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Recent progress in the development of β-Ga_2O_3 scintillator crystals grown by the Czochralski method

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Abstract: A high-quality bulk single crystal of β-Ga_2O_3 has been grown by the Czochralski method and its basic scintillation characteristics (light yield, energy resolution, proportionality, and scintillation decay times) have been investigated. All the samples cut from the crystal show promising scintillation yields between 8400 and 8920 ph/MeV, which is a noticeable step forward compared to previous studies. The remaining parameters, i.e. the energy resolution slightly above 10% (at 662 keV) and the scintillation mean decay time just under 1 μs, are at the same level as we have formerly recognized for β-Ga_2O_3. The proportionality of yield seems not to deviate from standards determined by other commercial scintillators.

1. Introduction

β-Ga_2O_3, one of the most perspective representatives of transparent semiconducting oxides, is considered as a promising candidate for manifold applications, most of them related to novel (opto)electronic devices [1]. Since it has been observed that β-Ga_2O_3 produces scintillation light when excited with ionizing radiation [2–5], it has also attracted attention of the scintillator market and scientists carrying out their research on this class of materials. Besides pure β-Ga_2O_3 crystals, doped ones have also been investigated [6–8], aiming at maximizing the scintillation yield and shortening the scintillation decay times. Nevertheless, based on the most recent publications [8–10], none of the dopants considered so far has led to an increase of the scintillation yield, which has been indicated to be strongly related to the free electron concentration in the material. For Czochralski-grown crystals the highest yield of 7040 ph/MeV has been reported up till now [9].

Our previous works have been aimed at identifying factors that affect the scintillation yield of β-Ga_2O_3. For that purpose, we have grown and studied a wide spectrum of crystals using different growth conditions and intentional doping. From that picture we have concluded that the highest values of the scintillation yield are confined to a relatively narrow range of the free electron concentration (at an order of 10^{16} cm^{-3}), which is the focus of the present manuscript. Therein we present the results of pulse height and scintillation time profile measurements performed on a series of samples prepared from a new bulk, Czochralski-grown, β-Ga_2O_3 crystal, which turns out to have much better performance as compared to any previous ones with respect to the scintillation yield: all the samples display clearly higher yields (by ~25%) than the above-cited 7040 ph/MeV. In addition to the standard 662 keV excited pulse height spectra we show for the first time the proportionality of the scintillation yield, examined between 59.6 and 1275 keV. Next, for the scintillation time profiles, which look very similar to those reported before [8,9],

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we propose a modified method of analysis, which sheds a new light on the question of decay components (their number and decay times).

2. Materials and experiment

Details of an impact of the growth conditions on the electrical properties are already recognized and described by Galazka et al. [10,11], which enabled to grow, by the Czochralski method, a high-quality bulk β-Ga_2O_3 single crystal with a low level of free electron concentration that would generate the highest scintillation yield, as concluded from our previous studies [7–10]. In particular, knowing the origin of the electrical conductivity in β-Ga_2O_3 (mainly silicon and hydrogen), as well as main compensation defects (gallium vacancies), we could balance shallow donor and acceptors by adjusting the oxygen concentration in the growth atmosphere (note that the concentration of Ga vacancies increases with O_2 concentration) without any intentional doping. By using a given Ga_2O_3 powder of 5N purity (containing traces of Si < 2 wt. ppm) and a gas atmosphere ($Ar + O_2$, 5N purity) we found out for given growth conditions an oxygen concentration in the growth atmosphere of 1.9% that resulted in a low free electron concentration, which indeed led to the highest scintillation yield as compared with our previous works [8–10]. To prepare plate samples necessary for pulse height spectra and scintillation time profile measurements, first (010)-oriented 5 mm thick slabs were cut from the bulk crystal, from which bars with 5×5 mm^2 cross-sections parallel to the (100) plane (which is an easy cleavage plane) were prepared. Then, about 0.5-0.6 mm thick (100)-oriented samples were cleaved from the bars. The advantage of freshly cleaved surfaces was the avoidance of any contamination and surface damage that could arise from polishing. The samples had a free electron concentration and an electron mobility of about $2.5 \cdot 10^{16}$ cm^{-3} and 130 cm^2 V^{-1} s^{-1}, respectively, according to Hall effect measurements.

