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Synthesis and luminescent properties of CaF_2:Eu^{2+} nanocrystals

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The synthesis of CaF_2 nanocryatals activated by Eu^{2+} ions and soluble in nonpolar media is described, their luminescent properties are studied. It is shown that in nanocrystals of this type there are some channels of radiationless energy loss. These losses significantly decrease the quantum yield of luminescence of CaF_2 nanocryatals.

Описан синтез нанокристаллов CaF_2, активированных ионами Eu^{2+} и растворимых в неполярной среде. Изучены их люминесцентные свойства. Показано, что в нанокристаллах этого типа имеются каналы безрадиационной потери энергии. Эти потери существенно снижают квантовый выход люминесценции нанокристаллов CaF_2.

1. Introduction

Fluorescent properties of nanoparticles are the subject of a great number of investigations [1–4]. The interest to these investigations is determined by the possibility of nanoparticles application in creating new generation of medical and biological marks, new solar concentrators, laser sources of light, etc. Last years the interest increases as for the use of nanoparticles for creating polymer-based composite materials, for instance, to modify plastic scintillators properties. Thus, inserting nanoparticles into scintillator's polymer base allow to change its energy dependence in different energy diapasons, and to increase its sensitivity to specific ionizing radiation. Unfortunately, there is still no possibility of direct inserting nanoparticles in a polymer medium due to their different polarity, which as a rule leads to their quick agglomeration with further precipitation of inorganic fraction. To avoid this negative phenomenon the nanoparticle surface modification is necessary to prevent nanoparticle aggregation in a polymer base.

Usually nanoparticles activated by rare earth ions are obtained by high-temperature pyrolysis [3], which leads to loss of organic layer on the nanoparticles surfaces and, therefore, makes impossible their dispergation in a polymer medium [3]. Some groups of nanoparticles obtained by low-temperature synthesis are known today: there are fluorides, phosphates, and vanadates [4, 5]. Nanocrystals of calcium fluoride take the special place among above compounds. CaF_2:Eu^{2+} crystals are rather widespread scintillating material due to their high light yield and transparency. All previously obtained nanoparticles which can be dispersed in organic medium are activated by three-valence europiumm [4–7]. But synthesis of two-valence europium-activated CaF_2 nanocrystals with modified surface still has not been described. In the present work we describe the synthesis and optical properties of CaF_2:Eu^{2+} nanocrystals with surfaces modified by oleic acid (OA).

2. Experimental

Synthesis of surface-modified $CaF_2:Eu^{2+}$ nanocrystals.

To synthesize $CaF_2:Eu^{2+}$ nanocrystals we used $CaCl_2$ (pure for analysis), NH_4F (pure for analysis), oleic acid (monounsaturated omega-9 fatty acid), methanol (chemically pure) and dichlorethan (pure for analysis) without further purification. $EuCl_2$ was obtained by $EuCl_3$ reduction using amalgamated zinc in hydrochloric acid according to the method described in [8].

To obtain $CaF_2:Eu^{2+}$ nanoparticles modified by oleic acid, we dissolved 6 mmol of $CaCl_2$, 0.06 mmol of $EuCl_2$ and 1.7 g of oleic acid in 20 ml of methanol in nitrogen atmosphere. Obtained solution was heated to 65°C and under intensive mixing and nitrogen barbotaging the 10 ml of NH_4F water solution (12 mmol) were added to ones. Suspension obtained was mixed at 65°C temperature during 2 h. After cooling to room temperature the precipitate was centrifuged, many times washed by water and methanol, dispersed in dichlorethan and precipitated by methanol. Nanoparticles were dried in vacuum under P_2O_5 during 24 h. The final product with Eu concentration about 1 % obtained in such a way was used for obtaining as dry samples and transparent dispersed solutions in toluene. Toluene in our experiments was used as a model solvent whose properties are nearly the same as that of polystyrene.

Measurements

Phase content of synthesized nanoparticles was determined by X-ray diffractometric replica. The morphology of synthesized nanoparticles was characterized by analysis of images obtained by transmission electron microscope (TEM). Excitation and fluorescence spectra of $CaF_2:Eu^{2+}$ nanocrystals are obtained by means of Fluoromax-4 (HORIBA, Joben Ivon Inc.) spectrofluorometer. Decay kinetics was measured by Combined Steady State and Lifetime Spectrometer FLS-920 (Edinburgh Instruments). As an excitation source a nanosecond flash lamp with 1 ns pulse width and 40 kHz repetition rate was used. Fluorescence decay was observed at 307 nm wavelength.

3. Results and discussion

Nanosize of the particles obtained can be estimated from TEM images (Fig. 1).

It is seen in the figure that an average size of nanoparticles is much less than 20 nm. To more precise determination of the obtained nanoparticles structure X-ray scattering technique was used which results are presented in Fig. 2.

