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Synthesis of Upconversion Luminophores Based on Calcium Fluoride

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Abstract

The aim of our study was to synthesize a luminophore based on calcium fluoride doped with rare-earth elements: 5 % Yb and 1 % Er, using the molten salt synthesis method.

NaNO₃ was used as a solvent and sodium fluoride NaF served as the fluorinating agent. The obtained samples were analysed and described using X-ray powder diffraction analysis, energy dispersive X-ray spectroscopy, scanning electron microscopy, and luminescence spectroscopy.

During the study we also investigated the effect of the synthesis conditions on the phase composition and the particles morphology. It was determined that single-phase samples (solid solutions based on calcium fluoride) can only be obtained at a temperature of at least 400 °C, with the optimal exposure time being 3 hours. The composition of the obtained samples was determined. It differs from the nominal composition and can be described as Ca_{0.88}(Yb, Er)_{0.06}Na_{0.06}F₂. It was demonstrated that the parallel insertion of sodium and rare-earth element ions increases the solubility limit of sodium fluoride in calcium fluoride. The luminescence efficiency was 1.21 %.

As a result of this study we obtained a new material with upconversion properties.

Keywords: luminophores, molten salt synthesis, inorganic fluorides, upconversion, nanopowders, rare-earth elements.

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1. Introduction

Anti-Stokes luminescence, or upconversion, occurs when a luminophore, excited by electromagnetic radiation at a certain wavelength, emits radiation with a shorter wavelength and thus with more energy. This phenomenon was independently discovered by V. Ovsyankin and P. Feofilov [1] and F. Auzel [2] in the mid-1960s. Since then, quite

a number of upconversion luminophores have been synthesized. Fluorides are among the most promising classes of compounds used for synthesizing upconversion luminophores. Due to low-energy phonons, their mechanical and optical properties, as well as high isomorphic capacity, fluorides are good host matrices for doping with rare-earth ions. Due to the high upconversion efficiency of luminescence the most commonly used fluoride matrices include hexagonal modifications NaYF₄ [3] and

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NaGdF₄ [4], as well as fluorides of alkaline earth techniques, doped with Yb³⁺, Er³⁺ [3,5–6].

At the moment, there are several common methods for the synthesis of fluorides, including coprecipitation from aqueous solutions [7–8], hydrothermal synthesis [9–10], solvothermal synthesis [5], the sol-gel method [11], mechanochemical synthesis [12], molten salt synthesis [13], combustion synthesis (CS) [6], and thermal decomposition of the precursors [14]. There are also methods which use ionic liquids as fluorinating agents, templates, and reaction media [15–16].

It is still important to search for new upconversion luminophores and develop new synthesis methods. Upconversion luminophores are applied in various areas of science and technology, including biomedicine [17], solar cells production [18], and thermometry [19]. Other applications of upconversion materials include the visualisation of infrared radiation [20] and synthesis of white light luminophores [21].

The aim of this study was to synthesise an upconversion luminophore based on a calcium fluoride matrix with a fluorite structure, doped with rare-earth elements (REE). Since the method of coprecipitation from aqueous solutions has certain drawbacks [6], our aim was also to determine the optimal conditions for the molten salt synthesis of single-phase calcium fluoride powders, doped with ytterbium and erbium. The choice of the concentrations of the doping rare-earth additives (5 mol% of Yb³⁺ and 1 mol% of Er³⁺) was based on the fact that the highest upconversion efficiency of a similar fluorite matrix of SrF₂ was observed, when the concentration range of Yb³⁺ was between 2 mol% and 12 mol%, and of Er³⁺ between 0.25 mol% and 2.25 mol% [3,22].

2. Experimental

The starting materials were: calcium nitrate tetrahydrate Ca(NO₃)₂·4H₂O (Lanhit®, 99.99 %), yttrium(III) nitrate hexahydrate Yb(NO₃)₃·6H₂O (Lanhit®, 99.9%), erbium nitrate pentahydrate Er(NO₃)₃·5H₂O (Lanhit®, 99.99 %), sodium nitrate NaNO₃ (Chimmed Group, CP), and sodium fluoride NaF (Lanhit®, P.A.). All the substances were used without additional purification.

