Institute of Technical Sciences Serbian Academy of Sciences and Arts

Photoluminescent Properties of Nanostructured $Y_2O_3:Eu^{3+}$ and $(Y_{1-x}Gd_x)_2O_3:Eu^{3+}$ Powders Obtained by Aerosol Synthesis

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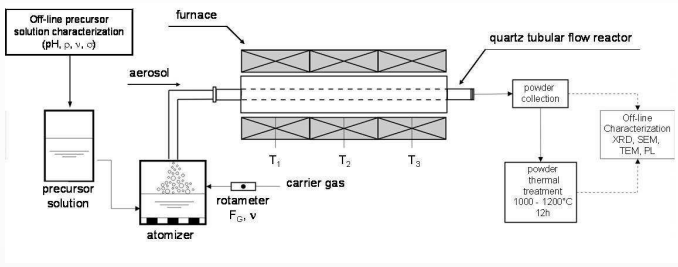
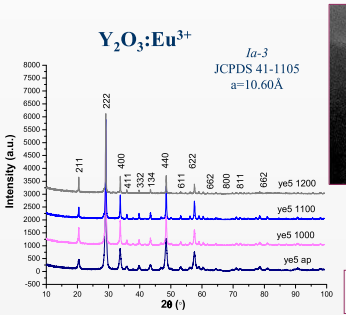
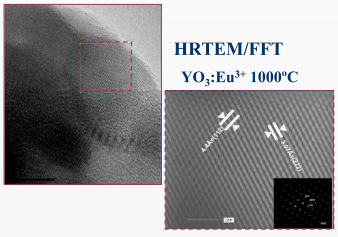
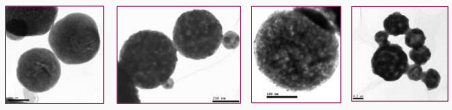
The nanostructured phosphor particles of $Y_2O_3:Eu^{3+}$ and $(Y_{1-x}Gd_x)_2O_3:Eu^{3+}$ (x=0.25, 0.50, 0.75) systems were synthesized through aerosol method. The corresponding nitrate solutions were ultrasonically atomized (1.3MHz) and the obtained aerosol was decomposed at 900°C. The as-prepared powders were thermally treated at 1000-1200°C/12h. The employed synthesis method assured formation of spherical, full, non-agglomerated and polycrystalline particles with crystallite size around 20nm. Powders structural and morphological features were investigated by means of XRD, SEM, TEM/SAED and HRTEM/FFT methods. Functional properties were examined through photoluminescent analysis. A detail study of the emission spectra after excitation with 393nm wavelength and of the decay lifetimes for Eu^{3+} ion $^5D_0$ and $^5D_1$ levels gave an insight into improved luminescent properties of the obtained powders. The emission spectra showed typical Eu^{3+} $^5D_0 \rightarrow {}^7F_i$ (i=0, 1, 2, 3, 4) transitions with dominant red emission at 611nm, while the lifetime measurements gave an insight into the effect of dopant concentration (5 and 10 at%) and its distribution into host lattice according to the applied thermal treatment. Additionally, luminescent properties were correlated with the obtained structural and morphological features of the synthesized powders.



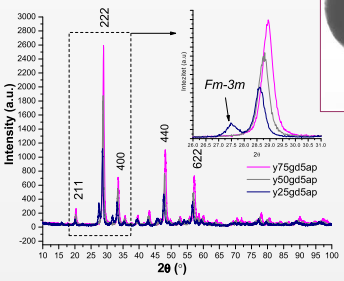


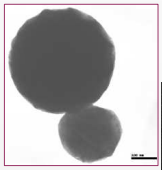


Domains of ordered crystal lattice, planes and FFT of *Ia-3* phase



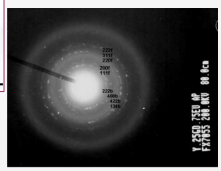
- full, spherical and non-agglomerated polycrystalline particles
- increase in temperature of thermal treatment led to higher particle roughness due higher crystallinity
- thermal treatment at 1200°C led to particle sintering





SAED

$(Y_{0.25}Gd_{0.75})_2O_3:Eu^{3+}$ as-prepared



D_{hkl}	hkl *bcc Ia-3*	hkl *fcc Fm-3m*
3,184	222	
3,289		111
2,795		200
2,716	400	
2,034		220
2,198	422	
2,052	134	
1,723		311
1,598		222

The presence of *Fm-3m* phase in as-prepared sample with highest Gd content was additionally confirmed by SAED analysis (correspond to $Gd_2Te_6O_{15}$ - JCPDS 37-1400, a=5.61Å)

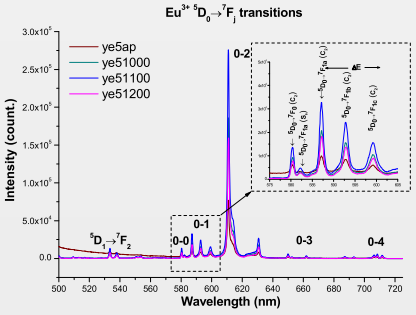
The increase in gadolinium content leads to the increase of lattice parameters and consequent pick shift towards lower 2θ angles.

