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Impact of codoping on structure, optical and scintillation properties of $Gd_2Si_2O_7$-based crystals

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Impact of codoping on structure, optical, and scintillation properties of $Gd_2Si_2O_7$:Ce (GPS:Ce) crystals doped with La^{3+} and Sc^{3+} have been considered. GPS:Sc,Ce and GPS:La,Ce crystals have been obtained by the Top Seeded Solution Growth method with SiO_2 self-flux. Codoping influences the type of structure, density, as well as decreases self-absorption of luminescence in crystals. Temperature dependence of light yield at elevated temperatures have been obtained and compared to other pyrosilicate based crystals.

Рассмотрено влияние соактивирования на структуру, оптические и сцинтилляционные свойства кристаллов $Gd_2Si_2O_7$:Ce (GPS:Ce), активированных La^{3+} и Sc^{3+}. Кристаллы GPS:Sc, Ce и GPS:La, Ce были получены Top Seeded Solution Growth методом. Показано, что соактивирование изменяет тип кристаллической структуры, плотность, а также снижает перепоглощение люминесценции в кристаллах. Получены температурные зависимости светового выхода при повышенных температурах в сравнении с другими кристаллами пиросиликатов.

1. Introduction

Complex rare earth silicate oxide single crystals are widely used in detector systems for medicine, security, and high energy physics. Technology of large size crystal growth is more developed for Lu_2SiO_5:Ce (LSO:Ce) [1] and $Lu_{2x}Y_{2-2x}SiO_5$:Ce (LYSO:Ce) [2]. Lutetium pyrosilicate scintillator $Lu_2Si_2O_7$:Ce (LPS:Ce) demonstrates excellent temperature stability of light yield at elevated temperatures together with high light yield and fast nanosecond decay [3]. This feature is of special importance for well logging applications. However, no evidences of LPS:Ce industrial production have been obtained so far. Well known drawbacks of abovementioned scintillators include inhomogeneity of characteristics along the crystal, extremely high crystallization temperatures (1900–2150°C), and high cost of Lu_2O_3 raw material.

In this context, development of scintillators based on gadolinium pyrosilicate $Gd_2Si_2O_7$ (GPS) is of special interest. Besides the abovementioned advantages of pyrosilicate family scintillators (Table 1), GPS:Ce efficiently registers thermal neutrons due to the presence of ^{155}Gd and ^{157}Gd isotopes with enormously high thermal neutron capture cross section. It is im-

Table 1. Basic characteristics of Ce-doped rare earth silicate scintillators [4–6]

Crystal	γ-Excitation, 662 KeV ^{137}Cs			T_m, °C
	Light yield, phot/MeV	Energy resolution, %	Decay time, ns	
GSO:Ce	8500	9–11	56	1950
LSO:Ce	27000	7.3—9.7	40	2100
LPS:Ce	26000	9.5	38	1900
GPS:Ce	26000	5.1	40	1750

portant that GPS crystals do not contain Lu and can be grown from significantly cheaper raw materials. However, GPS:Ce is an incongruent melting compound. It was shown that growth of GPS:Ce crystals from melt is possible only at doping with 10–30 at.% Ce (in respect to Gd). In accordance with [7], heavy Ce-doping leads to changes in the Gd_2O_3–SiO_2–Ce_2O_3 phase diagram and stabilizes orthorhombic phase of pyrosilicate. Therefore, in such crystals Ce^{3+} is both the host cation modifying the phase diagram, and activator of luminescence. However, large amount of Ce^{3+} leads to significant luminescence self absorption of self and, as the issue, to light yield decrease in bulk samples. Therefore, search for codopants, which are able to stabilize pyrosilicate phase and decrease cerium content in crystal is of special importance.

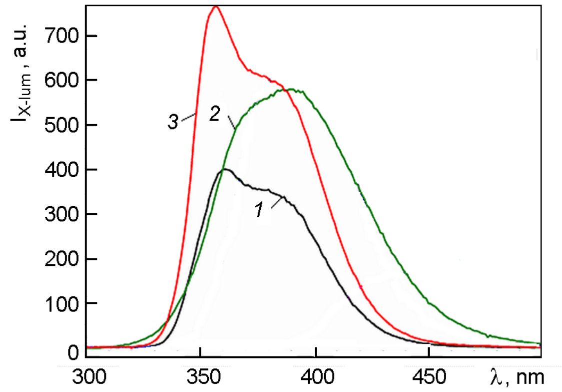

Fig. 1. X-ray luminescence spectra of the obtained crystals: *1* — GPS: 10 at. % Ce (orthorhombic), *2* — GPS: 10 at. % La, 1 at. % Ce (tetragonal); *3* — GPS: 5 at. % Sc, 0.2 at. % Ce (orthorhombic).

