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DEVELOPMENT OF RADIATION RESISTANT SCINTILLATORS BASED ON RARE-EARTH ALUMINATES

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LuYAG:Ce and YAG:Ce,Ca crystals were obtained by the Czochralski method using tungsten crucibles in reducing surroundings. Crystals $(Lu_xY_{1-x})_3Al_5O_{12}$:1%Ce and crystals of YAG:Ce,Ca with different concentrations of Ce and Ca were grown. Studies and analyses of their characteristics were carried out. The analysis of their characteristics is based on experimental data that we obtained by measurements of light output, decay time, spectra of luminescence, excitation, and light transmittance.

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INTRODUCTION

The work is devoted to the search for new alternative scintillation materials for solving modern problems of radiation materials science and instrumentation. This is, first of all, obtaining scintillation materials for creating ionizing radiation detectors for conducting the latest experiments in high-energy physics, which requires registration of super-large fluxes of ionizing radiation with a short decay time.

A characteristic feature of experiments planned and carried out at new generation charged particle and ion accelerators (such as, for example, the Large Hadron Collider (LHC at CERN) is the exposure of detectors to high doses of radiation (up to several tens and even hundreds of Mrad). The dose load on the subsystems of the detectors of experiments at the LHC is proportional to the peak luminosity of the collider, which by the end of the 2nd session of its operation (2018) had already reached 20 $fb^{-1}s^{-1}$, which was 2 times higher than the corresponding design value. Over the next few years, it is planned to increase the luminosity of the LHC several times more. By the end of the work of the accelerator complex (in ~ 20 years), it is planned to obtain a data array that will correspond to an integral luminosity of 3,000 fb^{-1}. At present, none of the detectors of the main experiments at the LHC meets such conditions, and work on their modernization is becoming extremely relevant. In this case, the search for and development of new scintillation materials characterized by high radiation resistance and fast response are of particular importance [1].

Given the above, interest in fast radiation-resistant scintillators is growing. YAG-based garnet crystals are considered to be an efficient material for laser, phosphor, and scintillation materials. The Ce-activated garnet did not attract much attention. Everything changed after the discovery of effective solid multicomponent solutions of garnets in which the substitution of Al/Ga cations with a light output of up to 58,000 phot./MeV is used. This value approaches the theoretical limit given the band gap of these materials. The improvement in the light output was due to the disappearance of the electronic levels of the charge carrier traps. This occurred due to the modification of the electronic structure by cationic substitution.

Therefore, it should be investigated whether the capture of charge carriers can be reduced and the efficiency of complex crystals based on available YAG:Ce can be improved.

One possible solid solution with a modified band structure is LuYAG. Thus, LuYAG:Pr crystals have an improved light output, reaching 33,000 phot./MeV compared to 19,000 phot./MeV in LuAG:Pr, and a shorter decay time. Thus, LuYAG:Pr crystals have an improved light output, reaching 33,000 phot./MeV compared to 19,000 phot./MeV in LuAG:Pr, and a shorter decay time.

1. EXPERIMENTAL DETAILS

1.1. CRYSTAL GROWTH

LuYAG:Ce crystals were obtained by the Czochralski method using tungsten crucibles in a reducing surroundings. Until recently, the main method for obtaining rare-earth garnet crystals was their growth by the Czochralski method from iridium crucibles. The only alternatives were crucible-free methods or growth in molybdenum by the Stockbarger method [2].

Recently, the possibility of growing YAG:Ce and YAG crystals by the Czochralski method using tungsten crucibles was shown in [3]. Thus, evaporating oxygen from the surface of the melt interacts with carbon contained in the atmosphere according to the following formulas:

$$O_2 + C = CO_2,$$
$$CO_2 + C = 2CO \text{ (at } > 950 \text{ ºC)}.$$

This prevents oxidation of the wolfram tooling.

Thus, in this work, LuYAG:Ce crystals were obtained by the Czochralski method using wolfram crucibles in a CO-containing atmosphere.

