Synthesis of rare-earth nanosized phosphors using microwave processing

A B Vlasenko and V V Bakhmetyev
Saint-Petersburg State Institute of Technology (Technical University), Russia

E-mail: vlasenkoab@bk.ru

Abstract. Nanomaterials find permanently extending applications in various areas of life. In particular, nanosized phosphors can be used as pharmaceutical carriers capable of emitting ultraviolet or visible light that activates a photosensitizer, thus significantly expanding the possibilities of photodynamic therapy in the treatment of oncological, bacterial and viral diseases. The conditions required for the use of nanosized phosphors in medicine include their fine dispersion and effective luminescence in the red region of visible light spectrum upon stimulation by X-ray radiation of the range accepted for medical applications, particularly for diagnostic and therapeutic purposes in many diseases. The aim of this work was to study the effect of microwave treatment of Y₂O₃:Eu phosphors prepared by hydrothermal synthesis in ethylene glycol at 230 °C for 6 hours, involving the decomposition of mixed acetate. In order to reduce the aggregation and growth of the resulting particles, Aerosil A300 with average particle size 7 nm was added to the reaction mixture in the course of hydrothermal synthesis in the ratio 1:1 relating to the obtained phosphor. The microwave treatment was carried out at 800 °C for 5 minutes. The developed method provided Y₂O₃:Eu phosphor samples featuring with increased luminescence intensity in the region 610…700 nm compared to similar phosphors earlier prepared using the rapid thermal annealing (RTA) procedure.

1. Introduction
Phosphors based on rare earths, in particular, Y₂O₃:Eu, are widely used in various fields. One of the promising areas of application of phosphors of this composition is the improvement of photodynamic therapy (PDT). The PDT method is increasingly used in the treatment of various diseases, including cancer [1, 2, 3]. But the possibilities of this type of therapy are limited by its use for the treatment of deep-seated lesions. At the moment, it is suitable only for superficially located tumors, as well as purulent skin lesions. There are a number of ways to expand this method of therapy from the development of new photosensitizers to the creation of a new pharmacological drug that includes a photosensitizer and a nanosized phosphor that will convert X-rays into visible light with the wavelength necessary for the photosensitizer to work [4]. The main requirements for the phosphor to improve PDT are biocompatibility, small particle size that allows obtaining a stable colloidal solution suitable for introduction into the body, as well as light radiation in the area of the absorption bands of industrial photosensitizers (590-730) nm.

The finest dispersion of the obtained materials can be achieved via hydrothermal synthesis by treating a solution of the initial components in an autoclave [5, 6]. However, to obtain the necessary phase of yttrium oxide after hydrothermal treatment, high-temperature annealing at the temperature of at least 800 °C is required. At this stage, sintering and size growth of nanoparticles can occur. In order...
to avoid these undesirable effects, we used such methods as rapid thermal annealing (RTA), microwave annealing, as well as the addition of highly dispersed pyrogenic silica (Aerosil) to the phosphor composition, thus preventing form sintering of the phosphor particles during heat treatment.

For this purpose, a number of samples were synthesized with and without the addition of pyrogenic silica (Aerosil) and characterized by X-ray phase analysis and measuring the luminescence parameters, including brightness and intensity.

2. Experimental

To obtain finely dispersed phosphors, hydrothermal synthesis method was used in an ethylene glycol medium at 230 °C for 6 hours. YCl$_3$ and EuCl$_3$ were used as starting materials. First, a mixed acetate of the composition Y$_{0.85}$Eu$_{0.15}$(CH$_3$COO)$_3$ was prepared by dissolving yttrium and europium oxides in acetic acid, followed by evaporation of the resulting solution. Polyethylene glycol with a molecular weight of 2000 g/mol (PEG 2000) was used as a dispersant. After hydrothermal treatment, the resulting sample was separated from the solution by centrifugation. Next, the obtained substances were washed in ethyl alcohol and bidistilled water. In order to reduce the coalescence of the particles during calcination, heat treatment of the samples was carried out in the following two ways.

