Luminescence performance of laser synthesized \( \text{Al}_2\text{O}_3: \text{Eu}^{3+} \) nanophosphors depending on synthesis conditions

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Abstract. Al\(_2\)O\(_3\):Eu\(^{3+}\) nanophosphors were prepared by laser vaporization method in a flowing mixture of Ar/He and O\(_2\). Luminescence properties of Al\(_2\)O\(_3\):Eu\(^{3+}\) nanophosphors are predominantly determined by Eu\(^{3+}\) ions red emission with inhomogeneously broadened bands in the region of 550-750 nm corresponding to \( ^5\text{D}_0 \rightarrow ^7\text{F}_2 \) transitions of Eu\(^{3+}\) (\(J = 0 - 4\)). Hypersensitive electric dipole transition \( ^5\text{D}_0 \rightarrow ^7\text{F}_2 \) dominates in the spectrum and is responsible for the red emission. The effect of crystallite size on luminescence properties of Al\(_2\)O\(_3\):Eu\(^{3+}\) nanocrystals was observed. It was shown that the introduction of oxygen during the synthesis improves the luminescence performance. The obtained chromaticity coordinates and high absolute QY (~ 14%) indicate the possibility of using red nanophosphors based on Al\(_2\)O\(_3\):Eu\(^{3+}\).

1. Introduction

Currently, investigations of the nanophosphors with red emission are of interest to the material research community [1-8]. Alumina (Al\(_2\)O\(_3\)) is one of the standard phosphor matrices for activators emitting in the red spectral region [6, 9, 10]. Al\(_2\)O\(_3\) possesses some unique properties, among which is a large transparency window from the short UV to the near-IR spectral region, and has good mechanical properties and excellent chemical stability. Therefore, Al\(_2\)O\(_3\) is a suitable host for Eu\(^{3+}\) ions. Eu\(^{3+}\) ions in Al\(_2\)O\(_3\) combine an intense red photoluminescence and a relatively easily interpretable luminescence spectrum. There are low-temperature \( \eta, \chi, \theta \), and high-temperature \( \delta, \kappa \), \( \alpha \)-polymorphs of Al\(_2\)O\(_3\). The only thermodynamically stable phase of Al\(_2\)O\(_3\) is \( \alpha \)-polymorph (corundum). All metastable phases of Al\(_2\)O\(_3\) irreversibly transform into the \( \alpha \)-polymorph upon heat treatment over 1200 °C of the starting hydroxides and oxides. The photoluminescent properties of Eu\(^{3+}\) ions are best studied in \( \alpha \)-Al\(_2\)O\(_3\) and \( \gamma \)-Al\(_2\)O\(_3\) matrices [11, 12]. When studying nano-sized Al\(_2\)O\(_3\) with particle sizes less than 100 nm, one usually deals with low-temperature modifications, since the particle size for \( \alpha \)-Al\(_2\)O\(_3\) most often exceeds 100 nm. Laser methods are capable of providing the synthesis of Al\(_2\)O\(_3\) with the required particle size.

In this study, the CO\(_2\) laser vaporization technique was used for the preparation of Al\(_2\)O\(_3\):Eu\(^{3+}\) nanophosphors. The use of the laser method with its wide range of possibilities for the production of nanoparticles with different chemical compositions makes it possible to vary the properties of the obtained nanomaterials in a wide range. The most important among these possibilities is the opportunity of synthesizing nanoparticles with a size range from 1-2 nm to 100 nm. Condensation of nanoparticles in this method occurs in a flow of buffer gases at different pressures, which provides particles with different properties. To the best of our knowledge, the photoluminescent properties of laser synthesized Eu doped Al\(_2\)O\(_3\) nanophosphors especially with the particle size below 10 nm were
comprehensively studied only in our early work [6]. This work focuses on the study of quantum efficiency and color coordinates of laser synthesized Al<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> nanophosphors depending on synthesis conditions.

2. Experimental techniques

2.1. Synthesis of europium doped Al<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> nanophosphors

Al<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> nanophosphors were obtained by laser vaporization of α-Al<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> (Eu concentration is 1.0 ± 0.2 wt%, T<sub>calc</sub> = 1250 °C/4h) ceramic targets irradiated by a cw CO<sub>2</sub> laser (the power density up to ~ 0.06 MW/cm<sup>2</sup>) with subsequent condensation of vapor in buffer gas flow in a vaporization chamber [6-8, 13-15]. To investigate the influence of synthesis conditions on PL properties of Eu<sup>3+</sup>, the Al<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> nanophosphors were synthesized in different buffer gas: a) helium (99.99%), b) argon (99.99%), and c) helium supplemented with oxygen (99.7%). To obtain nanophosphors with the different mean sizes of nanoparticles, the gas pressure in the vaporization chamber was varied from 0.1 to 0.9 bar.

2.2. Characterization

Elemental analysis of the Al<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> nanophosphors was made using X-ray fluorescence spectroscopy (XRF) on an ARL – Advant’x analyzer with the Rh anode of the X-ray tube.

The morphology of the synthesized samples was characterized by transmission electron microscopy (TEM) on a JEM-2010 electron microscope.

