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TECHNIQUE FOR OBTAINING LARGE COMPLEX OXIDE CRYSTALS FOR EXPERIMENTS ON MUON-TO-ELECTRON CONVERSION REGISTRATION IN HIGH ENERGY PHYSICS

Technological approaches for growing qualitative large size scintillation crystals based on rare-earth silicates have been proposed. A method of charging the iridium crucibles using the eutectic phase instead of the oxyorthosilicate has deen developed.

Key words: large size single crystal, Czochralski method, scintillator, and luminescence.

Nowadays, the development of techniques for growing large scintillation crystals is the subject of many researches [1—3], insofar as the practical application of these crystals in some cases is limited with the size of single-crystal boules that would ensure the most effective recording of certain types of ionizing radiation. For example, a calorimeter consisting of scintillation elements made of large (30 × 30 × 110 mm^3) oxyorthosilicate lutetium-yttrium ($(Lu_xY_{1-x})_2SiO_5 : Ce$) crystals is expected to be used in Mu2e experiment [4]. These elements will constitute four detecting lines, each having 11 series of 44 scintillation elements (Fig. 1).

Due to high density, effective atomic number, chemical stability, good moisture resistance, rapid (nanosecond) attenuation of luminescence, significant light yield and radiation resistance the cerium activated crystals based on complex oxides are one of the most promising classes of scintillators for their use as particle detectors in high-energy physics experiments, such as Mu2e, COMET, etc. [5, 6]. The rare-earth oxyorthosilicate crystals activated with cerium can fully meet the requirements of projects dealing with the muon-to-electron conversion, as they can have an energy resolution of 1% at 105 MeV and a decay time of less than 100 ns [5]. It is important to pay special attention to mixed scintillation crystals inasmuch as they surpass the constituents by some characteristics (e.g. light yield), or the drawbacks and weaknesses typical for their component parts can be minimized or even eliminated. For example, according to [7, 8], the light yield of Ce-activated mixed lutetium-yttrium-aluminum perovskite ($Lu_x Y_{1-x}AlO_3 : Ce$) is approximately twice higher as compared with the yttrium-aluminum perovskite ($YAlO_3$:Ce) and the lutetium-aluminum perovskite ($LuAlO_3 : Ce$). A similar phenomena has been recently observed for lutetium-gadolinium-aluminum-gallium garnet $(Lu_{1-y}Gd_y)_3(Al_{1-x}Ga_x)_5O_{12} : Ce$ [9]. A successful example of engineering of rare-earth orthosilicate mixed crystals is the lutetium-yttrium orthosilicate with improved energy division and light yield as compared with the lutetium oxyorthosilicate ($Lu_2SiO_5 : Ce$) [10, 11].

The paper deals with techniques for growing large-sized crystals of oxyorthosilicate lutetium-gadolinium ($(Lu_xGd_{1-x})_2SiO_5 : Ce$), yttrium ($Y_2SiO_5 : Ce$), and lutetium-yttrium ($(Lu_xY_{1-x})_2SiO_5 : Ce$). The Czochralski method was chosen

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for growing large oxyorthosilicate crystals. This method is often used for growing oxide crystals that melt congruently, including the silicates.

The process of obtaining the crystals can be presented in several stages: 1) preparation of primary (basic) materials; 2) filling of crucible with basic materials; 3) crystal growth; and 4) testing of crystals.

PREPARATION OF BASIC MATERIALS

The batch for growing the REE silicate crystals activated by cerium ions was prepared by the solid-phase synthesis technique using the following primary oxides: Gd_2O_3(4N), SiO_2(5N), CeO_2(4N), Y_2O_3(4N), and Lu_2O_3(4N). At the first stage of the solid-phase synthesis, the batch primary components were annealed in a Joule furnace at 300 °C (silicon oxide) and at 1100 °C (rare-earth oxides) to remove absorbed moisture and CO_2. The components were weighed and mixed in stoichiometric ratio. The mixture was loaded into a platinum boat pan and annealed for 8 hours at a temperature of 1200 °C until respective REE silicate formed.

