

Preparation and scintillation properties of LGSO:Ce crystals

*O.Ts.Sidletskiy, V.G.Bondar, B.V.Grinyov,
D.A.Kurtsev, V.N.Baumer*, K.N.Belikov*,
Z.V.Shtitelman*, S.A.Tkachenko, O.V.Zelenskaya,
N.G.Starzhinsky, K.A.Katrunov, V.A.Tarasov*

Institute for Scintillation Materials, STC "Institute for Single Crystals"

National Academy of Sciences of Ukraine,

*Institute for Single Crystals STC "Institute for Single Crystals",

National Academy of Sciences of Ukraine,

60 Lenin Ave., 61001 Kharkiv, Ukraine

Received October 11, 2008

$\text{Lu}_{2x}\text{Gd}_{2-2x}\text{SiO}_5\text{:Ce}$ single crystals with different $\text{Lu}/(\text{Lu}+\text{Gd})$ atomic ratio have been obtained by the Czochralski technique. It has been shown that the polymorph transition $P2_1/c-C2/c$ space symmetry at substitution of Gd atoms by Lu takes place at $\text{Lu}/(\text{Lu} + \text{Gd}) = 0.1-0.2$. The obtained crystals with $C2/c$ symmetry type demonstrate good scintillation characteristics. High Ce^{3+} segregation coefficient together with preferred inclusion of cerium into the seven-fold oxygen — coordinated position provide high light yield and good energy resolution of the crystals.

Методом Чохральского выращены монокристаллы $\text{Lu}_{2x}\text{Gd}_{2-2x}\text{SiO}_5\text{:Ce}$ с различным атомным соотношением $\text{Lu}/(\text{Lu}+\text{Gd})$. Показано, что полиморфный переход при смене пространственной симметрии с $P2_1/c$ на $C2/c$ в процессе замещения атомов гадолиния на лютеций происходит при соотношении $\text{Lu}/(\text{Lu}+\text{Gd}) = 0.1-0.2$. Полученные кристаллы с типом пространственной симметрии $C2/c$ демонстрируют высокие сцинтилляционные характеристики. Высокий коэффициент вхождения ионов Ce^{3+} в матрицу в совокупности с предпочтительным вхождением церия в семикоординированную позицию по кислороду обуславливают высокий световой выход и энергетическое разрешение кристаллов.

Crystals of high-temperature oxides, such as rare-earth silicates and aluminates, doped with cerium, are well-known scintillators used in detectors for high-energy physics, nuclear physics, medical diagnostics, and well-logging. The main advantages of rare-earth orthosilicates are good chemical stability, non-hygroscopicity, high density and high effective atomic number. Efficient scintillators based on $\text{Gd}_2\text{SiO}_5\text{:Ce}$ (GSO) and $\text{Lu}_2\text{SiO}_5\text{:Ce}$ (LSO) were developed in 1980th–1990th. These materials possess high light yield and fast decay (LSO), good energy resolution and moderate cost (GSO) [1–4]. The main drawbacks of LSO are back-

ground radioactivity and afterglow. Gadolinium orthosilicate crystals possess rather low light yield about 10000 Ph/MeV and tend to cracking during growing and manufacturing of elements.

During last two decades, mixed orthosilicates $\text{Lu}_{2x}\text{Y}_{2-2x}\text{SiO}_5$ (LYSO), $\text{Gd}_{2x}\text{Y}_{2-2x}\text{SiO}_5$ (GYSO), $\text{Lu}_{2x}\text{Gd}_{2-2x}\text{SiO}_5$ (LGSO) are in development in order to minimize the above-mentioned drawbacks. Today, large LYSO crystals with low yttrium content [5], and crack-free LSO crystals of up to 80 mm diameter and with high scintillation characteristics [6] are commercially produced. However, problem of high afterglow and

background in lutetium-containing orthosilicates is still unsolved. Attempts to modify the GSO crystal properties by yttrium addition were also made. Improvement of radiation resistance and mechanical properties of $Gd_{2x}Y_{2-2x}SiO_5:Ce$ have been reported, but no substantial increase of scintillation characteristics was observed [7, 8].

