

Features of the Phase Composition and Structure of Eu Doped Y_2O_3 Submicrospheres

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Polycrystalline, non-agglomerated nanopowders based on monosized $(Y_{1-x}Eu_x)_2O_3$ submicrospheres were prepared. It was shown that the annealing temperature strongly influences on the structure, morphology and composition of the spherical $(Y_{1-x}Eu_x)_2O_3$ phosphors obtained. It was found that the concentration quenching effects of Eu^{3+} luminescence in the $(Y_{1-x}Eu_x)_2O_3$ spheres with 70-280 nm diameter is shifted to lower Eu^{3+} concentrations ($x = 0,02; 0,05$ for 70 and 280 nm spheres respectively) compared with the microcrystalline powders with similar composition ($x = 0,09$). The reason of this phenomenon probably is formation of inhomogeneous phase of $(Y_{1-x}Eu_x)_2O_3$ solid solution in the nanopowders with the primary location of bigger Eu^{3+} ions in the surface area due to active diffusion processes.

Keywords: Solid Solution, Structure, Yttrium Oxide, Sphere, Luminescence, Segregation.

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1. INTRODUCTION

Within last several years, researchers have shifted the focus of their investigations toward the nanotechnology of new nano-objects based on rare-earth oxides $(R_{1-x}R_2)_2O_3$, $R_1 = Y, Gd, Lu$, $R_2 = Eu, Yb, Nd$ from individual nanoparticles to bulk materials with ordered nanostructure [1-5]. This new interest has emerged due to the prospective applications in photonics, lasers, energy and environmental technologies. To extend phosphor nanopowders to high resolution applications fine individual particles with ideal spherical morphology, controllable diameters, narrow size distribution as well as perfect crystalline structure and homogeneous composition can be highly desirable. Among the lot of methods of spherical particles formation, low cost soft chemistry co-precipitation route from water solutions attract much attention due to its simplicity, ecological compatibility and possibility to control the shape and the sizes of particles at high level, and also providing narrow size distribution of the particles [6-9]. However, the principal drawback of the luminescent nano- and submicrospheres $(R_{1-x}R_2)_2O_3$ ($D=70-400$ nm) is lower luminescence efficiency comparatively with bulk materials due to the surface quenching processes through the decrease of the volume/surface ratio of the phosphor layer.

That is why, it is necessary to establishment of the thermolysis parameters and crystallization processes of the spheres to minimize the activator activity diffusion, as well as select the optimal activator concentration to eliminate the of luminescence quenching. It was demonstrated in the present study for the model crystalline spheres phosphor $(Y_{1-x}Eu_x)_2O_3$ ($^5D_0 \rightarrow ^7F_2$ transition).

2. EXPERIMENT

Crystalline $Y_2O_3:Eu^{3+}$ powders have been obtained by the soft chemistry co-precipitation method from the water solutions with subsequent annealing for powders

crystallization. Initially, high-purity yttrium oxide (Y_2O_3 , 99.99%) and europium oxide (Eu_2O_3 , 99.99%) powders were dissolved in nitric acid to form $Y(NO_3)_3$ and $Eu(NO_3)_3$ solutions. Urea $((NH_2)_2CO)$ have been used as a precipitant. Synthesis procedure was carried out in watersolution, which contains $Y(NO_3)_3$ (0.5 mol L^{-1}), $Eu(NO_3)_3$ and urea $((NH_2)_2CO)$. The mixture was heated at 90°C to decompose the urea and stirred during 2 h. Europium content was 0-15 at.% with respect to yttrium in all experiments. The resulting suspension aged during 24 h and then the amorphous precursor was separated by centrifugation or filtration, washed several times with deionized water and ethanol, and dried in air at 50°C. The powders obtained was crushed and annealed at 400-1000 °C in air for the crystallization. The morphology of the samples obtained were studied by means of transmission electron microscopy (TEM) using a EM-125 (Selmi, Ukraine). The X-ray luminescence spectra were obtained using SDL- 2 (LOMO, Russia) automated complex. Luminescence was excited by REIS-E X-ray source (Cu-anticathode, deceleration radiation with the energy $E = 30$ keV), operating at $U=30$ kV and $I = 50$ mA.

3. RESULT AND DISCUSSION

Polycrystalline, non-agglomerated nanopowders based on monosized $(Y_{1-x}Eu_x)_2O_3$ nano- and submicrospheres was prepared (see Fig. 1a). The selected area electron diffraction (SAED) pattern (Fig. 2) confirmed a polycrystalline nature of $(Y_{1-x}Eu_x)_2O_3$ spheres with cubic structures.

