



X-ray excited luminescence of polystyrene composites loaded with SrF₂ nanoparticles



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ABSTRACT

The polystyrene film nanocomposites of 0.3 mm thickness with embedded SrF₂ nanoparticles up to 40 wt% have been synthesized. The luminescent and kinetic properties of the polystyrene composites with embedded SrF₂ nanoparticles upon the pulse X-ray excitation have been investigated. The luminescence intensity of the pure polystyrene scintillator film significantly increases when it is loaded with the inorganic SrF₂ nanoparticles. The film nanocomposites show fast (~2.8 ns) and slow (~700 ns) luminescence decay components typical for a luminescence of polystyrene activators (p-Terphenyl and POPOP) and SrF₂ nanoparticles, respectively. It is revealed that the fast decay luminescence component of the polystyrene composites is caused by the excitation of polystyrene by the photoelectrons escaped from the nanoparticles due to photoeffect, and the slow component is caused by reabsorption of the self-trapped exciton luminescence of SrF₂ nanoparticles by polystyrene.

1. Introduction

Considering the new possibilities which one can obtain using the luminescent properties of nanoparticles the creation of the new scintillation materials based on ones looks attractive. However, there are still no messages about the creation of a scintillator based on the nanoparticles, which would exceed the parameters of the bulk analogs. Recently, the high effective atomic number (effective *Z*) nanoparticles have been proposed to embed in polymer systems to increase the γ -stopping power for plastic scintillators. The polystyrene scintillator loaded with 3 wt% of gadolinium is reported to be used to register the thermal neutrons [1]. Upon loading of 0.5 wt% of gadolinium such the scintillators had registered 46% of neutrons. The polymer scintillator loaded with Hf_xSi_{1-x}O₂ (10 wt%) was used to carry out X-ray resonant scattering measurements [2]. This composite scintillator demonstrates registration efficiency 2.6 times greater than similar polystyrene scintillator retaining the 2.6 ns scintillation decay time of polystyrene scintillator. The transparent nanocomposite monoliths with hafnium oxide nanoparticles loaded up to 40 wt% (net hafnium wt% up to 28.5%) produce a full energy photopeak for 662 keV gamma rays [3].

The complexity to obtain the nanoscintillators which will compete with the bulk analogs becomes evident after the detailed analysis of the recombination luminescence mechanism in the case of space confine-

ment. Recently the ratio between the average sizes of the nanoparticles and the mean free path or the thermalization length of the electrons significantly was shown to affect on the luminescent intensity of the nanoparticles. In particular, the study of the luminescent intensity features of BaF₂ [4] CaF₂ [5] LaPO₄:Pr, LaPO₄:Eu [6] LuPO₄:Ce [7] nanoparticles in the case of excitation with high-energy quanta of the synchrotron or X-ray radiation have revealed the restrictions of their luminescence intensity related to the change of the nanoparticles sizes. For example the luminescent intensity of BaF₂ nanoparticles significantly decreases when the thermalization length or the mean free path of electrons equals or exceeds the nanoparticles sizes [4]. In this case the electrons escape from the nanoparticles and don't take part in the recombination luminescence. Under these conditions the external photoelectric effect caused by ionizing radiation dominates over the internal photoelectric effect. Thus, if the thermalization length or the mean free path of electrons is less than the sizes of nanoparticles, the external photoelectric effect prevails. The photoelectrons, which are created owing to the internal photoeffect provide the recombination luminescence of BaF₂ nanoparticles.

The existence of the external photoeffect can be used for creation of the new generation of the nanocomposite scintillators based on luminescent polymers with the embedded nanoparticles. In this case the electrons emitted by the nanoparticles will excite the luminescence

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of polystyrene scintillator matrix. Such the composites loaded with nanoparticles containing elements with effective atomic number Z will possess considerably higher an absorbing ability comparing with unloaded polystyrene scintillator and will keep fast time response inherent for one [2,3,8–10].