DEVELOPMENT OF TECHNIQUES FOR FILLING CRUCIBLE WITH BASIC MATERIAL

Growth of crystals by the Czochralski method involves the use of crucibles, with the melt therein leveling 5—10 mm below the upper edge of the crucible (depending on the size thereof). This is because of the fact that this level of melt in the crucible provides visual control over the seeding process and makes it possible to create a distribution of thermal fields for ensuring steady growth of the crystal at the early stage. The batch for growing the oxide crystals has a low bulk density, therefore filling of the crucible before growing crystal includes phased feeding of basic material to the crucible with repetition of the cycle «*batch feeding into the crucible — melting of batch — cooling of crucible with basic materials*» to obtain the necessary level of melt in the crucible. The repetitive cooling of crucible leads to its destruction caused by the recrystallization of crucible material and its mechanical deformation with cracking of the walls and the bottom, as a result of the formation of gas bubbles in crystallized melt and the difference in thermal expansion factors of the crucible material and the basic components. To eliminate this problem, two techniques for filling the crucible with basic material were used. The first one implies that the batch is fed to the crucible through the hopper. The hopper where the batch is fused is placed above the crucible, in the induction block. Having been heated in argon, the batch melts and outpours filling the crucible.

However, the method that works well for filling the crucibles with batch of up to 1 kg proves itself to be inadmissible for large crucibles loaded up to 3 kg. In a limited space of growth chamber, it is problematic to heat uniformly the entire volume of the hopper to the melting point, with overheating of some parts of the furnace being unacceptable. In practice, the attempts to use this technique led to overheating of some parts of iridium hopper causing a risk of iridium melting. At the same time, the lower part of the hopper located near the crucible that is placed in the cold zone does not warm up enough. As a result, a cork arises and prevents the melt from pouring to the crucible. This entails a short lifespan of the hop-

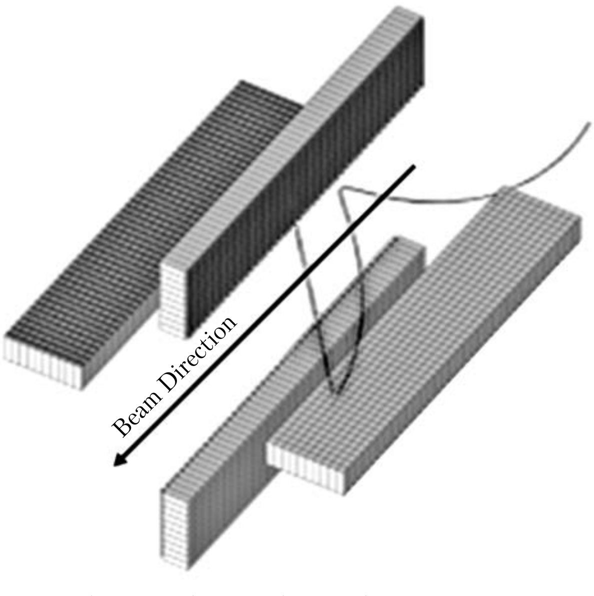

Fig. 1. Calorimeter detecting lines in the Mu2e experiment [4]

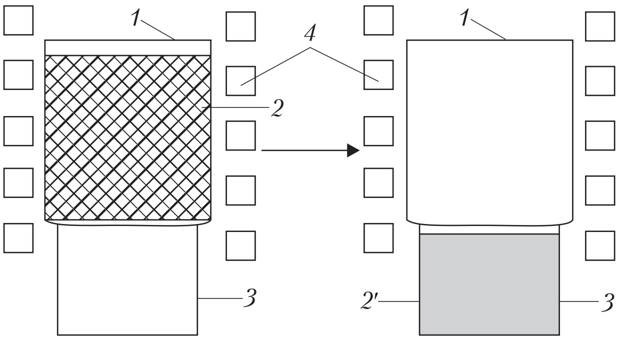

Fig. 2. Schematic flow chart of the process: *1* — hopper, *2* — charging material, *2′* — melt, *3* — crucible, *4* — inductor