The LGSO crystals are also materials of promise, because a substantial number of Lu atoms can be substituted by Gd without polymorph transition. Addition of Gd results in a reduced radioactive background caused by ^{176}Lu isotope, and a decreased crystal cost. Rather high values of light yield [9, 10] and energy resolution (up to 6.5 % [11]) were obtained for crystals with the same space symmetry type as LSO (monoclinic, $C2/c$). The preparation of LGSO crystals is somewhat difficult due to polymorph transition from monoclinic lattice $P2_1/c$ (GSO) to $C2/c$ (LSO) resulting in a lowered crystal transmission and cracking of boules. This seems to be the cause of fairly high afterglow observed in LGSO [12] exceeding that for LSO.

Thus, an actual task is to obtain LGSO crystals with low Lu/Gd ratio, high light yield, energy resolution, and low afterglow. Also, mechanisms of cation substitution and activator entry into this matrix should be studied, and influence of these factors on scintillation characteristics should be checked.

The consideration of above-mentioned publications shows that it is just oxyorthosilicate scintillators having a matrix of monoclinic $C2/c$ space group that demonstrate the best efficiency. Also, a considerable Lu content in the matrix seems to be necessary because the similarity of electronic properties for Ce^{3+} and Lu^{3+} d -orbitals provides efficient energy transfer of excited state from the matrix to the activator ion. Such a transfer depends strongly on the energy difference between the conduction band bottom and the activator ion excited state. The smaller is this value, the more efficient transfer must occur. The LSO:Ce crystal is characterized by a small energy difference. Therefore, the excited d -state of Ce^{3+} activator ions is situated near bottom of the conduction band formed by external (hollow) d -orbitals of Lu^{3+} ions. At too small energy difference between the activator ion excited state and the conduction band bottom, negative effects for scintillator are possible, such as the activator ion ionization and electron capture by traps. An af-

terglow is observed in the case of continuous retention of these electrons in traps, causing a deterioration of the scintillator operating characteristics. That is why a possibility to control that energy difference is of importance in obtaining of new luminescent materials. The change in the covalence extent of the ion-ligand bindings defined by the structure of the crystal matrix being activated is among the methods of that difference variation [13].

LGSO:Ce crystals with different Lu/Gd ratio were obtained by the Czochralski method from mixture of starting oxides Gd_2O_3 , Lu_2O_3 , SiO_2 and CeO_2 with purity of at least 99.99 %. Crystals of 30 mm in diameter and up to 50 mm length were grown using iridium crucibles of 60 mm in diameter and 60 mm height under argon atmosphere with addition of up to 1.0 vol.% O_2 . The pulling speed was 1.2 to 3 mm/h, the crystal rotation speed, was 30–35 rot./min. Cerium concentration in melt was 1 mol.%. The growth direction was [010] on seeds of the $P2_1/c$ structure, and [210] on seeds of the $C2/c$ one. The grown crystals were annealed at 1500°C.

X-ray studies of LGSO samples were carried out using an Xcalibur-3 single crystal diffractometer (Oxford Diffraction, MoK α radiation, $\lambda = 0.71073\text{\AA}$, graphite monochromator, a Sapphire-3 CCD-detector, ω/θ — scanning in the 2θ range up to 90°, account for absorption by equivalent reflections). The structures were calculated using SHELX-97 and WinGX software. The unit cell parameters were refined by the Rietveld method using diffractograms obtained for powders of the same crystal samples using a Siemens D500 powder diffractometer. Results obtained by the single crystal method were taken as initial data for refinement by the Rietveld method.

Lu and Gd concentrations were determined using an atomic emission spectrometer with inductively coupled plasma (TRACE SCAN Advantage, Thermo Jarrell Ash, USA). The analytical lines 2615 Å and 3350 Å were used for Lu and Gd, respectively. Lu and Gd concentrations were determined by the external standard method. The calibration samples were prepared in water solutions of these elements in the presence of phosphoric acid. The relative standard deviation did not exceed 0.02. Cerium concentrations in LGSO crystals were determined by atomic emission spectrography based on evaporation of the substance in an

AC arc discharge, and registration of the emission by a DFS-1 spectrograph. The detection limit was 0.001 wt. %.