1. Rapid thermal annealing (RTA) at 800 °C within 5 minutes. The RTA mode was chosen based on the results of our previous studies [5, 6], during which it was found that a lower annealing temperature does not allow obtaining the required phase composition, while insufficient annealing duration, results in remaining of unburned carbon in the samples.

2. Microwave annealing. For its implementation, a special microwave installation was used [7], the scheme of which is shown in figure 1. The frequency of the magnetron was 2.45 GHz, which corresponds to the wavelength of microwave radiation of 12.3 cm. The dimensions of the microwave chamber 2 were selected in such a way that a resonance occurred in it and a standing wave was formed, in the antinode of which a quartz crucible with the sample to be processed was placed (figure 2). This design of the installation made it possible to significantly increase the intensity of the effect of microwave radiation on the sample material. The heat treatment mode of the microwave annealing was the same as that of the RTA: temperature-800 °C, duration-5 minutes.

Also, to prevent sintering of the particles during annealing, we investigated the addition of a highly dispersed neutral filler to the samples at the hydrothermal treatment stage. As such a filler, we used highly dispersed amorphous SiO$_2$ pyrogenic silica (Aerosil) brands A-300. This choice of filler is due to the fact that SiO$_2$ has a high melting point (1600 °C). It was assumed that it would not react with the phosphor material either at the hydrothermal synthesis temperature (230 °C) or at the further processing temperature (800 °C). Due to its low toxicity, pyrogenic silica (Aerosil) is widely used in pharmacy, which will allow the use of phosphor in the composition of pharmacological preparations for PDT. The content of pyrogenic silica (Aerosil) in the composition of samples based on the mass of the finished phosphor Y$_2$O$_3$:Eu was 1:1. After hydrothermal treatment, samples with the addition of pyrogenic silica (Aerosil) were annealed using RTA and microwave annealing methods under the same conditions as samples without pyrogenic silica (Aerosil).

X-ray phase analysis of the synthesized samples was performed using a Rigaku SmartLAB 3 diffractometer (Japan). Electron micrographs were obtained using a TESCAN VEGA 3 SBH scanning electron microscope (Czech Republic). The luminescence spectra were measured using an AvaSpec-3648 spectrofluorometer (Netherlands). The IL-1700 research radiometer (USA) was used to measure the brightness.
3. Result and Discussion
X-ray diffractograms of Aerosil-containing and Aerosil-free samples prepared by RTA and microwave annealing methods, are shown in figure 3. The diffractograms of the samples synthesized using RTA and microwave annealing without adding pyrogenic silica (Aerosil) correspond to the PDF card of yttrium oxide 41-1105. The sample obtained using the microwave annealing features with narrower peaks, which indicates larger crystallite sizes. According to the Scherrer formula, the size of the crystallites was calculated as about 12 nm for the phosphor synthesized using RTA and 26 nm in the case of the sample obtained by microwave annealing. These data suggest that the use of microwave annealing at the same duration and temperature leads to a more than twofold increase in the size of the crystallites, which is probably due to a more intense energy impact compared to RTA. When adding
pyrogenic silica (Aerosil) to the samples, the type of diffractograms changes significantly. The diffractogram of the sample synthesized with the addition of pyrogenic silica (Aerosil) followed by rapid thermal annealing (RTA) features with a wide halo. Obviously, this phosphor has an amorphous or nanocrystalline structure due to fine grinding of the particles. To test this assumption, the samples synthesized with and without the addition of pyrogenic silica (Aerosil) were studied by SEM technique. The resulting images (figure 4) indicate that the particle size for Aerosil-free sample is 100...300 nm, while the addition of Aerosil leads to the particle size decrease below 100 nm. Obviously, this is due to the fact that the particles of highly dispersed refractory pyrogenic silica (Aerosil) separate the phosphor particles from each other and, thereby, prevent their fusion during the hydrothermal synthesis and subsequent heat treatment.