The samples were obtained by molten salt synthesis [13]. First, the weighed quantities of hydrates of calcium nitrate and REEs were

homogenized in an agate mortar. Then, sodium nitrate was added to the mixture. It acted both as a solvent and the medium for the chemical reaction. Next, sodium fluoride was added, which acted as a fluorinating agent. The mixture was homogenized, put into a glazed porcelain crucible, covered, and annealed at a temperature of 300 or 400 °C for 1 or 3 hours. After the crucible cooled down, the reaction mass was taken out and put in a polypropylene reactor, where the nitrates were washed off the samples. The reactor is filled with 900 ml of double distilled water. Next, the anchor of the magnetic stirrer was put inside the reactor, and the mixture was stirred for 30 minutes. The presence of nitrate-ions was determined by the qualitative reaction with diphenylamine. It was usually enough to wash the samples three times to remove the nitrates. After the last washing the samples were dried in air at the temperature of 60 °C for 4 hours.

The characterisation of the obtained samples was performed using the X-ray powder diffraction analysis (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), and luminescence spectroscopy. The XRD analysis was performed using a Bruker D8 Advanced diffractometer (Germany) with CuK α radiation. The obtained diffraction pattern were analysed using DifWin and Powder2.0 software packages ($\Delta Q < 10$). The size of the particles and the morphology of the samples were studied by means of SEM using a Carl Zeiss NVision 40 scanning electron microscope (Germany) with an Oxford Instruments XMAX microprobe analyser (UK) (80 mm²) for energy dispersive X-ray spectroscopy. The spectroscopic analysis included registering the spectra of upconversion luminescence and diffusely scattered laser radiation within the range of 300–1000 nm, and calculating the upconversion efficiency of upconversion luminescence. In order to conduct the measurements we used a combination of the fibre optic spectrometer LESA-01-BIOSPEC (BIOSPEC, Russia) with the UnoMomento software package, and a modified integrating sphere (Avantes, the Netherlands) connected by fibre-optic light carriers [23].

To carry out the measurements, the powder sample placed between two cover slips was put inside the integrating sphere. The radiation

of the diode laser (974 nm wavelength) was focused on the sample so that the power density on the surface of the sample was 1 W/cm². The integrating sphere had been preliminary calibrated with LEDs of various wavelengths and known power, measured with a LabMax[®]-TO (Coherent, USA) [24]. The scattered laser radiation and upconversion luminescence were captured by optic fiber and transmitted to the spectrometer. The upconversion luminescence efficiency was calculated using the formula

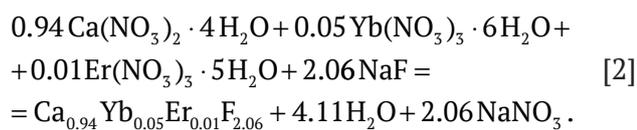
$$EQ = \frac{P_e^S}{P_{974_ab}^S} = \frac{P_e^S}{P_{974_sc}^R - P_{974_sc}^S}, \quad (1)$$

where P_e^S is the radiation power of the sample in the visible range, $P_{974_ab}^S$ is the laser power absorbed by the sample.

The latter is calculated as the difference between $P_{974_sc}^R$ – the power of the scattered radiation of the non-absorbing reference sample and $P_{974_sc}^S$ – the power of the scattered radiation of the studied sample.

3. Results and discussion

In our study the synthesis was performed several times. The nominal composition of sample No. 1 was pure calcium fluoride. The other experiments were conducted in order to synthesise samples with the nominal composition $\text{Ca}_{0.94}\text{Yb}_{0.05}\text{Er}_{0.01}\text{F}_{2.06}$, using the equation:



The conditions of the synthesis process and the actual yield are given in Table 1.

The X-ray diffraction patterns of the synthesised samples are shown in Fig.1. The calculated lattice parameters and the size of coherent scattering regions (CSR) are given in Table 2.

