



Luminescence of polystyrene composites loaded with CeF₃ nanoparticles

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ABSTRACT

Luminescence and kinetic characteristics of polystyrene nanocomposites with luminescence impurities of p-Terphenyl, POPOP and CeF₃ nanoparticles were studied. Intensity of X-ray excited luminescence of the polystyrene scintillation composites containing CeF₃ nanoparticles (40 wt%) has been established to substantially increase (up to 16 times), mainly due to excitation energy transfer from the CeF₃ nanoparticles to the polystyrene matrix by means of the electron escape mechanism.

1. Introduction

Polymer and crystalline detectors are widely used to detect ionizing radiation. Each of these types of detectors has advantages and disadvantages regarding scintillation parameters. However, taking into account the growing needs of detector use for environmental monitoring, large-scale experiments in high-energy physics, significant amounts of scintillator output and their cost are becoming key determinants. An optimal solution to this problem is the development of scintillation materials that are comparable in price with plastic scintillators, and in absorbing ability – with inorganic materials.

Promising materials that are able to combine the benefits of organic and inorganic scintillators are composite materials based on polystyrene, polyvinyl toluene or other polymeric matrices loaded with inorganic nanoparticles. Study of scintillation mechanism in such the composite materials is at the stage of accumulation of initial experimental results and development of models [1–11].

Designing the nanocomposite polymer scintillators, the following approaches can be presumably applied: excitation energy transfer from the nanoparticles to the polymer matrix [5,6,8], energy transfer from the polymer matrix to nanoparticles [2] or simply the use of polymer matrix to protect nanoparticles from environmental influence [12]. For the case of excitation energy transfer from the nanoparticles to the polystyrene matrix, several approaches can be considered: (i) the non-radiative resonance energy transfer from the nanoparticles to the polystyrene or the polystyrene's activators (p-Terphenyl and POPOP); (ii) the re-absorption of the nanoparticle emission by the polymeric

matrix; (iii) the excitation of the polymer matrix by the electrons escaping from the nanoparticles. All of these three approaches can be realized simultaneously, but in the case of small-size nanoparticles, the electron escape outside the nanoparticle is the determining mechanism of excitation of the polystyrene matrix [13,14].

Recent studies [10] have shown that intrinsic luminescence of CaF₂, SrF₂, BaF₂ fluoride nanoparticles decreases significantly with the decrease of nanoparticle sizes. The observed luminescence quenching is due to the escape of electrons from nanoparticles in the case when the thermalization length or the mean free path of electrons becomes larger than nanoparticle size [10–15]. However, when these nanoparticles are embedded in the polystyrene, its luminescence increases tenfold, confirming the electron escape mechanism.

For further clarification of energy transfer mechanisms from inorganic nanoparticles to organic polystyrene matrix with luminescence impurities, the composite based on polystyrene loaded with CeF₃ nanoparticles was studied. CeF₃ crystal is known as an attractive scintillation material due to its substantial density and short luminescence decay time [16]. CeF₃ nanoparticles are interesting for nanocomposite fabrication because they have luminescence at 280–320 nm due to 4d-5f transitions in cerium ion, which coincides with absorption spectra of the p-Terphenyl and partly with the polystyrene itself. In addition, CeF₃ also has a band with maximum at 360 nm, which is attributed to perturbed cerium. The band overlaps with absorption of POPOP (1,4-bis (5-phenyloxazol-2-yl) benzene). For composite loaded with CeF₃ nanoparticles, all three above-mentioned mechanisms of energy transfer are possible: the non-radiative, radiative and electron escape

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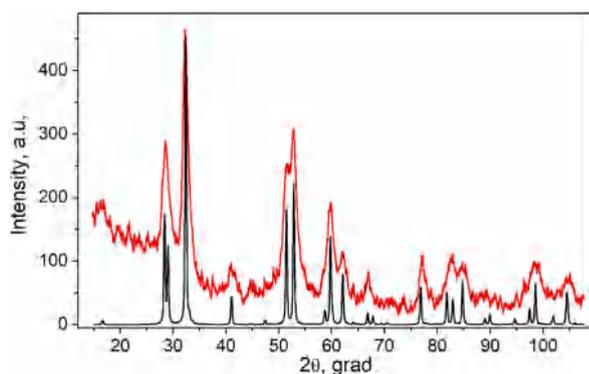


Fig. 1. XRD pattern of as synthesized CeF_3 nanoparticles. The standard pattern of CeF_3 is also supplied.