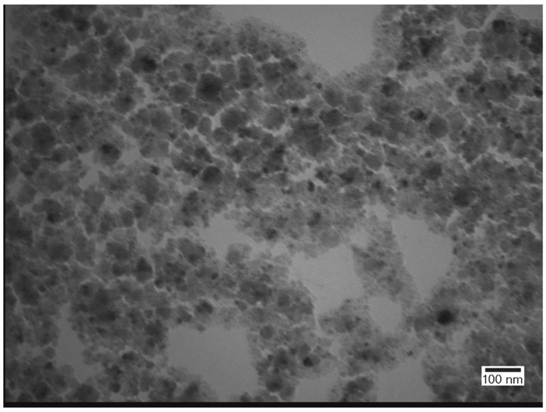

Fig. 1. TEM image of CaF_2 nanoparticles.

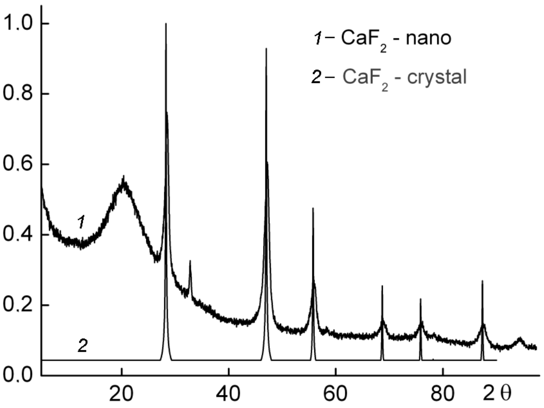

Fig. 2. Diffraction patterns of CaF_2 crystals and nanoparticles.

It can be seen in the figure that sharp maxima of diffraction patterns as CaF_2 crystals and nanoparticles coincide. It means that most of synthesized nanoparticles are CaF_2 nanocrystals. But what about charge state of activated europium ion in CaF_2 nanocrystals? To answer this question we used spectrometric method based on peculiarity of two- and three-valence ion of europium. This peculiarity is connected with different nature of these two ions fluorescence. For two-valence ion of europium the dipole resolved $4f^7 - 4f^6 5d$ transitions with small life-times placed in UV diapason are typical while optical property of three-charged ion of europium is characterized by electron transitions inside $4f^6$ electron shell which forbidden transitions are only partially allowed due to influence of external crystal field. As a rule, the life time of these optical transitions is about some milliseconds which differ from that of two-charge ion. Therefore, the spectral position of base lines of optical transitions of observed optical center and its life-time allow precise identification of europium ion which creates this center.

Fluorescence properties of CaF_2:Eu^{2+} *nanocrystals.*

The simplest method of establishing the Eu^{3+} admixture centers presence is an observation of specific for given center fluorescent lines at 610 nm which related to electron transitions from $^5D_0$ states to $^7F_{1,2,3,4}$ levels of multiplets. The most intensive excitation line responsible for such fluorescence is at 395 nm. In all nanocrystal samples synthesized by the method described above the line of this fluorescence at 610 nm was out of limits of the possible sensitivity. Therefore it can be concluded that reaction conditions of europium reduction allow it to enter to the nanocrystal in Eu^{2+} state only.

At the same time, fluorescence in 400 nm region was registered with confidence in all synthesized CaF_2 nanocrystals. Fig. 3 presents typical excitation and fluorescent spectra of CaF_2:Eu^{2+} nanocrystals, which were upset on a glass substrate.

It is seen in the Fig. 3 that the main peak of observed fluorescence of CaF_2:Eu^{2+} nanocrystals is placed at 421 nm wavelength while the excitation peak maximum of observed fluorescence is at 341 nm. Observed fluorescence is specific for electron transitions $4f^7 - 4f^65d$ of Eu^{2+} optical center in CaF_2 nanocrystals. Analogous fluorescent properties are also observed in bulk crystals of CaF_2:Eu^{2+}, which can indicate the identity of optical centers that are formed by Eu^{2+} ions as in nanocrystals and in bulk crystals.

Nanocrystals surface modification by oleic acid creates conditions of their ease dispergation in organic solvents. It was found that the nanoparticles are easy dispersed in toluene which from nanocrystals dissolving point of view is very close to styrene (which is the base monomer of most polymer bases of plastic scintillators) by its properties. And if the fluorescence spectrum of dispersed nanocrystals in toluene saves its maximum position compared to those of precipitated on substrate nanoparticles, than excitation spectrum is substantively modified (Fig. 4).

Thus in the excitation spectrum peaks at 337 nm, 355 nm and 366 nm are clearly distinguished, i.e. whole excitation spectrum acquires an additional shoulder in more long-wave region. This redistribution of excitation lines intensities can be connected with modification of phonon spectrum of the nanocrystals in toluene solution by means of activation of vibration freedom degrees of surface modified layer.