2. Experimental procedure

Crystals were grown by the Top Seeded Solution Growth (TSSG) method in conventional induction heating setups in Ar atmosphere using Ir crucibles of 60 mm in diameter and 60 mm in height. Ir wire with the 1 mm diameter was used as a seed. Crystal pulling rate was 0.3–0.5 mm/h, and crystal rotation rate was 5–10 rot/min. Using this method, several GPS-based crystals with diameter up to 20 mm and length up to 50 mm were obtained. Rare earth oxides and SiO_2 with purity not worse than 4N were used as raw materials.

X-ray studies of samples were carried out using a single crystal diffractometer "Xcalibur-3" by Oxford Diffraction (MoKα-radiation, $\lambda = 0.71073$ Å, graphite monochromator, a Sapphire-3 CCD-detector, ω/θ — scanning in the range $2\theta \le 90°$, accounting for absorption by equivalent reflections). Structure calculations were carried out using a SHELX-97 and WinGX software. Elementary cell parameters were refined by the Rietveld method, from diffractogramms obtained on powders of the same crystalline samples using a Siemens D500 powder diffractometer. Results obtained by the single crystalline method were taken as initial data for refinement.

Density of samples were evaluated by weighing the samples of regular shape using electronic balance with 10^{-4} g precision and measuring their volume using a micrometer.

Emission spectra in the 230–800 nm range were determined using combined fluorescent lifetime and steady-state spectrometer FLS 920 (Edinburgh Instruments). Xe lamp was used for steady-state measurements, and nanosecond hydrogen-filled flashlamp was used for decay time measurements.

Light yield and energy resolution were measured on 2×2×2 mm^3 and 3×3×3 mm^3 samples with polished faces. Scintillation parameters were tested for 662 keV Cs-137 gamma source by a R1307 Hamamatsu PMT ran at −800V HV with linear dynode voltage divider. PMT output was connected to the charge-sensitive preamplifier BUS 2-95 and AMA-03F multichannel analyzer. Signal from preamplifier was transferred to cus-

Table 2. Some properties of the obtained crystals

Crystal	GPS	GPS:Ce	GPS:Sc, Ce	GPS:La, Ce
Growth method	TSSG	Czochralski	TSSG	TSSG
Lattice type	Orthorhombic, $Pna2_1$	Orthorhombic, $Pna2_1$	Orthorhombic, $Pna2_1$	Tetragonal, $P4_3$
Lattice parameters (Å) and volume of elementary cell	a = 13.88836	a = 13.88915	a = 13.85034	a = 6.67299
	b = 5.05569	b = 5.05596	b = 5.05003	c = 24.33233
	c = 8.32054	c = 8.32015	c = 8.29361	V = 1083.49
	V = 584.229	V = 584.266	V = 580.093	
Density, g/cm^3	5.39	5.20	5.68	5.72
Integral intensity of X-ray luminescence (GSO:Ce = 100 %)	–	170	330	320
Decay times at photo-excitation, ns	–	31	26	25
FWHM of 662 keV peak, %	–	13.6	9.9	ND
Light yield, phot/MeV	–	36500	39000	38000 (evaluation)

tom shaping amplifier with the shaping time 2 μs. During measurements, crystals were coupled to the PMT entrance window using silicon optical compound Visilox V-788. In order to collect the whole scintillation light, the crystal together with open part of PMT photocathode were covered by 3 layers of Teflon tape.

Temperature dependence of the integral luminescence was measured in the 300–500 K range at irradiation by an X-ray emitter (U = 40 kV, I_a = 25 mA, Cu anode); temperature was controlled using a RP1-16 A controller.

