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# Preparation and structural properties of $Lu_2O_3$:$Eu^{3+}$ submicrometer spherical phosphors

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ABSTRACT

Monodisperse non-agglomerated $Lu_2O_3$:$Eu^{3+}$ submicrometer spheres were obtained by the homogeneous precipitation technique with subsequent annealing for spheres crystallization. The morphological and structural parameters of the $Lu_2O_3$:$Eu^{3+}$ crystalline spheres prepared were investigated by the electron microscopy methods, thermal analysis (TG-DTA), X-ray diffractometry (XRD), X-ray photoelectron (XPS) and FT-IR spectroscopy. The influence of the annealing temperature on the morphology and sphericity was shown. $Eu^{3+}$-doped lutetium oxide spheres were characterized by effective luminescence under X-ray excitation in the $\lambda$ = 575–725 nm range corresponding to $^5D_0 \rightarrow {}^7F_J$ transitions ($J$ = 0–4) of $Eu^{3+}$ ions. It was shown that the X-ray luminescence efficiency of the $Lu_2O_3$:$Eu^{3+}$ spherical phosphors prepared strongly depend on annealing temperature and dopant concentration.



## 1. Introduction

Nowadays, monodisperse spherical particles of the varied compositions are widely studied due to the prospective application both in practical and fundamental aspects. Colloidal suspensions of the nano- and submicrospheres ($SiO_2$, $TiO_2$, polymer etc. [1–3]) are playing an increasingly important role as model systems to study a variety of phenomena in condensed matter physics in real space, such as nucleation, growth mechanisms and rheology aspects.

Moreover spherical particles show ability to self-organization in ordered photonic crystals (PhCs), a promising optical materials due to the possibility Bragg-reflect the light with the wavelength defined by the spheres diameter [4,5]. Highly efficient light-emitting materials for display technologies (cathode ray tubes, plasma display panels, and field emission displays) can be achieved by the placing of the luminescent component inside the PhC, it can be realized by using of the phosphor spheres as structural units for such photonic crystals preparing. Thus, its stimulate active progress in development and study of the inorganic luminescent spherical nano- and submicron particles of the mixed compositions (rare-earth doped $SiO_2$, $Y_2O_3$:$Eu^{3+}$, $(Y_{1-x}Gd_x)_2O_3$:$Eu^{3+}$, etc. [6–8]) or with core–shell structure [9,10].

To extend phosphors to high resolution applications, fine phosphor particles with ideal spherical morphology, controllable diameters, narrow size distribution and homogeneous composition as well as required surface properties for the self-assembling would be highly desirable. A variety of methods have been successfully applied to the preparation of the spherical phosphors, including sol–gel and hydrothermal technology, precipitation route, combustion and spray pyrolysis methods [8,11–15]. Among these methods, urea-based homogeneous precipitation (UBHP) technique is widely used for the synthesis of the inorganic particles with the highly controllable sizes and well-defined morphologies by taking advantages of the slow decomposition of urea at the temperatures above 80 °C. The in situ decomposition of urea releases of the precipitating ligands ($OH^-$ and $CO_3^{2-}$) slowly and homogeneously into the reaction system, avoiding localized distribution of the reactants and thus making it possible to exercise control over nucleation and growth. The UBHP technique was employed to precipitate amorphous colloidal spheres of the mixed Y/Gd, Y/Eu, Gd/Eu basic carbonates (precursor) with subsequent annealing for the polycrystalline rare-earth oxides resultant particles obtaining [7,12,14].

The luminescence parameters of the phosphor particles are strongly depend on its morphology, surface area, crystallite sizes, which is defined by the synthesis conditions, reagents concentration, etc. The morphology dependent luminescence properties of $Y_2O_3$:$Eu^{3+}$ phosphors prepared were analyzed earlier [8,16,17]. Thus, it was concluded that the spherical morphology is good for improving the emission intensity as well as that particles with

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a smaller surface area showed higher photoluminescence intensity. The luminescence intensities were also found to be strongly dependent on crystallites size for $Y_2O_3$:$Eu^{3+}$ and $Gd_2O_3$:$Eu^{3+}$ polycrystalline particles [8,18].

