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Synthesis and Study of Y_2O_3:Eu^{3+} Nanoparticles

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Abstract—The synthesis method of weakly agglomerated Y_2O_3 powders based on the decomposition of metal–polymer gel (Pechini method) has been developed. The physicochemical properties of powders synthesized by the standard Pechini method and a method using foaming components have been compared. The luminescence properties of Eu^{3+}-doped Y_2O_3 have also been studied.

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INTRODUCTION

Preparing ultramicroheterogeneous freely dispersed systems in which the particle size is 1–100 nm is extremely challenging. First of all, this is determined by the strongly developed surface of the dispersed substance. In an aggregatively unstable system, the spontaneous enlargement of particles occurs, which reduces the surface energy. The aggregation process takes place during both the synthesis and further storage and the use of the dispersed material [1].

The problem of the synthesis of individual nanosized particles is being solved when studying materials used in the area of medicine, drug therapy, mechanical and tool engineering, etc. For example, preparing colloidal solutions of particles that do not mutually interact is required for luminescence and magnetic labels. When producing optical ceramics, particular attention is paid to the challenge of the energy efficiency of compaction and the synthesis of dispersed raw material, which should consist of easily deformable agglomerates. Also, the properties of initial materials such as chemical and phase purity, particle size, particle size distribution, uniformity of particle shape, and absence of rigid agglomeration are critical factors [2].

The aim of this work is to develop the synthesis method for weakly agglomerated nanosized particles of europium-doped yttrium oxide and study their structural and luminescence properties.

SYNTHESIS METHODS AND STUDIES

Studying the process of synthesizing yttrium oxide via the Pechini method made it possible to modify the procedure to improve the properties of the powders being obtained, which are precursors for optic ceramics. In synthesis via the Pechini method, the product is obtained by the thermal treatment of the polymer gel, which is a structured colloidal system. Solid particles of the dispersed phase are interconnected, forming a flocculent spatial grid containing a liquid dispersed media in its cells. The contacts between the particles break down under thermal action and gel annealing. It is proposed to introduce a process of intense gas evolution preventing the agglomeration and caking of the particles, similarly to the principle of the method of self-propagating high-temperature synthesis (SHS), to this final stage. For this, it is necessary to introduce a foaming component that will further fill the structural grid of the gel into the system before the polymer is formed. When choosing such a component, it is necessary to meet the following requirements:

(1) The compound being introduced into the synthesis should not react with the main components of the system (in this case, with yttrium and europium oxides) or form substances reacting with them.

(2) The foaming component should not prevent the completion of the synthesis.

(3) Side substances should be easily removable from the product with a solvent that does not contaminate the product being obtained.

A mixture of aluminum nitrate and potassium chloride was chosen as the foaming component for the synthesis of Y_2O_3. Under the condition of the excess of citric acid in the solution, a reaction that provides the uniform foaming of the mass proceeds during the thermal treatment of the gel.