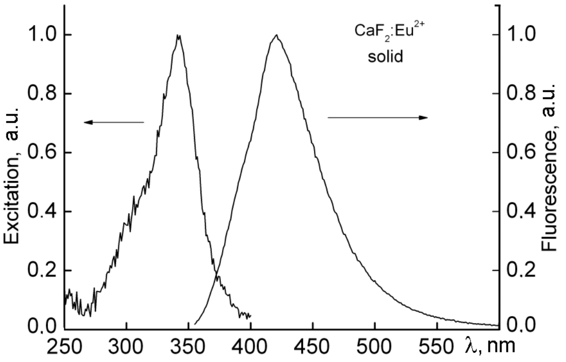

Fig. 3. Excitation and fluorescence spectra of CaF_2:Eu^{2+} nanoparticles.

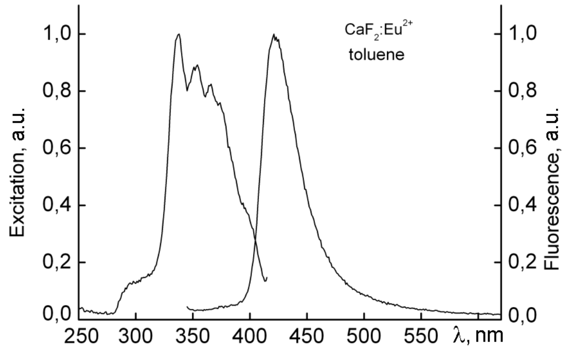

Fig. 4. Excitation and luminescence spectra of CaF_2:Eu^{2+} nanoparticles dispersed in toluene.

Additional proof of the fact that observed emission is Eu^{2+} fluorescence in CaF_2 nanocrystals is its decay curves presented in Fig. 5.

It is seen in the figure that the life time of excited state is in sub-microsecond diapason which is specific for $4f^7 - 4f^65d$ transition of Eu^{2+} optical center. But in contrast to analogues decay curves in bulk crystals observed curve can not be fitted by a single exponential. It is known that decay curves deviate from exponential when some quenching centers are exist which can be acceptors of radiationless energy transfer. In this case the decay curves are described by the root dependence:

$$I/I_0 = \exp(-t/\tau_0 - qc_aR_0^3\sqrt{t/\tau_0})$$

where τ_0 — life time of an optical center without quenchers, c_a — concentration of

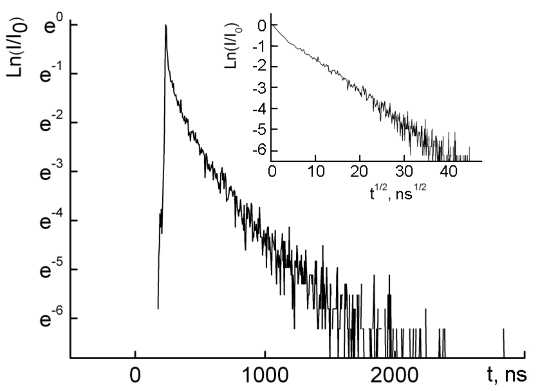

Fig. 5. Fluorescence decay curve of CaF_2:Eu^{2+} nanocrystals dispersed in toluene.

quenching centers, R_0 — Fцrster radius, q — constant, approximately equals to 7.4.

The existence of radiationless channel of energy loss is clearly seen after redrawing the decay curve in $\ln(I/I_0) + t/\tau_0$, $\sqrt{t}$ coordinates (insertion in Fig. 5) 800 ns was chosen as τ_0 which is specific life time of Eu^{2+} centers in CaF_2 bulk crystals. The channel of radiationless energy loss can cause significant reduction of the optical center fluorescence efficiency. The slope of the line in the insertion of Fig. 5 allows to estimate the quenching constant $\gamma = qc_aR_0^3/2$, which equals approximately to 1.41. Awareness of this quenching constant value allows to evaluate the center fluorescence efficiency according to following equation:

$$f/f_0 = 1-\sqrt{\pi}\gamma\,\exp(\gamma^2)(1-\mathrm{erf}(\gamma)).$$

Calculations have shown that fluorescence yield of Eu^{2+} optical center in CaF_2 is only 16 % compared to that of fluorescence center in bulk crystals. The rest of excitation energy is lost on the energy traps in radiationless way. The nanocrystal surface can contain such traps.

4. Conclusions

The described method of synthesis enables obtaining CaF_2 nanoparticles activated by europium ions in Eu^{2+} charge state. Modification of the nanocrystals surfaces by oleic acid allows to distribute them rather effectively in a bulk of nonpolar solvents such as toluene. This indicates the possibility of their dispersion in a polymer base of plastic scintillator. But surface modification can not eliminate channels of radiationless energy loss which leads to significant reduction of fluorescence. Therefore, to efficient use of nanoparticles for modification of plastic scintillator properties it is necessary to develop methods of surface modification which significantly reduce channels of radiationless energy losses.

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Синтез и люмінесцентні властивості нанокристалів CaF_2:Eu^{2+}

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Описано синтез нанокристалів CaF_2 активованих іонами Eu^{2+} які є розчинними у неполярному середовищі. Показано, що у нанокристалах цього типа є канали безрадиаційної втрати енергії. Ці втрати суттєво знижують квантовий вихід люмінесценції нанокристалів CaF_2.