Phase composition of the Al<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> nanophosphors was revealed by X-ray diffraction (XRD) analysis. X-ray diffraction patterns were recorded on a Bruker D8 diffractometer. Measurements were performed in the 2θ range of 20 – 70° with a step of 0.05° and acquisition time of 3 s. The ICDD PDF-2 database (Powder Diffraction File database PDF-2, International Center for Diffraction Data, USA, 2009) was used for phase identification.

Photoluminescence (PL) spectra were measured on a Cary Eclipse (Varian) fluorescence spectrophotometer. To measure an absolute quantum yield (QY) of the Al<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> nanophosphors, a Spectalon covered G8 integration sphere (GMP SA, Switzerland) was coupled to the Fluorolog 3 (Horiba Jobin Yvon) spectrofluorometer. At least three measurements of QY were made and the average value is reported. According to estimations, a consistent experimental error for the QY measurements did not exceed 15%. The color coordinates of luminescence chromaticity of the samples (in the Commission International de l’Eclairage (CIE) 1931 diagram) were calculated for the PL spectral range 565 – 725 nm. A color calculator was used to calculate the x, y color chromaticity coordinates.

3. Results and discussion

The XRF analysis reveals that after vaporization of the α-Al<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> targets and subsequent condensation of vapor, europium enters the composition of the produced Al<sub>2</sub>O<sub>3</sub> nanoparticles with the concentration 0.92 ± 0.04 wt%. The phase composition of the synthesized Al<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> nanophosphors is represented mostly by γ-Al<sub>2</sub>O<sub>3</sub> with the cubic structure (Fd<sub>3</sub>m).

Vaporization in He and Ar buffer gas at 0.1 – 0.9 bar pressures leads to the formation of Al<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> nanometer particles, Fig.1. The sample obtained at 0.1 bar (He) contains predominantly faceted nanoparticles with the mean size of 7.2 ± 4.1 nm. An increase in the He pressure to 0.9 bar leads to growth in the average particle size to 20.9 ± 17.7 nm, while the shape of the nanoparticles becomes close to spherical. Similar changes occur when He is replaced by Ar as a buffer gas. The particle sizes obtained at a pressure of 0.1 bar (Ar) and 0.3 bar (Ar) are 14.9 ± 9.0 nm and 16 ± 9.4 nm, respectively.

PL properties of Al<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> nanophosphors under indirect (to charge transfer O<sup>2-</sup>→Eu<sup>3+</sup> transition, λ<sub>exc</sub> = 232 nm) excitation are predominantly determined by Eu<sup>3+</sup> ions red emission with inhomogeneously broadened bands in the region of 565-725 nm, Fig.2. These bands correspond to
The hypersensitive electric dipole transition $^5\text{D}_0 \rightarrow ^7\text{F}_2$ dominates in the spectrum and is responsible for the red emission of nanophosphors. It was shown that Eu$^{3+}$ ions incorporate into the nanosized Al$_2$O$_3$ matrix in positions with $C_{3v}$ local symmetry. Similar structural positions of Eu$^{3+}$ were observed by the authors for phosphors based on $\alpha$-Al$_2$O$_3$ and $\gamma$-Al$_2$O$_3$ obtained by other synthesis methods [11, 12].

The PL decay of Eu$^{3+}$ in the region of the most intense transition $^5\text{D}_0 \rightarrow ^7\text{F}_2$ falls within the millisecond range and is adequately described by the bi-exponential decay with “slow” and “fast” components.

**Figure 1.** TEM image of the size series of Al$_2$O$_3$:Eu$^{3+}$ nanophosphors obtained at different pressures and compositions of the ambient gas: a – 0.1 bar He, b – 0.9 bar He, c – 0.1 bar Ar, d – 0.3 bar Ar.
Figure 2. PL spectra of the size series of Al₂O₃:Eu³⁺ nanophosphors obtained at different pressures and compositions of the ambient gas (a) and Al₂O₃:Eu³⁺ nanophosphor obtained at 0.1 He supplemented with O₂ (b). All PL spectra were recorded at λ_{ex} = 232 nm.

Normalized intensities of ⁵D₀ → ⁷F₂ transition, the calculated values of asymmetry parameter R, and lifetimes ("slow" component) are presented in Fig. 3 as a function of the particle size.

Figure 3. Normalized intensities of ⁵D₀ → ⁷F₂ transition, asymmetry parameter R, and lifetimes ("slow" component) as a function of the particle size of Al₂O₃:Eu³⁺ nanophosphors.

With a decrease in the nanoparticle size, a shortening of the PL lifetime (λ_{em} = 618 nm, λ_{ex} = 232 nm) was observed, which is due to an increase in the probability of nonradiative energy transfer from Eu³⁺ ions to adsorbed OH groups. It can be noted that the parameter R increases with increasing nanoparticle size. Thus, it can be concluded that the local symmetry of Eu³⁺ decreases with increasing nanoparticle size. In the work for Eu³⁺:KGd(WO₄)₂ nanoparticles, the opposite effect of decreasing the R-value was observed [16]. The authors associated this effect with the contribution of the surface. In our case, the above effects are due to the conditions for the synthesis of this material, namely the pressure and the composition of the atmosphere in the vaporization chamber. Comparison of the luminescence characteristics of Al₂O₃:Eu³⁺ nanoparticles obtained in different atmospheres showed that the introduction of oxygen into the composition of the buffer gas mixture during the synthesis of the samples increases the intensity and lifetime of photoluminescence. The role of oxygen addition in
the preparation of nanoparticles by laser vaporization was discussed by us earlier and is associated
with a decrease in oxygen vacancies in the samples [6].