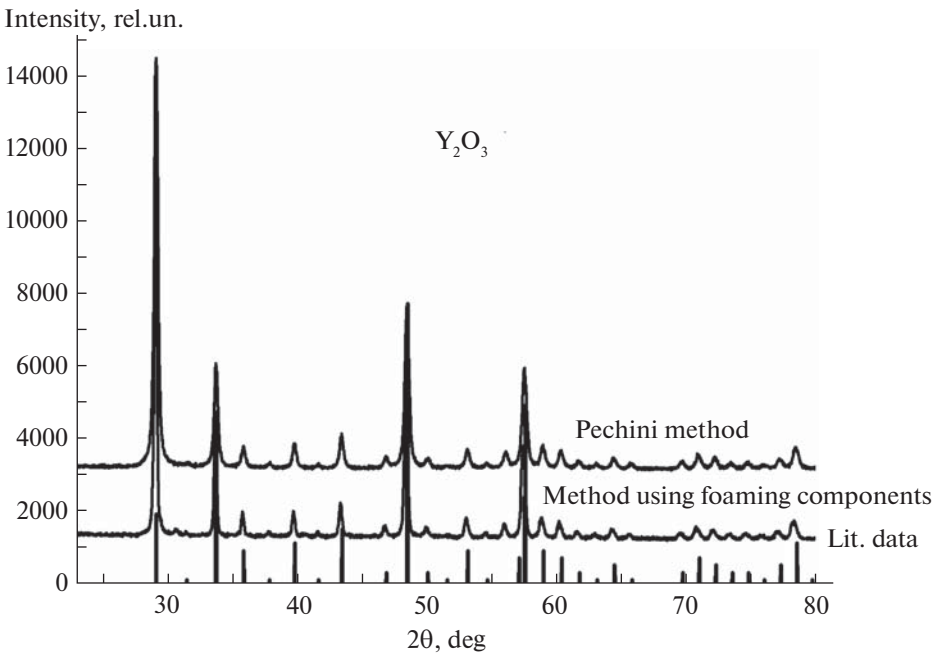

Fig. 1. Diffraction patterns of the samples of Y_2O_3 synthesized via the Pechini method and a method using foaming components under similar temperature and time modes (900°C, 2 h).

According to the data of thermodynamic calculation, potassium chloride reacts with citric acid under heating:

$$H_3C_6H_5O_7 + KCl \rightarrow KH_2C_6H_5O_7 + HCl\uparrow$$

During the subsequent annealing, the potassium citrate dehydrate burns in the oxygen atmosphere:

$$4KH_2C_6H_5O_7 + 7O_2 = 2K_2CO_3 + 14H_2O + 22CO\uparrow$$

(At $T > 150$°C)

Potassium carbonate reacts with aluminum oxide, forming an aluminate that is removed from the sample during rinsing with distilled water:

$$Al_2O_3 + K_2CO_3 = 2KAlO_2 + CO_2\uparrow \text{ (600°C)}$$

The gel was annealed at 1000°C for 2 h for all the obtained samples. During annealing, the nanoparticles of yttrium oxide turn out to be distributed in the medium of molten potassium chloride and solid potassium aluminate. After the synthesis, the potassium chloride and aluminate is completely removed from the sample by rinsing with distilled water.

Qualitative X-ray phase analysis was performed on D2 Phaser (Bruker) and Ultima IV (Rigaku) X-ray powder diffraction apparatuses (CuK_α radiation). The dispersity of the powder was determined via laser diffraction on a Mastersizer 3000 particle-size analyzer with a range from 0.01 to 3500 μm. The specific surface was measured on ASAP 2020MP equipment. The micrographs of the particles were preformed on a SUPRA 40VP WDS scanning electron microscope with a resolving power of 4 nm. The luminescence and luminescence excitation spectra were studied on a Fluorolog-3 spectrofluorometer. The kinetics of luminescence was studied on this same instrument, but a pulsed xenon lamp was used as the excitation source. All spectroscopic measurements were carried out at room temperature.

EXPERIMENTAL RESULTS AND DISCUSSION

X-ray phase analysis confirms the presence of yttrium oxide as a single crystalline phase in the samples (Fig. 1).

The mean sizes of the crystallites were calculated by the broadening of the diffraction lines using Bruker TOPAS 4.2 software. In the case of particles synthesized via the Pechini method, this value is 20 nm. In the case of the use of foaming components, the size of the crystallites reaches 50 nm.

The described modification of the Pechini method makes it possible to enhance the specific surface area up to 108 m^2/g (Fig. 2). Adsorption and desorption isotherms are shown in Fig. 2. The pore volume for the powders synthesized using foaming components is 0.37 cm^3/g. It follows from the data on the particle size distribution that the particles consist of agglomerates, which are easily broken into nanosized components after ultrasonic (US) treatment (Fig. 3).

According to the qualitative analysis of the micrographs (SEM), Y_2O_3 powder synthesized via the method using foaming components consists of weakly agglomerated particles with a size of ≈100 nm (Fig. 4).