Lutetium oxide ($Lu_2O_3$) doped with trivalent europium ($Eu^{3+}$) ions is a structural analog of effective commercial $Y_2O_3$:$Eu^{3+}$ red phosphor, and belongs to cubic structure, space group Ia3. It is reported earlier that lutetium is more favorable cation than yttrium for lanthanide dopant emission [19]. Moreover, $Lu_2O_3$:$Eu^{3+}$ is one of the most perspective material for X-ray detection and imaging due to high effective atomic number $Z_{eff.} = 67$ and its extremely high density ($\rho = 9.4\ g/cm^3$) in comparison with $Y_2O_3$ ($\rho = 4{,}8\ g/cm^3$) and $Gd_2O_3$ ($\rho = 7{,}6\ g/cm^3$). $Lu_2O_3$:$Eu^{3+}$ was obtained and studied in different forms such as powders (including nanocrystalline), sol–gel films and transparent ceramics [20,21]. Preparation, morphology and structure features of the $Lu_2O_3$:$Eu^{3+}$ spherical particles has not been properly described yet [22]. $Lu_2O_3$:$Eu^{3+}$ in the form of the nanoshells on $SiO_2$ spheres was prepared by us earlier for the creation of the spherical and size controlled phosphors [9]. However, the principal drawback of the luminescent nanoshells 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, the bare $Lu_2O_3$:$Eu^{3+}$ spherical particles were chosen as investigation object in the present study.

In this work, we report a systematic experimental study regarding the preparing of the $Lu_2O_3$:$Eu^{3+}$ spheres by UBHP method and their characterization and also the influence of the annealing temperature on the structure and morphology of the $Lu_2O_3$:$Eu^{3+}$ phosphors.

## 2. Experimental

The $Lu_2O_3$:$Eu^{3+}$ spheres were obtained by the UBHP technique. Europium content was ranged from 1 to 10 at.% with respect to lutetium. Firstly, high-purity lutetium oxide ($Lu_2O_3$, 99.99%) and europium oxide ($Eu_2O_3$, 99.99%) powders were dissolved in nitric acid to form $Lu(NO_3)_3$ and $Eu(NO_3)_3$ solutions. Synthesis procedure was carried out in water solution of $Lu(NO_3)_3$ ($2 \times 10^{-3}$ mol/L), $Eu(NO_3)_3$ and urea ($(NH_2)_2CO$) as a precipitant. The molar ratio [$Lu^{3+}$]/[urea] was 0.002 for preparing the precursor particles with the diameter about 130 nm [22]. The reactive mixture was heated at $85 \pm 1$ °C to decompose the urea and stirred during 5 h. The resulting precursor was separated by centrifugation, washed several times with ethanol and water, and dried at 60–80 °C to prevent "soft" agglomerates formation [22]. Finally, the precursor obtained was exposed by heating in air in 500–1200 °C temperature range for 2 h to produce the final crystalline spherical particles.

The morphology of the samples obtained was studied by means of scanning electron microscopy (SEM) using a JSM-6390 LV (JEOL, Japan) and a transmission electron microscopy (TEM) using a EM-125 (Selmi, Ukraine). The X-ray diffraction (XRD) of the powder samples was examined on a DRON-3M diffractometer using $CoK_\alpha$ radiation ($\lambda = 1.79021$ Å). The average sizes of $Lu_2O_3$:$Eu^{3+}$ crystallites were found from the broadening of the [2 2 2], [4 0 0] and [4 4 0] diffraction lines of the X-ray patterns according to Scherrer's formula: $D = K\lambda/(\beta\cos\Theta)$, where $\lambda$ is the X-ray wavelength, $\beta$ is the full-width at the half-maximum of the diffraction line located at $\Theta$ angle. The thermal analysis (TG-DTA) was conducted using a MOM Q-1500 derivatograph in air within a temperature interval 20–1000 °C at heating rate of 10 °C/min. Fourier transform infrared spectroscopy (FT-IR) spectra of the samples were measured on a FT-IR spectrometer SPECTRUM ONE (Perkin-Elmer) with the KBr pellet technique. The surface composition of the particles prepared was studied with X-ray photoelectron spectroscopy (XPS) with a spectrometer XSAM-800 Kratos using $MgK_\alpha$ – radiation ($h\gamma = 1253.6$ eV). X-ray luminescence spectra of the samples were obtained using SDL-2 (LOMO, Russia) automated complex. X-ray luminescence was excited by REIS-E X-ray source (Cu-anticathode, deceleration radiation with the energy $E \sim 30$ keV), operating at $U = 30$ kV and $I = 50$ mkA.