Thermal treatment at 1100ºC/12h led to the presence of solely bcc *Ia-3* phase

The summarized microstractural data and characteristics of emission spectra for $Y_2O_3:Eu^{3+}$ system

	ye5	ye5 1000	ye51100	ye5 1200	ye10	ye10 1000	ye10 1100	ye10 1200
cs (nm)	19.14	40.55	60.06	129.53	20.11	40.94	66.99	132.89
a (Å)	10.620	10.616	10.616	10.616	10.632	10.628	10.623	10.628
ms(%)	0.432	0.189	0.0607	0.0963	0.529	0.197	0.0794	0.0402
$^5D_0 \rightarrow {}^7F_0$ (C_2) (nm)	580.3	580.4	580.4	580.4	580.4	580.4	580.4	580.4
$^5D_0 \rightarrow {}^7F_{1a}$ (S_6) (nm)	582.1	582.3	582.2	582.2	582.2	582.0	582.1	582.1
$^5D_0 \rightarrow {}^7F_{1a}$ (C_2) nm)	587.1	587.2	587.1	587.2	587.1	587.2	587.2	587.2
$^5D_0 \rightarrow {}^7F_{1b}$ (C_2) nm	592.9	592.8	592.8	592.9	592.8	592.8	592.8	592.8
$^5D_0 \rightarrow {}^7F_{1c}$ (C_2) nm	599.2	599.1	599.2	599.4	599.2	599.2	599.2	599.2
ΔE (cm^{-1})	344.0	338.2	344.0	346.5	344	341	341	341
$\tau(^5D_0 \rightarrow {}^7F_2)$ (ms)	1.47	1.46	1.40	1.42	1.24	1.21	1.14	1.14
$\tau_{avr}(^5D_0 \rightarrow {}^7F_2)$ (μs)	11.33	18.97	19.74	19.78	/	/	/	/

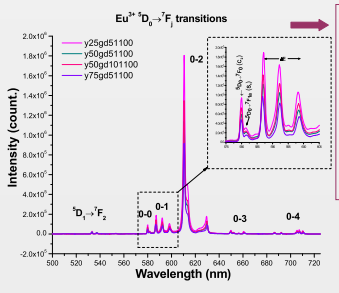
Concentration quenching for 10 at% of Eu^{3+}



λ_{ex}=393 nm

λ_{em}=611 nm

typical emission spectra of Eu^{3+} $^5D_0 \rightarrow {}^7F_i$ (i=0,1,2,3,4) transitions

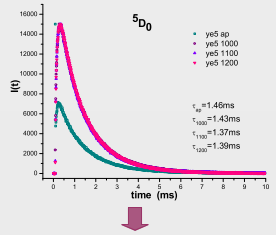


The increase of ΔE value with the increase of Gd content could be treated as a clear indication of almost perfect mixing in solid solutions of $(Y,Gd)_2O_3:Eu^{3+}$ system

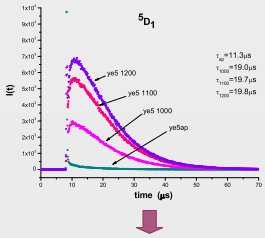
The summarized microstractural data and characteristics of emission spectra for $(Y_{1-x}Gd_x)_2O_3:Eu^{3+}$ system at 1100ºC

	y75 gd5	y50gd5	y25 gd5	y50 gd10
cs (nm)	155.94	202.63	55.25	191.36
a (Å)	10.667	10.724	10.771	10.730
ms(%)	0.0329	0.0563	0.0333	0.0195
$^5D_0 \rightarrow {}^7F_0$ (C_2) (nm)	579.9	580.0	580.0	579.9
$^5D_0 \rightarrow {}^7F_{1a}$ (S_6) (nm)	581.6	581.6	581.4	581.4
$^5D_0 \rightarrow {}^7F_{1a}$ (C_2) nm)	586.8	586.9	587.1	586.9
$^5D_0 \rightarrow {}^7F_{1b}$ (C_2) nm	592.3	592.3	592.2	592.2
$^5D_0 \rightarrow {}^7F_{1c}$ (C_2) nm	598.5	598.3	598.2	598.4
ΔE (cm^{-1})	333.2	324.7	316.1	327.5
$\tau(^5D_0 \rightarrow {}^7F_2)$ (ms)	1.36	1.25	1.32	0.86
$\tau_{avr}(^5D_0 \rightarrow {}^7F_2)$ (μs)	14.3	13.9	13.6	/

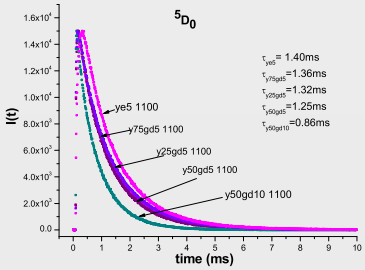
ΔE (Y_2O_3) = 355cm^{-1}, ΔE (Gd_2O_3) = 318cm^{-1}, $\tau(Gd_2O_3)_{bulk}$=1.1ms



Applied synthesis method (spray pyrolysis) led to the formation of nanostructured powders having longer lifetimes in comparison to $Y_2O_3:Eu^{3+}$ in its bulk form ($\tau(^5D_0 \rightarrow {}^7F_2)_{theor}$=1.0 ms).



Cross-relaxation effect is stronger in the case of as-prepared samples, indirectly depicting more homogeneous distribution of Eu^{3+} ions in the case of the annealed samples



$$I(t) = I(o)e^{-\frac{t}{\tau}}$$

$$\tau_{avr} = \frac{\int tI(t)dt}{\int I(t)dt}$$

Mixed oxides obtained through spray pyrolysis method have higher lifetimes in comparison to bulk form of pure $Y_2O_3:Eu^{3+}$ and $Gd_2O_3:Eu^{3+}$ oxides. For the case of $(Y_{0.50}Gd_{0.50})_2O_3$ with 10 at% of Eu^{3+} quit strong luminescence quenching is observed resulting in poorer properties even compared to bulk.

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