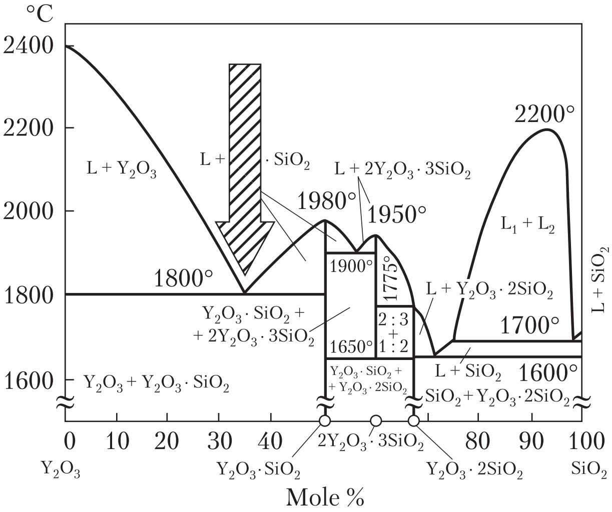

Fig. 3. Phase-rule diagram of $Y_2O_3 - SiO_2$ [13]

per made of precious iridium, which results in increased production costs.

To solve this problem, a new method has been proposed for filling the crucible with basic material [12]. This method is based on the same scheme as showed in Fig. 2, but the composition of basic materials is different. The hopper is fed with initial components taken in non-stoichiometric proportion, namely the share of rare-earth oxide exceeds that required by the stoichiometric ratio. The composition of basic material corresponds to the eutectic point (Fig. 3, *the arrow*); the melting temperature at this point is by 200 °C lower than the melting point of oxyorthosilicate phase, which provides easy filling of crucibles. To obtain the oxyorthosilicate phase, a mixture of oxides is added directly to the crucible in such a proportion as required for getting an oxyorthosilicate compound.

Usually, from 90 to 95 wt. % of eutectic material is fed to the hopper and from 5 to 10 wt. % of total mass required for the further growth of crystal is loaded to the crucible. The proposed method gives a significant reduction of energy and time for obtaining the oxide single crystals due to lowering the melting temperature by 150–200 °C as compared with the respective oxide crystal. In addition, the service life of crucibles and hopper (which are made of precious metals) extends significantly.

CRYSTAL GROWTH

The crystal grew in *Oxide-II* induction heater. An iridium crucible having a diameter of 90 mm and a height of 90 mm with the melt of respective structure located in the center of water-cooled inductor and separated with two zirconium ceramic layers and with one alundum ceramic layer was used for crystal growth by the Czochralski method (Fig. 4).

An iridium aperture located above the crucible was used to create the required thermal field. The position of aperture with respect to the crucible edge and the crucible edge with respect to the upper coil inductor was chosen and regulated experimentally. The optimal position of the aperture was established to be 5 mm above the crucible that has to be located 5 mm with respect to the upper inductor coil, with the melt level being, at least, by 10 mm lower than the crucible edge. Failure to comply with these conditions led to unstable growing process and poor quality of the crystals (Fig. 5).

Before heating the growth chamber was evacuated and filled with argon of 99.987% purity until the pressure reached the atmospheric value. The heating occurred in automatic mode, with the melt appearance controlled visually through the access holes, in ceramic insulation. After process operations, the seeds were introduced into the melt, and the crystals grew automatically according to the set program. The rate of crystal growth at different stages ranged from 1 to 3 mm per hour, while the rotation speed was 30—35 revolutions per minute. The stability of diameter of growing crystal was regulated by a diameter controller, according to the proportional integral differential law, on the basis of string weight sensor readings. The crystal was separated from the melt due to accelerated rod moving 20 mm up at a speed of 60 mm/h. The fact of the crystal separation from the melt was controlled based on the weight sensor readings, and the separation criterion was deemed met provided the weight of crystal boule did not change for 10 minutes after separation. The crystal was cooled by one step, with the temperature decreasing to the ambient one during 40—60 hours. The post-growth annealing of crystals occurred in inert atmosphere at a temperature of 1500 °C.

The $(Lu_xGd_{1-x})_2SiO_5$ crystals are known to crack in the course of post-growth cooling as a result of thermoelastic stresses arising in unevenly cooled crystal boule. Therefore, to prevent cracking of the $(Lu_xGd_{1-x})_2SiO_5$ crystal boule, it is necessary to create conditions in which there is no temperature gradient along the boule length during the cooling or this gradient is very small. To achieve this an additional Joule platinum heater was used. It was located in the top part of crystallization block above the crucible. The use of this active element of the block reduced the temperature gradient along the length of the crystal boule during the post-growth annealing.