There are 32 yttrium ions in the elementary cell of cubic Y_2O_3, which can be replaced by other rare earth

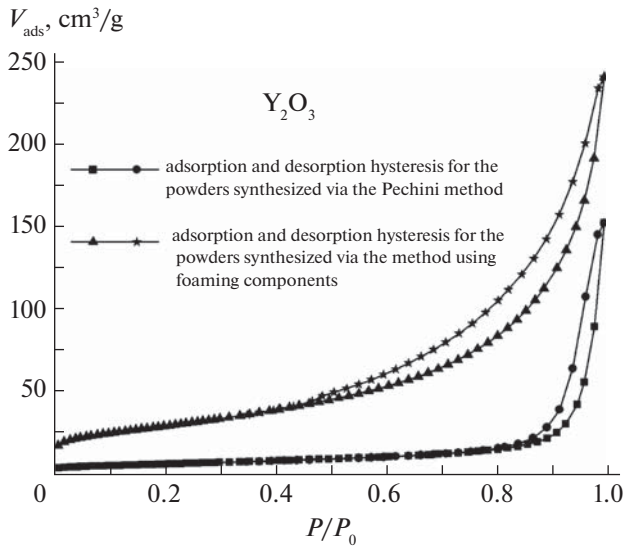

Fig. 2. Adsorption and desorption isotherms for the powders synthesized via the standard Pechini method and a method using foaming components.

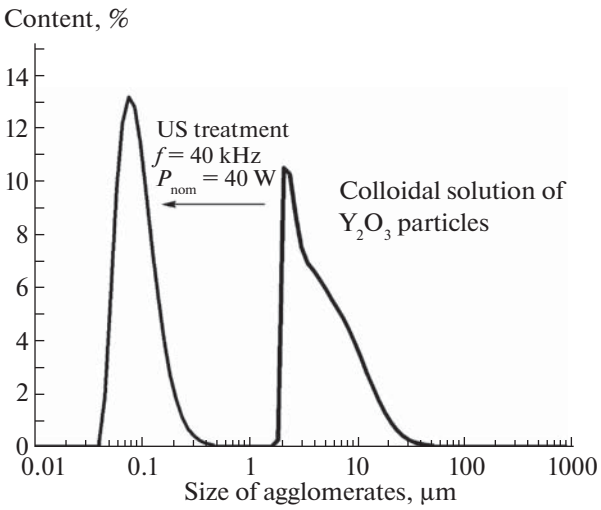

Fig. 3. Particle-size distribution of yttrium oxide before and after US treatment. Synthesis via the method using foaming components.

ions. Eight of them occupy a centrally symmetric position (C_{3i} symmetry), while the rest 24 have a lower C_2 symmetry [3].Therefore, europium ions may be found in either nonequivalent position, which leads to the difference in the luminescence spectra.

The luminescence spectra of the Y_2O_3:Eu^{3+} nanosized powders synthesized via the Pechini method and a method using foaming components are presented in Fig. 5. In both cases the luminescence was excited by the radiation with a wavelength of 393.5 nm. It is seen that the positions of the spectral lines are similar for different synthesis methods, and the diagrams differ only with respect to the intensity of the luminescence. It turned out that the intensity of the luminescence of the nanosized powders obtained via the method using foaming components was higher when compared to the nanosized powders obtained via the Pechini method.

