A method for solid phase synthesis of phosphors under increased pressure; creation of remote phosphors

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Abstract. A method for phosphors solid-phase synthesis under high pressure is proposed. Using the method, phosphors based on rare earth garnets were synthesized at a temperature considerably lower (1300 °C) than the temperature of the synthesis by conventional method (above 1650 °C). Using organic, inorganic ligaments and synthesized phosphors, remote phosphors were created. The chromaticity coordinates of created LEDs on the base of blue LEDs and remote phosphors fall into the bin of white and green colours. Luminous efficiency reaches 140 lm/W.

1. Introduction

Light is an integral part of human life. The last few years were crucial for the sciences studying light. Light technologies are rapidly evolving. In many ways, it is possible thanks to their rather wide application [1, 2], both in everyday life and in various industries.

The role of lighting technology is appreciated by the world community. So, in 2014, – Nobel Laureate in Physics [3] was awarded for the creation of energy-saving and environmentally friendly light sources - blue light-emitting diodes (LED). The efficiency of the LED (80%) is 10-fold higher than the efficiency of incandescent and twice the efficiency of fluorescent lamps, which contain highly toxic mercury vapors. However, the service life of the light-emitting heterostructures more than 100 000 hours, it is many times longer than incandescent and fluorescent lamps.

To raise global awareness of how light-based technologies provide solutions to global problems in the areas of health, energy, education and agriculture, United Nations General Assembly declared 2015 - the International Year of the light and light technologies (IYL 2015).

Currently yellow phosphors based on rare-earth garnet (Y₃Al₅O₁₂:Ce) are used in most commercial LEDs. The use of such phosphors for white LEDs is primarily due to high conversion efficiency and optimum light performance. However, the commercial synthesis of these phosphors is quite complex and energy-intensive because it being done at high temperatures (above 1650 °C). Phosphor powders of different fractions (typically 2 to 50 microns) for different applications are required and such high temperatures of the synthesis lead to the formation of agglomerated microparticles. This implies involvement of additional expensive processing methods to obtain powders of the desired gravimetric composition.

A method for the synthesis of phosphors based on rare earth garnets in a controlled high pressure is proposed in this paper. A prerequisite to the establishment of the proposed synthesis method is the fact that at higher pressures the cubic yttrium oxide phase becomes more disordered monoclinic yttrium oxide phase [4]. It is assumed that in a solid phase form reaction of Y₃Al₅O₁₂, the diffusion of
aluminum atoms in the disordered structure of yttrium oxide is faster, as a result of the reaction rate increases, intermediate phase YAlO$_3$ disappears, and as a consequence, the total synthesis phase Y$_3$Al$_5$O$_{12}$ occurs at a lower temperature and a shorter time.

Modern commercial LEDs are coated optical silicone mixed up with the phosphor powder. The disadvantage of this system is that the silicone has a low thermal conductivity. In operation, the LED phosphor is heated, this leads to lower conversion properties and loss luminous efficiency. Furthermore, since the optical silicone is an organic compound, the degradation of the silicone occurs under the action of radiation emission of a blue LED, and this also leads to a reduction in light transmittance. It should be noted that the optical silicon has a high price - the order of $1200 / \text{kg.}$ In order to avoid light and conversion losses associated with the heating of the phosphor, one possible way is to use a remote phosphor.

2. Fabrication

For the synthesis of the samples, the following original reagents are used:

| Table 1. Original reagents. |
|-----------------------------|
| Reagent        | Production | Purity, % | Grain size D50, µm |
| Y$_2$O$_3$     | South Korea | 99.99    | 2                   |
| Al$_2$O$_3$    | China       | 99.99    | 2                   |
| CeO$_2$        | Russia      | 99.95    | 2                   |
| Lu$_2$O$_3$    | China       | 99.99    | 2                   |

