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Radiation resistance of composite scintillators containing grains of Y_2SiO_5:Ce or $Y_3Al_5O_{12}$:Ce obtained by solid-phase synthesis

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The paper focuses on the study of radiation resistance of composite scintillators containing the grains of Y_2SiO_5:Ce or $Y_3Al_5O_{12}$:Ce. The paper compares the results obtained for composite scintillators when the grains were made in two ways: (i) by grinding the ingots of the above substances those were obtained by solid phase synthesis, and (ii) by grinding the single crystals growing from the melt. The samples were irradiated by 8.3 MeV beam electrons (at the dose rate 1500 Mrad/h). The paper presents the photoluminescence spectra and values of the relative detection efficiency of beta-radiation of the scintillators measured before and after irradiation by accumulated dose *D* of 30 and 50 Mrad.

Keywords: radiation resistance, composite scintillators, solid phase synthesis, yttrium orthosilicate, yttrium garnet.

Исследована радиационная стойкость композиционных сцинтилляторов, содержащих гранулы Y_2SiO_5:Ce или $Y_3Al_5O_{12}$:Ce. Проведено сравнение результатов, полученных для композиционных сцинтилляторов, изготовленных двумя способами: дроблением слитков вышеупомянутых веществ, полученных твердофазным синтезом и дроблением монокристаллов, выращенных из расплава. Образцы облучались электронами с энергией 8,3 МэВ (темп облучения 1500 Мрад/час). Представлены спектры фотолюминесценции и значения относительной эффективности регистрации бета-излучения сцинтилляторов, измеренные до и после облучения до накопленной дозы *D* 30 и 50 Мрад.

Радіаційна стійкість композиційних сцинтиляторів, що містять гранули Y_2SiO_5:Ce або $Y_3Al_5O_{12}$:Ce, які були отримані твердофазним синтезом. *А.Ю.Бояринцев, М.З.Галунов, Л.Г.Левчук, .В.Мартиненко, Т.А.Непокупна, Ю.Д.Онуфрієв, В.П.Попов, О.В.Волошина.*

Досліджено радіаційну стійкість композиційних сцинтиляторів, що містять гранули Y_2SiO_5:Ce або $Y_3Al_5O_{12}$:Ce. Порівняно результати, які отримано для композиційних сцинтиляторів, що виготовлени двома шляхами: подрібненням зливків вищезгаданих речовин, що отримані твердофазним синтезом та подрібненням монокристалів, які вирощені з розплаву. Зразки опромінювалися електронами з енергією 8,3 МеВ (темп опромінення 1500 Мрад/год). Наведено спектри фотолюмінесценції і значення відносної ефективності реєстрації бета-випромінювання сцинтиляторів, що виміряні до та після опромінення до накопиченої дози *D* 30 та 50 Мрад.

1. Introduction

Recently, there were developed new type scintillators with high radiation resistance, namely, the composite scintillators containing single crystal grains of some inorganic scintillation substances [1–9]. A composite scintillator consists of the grains of scintillation material distributed in optically transparent media (elastomer). Dielectric polydimethylsiloxane elastomer Sylgard-184 was chosen as such media with considering the results presented by [10]. According to [10] the light transmittance of Sylgard-184 practically did not change at least up to dose 90 Mrad.

Composite scintillators have a number of advantages over single crystals [1–5]. First of all it is possibility to create composite detectors of any shape with no limitation on window area. It is possible to make composite scintillators flexible due to flexibility of polydimethylsiloxane. Another important advantage of composite scintillators is lower price as compared with single crystals [1]. Crystals with different physical damage (e.g., cracks) as well as parts of single crystals remaining after their machining (cuts) can be used for production of scintillation grains. It makes composite scintillators essentially cheaper: prime cost of composite detector production is at least two times lower as compared with corresponding single crystal [1]. A light output of such composite detectors can reach 90 % as compared with analogous single crystal one [3, 7]. Changing material of scintillation grains, proportion of grains and elastomer, optimizing shape and size of grains one can modify parameters of composite detector for different applications [3–5]. On condition of selection of proper material for scintillation grains, such combination of properties makes composite scintillators promising for high energy physics as well as for other tasks when large amount of radiation-resistant scintillation materials are required [2–6]. So investigation of radiation resistance of these new type scintillators along with investigation of their scintillation and optical characteristics is important problem.

