

Spectroscopic studies of nanofluorides doped with Ln³⁺ synthesized *via* thermal decomposition of organic precursors

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Abstract. The results of recent investigation of wide band-gap luminescent cubic NaYF₄ nanocrystals doped with the optically active rare earth ions, RE=Pr, Eu, Er, as the converters of VUV radiation into visible emission, are presented. The materials have been synthesised by the thermal decomposition of the alkaline metals trifluoroacetate and lanthanide trifluoroacetate precursors. The high-boiling octadecene was selected as the growth medium for the nanoparticles and oleic acid were employed as the surfactant. Crystal structures of the compounds have been confirmed by X-ray diffraction powder diffraction. The morphology study of the materials was performed by Transmission electron microscope. The spectroscopic properties of the crystals have been determined based on excitation and emission spectra recorded in the UV–VIS–NIR spectral region. The optical and morphological properties of material have been presented and discussed.

1. Introduction

There has been a growing demand for quantum cutting and upconverting efficient nano luminescent materials during the last decades. Wide band gap luminescent materials, especially the fluorides, are one of the major role players. Due to a number of advantages such as the excellent transparency in the infrared (IR) to far ultraviolet (UV) range and low-energy phonons as well as low toxicity they have recently gathered considerable attention for their potential applications in bioimaging, disease detection and diagnostics. The same group of materials having downconversion characteristics can be applied for the improvement of solar cell efficiency in the quantum cutting processes.

2. Experimental

2.1. Synthesis of Nanocrystals NaYF₄:RE³⁺

Nanocrystals of NaYF₄:RE³⁺ (NC) were synthesized using a thermal decomposition method. First, the trifluoroacetates of selected rare earths were prepared. The lanthanide trifluoroacetate precursors were prepared from the corresponding lanthanide oxides and trifluoroacetic acid in the environment of butanol. The corresponding amount of sodium trifluoroacetate and RE (III) trifluoroacetates was added to the reaction vessel with octadecene and oleic acid. The mixture of sodium trifluoroacetate and oleic acid (90%, technical grade) in molar ratio 1:50 and corresponding amount of 1-octadecene (90%) were mixed in the three-necked flask. The resulting solution was then stirred and heated for 30 min at 120 °C. During this time the flask was purged with dry argon to remove water and oxygen. The

solution was then heated to 300 °C at a rate of about 10 °C per minute under argon gas protection and kept at this temperature under vigorous stirring for 2 h. A capillary was used to let the argon gas in and out during the synthesis. The mixture was cooled to room temperature. The nanoparticles were isolated via centrifuge at 3000 rpm after prior adding the absolute ethanol. The resulting precipitate was then washed several times with ethanol and isolated via centrifuge at 3000 rpm each time. The nanoparticles were stored in the ethanol and centrifuged for experiments if needed.

2.2. Structure and morphology.

The size and morphology of the nanocrystals were characterized by transmission electron microscopy (TEM) using a Philips CM100 microscope. The powder X-ray diffraction (XRD) patterns were recorded with a Bruker D8 ADVANCE diffractometer using Cu K α radiation (0.15418 nm). The 2 θ angle of the XRD spectra was recorded at a scanning rate of 1.2°/min.

2.3. Spectroscopic techniques.

The measurements of the luminescence excitation and emission spectra were performed at the Deutsches Elektronen Synchrotron (DESY, Hamburg) using the facility of the SUPERLUMI station at HASYLAB22. The luminescence spectra at room temperature and at 10 K were measured within the 300-1000 nm spectral range using 0.3 m (Acton Research Corporation) Spectra Pro308 monochromator-spectrograph in Czerny-Turner mounting equipped with a liquid nitrogen cooled (Princeton Instruments, Inc.) CCD detector. Spectral resolution of the analyzing monochromator was ~0.5 nm. The emission spectra were not corrected for the detector sensitivity and monochromator transmission. High resolution time-resolved luminescence excitation spectra were scanned within 60-300 nm with the primary 2 m monochromator in 15° McPherson mounting (3.2 Å resolution) using (Hamamatsu R6358P) a PMT detector with a secondary ARC monochromator. The excitation spectra were corrected for the incident photon flux compared to that of a reference sample of NaSal whose quantum efficiency is assumed to be about 58% and is constant over the excitation wavelength range from 4 to 25 eV¹. The temperature could be varied between 8 and 300 K by means of a liquid-helium cryostat (Cryovac GmbH).

