The hydrothermal synthesis and RTA conditions influence on the Y$_2$O$_3$:Eu nanosized phosphors microstructure

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Abstract. When developing new methods for the diagnosis and treatment of cancer, the use of nanomaterials may be promising. One of the ways to improve and expand the fields of application of radiation and photodynamic therapy of cancer is the use of drugs containing nanosized phosphors. The aim of the work was to study the effect of the duration of hydrothermal synthesis and the conditions of rapid thermal annealing (RTA) on the Y$_2$O$_3$:Eu nanosized phosphors microstructure. The hydrothermal synthesis technique was carried out in two ways: chloride (precipitation from a chloride solution using NaOH and NH$_4$OH precipitators) and acetate (decomposition of mixed acetate without a dispersant, as well as with PEG-200 and PEG-2000 dispersants). Hydrothermal synthesis was carried out at a temperature of 230 °C for 6–24 hours. Rapid thermal annealing was carried out at a temperature of 600–800 °C for 5–20 minutes. As a result of our work, the Y$_2$O$_3$:Eu nanosized phosphors which particle size does not exceed 200 nm is synthesized.

1. Introduction

Today, the development of new phosphors continues, as well as the expansion of the scope of previously synthesized ones. Nanotechnology has greatly expanded the ability to synthesize phosphors. At the same time, the obtained nanosized [1] phosphors can play an important role in the possibilities of expanding photodynamic therapy for the fight against cancer. Today, positive results have been obtained with the use of PDT in the treatment of skin cancer, but the use of this type of therapy is limited for perifocal tissues [2]. The main problem remains the difficulty of bringing light into the tumor with cavity localization. And to solve this problem, there may be the creation of a pharmacological preparation that will include a photosensitizer [3, 4] and a phosphor that converts x-ray radiation that easily penetrates through the tissues of the body into visible light with a wavelength necessary for the photosensitizer to work. And one of the requirements for such a phosphor is its small particle size, which makes it possible to prepare a stable colloidal solution [5, 6]. As one of the possible options for such a luminescent system, phosphors based on yttrium oxide activated by europium can be proposed.

The aim of this work was to obtain phosphors of the composition Y$_2$O$_3$:Eu by the hydrothermal method, followed by annealing and study of their properties. The hydrothermal method is known as a relatively simple and inexpensive method of synthesis, allowing to obtain highly dispersed particles. Phosphors of the selected composition are resistant to external factors, have low toxicity, and are also resistant to cathode rays [7, 8].

As a result of the work, a number of samples were synthesized in two ways (chloride and acetate), they were studied by X-ray phase analysis and scanning electron microscopy, and optimal synthesis
conditions were determined that made it possible to obtain samples of the required phase composition with minimum particle sizes.

2. Experimental
A hydrothermal method was used to obtain highly dispersed phosphors. Two synthesis methods were used in the work:

1. the chloride method, a method using two different precipitants (NaOH and NH₄OH);
2. the acetate method, a technique using yttrium acetate, without using a precipitant.

In the chloride synthesis method, YCl₃ and EuCl₃ were used as starting materials, and NaOH and NH₄OH as precipitants. Hydrothermal treatment was carried out in ethylene glycol at a temperature of 230 °C for 24 hours. The dispersant was polyethylene glycol with a molecular weight of 2000 g/mol. In the acetate synthesis method, a mixed acetate of the composition Y₁₋ₓEuₓ(CH₃COO)₃ was first prepared by dissolving the yttrium and europium oxides in acetic acid, followed by evaporation of the resulting solution. Hydrothermal treatment was also carried out in ethylene glycol. The processing time was 24 hours, 12 hours and 6 hours, at a temperature of 230 °C. Polyethylene glycols with molecular weights of 200 and 2000 g/mol (PEG-200 and PEG 2000, respectively) were used as dispersants. The synthesis was carried out without the use of a dispersant. After hydrothermal treatment, all samples obtained were separated from the solution by centrifugation, followed by washing: first, in ethanol, then in bidistilled water.

To obtain the Y₂O₃ phase after hydrothermal treatment, all samples were annealed in air. Samples obtained by the chloride method were stepwise annealed at temperatures of 300, 400, 500, and 600 °C. Samples obtained by the acetate method underwent rapid thermal annealing (RTA) at temperatures of 600 and 800 °C.

3. Result and Discussion
Figures 1 and 2 show scanning electron micrographs of unannealed Y₂O₃:Eu³⁺ samples obtained by the chloride method using NaOH and NH₄OH precipitators. All synthesized phosphors are polydisperse in nature. The particle size of the synthesized phosphors is more than 500 nm, there are also aggregated particles. It is also seen that in the case of precipitation of samples by the chloride method, finer particles were obtained using a NaOH precipitant.