In previous paper [3] it have been demonstrated that in the composite material loaded with BaF_2 nanoparticles the decay time is the same as in pure polystyrene scintillator, however the luminescent intensity increases by order. The aim of present work is to confirm that the similar regularities are observed in the composite material with SrF_2 nanoparticles. Unlike BaF_2 nanocrystals possessing in addition to emission of self-trapped excitons (STE) peaked at ~ 300 nm the fast core-valence luminescence (0.9 ns) at 225 nm the SrF_2 nanoparticles reveal only slow (700 ns) STE luminescence decay component (band peaked at ~ 300 nm) [11]. The absence of fast luminescence in SrF_2 allows to elucidate more clearly the nature of fast response for composite polystyrene loaded with nanoparticles.

2. Experimental

2.1. Synthesis of nanoparticles

The research of the X-ray luminescent intensity dependence on the nanoparticle sizes is performed for polystyrene scintillation films loaded with SrF_2 nanoparticles. SrF_2 nanoparticles with the average size of 16 ± 4 nm were synthesized by the chemical precipitation method from the aqueous solutions with presence of the ethanol [4]. The sizes of the nanoparticles were estimated by the XRD method. The size of synthesized nanoparticles was estimated from the half-width of diffraction maxima using the Scherrer equation. In order to obtain nanoparticles with larger size the high temperature annealing for 2 h at the temperatures of 200, 400, 600, 800 and 900 °C was used. In this case, the sizes of nanoparticles were equal 25, 29, 74, 96 and 110 nm, respectively.

2.2. Obtaining of polymeric composites with the embedded SrF_2 nanoparticles

The shavings of polystyrene scintillator of ISMA (Institute for Scintillation Materials NAS of Ukraine, Kharkiv) production were used to obtain the composite films. The polystyrene shavings contain the organic luminescence admixtures of p-Terphenyl (used as an activator) and POPOP (as the wavelength shifter) with concentrations of 1% and 0.1%, respectively. To disperse the inorganic nanoparticles into the polymer, the next few steps were performed. SrF_2 nanoparticles were added to solution of polystyrene in $\text{C}_2\text{H}_4\text{Cl}_2 + \text{CCl}_4$ azeotrope mixture and were mixed by ultrasonic disperser. The obtained transparent suspension was deposited on a glass slide and was dried on air for a day. The thickness of composite films, formed in this a way, was $h=0.3$ mm, the concentration of SrF_2 nanoparticles was $c=5$ wt% and $c=40$ wt%. As the concentration of SrF_2 nanoparticles in polystyrene is 40 wt% they can form aggregates causing the decreases of light collection and respectively the light yield of a composite. The optical quality of composite scintillation films can be examined from Fig. 1.

2.3. Spectral and kinetic studies of the polystyrene nanocomposites

The luminescence spectra and luminescence decay kinetics measurements of SrF_2 nanoparticles and polymeric composites containing the SrF_2 nanoparticles under pulsed X-ray excitation were performed at the laboratory setup, based on the diffraction monochromator MDR-2 (LOMO) with a the dispersion of 20 nm/mm. The facility allows the performing of the luminescence-kinetic measurements in 10^{-9} – 10^{-6} s time and 200–800 nm spectral range. Emission spectra were not corrected on spectral sensitivity of the grating monochromator and PMT registration channel. The parameters of X-ray tube: anode voltage

– 40 kV, average current – 0.5 mA, and time pulse width – 2 ns. The average energy of the X-ray excitation was 23 keV. All measurements were performed at room temperature.

3. Results and discussion

3.1. The X-ray excite luminescence of the polystyrene nanocomposite with the embedded SrF_2 nanoparticles

The luminescent spectra of the scintillation composite polystyrene films with embedded SrF_2 nanoparticles under X-ray excitation are shown in Fig. 2. Two luminescence bands with maxima at 350 and 420 nm are observed. These bands correspond to the luminescence of polystyrene activators: p-Terphenyl and POPOP respectively.

The luminescent intensity of polystyrene film without nanoparticles (Fig. 2, curve 1) is predictably low because of the low absorption ability of the polystyrene (effective $Z \sim 6$). The loading of the polystyrene films with 40 wt% of inorganic nanoparticles (SrF_2 , effective $Z \sim 38$) significantly increases the luminescent intensity of such the films. Thus, the luminescent intensity of the polystyrene composites, loaded with 40 wt % SrF_2 nanoparticles of 16 nm average size, increases by ~ 10 times in comparison with the polystyrene film without nanoparticles. The increase of the average nanoparticle size up to 110 nm leads to the increase of luminescent intensity approximately by 46 times. The luminescent intensity of the 0.3 mm thick polystyrene films with embedded SrF_2 nanoparticles of 110 nm size $\sim 36\%$ of the luminescent intensity of the 0.3 mm thick pellet pressed from the SrF_2 microcrystalline powder (emission maximum at ~ 300 nm [11]).