So, large crystals $(Lu_xGd_{1-x})_2SiO_5$ having a diameter of 35 mm and a length of cylindrical part up to 150 mm and crystals $Y_2SiO_5:Ce$ and $(Lu_xY_{1-x})_2SiO_5$ having a diameter of 45 mm and a length of 250 mm (Fig. 6) have been grown by Czochralski method. The crystals have neither cracks nor large impregnations.

TESTING OF THE GROWN CRYSTALS

The absorption spectra were measured using *Specord 40* spectrophotometer (*Analytik Jena AG*) with a measurement range of 190—1100 nm. The absorption spectra of $(Lu_xY_{1-x})_2SiO_5$ and $Y_2SiO_5:Ce$

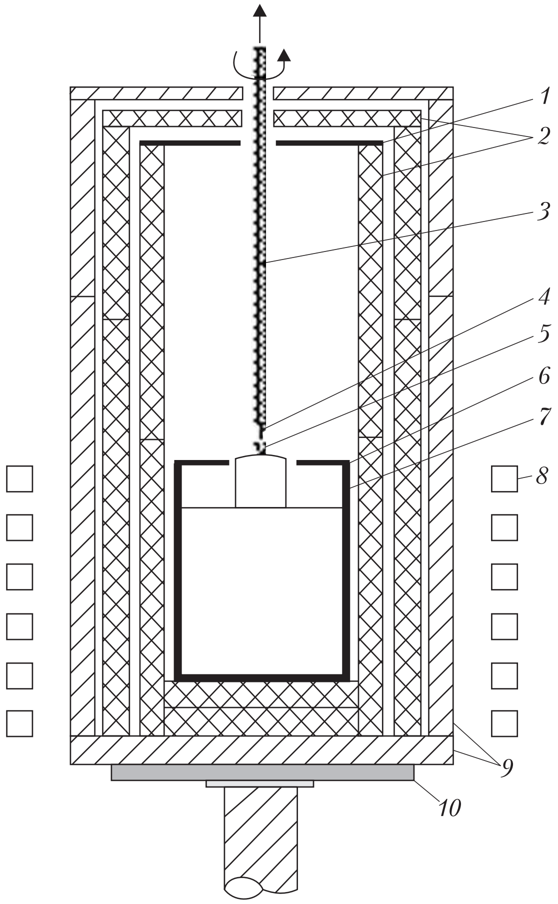

Fig. 4. Design of furnace for growing large RE silicate crystals: *1*) Pt covers, *2*) Zr ceramic, *3*) coupling rod, *4*) seed crystal, *5*) crystal, *6*) Ir aperture plate, *7*) Ir crucible, *8*) inductor, *9*) alundum ceramic, *10*) base