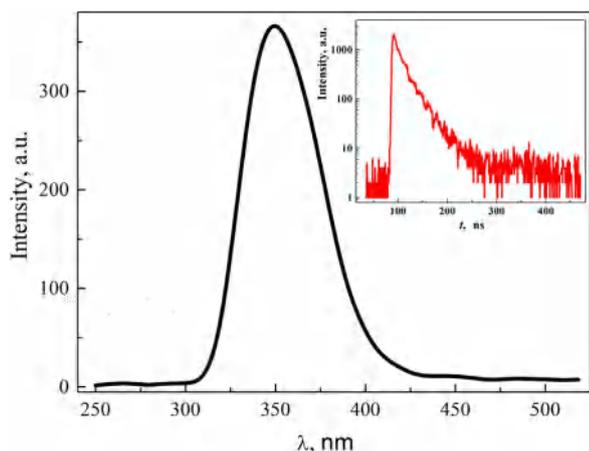


Fig. 2. X-ray excited luminescence of the CeF_3 nanoparticles. Inset – X-ray excited luminescence decay kinetics of the CeF_3 nanoparticles.

mechanisms. Therefore, the nanocomposite with CeF_3 may be a model for the revealing of dominating excitation mechanism of polystyrene scintillator with loaded nanoparticles.

2. Experimental

2.1. Synthesis of nanoparticles

Synthesis of CeF_3 nanoparticles from CeCl_3 and NH_4F raw materials was carried out in ethanol-aqueous solution according to the ionic substitution reaction: $\text{CeCl}_3 + 3\text{NH}_4\text{F} \rightarrow \text{CeF}_3 + 3\text{NH}_4\text{Cl}$. Ammonium fluoride (NH_4F) ethanol-aqueous solution was added dropwise at regular intervals to CeCl_3 solution to provide the absence of concentration gradients.

Absence of organic modifiers allows the purification of CeF_3 nanoparticles from other components of the mixture. For this, centrifuged at 6000 rpm CeF_3 nanoparticles were washed with distilled water and centrifuged again. The procedure of centrifuging and washing was carried out twice, and then nanoparticles were dried.

Sizes of the nanoparticles were determined on the basis of X-ray diffraction data with analyzing the width of diffraction peaks (Fig. 1) by the Sherrer's equation. The size of as synthesized CeF_3 nanoparticles was found to be 12 ± 4 nm.

2.2. Obtaining polymeric composites with the embedded CeF_3 nanoparticles

Composite films were produced using polystyrene scintillator shavings from the Institute of Scintillation Materials of the National Academy

of Sciences of Ukraine (Kharkiv), which contains organic luminescence impurities: p-Terphenyl (activator) and POPOP (spectrum shifter) in the amount of 2 wt% and 0.1 wt%, respectively. The polystyrene scintillator shavings were dissolved in an azeotropic mixture of $\text{C}_2\text{H}_4\text{Cl}_2 + \text{CCl}_4$ (dichloroethane + tetrachloromethane). After dissolving polystyrene, CeF_3 nanoparticles (40 wt%) were added to the mixture. To achieve a uniform distribution of nanoparticles in a polystyrene solution, the mixture was treated ultrasonically. As a result of ultrasound influence with the power of 150 W for 15 min, a colorless, completely transparent suspension of nanoparticles in polystyrene solution was obtained. To fabricate composite films, the resulting suspension was put drop-by-drop on the slide glass. After this, the film was kept for 24 h to achieve a complete evaporation of the solvent.

