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Synthesis and luminescence properties of Eu^{3+}-doped $LaAlO_3$ nanocrystals

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Abstract

The preparation, morphology and structural properties of Eu^{3+}-doped $LaAlO_3$ nanocrystallites based on Pechini's method is presented. The annealing temperature and Eu-ion content on the forming process of nanocrystallites is investigated. Preliminary studies on the size effect of the $LaAlO_3$ nanocrystallites on the luminescence properties of Eu-ions are done. The time resolved luminescence spectra and decays were recorded for powders characterized by a different size of grains. The effect of nanocrystallite sizes on the radiative relaxations of Eu^{3+} luminescence was found.

Keywords: Nanostructures; Sol–gel synthesis; Luminescence; Time-resolved optical spectroscopy

1. Introduction

The powders of rare earth (RE) doped nanocrystals are considered as efficient hosts for full-color phosphors [1,2]. Recently, a lot of new low-temperature synthesis methods of such materials based on various wet-chemical processes have been reported. In this work we present the preparation, morphology and structural properties of rare earth ions (RE)-doped $LaAlO_3$ nanocrystallites based on sol–gel derived Pechnini's method [3]. Our interest was primarily concerned with the studies on luminescence properties of the fine nano-sized crystallites of perovskite $LaAlO_3$ type doped with RE ions for application in optoelectronic systems.

2. Results and discussion

Stoichiometric amounts of lanthanide and aluminum salts were dissolved in aqueous citric acid and ethylene glycol solution to give an appropriate molar ratio. The hydrous salt of the Eu was added in the homogeneous solutions to give a different nominal Eu:La atomic ratios in range 0.5–10%. All solutions were stirred for 2 h at room temperature. Then a mixture of substrates was heated at 80 °C for several hours and dried at 110 °C during the period of 3 days in order to obtain gels. Samples of the crushed gel were heat-treated in range 800–1100 °C in the air conditions in an electric oven. The structure of all prepared samples was confirmed by the X-ray diffraction (filtered Cu $K\alpha_1$ radiation) as $LaAlO_3$ perovskite with $R3m$ space group (PDF 31-0022) (Fig. 1a). The averaged sizes of crystallites were estimated from the broadening of diffraction peaks by the well-known Scherrer's formula [4]. The results are shown in Fig. 1b. The obtained values were in agreement with results of measurements performed by TEM (the picture of sample annealed at 900 °C is shown in Fig. 2).

The time-resolved emission spectra measured at RT for the sample of $LaAlO_3$ after annealing at 800 °C ($D = 32$ nm) are shown in Fig. 3. The energies of observed bands corresponding to $^5D_J \rightarrow {}^7F_J$ transitions were found to be similar as for the bulk crystal of $LaAlO_3$:Eu^{3+} [5]. No distinct changes were recorded for the samples annealed at higher temperatures. One can note that even for the smallest nanocrystallites

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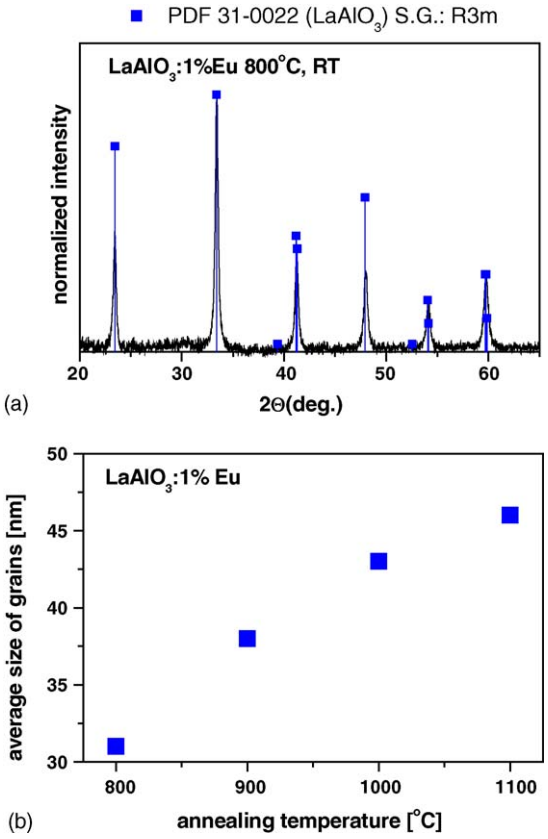

Fig. 1. X-ray pattern (a) and average sizes of grains for sample of $LaAlO_3$ after different annealing temperature (b).

