Study of the properties of Ce$^{3+}$-doped fluoride nanophosphors: phase composition, morphology, luminescence

A M Dorokhina$^{1,2}$, V V Bakhmetyev$^1$, H Kominami$^2$, A Toru$^3$ and M Hisashi$^3$

$^1$Saint-Petersburg State Institute of Technology (Technical University), Russia
$^2$Shizuoka University, Research Institute of Electronics, Japan
$^3$ANSeeN Inc., Japan

E-mail: vadim_bakhmetyev@mail.ru

Abstract. To date, nanophosphors have found application in various fields, one of which is medicine. These phosphors were developed with the aim to become one of the components of a drug for photodynamic therapy of oncological diseases. The aim of this work was to study the effect of the duration, environment, and stabilizers of solvothermal synthesis on the microstructure and luminescent properties of the YF$_3$:Ce nanophosphor. The solvothermal synthesis technique was carried out in three different media: water, ethanol, and ethylene glycol. The optimal duration of the synthesis was also determined (the synthesis was carried out at a temperature of 200°C for 4...20 hours). The dependence of the YF$_3$ luminescence on the phase composition and the solvothermal synthesis medium was studied. Using SEM, the morphology and particle size of YF$_3$:Ce phosphors were studied depending on different stabilizers (polyethylene glycol, polyethyleneimine, polyvinylpyrrolidone). The luminescence intensity of YF$_3$:Ce and Na(Y$_{1,5}$Na$_{0,5}$)F$_6$:Ce samples was compared.

1. Introduction

The synthesis of nanosized inorganic materials with a certain morphology attracts much attention from the point of view both of fundamental scientific interest and potential technological applications in various fields, such as photochemistry, superconductors, optoelectronics, solar cells, and medicine [1, 2]. Thus, it remains an important goal of modern materials chemistry. Much recent research has focused on controlled morphology and spatial structuring of various materials, which is an important step towards creating multifunctional nanosystems. Typically, chemical vapor deposition or solution chemistry processes are used to achieve this objective. However, this usually requires: catalysts; expensive and even toxic matrices or surfactants; high temperatures; and a number of complex procedures.

This work is devoted to the solvothermal synthesis method, which makes it possible to obtain nanosized particles while avoiding high-temperature processing.

YF$_3$ has great potential as a phosphor. On its basis, lanthanide-doped phosphors with Stokes and anti-Stokes luminescence have been synthesized [3, 4]. Fluoride materials have advantages in terms of high density, mechanical hardness, and radiation resistance. Phosphors based on LnF$_3$ fluorides (Ln = lanthanide) are preferred matrices for lanthanide phosphors (since they have a low phonon energy state) and for downconversion due to their wide band gap (9–10 eV) [5].
To ensure the applicability of phosphors in medicine, in particular in the composition of pharmacological preparations for photodynamic therapy of oncological diseases (PDT), a phosphor with certain properties is required, such as: particle size less than 100 nm, excitation by radiation, ability to penetrate through body tissues - X-ray or infrared, and emitting light with a wavelength corresponding to the absorption band of industrial photosensitizers [6, 7].

In our previous studies [8–10], the main problem in obtaining phosphors is the need for high-temperature (more than 800°C) annealing, which leads to the agglomeration of phosphor nanoparticles into large agglomerates. To solve this problem, a solvothermal method for the synthesis of phosphors was proposed, which consists of thermal treatment of a liquid medium in an autoclave at moderate temperatures (200°C and below).

In particular, this approach is applicable to the synthesis of lanthanide fluorides activated by cerium, which are advantageous in terms of efficient X-ray luminescence in addition to high density and non-toxicity. Since the scattering of X-rays in tissues is negligible, lanthanides are effective additives for such phosphors, since they have a high atomic number and electronic energy states that provide radiation in the visible and ultraviolet regions. The inclusion of elements with high atomic numbers in the matrix provides the generation of electrons with an energy sufficient for conversion with a decrease in frequency, with an appropriate choice of lanthanide sensitizers and luminescent centers.