Crystals $(Lu_xY_{1-x})_3Al_5O_{12}$:1%Ce were grown. After that, the samples 5x5x2 mm were cut and polished from the obtained crystals. The samples were cut at the same height in order to cancel the influence of the uneven distribution of Ce.

Also, crystals of YAG:Ce,Ca with different concentrations of Ce and Ca were grown.

1.2. MEASUREMENTS OF SCINTILLATION LIGHT YIELD AND DECAY TIME

Light yield and energy resolution were measured under irradiation with a ^{137}Cs γ-source at the 662 keV energy. As a photodetector a R1307 Hamamatsu PMT ran at 800…960 V with a linear dynode voltage divider was used. The photomultiplier tube (PMT) output was connected to a charge-sensitive preamplifier BUS 2−94 and then to a BUI-3K shaping amplifier. The signal from the preamplifier was formed by a shaping amplifier with a 2 μs shaping time. To collect the whole scintillation light, the samples and the open part of PMT photocathode were covered with a Teflon reflector. No optical contact between samples and the PMT window was provided. For absolute light yield determination, the light yields were compared to $Bi_4Ge_3O_{12}$ (BGO) etalon with a light yield of 8,600 phot./MeV produced at ISMA. The energy resolution of ^{137}Cs 662 keV peak was determined by approximation of the obtained pulse height spectra with the Gaussian function.

Scintillation decay curves were measured with Hamamatsu R6231 PMT and excitation with 662 keV gamma ray from ^{137}Cs source. A signal from the PMT anode was fed to the 50 Ω terminated input of the Rigol DS6064 oscilloscope.

1.3. MEASUREMENTS OF LIGHT TRANSMITTANCE

The measurements of the luminous transmittance T in the range from 300 to 700 nm were performed by Shimadzu-2450 spectrophotometer with the integrating sphere. The comparison channel remained blank and the light flux inside it was calibrated to be the same as the light flux falling on a sample in the measuring channel. The inaccuracy of the calibration was limited by 0.5%. The value of T was calculated as follows:

$$T = (I/I_0)\cdot 100\%, \quad (1)$$

where I_0 is the light flux in the comparison channel, I is the light flux, which has passed through a sample in the measuring channel. Actually, the T – value (1) is a relative luminous transmittance, where $T = 100\%$ is the luminous transmittance of air.

1.4. MEASUREMENTS OF LUMINESCENCE AND EXCITATION SPECTRA

To obtain luminescence spectra and absorption spectra we use spectrofluorimeter Varian Cary Eclipse. In our experiments, the range of wavelengths is 300…700 nm.

2. RESULTS AND DISCUSSION

First of all, measurements of the scintillation yield of samples of different chemical compositions were carried out, but they were taken from the same part of the crystal. The results of measuring the light output (L) and resolution (R) for all studied samples are shown in Table 1. At a value of 100% light output, the light output of the BGO crystal was chosen.

Table 1

Relative light output L_{rel} and resolution R of samples based on $(Lu_xY_{1-x})_3Al_5O_{12}$:Ce

Sample	Without optical contact		With optical contact	
	L_{rel}, %	R, %	L_{rel}, %	R, %
x = 0.25	186.5	15.6	206.7	13.2
x = 0.5	179.4	14.2	188.7	12.9
x = 0.75	148.5	14.1	169.8	11.5
x = 1	180.6	13.7	189.3	11.3

Table 1 shows that the light output decreases with increasing lutetium concentration in the crystal. In this case, high light output is observed for samples that do not contain yttrium in their composition. Also, samples of this composition show the high efficiency of registration of ionizing radiation.

Using the method of direct digitization of the scintillation pulse, the decay time of the scintillation pulse was studied. The experimental curves were described using an exponential function, and thus the decay times were obtained for each of the samples. Fig. 1 shows the kinetics of scintillation decay time for samples of scintillators of the crystals $(Lu_xY_{1-x})_3Al_5O_{12}$:Ce. The change in the scintillation time was observed experimentally.