In the acetate method, synthesis was carried out both without a dispersant and using PEG-200 and PEG-2000 as a dispersant. As can be clearly seen from figure 3, the synthesized phosphors using PEG-2000 as a dispersant are most suitable for PDT, since they have the smallest particle size, but the particles continue to aggregate. The size of the smallest particles of the synthesized samples is less than 200 nm, which meets the requirements for phosphors for PDT.

![Figure 1. SEM images of unannealed samples obtained by the chloride method NaOH precipitant.](image-url)
Figure 2. SEM images of unannealed samples obtained by the chloride method. NH$_4$OH precipitant.

Figure 3. SEM images of unannealed samples obtained by the acetate method:

a - without dispersant; b - with a dispersant PEG-200; c - with a dispersant PEG-2000.

As mentioned above, in order to obtain the yttrium oxide phase after the hydrothermal process, the obtained samples were heat treated. In order to determine the optimal heat treatment temperature, step-by-step annealing in air was carried out for samples obtained by the chloride method at temperatures of 300, 400, 500, and 600 °C for 1 hour. It was found that the phase of cubic Y$_2$O$_3$ begins to form even at an annealing temperature of 400 °C; however, a temperature of at least 600° C was required to burn out the carbon impurities generated during the decomposition of polyethylene glycol. X-ray diffraction patterns of samples after various stages of step annealing are presented in figure 4. According to XRD data, using the Scherrer formula, the crystallite size in the particles of the synthesized samples was calculated. The results are presented in table 1. It can be seen that when using NaOH as a precipitant, the samples have a smaller initial crystallite size, however, after the heat treatment stage at a temperature of 600 °C, the crystallite size is larger than that of samples precipitated using NH$_4$OH. Thus, the use of NaOH as a precipitant makes it possible to obtain phosphors with a higher dispersion and, at the same time, with a more perfect crystalline structure.

After the heat treatment, a phosphor of the required phase composition was obtained, but as a result of annealing, particles fused into large aggregates (figure 5a), which does not allow the use of the synthesized phosphor in medicine. To reduce particle growth during heat treatment, Rapid Thermal Annealing (RTA) was used for samples prepared using the acetate method. Samples subjected to hydrothermal treatment for 24 hours were annealed at a temperature of 600 °C in two stages. After the first stage of annealing for 10 minutes, the samples were gray, indicating the presence of unburned carbon residues. After the second ten-minute annealing stage, the samples were white. According to the XRD data (figure 6), they have the structure of cubic Y$_2$O$_3$ and do not contain extraneous phases.
To shorten the duration of RTA, samples subjected to hydrothermal treatment for 12 and 6 hours were annealed at 800 °C for 5 minutes. After this heat treatment, the phosphors also had the structure of cubic yttrium oxide without impurity phases (figure 6).

Figure 4. X-ray diffraction patterns of annealed Y$_2$O$_3$:Eu nanosized phosphors synthesized using the chloride method:
- a - NaOH precipitant, annealing temperature 400 °C;
- b - NaOH precipitant, annealing temperature 500 °C;
- c - NaOH precipitant, annealing temperature 400 °C;
- d - NH$_4$OH precipitant, annealing temperature 400 °C;
- e - NH$_4$OH precipitant, annealing temperature 500 °C;
- f - NH$_4$OH precipitant, annealing temperature 400 °C;
- g - the cubic phase of Y$_2$O$_3$ (PDF card 41-1105).

Table 1. Comparing of the X-ray luminescence intensities of the synthesized phosphors.

| Precipitant | Annealing temperature, °C | Crystallite size, Å |
|-------------|----------------------------|-------------------|
| NaOH        | 400                        | 1.1               |
|             | 500                        | 11.1              |
|             | 600                        | 66                |
| NH$_4$OH    | 400                        | 12                |
|             | 500                        | 13                |
|             | 600                        | 36                |

Table 2 presents the results of calculations by the Scherrer equation of crystallite sizes of annealed samples synthesized using the acetate method. It can be seen that an increase in the crystallite size of the finished phosphor results in both an increase in the duration of hydrothermal treatment and an increase in the molecular weight of the dispersant used. Thus, the use of dispersants leads to a
decrease in the particle size of unannealed samples and, at the same time, increases the crystallite size of the finished phosphors. This can be explained by the fact that the smaller particles of the sample obtained as a result of hydrothermal synthesis are more intensively recrystallized during the heat treatment, which leads to the formation of larger crystallites.

Figure 5. SEM images of annealed samples:

- a - precipitation by the chloride method, NaOH precipitant, annealing for 1 hour;
- b – deposition acetate method, without dispersant, annealing RTA for 20 minutes.