Room temperature pulse height spectra were measured under ^{137}Cs (662 keV, 210 kBq) γ-excitation. The output signal from a Hamamatsu R878 photomultiplier (PMT) biased with a voltage of 1250 V was processed by a Canberra 2005 integrating preamplifier, a Canberra 2022 spectroscopy amplifier (working with a 2 μs shaping time), and a TUKAN-8K-USB multichannel analyzer. To improve the light collection efficiency, a thin layer of Viscasil grease was injected between the sample and the PMT window, and the sample was covered with several layers of Teflon tape. To provide the most accurate values of the photoelectron yield, pulse height spectra of each sample were recorded twice (i.e. sticking both sides of the plate to the PMT window; from the two values, quite close to each other, the higher one was credited as the photoelectron yield of the sample), as well as single photoelectron spectra were taken prior to and after examination of each sample. The photoelectron yields (expressed in phe/MeV) were afterward converted into the scintillation yields (in ph/MeV), considering the spectral matching of the β-Ga_2O_3 luminescence to the PMT characteristics.

The delayed coincidence single photon counting method proposed by Bollinger and Thomas [12] was chosen for scintillation time profile measurements. The setup was constructed from two Hamamatsu PMTs (R1104 and R928 for "starts" and "stops", respectively), a Canberra 2145 time-to-amplitude converter, and a TUKAN-8K-USB multichannel analyzer. The same ^{137}Cs source as specified above was used for excitation.

3. Results and discussion

3.1. Scintillation yield and energy resolution

^{137}Cs pulse height spectra of four of the investigated samples (U2a,b,d,e) are presented in Fig. 1 (the spectrum of the remaining U2c sample appears in Fig. 2). All of them display a clearly resolved full energy peak, which is essential for determination of the basic scintillation parameters: scintillation yield and energy resolution. Their values are summarized in Table 1 and also

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included in Fig. 1. It turns out that this series consists of the brightest β-Ga_2O_3 samples ever characterized at our laboratory. The yields from 8400 to 8920 ph/MeV indicate a significant step forward compared to our previous reports [8,9], in which the highest yield was equal to 7040 ph/MeV. A small spread of the yield values reflects the differences in heights [7] and possibly in surface qualities. The resolution of the new samples is maintained at the same level as of the best samples from the preceding series [8,9].