Earlier inorganic composite scintillators based on grains of $Lu_{2(1-x)}Y_{2x}SiO_5$ (LYSO:Ce), Gd_2SiO_5:Ce (GSO:Ce), $Gd_2Si_2O_7$:Ce (GPS:Ce), $Al_2O_3:Ti^{3+}$, Y_2SiO_5:Ce (YSO:Ce) and $Y_3Al_5O_{12}$:Ce (YAG:Ce) single crystals were made and investigated [1–9]. The values of relative scintillation efficiency [1], relative light yield [2, 4, 6–9], light transmittance [2, 7–9] and luminescence [7–9] spectra were obtained for investigated composite scintillators for different integrated doses accumulated at various dose rates. Obtained results showed that:

— composite scintillators based on $Al_2O_3:Ti^{3+}$ single crystal grains are radiation-resistant at least up to doses 125 Mrad and 550 Mrad when the dose rates are 0.20 Mrad/hour and 1500 Mrad/h, correspondently [2, 6, 8];

— composite scintillators based on GSO:Ce, GPS:Ce single crystal grains are radiation- resistant at least up to doses 200 Mrad and 250 Mrad when the dose rates are 0.20 Mrad/hour and 1500 Mrad/hour, correspondently [1, 2, 6, 7];

— composite scintillators based on YSO:Ce and YAG:Ce single crystal grains are radiation-resistant at least up to doses 25 Mrad and 150 Mrad when the dose rates are 0.10 Mrad/h and 1500 Mrad/h, correspondently [1, 4, 9];

— composite scintillators based on LYSO:Ce single crystal grains are radiation-resistant at least up to doses 25 Mrad [1].

Such impressive results have shown prospects of further development of radiation-resistant composite scintillators.

Returning to such the advantage of composite scintillators, as cheapness it is worth to note, that cost of scintillators is important and sometimes determining parameter at their practical application. The most expensive stage of a composite scintillator creation is growth of single crystal. It is obviously that riddance of this stage from technological chain of inorganic composite scintillator production has to make their prime cost yet lower. Therefore we have advanced the idea to use scintillation materials obtained by solid phase synthesis for making the grains [4]. It would permit to avoid the stage of crystal growth. Using YSO:Ce as an example, we realized our first attempt to make a composite scintillators on the basis of grains obtained by solid phase synthesis. We also carried out preliminary tests of their radiation resistance in comparison with YSO:Ce single crystal as well as YSO:Ce composite scintillators made of single crystal grains [4]. The investigated samples were irradiated with 8.3 MeV electrons up to integrated dose 50 Mrad. Obtained results showed that light yield of single crystal and composite scintillators decreased no more than 2 % after irradiation. Composite scintillators on the basis of grains obtained by solid phase synthesis demonstrated radiation damage comparable

with it for composite scintillators made of single crystal grains. So, preliminary tests showed high radiation stability of YSO:Ce composite scintillators on the basis of grains obtained by solid phase synthesis. Such results are very promising and indicate prospects of technological procedure when grains obtained by solid phase synthesis are used for making of composite scintillators.

This paper is continuation of our investigations begun in [4] and dedicated to the study of radiation resistance of YSO:Ce and YAG:Ce composite scintillators containing the grains obtained by solid phase synthesis. YSO:Ce and YAG:Ce are known as radiation-resistant scintillation materials with high light yield and rather shot decay time [11–15]. They can be used at nuclear medicine (positron-emission tomography), astrophysics and geophysics, for beta-, gamma- and X-ray-visualization and for some other purposes. Also scintillation materials YSO:Ce and YAG:Ce are considered as possible candidates for high energy physics tasks [12–14]. According to above-mentioned, such range of practical use of these scintillation materials allows to suppose that YSO:Ce and YAG:Ce composite materials will be in demand.