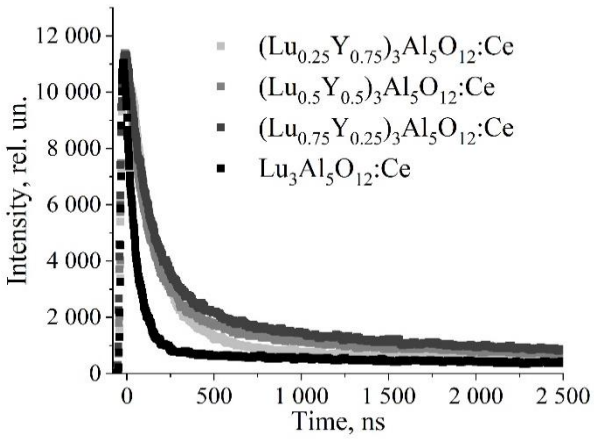

Fig. 1. Dependence of the decay time of scintillations on the concentration of lutetium

The decay time of scintillations depends on the concentration. Fig. 1 shows that an increase in the concentration of yttrium leads to a reduction in the luminescence time of the scintillation pulse. And samples that do not contain yttrium have the shortest decay time.

According to the data presented in Fig. 1, the following Table 2 was built.

In this study, the effect of changing the scintillation time for samples of new scintillators with different Lu/Y ratios, first obtained at ISMA, is experimentally confirmed.

Table 2

The decay time of crystals based on $(Lu_xY_{1-x})_3Al_5O_{12}$:Ce

Sample	Decay time, ns
$(Lu_{0.25}Y_{0.75})_3Al_5O_{12}$:Ce	190
$(Lu_{0.5}Y_{0.5})_3Al_5O_{12}$:Ce	181
$(Lu_{0.75}Y_{0.25})_3Al_5O_{12}$:Ce	206
$Lu_3Al_5O_{12}$:Ce	70

The obtained scintillation decay times are within the range of values given in the literature for scintillators activated by Ce^{2+} ions (literature data). Based on the obtained scintillation decay time, the optimal value of the pulse formation time (8 μs) was chosen to obtain the maximum value of its amplitude.

Also, using the above method, the kinetic characteristics of the YAG:Ce,Ca samples before and after annealing were determined. The results of processing the decay curves of the scintillation pulse for these samples are presented in Table 3.

Table 3

The decay time of crystals based on YAG(Ce, Ca) before and after annealing

Sample	Decay time, ns	
	Before annealing	After annealing
YAG(Ce,Ca) 0.3/0.6	202	63
YAG(Ce,Ca) 1%/1%	176	60

Also, the optical transmittance of light was studied for samples of single crystals $(Lu_xY_{1-x})_3Al_5O_{12}$:Ce. The research results are shown below.

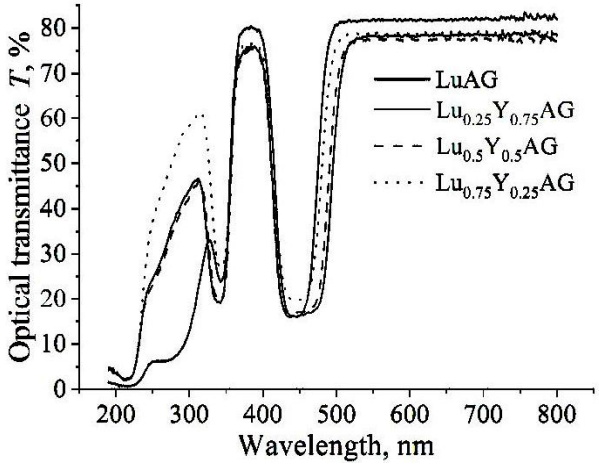

Fig. 2. Comparison of optical light transmittance for samples of single crystal scintillators based on $(Lu_xY_{1-x})_3Al_5O_{12}$:Ce with different Y and Lu ratios

Fig. 2 shows a comparison of the light transmittance spectra of samples of different chemical compositions.