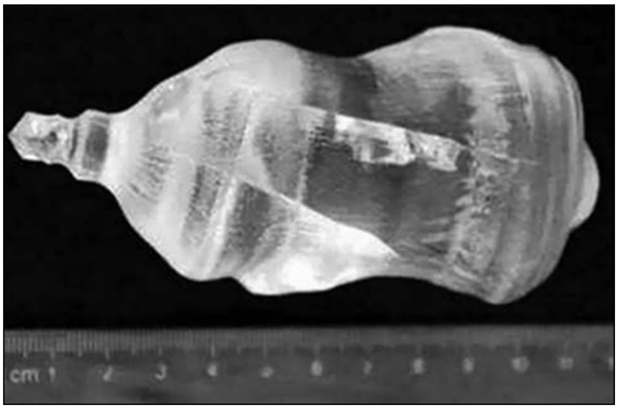

Fig. 5. LYSO:Ce crystal grown in furnace of nonoptimal configuration

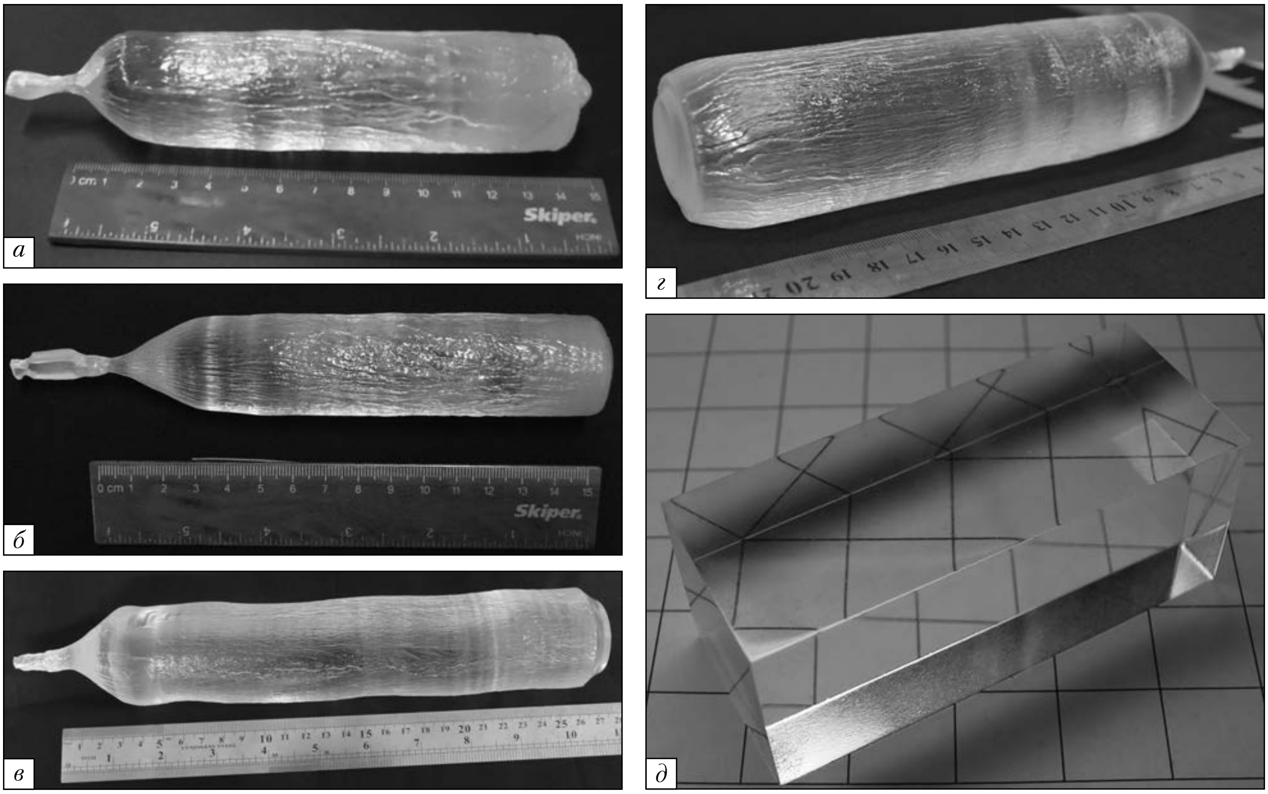

Fig. 6. The grown crystals: *a*) $(Lu_xGd_{1-x})_2SiO_5 : Ce$; *b*) $(Lu_xY_{1-x})_2SiO_5 : Ce$; *c*, *d*) $Y_2SiO_5 : Ce$; *e*) $(Lu_xGd_{1-x})_2SiO_5 : Ce$

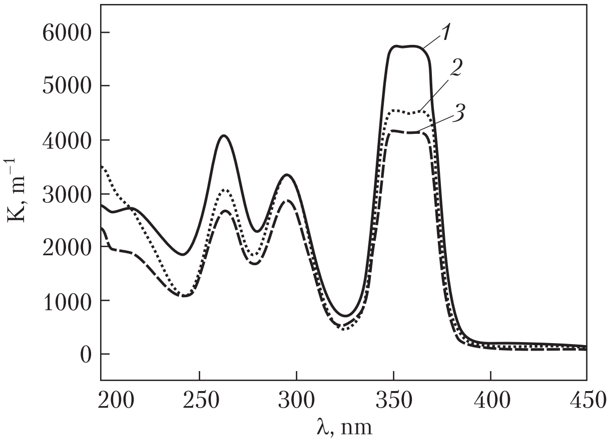

Fig. 7. Absorbtion spectra of $(Lu_xY_{1-x})_2SiO_5 : Ce$ (*1*), $Y_2SiO_5 : Ce$ (*2*) as compared with $Lu_2SiO_5 : Ce$ (*3*)