3. Results and discussion

3.1. Choice of codopant

Growth of undoped rare earth pyrosilicates by direct crystallization from melt by Floating Zone or Czochralski methods is possible for rare earth cations with the radii <0.87 Å, otherwise pyrosilicates melt with decomposition [8]. Gd^{3+} ionic radius equals 0.94 Å [9]. Basically, type of phase and shape of phase diagram of pyrosilicates is strongly dependent on the averaged ionic radius of trivalent cations and crystallization temperature. Basing on detailed study of $(Gd,Ce)_2O_3$–SiO_2 phase diagram [7] the Top Seeded Solution Growth (TSSG) method with SiO_2 self flux was implemented in the present work. The excess of SiO_2 in melt was up to 4 mol. % relatively the stoichiometric composition.

Optically inactive La^{3+} with the ionic radius similar to one in Ce^{3+} (1.02 Å in Ce^{3+} and 1.03 Å in La^{3+}, correspondingly) was chosen in the first case, assuming that these two cations will identically shift the averaged lanthanide cation radius and, as a sequence, identically modify the phase diagram. In this case, Ce^{3+} with concentration up to 1 at.% is the activator of luminescence, and efficient cation radii is changed mainly due to the addition of 10 at.% of La^{3+}. In case of Sc^{3+} codoping with significantly smaller ionic radius compared to lanthanides, its addition to melt leads to decrease of trivalent cation averaged radius. Besides this, it is known that melts of some complex borates melting with decomposition can be stabilized by scandium addition. As the result, congruent melting compound was obtained [10, 11].

As the result, single crystals with the following compositions were grown: GPS, GPS: 5 at. % Sc, 0.2 at. % Ce, GPS: 10 at. % La, 1 at. % Ce (Table 2).

3.2. Structure and density of codoped GPS crystals

Seven types of polymorph modifications are inherent to rare earth pyrosilicates [12]. The crystal samples obtained in the present work are related to orthorhombic and tetragonal structures. This is conditioned by

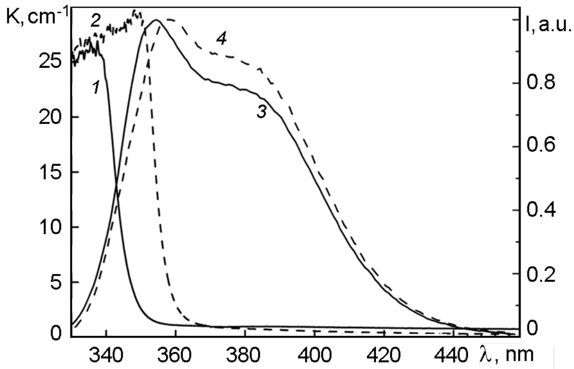

Fig. 2. Absorption spectra of GPS: 5 at. % Sc, 0.2 at. % Ce (*1*) and GPS: 10 at. % Ce (*2*) and normalized X-ray luminescence spectra: GPS: 5 at. % Sc, 0.2 at. % Ce (*3*) and GPS: 10 at. % Ce (*4*).

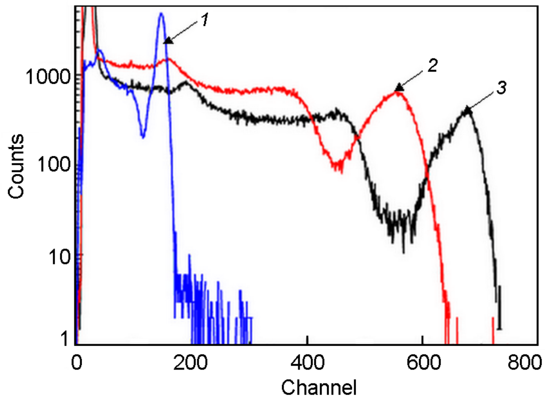

Fig. 3. Pulse height spectra of pyrosilicate samples in comparison with BGO at γ-excitation (^{137}Cs, 662 keV): *1* — BGO, *2* — GPS: 10 at. % Ce, *3* — GPS: 5 at. % Sc, 0.2 at. % Ce.