As can be seen from Fig. 2, the largest value of optical transmission in the luminescence region (light wavelengths greater than 500 nm) of samples of single crystals based on $(Lu_xY_{1-x})_3Al_5O_{12}$:Ce are samples of $Lu_3Al_5O_{12}$:Ce, which do not contain yttrium at all.

Fig. 3 shows a comparison of the excitation spectra for single-crystal samples of scintillators based on $(Lu_xY_{1-x})_3Al_5O_{12}$:Ce with different chemical compositions for a luminescence wavelength of 510 nm.

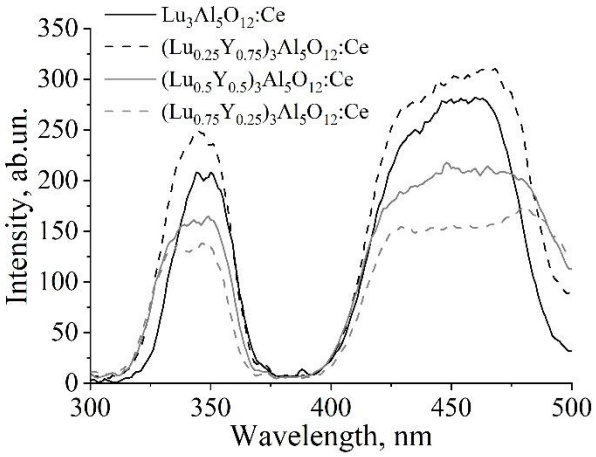

Fig. 3. Comparison of excitation spectra for single crystal samples of scintillators based on $(Lu_xY_{1-x})_3Al_5O_{12}$:Ce with different chemical compositions for a luminescence wavelength of 510 nm

Fig. 3 shows that when the chemical composition of $(Lu_xY_{1-x})_3Al_5O_{12}$:Ce single crystals changes (the Lu and Y ratio changes), the shape of the luminescence excitation spectra almost does not change, and only the light wavelength changes.

For samples of single crystal scintillators based on $(Lu_xY_{1-x})_3Al_5O_{12}$:Ce, the luminescence spectra were studied. The intensity is given in arbitrary units; therefore, only the estimate of the shape and wavelengths of luminescence, and not their intensity, will be correct.

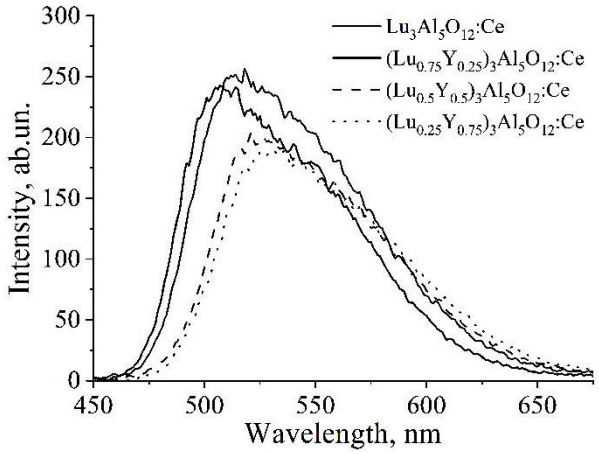

Fig. 4. Comparison of the luminescence spectra of single crystal scintillators based on $(Lu_xY_{1-x})_3Al_5O_{12}$:Ce with excitation of the light wavelength of 345 nm

For comparison, Fig. 4 shows the luminescence spectra of samples of single crystal scintillators based on $(Lu_xY_{1-x})_3Al_5O_{12}$:Ce of different chemical compo-

sitions (different ratios of lutetium and yttrium) with excitation of the light wavelength of 345 nm.

Fig. 4 shows that with an increase in the Y content in mixed crystals $(Lu_xY_{1-x})_3Al_5O_{12}$:Ce, a slight shift of the luminescence spectrum to a longer wave-length region is observed. At the same time, the shape of the spectrum does not undergo significant changes with a change in the chemical composition (a change in the ratio of yttrium and lutetium).

