

Compositionally Disordered Doped with Cerium Crystalline Garnet Type Materials for Brighter and Faster Scintillations

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Abstract

Ce-doped tetracationic garnets $(\text{Gd}, \text{M})_3\text{Al}_2\text{Ga}_3\text{O}_{12}$ ($\text{M}=\text{Y}, \text{Lu}$) form a family of new multipurpose promising scintillation materials. The aim of this work was to evaluate the scintillation yield in the materials of quaternary garnets activated by cerium ions with partial isovalent substitution of the matrix-forming gadolinium ions by yttrium or lutetium ions.

Materials were obtained in the form of polycrystalline ceramic samples, and the best results were shown by samples obtained from the raw materials produced by the coprecipitation method. It was found that ceramics obtained from coprecipitated raw materials ensure a uniform distribution of activator ions in the multi-cationic matrices, which enables the high light yield and fast scintillation kinetics of the scintillation. It was demonstrated that the superstoichiometric content of lutetium/gadolinium in the material is an effective method to suppress phosphorescence accompanied scintillation. For ceramics with the composition $(\text{Gd}, \text{Lu})_3\text{Al}_2\text{Ga}_3\text{O}_{12}$, a scintillation yield of more than 50.000 ph/MeV was achieved. The scintillation kinetics was measured to be close to the kinetics with a decay constant of 50 ns.

In terms of the set of the parameters, the developed scintillation materials are close to the recently developed alkali halide materials $\text{LaBr}_3:\text{Ce}$, $\text{GdBr}_3:\text{Ce}$. Moreover, they have high mechanical hardness, are characterized by the absence of hygroscopicity, and are better adapted to the manufacture of pixel detectors used in modern devices for medical diagnostics.

Keywords: scintillator, crystal, garnet, light output, gadolinium.

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Композиционно неупорядоченные активированные ионами церия кристаллы типа граната для более ярких и быстрых сцинтилляций

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Четырёхкатионные гранаты $(Gd,M)_3Al_2Ga_3O_{12}$ ($M=Y, Lu$), легированные ионами Ce, формируют семейство новых многоцелевых перспективных сцинтилляционных материалов. Целью работы являлось проведение оценки выхода сцинтилляций в сцинтилляционных материалах четверных гранатов, активированных ионами церия при частичной изовалентной замене матрицеобразующих ионов гадолиния ионами иттрия или лютеция.

Материалы были получены в виде поликристаллических пластин, причём наилучшие результаты показали образцы, полученные из сырья, произведённого методом соосаждения. Установлено, что керамика, полученная из соосаждённого сырья, обеспечивает однородность распределения активаторных ионов в многокатионных матрицах. Это, в свою очередь, обеспечивает достижение высокого световыхода и быстрой кинетики сцинтилляции. Показано, что сверхстехиометрическое содержание лютеция/гадолиния в материале для изготовления керамики является эффективным средством подавления фосфоресценции. Для керамики состава $(Gd,Lu)_3Al_2Ga_3O_{12}$ достигнут выход сцинтилляций более 50000 фот./МэВ, а усреднённая константа затухания кинетики сцинтилляций близка к 50 нс.

По совокупности параметров разработанные сцинтилляционные материалы близки к недавно разработанным щелочно-галогидным материалам $LaBr_3:Ce$, $GdBr_3:Ce$, к тому же обладают высокой твёрдостью, характеризуются отсутствием гигроскопичности и лучше приспособлены к изготовлению пиксельных детекторов, используемых в современных устройствах для медицинской диагностики.

Ключевые слова: сцинтиллятор, кристалл, гранат, световыход, гадолиний.