The decay time parameters of the X-ray excited luminescence of the polystyrene composites with nanoparticles of different size are shown in Fig. 3. Taking into account the similarity of time constants for p-terphenyl and POPOP in the case of optical excitation, 1.0 and 1.3 ns, respectively, the duration of exciting X-ray impulse of ~ 2 ns, the study of luminescence time parameters of nanocomposite were carried out in the integrated mode. There are fast and slow decay components with the time constants of ~ 2.8 ns and ~ 700 ns respectively (curve 5) in a scintillation pulse for the large nanoparticles (110 nm). The fast decay component (2.8 ns) corresponds to the polystyrene scintillator decay and the slow component (700 ns) corresponds to the luminescence decay time of self-trapped exciton in SrF_2 [11,12]. The luminescence decay constant of SrF_2 nanoparticles of 110 nm average size is similar to that for SrF_2 single crystal (curves 6 and 7). The presence of various decay parameters can be a result of the several mechanisms of the energy transfer from the nanoparticles to the polystyrene matrix. The presence of slow component indicates the radiative nature of the energy transfer due to the SrF_2 STE luminescence reabsorption by polystyrene. This is proved by the fact that the STE emission band energy position is consistent with the absorption band of the p-Terphenyl polystyrene activator. The fast component reproducing the polystyrene kinetic parameters can correspond to polystyrene excitation by the high-energy electrons emitted by the nanoparticles due to photoeffect. In the case of the composite with nanoparticles of 16 nm size the luminescence decay curve (curve 1) exactly reproduces the decay curve of pure polystyrene scintillator with the decay time constant of ~ 2.8 ns.

The luminescence intensity dependences of the fast and slow decay components of the polystyrene films with the embedded SrF_2 nanoparticles of different sizes are presented in Fig. 4. The luminescence intensity of the slow component (curve 1) significantly decreases at the nanoparticle size decrease while the fast component (curve 2) reveals a tendency to slight growth ($\sim 20\%$).

3.2. Discussion

The observed dependencies of spectral and kinetic parameters of nanocomposites and their luminescence intensity on the nanoparticles