3. Results

3.1. Morphology and structure results.

The morphology of the materials was evaluated by the TEM. **Figure 1** shows the TEM images of NaYF₄:RE nanocrystals synthesized by thermal decomposition of trifluoroacetates precursors.

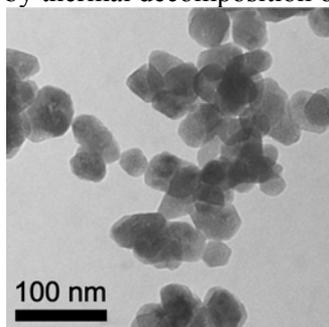


Figure 1. TEM images of NaYF₄:RE powders displaying uniformity of the particles.

The synthesized nanoparticles are equiaxed and clearly faceted which in turn is a good indication of their crystallinity. The crystallinity of the synthesized nanoparticles has been subsequently confirmed by powder XRD. The obtained nanocrystals belong to the cubic system, space group Fm $\bar{3}$ m. The diffraction patterns presented in **Figure 2** disclose reflexes which can be assigned to the (111), (002), (022), (113) (004) (133) and (224) of the (hkl) planes of the standard ICSD-60257 cubic NaYF₄.

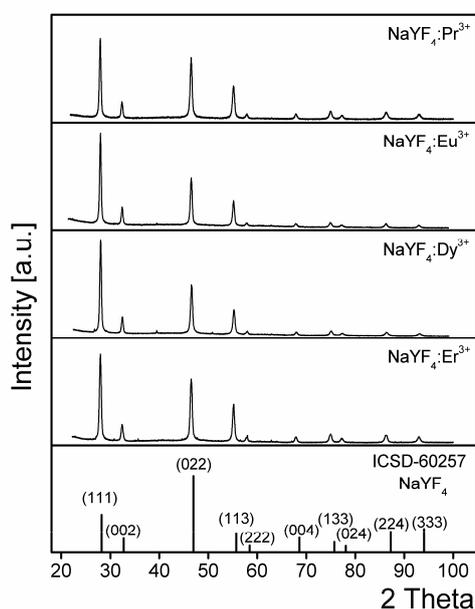


Figure 2. X-ray powder diffraction pattern of NaYF₄ nanocrystals doped with RE³⁺ ions compared with the pattern generated based on the monocrystal NaYF₄ cubic structure ICSD-60257 standard.

The pattern generated based on cubic NaYF₄ monocrystal data from ICSD-60257 is shown for comparison (the bottom of **Figure 2**). It is evident that the prepared nanomaterial is highly crystalline. The positions of the XRD peaks correspond to the standard ICSD-60257 cubic pattern of NaYF₄ and no peaks from other phases or impurities have been observed. The XRD peaks have very broad widths originating from the size effect. The average crystallite size of the nanocrystals was calculated according to the Scherrer's equation.

$$D = K\lambda / \beta \cos \theta \text{ (eq 1)}$$

where D is average crystal size (in nanometers), $K=0.89$, λ is the wavelength of the Cu K α radiation equal to 0.154 nm, β is the full width at half maximum of the diffraction peak ($\text{FWHM } 2\theta = 0.392 = \text{FWHM } \theta = 0.196 = 0.0034$ radians) and θ is Bragg's angle of the diffraction peak. For our calculations the most intense peak at 2θ equal to 28° , giving Bragg θ equal to 14° , was taken. According to equation (eq 1) the average nanocrystal size was calculated to be about 42 nm, which is consistent with the TEM results.