As well-known the effect of the phase-forming cations has great influence on the final diameter of the spheres. Size dependence of the spheres on the europium concentration were investigated. It was shown that doping by the Eu^{3+} activator ($x = 0-0,1$) at the stage of amorphous precursor preparing leads to reduction of the final spheres diameter (see Fig. 2) due to differences in the kinetics growth of the spheres in accordance with the known growth mechanisms. It may be

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due to increases of nucleation density as result of Eu addition caused to differential nucleation energy of $Y(OH)CO_3$ and $Eu(OH)CO_3$ during hydrocarbonate

formation. The decrease average size of the colloidal spheres take place as result of this phenomena [10, 11].

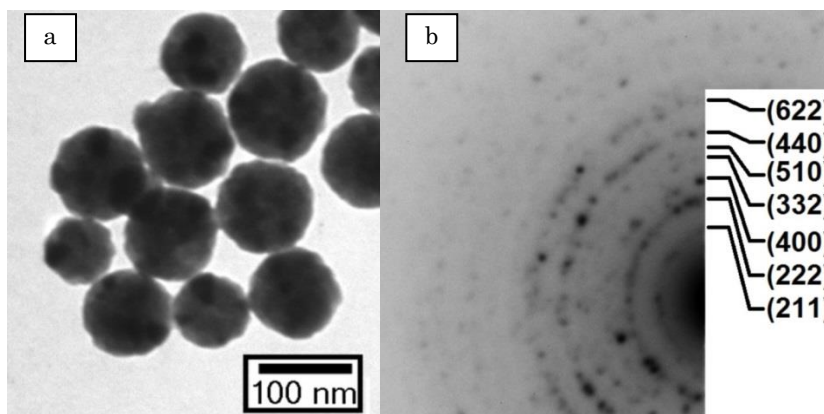


Fig. 1 – TEM image (a) and SAED (b) of the $(Y_{1-x}Eu_x)_2O_3$ spheres

The effects of the annealing conditions on the spheres diameter, their morphology and light yieldemission were studied in detail. The diameters of spheres depending on the annealing temperature are shown in Fig. 3a. Dependence of mean spheres diameter on the annealing temperature can be catted on three steps was found. Active reduction of the spheres diameter during thermolysis of the amorphous precursor corresponded with active weight loss processes. During crystallization step the spheres diameter changes slightly. It should be noted that the temperature threshold of morphological stability of spheres particles has been found. During the annealing at 1000°C and more, particles are begun to sintering (see Fig. 3a).

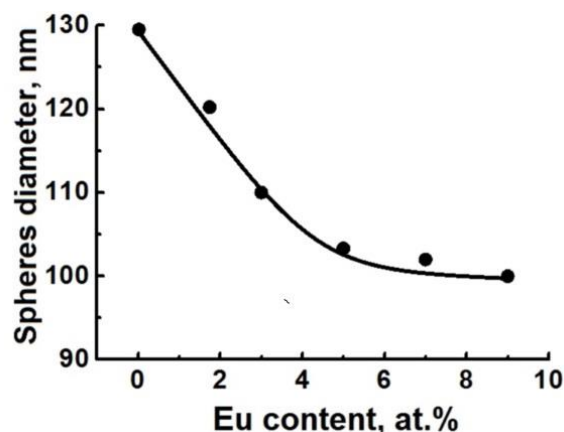


Fig. 2 –Diameter of the $(Y_{1-x}Eu_x)_2O_3$ spheres depending on the europium content.

