Institute of Technical Sciences Serbian Academy of Sciences and Arts

RARE-EARTH-BASED PHOSPHOR PARTICLES SYNTHESIS THROUGH HYDOTHERMAL AND SPRAY PYROLYSED ROUTES

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The synthesis of nanomaterials with controlled morphology is a subject of special interest in current trend of miniaturisation. It is already shown that "soft solution chemical processing" is superior to other synthesis techniques for the preparation of such materials. When one-dimensional nanomaterials are considered, the hydrothermal method is shown to be one of the simplest techniques for their obtaining. On the other side, processing of highly spherical three-dimensional nanostructured particles is feature of the powders obtained via spray pyrolysis process. Currently there is a great interest in synthesis of nano-phosphors, mainly due to a number of potential advantages which they posses over traditional luminescent materials. Here, we present the results related to the $(Y_{0.75}Gd_{0.25})_2O_3:Eu^{3+}$ (5at%) system synthesized by both hydrothermal and spray pyrolysis processes. Conversion of the starting nitrates mixture into desired oxide composition is performed with a help of ammonium hydrogen carbonate solution during hydrothermal treatment of precipitated mixture at 200°C/3h, while pure nitrate precursors in dispersed phase (aerosol) are thermally decomposed at 900°C within a tubular flow reactor in a spray pyrolysis process. The obtained powders are additionally thermally treated either at 600/1000°C - 3h (for those hydrothermally processed) or 1100°C – 12h (for the spray pyrolyzed ones). Comparison of the morphological, structural and functional characteristics of the powders is done based on the results of X-ray powder diffractometry, laser particle size analysis, X-ray energy dispersive spectroscopy, transmission electron microscopy and photoluminescence measurements.

HYDOTHERMAL ROUTE (HT)

Reverse precipitation with 4M NH_3HCO_3
HT treatment at 200°C, time 3h, 400rpm, p=20 bars
filtrated and washed up to pH~7, dried at 80°C, 1h
as-prepared

Thermal treatment:
600/1000°C – 3h

COMMON NITRATES SOLUTION

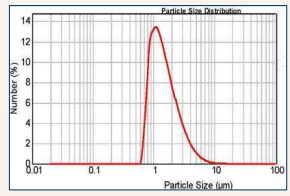
c=0.1 mol/dm³
$Y(NO_3)_3$ x $6H_2O$ $Gd(NO_3)_3$ x $6H_2O$
$Eu(NO_3)_3$ x $5H_2O$

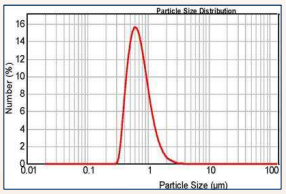
SPRAY PYROLYSIS ROUTE (SP)

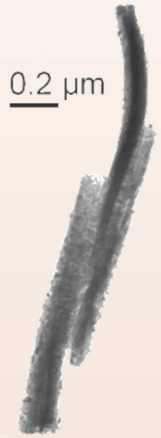
Ultrasonic atomization , 1,3MHz droplets generation
3.39 µm
time: 63s

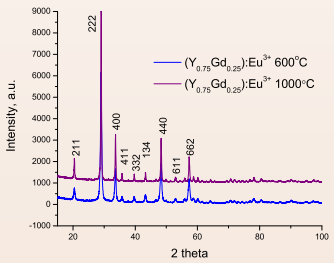
Decomposition up to 900°C particle generation
567 nm
as-prepared

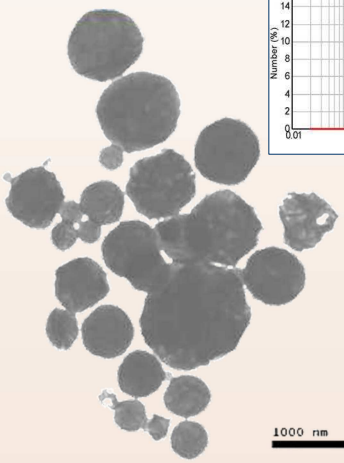
Thermal treatment:
1100°C – 12h

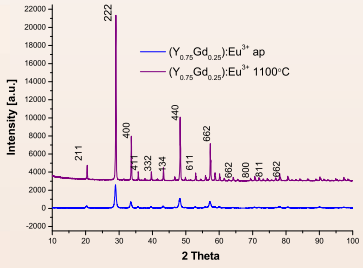












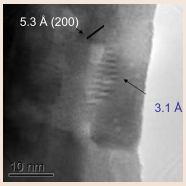
Microstructural characteristics of HT produced powders (Topas Academic)

	gof	r_{wpg}	a, Å	cs, nm	ms, %
$(Y_{0.75}Gd_{0.25})_2O_3$ 600	1.122	1.103	10.677(1)	19.6(3)	0.39(2)
$(Y_{0.75}Gd_{0.25})_2O_3$ 1000	1.251	1.852	10.669(1)	51(1)	0.20(1)