grown crystals as compared with Lu_2SiO_5 : Ce crystal are showed in Fig. 7. Within the range 200—375 nm, all studied crystals feature bands corresponding to 4*f*-5*d*-transitions in Ce^{3+} ions.

The luminescence spectra of X-ray excited crystals consist of two bands, at 410 and at 430 nm, which correspond to emitting 5*d*-4*f* transitions of Ce^{3+} ions in two non-equivalent positions in the crystal lattice. The spectra of $(Lu_xGd_{1-x})_2SiO_5$:Ce, $(Lu_xY_{1-x})_2SiO_5$, and Y_2SiO_5:Ce are very similar to each other. The only difference is $(Lu_x Gd_{1-x})_2SiO_5$ spectra featuring a more intense long-wave spectral shoulder caused by stronger reabsorption of short-wave part and/or redistribution of ions in the crystal lattice $(Lu_xGd_{1-x})_2SiO_5$ for the sake of CeO_6 polyhedron with a longer wavelength luminescence (Fig. 8).

The light yield and energy resolution of the samples excited by ^{137}Cs sourced gamma rays having an energy of 662 keV were measured by the pulse technique using a standard spectrometer consisting of preamplifier BUS-94b, line amplifier BUI-3K, and multichannel pulse-height analyzer AMA-3F. To determine the absolute light

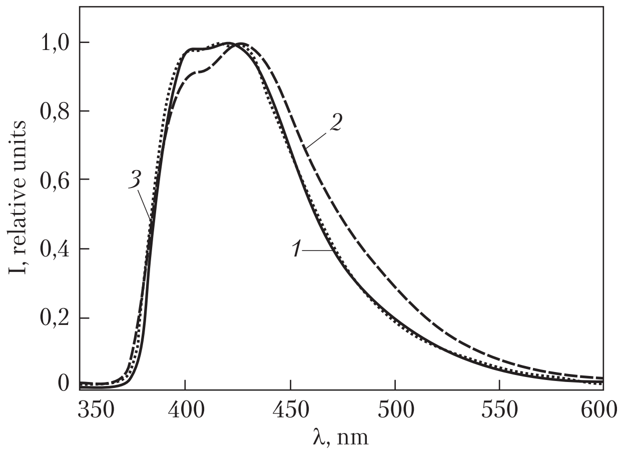

Fig. 8. Luminescence spectra of X-ray excited samples: *1* — $Y_2SiO_5 : Ce$; *2* — $(Lu_xGd_{1-x})_2SiO_5 : Ce$; *3* — $(Lu_xY_{1-x})_2SiO_5 : Ce$

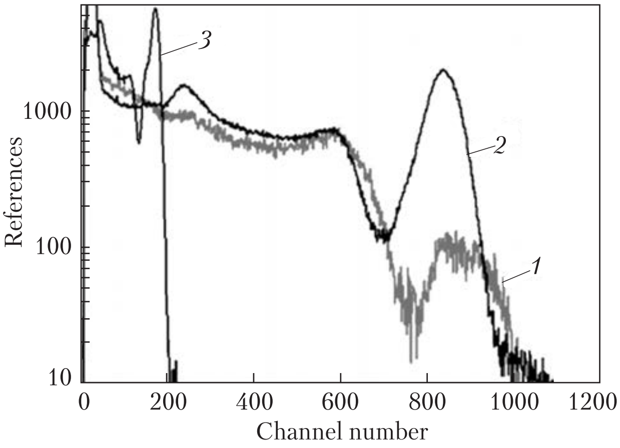

Fig. 9. Amplitude spectra of $Y_2SiO_5 : Ce$ (*1*) and $(Lu_xY_{1-x})_2SiO_5 : Ce$ (*2*) as compared with $Bi_4Ge_3O_{12}$ (*3*) excited by ^{137}Cs (662 KeV)

yield the matching factors for the crystal luminescence spectrum and the photomultiplier sensitivity band were simulated by Monte Carlo method. *Hamamatsu* R1307 photomultiplier with a photocathode having 3 inches in diameter was used as photoelectric receiver. To improve the light-gathering parameters the measured samples and the open part of photocathode were coated with three layers of Teflon tape.