## 3. Results and discussion

### 3.1. Crystallization, structure and temperature effects

The urea-precipitated and dried at 60 °C precursor spheres of the europium-doped lutetium basic carbonate ($Lu(OH)CO_3$:$Eu{\cdot}H_2O$) composition were amorphous to X-rays. Scanning electron microscopy (SEM) was used for the morphology analysis in a large scale of the freshly prepared spheres (Fig. 1a). It is clearly seen that $Lu(OH)CO_3$:$Eu{\cdot}H_2O$ particles have perfect spherical shape, uniform size distribution and keep they individuality without agglomeration. Energy dispersive X-ray spectrum of precursor particles includes the peaks attributed to Lu, O and C elements presence (Fig. 1b). Statistical analysis of the particles size distribution carried out using SEM data points to a narrow size distribution for the obtained samples (Fig. 1c).

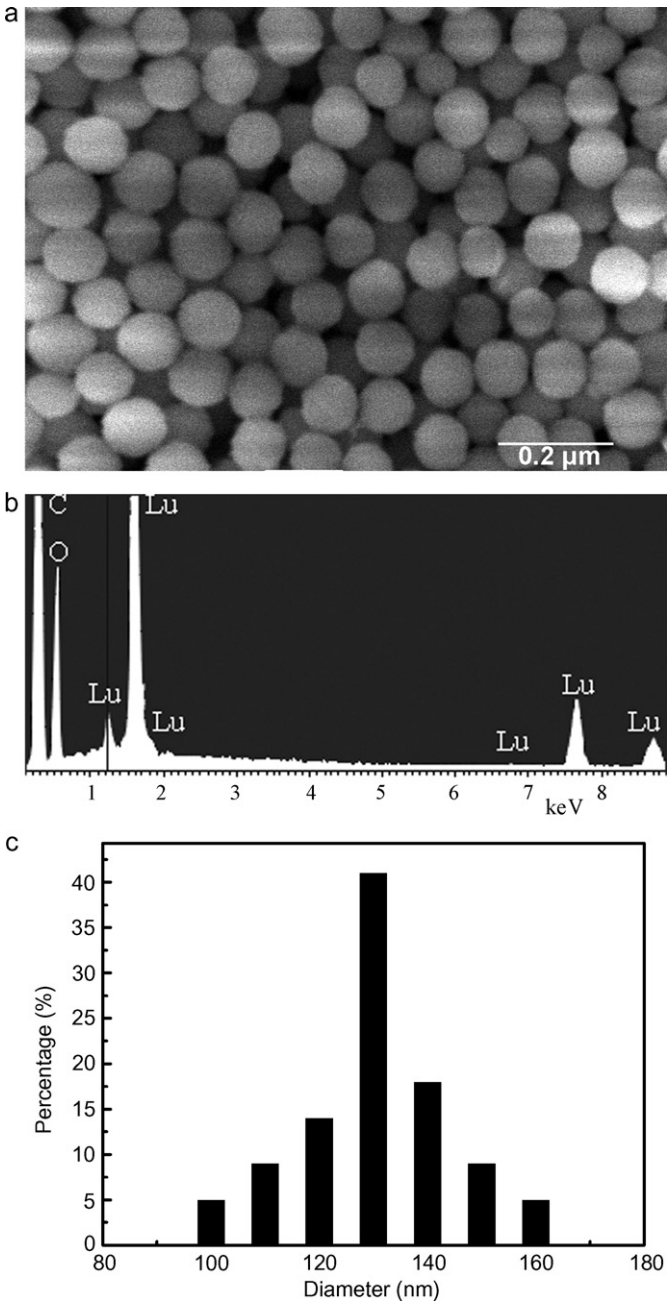


**Fig. 1.** SEM image (a), EDS analysis (b) and histogram for the size distribution (c) of the $Lu(OH)CO_3$:$Eu{\cdot}H_2O$ precursor particles.

The thermal analysis was used for the studying of the precursor particles decomposition and crystallization process. TG-DTA curves of the precursor powders dried at 60 °C are given in Fig. 2. DTA shows one endothermic peak at about 190 °C corresponds to release of hydration water, a shallow peak in the region of 320–530 °C, which is related with precursor decomposition and exothermic