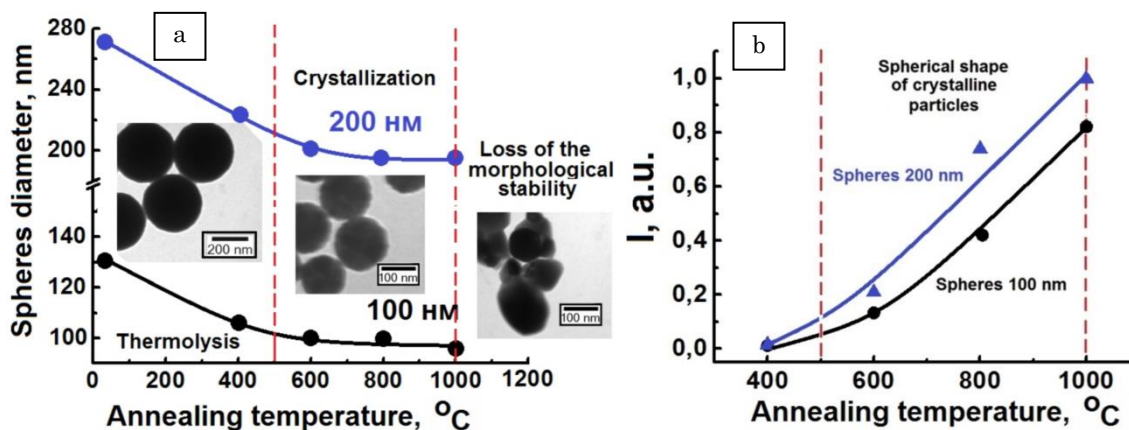


Fig. 3 –Diameter of the $(Y_{1-x}Eu_x)_2O_3$ ($x = 0.05$) spheres depending on the annealing temperature (a), and X-Ray luminescence Intensity of the $(Y_{1-x}Eu_x)_2O_3$ ($x = 0.05$) spheres depending on the annealing temperature (b). Annealing time - 2 hours.

Fig. 3b presents the dependence of luminescence intensity of $(Y_{1-x}Eu_x)_2O_3$ ($x=0,05$) spherical powders under X-ray excitation on the annealing temperature. The increasing of the luminescence intensity was observed with the increasing of the annealing temperature. Such

luminescence increase can be explained both by the elimination of the residualOHgroups in crystalline europium-doped yttrium oxide and improvement of the powders crystallinity with the rising of the annealing temperature [12-14].

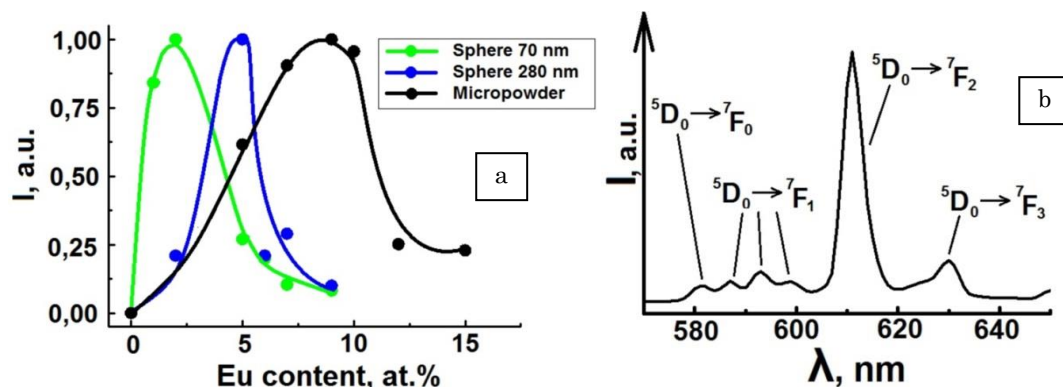


Fig. 4 – Relative intensity of the X-ray luminescence of the $(Y_{1-x}Eu_x)_2O_3$ spheres depending on the concentration of europium (a), the typical range of X-ray luminescence (b)

It was shown that the concentration quenching effects of Eu^{3+} luminescence in the $(Y_{1-x}Eu_x)_2O_3$ spheres with 70-280 nm diameter is shifted to lower Eu^{3+} concentrations ($x = 0,02; 0,05$ for 70 and 280 nm spheres respectively) compared with the microcrystalline powders with similar composition ($x = 0,09$). The reason of this phenomenon probably is formation of inhomogeneous phase of $(Y_{1-x}Eu_x)_2O_3$ solid solution in the nanolayers with the primary location of bigger Eu^{3+} ions in the surface area due to active diffusion processes [15].

4. CONCLUSIONS

Polycrystalline, non-agglomerated nanopowders based on monosized $(Y_{1-x}Eu_x)_2O_3$ nano- and submicrospheres was prepared by co-precipitation method. It was

shown that doping by the Eu^{3+} activator ($x = 0,01-0,10$) at the stage of amorphous precursor preparing leads to reduction of the final spheres diameter due to differences in the kinetics growth of the spheres in accordance with the known growth mechanisms. The optimum temperature-time conditions for preparing spheres with maximum light yield without loss of morphological stability of the spherical shape of the individual particles was discovered (800°C/2h). It was shown that the concentration quenching effects of Eu^{3+} luminescence in the $(Y_{1-x}Eu_x)_2O_3$ spheres with 70-280 nm diameter is shifted to lower Eu^{3+} concentrations ($x = 0,02; 0,05$ for 70 and 280 nm spheres respectively) compared with the microcrystalline powders with similar composition ($x = 0,09$).

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