

Luminescence decay of Sm:LaF₃@LaF₃ core-shell crystalline nanoparticles

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Abstract. Luminescent properties in visible spectral range of crystalline LaF₃ nanoparticles containing 1 % and 5 % of Sm³⁺ ions before and after microwave hydrothermal treatment and also Sm:LaF₃@LaF₃ core-shell nanoparticles were studied. The LaF₃ surface layer resulted in lowering the luminescence decay time apparently due to eliminating surface quenching factors. This opens the way to manage luminescence and energy transfer properties of the material.

1 Introduction

Crystalline nanoparticles of LaF₃ compound, doped with various rare-earth ions are of great interest today for unique combination of optical and physical properties. Depending on luminescence and excitation spectral ranges of action these materials are prospective in bioimaging, lamp phosphors, quantum cutting, up-conversion, luminescent material for combined photodynamic therapy [1,2]. Composite materials based on these nanoparticles can be utilized as elements for quantum devices. Aim of this work is to study opportunities to manage luminescence decay properties of Sm³⁺ ions in LaF₃ nanoparticles by chemical approach.

2 Experimental

Crystalline Sm:LaF₃ nanoparticles were fabricated via co-precipitation method described earlier [3,4]. Nanoparticles of Sm:LaF₃ (C_{Sm} = at. 1 %, C_{Sm} = at. 5 %, samples N1 and N2 respectively) were used in experiments after washing and drying directly after synthesis. The hydrothermal treated (60 minutes exposure in the microwave oven) samples were prepared as it can improve crystallinity of the particles (sample N3). Also the approach of core-shell was tested. The sample of N2 was dispersed in distilled water by sonication treatment. Then 1.2 mmol of NH₄F was added into suspension. Then the solution was heated to 50 °C, and stirred for 15 min and the 0.4 mmol of La(NO₃)₃·was introduced to it. The prepared suspension was placed into the microwave oven for 60 minutes. The following procedures of washing and drying were the same as that was stated for previous samples.

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3 Results and discussion

Luminescence spectra of all Sm:LaF₃ samples registered under 405 nm excitation contain well known lines of transitions from ⁴G_{5/2} state to ⁶H_J terms (see Fig. 1a).

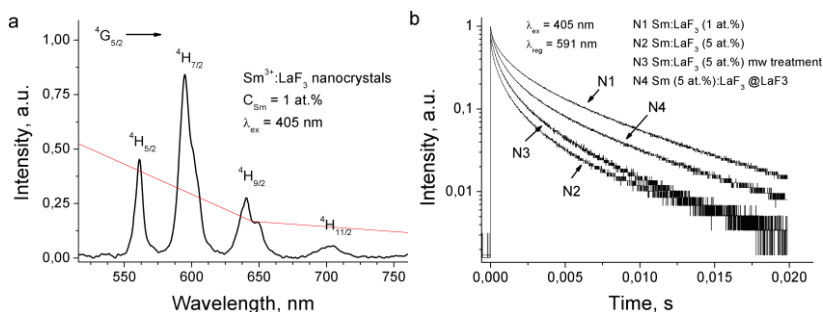


Fig.1. Room temperature luminescence spectrum (a) and luminescence decay curves (b) of LaF₃:Sm nanoparticles dried sample under 405 nm excitation.

Changes in preparation method have found reflection in luminescence decay of the samples. The decay curves of all four samples of Sm:LaF₃ nanoparticles are presented in Figure 1b. All samples of Sm:LaF₃ nanocrystals have exhibited non-exponential decay which is common for nanoparticles due to large surface to volume ratio and significant amount of surface perturbed sites [5] and which empirically can be divided into fast and slow components. The results of two-exponential fitting are presented in Table 1.

Table 1. Luminescence decay components of Sm:LaF₃ nanoparticles samples.

	N1 (C _{Sm} 1%)	N2 (C _{Sm} 5%)	N3 (C _{Sm} 5% microwaved)	N4 (C _{Sm} 5% core-shell)
t1, ms	4.79±0.02	3.27±0.02	3.33±0.02	4.26±0.02
t2, ms	0.85±0.02	0.67±0.02	0.66±0.02	0.77±0.02

The decay of heavier doped sample N2 is faster both in slow and fast components as it should be due to concentration quenching. Existence of LaF₃ shell lowers the decay times back apparently due to covering impurity sites at the surface thus eliminating surface quenching factors. The microwave treatment of nanoparticles on the contrary has not introduced any effect in implemented conditions which can speak for deficient fluorination or exposition during reaction.

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