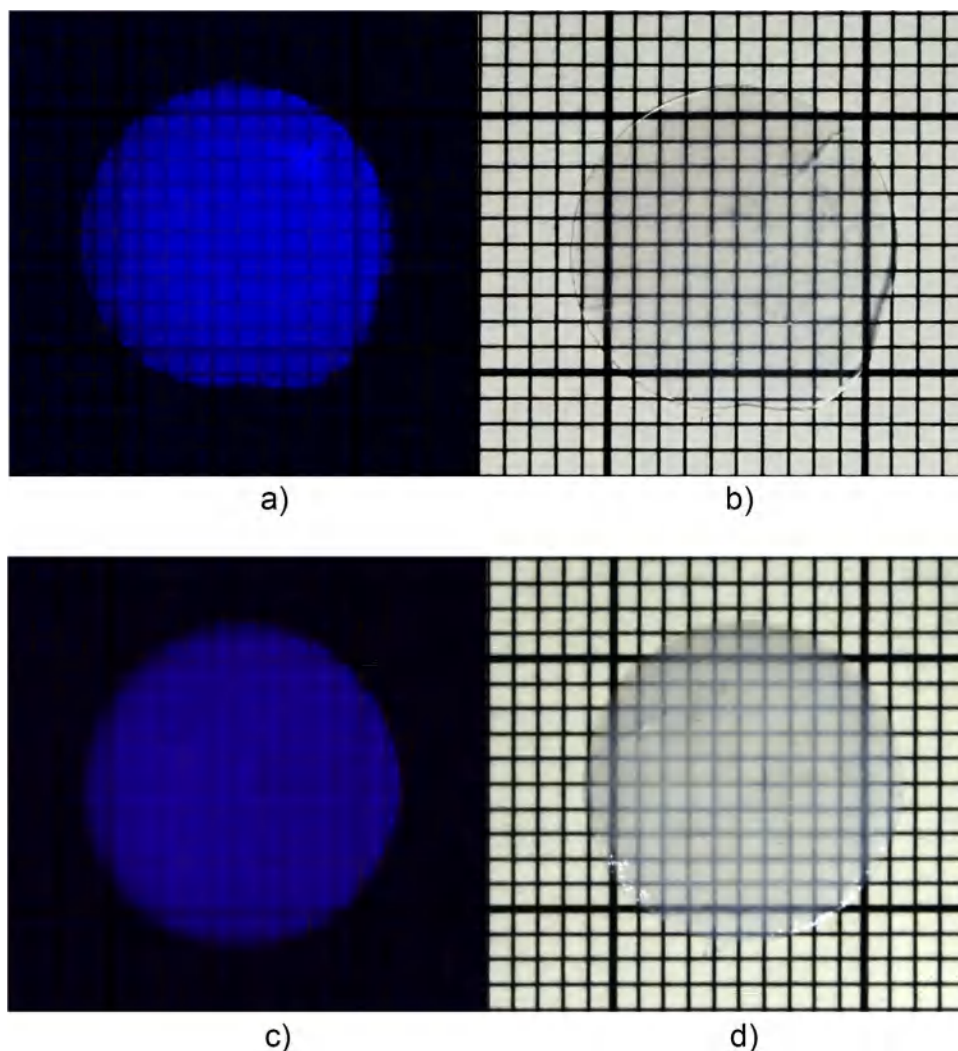


Fig. 1. Photos of the polystyrene film scintillators with embedded SrF₂ nanoparticles of 16 nm size at visible light (b), (d) and at UV-excitation (a), (c): (a), (b) – 5 wt% of SrF₂ nanoparticles, (c), (d) – 40 wt% of SrF₂ nanoparticles. The thickness of films – 0.3 mm.

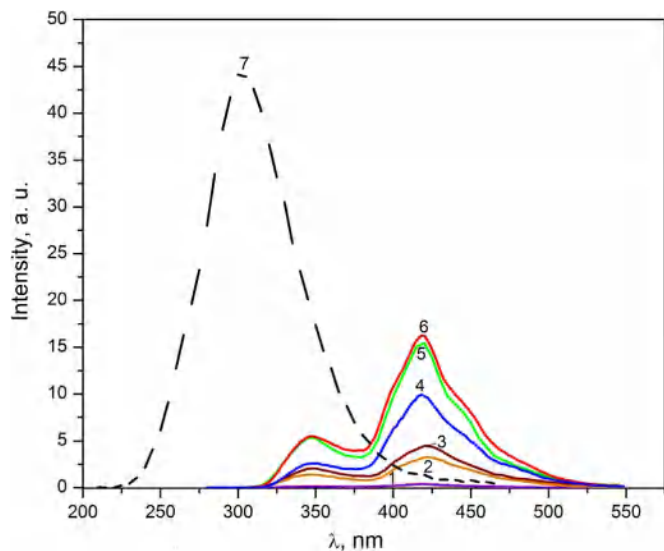


Fig. 2. The X-ray excited luminescence spectra of the pure polystyrene scintillator film (1) and composite polystyrene films loaded with the SrF₂ nanoparticles of different size: 2–16 nm, 3–29 nm, 4–74 nm, 5–96 nm, 6–110 nm. Thickness of films was 0.3 mm, concentration of nanoparticles – 40 wt%. Curve 7 – spectrum of the SrF₂ microcrystalline powder pellet of same thickness as film.