Light yield and energy resolution were determined by pulse method using a standard spectrometric setup including a BUS2-94b preamplifier, BUI-3K linear amplifier, and AMA-3F multichannel amplitude analyzer. A Hamamatsu R1307 PMT with 3 in. cathode was used as photodetector. The afterglow level after a certain time was measured using a special measuring setup consisting of a RAPAN-200 pulse X-ray emitter ($E_x = 100-160$ KeV), an S8594 photodiode, a current-to-voltage converter, multiplexer, controller, A/D converter, PC, a C1-102 oscillograph, and control unit for the X-ray emitter.

The scintillation characteristics of the grown crystals are presented in Table 1. A sharp improvement of scintillation properties (decrease of afterglow and about triple increase of light yield) is observed at change of space symmetry group near 20 at. % Lu. A very low afterglow as compared with literature data for LSO [15] is of a special interest.

It has been shown before that a polymorph transition in LGSO takes place at $\text{Lu}/(\text{Lu}+\text{Gd}) = 0.5$ (in accordance with [9]), and 0.1 (in accordance with [10]). In general, the data from [10] were confirmed in this work. The crystallization in monoclinic $P2_1/c$ structure is observed in the range $0 \leq \text{Lu}/(\text{Lu}+\text{Gd}) < 0.1$ independently of the seed space symmetry. The phase with monoclinic $C2/c$ group is crystallized at $\text{Lu}/(\text{Lu}+\text{Gd}) > 0.2$. The formation of crystals of both types is possible in melt with $\text{Lu}/(\text{Lu}+\text{Gd})$ ratio of 0.1 to 0.2. The crystal

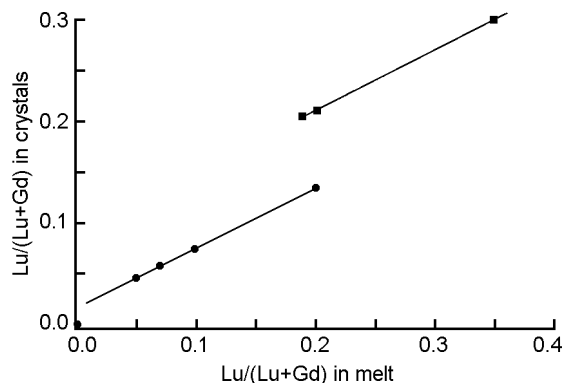


Fig. 1. Concentration of Lu ions in melt and in grown crystals.

lattice type of the used seed is of major importance in this case.

Light yield increase can be explained when considering the Lu/Gd substitution character in the matrices with the different space symmetries (Fig. 1). When lutetium is added to the $P2_1/c$ matrix, the crystal quality and scintillation properties degrade gradually. A noticeable increase of Lu concentration in crystals is observed at transition to $C2/c$ lattice. The unit cell volume decreases with Lu addition due to diminishing effective cation radius in the matrix (Fig. 2). The structure transition is observed at cation effective radius of about 0.92 Å.

Thus, the effective cation radius in the $C2/c$ matrix can be increased from 0.86 Å (Lu ionic radius) to 0.92 Å without changing the space symmetry type. This must result in increasing Ce segregation coefficient, because the smaller the difference between ionic radii of matrix and activator, the larger the segregation coefficient [17].