3.2. Spectroscopic results and discussion

Figure 3A presents the room temperature excitation spectrum monitoring the 396 nm $^1S_0 \rightarrow ^1I_6$ transition of Pr³⁺ in NaYF₄ nanocrystals. The intensity of the $^1S_0 \rightarrow ^1I_6$ transition is increasing for incident photons with energy corresponding to around 210 nm wavelength where the onset of interconfiguration $4f^2 \rightarrow 4f^5d$ transitions begins. The $^1S_0 \rightarrow ^1I_6$ luminescence increased with changing the wavelengths of excitation up to a maximum at 180 nm. There is no evidence of any transfer from matrix to the $4f5d$ configuration which can increase the luminescence intensity of $^1S_0 \rightarrow ^1I_6$ transitions. In the luminescence spectrum presented in Figure 3B nine bands are clearly resolved; having maxima at 249, 269, 334, 396 nm assigned to $^1S_0 \rightarrow ^3H_6$, 3F_4 , 1D_2 , 1I_6 transitions and at 482, 530, 600, 636 nm which correspond to $^3P_0 \rightarrow ^3H_4$, 3H_5 , 3H_6 , 3F_2 , $^3F_{3,4}$ transitions of the Pr³⁺ ions, respectively.² When Pr³⁺ ions are excited into the $4f5d$ configuration, firstly relaxation from the lowest $4f5d$ level to the 1S_0 level takes place. It is followed by a photon cascade emission, i.e. the emissions of $^1S_0 \rightarrow ^1I_6$ and followed by the emission of $^3P_0 \rightarrow ^3H_J$, 3F_J .

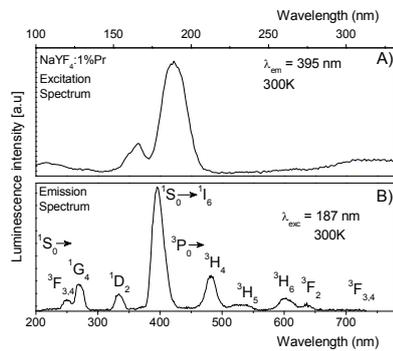


Figure 3. Excitation and emission spectrum of NaYF₄:1%Pr NC.

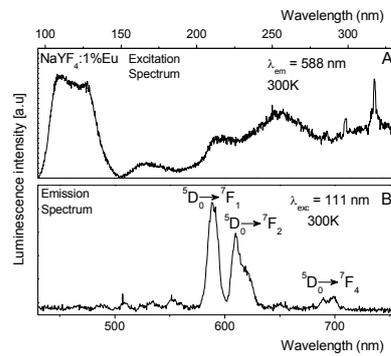


Figure 4. Excitation and emission spectrum of NaYF₄:1%Eu NC..

The excitation spectrum monitoring the $^5D_0 \rightarrow ^7F_1$ emission is presented in Figure 4A. In the region above 150 nm the spectrum is dominated by the broad band which origin can be ascribed to the absorption of NaYF₄ nanocrystals matrix overlapping with the *fd* band which can be close to the host lattice absorption edge which was previously observed in LiYF₄.³ The broad band observed in the region 150 to 200 nm with a maximum at 166 nm is assigned to the fluoride-europium charge-transfer band. The origin of the broad bands in the region 200 -300 nm where ascribed to the defect and the contaminations of the nanocrystals by the surfactant used for synthesis. Interesting is the observation that they also transfer the energy to the optically active centers and feed the emission from the 5D_0 level. In Figure 4B the luminescence of NaYF₄:Eu³⁺ nanocrystals is presented The main emissions channels are $^5D_0 - ^7F_1$ and $^5D_0 - ^7F_2$ but in the region 450 to 550 nm very weak transitions with the origin of 5D_1 and 5D_2 are also observed.

Figure 5A presents the VUV excitation spectrum of $^4F_{9/2}$ to $^6H_{13/2}$ emission of Dy³⁺ in NaYF₄ nanocrystals. The edge of the matrix absorption is evident at the 125 nm, the band responsible for matrix absorption similar to this one presented in the Er excitation picture was removed for the clarity. In this spectrum the lowest LS *fd* transition of Dy³⁺ is observed at the 175 nm. Its structure is very similar to the transitions of Dy³⁺ observed in the LiYF₄ crystals.⁴ The expected *fd* HS high-spin transitions of Dy³⁺ around 190 nm are fully covered by the intense broad band transitions originating from the traces of surfactant-covered nanoparticles. Figure 5B presents the emission spectrum of NaYF₄: 1%Dy NCs measured after excitation of the band gap at 91 nm which was registered at room temperature. In the spectrum the four Dy³⁺ bands are clearly resolved; having maxima at 477, 573, 663, 754 nm, assigned to $^4F_{9/2} \rightarrow ^6H_{15/2}$, $^6H_{13/2}$, $^6H_{11/2}$ and $^6H_{9/2} + ^6F_{11/2}$ transitions.

