POLYSTYRENE COMPOSITES WITH LOADED LaF_3 NANOPARTICLES FOR REGISTRATION OF IONIZING RADIATION

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Film polymer composite scintillators based on scintillation polystyrene with n-terphenyl and POPOP activators and loaded LaF_3 nanoparticles have been developed for the registration of ionizing radiation. LaF_3 nanoparticles were obtained through precipitation involving ion substitution from $LaCl_3$ water and water-alcohol solution with the addition of NH_4F solution. The spectral and kinetic properties of polymer nanocomposites under X-ray irradiation have been studied. It was found that the efficiency of the ionizing radiation detection for a polystyrene composite with loaded non-luminescence LaF_3 nanoparticles increases by an order of magnitude compared to the efficiency of a polystyrene scintillator without nanoparticles, maintaining the spectral composition of the polystyrene scintillator radiation and its speed was 3 ns. It is proposed that the main mechanism of the scintillation generation is the excitation of polystyrene matrix by electrons that escape from the nanoparticle by the mechanism of photoeffect under the influence of ionizing radiation.

Key words: luminescence of nanoparticles, polystyrene nanocomposite, loaded LaF_3 nanoparticles, spectral and kinetic properties.

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I. INTRODUCTION

The growing need for radiation control over the movement of goods and monitoring the radiation background on large areas requires a significant amount of materials with high light output and speed performance to detect ionizing radiation, which would be technological and cheap in fabrication. The material for ionizing radiation detectors that meets the above mentioned requirements could be luminescence polystyrene. It is cheap, technological, and exhibits luminescence under the influence of X-rays with a decay time of about 3 ns. However, the low absorption capacity of polystyrene as to high-energy radiation due to its low effective atomic number Zeff substantially limits its use as a material for scintillation detectors of ionizing, and in particular X-ray radiation [1].

Nanocomposite scintillation materials, in which inorganic luminescence nanoparticles are used as a filler, show a significant increase in the efficiency of the registration of ionizing radiation [2, 3], when the size of nanoparticles is much larger than the free path of electrons in them. It turned out that this efficiency is determined by the size of nanoparticles and depends on the ratio between the free path of electron and the size of nanoparticles. The high-speed performance of such luminescence composites in the case of nanoparticles, for which the free path length l is less than the size of nanoparticles a ($l < a$), is ensured by radiative or resonance mechanisms of energy transfer from the nanoparticles to the polystyrene matrix [4–9]. In this case, the decay kinetics of the composite reproduces the luminescence decay parameters of inorganic dielectric particles and is an order of magnitude slower than the luminescence of the polystyrene matrix with n-terphenyl and POPOP activators. When the size of nanoparticles loaded in the polystyrene matrix is comparable or less than the free path length of the electrons in them ($l \geq a$), the luminescence of the polystyrene composite is associated with the electronic mechanism of energy transfer from nanoparticles to the polystyrene matrix and is determined by the luminescence decay kinetics of the polystyrene matrix [10, 11] which lies in the nanosecond range (2–3 ns). In order to study the efficiency of the electronic excitation mechanism of the scintillation polystyrene, it is proposed to exclude the radiation mechanism of the energy transfer from nanoparticles to polystyrene by synthesizing polystyrene nanocomposites loaded with non-luminescence LaF_3 nanoparticles and conducting spectral and kinetic studies of the obtained nanocomposites.

II. PRODUCTION TECHNOLOGY AND METHODS FOR MEASURING THE LUMINESCENCE CHARACTERISTICS OF LaF_3 NANOPARTICLES AND COMPOSITES BASED ON THEM

A. Synthesis of LaF_3 nanoparticles

LaF_3 nanoparticles were obtained from $La(NO_3)_3$ i NH_4F starting materials in water or water-ethyl-alcohol solution by the ion substitution reaction:

$$La(NO_3)_3 + 3NH_4F \rightarrow LaF_3 + 3NH_4\ NO_3.$$

To avoid concentration gradients, water-alcohol solution of ammonium fluoride NH_4F was added drop-by-drop in regular intervals to the lanthanum nitrate solution $La(NO_3)_3$.

The obtained nanoparticles were precipitated by centrifugation at a speed of 6000 rpm. Then they were washed with distilled water and centrifuged again. The procedure of centrifugation and washing of the nanoparticles was repeated once again. The washed nanoparticles were dried at 120°C and used for further studies.