The luminescence spectrum consists of narrow lines characteristic for rare earth metal ions. All the lines in the spectrum correspond to the transitions from the $^5D_0$ excitation level to the Stark split sublevels of the lower ^7F_J level (J = 0–4). The $^5D_0$–$^7F_2$ electric dipole transition with the maximum at the wavelength of 610.2 nm is the most intensive. This transition is only possible in Eu^{3+} ions located in positions with C_2 symmetry because, in this case, due to the influence of the electric field of the environment, the transition becomes partially permitted. The $^5D_0$–$^7F_1$ magnetic dipole transition is possible for all Eu^{3+} ions irrespective of their point symmetry. The position of the tran-

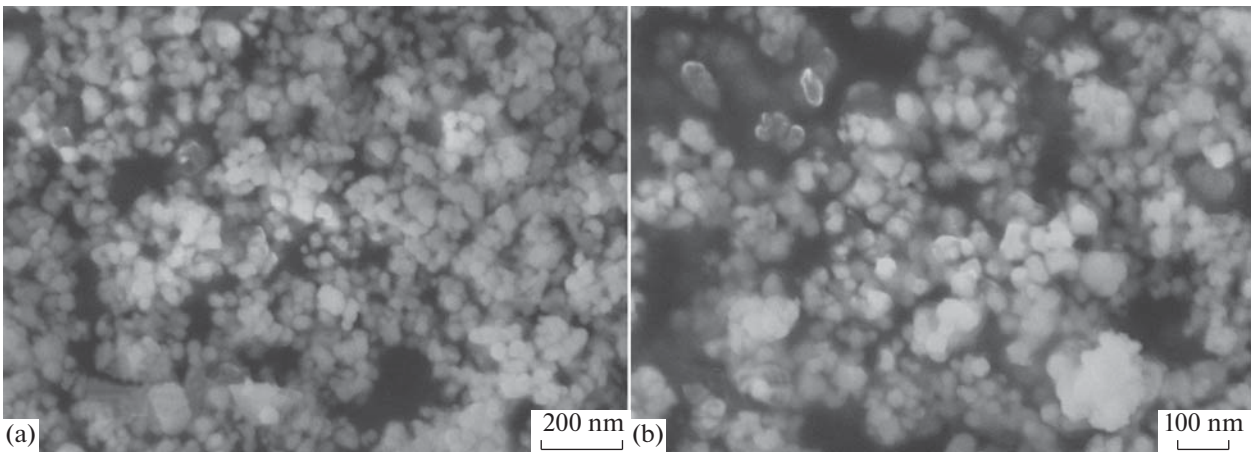

Fig. 4. Micrographs of the samples of Y_2O_3 synthesized via the method using foaming components at 1000°C, 2 h.

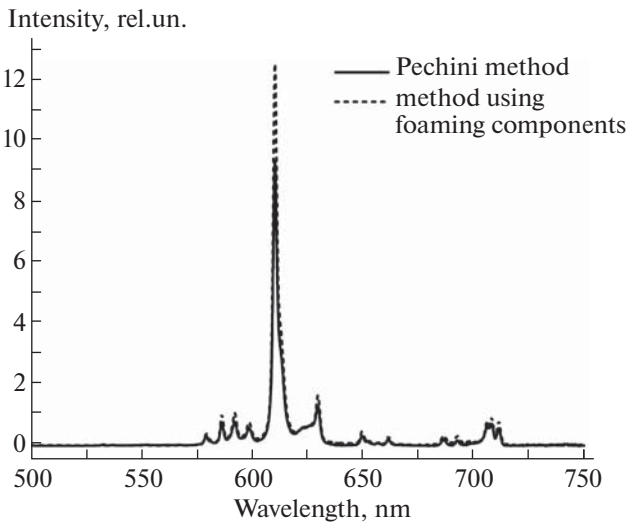

Fig. 5. Luminescence spectra of the samples of Y_2O_3:Eu^{3+} synthesized via the Pechini method and the method using foaming components (λ_{exc} = 393.5 nm).

sition maximum for ions with C_{3i} symmetry is 581.2 nm, while that for the C_2 symmetry is 586.4, 592.2, and 598.6 nm. Less intensive lines in the spectrum correspond to the $^5D_0$–$^7F_0$ (579.2 nm), $^5D_0$–$^7F_3$ (647–665 nm), and $^5D_0$–$^7F_4$ (683–695; 700–715 nm) transitions. In addition, there is a low-intensity transition from the higher $^5D_1$: $^5D_1$–$^7F_1$ excitation level (532.4 and 538 nm) in the spectrum.