The peaks of the cubic phase were indexed on all the XRD patterns. They correspond to the cubic fluorite phase of calcium fluoride (JCPDS card No. 35-0816). Samples No. 2 and 3, in addition to the cubic phase, demonstrated the peaks of the hexagonal phase. The XRD patterns of samples No. 4 and 5 demonstrated five peaks. A (200) peak appeared, which was suppressed in case of pure calcium fluoride. A broadening of the cubic phase peaks was observed. The size of the CSRs was calculated according to the Scherrer equation.

The lattice parameters of the cubic phase of samples No. 2 and 3 coincide with the parameters of pure calcium fluoride $a = 5.463 \text{ \AA}$. Samples No. 4 and 5 are single-phase. The lattice parameters of their cubic phases should increase, since their unit cells contained ions of rare-earth elements [25]. However, the lattice parameters of samples No. 4 and 5 are lower than the lattice parameters of pure CaF_2 . This means that the crystal lattice was intercalated with ions with smaller ionic radii, which is quite possible, since there was a lot of sodium in the system. According to the EDX results presented in Table 3, there actually was sodium in the samples, and its amount is comparable to the number of rare-earth ions. The concentration of erbium is within the margin of error for the EDX method.

Table 1. Synthesis conditions and actual yield

Sample No.	Sample code	Annealing temperature, °C	Annealing time, hours	Concentrations of the starting materials, mol. (M, Ln)(NO ₃) _x : NaF:NaNO ₃	Actual yield, %
1	F1804	300	1	1:3:2	87.0
2	F1814	300	1	1:3:2	86.2
3	F1826	300	3	1:3:2	91.2
4	F1699	400	1	1:3:10	77.2
5	F1836	400	3	1:3:2	76.0

Table 2. The results of the XRD analysis

Sample No.	Lattice parameter a (cubic phase), Å	CSR size, nm
1	5.460(1)	32
2	5.463(2)	24
3	5.464(1)	24
4	5.452(1)	23
5	5.455(1)	41