As prepared film composites were of good transparency and homogeneity. Luminescence studies of film composites were carried out on the samples of 10 mm in diameter and 0.3 mm in thickness.

2.3. Measurement of X-ray excited luminescence parameters

Measurement of the luminescence spectra and the luminescence decay kinetics of CeF_3 nanoparticles and polymeric composites containing CeF_3 nanoparticles were performed using laboratory setup based on the LOMO MDR-2 monochromator and pulse X-ray source. Such an equipment allows the performing of the luminescence-kinetic measurements in 10^{-9} – 10^{-6} s time interval and 200–800 nm spectral range. The anode voltage of X-ray tube was equal to 40 kV, average current – 0.5 mA and pulse width – 2 ns [14]. The average energy of X-ray quanta was 23 keV.

All measurements were performed at room temperature.

3. Results and discussion

In the case of X-ray excitation, CeF_3 nanoparticles exhibit a broad, unstructured band (Fig. 2) peaked at 350 nm, which is like to the luminescence band of so-called perturbed cerium in CeF_3 single crystals [17–19]. The spectral position of this band is consistent with POPOP absorption band [2]. Luminescence decay kinetics curve of nanoparticles is close to the exponential curve with decay time ~ 20 ns (Fig. 2, inset).

X-ray excited luminescence of the polystyrene scintillator (curve 1), the polystyrene without activator but with CeF_3 nanoparticles of 40 wt% (curve 2) and the polystyrene composite with the CeF_3 nanoparticles content of 40 wt% (curve 3) is presented in Fig. 3. In absence of inorganic nanoparticles, the spectrum of the polystyrene scintillator exhibits a weak emission (curve 1) in the form of a band with maxima of ~ 350 nm and ~ 420 nm corresponding to luminescence of p-Terphenyl and POPOP, respectively [20]. The weak emission of polystyrene is due to its low effective atomic number ($Z_{\text{eff}} \sim 6$).

Polystyrene film without activators but with CeF_3 nanoparticles (40 wt%) exhibits luminescence characteristic of CeF_3 nanoparticles with the maximum at 350 nm (Fig. 3, curve 2). The polystyrene scintillation nanocomposite with embedded CeF_3 nanoparticles (40 wt%) reproduces the luminescence of the polystyrene with activators, but it reveals 16-fold increase of the luminescence intensity. Time parameters of the composite coincide with decay time of polystyrene scintillator (Fig. 4). The decay curves for polystyrene and nanocomposite scintillator can be approximated by the exponent with the decay time of ~ 2.7 ns.

Let us consider possible mechanisms for increasing of luminescence intensity for the nanocomposite polystyrene scintillator in the case of X-ray excitation. X-ray quanta with energy $h\nu \gg E_g$ create high-energy photoelectrons with kinetic energy much higher than the forbidden energy band gap ($E > E_g$) [10,11]. Relaxation processes of photoelectrons occur due to their scattering on the electrons and phonons of the crystalline lattice. The relaxation of this high-energy electron occurs as a result of inelastic electron–electron scattering, provided that the electron kinetic energy is greater than the forbidden energy bandgap value. The distance on which the electron propagates between two consecutive collisions determines the length of the free electron

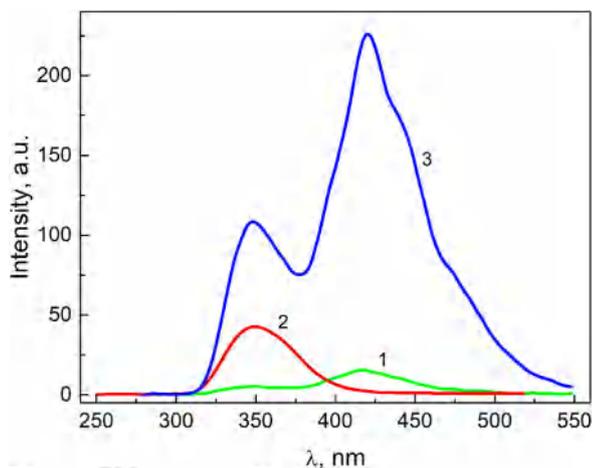


Fig. 3. X-ray excited luminescence spectra. Curves: 1 – polystyrene scintillator film without nanoparticles; 2 – CeF_3 nanoparticles (40 wt%) in polystyrene film without activators; 3 – polystyrene scintillator film loaded with CeF_3 nanoparticles (40 wt%).