In this experiment, we implement a one-stage solvothermal synthesis of YF$_3$:Ce$^{3+}$ nanocrystals in three different media (in water, ethanol, and ethylene glycol), which are the most promising in this synthesis method. The selection of the optimal synthesis duration in the ethylene glycol medium is carried out, and the morphology of the obtained particles is investigated depending on various stabilizers (polyethylene glycol, polyethyleneimine, polyvinylpyrrolidone). A comparison of the cerium-activated Na(Y$_{1.5}$Na$_{0.5}$)F$_6$ and YF$_3$ images is also provided.

2. Experimental

A series of fluoride luminophores with the composition YF$_3$:Ce$^{3+}$ 2 mol% was synthesized. A typical synthesis [5] was carried out in various media, both aqueous and organic (ethylene glycol and ethanol) at 200°C for 22 hours. Chlorides of cerium and yttrium and the stabilizer polyethylene glycol M$_w$ = 2000 (PEG-2000) were vigorously stirred on a magnetic stirrer at room temperature. Then, ammonium fluoride NH$_4$F was dissolved in a suitable medium (water, ethylene glycol or ethanol), added to the above solution, and again stirred vigorously at room temperature for 30 minutes. Finally, the mixture was transferred to a Teflon liner, placed in a sealed stainless steel autoclave, where it was subjected to a solvothermal treatment, and cooled naturally to room temperature. The precipitate was washed in ethanol and deionized water, and the final products were dried at 50°C for 6 hours in a normal atmosphere. Further, according to the same method (but only in an ethylene glycol medium), a number of YF$_3$:Ce samples with a cerium concentration of 1 ... 6 mol.% were synthesized.

To determine the optimal synthesis time, the solvothermal synthesis of YF$_3$ samples was carried out without doping with Ce$^{3+}$ in an ethylene glycol medium without the use of stabilizers for 4, 8, 12, 16, and 20 hours.

A sample of Na(Y$_{1.5}$Na$_{0.5}$)F$_6$ was synthesized in an aqueous medium for 22 hours at 200°C with PEG-2000 as a stabilizer.

The structural characteristics of the final products were investigated by powder X-ray diffraction (XRD) using Cu-Ka radiation ($\lambda = 0.15405$ nm) on a Rigaku-RINT2200 diffractometer. The morphology and size of the obtained samples were observed using field emission scanning electron microscope (FE-SEM, JSM-6335F, JEOL). The emission spectra of ultraviolet and visible photoluminescence were recorded using a laboratory setup - a spectrofluorometer with two monochromators (model of an ultramonochromatic light source) equipped with a xenon lamp as an exciter. The X-ray luminescence spectra were measured on a laboratory setup with a copper anode at a voltage of 80 kV and a current of 62 mA. The decay time was measured with a Hamamatsu Photonics DG645 setup. All measurements were carried out at room temperature.
3. Result and Discussion
To find out the optimal synthesis medium it was decided to carry out solvothermal synthesis in various media, in which it is possible to obtain spherical particles less than 100 nm. Figure 1 shows the diffraction patterns of YF$_3$:Ce$^{3+}$ (2 mol%) samples synthesized in ethanol, aqueous solution, and ethylene glycol respectively. As can be seen, the obtained X-ray diffraction patterns fully correspond to the orthorhombic phase of yttrium fluoride (PDF card 32-1531). According to the X-ray diffraction data, the crystallite sizes were calculated (according to the Scherrer formula) for each of the samples (Table 1). The sample synthesized in ethylene glycol has the smallest crystallite size.

![Figure 1. Diffraction patterns of YF$_3$:Ce$^{3+}$ samples synthesized in different media: a - ethylene glycol, b - water, c - ethanol, d – orthorhombic YF$_3$ (PDF card 70-1935).](image1)

The photoluminescence (excitation and emission) spectra recorded of these samples are shown in figure 2.