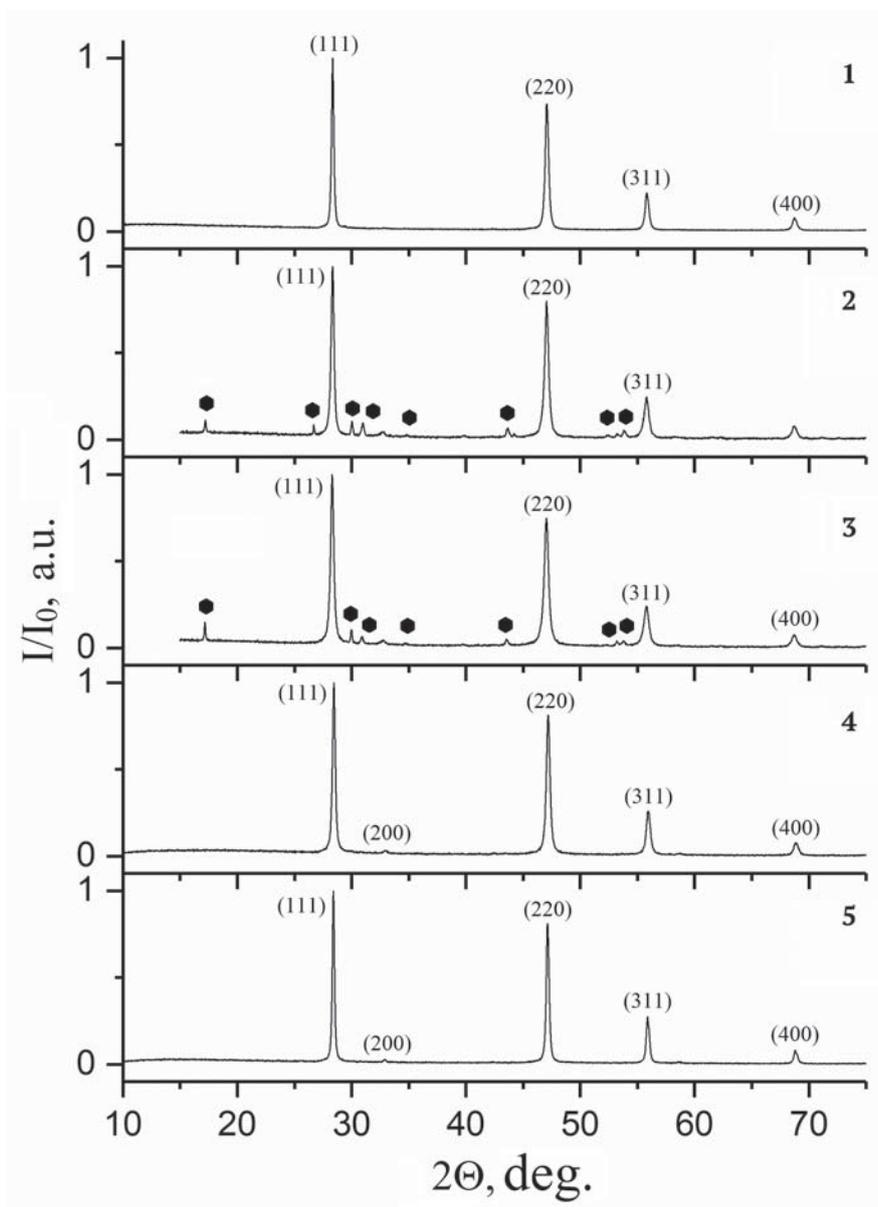


Fig. 1. Results of the XRD analysis. Dots denote the peaks of the hexagonal NaYF_4 phase. Sample numbers are the same as in Table 1

Table 3. The EDX results, in atomic percent

Sample No.	Na, at. %	Ca, at. %	Yb, at. %
4	6	88	6
5	6	88	6

Thus, the composition of the single-phase samples is different from the nominal composition. Certain lattices contained sodium, which was inserted together with REEs. Isomorphic substitutions can be represented as



where $\text{Ln} = \text{Yb}, \text{Er}$. This kind of joint intercalation means that the sodium ions had an in-

creased solubility limit. The maximal solubility in the system $\text{NaF} - \text{CaF}_2$ is 2.2 mol. % [26]. Heterovalent isomorphism of this type is common for $\text{NaF} - \text{CaF}_2 - \text{LnF}_3$ systems [27–28].

SEM photographs of samples No. 3, 4, and 5 and their resolutions are given in Figures 2–4.

Fig. 2 shows a rod-like particle, several microns in size, with a hexagonal cross-section surrounded by an agglomeration of particles (a few dozen nanometres) with no definite faceting, which implicitly confirms that sample No. 3 is two-phase. Microphotographs in Fig. 3 and 4 demonstrate the morphological homogeneity