Generally, the local environment of the luminescence ion has almost no effect on most *f*–*f* transitions in rare earth metals. For example, the magnetic dipole transition ($^5D_0$–$^7F_1$) is not sensitive to the local symmetry because it is permitted by the G-parity selection rules. Nevertheless, there are certain transitions sensitive to the environment. Such transitions are called hypersensitive transitions. The $^5D_0$–$^7F_2$ electric dipole transition with $\Delta J = 2$ is hypersensitive and its sensitivity may vary depending on the local symmetry of the luminescence ion. The ratio of the intensities of the $^5D_0$–$^7F_2$ and $^5D_0$–$^7F_1$ transitions can be used for the analysis of the local environment and symmetry of the luminescence center. This ratio is called an asymmetry factor *k*. The table shows the asymmetry factors for the nanosized powders synthesized via the Pechini method and a method using foaming components. The calculation factors differ slightly; hence, the position of the doping europium ions in the elementary cell does not depend on the synthesis method.

The luminescence excitation spectra of the most intensive $^5D_0$–$^7F_2$ transition (610.2 nm) of the nanosized powders synthesized via different methods are presented in Fig. 6. The measurements were carried out within the spectral range of 260–600 nm. The luminescence excitation spectrum consists of an intensive broad line associated with the Eu–O charge transfer and weak

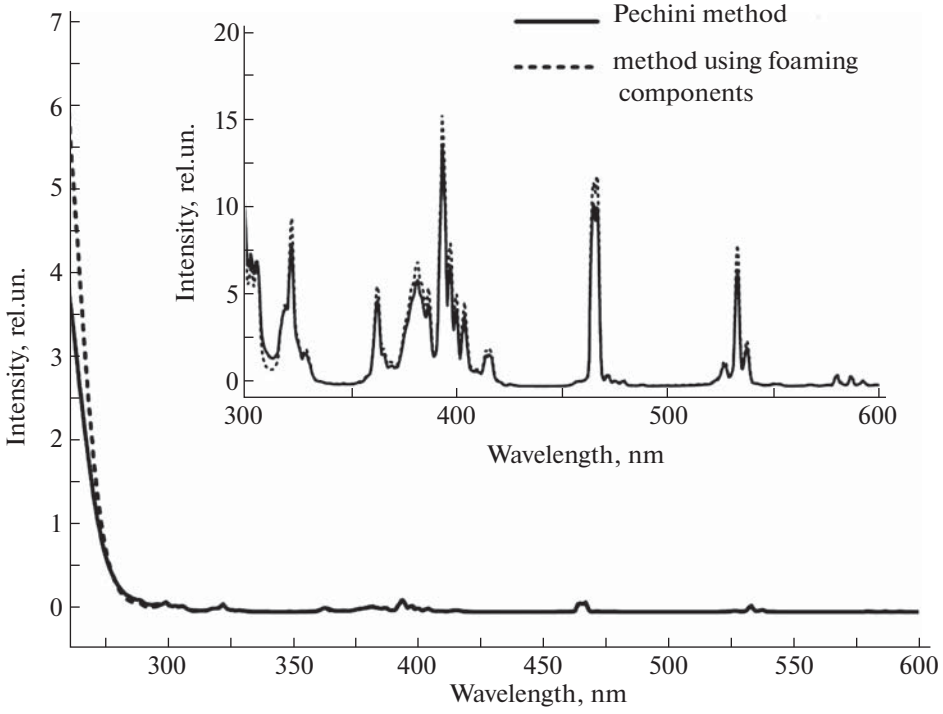

Fig. 6. Luminescence excitation spectra of the samples of Y_2O_3:Eu^{3+} synthesized via the Pechini method and the method using foaming components (λ_{lum} = 610.2 nm).