Like in [4], we will compare composite scintillators on the basis of grains obtained by solid phase synthesis with corresponding single crystal as well as composite scintillators made of single crystal grains. It should be noted, that in earlier publications one of the main parameter for estimation of radiation resistance of composite scintillators was the value of light output [2, 4, 6–9]. But in technical application sometimes it is important to know how the ionizing radiation detection efficiency of a scintillator will change as the result of the irradiation. Therefore in this work we will estimate radiation resistance of investigated scintillators, first of all, by changes in the value of detection efficiency for the example of beta irradiation. We will also take into account changes in luminescence spectra of investigated scintillators obtained before and after irradiation. Similarly to [2, 9] and according to [16], we will consider scintillation material as radiation-resistant by chosen parameter A up to some dose D, if the value of the parameter for this dose A_D changes no more than on a half of its initial value A_0 (i.e. its value for $D = 0$). As it was mentioned above, in present work detection efficiency of betaradiation as well as normalized intensity of luminescence were chosen as such the parameters.

2. Experimental

2.1 Solid phase synthesis

The method of YSO:Ce and YAG:Ce solid phase synthesis includes the following stages: preliminary drying of starting oxides, their mixing in stoichiometric proportion, pressing and high-temperature annealing. As starting we used the oxides of Y_2O_3 (Shenzhen Nexconn Pharmatechs Ltd, China), CeO_2 (Stanford Materials Corporation, USA) SiO_2 and Al_2O_3 (HimLaborReaktiv, Ukraine) with purity not less than 99.99 % to exclude possible influence of impurity ions on activator luminescence. To remove adsorbed moisture and carbon dioxide the starting oxides were preliminary annealed at a temperature of 1100°C for yttrium and cerium oxides, and at a temperature of 600°C for silicon and aluminium oxides. The oxides were weighed in stoichiometric proportion accurate to ±0.0001 g. The proportions were the following Y_2O_3:SiO_2 = 1:1 for yttrium orthosilicate and Y_2O_3:Al_2O_3 = 1:1.67 for yttrium garnet. The mixture of the oxides was charged into a ball mill and was intermixed for 30 min to achieve high degree of homogeneity of initial components. The Ce^{3+} content of starting mixtures is 0.2 at.% for YSO:Ce and 0.3 at.% for YAG:Ce, respectively. The activator was added at the stage of stoichiometric mixture obtaining. Then obtained mixture was pressed to increase contact surface of the reacting components that leads to speed increase of solid phase synthesis. The final stage of the process is high-temperature annealing in inert atmosphere of Ar at a temperature of 1300±100°C during 8–10 h for YSO:Ce and in reducing atmosphere of Ar + CO at a temperature of 1650±100°C during 5–6 h for YAG:Ce. The inert and reducing atmospheres of annealing were used to convert the activator from tetravalent state to trivalent one by reaction: $2CeO_2 \rightarrow Ce_2O_3 + 1/2\ O_2$. After carrying out of solid phase synthesis X-ray phase analysis data of the samples showed that phase content of yttrium orthosilicate and yttrium garnet is 99 wt.% and 98 wt.%, respectively.

2.2 Preparation of the experimental samples

Single crystals YSO:Ce and YAG:Ce were grown by the Czochralski method. To make composite scintillators a single crystal or an ingot obtained by solid phase synthesis were mechanically ground. Then by means of the set of calibrated sieves grains with size 45–

63 μm were selected. The selected grains were introduced into the dielectric polydimethylsiloxane elastomer Sylgard-184 [10] prepared as follows. Two components of the elastomer were mixed and after that the elastomer was treated under vacuum to remove air bubbles. Then we introduced the grains into the prepared elastomer, mixed and treated under vacuum again. After that we polymerized it in a forming container at a temperature of +120°C during 2 h up to complete hardening of the composite scintillator. The proportion of scintillation grains and elastomer was 75 wt.% and 25 wt.%, respectively. All obtained composite samples were 20×20×0.5 mm^3 and single crystal samples were 20×20×2 mm^3.

2.3 Irradiation of the samples

The irradiation of the samples was carried out at the electron accelerator of NSC "Kharkiv Institute of Physics and Technology". The samples of YSO:Ce and YAG:Ce single crystals as well as composite scintillators based on YSO:Ce and YAG:Ce were irradiated by 8.3 MeV beam electrons at the room temperature. The average dose rate was 1500 Mrad/h. The samples were consistently exposed to radiation until the prescribed integrated dose D was accumulated. Then for given value of accumulated dose D we carried out the measurements of photoluminescence spectra and determined the relative detection efficiency of beta-radiation of the samples. After that the samples again were exposed to radiation until the next prescribed value of integrated dose was reached and the measurements of luminescent and scintillation characteristics were repeated. The prescribed values of integrated dose were 30 Mrad and 50 Mrad. The error of determination of the value of accumulated integrated dose was ±3 %.