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Introduction

Exploiting the disordered crystalline compounds is found to be a promising approach for imparting new features to crystalline compounds. The disorder of the crystal lattice can be purposely introduced into the inorganic material during production, and its effect on their physical properties can be significant. Among the various types of disorder in a crystal system [1], the compositional disorder is of particular interest for the development of materials for photonics operating on the principles of creation, transfer, and relaxation of electronic excitations. Worth noting, scintillation materials utilized to detect various types of ionizing radiation demonstrate an impressive improvement in parameters due to the introduction of disorder into the cationic or anionic sublattices of the crystal [2]. A relatively simple type of disorder is introduced into the crystal due to isomorphous or isovalent substitutions of cations in the matrix. The advantage of this approach to improve the scintillation properties of crystalline materials based on oxides doped with Ce ions was demonstrated almost two decades ago [3–7]. Ternary mixed $\text{Lu}_x\text{Y}_{1-x}\text{AlO}_3:\text{Ce}$ crystals of the perovskite structure and oxyorthosilicate $(\text{Lu}_x\text{Y}_{1-x})_2\text{SiO}_5:\text{Ce}$ (LYSO) structure crystals were found to be superior in scintillation performance to binary $\text{LuAlO}_3:\text{Ce}$ and $\text{Lu}_2\text{SiO}_5:\text{Ce}$ correspondingly. A combinatorial search for the best composition of multicomponent Ce-doped garnet compounds containing Y, Gd, Ga, and Al has shown that a balanced combination of Gd and Ga makes it possible to increase the scintillation light yield (LY) above 40.000 ph/MeV [8]. The incorporation of Gd in the composition of multicationic garnets for brighter scintillation is preferable because of the ability of the Gd sublattice in the crystal to be a reservoir for Frenkel-type excitons, providing further transfer of electronic excitations to luminescence centers [9]. An influence of the Ga/Al ratio in the crystal composition on the luminescence kinetics and other scintillation properties of gadolinium-aluminum-gallium garnets was studied in [10–12]. In addition to the mixing of Ga and Al ions in the lattice, the isovalent substitution of gadolinium ions with yttrium or lutetium ions is considered as well. A competition in occupying the dodecahedral positions in the garnet structure introduces additional disorder into the cation sublattice. A very positive effect of partial substitution of the Gd ions by Y was confirmed in single crystals grown by the

Czochralski method. A GYAGG: Ce single crystal with equal atomic percentages of Y and Gd ions in the composition demonstrates a high light yield of 52.000 ph/MeV and a scintillation decay time of 50 ns [13]. The drawback of the material is a relatively low density of 5.9 g/cm³. Low density leads to a low stopping power to gamma-quanta, the measurement of which is widely used in medical diagnostics. For this reason, the material proved to be less competitive for computer tomography and positron emission tomography scanners. Replacement the Y with Lu in a quaternary garnet would solve this problem. At a Gd/Lu ratio of 1/1, the density of the material reaches 7 g/cm³, which is comparable to the density of lutetium orthosilicate, in which 20 at.% Lu is substituted by Y ions. However, the use of Lu in the garnet matrix creates some technological problems, the main of which are: creation of defect-centers due to the possible localization of small Lu^{3+} ions in oxygen octahedra [14–16] in the garnet matrices. This creates cation vacancies in the dodecahedral positions of lutetium ion localization, and, therefore, gives a rise to the formation of traps of nonequilibrium carriers, which cause the phosphorescence of the material.

This work is devoted to a comparison of the spectroscopic and scintillation properties of ceramic scintillators $(\text{Gd},\text{Y})_3\text{Ga}_3\text{Al}_2\text{O}_{12}$ (GYAGG) and $(\text{Gd},\text{Lu})_3\text{Ga}_3\text{Al}_2\text{O}_{12}$ (GLAGG) obtained from nonstoichiometric raw material compositions and to assess the prospects for their use in novel medical imaging equipment.