The CIE color chromaticity coordinates of nanosized Al₂O₃:Eu³⁺ obtained from the PL spectra are
marked on the CIE 1931 chromaticity diagram, Fig. 4. The values of the color chromaticity
coordinates (x, y) were found to be (0.613, 0.386), (0.679, 0.320), (0.615, 0.385), (0.609, 0.391),
(0.606, 0.393), and (0.704, 0.296) for Al₂O₃:Eu³⁺ nanophosphors obtained at 0.1 bar (He), 0.1 bar
(He+O₂), 0.1 bar (Ar), 0.3 bar (Ar), 0.9 bar (He), and 0.9 bar (He+O₂), respectively. The obtained
chromaticity coordinates are close to the ideal red light (0.67, 0.33), which makes it possible to use
Al₂O₃:Eu³⁺ as luminescent devices and applications.

![CIE 1931 Chromaticity Diagram](image)

**Figure 4.** The CIE 1931 chromaticity diagram for Al₂O₃:Eu³⁺ nanophosphors: a - 0.1 bar (He),
b - 0.1 bar (He+O₂), c - 0.1 bar (Ar), d - 0.3 bar (Ar), e - 0.9 bar (He), f - 0.9 bar (He+O₂).

The absolute quantum yield (QY) measured using integrating sphere pumped at 395 nm (to
⁷F₀ → ⁵L₆ transition) for the Al₂O₃:Eu³⁺ nanophosphors obtained at 0.1 bar (He), 0.1 bar (He+O₂), 0.1
bar (Ar), 0.3 bar (Ar), 0.9 bar (He), and 0.9 bar (He+O₂) was 2.8, 6.4, 3.6, 4.6, 11, and 14.3%,
respectively. It can be seen that the quantum yield is maximum for particles with the largest sizes in
the series. From an analysis of the luminescence decay, it was concluded that, for particles with the
smallest sizes, the probability of nonradiative relaxation is maximal, which in turn leads to a decrease
in the luminescence intensity and quantum efficiency. Earlier studies of the quantum efficiency of
Gd₂O₃:Eu³⁺ and Y₂O₃:Eu³⁺ laser synthesized nanopowders showed that for particles with close sizes to
Al₂O₃:Eu³⁺ nanophosphors, the QY values are 4% and 21%, respectively [7, 8]. The values obtained in
this work are significantly higher than for Gd₂O₃:Eu³⁺ and lower than for the Y₂O₃:Eu³⁺ nanophosphor.
Since the QY of nanophosphors strongly depends on many factors (for example, the concentration of
europium, the size of nanoparticles and their crystallinity, etc.), there is every reason to believe that,
with the help of further optimization of a number of parameters, it is possible to achieve a higher QY
for red Al₂O₃:Eu³⁺ emission.
4. Conclusion

Laser vaporization by a cw CO₂ laser in flowing mixture of Ar/He and O₂ was used to obtain Al₂O₃:Eu³⁺ nanophosphors. The particle size was varied from 7.2 ± 4.1 nm to 20.9 ± 17.7 nm by changing the gas composition and pressure in the vaporization chamber. As follows from TEM images, such particles are represented by faceted and spherically nanocrystallites. XRD studies demonstrated that the phase composition of Al₂O₃:Eu³⁺ nanophosphors is represented predominantly by γ-Al₂O₃ with the cubic structure. Photoluminescence of Al₂O₃:Eu³⁺ nanoparticles was studied under direct (to ⁵F₀ → ⁵L₆ transition) and indirect (to charge transfer O²⁻→Eu³⁺ transition) excitation with λexc = 232 and 395 nm. Luminescence properties of Al₂O₃:Eu³⁺ nanophosphors are predominantly determined by Eu³⁺ ions red emission with inhomogeneously broadened bands in the region of 550-750 nm corresponding to ³D₀ → ³F₃ (J = 0 - 4) transitions of Eu³⁺. Hypersensitive transition ³D₀ → ³F₂ dominates in the spectrum and is responsible for the red emission. The effect of crystallite size on luminescence intensity, decay times, color coordinates and quantum efficiency of Al₂O₃:Eu³⁺ nanocrystals was observed. It was shown that the introduction of oxygen during the synthesis improves the luminescence performance. The obtained chromaticity coordinates and absolute QY (~14%) indicate the possibility of using red nanophosphors based on Al₂O₃:Eu³⁺.

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CRediT authorship contribution statement

A. I. Kostyukov: Conceptualization, Investigation, Writing-original draft. A. A. Nashivochnikov: Investigation. M. I. Rakhmanova: Investigation. V. N. Snytnikov: Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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