Table 1. Scintillation characteristics of the obtained crystals

Matrix composition	Space symmetry type	Light yield to BGO, % under excitation by $E_\gamma = 662$ KeV	Energy resolution, % under excitation $E_\gamma = 662$ KeV	Afterglow after 5 ms, %
Gd_2SiO_5	$P2_1/c$	112.5	9.5	0.024
$\text{Lu}_{0.090}\text{Gd}_{1.910}\text{SiO}_5$	$P2_1/c$	104.1	10.1	0.049
$\text{Lu}_{0.148}\text{Gd}_{1.852}\text{SiO}_5$	$P2_1/c$	95.3	10.3	0.073
$\text{Lu}_{0.268}\text{Gd}_{1.732}\text{SiO}_5$	$P2_1/c$	88.0	11.2	0.115
$\text{Lu}_{0.410}\text{Gd}_{1.590}\text{SiO}_5$	$C2/c$	260.1	7.7	0.043
$\text{Lu}_{0.420}\text{Gd}_{1.580}\text{SiO}_5$	$C2/c$	–	–	0.034
$\text{Lu}_{0.798}\text{Gd}_{1.202}\text{SiO}_5$	$C2/c$	304.8	11.4	0.052
Lu_2SiO_5	$C2/c$	≈300 [14]	7.3–9.7 [14]	1.6 [15]

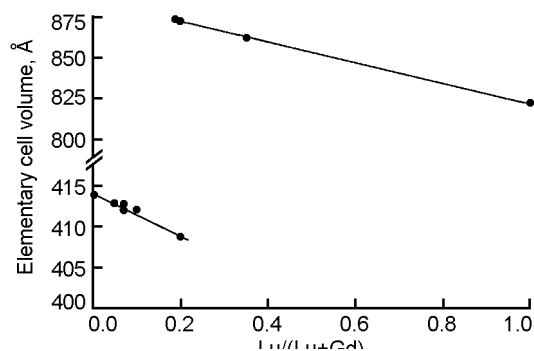


Fig. 2. Unit cell volume of the grown crystals (the value for LSO corresponds to [16]).

Direct measurements of $k(\text{Ce})$ confirm this law (Fig. 3). The segregation coefficient is in the range 0.52 to 0.83. It is about the same as that for GSO, and exceeds substantially $k(\text{Ce})$ for LSO (~ 0.2) [17]. For comparison, the $k(\text{Ce})$ value for LGSO (20 at. % Lu) obtained in [18] is presented in the same Figure.

The increase of activator segregation coefficient itself cannot explain so sharp changes of scintillation properties. Let the structure of $C2/c$ crystal lattice be considered taking LSO as the example. This space group contains 64 ions in unit cell; in particular, each of 8 Lu ions of first type (Lu_1) being coordinated with 7 oxygen atoms, while each of 8 second type ions (Lu_2) are coordinated with 6 oxygens. It is known that energy of $\text{Ce}^{3+} \rightarrow \text{Lu}_1$ substitution amounts +6.90 eV, while that of $\text{Ce}^{3+} \rightarrow \text{Lu}_2$ one, +7.25 eV. In both cases the energy is positive, because Ce^{3+} ionic radius is larger than that of Lu^{3+} . Different displacement of oxygen ions after $\text{Ce}^{3+} \rightarrow \text{Lu}_1$, Lu_2 substitution in LuO_7 and LuO_6 polyhedra provides substantially different scintillation characteristics of the substance. Light yield, luminescence maximum wavelength, and decay

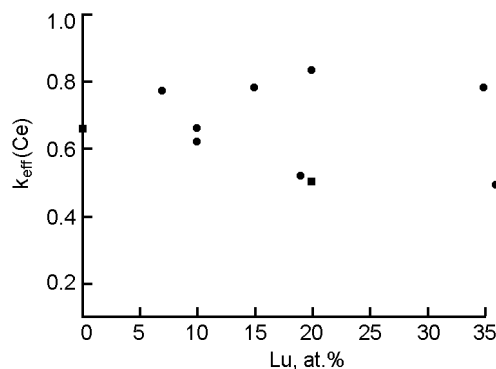


Fig. 3. Cerium segregation coefficient vs. lutetium concentration in melt. Data from [17, 18] are denoted by squares.

time depend on the number of Ce^{3+} ions substituting Lu_1 and Lu_2 ones. The decay time of Ce_1 luminescence center (polyhedron LuO_7) is 30–38 ns, and luminescence maximum is at 410–418 nm. The decay time of Ce_2 luminescence center (polyhedron LuO_6) is 50–60 ns and luminescence band is around 450–520 nm. The simultaneous presence of Ce^{3+} in both LuO_6 and LuO_7 causes the substantial decreased light yield, increased luminescence time up to 40–50 ns, and decay time shift towards the band of reduced PMT sensitivity. The best characteristics are observed in crystals containing Ce^{3+} ions only in LuO_7 polyhedra [9, 19–21].