Samples

Quaternary polycrystalline compounds with a garnet structure exhibit various type of disorder. First, the polycrystalline material consists of separate grains, misoriented relative to each other. Second, in such crystallites, there is a disordering of the cation sublattice, which arises due to the competition of different cations for identical crystallographic positions. In the studied compounds, Gd, Lu, and Y can occupy positions with a dodecahedral oxygen environment, and Ga and Al – with octahedral and tetrahedral sites (Figure 1). Samples of GYAGG and GLAGG translucent ceramics were obtained at the National Research Center Kurchatov Institute (Russia) from coprecipitated raw materials with a purity not worse than 5N, compacted into tablets 15 mm in diameter by uniaxial pressing at a pressure of 60 MPa

and annealed in an argon atmosphere at a temperature of 1600 °C for 4 hours. An additive in the form of a suspension of Gd₂O₃ oxide was dropped into the solution at the final stage during the coprecipitation of the composition. After sintering, the samples were polished on both sides to a thickness of 0.5 mm, their density was no less than 98.6 % of the theoretical value, and the optical transmission was no worse than 30 %. The hardness of the samples was 8 (Moos). The studied samples of ceramics, according to X-ray luminescence analysis, contained a single garnet phase (PDF [00-046-0448]), and the grain size according to scanning electron microscopy was 5–10 μm.

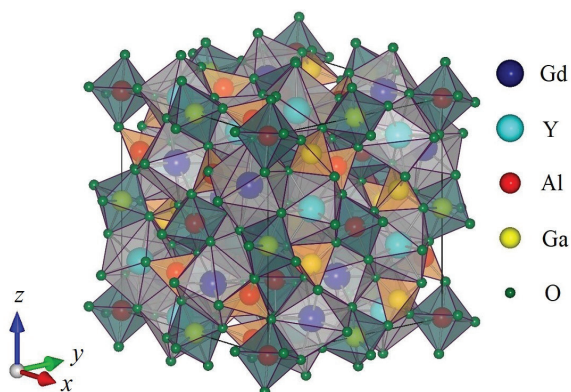


Figure 1 – Schematic presentation of the crystal structure of the quaternary garnet Gd_{1.5}Y_{1.5}Al₂Ga₃O₁₂ created with VESTA software package [17]

A single crystal sample (Gd,Y)₃Ga₃Al₂O₁₂:Ce [13] with a scintillation yield of 50.000 ph/MeV was chosen to be a reference. To mimic translucent ceramic the crystal surface was ground. Since the ceramic scintillator samples were translucent, the scintillation yield was estimated by comparison of the radioluminescence (XRL) spectra. The radioluminescent properties were evaluated at excitation with BSV-2 X-ray tube (copper anode, 30 kV, 10 mA) by MDR-23 LOMO monochromator (spectral width 2 nm) and FEU-106 V photomultiplier tube in a photon counting mode. The spectra were corrected for spectral sensitivity. The scintillation kinetics was measured by the standard start-stop method as described in [2].

Results and discussion

Figure 2 shows the XRL spectra of ceramic samples in comparison with a single crystal sample, measured in the geometry of 45°. Comparison of the areas under the XRL curves allows to estimate the scintillation yield of GLAGG samples as 52650

+/- 1000 ph/MeV, respectively, while for GYAGG ceramics at the level of 48250 +/- 1000 ph/MeV. The good coincidence of the X-ray spectra of the GLAGG samples is remarkable, which indicates the reproducibility of the technology for the scintillation ceramics. All bands have a complex structure; a long-wavelength shoulder is observed in the XRL spectra, which is apparently due to the difference in the emission spectra of Ce³⁺ ions depending on the cationic environment of Ga and Al ions.

