillo 9500, 8400, San Carlos de Bariloche, Rio Negro, Argentina.

⁵Applied Physics Center, Institute of Physics, University of Brasilia, DF, 70910-900, Brazil.

^fRegional Centre for Advanced Technologies and Materials, Palacky University Šlechtitelů 27, 78371, Olomouc, Czech Republic.

^gDepartment of Physics, University of Agriculture, Faisalabad, Pakistan.

^hUGC-DAE Consortium for Scientific Research, Indore Centre, University Campus, Khandwa Road, Indore 452017, India.

ⁱNuclear and Energy Research Institute - IPEN, University of Sao Paulo, Av. Prof. Lineu Prestes, 2242 - SP, 05508-000, São Paulo-SP, Brazil.

Corresponding Email: **<u>surender76@gmail.com</u> * latifmwt@hotmail.com S1: Powder X-Ray Diffraction and Analysis of Rietveld refinement of Samples

Samples	Lattice Par	rameters (Å)	Volume	R _{wp}	χ^2
LaF ₃ :xCe ³⁺ ,xGd ³⁺ ,yEu ³⁺	$\mathbf{a} = \mathbf{b}$	c	V (ų)	(%)	
(x = 5, y = 1 mol-%)	4.133 (3)	7.323 (6)	108.3 (2)	8.45	1.56
(x = 5, y = 5 mol-%)	4.135 (3)	7.332 (5)	108.6 (2)	9.12	1.22
(x = 5, y = 10 mol-%)	4.126 (3)	7.313 (5)	107.8 (2)	10.01	1.14
(x = 5, y = 1 mol-%)	4.122 (3)	7.304 (5)	107.5 (2)	10.33	1.28

Table T1- Lattice parameters (a, c), volume (V), goodness of fitting (R_{wp}), and chi-square (χ^2)

Table T2- Anisotropic crystalite size analysis and microstrain

Samples	Crystallit	Strain	
LaF ₃ :xCe ³⁺ ,xGd ³⁺ ,yEu ³⁺	Parallel to [110]	(%)	
	Perpendicular t		
(x = 5, y = 1 mol-%)	8.22	3.43	0.94
(x = 5, y = 5 mol-%)	12.1	5.36	0.80
(x = 5, y = 10 mol-%)	8.96	8.77	0.57
(x = 5, y = 15 mol-%)	13.3	6.78	0,65

S2:Transmission Electron Microscopy (TEM) and Electron Dispersive Spectroscopy (EDS) There were acquired several spectra and elemental maps distribution for the for $LaF_3:xCe^{3+},xGd^{3+},yEu^{3+}$ (x = y = 5 and 15 mol-%) samples. The top of the Fig. S1(i) shows the EDS layered images of both samples, and the bottom, its respective SAED patterns, highlighting three major crystallographic planes.



Fig. S2(i). Chemical maps distribution and Selected Area Electron Diffraction patterns of for $LaF_3:xCe^{3+},xGd^{3+},yEu^{3+}$ (x = y = 5 mol-%)(a-top / a-bottom) and(x = 5; y = 15 mol-%) (b-top / b-bottom) samples.



Figure S2-(ii). EDS spectrum for $LaF_3:xCe^{3+},xGd^{3+},yEu^{3+}$ (x = y = 5 mol-%) sample for spot/Frame 5.



Figure S2-(iii).High-Angle Annular Dark-Field (HAADF) image and EDS elemental mappings, acquired in the JEM-2100F microscope, showing the homogeneous and uniform distribution La, F, Ce, Gd and Eu elements in sample of $LaF_3:xCe^{3+},xGd^{3+},yEu^{3+}$ (x = y = 5 mol-%) nanocomposite.



Figure S2-(iv). EDS map sum spectrum for $LaF_3:xCe^{3+},xGd^{3+},yEu^{3+}$ (x = 5; y = 15 mol.%) sample for all four spectrum.



Figure S2-(v). High-Angle Annular Dark-Field (HAADF) image and EDS elemental mappings, acquired in the JEM-2100F microscope, showing the homogeneous and uniform distribution La, F, Ce, Gd and Eu elements in sample of LaF₃: xCe^{3+} , xGd^{3+} , yEu^{3+} (x = 5; y = 15 mol-%) nanocomposite.

EDS spectra for LaF₃:xCe³⁺,xGd³⁺,yEu³⁺ (x = 5; y = 5 and 15 mol-%) samples have been acquired in the JEM-2100F microscope for different spots/frames. The electron beam was focused on agglomerated particles. The observed peaks confirm the existence of La, F, Ce, Gd and Eu elements. The Cu and C peaks may be due to copper grids of ultrathin Carbon film with Lacey Carbon. Since EDS analysis is a local measurement of small number of particles seen in the image, hence it may represent a difference in stoichiometry information. The following tables 1 and 2 show the average % elemental composition measured at different spots of the samples LaF₃:xCe³⁺,xGd³⁺,yEu³⁺ (x = 5; y = 5 and 15 mol%).