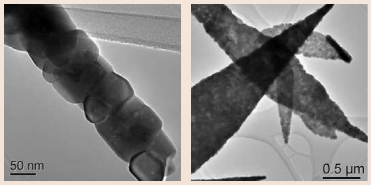
Microstructural characteristics of SP produced powders (Topas Academic)

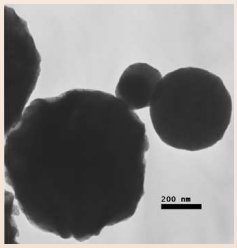
	gof	r_{wpg}	a, Å	cs, nm	ms, %
$(Y_{0.75}Gd_{0.25})_2O_3$ ap	1.059	1.042	10.672(5)	21.49(36)	0.479(2)
$(Y_{0.75}Gd_{0.25})_2O_3$ 1100	1.354	3.365	10.667(1)	156(6)	0.032(2)

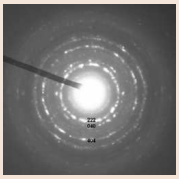
TEM $(Y_{0.75}Gd_{0.25})_2O_3$ 600 polycrystalline rods



TEM $(Y_{0.75}Gd_{0.25})_2O_3$ 1000 - polycrystalline fibrous & leaf-like particles





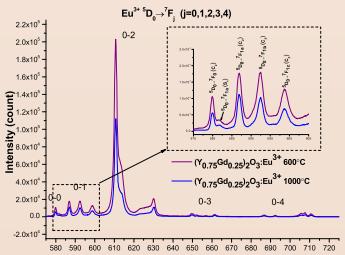


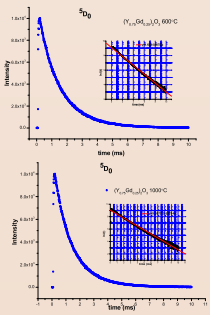
D_{HKL}	hkl
3,078	222
2,716	400
2,320	420
2,137	422
1,931	440
1,592	622
1,539	444

TEM $(Y_{0.75}Gd_{0.25})_2O_3$ 1100

-spherical
-unagglomerated
-dense &
-polycrystalline particles.

λ_{ex}=466nm $^7F_0 \rightarrow {}^5D_2$



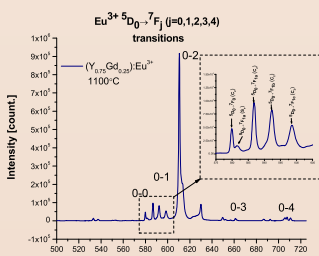


τ_{600} = 1.65 ms

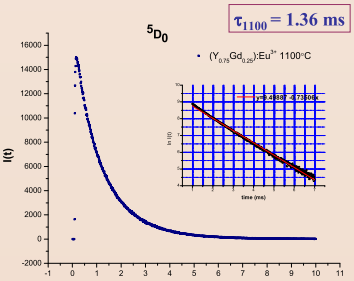
$I(t) = I(0)e^{-\frac{t}{\tau}}$

τ_{1000} = 1.57 ms

λ_{ex}=393nm $^7F_0 \rightarrow {}^5L_6$



τ_{1100} = 1.36 ms



The $(Y_{0.75}Gd_{0.25})_2O_3$:Eu (5at%) phosphors with the different particle morphologies were succesfully synthesized through HT and SP methods. Submicronic sized particles exhibit well-defined polycrystalline nature. HT – derived particles posses exclusively one-dimensional morphology (rods) up to the temperatures of 600°C, whilist leaf-like particles starts to grow afterwards. SP – derived particles keep their higly spherical shape up to the temperatures of 1100°C. All produced powders have improved optical characteristics in comparison to the bulk due to their nanocrystalline nature, while the HT-$(Y_{0.75}Gd_{0.25})_2O_3$ 600 sample shown the longest lifetime among them.

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