![Figure 2. Photoluminescence spectra (excitation and emission) of YF$_3$:Ce 2%mol. samples synthesized in various media.](image2)
Table 1. Sizes of crystallites of the obtained samples.

| Sample name                     | Crystallite sizes, nm |
|---------------------------------|-----------------------|
| YF$_3$:Ce in water              | 35.61                 |
| YF$_3$:Ce in ethanol             | 29.84                 |
| YF$_3$:Ce in ethylene glycol     | 27.05                 |
| YF$_3$ 4 hours                   | 48.91                 |
| YF$_3$ 8 hours                   | 37.68                 |
| YF$_3$ 12 hours                  | 35.78                 |
| YF$_3$ 16 hours                  | 27.23                 |
| YF$_3$ 20 hours                  | 30.39                 |
| YF$_3$:Ce PEG-2000               | 29.21                 |
| YF$_3$:Ce PVP                    | 33.04                 |
| YF$_3$:Ce PEI                    | 38.64                 |
| Na(Y$_{1,5}$Na$_{0,5}$)F$_6$:Ce  | 63.07                 |

As can be seen from the graph of the spectra (figure 2), the emissions of all 3 samples have 2 peaks at $\lambda = 260$ nm and $\lambda = 310$ nm, which corresponds to the 5d-$^2$F$_{7/2}$ and 5d-$^2$F$_{5/2}$ transitions of cerium, respectively. The sample synthesized in ethanol has the highest intensity. The excitation spectra were recorded at $\lambda_{\text{em}} = 260$nm.

For phosphors intended for use in photodynamic therapy, it is important that the half-life is as long as possible. Thus, the time of exposure to X-rays is reduced.

The X-ray luminescence of a YF$_3$:Ce 5%mol. sample was measured. (figure 4d), the shape of the spectrum corresponds to the shape obtained upon UV excitation.

In the course of the experiment, a sample of Na(Y$_{1,5}$Na$_{0,5}$)F$_6$ of the hexagonal phase was also synthesized, since according to the literature data [11], yttrium fluoride is somewhat inferior to it in some characteristics (band gap, half-life, etc.). The photoluminescence spectra of YF$_3$:Ce and Na(Y$_{1,5}$Na$_{0,5}$)F$_6$:Ce are shown in figure 5a. Both samples were synthesized in water and have a cerium concentration of 5% mol. As can be seen, the YF$_3$:Ce sample is inferior to Na(Y$_{1,5}$Na$_{0,5}$)F$_6$:Ce in intensity and has a shorter-wavelength peak $\lambda = 300$ nm.

![Figure 3. X-Ray diffraction patterns with different concentrations of cerium: a – 1%mol.; b – 2%mol.; c – 3%mol.; d – 4%mol.; e – 5%mol.; f – 6%mol.](image-url)
Figure 3 shows X-ray diffraction patterns of yttrium fluoride samples with different cerium concentrations from 1 to 6% mol. As can be seen from the X-ray diffraction patterns, the samples of 1%, 3%, and 4% have an insignificant amount of impurity phases - cubic yttrium fluoride and CeF₂, which dramatically affected the shape of the luminescence peaks (figure 4 a, b). As can be seen from the above spectra, the samples containing the cubic phase of yttrium fluoride differ in the intensity of the emission peaks: the most intense peak is $\lambda = 315$ nm (figure 4b), while the pure orthorhombic phase has the maximum peak $\lambda = 296$ nm (figure 4a). YF$_3$:Ce 5% mol. has the highest intensity among the obtained samples. Figure 4c shows the decay time measurement of this sample, which corresponds to 28.7 ns.

Figure 4. Luminescence characteristics of samples YF$_3$:Ce: a - photoluminescence spectra of YF$_3$:Ce (orthorhombic phase); b - photoluminescence spectra of YF$_3$:Ce samples (orthorhombic phase with an admixture of the cubic phase); c - graph of decay time of YF$_3$:Ce 5% mol. sample; d - X-ray luminescence spectrum YF$_3$:Ce 5% mol. sample.

YF$_3$:Ce with different phase compositions was synthesized as well: cubic and orthorhombic. The photoluminescence spectra are shown in figure 5b. As can be seen, in the case of a sample of the cubic phase, the spectrum is strongly shifted to longer wavelengths and has a noticeably lower luminescence intensity.

