



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

L. Mancic¹, K. Marinkovic¹, B. Marinkovic², M. Dramicanin³, O. Milosevic¹

¹Institute of Technical Sciences of the Serbian Academy of Sciences and Arts, Belgrade, Serbia,

²Departamento de Ciência dos Materiais e Metalurgia, Pontifícia Universidade Católica do Rio de Janeiro, Rio de Janeiro, Brazil

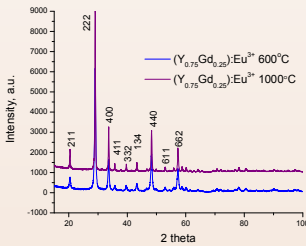
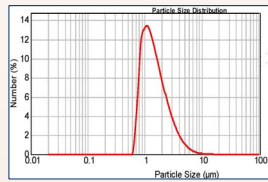
³Institute Vinca, Belgrade, Serbia

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 possess 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.

HYDROTHERMAL ROUTE (HT)

Reverse precipitation with 4M NH_4HCO_3
HT treatment at 200°C, time 3h, 400rpm, p=20 bars
filtered and washed up to pH=7, dried at 80°C, 1h
as-prepared

Thermal treatment:
600/1000°C - 3h



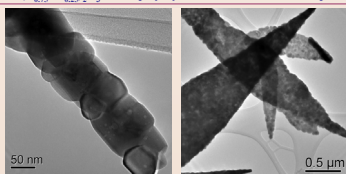
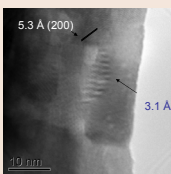
Microstructural characteristics of HT produced powders (Topas Academic)

| | gof | r_{int} | 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) |

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



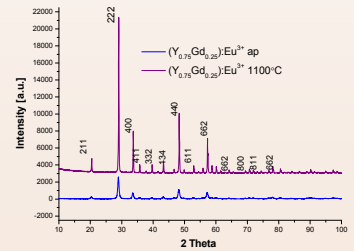
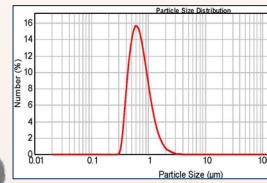
TEM $(Y_{0.75}Gd_{0.25})_2O_3$ 600 polycrystalline rods



SPRAY PYROLYSIS ROUTE (SP)

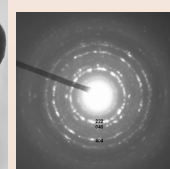
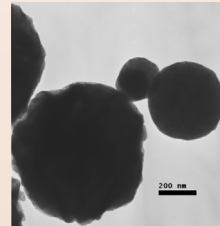
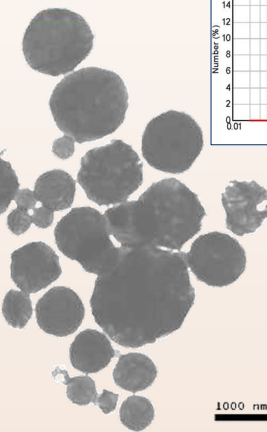
Ultrasonic atomization, 1.3MHz
droplets generation 3.39 µm
Decomposition up to 900°C
particle generation 567 nm
time: 63s
as-prepared

Thermal treatment:
1100°C - 12h



Microstructural characteristics of SP produced powders (Topas Academic)

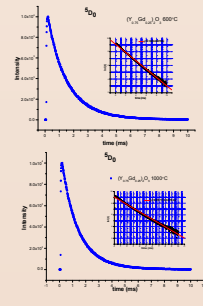
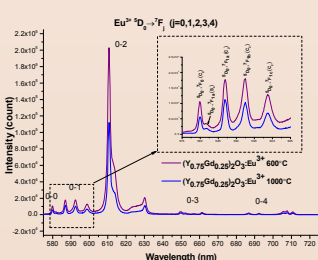
| | gof | r_{int} | a, Å | cs, nm | ms, % |
|---------------------------------|-------|-----------|-----------|-----------|----------|
| $(Y_{0.75}Gd_{0.25})_2O_3$ ap | 1.059 | 1.042 | 10.672(5) | 21.49(36) | 0.479(2) |
| $(Y_{0.75}Gd_{0.25})_2O_3$ 1100 | 1.354 | 3.365 | 10.667(1) | 156(6) | 0.032(2)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



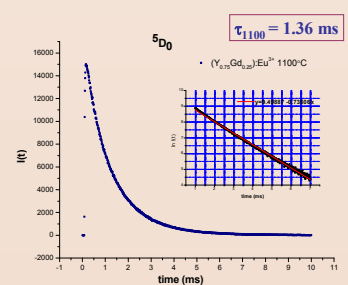
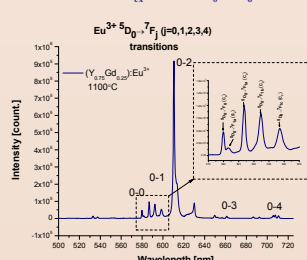
| D_{hkl} | hkl |
|-----------|-------|
| 3.078 | 222 |
| 2.716 | 400 |
| 2.320 | 420 |
| 2.137 | 422 |
| 1.931 | 440 |
| 1.592 | 622 |
| 1.539 | 444 |

TEM $(Y_{0.75}Gd_{0.25})_2O_3$ 1100
-spherical
-agglomerated
-dense &
-polycrystalline particles.

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



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



The $(Y_{0.75}Gd_{0.25})_2O_3:Eu$ (5at%) phosphors with the different particle morphologies were successfully synthesized through HT and SP methods. Submicronic sized particles exhibit well-defined polycrystalline nature. HT - derived particles possess exclusively one-dimensional morphology (rods) up to the temperatures of 600°C, whilst leaf-like particles start to grow afterwards. SP - derived particles keep their highly spherical shape up to the temperatures of 1100°C. All produced powders had 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.

Acknowledgement: This research is supported by the Ministry of Science, Republic of Serbia (Project No. 142010) & COST 539 Action.