Asymmetry factors (k) of the nanosized powders synthesized via different methods

Synthesis method	Integral intensity		k
	$^5D_0$–$^7F_1$	$^5D_0$–$^7F_2$	
Pechini	7.2×10^6	4.3×10^7	6.0
Foaming	9.5×10^6	5.5×10^7	5.7

narrow lines corresponding to the f–f transitions inside europium ions [4, 5]. The line with the maximum at the wavelength of 393.5 nm, which corresponds to the $^7F_0$–$^5L_6$ transition, is the most intensive of long-wavelength lines. In addition to it, the following transitions are observed in the spectrum: $^7F_0$–$^5L_8$(322 nm), $^7F_0$–$^5D_4$(363 nm), $^7F_0$–$^5L_7$(381.5 nm), $^7F_0$–$^5D_3$(416 nm), $^7F_0$–$^5D_2$(466.5 nm), $^7F_0$–$^5D_1$ (533 nm), and $^7F_1$–$^5D_0$(587 nm). The synthesis method does not affect the position of the spectral lines.

Lifetime is one of the important characteristics of the excitation level. All processes resulting in the relaxation of electron are divided into radiative and nonradiative. The lifetime being measured takes into account the contribution of both processes. In order to find the lifetime of the $^5D_0$ excitation level, luminescence attenuation curves (Fig. 7) were measured for the $^5D_0$–$^7F_2$ electric dipole transition (610.2 nm). The experimental curves were approximated by the exponential dependence:

$$y = Ae^{-\frac{\tau}{\tau_f}},$$

where τ_f is the lifetime of the excitation level.

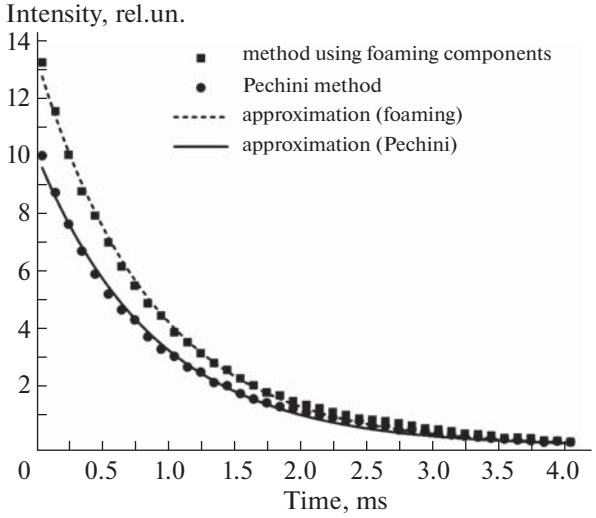

Fig. 7. Kinetics of the luminescence of the samples of Y_2O_3:Eu^{3+} synthesized via the Pechini method and the method using foaming components (λ_{exc} = 393.5 nm and λ_{lum} = 610.2 nm).

The lifetime of the $^5D_0$ excitation level of europium in the Y_2O_3:Eu^{3+} 12 at % nanosized powders is 0.88 ms for those synthesized via the Pechini method and 0.9 ms for those synthesized via the method using foaming components.

CONCLUSIONS

A liquid-phase procedure for the synthesis of weakly agglomerated particles of yttrium oxide has been developed. The sizes of the obtained particles fall within a nanometer range and are 100 nm on the average. The modification makes it possible to enhance the specific surface of the material more than twofold when compared to the powder synthesized via the Pechini method. The position of the luminescence bands for the samples synthesized via the Pechini method and method using foaming components is completely the same. However, the luminescence of the nanosized powder obtained via the method using foaming components possesses high intensity. The luminescence excitation spectrum consists of an intensive broad line associated with the Eu–O charge transfer and weak narrow lines corresponding to the *f–f* transitions inside europium ions. The lifetime of the $^5D_0$ excitation level of europium in the Y_2O_3:Eu^{3+} 12 at % nanosized powders does not depend on the synthesis method and is 0.9 ms.

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