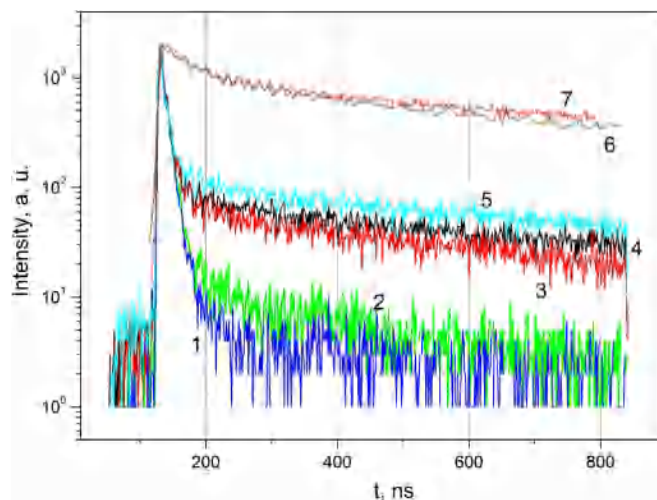


Fig. 3. The X-ray excited luminescence decay kinetics of the polystyrene composites with embedded SrF₂ nanoparticles of different sizes: 1–16 nm, 2–29 nm, 3–74 nm, 4–96 nm, 5–110 nm. Luminescence decay kinetics of SrF₂ nanoparticles with the size of 110 nm (6) and of SrF₂ single crystal (7).

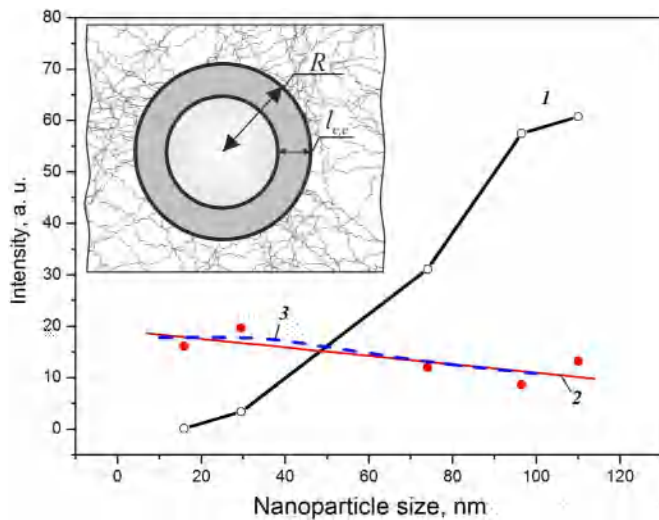


Fig. 4. The X-ray excited luminescence intensities of the polystyrene films loaded with SrF₂ nanoparticles of different nanoparticle sizes: 1 – slow component; 2 – fast component; 3 – calculated intensity of the fast component.

sizes can be explained taking into account the ratio between the mean free path of electrons, the electron thermalization length and the nanoparticles sizes. Such approach was used for an explanation of the luminescent parameters of the polystyrene composites loaded with BaF₂ nanoparticles [3].

In result of the X-ray photon absorption the high-energy electron (photoelectron) is created. Already at the first stage of photoelectron relaxation due to scattering on valence electrons its mean free path $l_{e,e}$ can exceed the nanoparticle size doing the recombination luminescence of in a volume of nanoparticles impossible. The mean free path $l_{e,e}$ of the high-energy photoelectron due to scattering of photoelectron on valence electrons can be found from the universal curve of electron-electron scattering. For the photoelectrons with kinetic energy of $E_0=23$ keV the mean free path of electron is about 30–40 nm [13]. Thus, the mean free path is the important parameter for a luminescence of the polystyrene nanocomposites because the photoelectrons emitted from the nanoparticles cause a luminescence of the polystyrene matrix. Therefore, the presence of fast component (Figs. 3 and 4, curve 3) which reproduces the polystyrene luminescence kinetic parameters corresponds to the excitation of polystyrene by electrons emitted from the nanoparticle owing to the photoelectric effect mechanism.