The amplitude spectra of $Y_2SiO_5 : Ce$ and $(Lu_xY_{1-x})_2SiO_5 : Ce$ are showed in Fig. 9. The positions of peaks are almost identical. The absolute light yield of $(Lu_xY_{1-x})_2SiO_5$ and $Y_2SiO_5 : Ce$ crystals (light-gathering factor is 0.700; PHM matching factor is 0.903) was 28000 and 29500 ph/MeV, respectively. The energy resolution of $(Lu_xY_{1-x})_2 SiO_5$ crystals excited by ^{137}Cs emitted 662 keV gamma rays was 9.7%. For $Y_2SiO_5 : Ce$ the peak was too vague to accurately determine its width at half-height. The resolution of $Y_2SiO_5 : Ce$ can be estimated at about 15–20%.

The decay time for gamma (662 keV) excited $Y_2SiO_5 : Ce$ crystal is 60 ns, which is typical for Ce-containing scintillators.

CONCLUSIONS

The project has brought the following results:

1. The $Y_2SiO_5 : Ce$ and $(Lu_xY_{1-x})_2SiO_5 : Ce$ large crystals having a diameter of 50 mm and a length of 250 mm have been obtained. The $(Lu_xGd_{1-x})_2SiO_5 : Ce$ large crystals having a diameter of 30 mm and a length of 150 mm have been grown for the first time in the world practice.
2. The grown crystals comply with requirements for recording muon-to-electron conversion in high-energy physics, namely, they have a light yield of 28 000–30 000 ph/MeV (vs required 20 000 ph/MeV, at least);
3. The properties of crystals make it possible to apply $Y_2SiO_5 : Ce$, $(Lu_xY_{1-x})_2SiO_5 : Ce$; and $(Lu_xGd_{1-x})_2SiO_5 : Ce$ to diagnostic medical devices (*positron emission tomography and computer tomography*), and to the systems controlling the unauthorized movement of hazardous substances (X-ray scanners).

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РОЗРОБКА ТЕХНОЛОГІЇ ОТРИМАННЯ ВЕЛИКОГАБАРИТНИХ КРИСТАЛІВ СКЛАДНИХ ОКСИДІВ ДЛЯ ЕКСПЕРИМЕНТІВ З РЕЄСТРАЦІЇ МЮОН-ЕЛЕКТРОННОЇ КОНВЕРСІЇ В ФІЗИЦІ ВИСОКИХ ЕНЕРГІЙ

Запропоновано технологічні прийоми для отримання якісних великогабаритних сцинтиляційних кристалів на основі силікатів рідкісноземельних елементів. Розроблено спосіб наплавлення іридієвих тиглів за рахунок використання евтектичної суміші замість фази того чи іншого оксиортосилікату.

Ключові слова: великогабаритний монокристал, метод Чохральського, сцинтилятор, люмінесценція.

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РАЗРАБОТКА ТЕХНОЛОГИИ ПОЛУЧЕНИЯ КРУПНОГАБАРИТНЫХ КРИСТАЛЛОВ СЛОЖНЫХ ОКСИДОВ ДЛЯ ЭКСПЕРИМЕНТОВ ПО РЕГИСТРАЦИИ МЮОН-ЭЛЕКТРОННОЙ КОНВЕРСИИ В ФИЗИКЕ ВЫСОКИХ ЭНЕРГИЙ

Предложены технологические подходы для получения качественных крупногабаритных сцинтиляционных кристаллов на основе силикатов редкоземельных элементов. Разработан способ наплавления иридиевых тиглей за счет использования эвтектической смеси вместо фазы того или иного оксиортосиликата.

Ключевые слова: крупногабаритный монокристалл, метод Чохральского, сцинтиллятор, люминесценция.

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