2.4 Determination of the relative detection efficiency of beta-radiation

We used measuring system Canberra and photomultiplier R1306 Hamamatsu as a photodetector to determine the relative detection efficiency of beta-radiation of investigated scintillators. The scintillators were excited by ^{90}Sr–^{90}Y beta-radiation source that was placed on the center of a scintillator. We used the diffuse reflector Tetratek as a reflective scintillator coating. To create an optical contact between scintillator output window and photomultiplier window we used optical grease. We obtained scintillation amplitude spectra for investigated samples and the reference sample under excitation by ^{90}Sr–^{90}Y source using multichannel pulse-height analyzer. The spectra were accumulated during the same time and under the same excitation conditions. We used corresponding not irradiated single crystal (YSO:Ce or YAG:Ce) as the reference scintillator. The measurements were run before irradiation of the samples and after they have accumulated the necessary dose D.

We determined the relative integrated efficiency of beta-radiation detection ξ of a scintillator, which has accumulated integrated dose D, as follows:

$$\xi = \left(\sum_{i=50}^{1024} N_i^2 / \sum_{i=50}^{1024} R_i^2 \right) / \left(\sum_{i=50}^{1024} N_i^1 / \sum_{i=50}^{1024} R_i^1 \right) \qquad (1)$$

where N_i is a number of pulses accumulated in i channel of scintillation amplitude spectrum for investigated scintillator under excitation by ^{90}Sr–^{90}Y source; R_i is a number of pulses accumulated in i channel of scintillation amplitude spectrum for the reference scintillator under excitation by ^{90}Sr–^{90}Y source. The superscript 1 refers to the measurements run before irradiation of an investigated sample ($D = 0$) and the superscript 2 — to the measurements run after accumulation by it the prescribed dose value D. The relative integrated efficiency ξ of investigated scintillators when $D = 0$ was taken as 1.

2.5 The measurement of photoluminescence spectra

We obtained the luminescence spectra with combined spectrofluorimeter FLS 920 Edinburg Instruments under excitation by photons over the energy range 1.55–6.0 eV. The arc discharge xenon lamp Xe 900 450W was used as a source of excitation. The photomultiplier Hamamatsu R1527 was used as a photodetector over the range from 230 to 800 nm.

3. Results and discussion

3.1. YSO:Ce scintillators

We determined the relative efficiency of beta-radiation detection ξ (1) as a function of accumulated integrated dose D for single crystal and composite scintillators. Fig. 1 demonstrates the obtained results. Fig. 1 shows that the detection efficiency ξ varies insignificantly within the range of the doses considered both for YSO:Ce single crystal

and for YSO:Ce composite scintillators. The maximum deviation of the ξ value is observed for composite scintillator containing grains obtained by solid phase synthesis ($D = 50$ Mrad) and corresponds to 5 % ± 0.5 %, only. These results indicate that the composite scintillators containing grains of YSO:Ce obtained by solid phase synthesis at least up to doses 50 Mrad when the dose rate is 1500 Mrad/h are radiation resistant. It is in a good agreement with the results we obtained in [4].

Fig. 2 shows normalized luminescence spectra measured before ($D = 0$) and after ($D = 50$ Mrad) irradiation for YSO:Ce composite scintillator containing the grains obtained by solid phase synthesis. The scintillator was excited with light of wavelength 355 nm. Obtained luminescence spectra are similar to ones of composite scintillators based on YSO:Ce single crystal grains as well as to ones of YSO:Ce single crystal [9, 11]. Fig. 2 demonstrated that there are no significant changes in the luminescence spectra obtained before and after irradiation for the YSO:Ce composite scintillator. As a result of irradiation, a weak redistribution of the intensity within the luminescence band is observed. However, this effect is insignificant. Thus, the width at half the height for the spectra obtained before and after irradiation differs by about 8 %, and the areas under the spectra curves by about 14 %. These results are in a good agreement with the results presented in Fig. 1 and prove that composite scintillators containing the grains of YSO:Ce obtained by solid phase synthesis are radiation resistant over the considered dose range.