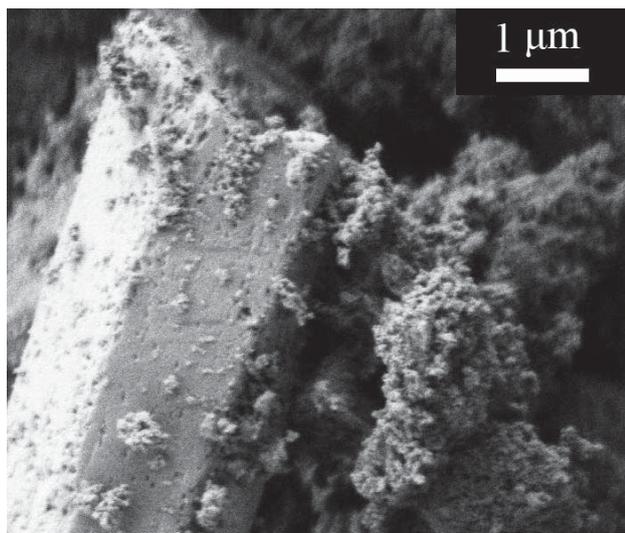


Fig. 2. SEM photograph of sample No. 3

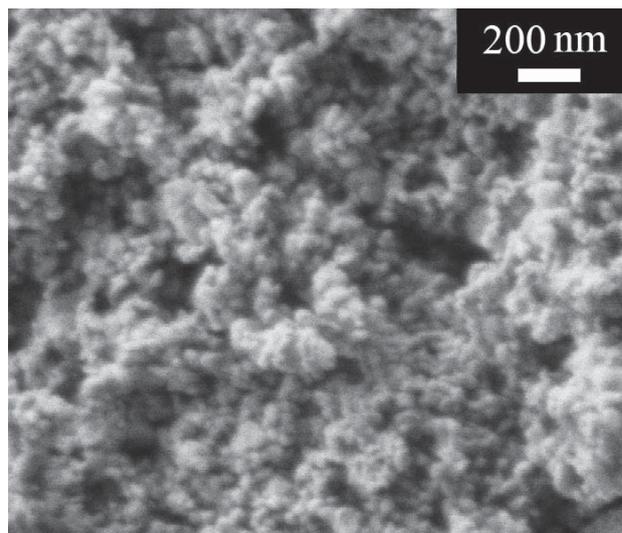


Fig. 3. SEM photograph of sample No. 4

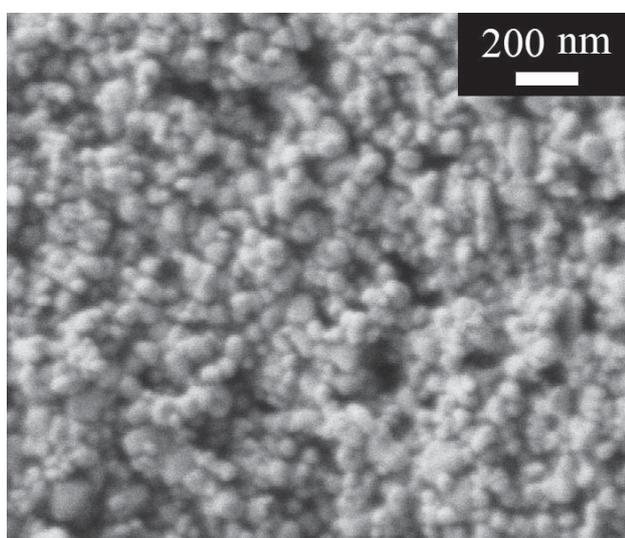


Fig. 4. SEM photograph of sample No. 5

and high dispersion of particles in samples No. 4 and 5. The particles in sample No. 5 are larger than those in sample No. 4, which complies with the calculations of CSR size. The average size of the particles in both samples is below 120 nm.

The luminescence spectra of samples No. 4 and 5 are given in Fig. 5.

The luminescence spectra of the samples show green (510–575 nm) and red (625–670 nm) bands, corresponding to the radiative transitions of the erbium ions ${}^2\text{H}_{11/2}, {}^4\text{S}_{3/2} \rightarrow {}^4\text{I}_{15/2}$ and ${}^4\text{F}_{9/2} \rightarrow {}^4\text{I}_{15/2}$. The upconversion efficiency was 0.02 % for sample No. 4, and 1.21 % for sample No. 5. The difference in the values of upconversion efficiency may be accounted for by the larger size

of the particles in sample No. 5 (resulting from the longer synthesis), which leads to the decrease in the surface area to volume ratio.

The obtained results lead to several conclusions. First, when the temperature is 300 °C, two-phase samples are formed. At higher temperatures the hexagonal phase NaLnF_4 disappears from the reaction system. According to the XRD results, the samples obtained at 400 °C are single-phase. Also, the calculated lattice parameters are lower than those of calcium fluoride, even though their crystal lattices were intercalated with REE ions. Our assumption that the lattice contained sodium ions was confirmed by the EDX results. The concentration of sodium is comparable to the concentration of Yb^{3+} and Er^{3+} . Thus, while developing the technology, we obtained a new material $\text{CaF}_2:\text{Na}^+, \text{Yb}^{3+}, \text{Er}^{3+}$ with upconversion properties.

Second, the SEM analysis allowed us to describe the morphology of the particles of single-phase powders. The particles are spherical, highly homogeneous, and have particle size distribution within a narrow range. When the samples are annealed for a longer time, the particles continue growing, and their size reaches 60–120 nm. This results in a higher volume to surface area ratio, and hence increased luminescence.