Experimentally obtained data on cation distribution in the positions in the matrix are presented in Table 2. Lu^{3+} ions are situated preferably in 7-coordinated polyhedra LnO_7 in crystals with $P2_1/c$ space symmetry. In contrast, lutetium ions in crystals of $C2/c$ space group are situated preferably in 6-coordinated polyhedra. These results are quite expectable, accounting for the smaller Ln–O average bond length (2.23 Å) for LnO_6

Table 2. Population of cation positions in the matrices

Lu/(Lu+Gd), % in melt	Lu/(Lu+Gd), % in crystal	Space symmetry type	Fraction of Lu atoms (%) in polyhedra	
			In 7-fold	In 9-fold
5	4.5	$P2_1/c$	9	Not observed
10	7.4	$P2_1/c$	15	Not observed
20	13.4	$P2_1/c$	18	9
			In 6-fold	In 7-fold
19	20.5	$C2/c$	41	Not observed
20	21.0	$C2/c$	35	7
35	29.9	$C2/c$	50	10

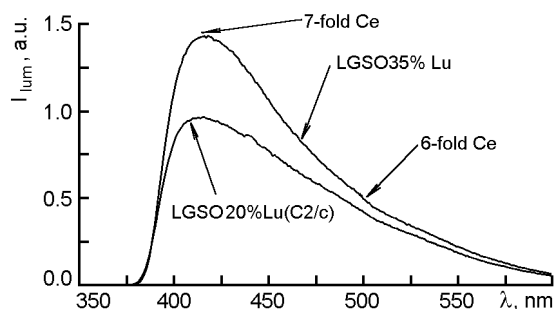


Fig. 4. X-ray luminescence spectra of the obtained single crystals.

in comparison with that for LnO_7 (2.32 \AA) in LSO [22]. Smaller Lu^{3+} ions and larger Gd^{3+} at high probability will be situated in LnO_6 and LnO_7 polyhedra, respectively. This distribution of lutetium and gadolinium ions is energy-favorable and must promote situation of Ce^{3+} ions with larger ionic radius (1.01 \AA) in the seven-fold oxygen-coordinated position.

The distribution of Ce^{3+} ions in LuO_7 and LuO_6 polyhedra can be estimated from X-ray luminescence spectra of grown crystals (Fig. 4). For crystals with space group $C2/c$ (20 % and 35 % Lu), intensity of the 420 nm peak corresponding to seven-fold coordinated Ce^{3+} is substantially higher than that of the second peak near 500 nm. This result confirms the hypothesis on the preferred situation of activator ions in the seven-fold coordinated position with higher luminescence intensity.

Thus, $\text{Lu}_{2x}\text{Gd}_{2-2x}\text{SiO}_5:\text{Ce}$ crystals in the range $x = 0-0.35$ have been studied. A sharp improvement of scintillation properties at transition from monoclinic $P2_1/c$ to $C2/c$ symmetry has been observed. High light yield values at $x \geq 0.2$ are connected with high cerium inclusion coefficient and preferred situation of activator in the seven-fold oxygen-coordinated position. The causes of substantial afterglow decrease observed in this work as compared with other authors are not known at the moment. A detailed study of LGSO energy-band structure is now in progress.

Acknowledgment. Authors are grateful to Mr. Igor Zenya (Institute for Scintillation Materials) who has measured the afterglow levels in the crystals.