3.2. YAG:Ce scintillators

For YAG:Ce scintillators we also determined values of the relative efficiency of beta-radiation detection ξ (1) versus accumulated integrated dose D. The obtained results are presented in Fig. 3. Fig. 3 shows that in the considered dose range for the investigated samples YAG:Ce the ξ value decreases slightly more significantly than for corresponding YSO:Ce scintillators. However, the changes of ξ value were small for all YAG:Ce scintillators, just like it was for YSO:Ce scintillators. Thus, the maximum deviation of ξ value is about 7 %±0.5 %. As in the case of YSO:Ce scintillators, it is observed for dose 50 Mrad for the composite scintillator containing the grains obtained by solid phase synthesis. Such small

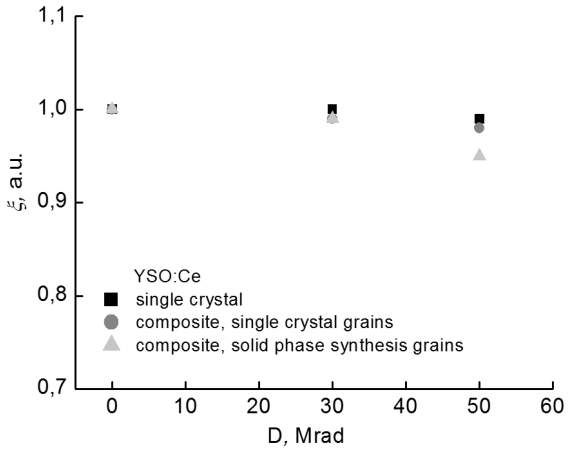

Fig. 1. The relative detection efficiency ξ (*1*) of ^{90}Sr–^{90}Y source beta-radiation for YSO:Ce scintillators as a function of accumulated integrated dose D. Squares — the single crystal; circles — the composite scintillator containing the single crystal grains; triangles — the composite scintillator containing the grains of the ingot obtained by solid phase synthesis.

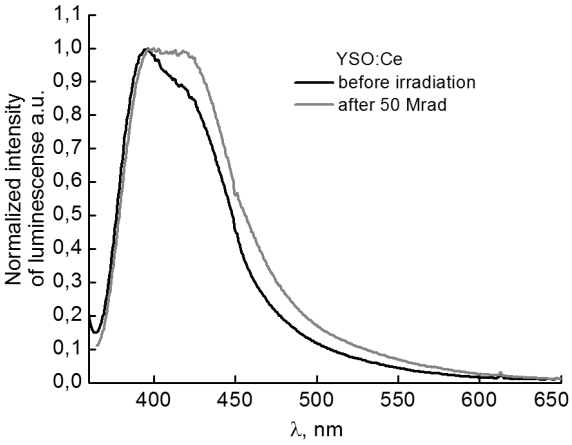

Fig. 2. Normalized photoluminescence spectra of the YSO:Ce composite scintillator containing the grains of ingot obtained by solid phase synthesis.

changes of ξ value evidence of radiation resistance of YAG:Ce composite scintillators containing the grains obtained by solid phase synthesis at least up to doses 50 Mrad when the dose rate is 1500 Mrad/h.

Fig. 4 presents normalized luminescence spectra measured before ($D = 0$) and after ($D = 50$ Mrad) irradiation for YAG:Ce composite scintillator containing the grains obtained by solid phase synthesis. The scintillator was excited with light of wavelength 455 nm. Obtained luminescence spectra are similar to ones of composite scintillators

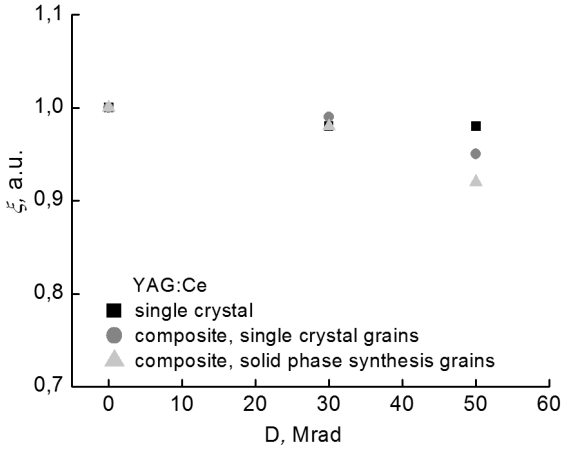

Fig. 3. The relative detection efficiency ξ (*1*) of ^{90}Sr–^{90}Y source beta-radiation for YAG:Ce scintillators as a function of accumulated integrated dose *D*. Squares — the single crystal; circles — the composite scintillator containing the single crystal grains; triangles — the composite scintillator containing the grains of the ingot obtained by solid phase synthesis.