The starting reagents are hung in the ratios equal gross formulas (Y$_{0.98}$Ce$_{0.02}$)$_3$Al$_5$O$_{12}$, (Y$_{0.78}$-Gd$_{0.2}$Ce$_{0.02}$)$_3$Al$_5$O$_{12}$ and (Lu$_{0.98}$Ce$_{0.02}$)$_3$Al$_5$O$_{12}$ on laboratory scale (VC-3000) with a precision weighing 50 mg. Further starting reactants are placed into a mixer (Frich firm) of the type "drunken barrel" and mixed in ethanol for 12 hours. The mixture is placed in an oven desiccator and dried for 12 hours at a temperature of 120 ºC. Then the dried blend is placed into an alumina crucible and covered with a lid made of the same material. The crucibles were placed in a high-pressure synthesis unit. Working chamber installation was evacuated to $10^{-2}$ Pa, and then a graphite heater heats up to a temperature of 1300 ºC. When the temperature reached 1300 ºC installation is filled with reducing argon - hydrogen gas mixture (95% Ar, 5% H$_2$) until the pressure reached 10$^7$ Pa. Under these conditions the samples were incubated for 3 hours. Thereafter, the heater power setting is disabled and installation is cooled to room temperature for 12 hours.

In the described method the following examples were prepared: (Y$_{0.98}$Ce$_{0.02}$)$_3$Al$_5$O$_{12}$ and (Y$_{0.78}$Gd$_{0.2}$Ce$_{0.02}$)$_3$Al$_5$O$_{12}$, (Lu$_{0.98}$Ce$_{0.02}$)$_3$Al$_5$O$_{12}$.

![Figure 1. Synthesized phosphors: (Lu$_{0.98}$Ce$_{0.02}$)$_3$Al$_5$O$_{12}$ and (Y$_{0.98}$Ce$_{0.02}$)$_3$Al$_5$O$_{12}$.](image1)

![Figure 2. The luminescence of the phosphors due to irradiation of blue.](image2)
3. Results
X-ray diffraction analysis (copper radiation $\lambda=1.5418$ Å) of the samples showed that samples were synthesized at a temperature of 1300 °C and a pressure of $10^5$ Pa (Figure 3) in addition to garnet phase have extraneous phases of reaction products of synthesis. At a temperature of 1650 °C and a pressure of $10^5$ Pa (Figure 4) the amount of foreign phases is reduced, but not completely. Electron microscopy showed that the particles are agglomerated and have a non-uniform surface shape (Figure 5).

![Figure 3](image1.png)  
**Figure 3.** Synthesis of $(Y_{0.98}Ce_{0.02})_3Al_5O_{12}$ at a conditions $T=1300$ °C and $P=10^5$ Pa.

![Figure 4](image2.png)  
**Figure 4.** Synthesis of $(Y_{0.98}Ce_{0.02})_3Al_5O_{12}$ at a conditions $T=1650$ °C and $P=10^5$ Pa.

![Figure 5](image3.png)  
**Figure 5.** Electron microscopy of $(Y_{0.98}Ce_{0.02})_3Al_5O_{12}$ at a conditions of synthesis $T=1650$ °C and $P=10^5$ Pa.
X-ray diffraction analysis of the samples showed that samples were synthesized at a temperature of 1300 °C and a pressure of 10^7 Pa (Figure 6) have only garnet phase. Electron microscopy showed that the particles are not agglomerated and have faceted surface (Figure 7). According to the data of laser particle size analyser it was found that all the samples synthesized at high pressures have particle sizes from 10 to 20 µm.

Using organic, inorganic ligaments and synthesized phosphors remote phosphors (Figure 8) were created. The chromaticity coordinates of created LEDs on the base of blue LEDs and remote phosphors fall into the bin of white and green colors. Luminous efficiency was 140, 130, and 120 lm, respectively for Y₃Al₅O₁₂:Ce, Gd₃Al₅O₁₂:Ce, Lu₃Al₅O₁₂:Ce remote phosphor.

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