In Figure 6A the excitation spectrum of $^4S_{3/2} \rightarrow ^4I_{15/2}$ in NaYF₄ doped with Er³⁺, registered at 10 K is presented. In the spectrum the host lattice absorption at wavelengths shorter than 120 nm is clearly seen. The energy from the matrices is efficiently transferred to the luminescence levels of Er³⁺ and has determined the main channel of the excitation of $^4S_{3/2} \rightarrow ^4I_{15/2}$ emission. In the excitation spectrum the bands in the region 120 - 300 nm are not well resolved and do not show the fine structure. In the emission spectrum in Fig.5B the main emissions are due to the Er³⁺ $^2P_{3/2} \rightarrow ^4I_{13/2}$, $^4I_{11/2}$, $^4I_{9/2}$ transitions (399, 467 and 521 nm) and $^4S_{3/2} \rightarrow ^4I_{15/2}$ transition (around 550 nm). The lines around 525 nm can be partly due to the emission from the $^2H(2)_{11/2}$ state, which lies just above the $^4S_{3/2}$ level and

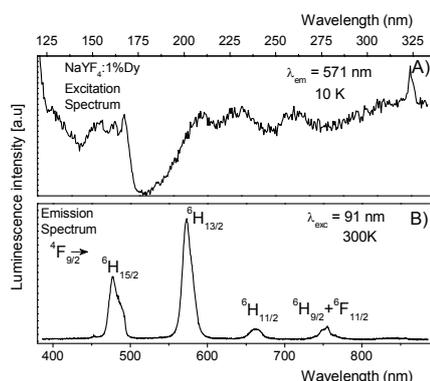


Figure 5. Excitation and emission spectrum of NaYF₄:1%Dy NC.

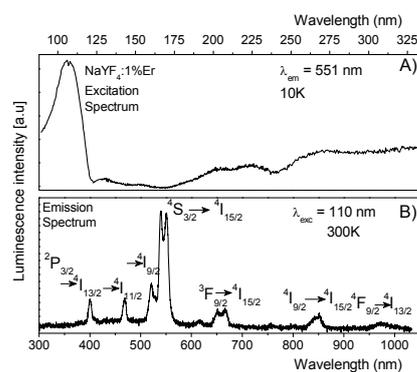


Figure 6. Excitation and emission spectrum of NaYF₄:1%Er NC.

being thermally populated at room temperature, as well as from the ${}^2P_{3/2}$ level. In the spectrum we can also observe the transitions ${}^4F_{9/2} \rightarrow {}^4I_{15/2}$ and the transitions within ${}^4I_{9/2} \rightarrow {}^4I_{15/2}$ and ${}^4F_{9/2} \rightarrow {}^4I_{13/2}$. The band assignments were done based on the previously studied YAlO₃ and LiGdF₄ systems.⁵⁻⁶

4. Conclusions.

The crystalline nanocrystals of the NaYF₄ doped with RE were successfully synthesized by thermal decomposition of trifluoroacetates precursors. The size and the crystallinity of the particles were confirmed by the TEM and XRD techniques. The luminescence characteristics of prepared nanoparticles were studied. In the case of the NaYF₄:1% Pr the quantum-cutting (QC) effect on the photoluminescent (PL) spectra of colloidal NaYF₄ nanocrystals doped with 1% Pr³⁺ ions has been clearly evident under interconfiguration $4f^2 \rightarrow 4f5d$ excitation. The main channel of luminescence is around 396 nm which originates from the ${}^1S_0 \rightarrow {}^1I_6$ transition being responsible for the feeding of the photon cascade. The surfactant influence has been evident in all the samples causing the difficulty in the proper interpretations of the spectroscopic results.

References

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