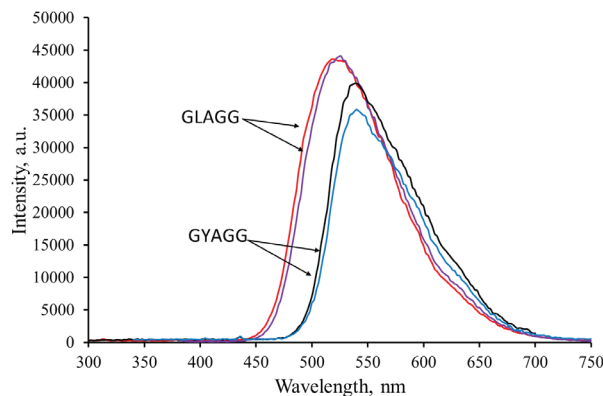
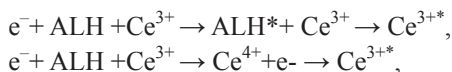


Figure 2 – Radioluminescence spectra of GLAGG ceramic samples (violet and red curves), a GYAGG ceramic sample (blue curve) and a GYAGG single crystal (black curve) measured at room temperature

Table shows some of the physical and scintillation properties of the obtained ceramics in a comparison with the GYAGG single-crystal sample, which allows considering the possibility of the application.

The sample with lutetium shows the highest scintillation yield. An incorporation of Lu ions into the lattice leads to an increase in the role of scintillation creation mechanisms due to interaction with self-trapped states in the lattice: auto-localized holes (ALH) and auto-localized excitons (ALE). In contrast to the yttrium ion, lutetium has a high nucleus charge, higher than that of gadolinium; therefore, the formation of photoelectrons when interacting with gamma-quanta occurs mainly on electronic shells of lutetium ions. For this reason, holes are formed and localized primarily in polyhedra occupied by lutetium ions. Lattice excitons of the ALE type are rapidly converted into excitons of the Frenkel type, localized on the gadolinium sublattice; however, self-trapped holes can additionally excite Ce³⁺ ions both due to dipole-dipole interaction and due to sequential capture:



where * means an excited state.

Table

Density and scintillation parameters of the materials

Sample	Density, g/cm ³	Light yield, ph/MeV	Decay constant, ns (%)	XRL maximum, nm
GYAGG (single crystal)	5.86	50 000	36 (80) 97 (20)	535
GYAGG (ceramics)	5.85	48 250	20(10) 51(85) 120(5)	535
GLAGG (ceramics)	7	52 650	23(60) 61(30) 600(10)	525

This additional channel for the transfer of the electronic excitations leads to an increase in the scintillation yield in GLAGG, respectively.

Thus, it can be argued that an enlarging in the structural disorder in the crystal upon partial replacement of gadolinium by lutetium ions leads to an increase in the set of mechanisms for the transfer of excitations of nonequilibrium carriers to Ce³⁺ ions, which enhances the scintillation yield.

As seen from Table 1, the presence of a ten percent fraction of 600 ns slow scintillation component in the GLAGG sample is noteworthy. At the same time, ceramics samples do not exhibit phosphorescence, which is a characteristic property of the crystals of the gadolinium-aluminum-gallium garnet family [2].

Conclusion

The results of evaluating the scintillation properties of ceramic samples of Ce doped quaternary garnets (Gd,Y)₃Ga₃Al₂O₁₂ and (Gd,Lu)₃Ga₃Al₂O₁₂ are presented. It was shown that the samples prepared with deviation from the stoichiometry in Gd content, particularly the Lu-containing sample, demonstrate a light yield of ≈ 52.000 ph/MeV. This is comparable to the GYAGG single crystal scintillator, which was recently produced. At the same time, a significant fraction (≈ 60 %) of the component with a decay constant of ≈ 20 ns is observed in the scintillation kinetics. A combination of GLAGG density, high scintillation yield, and short decay time makes this material a promising candidate for use in the next generation of medical diagnostic devices, especially in positron emission tomography scanners.

The disordered materials of quaternary garnets have a great potential for further improvement. It can be assumed that in a four-cation system with a garnet structure, the additional disorder introduced by the random distribution of Gd and Lu ions, like Al and Ga ions, also affects the multiplicity of non-equivalent positions of the localization of Ce ions. Of particular interest is the search for technological solutions that preferentially stabilize Ce ions in polyhedrons that provide the fastest scintillation kinetics.

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