Figure 6. X-ray diffraction patterns of annealed Y₂O₃:Eu nanosized phosphors synthesized using the acetate method:

- a - deposition of 24 hours without a dispersant;
- b - deposition of 24 hours with a dispersant PEG-200;
- c - deposition of 24 hours with a dispersant PEG-2000;
- d - deposition of 12 hours with a dispersant PEG-2000;
- e - deposition of 6 hours with a dispersant PEG-2000;
- f - the cubic phase of Y₂O₃ (PDF card 41-1105).
Table 2. Crystallite size of Y$_2$O$_3$:Eu nanosized phosphors synthesized using the acetate method.

| Duration of hydrothermal treatment, h | Dispersant used | Crystallite size, Å |
|--------------------------------------|-----------------|---------------------|
| 24                                   | Without dispersant | 28                  |
| 24                                   | PEG-200         | 99                  |
| 24                                   | PEG-2000        | 102                 |
| 12                                   | PEG-2000        | 80                  |
| 6                                    | PEG-2000        | 75                  |

The particle size of the phosphors synthesized using the acetate method is smaller than the samples synthesized using the chloride method, but aggregated particles are also available. Therefore, it was decided to continue the synthesis and study of phosphors obtained by the acetate method using the PEG-2000 dispersant by hydrothermal synthesis at a temperature of 230 °C for 24, 12, and 6 hours.

As can be seen from SEM images (figure 7, 8) of the presented samples, the hydrothermal synthesis time affects both the crystallite size and their aggregation. It is also seen that the aggregation of particles did not occur during annealing, but already at the time of hydrothermal treatment.

Figure 7. SEM images of samples after hydrothermal synthesis: a - 24 hours, b - 12 hours.

Figure 8. SEM images of samples after RTA: a - after hydrothermal synthesis for 24 hours, b - after hydrothermal synthesis for 12 hours.

Figure 9 shows the luminescence spectra of the samples annealed at a temperature of 600 °C. The luminescence intensities were calculated from the area under the spectral curves. The results are
shown in figure 10. It is seen that the phosphors synthesized using the acetate method have not only the smallest particle size, but also the highest luminescence intensity, and therefore are most suitable for use in photodynamic therapy. In the luminescence spectra, the bands with maxima $\lambda_{\text{max}} = 613$ nm and $\lambda_{\text{max}} = 626$ nm, which are related to electronic transitions in europium ions $^5\text{D}_0 \rightarrow ^7\text{F}_2$ and $^5\text{D}_0 \rightarrow ^7\text{F}_3$, respectively, have the highest intensity. The band with $\lambda_{\text{max}} = 626$ nm is closer to the absorption band of industrial photosensitizers, which should provide more efficient generation of active oxygen by the X-ray phosphor-photosensitizer system. This band has the highest intensity in the luminescence spectrum of a sample synthesized by the acetate method without the use of a dispersant. Therefore, this sample is most suitable for use in PDT both in dispersion and in luminescent properties.

Figure 9. Luminescence spectra of Y$_2$O$_3$: Eu samples annealed at a temperature of 600 °C.

Figure 10. Relative intensities of Y$_2$O$_3$: Eu samples annealed at a temperature of 600 °C.

Though we can say that phosphor synthesized in the reducing atmosphere with injection of the sodium pyrophosphate has the highest intensity of the X-ray luminescence of all synthesized phosphors. The average grain size of this phosphor is 9.9 μm. Such dispersity allows getting the roentgenograms of rather high definition when using this phosphor in the X-ray intensifying screens.
It is interesting to note that the ratio of the intensities of the luminescence bands with $\lambda_{\text{max}} = 626$ nm and $\lambda_{\text{max}} = 613$ nm has an inverse correlation with the crystallite size of the samples (correlation coefficient $-0.92$). Thus, a decrease in crystallite sizes allows one to increase the relative intensity in the luminescence spectrum of the band with $\lambda_{\text{max}} = 626$ nm, which is more suitable for using phosphors in PDT.

4. Conclusions
As a result of the work done using the hydrothermal method and rapid thermal annealing (RTA), highly dispersed phosphors $\text{Y}_2\text{O}_3:\text{Eu}$ were synthesized. It has been established that the use of dispersants in the hydrothermal treatment process, in addition to reducing the particle size of unannealed samples, leads to an increase in the crystallite size of annealed phosphors. At the same time, a decrease in the crystallite sizes of $\text{Y}_2\text{O}_3:\text{Eu}$ phosphors leads to an increase in the relative intensity in the spectrum of the band with $\lambda_{\text{max}} = 626$ nm, which is related to the $^5\text{D}_0 \rightarrow ^7\text{F}_3$ electronic transition. Based on the studies, it was found that the most suitable for use in PDT is $\text{Y}_2\text{O}_3:\text{Eu}$ nanosized phosphor synthesized by the acetate method without the use of dispersants and using RTA.

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