The electron with kinetic energy of $E_0 < E_g$, energy of which is not enough for further multiplication of electronic excitations will lose its energy due to the scattering on phonons until it becomes equal to the thermal energy of a lattice. During energy relaxation on phonons the thermalization electron overcomes a distance known as thermalization length $l_{e,ph}$. In particular, the average thermalization length of electrons for BaF₂ is approximately $l_{e,ph}=80$ nm [14]. It can be assumed that the electron thermalization length in SrF₂ is comparable with that in BaF₂. A ratio between thermalization length of electron and the nanoparticle size will define the recombination probability of electrons and holes in nanoparticle volume and the intensity of STE recombinational luminescence of nanoparticles. When the thermalization length exceeds the nanoparticles sizes the STE luminescence would have to decrease. Indeed, such the dependence is observed for the luminescence intensity of a slow decay component of composite (Fig. 4, curve 1). The essential decrease of the luminescence intensity of a slow component occurs for composites with embedded nanoparticles with size of ~75 nm and less. This size can attribute to the average thermalization length of electron in SrF₂.

A slight dependence of a slow decay time constant of composite on the sizes of loaded nanoparticle is an additional confirmation of thermalization electrons escape from the nanoparticle (Fig. 3). Thus,

for nanoparticles with the size of 110 nm decay time constant is $\tau \approx 700$ ns and for 74 nm nanoparticles is $\tau \approx 620$ ns. The difference between these constants is insignificant comparing with luminescence intensity decrease. This negligible change of slow decay time constant does not agree with the drastic decrease of luminescent intensity (about two times). In a case of luminescence quenching due to the energy transfer from excited states of the luminescent centers towards the surface defects through the multipolar interaction mechanism the luminescence decay kinetics would have to reveal an essential reduction. In this case the dynamics of the luminescent intensity decrease correlates with the luminescence decay time constant reduction. The opposite situation is expected when luminescence quenching is caused by the decrease of electron-hole recombination number due to the electron escape from the nanoparticle. Such a type of quenching is followed by essential decrease of the luminescent intensity, while the decay time constant changes slightly. Such the regularity for the luminescence parameters depending on the nanoparticles sizes is observed for the luminescence of the SrF₂ and other nanoparticles [4–7].

At the same time the luminescence intensity of the fast decay time component increases since the photoelectrons and the thermalization electrons escaped from nanoparticles contributes to the luminescent intensity of the polystyrene. Only part of thermalization electrons possessing the kinetic energy in the range of 4–10 eV is able to excite a polystyrene luminescence. Therefore it is more likely that the polystyrene luminescence will be caused mainly by the high-energy photoelectrons with energy much higher than $E_g=10$ eV. The mean free path of photoelectrons created in result of absorption of 23 keV X-ray quanta is about 30 nm. The surface layer with the size 30 nm can be considered as optimal for the external photoelectric effect. When the nanoparticle size will decrease the conditions for escape of the photoelectrons will be improved.

The increase of the nanocomposite luminescence intensity owing to the additional absorption of X-rays by nanoparticles is reasonable to estimate for nanocomposite loaded with nanoparticles of 16 nm size. In this case the increase of registration effectiveness due to the radiation channel of energy transfer from nanoparticles to polystyrene would be excluded as STE luminescence is almost absent in the nanoparticles of 16 nm size. Then, the increase of the efficiency would be associated with the increase of X-ray absorption capacity of nanoparticles comparing with the polystyrene absorption capacity. The ratio of absorption capacities of polystyrene with nanoparticles and pure polystyrene can be evaluated on the base of known values of attenuation lengths for SrF₂ and polystyrene, given in [15] as well as SrF₂ and polystyrene densities. In the case of 40 wt% SrF₂ concentration this ratio is close to 10. Similar ratio for the intensities was obtained on the base of analysis of SrF₂ and polystyrene X-ray excited luminescence intensity. The coincidence of experimentally observed and calculated ratios can be the evidence that light outputs of the composite and polystyrene are similar. Not in all cases the light output of the composite corresponds to the light output of the matrix. For example, for polystyrene containing 10 wt% of Hf_xSi_{1-x}O₂ nanoparticles the increase of light output by 20 wt% is observed [2]. Another situation is observed when polystyrene is loaded with metal-organic compounds of gadolinium. In the case of 10 wt% Gd the light output is 25 wt% smaller than in polystyrene [10].