Table T3. Chemical distribution of LaF_3 :xCe³⁺,xGd³⁺,yEu³⁺ (x = 5; y = 5 mol-%)samples.

	Spectrum 1		Spectrum 2		Spectrum 3		Map 1		Map 2	
		Wt%		Wt%		Wt%		Wt%		Wt%
Element	Wt%	Sigma	Wt%	Sigma	Wt%	Sigma	Wt%	Sigma	Wt%	Sigma
F	31.62	0.33	30.45	0.31	32.43	0.33	30.92	0.35	31.55	0.32
La	58.5	0.42	59.15	0.41	57.55	0.42	58.93	0.46	57.92	0.42
Ce	3.52	0.35	3.12	0.35	3.36	0.35	3.37	0.37	3.5	0.33
Eu	3.48	0.25	3.83	0.24	3.96	0.27	3.37	0.28	4.32	0.27
Gd	2.88	0.24	3.45	0.23	2.71	0.25	3.41	0.27	2.71	0.26

Table T4. Chemical distribution of LaF_3 :xCe³⁺,xGd³⁺,yEu³⁺ (x = 5; y = 15 mol-%)samples

	Spe	ctrum 1	Spe	ctrum 2	Spe	ctrum 3	Spe	ctrum 4	N	Map 1		Map 2	
		Wt%		Wt%		Wt%		Wt%		Wt%		Wt%	
Element	Wt%	Sigma	Wt%	Sigma	Wt%	Sigma	Wt%	Sigma	Wt%	Sigma	Wt%	Sigma	
F	32.27	0.33	9.18	0.19	1.62	0.12	15.36	0.28	31.09	0.58	33.12	0.39	
La	51.58	0.41	62.12	0.49	62.07	0.6	60.87	0.55	51.76	0.72	50.54	0.48	
Ce	2.89	0.34	3.92	0.38	3.44	0.47	3.6	0.44	3.42	0.59	3.46	0.39	
Eu	10.16	0.28	18.17	0.37	23.15	0.48	15.19	0.4	10.42	0.52	9.96	0.34	
Gd	3.11	0.25	6.62	0.33	9.72	0.44	4.99	0.36	3.3	0.48	2.92	0.31	

S3: Photoluminescence (PL) measurement-



Following figure explains the emission/excitation spectrum of $LaF_3:xCe^{3+},xGd^{3+}$ (x = 5 mol%).

Figure S3. Excitation and emission of $LaF_3:xCe^{3+}.xGd^{3+}$ (x = 5; mol%) nanoluminescent material.

S4: Lifetime versus concentration



Figure S4. Lifetime of ${}^{5}D_{0}$ level of Eu^{3+} ion in a triply doped $LaF_{3}:xCe^{3+}.xGd^{3+}.yEu^{3+}$ (x = 5; y = 1. 5. 10 and 15 mol-%) nanoluminescent material.

S5: X-ray Absorption Spectroscopy

The X-ray absorption spectra (XAS) across Eu M-edges were collected for all samples along with reference compound Eu_2O_3 . These XAS measurements were performed at soft X-ray absorption spectroscopy (SXAS) beam line BL-01(operating range 100-1200 eV), at Indus-2, RRCAT, Indore, in total electron yield (TEY) mode.

This technique has been employed to determine more thoroughly the valence state of Eu cations as well as to study the local geometrical structure. **Figure S5** shows the Eu $M_{5,4}$ edge XAS of all doped samples, along with the reference compound, Eu₂O₃. These spectra show two clear features marked in **Figure S5** as M_5 and M_4 , signatures that arise to spin-orbit splitting. For a symmetrical molecule, XAS is dominated by dipolar transitions. The M_5 fingerprint is associated to transitions from $3d^{5/2}$ to 4f states, while M_4 arises from $3d^{3/2}$ to 4f states. The dotted line in **Figure S5** shows the expected $3d^{5/2}$ to 4f transition peak position for Eu^{2+} cation, which falls around 2 eV. These results indicate that all the investigated samples certainly possess Eu in (3+) valence state, but remains unclear the presence of Eu^{2+} , because only shoulders around 1128 eV were detected. Stronger evidences of the presence of Eu^{2+} cations in the samples emerged indeed from analysis of the photoluminescence spectra.



Figure S5. The Eu-M_{5,4} X-ray absorption spectra of all the samples LaF₃:xCe³⁺,xGd³⁺,yEu³⁺ (x = 5; y = 1, 5, 10 and 15 mol-%) along with reference Eu₂O₃ spectrum (Eu³⁺). The spectra were divided by their respective maxima and vertically shifted to enhance direct comparison.

S6: Magnetic Measurement



Figure S6. Magnetization as a function of magnetic field for $LaF_3:xCe^{3+},xGd^{3+},yEu^{3+}(x = 5; y = 1, 5, 10 \text{ and } 15 \text{ mol-}\%)$ samples at 300 and 2 K.