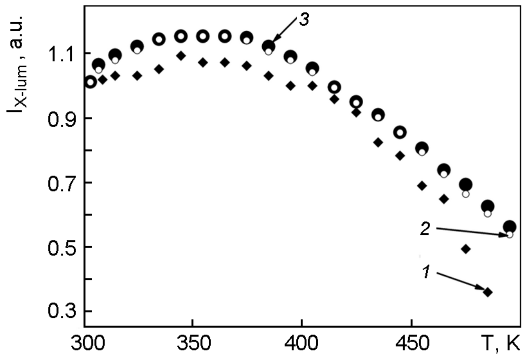

Fig. 4. Temperature stability of light yield: *1* — LPS:Ce; *2* — GPS: 10 % La, 1 % Ce (tetragonal), *3* — GPS: 10 % Ce (orthorhombic).

the averaged ionic radius of rare earth cations in every compound, as well as crystallization temperatures. Crystal structures of the obtained samples are presented in Table 2. Clear XRD peaks of the corresponding phases without broadening of characteristic lines, and increase of lattice parameters compared to undoped GPS certify that Sc^{3+} and La^{3+} enter into the lattice as host cations substituting Gd^{3+} in corresponding sites and forming solid solution. The measured density significantly increases due to the codoping. In the case of Sc^{3+} codoping, density increases due to the decrease of averaged ionic radius and lattice parameters of orthorhombic lattice. Increase in density for La^{3+} codoped crystal up to 5.72 g/cm^3, probably, is caused by the change in lattice type and more close packing of atoms in tetragonal structure. As the result of the applied codoping, crystal density significantly increases in both cases, which is favorable for scintillator applications.

3.2. Luminescent and scintillation properties

X-ray luminescence of Ce-doped GPS crystals with different crystal structures are attributed to $5d$–$4f$ in Ce^{3+} ions [13]. Both the studied codoped samples demonstrate nearly the same integrated luminescence intensity, around 3× in respect to GSO:Ce (Fig. 1, Table 2). Decrease of luminescence self absorption in codoped crystal due to the lowering the Ce concentration and weakening of absorption band associated with $4f$–$5d_1$ transition in Ce^{3+} is well illustrated with GPS:Sc,Ce having the same crystal structure, as GPS:Ce (Fig. 2). Minimization of self absorption in scintillator is important at utilization of large volume crystal detectors.

Absolute light yield of crystals determined with account for matching of scintillator luminescence band with PMT sensitivity spectral range, and reabsorption in crystals is 39000 and 36500 phot/MeV for GPS:Sc,Ce and GPS:Ce, correspondingly. Pulse height spectra of the samples in comparison with BGO scintillator at γ-excitation ^{137}Cs (662 keV) are presented in Fig. 3. Absolute light yield of La, Ce-codoped sample have not been measured because of small size of the sample. Basing on its X-ray luminescence intensity (Table 2), its light yield can be evaluated as ~38000 phot/MeV. Rather bad values of energy resolution (Table 2) determined from the same spectra, probably, indicate significant inhomogeneity in grown crystals. From the other side, it evidences a potential for further improvement of light yield in crystals by optimization of crystal growth technology.

Excellent stability of light yield at elevated temperatures is the key advantage of pyrosilicate-based scintillators. This feature was illustrated before on example of LPS:Ce [3] and GPS:10 % Ce [14]. In the present work, temperature dependence of light yield was determined with La, Ce-codoped crystal. One may see that it is not behind those analogues (Fig. 4). Increase in light yield by 10–15 % at heating from room temperature up to 100–150°C is observed, and more than 50 % of light yield at room temperature retains at 230°C.

4. Conclusions

Absolute light yield of GPS-based crystals was evaluated as 39000, 38000, and 36500 phot/MeV in GPS:Sc,Ce, GPS:La,Ce, and GPS:Ce, correspondingly. GPS:Ce codoping with La^{3+} or Sc^{3+} leads to significant luminescence self absorption in crystals. This factor is important at utilization of large-size bulk detectors. Codoped crystals demonstrate excellent stability of light yield at elevated temperatures. This is a crucial advantage for scintillator application in standard, high-temperature (above 150°C), and ultra-high temperature (above 220°C) well logging.

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Вплив соактивування на структуру, оптичні та сцинтиляційні властивості кристалів на основі $Gd_2Si_2O_7$

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Розглянуто вплив соактивування на структуру, оптичні та сцинтиляційні властивості кристалів $Gd_2Si_2O_7$:Ce (GPS:Ce), активованих La^{3+} та Sc^{3+}. Кристали GPS:Sc, Ce та GPS:La, Ce отримано Top Seeded Solution Growth методом. Показано, що соактивування змінює тип кристалічної структури, щільність, а також знижує перепоглинання люмінесценції у кристалах. Отримано температурні залежності світлового виходу при високих температурах у порівнянні з іншими кристалами піросилікатів.