The luminescence spectra confirm the upconversion properties of the material. When excited with IR laser at a wavelength of 974 nm, the material demonstrates two luminescence bands in the visible range: in the green and

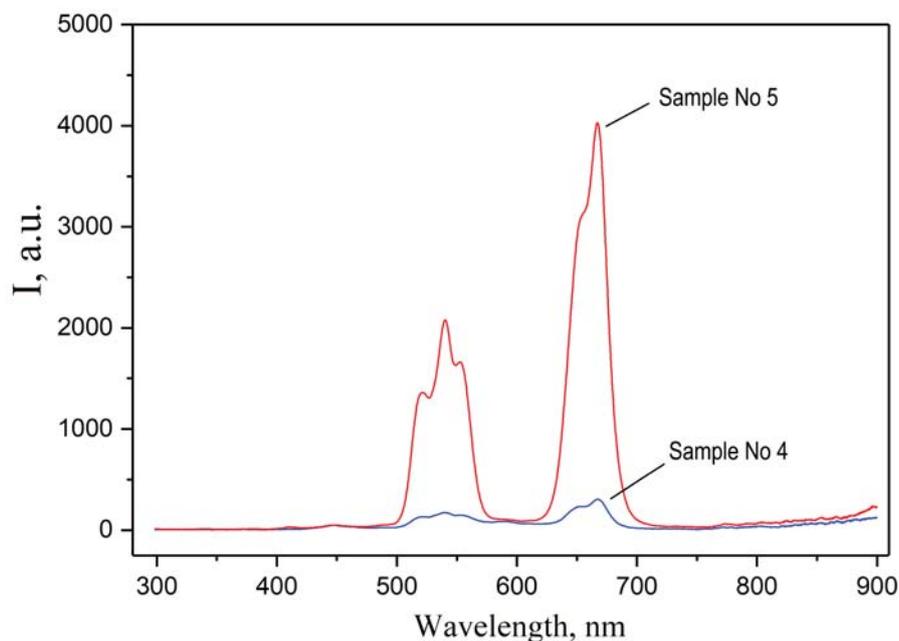


Fig. 5. Luminescence spectra of samples No. 4 and 5. The wavelength of the pumping laser is 974 nm

red spectra. The upconversion luminescence efficiency of the samples is lower than that of a similar material obtained by coprecipitation from aqueous solutions: 1.21 % as compared to 3.11 % [8]. This is partly accounted for by the insertion of sodium in the crystal lattice. Nevertheless, the molten salt synthesis method has a number of advantages. For instance, the pyrohydrolysis process is slower, and the EDX results confirm that the samples do not contain oxygen. The molten salt synthesis is also easy to perform, does not involve dangerous reagents, such as hydrofluoric acid, and there is no need to reconstruct the precise synthesis conditions to reproduce the results. Also, the adsorbed water can be removed without further thermal treatment.

4. Conclusions

During our study, we determined the conditions for the synthesis of calcium fluoride powder doped with ytterbium and erbium ions with upconversion properties. We obtained a single-phase sample with the composition $\text{Ca}_{0.88}(\text{Yb}, \text{Er})_{0.06}\text{Na}_{0.06}\text{F}_2$, which differs from the nominal. It was determined, that the crystal lattice of the obtained solid solution included sodium ions. The joint intercalation of sodium and REE ions increases the solubility limit of sodium fluoride in calcium fluoride up

to 6 mol. % against 2.2 mol. %, as determined by previous studies. The study demonstrated that the synthesis conditions influence the morphology and phase composition of the particles. Two-phase samples are obtained at 300 °C ($\text{CaF}_2 + \text{NaLnF}_4$), and single-phase samples at 400 °C. The size of the particles increases with longer annealing time. The obtained sample demonstrates upconversion properties. When pumped with 974 nm wavelength laser, green and red luminescence bands are detected. Due to its upconversion luminescence properties, the obtained material can find various applications in biomedicine.

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Conflict of interests

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

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