The diffractogram of the sample synthesized with the addition of pyrogenic silica (Aerosil) and subsequent microwave annealing (figure 3) features with narrow peaks and corresponds to yttrium silicate $Y_2Si_2O_7$ (PDF-card 21-1457). Thus, at the same temperature and duration of annealing, the RTA and microwave methods give different results. Obviously, the microwave field provides a much more intense impact onto the material compared to thermal heating, allowing yttrium and silicon oxides to react with each other at the temperature about 800 °C. Without the application of microwave field, $Y_2O_3$ and $SiO_2$ do not react with each other at this temperature.

![Figure 3](image-url)

**Figure 3.** XRD profiles of the synthesized phosphors: a – RTA, without Aerosil; b – microwave annealing, without Aerosil; c – RTA, with Aerosil; d – microwave annealing, with Aerosil; e – $Y_2O_3$ (PDF card 41-1105); f – $Y_2Si_2O_7$ (PDF card 21-1457).
Figure 4. SEM images of Y$_2$O$_3$:Eu phosphors synthesized using RTA method without (a) and with (b) Aerosil addition.

Figure 5 shows the luminescence spectra of the obtained samples. The spectra of Aerosil-free samples prepared by both RTA and microwave annealing feature with narrow bands typical for Y$_2$O$_3$:Eu with the maximum at 612 nm, corresponding to the electronic transition $^5$D$_0$ $\rightarrow$ $^7$F$_2$. The sample synthesized with the addition of pyrogenic silica (Aerosil) sing RTA procedure also has a maximum with a wavelength of 612 nm, but the addition of pyrogenic silica (Aerosil) leads to an increase in the width of this luminescence bands, probably due to the decrease of the phosphor particle size and amorphization of the phosphor structure. Remaining of the peak position in couple with a significant decrease in its intensity may indicate that yttrium oxide did not react with pyrogenic silica during RTA. Probably, the synthesized sample is a mixture of nanosized Y$_2$O$_3$:Eu and SiO$_2$ particles. The presence of non-luminous SiO$_2$ in the sample reduces the luminescence intensity, but significantly enhances the dispersion, which is required for the use of the phosphor in PDT. During the synthesis of phosphor with the addition of pyrogenic silica (Aerosil) and subsequent microwave annealing, the intensity of the bands in the luminescence spectrum is redistributed. The maximum with a wavelength of 621 nm, relating to the $^5$D$_0$ $\rightarrow$ $^7$F$_3$ electron transition, becomes the most intense. The intensity of the peaks at 590 nm (transition $^5$D$_0$ $\rightarrow$ $^7$F$_0$), 600 nm (transition $^5$D$_0$ $\rightarrow$ $^7$F$_1$) and 700 nm (transition $^5$D$_0$ $\rightarrow$ $^7$F$_4$) also increases. The drastic change in the luminescence spectrum in this case is explained by the fact that instead of Y$_2$O$_3$:Eu, a phosphor of a completely different composition comprising Y$_2$Si$_2$O$_7$:Eu is obtained. It should be noted that regardless of pyrogenic silica addition, the samples synthesized using microwave annealing have a much higher intensity of the luminescence bands compared to samples synthetized using RTA process. This is obviously due to the fact that the microwave effect on the material is more intense than the thermal one, which leads to an increase in the perfection of the crystal structure of the phosphors, as well as to an increase in the uniformity of the activator distribution in the particles.