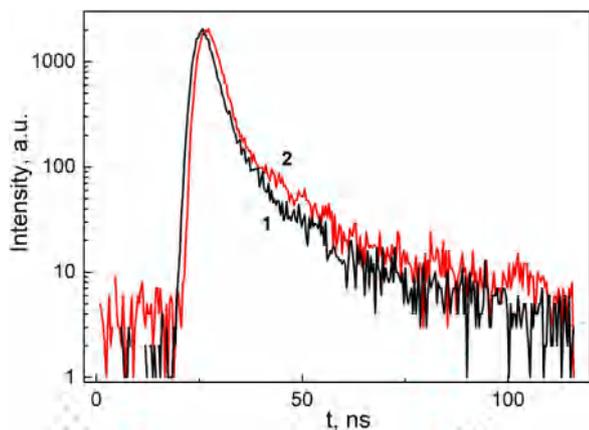


Fig. 4. X-ray excited luminescence decay kinetics: 1 – the polystyrene scintillator film without nanoparticles; 2 – the polystyrene scintillation film loaded with the CeF_3 nanoparticles (40 wt%).

path. Electrons with kinetic energy less than E_g lose their energy due to electron–phonon interaction, this is so-called thermalization stage for electron excitation relaxation. The spatial parameters of these interactions (mean free path length and electron thermalization length) under certain conditions can exceed the size of nanoparticles. In such a case the electrons leave nanoparticles by means of mechanism of the external photoelectric effect, and, naturally, the luminescence intensity of nanoparticles will be significantly weakened. Mean free path length is estimated from the universal curve of electron–electronic scattering. For X-ray quanta with an energy of 23 keV it amounts to ~ 30 nm [21]. The electron thermalization length for CeF_3 can be assumed to have a value characteristic for BaF_2 , SrF_2 , CaF_2 fluoride crystals, which according to experimental estimates is ~ 80 nm [22]. For comparison, the thermalization length is about 20 nm for phosphate crystals [22]. In view of these spatial interaction parameters, the size of nanoparticles which is smaller than mean free path length and electron thermalization length is critical for luminescence observation [10–12]. However, the significant increase of electron escape from the nanoparticles starts at these sizes. If such nanoparticles are loaded in polystyrene, the electrons leaving the nanoparticles under the influence of X-rays will excite the luminescence of the polystyrene. Under these conditions, the polystyrene luminescence should grow proportionally to the concentration of nanoparticles in the polystyrene. In this case, the luminescence

of such the composite would have to reproduce the spectral and time characteristics of the polystyrene matrix. Such a process, associated with electron escape outside the nanoparticle, could be one of the excitation mechanisms of polystyrene matrix luminescence. Another mechanism could be related to radiative or non-radiative energy transfer from cerium ions to polystyrene matrix. The reason for this is the overlapping of CeF_3 5d-4f luminescence band peaked at 360 nm with POPOP absorption band in the region of 300–400 nm [5]. This makes possible both the reabsorption of intrinsic emission of the CeF_3 nanoparticles (Fig. 2) by the POPOP polystyrene activator and the resonance energy transfer from the excited states of Ce^{3+} ion in CeF_3 to the POPOP.