To obtain larger LaF_3 nanoparticles, the method of hydrothermal synthesis in autoclave at the temperature of 200°C for 12–24 hours was used.

B. Identification of phase composition and evaluation of the size of LaF_3 nanoparticles

To study the structure and phase composition of LaF_3, methods of X-ray phase analysis were used. X-ray diagrams were measured on a DRON-4 diffractometer with a nickel filter and a copper anticathode (CuK_α radiation, $\lambda = 1.5406$ Å) in the range of angles $10° < 2\Theta < 80°$ with a scanning step of 0.05°.

According to the width of the diffraction maxima using to Scherer's formula, the average size of nanoparticles was found.

Figures 1 and 2 show the diffraction patterns of the synthesized LaF_3 particles. In Figs. 1 and 2, the diffraction patterns of LaF_3 nanoparticles obtained by the ionic substitution reaction with and without the addition of alcohol are shown, respectively. The diffractograms show that both methods allow producing nanoparticles of LaF_3 composition with the following average sizes: 29 nm — without the use of alcohol; 5 nm — using alcohol. Hydrothermal growth in a water-alcohol solution in an autoclave at a temperature of 200 °C led to an increase in the average size of the nanoparticles to 25 nm and 47 nm depending on the synthesis duration (12 and 24 hours, respectively). Hydrothermal growth in an aqueous solution in an autoclave at a temperature of 200°C led to an increase in the average size of the nanoparticles from 29 nm to 35 nm for 24 hour synthesis.

The proposed methods allowed us to obtain a wide set of LaF_3 nanoparticles with the average size from 5 nm to 49 nm.

C. Preparation of polystyrene films

Composite films were made from polystyrene scintillator chips produced by the Institute of Scintillation Materials of the National Academy of Sciences of Ukraine (Kharkiv), which contain organic luminescence impurities: n-terphenyl luminescence activator (2 wt.%) and POPOP spectrum shifter (0.1 wt.%).

The polystyrene scintillator chips were dissolved in an azeotropic mixture of $C_2H_4Cl_2 + CCl_4$ (dichloroethane + carbon tetrachloride). After the complete dissolution of the polystyrene, LaF_3 nanoparticles (40 wt%) were added to the mixture. The mixture was sonicated at 150 W for 15 minutes to obtain a uniform distribution of nanoparticles in the polystyrene solution. A colorless and completely transparent suspension of nanoparticles in the polystyrene solution was obtained. To obtain composite films, the suspension was applied drop-by-drop to a glass slide and held for 24 hours until the solvent completely evaporated.

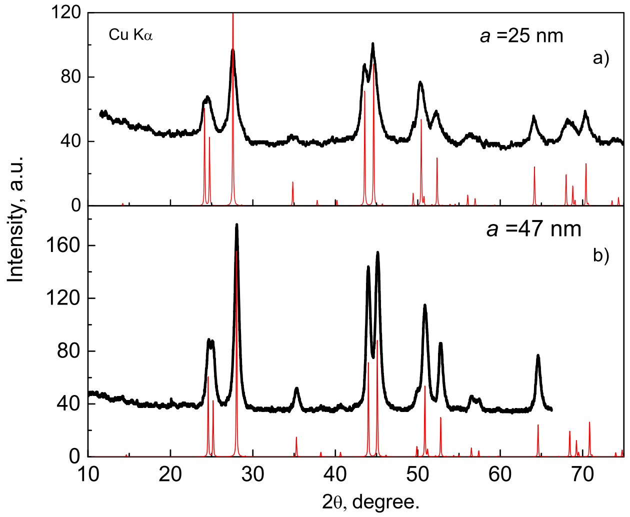

Fig. 1. Diffractograms of LaF_3 nanoparticles obtained from a water-alcohol solution in an autoclave at the annealing temperature of 200°C for 12 h (a) and 24 h (b)

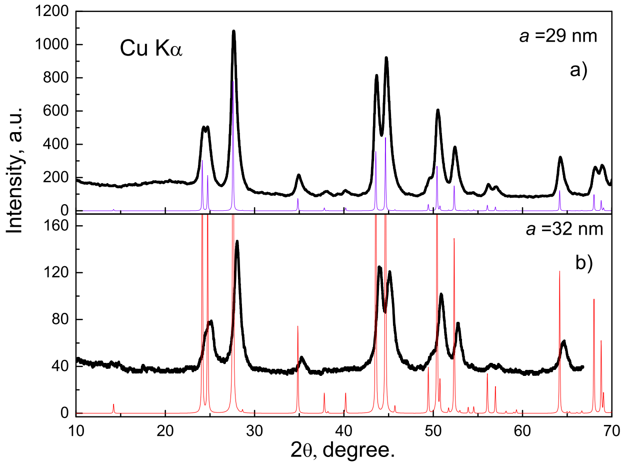

Fig. 2. Diffractograms of LaF_3 nanoparticles obtained from an aqueous solution (a) and in an autoclave at the annealing temperature of 200 °C for 24 hours (b)