3.3. Theoretical calculation

Since the existence of fast decay time component of the luminescence is caused by the photoelectrons emitted from the nanoparticles due to photoeffect, the luminescent intensity of fast component of composite has to be proportional to a part of volume V_0 of SrF₂ nanoparticle from which electrons can be emitted into the polystyrene. Based on this assumption the model for calculation of luminescence intensity dependence of fast decay time component of composite

polystyrene material with the embedded SrF₂ nanoparticles depending on nanoparticles sizes R is proposed (see the inset of Fig. 4). Thickness of nanoparticle surface layer from which the electrons can escape from nanoparticle is defined by the mean free path of an electron $l_{e,e}$. As it was already noted, the mean free path of photoelectron $l_{e,e}$ for the average X-ray excitation energy of 23 keV is equal ~ 30 nm for SrF₂ nanoparticles. The luminescent intensity was calculated for the polystyrene scintillator with concentration 40 wt% of SrF₂ nanoparticles. It should be noted that for the identical volume of nanocomposites the mass of SrF₂ nanoparticles m was identical in studied composite polystyrene samples loaded with nanoparticles of various sizes. Therefore, when the nanoparticles size R decreases the quantity of nanoparticles $N = \frac{3m}{4\pi\rho R^3}$ (ρ – density of SrF₂) in the polystyrene scintillator increases. In a case of $R > l_{e,e}$ the nanoparticle volume V , from which electrons can be emitted into polymer, is determined by the expression $V = NV_0 = \frac{4}{3}N\pi(R^3 - (R - l_{e,e})^3)$. In a case of $l_{e,e} \geq R$ the volume is $V = m/\rho$.

The calculation results of the dependence of the fast luminescence component intensity for the polystyrene composites on SrF₂ nanoparticles size are presented in Fig. 4 (curve 3). The calculated fast luminescence component intensity of nanocomposite increases when the SrF₂ nanoparticles size R decreases until the size is more than the mean free path of electron $l_{e,e}$ ($R > l_{e,e}$). Under this condition the part of photoelectrons created in a nanoparticle cannot leave its volume and as a result they do not give the contribution to the fast component of luminescence. The electrons can escape from the whole volume of SrF₂ nanoparticles into the polymer and give a contribution in luminescence when the nanoparticle size R is equal or less the mean free path of electron ($R \leq l_{e,e}$). For nanoparticles of such the sizes the fast luminescence intensity is maximal and it ceases to depend on nanoparticle size R (curve 3). Theoretically calculated curve 3 (Fig. 4) is in a good agreement with the experimental curve 2. Such the result is an additional evidence of fact that the fast decay time component of the luminescence of nanocomposite is caused by excitation of polystyrene by the electrons escaped from SrF₂ nanoparticles due to the photoeffect under the X-ray excitation.

4. Conclusions

The X-ray excited luminescence of nanocomposite films based on the polystyrene loaded with SrF₂ nanoparticles reveals an emission bands at 350 and 420 nm inherent for emission of polystyrene's activators (p-Terphenyl and POPOP). The luminescence intensity of

polystyrene nanocomposite is significantly increased due to embedding of inorganic SrF₂ nanoparticles. In particular, the luminescence intensity of the polystyrene composite film of 0.3 mm thickness loaded with 40 wt% of SrF₂ nanoparticles with size 16 nm increases by ~ 10 times in comparison with the unloaded polystyrene film of the same thickness.

The X-ray excited luminescence of nanocomposite films based on the polystyrene with embedded SrF₂ nanoparticles reveals the slow (~ 700 ns) and fast (~ 2.8 ns) decay time components. Contribution of the fast component increases with decreasing of nanoparticles size and becomes determinative at the size of 16 nm. The slow component is caused by the reabsorption of the self-trapped exciton luminescence of SrF₂ nanoparticles. The fast component is caused by the excitation of polystyrene with high-energy electrons emitted from the SrF₂ nanoparticle due to the photoeffect. The behavior of fast luminescence intensity represents the dependence of the external photoelectric effect effectiveness on the nanoparticles sizes. When the nanoparticle sizes are changed from 110 to 16 nm the fast component luminescence intensity of composite increases by $\sim 20\%$ because the conditions of photoelectron escape from nanoparticles is improved at decrease of their sizes.

In the composite loaded with the small nanoparticles when the emission mechanism of energy transfer from STE to polystyrene is absent, the polystyrene matrix is excited by the electrons that have escaped from the nanoparticles, demonstrating time scintillation parameters typical for polystyrene.

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