References

1. H. Ishibashi, K. Shimizu, K. Susa, S. Kubota, *IEEE Trans. Nucl. Sci.*, **36**, 170 (1989).
2. C.L. Melcher, J.S. Schweitzer, *IEEE Trans. Nucl. Sci.*, **39**, 502 (1992).
3. L. Pidol, A. Kahn-Harari, B. Viana et al., *Trans. Nucl. Sci.*, **51**, 1084 (2004).
4. V.M. Garmash, S. Ya. Beloglovski, S.L. Lubetsi, *Nucl. Instr. Meth. in Phys. Res. A*, **486**, 106 (2002).
5. J. Chen, L. Zhang, R.-Y. Zhu, *IEEE Trans. Nucl. Sci.*, **52**, 3133 (2005).
6. Yu. D. Zavartsev, A. I. Zagumennyi, S. A. Koutovoi et al., in: Proc. 4th Int. Workshop on Crystal Growth Technology, Beatenderg, Switzerland (2008), p.85.
7. V. Bondar, L. Nagornaya, V. Martynov et al., in: Proc. Int. Conf. on Inorganic Scintillators and Their Applications SCINT-2005, Alushta, Ukraine (2006), p.98.
8. M. Jie, G. Zhao, X. Zeng, *J. Cryst. Growth*, **277**, 175 (2005).
9. Patent US 6.278.832 B1 (2001).
10. Patent US 2006/054831 A1 (2006).
11. M. Moszynski, A. Nassalski, W. Czarnacki et al., *IEEE Trans. Nucl. Sci.*, **37**, 1493 (2007).
12. A. Nassalski, M. Kapusta, T. Batsch et al., *IEEE Trans. Nucl. Sci.*, **54**, 3 (2007).
13. P. N. Zhmurin, Yu. V. Malyukin, Spectroscopy of Rare-Earth Ions in Volume and Nanosize Crystals, Institute for Single Crystals, Kharkiv, (2007) [in Russian].
14. M. E. Globus, B. V. Grinyov, Inorganic Scintillators, Akta, Kharkiv (2001) [in Russian].
15. A. Masalov, O. Vyagin, I. Ganina et al., *Pis'ma v Zh. Eksper. Teor. Fiz.*, **35**, 6 (2009).
16. S. A. Speakman, W. D. Porter, M. A. Spurrier, C. L. Melcher, *Materials Res. Bull.*, **41**, 423 (2006).
17. C. D. Brandle, A. J. Valentino, G. W. Berkstreser, *J. Cryst. Growth*, **79**, 308 (1986).
18. T. Usui, H. Yamamoto, Y. Yokoyama et al., *IEEE Trans. Nucl. Sci.*, **N24-206**, 412 (2007).
19. H. Matsumura, S. Watanabe, O. Nakamura, Takeshi Ito, *J. Cryst. Growth*, **308**, 348 (2007).
20. Bo Liu, Ch. Shi, M. Yin et al., *J. Luminescence*, **117**, 129 (2006).
21. D. W. Cooke, B. L. Bennett, K. J. McClellan et al., *Phys. Rev. B*, **18**, 11973 (2000).
22. L. Pidol, O. Guillot-Noel, A. Kahn-Harari et al., *J. Phys. Chem. Solids*, **67**, 643 (2006).

Одержання та сцинтиляційні властивості кристалів LGSO:Ce

**О.Ц.Сідлецький, В.Г.Бондар, Б.В.Гриньов,
Д.О.Курцев, В.М.Баумер, К.М.Беліков,
З.В.Штителъман, С.А.Ткаченко, О.В.Зеленська,
М.Г.Старжинський, К.А.Катрунов, В.О.Тарасов**

Методом Чохральського вирошено монокристали $\text{Lu}_{2x}\text{Gd}_{2-2x}\text{SiO}_5:\text{Ce}$ з різним атомним співвідношенням $\text{Lu}/(\text{Lu}+\text{Gd})$. Показано, що поліморфний перехід від просторової симетрії $P2_1/c$ до $C2/c$ в процесі заміщення атомів гадолінію на лютецій відбувається при співвідношенні $\text{Lu}/(\text{Lu}+\text{Gd})=0.1-0.2$. Отримані кристали з типом просторової симетрії $C2/c$ демонструють високі сцинтиляційні характеристики. Високий коефіцієнт входження іонів Ce^{3+} у матрицю у поєднанні з переважним входженням церію у семикоординовану позицію киснем обумовлює високий світловий вихід та енергетичну роздільну здатність кристалів.