The film composites formed in this way had good transparency and homogeneity. For luminescence studies, samples, 10 mm in diameter and 0.3 mm thick, were cut from film composites.

D. Measurement of spectral and kinetic luminescence parameters

The luminescence spectra, excitation spectra, and luminescence decay kinetics of LaF_3 nanoparticles and polymer composites with loaded LaF_3 nanoparticles under pulsed X-ray excitation were measured on an apparatus based on a LOMO MDR-2 diffraction monochromator with 20 nm/mm dispersion and pulsed X-ray source. The installation allows conducting luminescence and kinetic measurements in the 10^{-9}–10^{-6} s time interval and 200–800 nm spectral range. The anode voltage on the X-ray tube was $U = 40$ kV, the average current was about 100 μA, and the pulse duration was 2 ns. The average energy of the X-ray quanta was 23 keV. All measurements were made at room temperature.

III. RESULTS AND DISCUSSION

LaF_3 nanoparticles have an effective atomic number of $Z_{\text{eff}} \approx 51$, which indicates a much greater ability to absorb X-rays compared to a polystyrene matrix. However, in the case of excitation by X-ray quanta at $T = 300$ K, LaF_3 nanoparticles practically do not emit (3, curve 2). This is confirmed by the fact that their emission intensity is of the same order as the luminescence intensity of pure polystyrene (3, curve 1), which also practically does not emit under X-ray excitation.

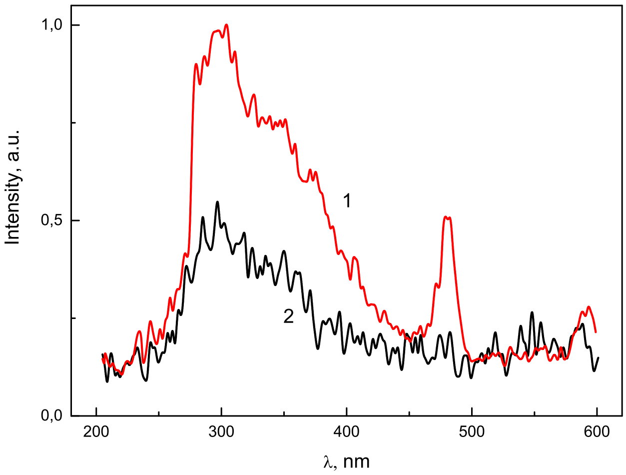

Fig. 3. Luminescence spectra: 1 — a polystyrene film without activators; 2 — LaF_3 nanoparticles with the average size of 25 nm under X-ray excitation

Figure 4 shows the luminescence of the polystyrene film scintillator (PSL) 0.3 mm thick without nanoparticles (curve 2) and with loaded different-size LaF_3 nanoparticles with 40 wt.% concentration (curves 3–5) in the case of X-rays excitation. For comparison, the luminescence of a PS polystyrene film without activators is shown (curve 1).

When inorganic LaF_3 nanoparticles are not present, the polystyrene scintillator has a weak emission (curve 2) in the form of two bands with maxima at 350 nm and 420 nm, which correspond to the luminescence of n-terphenyl and POPOP, respectively [12]. The luminescence of the polystyrene composite scintillator loaded with non-luminescence LaF_3 nanoparticles shows approximately 16 times more intense luminescence (curves 3–5) compared to the luminescence intensity of the polystyrene film with activators (curve 2) (PSL). The structure of the luminescence spectra of polystyrene composite with loaded nanoparticles is similar to the luminescence spectra of polystyrene films with n-terphenyl and POPOP activators and reveals two emisstion bands with the maxima of about 350 and 420 nm. Note that the luminescence intensity of composites with loaded LaF_3 nanoparticles under X-ray excitation is much higher than the intensity of a polystyrene scintillator without nanoparticles. With an increase in LaF_3 nanoparticle size from 5 nm to 47 nm at a constant concentration, if the size of nanoparticles is larder than 20 nm, the composite luminescence intensity decreases slightly (Fig. 4, insert).