Figure 6 presents the comparison of luminescence brightness of the synthesized phosphors. It can be seen that the use of microwave annealing instead of RTA leads to an increase in brightness regardless of Aerosil addition. As mentioned above, this is probably due to an increase in the perfection of the crystal structure and improvement of the activator distribution uniformity. For samples synthesized using RTA annealing, the addition of Aerosil results in a decrease in the luminescence brightness, apparently due to the dilution of the luminous phosphor Y$_2$O$_3$:Eu with non-luminous SiO$_2$ powder. However, despite the fact that the mass of Aerosil added to the autoclave is equal to the calculated mass of the synthesized phosphor, the observed brightness decrease was only 32% instead of the expected 2-fold. On the contrary, for the samples synthesized using microwave annealing, the addition of pyrogenic silica led to an increase in the luminescence brightness by 11%. This effect is probably determined by a higher luminescence efficiency of Y$_2$Si$_2$O$_7$:Eu compared with
Y$_2$O$_3$:Eu, due to the presence of luminescence bands in the short-wave region with maxima of 590 nm and 600 nm, closer to the area of the maximum sensitivity of the human eye.

**Figure 5.** Luminescence spectra of the synthesized phosphors.

**Figure 6.** Luminescence brightness of the synthesized phosphors: a – RTA, without Aerosil; b – microwave annealing, without Aerosil; c – RTA, with Aerosil; d – microwave annealing, with Aerosil.
4. Conclusions
Hydrothermal synthesis followed by RTA and microwave annealing, as well as the addition of pyrogenic silica (Aerosil) provided a series of Eu-activated rare earth (yttrium oxide) based luminescent phosphors. The application of microwave annealing for heat treatment of phosphors allows the increase of the luminescence brightness due to the improvement of the crystal structure perfection, as well as, presumably, by increasing the uniformity of the activator distribution in the phosphor particles. The combination of microwave annealing and pyrogenic silica addition yields phosphors of the composition Y$_2$Si$_2$O$_7$:Eu featuring with a significantly higher brightness compared to the Y$_2$O$_3$:Eu phosphor. In the case of RTA annealing, the addition of pyrogenic silica (Aerosil) provides a significant enhancement of Y$_2$O$_3$:Eu particles dispersion affording phosphors with the particle size less than 100 nm, suitable for medical applications as a component of drugs for photodynamic therapy.

References
[1] Meerovich G.A., Akhlustina E.V., Tiganova I. G., Makarova E. A. et al. 2018 Nanostructured Photosensitizer Based on a Tetracationic Derivative of Bacteriochlorin for Antibacterial Photodynamic Therapy. Bulletin of RSMU 6 80 – 85.
[2] Logunova E.V., Nasedkin A.N. 2015 Modern View on Antimicrobial Photodynamic Therapy (Review of Literature). Laser Medicine 19 (2) 44 – 52.
[3] Gelfond M L, Barchuk A S, Vasiliev D V and Stukov A N 2003 The possibilities of photodynamic therapy in oncological practice Russian Biotherapeutic Journal 2 4 pp 67–71.
[4] Bakhmetyev V.V., Sychev M.M., Orlova A.I., Potanina E.A., Sovestnov A.E., Kulvelis Yu.V. 2013 Nanophosphors for Roentgenophotodynamic Therapy of Oncological Diseases. Nanoindustry. 8 46 – 50.
[5] Vlasenko A.B. Bakhmetyev V.V. 2020 Synthesis of Y$_2$O$_3$:Eu Nanosized Phosphor Using Hydrothermal Technique and Rapid Thermal Annealing (RTA). Key Engineering Materials. 854 209 – 215.
[6] Vlasenko A.B. Bakhmetyev V.V., Khristyuk N.A. 2020 The Hydrothermal Synthesis and RTA Conditions Influence on the Y$_2$O$_3$:Eu Nanosized Phosphors Microstructure. Journal of Physics: Conference Series. 1560 (1) 012023.
[7] Keskinova M.V., Ogurtsov K.A., Sychev M.M., Kolobkova E.V., Turkin I.A., Nakanishi Y., Hara K. 2015 Synthesis of chlorine-silicate phosphors for white light-emitting diodes. Advanced Materials Research. 1117 48 – 51.