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Luminescence of $CaF_2:Eu^{2+}$ nanocrystals

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Introduction

Fluorescent properties of nanoparticles are the subject of a great number of investigations. [1 – 3] The interest to these investigations is determined by the possibility of nanoparticles using in creating new generation of medical and biological marks, new solar concentrators, laser sources of light, etc. Last years the interest is increases to 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 changing its energy dependence in different energy diapasons, increase its sensitivity to specific ionizing radiation. Unfortunately, there are 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 modifying the nanoparticle surface 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 now. They 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 [3 – 6]. But the synthesis two-valence europium-activated CaF_2 nanocrystals with modified surface is still not described.

The aim : The synthesis of $CaF_2:Eu^{2+}$ nanocrystals and studing their optical properties

General

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

To synthesized $CaF_2:Eu^{2+}$ 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 by amalgamated zinc in hydrochloric acid according to the method described in [7].

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 intencive mixing and nitrogen barbotage added to the 10 ml of NH_4F water solution of (12 mmol). Suspension obtained was mixed under 65°C temperature during 2 hours. After cooling to room temperature the precipitate was centrifugated, 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 hours. The final product 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 the model solvent whose properties are nearly the same as that of polystyrene.

Measurements

The 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). The excitation source was a nanosecond flash lamp with 1 ns pulse width and 40 kHz repetition rate. Fluorescence decay was observed at 307 nm wave-length.

The size of obtained particles was estimated from TEM images. It turns out that the average size of nanoparticles is much less than 20 nm. More precise determination of nanoparticles structure was made using X-ray scattering techniques Fig. 1. 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. As a rule, the life time of three-charge ion 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. Fig 2 presents typical excitation and fluorescent spectra of $CaF_2:Eu^{2+}$ nanocrystals, which were upset on a glass substrate. It is seen in the figure 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 $4f^7 – 4f^6 5d$ 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.

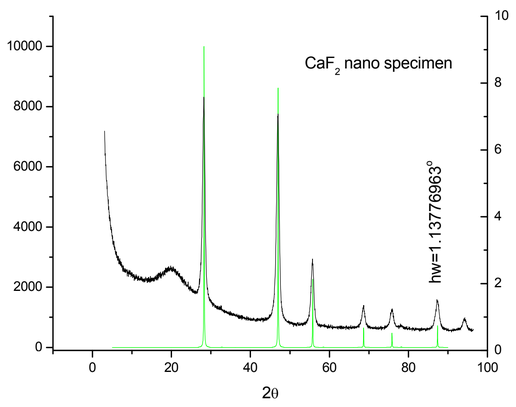

Fig. 1. X-ray pattern of obtained $CaF_2:Eu^{2+}$ nanocrystals

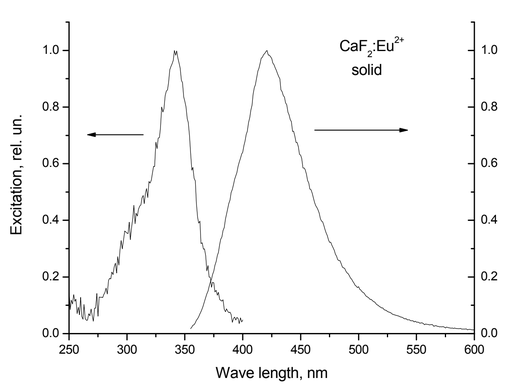

Fig.2 Excitation and fluorescence spectra of $CaF_2:Eu^{2+}$ nanoparticles

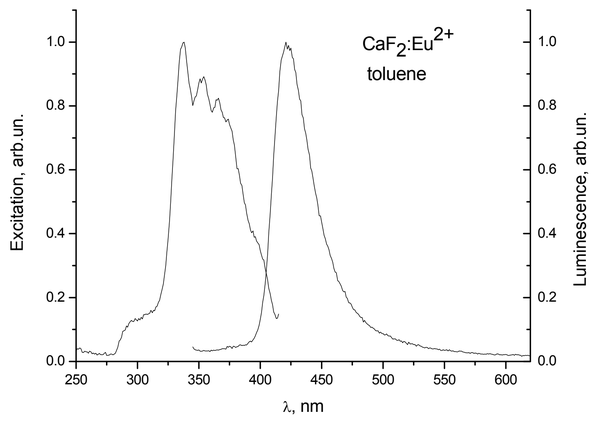

Fig.3. Luminescence and excitation spectra of $CaF_2:Eu^{2+}$ nanocrystals, dissolved in toluene

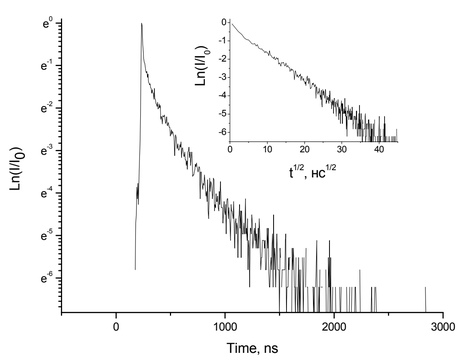

Fig.4 Decay curve of luminescence of $CaF_2:Eu^{2+}$ nanocrystals, dissolved in toluene

Nanocrystals surface modification by oleic acid creates conditions of their ease dispergation in organic solvents. It was found that nanoparticles easy disperses 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.3). Thus in the excitation spectrum the peaks at 337 nm, 355 nm and 366 nm are clearly distinguished, that is, 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 nanocrystals in a toluene solution by means of activation of vibration degrees of freedom of surface modified layer. Additional proof of the fact that observed emission is Eu^{2+} fluorescence in CaF_2 nanocrystals, is their decay curves presented in Fig. 4. 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 a root dependence:

$$I/I_0 = \exp(-t/\tau_0 - qc_a R_0^3 \sqrt{t/\tau_0})$$

were τ_0 – life time of an optical center without quenchers, c_a – concentration of quenching centers, R_0 – Förster radius, $q \approx 7.4$. The existence of a radiationless channel of energy loss is clearly seen after redrawing the decay curve in $\ln(I/I_0)+t/\tau_0$, coordinates (insertion in Fig.4). We choose τ_0=800 ns 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 allows estimation of the quenching constant $\gamma = qC_a R^3_2/2$ which equals approximately to 1.41. Knowing this quenching constant we can estimate the fluorescence efficiency according to following equation:

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

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. It is the nanocrystal surface that can be such a trap. The rest of excitation energy is lost on the energy traps in radiationless way. It is the nanocrystal surface that can be such a trap.

Conclusions

Described method of synthesis enables obtaining CaF_2 nanoparticles activated by europium ions in Eu^{2+} charge state. Modification of their surfaces by oleic acid allow in rather efficient way disperse them 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.

References

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