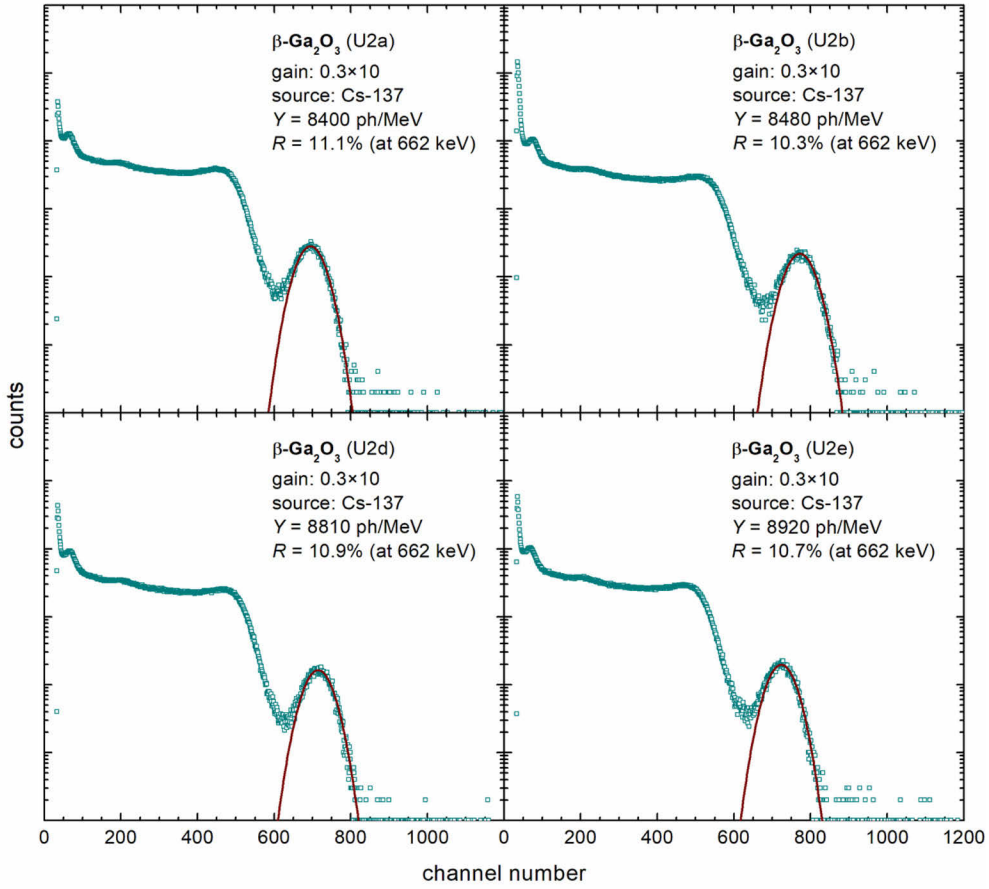

Fig. 1. ^{137}Cs pulse height spectra of β-Ga_2O_3 (samples: U2a,b,d,e).

Table 1. Summary of properties of the studied β-Ga_2O_3 samples (*Y* - scintillation yield, *R* - energy resolution at 662 keV, τ_i - scintillation decay time constants with their contributions in brackets, τ_{mean} - scintillation mean decay time)[a]

ID	size (mm^3)	*Y* (ph/MeV)	*R* (%)	τ_i (ns)	τ_{mean} (ns)
U2a	5 × 5 × 0.62	8400	11.1	20.0 (4.8%), 121 (15.4%), 1215 (79.8%)	989
U2b	5 × 5 × 0.58	8480	10.3	17.7 (2.6%), 113 (14.6%), 1187 (82.8%)	1000
U2c	5 × 5 × 0.49	8770	10.5	16.7 (3.5%), 110 (15.2%), 1169 (81.3%)	968
U2d	5 × 5 × 0.52	8810	10.9	16.2 (3.1%), 104 (14.5%), 1065 (82.4%)	894
U2e	5 × 5 × 0.56	8920	10.7	16.9 (3.1%), 107 (14.6%), 1182 (82.3%)	989

[a]The uncertainties of *Y* and *R* are below 5%, whereas those of τ_i and τ_{mean} are specified in Fig. 3.

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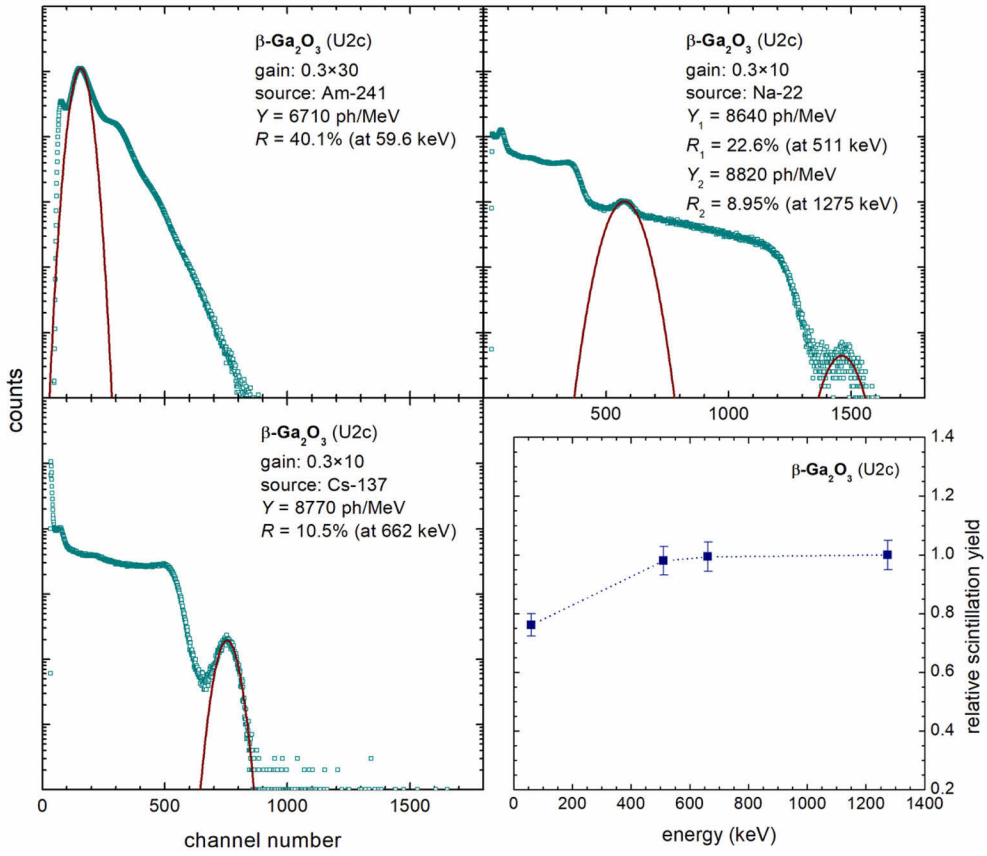