We have synthesized a number of samples of undoped YF$_3$ to establish the optimal duration of the synthesis. As a result, it would be possible to obtain yttrium fluoride of the orthorhombic phase. Figure 6 shows X-ray diffraction patterns of YF$_3$ samples synthesized by solvothermal methods in an ethylene glycol medium for different periods of time. The optimal duration is a synthesis time of 16 hours. When synthesizing within 12 hours, it is possible to obtain a cubic phase of yttrium fluoride.
Since the time parameter strongly influences the coalescence of particles, figure 7 shows the growth of YF$_3$ particles over time. Particles with a size of about 100 nm can be obtained at 4 hours without adding stabilizers, but the required phase is reached only after 16 hours of synthesis. Samples synthesized for 16 hours have the smallest crystallite size (see Table 1).

To study the effect of stabilizers on the morphology and size of YF$_3$: Ce particles, samples with various stabilizers were synthesized: polyethylene glycol (PEG), polyethyleneimine (PEI), and polyvinylpyrrolidone (PVP). Figure 8 shows photomicrographs of the respective samples. The optimal shape is often found in the case of polyethylene glycol, while the samples coated with PVP and PEI are generally needle-like or plate-like. In the case of PEI (figure 8 a, b), some particles significantly exceed nanosize and reach 1 μm in length.
Conclusions

As a result of the work done by the solvothermal method, the YF$_3$::Ce$^{3+}$ nanophosphor was synthesized in three ways - in an aqueous medium, in ethylene glycol, and in ethanol.

It was shown that, in contrast to works [5, 12], the duration of solvothermal synthesis can be less than 20 hours, specifically in the range of 16-18 hours.

Compared to synthesis in an aqueous medium, hydrothermal synthesis in an ethylene glycol medium using the PEG-2000 stabilizer allows the synthesis of phosphors with smaller particles (less than 100 nm), which have a high degree of crystallinity, which is more suitable for use in PDT.

In terms of particle size and X-ray luminescence characteristics, the synthesized phosphors YF$_3$::Ce$^{3+}$ and Na(Y$_{1.5}$Na$_{0.5}$)F$_6$:Ce$^{3+}$ are very promising for use in photodynamic therapy of oncological diseases.

References

[1] Xiaojie Wang, Tianqi Sheng, Zuoling Fu, Wenhao Li, Jung Hyun Jeong 2013 *Materials Research Bulletin* **48** 2143–2148.
[2] Y Cui, X P Fan, Z L Hong, M Q Wang, 2006 Nanosci. Nanotechnol. 6 830.
[3] S Sekiyama, M Umezawa, S Kuraoka, T Ube, M Kamimura, and K Soga 2018 Scientific Reports 8 (1)
[4] Y Gu, Q Ran, W She, and J Liu 2017 Advances in Materials Science and Engineering, 13
[5] L. Sudheendra, Gautom K. Das, Changqing Li, Daniel Stark, Jake Cena, Simon Cherry, Ian M. Kennedy 2014 Chem. Mater. 26 1881–1888.
[6] V V Semashko, M S Pudovkin, A C Cefalas et al., 2018 Nanoscale Research Letters 13(1) 370
[7] V V Bakhmetyev, A M Dorokhina, M M Sychov 2018 Izvestia (41)
[8] V V Bakhmetyev, M M Sychev, A I Orlova, E A Potanina, A E Sovestnov, Kulvelis Yu.V. 2013 Nanoindustriya (8) 46-50.
[9] T S Minakova, M M Sychov, V V Bakhmetyev, N S Eremina, S P Bogdanov, I A Zyatikov, L Yu Minakova 2014 Adv. Mater. Res. 872 106–111
[10] V V Malygin, L A Lebedev, V V Bakhmetyev, M V Keskinova, M M Sychov, S V Mjakin, Y Nakanishi 2016 Adv. Intell. Syst. Comput. 519 47–54
[11] A A Blistanov 2000 Crystals of quantum and nonlinear optics M.: MISIS 432 p.
[12] A M Korableva, M K Kaczmarek, and R Van Deun 2019 Nanoscale 11(3) 833–837.