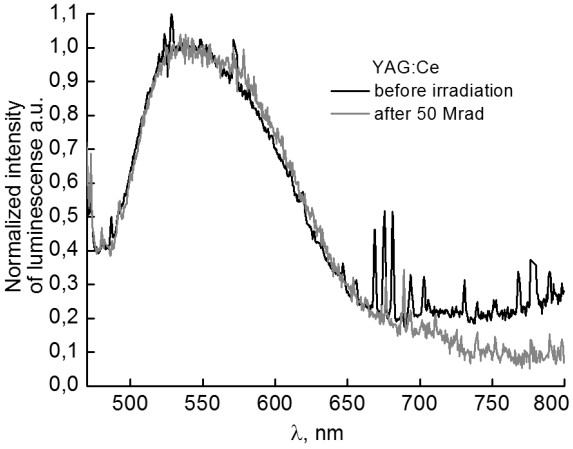

Fig. 4. Normalized photoluminescence spectra of the YAG:Ce composite scintillator containing the grains of ingot obtained by solid phase synthesis.

containing the YAG:Ce single crystal grains as well as to the spectrum of YAG:Ce single crystal [9, 11]. In the luminescence spectra of the composite scintillator YAG:Ce, made from grains obtained by solid-phase synthesis, no significant changes are observed as a result of irradiation to a dose of 50 Mrad (Fig. 4). Within band of YAG:Ce luminescence the spectra obtained before ($D = 0$) and after ($D = 50$ Mrad) irradiation actually coincide. Some decrease of intensity is observed in the spectrum of irradiated sample in the wavelength range, where YAG:Ce luminescence is not effective (> 700 nm). Comparison of the spectra of YAG:Ce composite scintillator obtained before and after irradiation shows that the width at half the height for the spectra differs by less than 2 % and the areas under the spectral curves differ by less than 8 %. Like the plots ξ versus *D* (Fig. 3), these results indicates radiation resistance of YAG:Ce composite scintillators containing grains obtained by solid phase synthesis over the considered dose range.

Thus the obtained results has shown that YSO:Ce and YAG:Ce composite scintillators containing the grains obtained by solid phase synthesis demonstrate radiation resistance at least up to doses 50 Mrad when the dose rate is 1500 Mrad/h. And the degree of radiation damage for the composite scintillator containing the grains obtained by solid phase synthesis is comparable with it for corresponding composite scintillator made of single crystal grains and single crystal within this dose range. Such small changes of scintillation and luminescent characteristics of investigated YSO:Ce and YAG:Ce composite scintillators allows us to suppose that these scintillators will be radiation-resistant for higher dose of irradiation.

4. Conclusions

Thys, we have carried out the investigations of radiation resistance of Y_2SiO_5:Ce and $Y_3Al_5O_{12}$:Ce composite scintillators containing the grains obtained by solid phase synthesis. We compare these results with ones obtained for Y_2SiO_5:Ce and $Y_3Al_5O_{12}$:Ce composite scintillators containing the single crystal grains, as well as Y_2SiO_5:Ce and $Y_3Al_5O_{12}$:Ce single crystals.

The obtained results indicate the radiation resistance of composite scintillators containing the grains of Y_2SiO_5:Ce and $Y_3Al_5O_{12}$:Ce at least up to doses 50 Mrad when the dose rate is 1500 Mrad/h. Moreover, composite scintillators containing the grains obtained by solid-phase synthesis show a level of radiation damage comparable to the corresponding composite scintillators containing the grains obtained from single crystal and even single crystals. The combination of radiation resistance comparable to single crystals and a significantly lower cost makes the composite scintillators containing the grains obtained by solid phase synthesis the most promising for practical use.

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