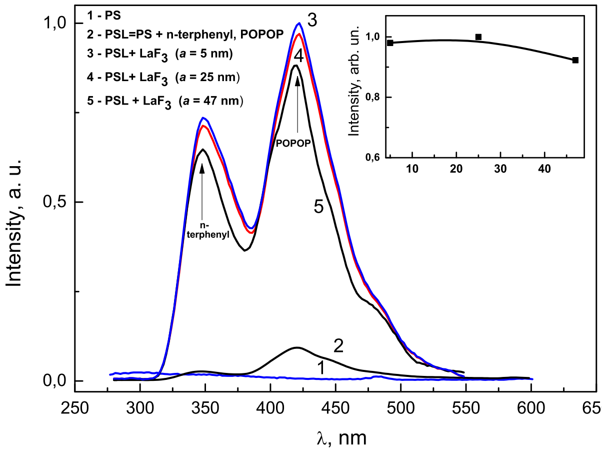

Fig. 4. X-ray luminescence of a polystyrene film without activators (PS) (curve 1); a scintillation polystyrene film without nanoparticles (PSL) (curve 2); a scintillation polystyrene films (PSL) with loaded LaF_3 nanoparticles with 40 wt.% concentration and average sizes of 5 nm (curve 3), 25 nm (curve 4) and 47 nm (curve 5). The film thickness is 0.3 mm

The observed behavior of the luminescence parameters of a polystyrene composite with loaded LaF_3 nanoparticles can be understood from the following considerations.

As the absorption capacity of polystyrene is low, the composite absorption capacity increases due to the loaded LaF_3 nanoparticles. In this case, the electrons under X-ray excitation move from the nanoparticles to the matrix and cause the emission by the polystyrene matrix (electronic excitation mechanism of polystyrene matrix [6–11], which is characteristic of scintillation polystyrene). The emission intensity will be determined by the ratio between the size of the nanoparticle and the electron free path. The most favorable conditions for increasing the luminescence intensity of the polystyrene composite are when the electron free path is greater than the size of the nanoparticles. In the case of excitation by X-ray quanta with 23 keV energy, the electron free path length is about 20 nm [13]. This value is larger or comparable with the size of LaF_3 nanoparticles. Under such conditions, the luminescence intensity of the composite film depends only on the volume from which the photoelectrons can escape to the polystyrene matrix and cause its emission. In [6], it was shown that the total volume of the scintillator inorganic component, from which electrons can exit into the polystyrene environment, slowly decreases as the size of the nanoparticles increases at a constant weight concentration. Accordingly, the luminescence intensity of the polystyrene nanocomposite with an increasing size of non-luminescence LaF_3 nanoparticles and constant concentration has a weak tendency to decrease.

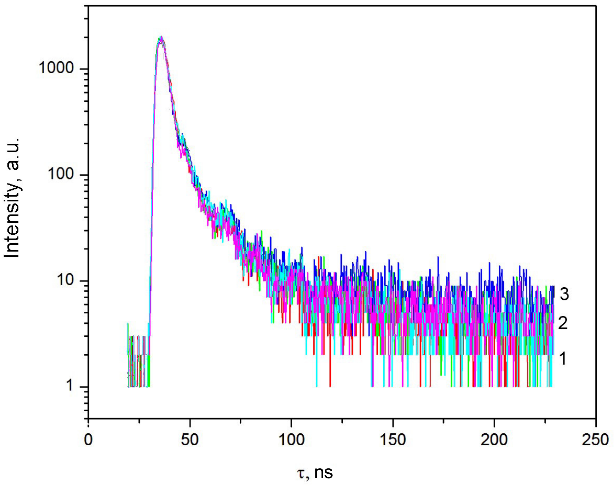

Fig. 5. Curves of X-ray luminescence decay kinetics: 1 — a scintillation polystyrene film (PSL) without nanoparticles (curve 1); film composites containing different-size LaF_3 nanoparticles (40 wt.%): curve 2 — 25 nm; curve 3 — 47 nm. The thickness of the films is 0.3 mm

It is not only the luminescence spectrum, but also the kinetics that reproduces the luminescence parameters of the polystyrene scintillator. The luminescence decay of the film without LaF_3 nanoparticles is characterized by monoexponential curves with the decay constant of 3 ns (Fig. 5, curves 1–3), which is characteristic of a polystyrene scintillator without nanoparticles. This indicates that the excitation energy from the non-luminescence LaF_3 nanoparticles is transferred to the polystyrene matrix by a non-radiating channel through the electronic mechanism via the injection of electrons that flew from outside the nanoparticle into the polystyrene matrix.