Let us consider the possibility of electron escape mechanism realization in polystyrene nanocomposites. From this point of view, the significant 16-fold increase of the luminescence intensity is very attractive. This result agrees with theoretical estimation of absorption capacity of polystyrene composite based on known absorption coefficients for CeF_3 and polystyrene [23]. If the composite is considered as a set of sequentially placed layers of cerium fluoride and polystyrene with thicknesses of d_{CeF_3} and d_{PS} , respectively, the attenuation coefficient of the composite will be written as:

$$\alpha = \frac{\alpha_{\text{CeF}_3} d_{\text{CeF}_3} + \alpha_{\text{PS}} d_{\text{PS}}}{d_{\text{CeF}_3} + d_{\text{PS}}}$$

The values of attenuation coefficients being $\alpha_{\text{CeF}_3} = 98.8 \text{ cm}^{-1}$ and $\alpha_{\text{PS}} = 0.436 \text{ cm}^{-1}$, an absorption of 0.3 mm thick polystyrene composite loaded with CeF_3 nanoparticles (40 wt%) in comparison with polystyrene film without nanoparticles of the same thickness increases by 22 times. This value is close to observed 16-fold increase of luminescence intensity. Thus, the increase of the luminescence intensity of polystyrene composite under X-ray excitation correlates with its absorption capacity increase due to the introduction of the CeF_3 nanoparticles in the polystyrene matrix. Consequently, the increase of luminescence intensity of nanocomposite in proportion to the concentration of embedded inorganic nanoparticles and the reproduction of spectral peculiarities and decay time constant of pure polystyrene scintillator can serve as an evidence of the electron escape mechanism. Similar mechanism was observed in polystyrene matrix loaded with other wide band gap nanoparticles. For example, in polystyrene composites with BaF_2 the luminescence intensity increased by 15 times [6], with SrF_2 by 46 times [7], and with $\text{LaPO}_4\text{-Pr}$ by 30 times [8].

Let us consider the possibility of realization of the radiative or non-radiative resonance energy transfer from the excited state of Ce^{3+} ion to the polystyrene. The radiative mechanism involves the reabsorption of CeF_3 luminescence with maximum at 360 nm by the POPOP activator. However, in the case of non-radiative mechanism, the luminescence decay time curve of the composite should have a time component comparable with CeF_3 decay time constant. Deficiency of the time component of 20 ns in the scintillation pulse of nanocomposite proves the absence of the radiative excitation channel from CeF_3 nanoparticles to the polystyrene. The authors of [24] observed resonance energy transfer from CeF_3 nanoparticles to polystyrene scintillator in the case of optical excitation. We do not exclude this mechanism, but contribution from it to the scintillation pulse should be much less than that of electron escape mechanism. The reasons for this are as follows. Light energy emitted by CeF_3 nanoparticles (40 wt%) (Fig. 3, curve 2) embedded in polystyrene without activators (p-Terphenyl and POPOP) is less than 11% of the energy emitted by the polymer composite loaded with CeF_3 nanoparticles under the same experimental conditions (Fig. 3, curve 3). Consequently, such transfer mechanism cannot increase luminescence intensity of the composite by an order of magnitude even if entire excitation energy is transmitted from CeF_3 to the POPOP by the resonance transfer. In addition, in view of the possible agglomeration of CeF_3 nanoparticles and their random arrangement, for the weight concentration of 40% CeF_3 and 0.1% POPOP, portion of CeF_3 nanoparticle – POPOP molecule pairs with a distance sufficient to exhibit a dipole–dipole resonance

interaction is negligible. This circumstance additionally reduces the resonance mechanism contribution to the scintillation pulse formation.

The significant increase of the luminescence intensity of the composite the luminescence of which repeats the spectral composition and time constants of polystyrene, observed when mean free path length and thermalization length exceed the size of nanoparticles, suggests that the main contribution to luminescence increase is caused by the electron escape mechanism.

4. Conclusions

The CeF₃ nanoparticles with size of 12 nm and polystyrene composites loaded with CeF₃ nanoparticles (40 wt%) were fabricated. The luminescence of the polystyrene nanocomposite has two bands with maxima at 350 and 420 nm and decay time (~2.7 ns), which are typical for polystyrene scintillator. The significant 16-fold increase in the luminescence intensity of nanocomposite is due to the energy transfer from CeF₃ nanoparticles to the polystyrene matrix, mainly in non-radiative way by means of the electron escape mechanism.

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