For comparison, Fig. 5 shows the luminescence spectra of samples of single crystal scintillators based on $(Lu_xY_{1-x})_3Al_5O_{12}$:Ce of different chemical compositions (different ratios of lutetium and yttrium) with excitation of the light wavelength of 460 nm.

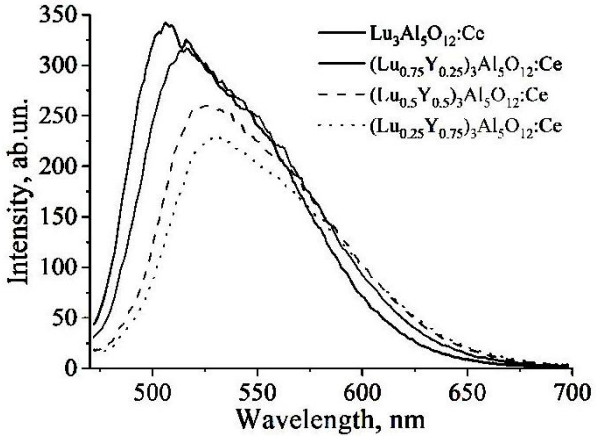

Fig. 5. Comparison of the luminescence spectra of single crystal scintillators based on $(Lu_xY_{1-x})_3Al_5O_{12}$:Ce with excitation of the light wavelength of 460 nm

Fig. 5 shows that with an increase in the Y content in mixed crystals $(Lu_xY_{1-x})_3Al_5O_{12}$:Ce, an insignificant shift of the luminescence spectrum to a longer wavelength region is observed. At the same time, the shape of the spectrum does not undergo significant changes with a change in the chemical composition (a change in the ratio of yttrium and lutetium).

We also studied the luminescence spectra of YAG:Ce,Ca samples before and after annealing with different concentrations of Ce and Ca.

A study of the luminescence spectra of samples of single crystal scintillators based on YAG:Ce,Ca with different concentrations of cerium and calcium after annealing showed that the luminescence intensity in the regions of 400 and 530 nm, upon excitation at 340 and 460 nm, is either absent or very low.

That is, in these samples of single crystals after annealing, there is no luminescence due to excitation by light photons, but luminescence can be observed due to excitation by ionizing radiation.

CONCLUSIONS

1. LuYAG:Ce mixed crystals with different Y/Lu ratios and YAG:Ce,Ca crystals with different Ce and Ca concentrations were grown.

2. Preliminary studies of optical transmission, luminescence, light output, and extinction time have been carried out.

3. It has been established that after annealing of LuYAG:Ce and YAG:Ce,C crystals, their light output increases from 1.5 to 2.5 times.

4. For crystals after annealing, a decrease in the decay time is observed. For example, for YAG:Ce,Ca with a Ce/Ca concentration ratio of 0.3/0.6%, the decay time before annealing was 202 ns, and after annealing it decreased to 63 ns.

5. Optimal crystals for creating high-speed composite scintillators at the next stage of work are YAG:Ce,Ca (after annealing) and LuAG:Ce crystals.

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РОЗРОБКА РАДІАЦІЙНО СТІЙКИХ СЦИНТИЛЯТОРІВ НА ОСНОВІ РІДКІСНОЗЕМЕЛЬНИХ АЛЮМІНАТІВ

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Кристали LuYAG:Ce та YAG:Ce,Ca отримані методом Чохральського з використанням вольфрамових тиглів у відновному середовищі. Вирощено кристали $(Lu_xY_{1-x})_3Al_5O_{12}$:1%Ce та кристали YAG:Ce,Ca з різними концентраціями Ce та Ca. Були проведені дослідження та аналіз їх характеристик. Аналіз їх характеристик ґрунтується на експериментальних даних, які отримані нами шляхом вимірювань світлового виходу, часу згасання, спектрів люмінесценції, збудження та пропускання світла.