IV. CONCLUSIONS

Thin-film polymer scintillators based on scintillation polystyrene with n-terphenyl and POPOP activators and loaded LaF_3 nanoparticles were obtained. The luminescence spectra of polystyrene composites with loaded different-size LaF_3 nanoparticles consist of two emission bands with maxima at 350 and 420 nm, which correspond to the luminescence of n-terphenyl and POPOP polystyrene activators. The luminescence intensity of the composites with loaded LaF_3 nanoparticles under X-ray excitation is an order of magnitude higher than the intensity of a polystyrene scintillator without nanoparticles. The luminescence decay kinetics of the composites with loaded different-size LaF_3 nanoparticles is characterized by the decay constant of 3 ns, which is typical of a polystyrene scintillator without nanoparticles.

The observed regularities of the luminescence of the composites suggest that the main mechanism of scintillation is the excitation of the polystyrene matrix by the electrons formed in the nanoparticles under the influence of ionizing radiation by the photoeffect mechanism, which escaped from them to the polystyrene environment and excite the polystyrene matrix.

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ПОЛІСТИРОЛЬНІ КОМПОЗИТИ З УКРАПЛЕНИМИ НАНОЧАСТИНКАМИ LaF_3 ДЛЯ РЕЄСТРАЦІЇ ЙОНІЗУВАЛЬНОГО ВИПРОМІНЮВАННЯ

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Розроблено плівкові полімерні сцинтилятори на основі сцинтиляційного полістиролу з активаторами n-терфенілом та POPOP і вкрапленими наночастинками LaF_3 для реєстрації йонізувального випромінювання з наносекундною швидкодією. Наночастинки LaF_3 отримано методом осадження за реакцією йонного заміщення з водно- та водно-спиртового розчинів LaF_3 із додаванням розчину $\mathrm{NH}_4\mathrm{F}$. Середній розмір наночастинок LaF_3 з водно-спиртового розчину становив 5 нм, з водного розчину — 29 нм. Збільшували розмір наночастинок LaF_3 гідротермальним відпалом в автоклаві за температури 200°C протягом 12–24 годин.

Досліджено спектрально-кінетичні властивості полімерних нанокомпозитів із украпленими наночастинками LaF_3 різного розміру у разі збудження X-променями. Спектри люмінесценції полістирольних композитів із украпленими наночастинками LaF_3 виявляють дві смуги випромінювання з максимумами за 350 і 420 нм, які відповідають свіченню активатора полістиролу n-терфенілу та зміщувача спектра POPOP, відповідно. Інтенсивність люмінесценції полістирольних композитів із украпленими наночастинками LaF_3 за збудження X-випромінюванням зростає до 16 разів порівняно з інтенсивністю полістирольного сцинтилятора без наночастинок. Зі збільшенням розміру наночастинок LaF_3 від 5 нм до 47 нм за незмінної їх концентрації (40 ваг.%) інтенсивність люмінесценції полістирольного нанокомпозиту незначно зменшується. Кінетика загасання полістирольних композитів становить приблизно 3 нс, що відповідає кінетиці загасання сцинтиляційного полістиролу ($\sim$ 3 нс). Використання нелюмінесцентних наночастинок LaF_3 виключає радіаційний механізм перенесення енерґії від наночастинок до полістирольної матриці. Тому основним механізмом виникнення сцинтиляцій у полістирольному нанокомпозиті з украпленими нелюмінесцентними наночастинками LaF_3 є електронний механізм. У цьому разі електрони, що вилітають із наночастинки внаслідок зовнішнього фотоефекту, збуджують сцинтиляції в полістирольній матриці. Найбільша ефективність перенесення енерґії досягається тоді, коли довжина вільного пробігу електрона більша за розміри наночастинки або сумірна з нею. За такої умови фотоелектрони, ґенеровані в наночастинці під дією йонізувального випромінювання, мають найбільшу ймовірність виходу за її межі.

Ключові слова: спектри люмінесценції, спектри збудження, довжина термалізації, довжина вільного пробігу, наночастинка.