we have observed the luminescence originating not only from $^5D_0$ but also from $^5D_1$, $^5D_2$ and $^5D_3$ levels. The luminescence from higher emissive states ($^5D_{3–1}$) was quenched faster compared to the $^5D_0$ state. The stronger luminescence quenching of the upper lying ^5D_J ($J = 1, 2, 3$) levels is due to the concentration quenching by the cross-relaxation processes [6] (for example, $(^5D_1 \rightarrow {}^5D_0) \leftrightarrow (^7F_0 \rightarrow {}^7F_3)$ or $(^5D_2 \rightarrow {}^5D_0) \leftrightarrow (^7F_0 \rightarrow {}^7F_5)$). Besides the concentration quenching the luminescence from all emitting levels can be quenched also by high energy phonons leading to the fast multiphonon relaxations [7]. The observed emission for the sample doped with 1% of Eu versus La atoms can point on the

Fig. 2. TEM picture for the sample of $LaAlO_3$ obtained at 900 °C.

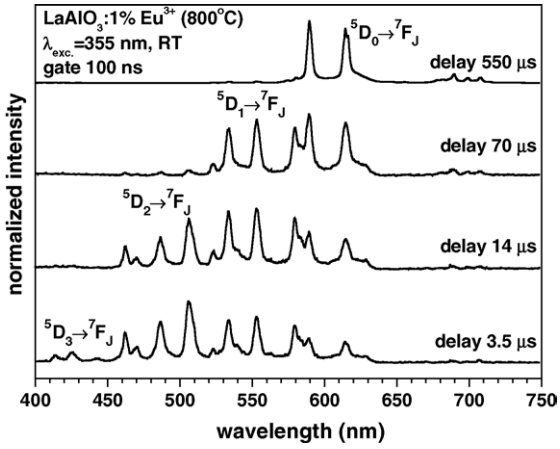

Fig. 3. Time-resolved spectra recorded for sample $LaAlO_3$:1% Eu annealed at 800 °C.

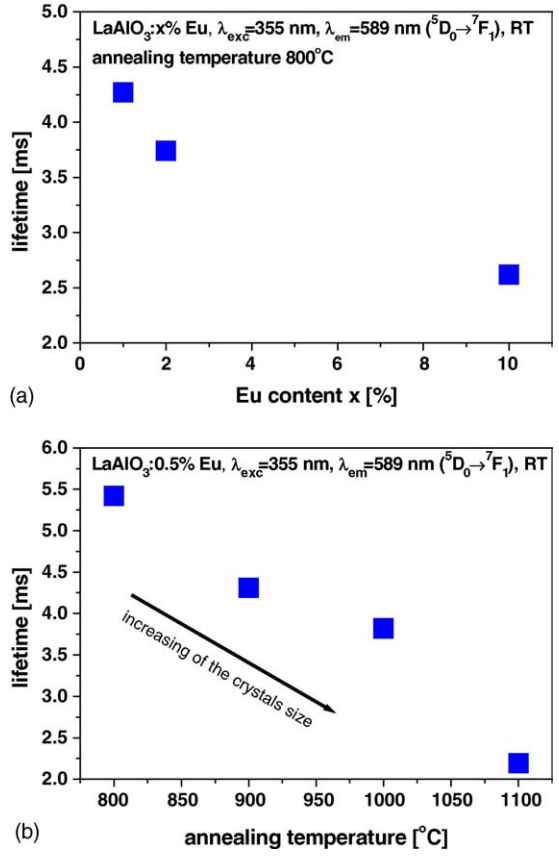

Fig. 4. The dependence of fluorescence lifetimes on the Eu concentration (a) and on the nanocrystal size (b).

high homogeneity and arrangement of Eu^{3+} ions in nanocrystals. For the more detail analyze of concentration effects on the luminescence behavior in the smallest nanocrystals the luminescence decays of the samples doped with different content of dopant prepared at 800 °C were measured at room temperature. The decay curves of $^5D_0$ emission were well fitted by exponential function. The values of lifetimes for three concentrations of Eu ions (1, 2 and 10%) are shown in Fig. 4a. One can note that a distinct decreasing of lifetime was observed for 10% of Eu concentration and equals 2.6 ms compared to 3.7 and 4.3 ms for the samples doped with 1 and 2% of Eu, respectively. The lifetimes are not shorter than in single crystal doped with this same concentration of Eu-ions [5]. It indicates on low content of OH^- group even in the sample prepared at 800 °C. In order to investigate the size effect on the radiative decay of the $^5D_0$ level the lifetimes for the samples doped with this same concentration (0.5% Eu) were determined at different temperatures. The results are shown in Fig. 4b. One can note increasing luminescence lifetimes with decreasing the nanocrystals sizes.

3. Conclusions

The preparation of nanocrystalline powders of $LaAlO_3$ doped with Eu^{3+} was presented. The effect of the crystallites size of the host on the luminescence decay of the luminescence Eu^{3+} ions was investigated. An enhancement of luminescence lifetimes with decreasing of the nanocrystals sizes was found.

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