Fig. 2. ^{241}Am, ^{22}Na, and ^{137}Cs pulse height spectra of β-Ga_2O_3 (sample: U2c), and the scintillation yield proportionality plot.

In order to assess the proportionality of scintillation yield of β-Ga_2O_3, besides the standard ^{137}Cs pulse height spectra we have performed measurements with two other radioactive sources: ^{22}Na (511 and 1275 keV) and ^{241}Am (59.6 keV). In Fig. 2 and Table 2 we show the results for one selected sample (U2c). The corresponding proportionality plot (Fig. 2) reveals a rather common tendency, i.e. the yield increases with excitation energy, likewise for e.g. $LaBr_3$:Ce [13], Lu_2SiO_5:Ce [14] or $Lu_3Al_5O_{12}$:Pr [15]. We note that almost identical plots have been obtained for the remaining β-Ga_2O_3 samples, hence for conciseness we limit the presentation of the yield proportionality to a single sample.

Table 2. Scintillation yield proportionality of β-Ga_2O_3 based on the U2c sample (*E* - excitation energy, *Y* - scintillation yield, Y_{rel} - scintillation yield normalized to 1.000 for 1275 keV excitation, *R* - energy resolution at particular excitation energy)[a]

ID	source	*E* (keV)	*Y* (ph/MeV)	Y_{rel}	*R* (%)
U2c	^{241}Am	59.6	6710	0.761	40.1
	^{22}Na	511	8640	0.980	22.6
	^{137}Cs	662	8770	0.994	10.5
	^{22}Na	1275	8820	1.000	8.95

[a]The uncertainties of *Y* and *R* determination are below 5%.

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3.2. Scintillation time profiles

Scintillation time profiles of all the studied β-Ga_2O_3 samples are shown in Fig. 3. Additionally, the lowest right window illustrates our new approach to the data analysis. It is based on an assumption that an *observed profile* is in fact a convolution of a *genuine profile* with an instrumental response (which is a profile recorded with the same apparatus settings, but without a sample between the PMTs). For each sample such a deconvolved *genuine profile* has been fitted with a 3-exponential decay function (included in Fig. 3), providing a reasonably good matching with one component less than when fitting an *observed profile*, like it was done in previous works [8,9]. We note that it is the fastest component (a few ns) that does not appear in *genuine profiles*, hence it must be associated with some instrumental response.

The decay times of the three other components, as well as the mean decay times, calculated as:

$$\tau_{mean} = \frac{\sum_{i=1}^{3} A_i \tau_i^2}{\sum_{i=1}^{3} A_i \tau_i}$$

(A_i and τ_i - amplitudes and decay time constants of each decay component, respectively), specified in Fig. 3 and Table 1, roughly agree with the previously obtained values for undoped semiconducting β-Ga_2O_3 crystals with lower free electron concentrations [8,9]. Of course, due to the absence of the fastest component, the contributions are now accordingly higher: ~5% for the prompt component (16.2-20.0 ns), ~15% for the middle one (104-121 ns), and ~80% for the slow one (~ 1 μs). Although the samples have very similar free electron concentrations, there are some differences amongst their time profiles and related decay times. To explain this observation we point out that the samples come from different parts of the same crystal. They can thus differ by some local trace impurities (electrically neutral) that could possibly introduce some additional trapping or scattering, affecting the scintillation kinetics (possibly also the scintillation yields, but in a lesser degree). Most of such trace impurities have a segregation coefficient different than unity, hence their concentration is not the same in various parts of the crystal [11]. This results in somewhat different scintillation time profiles of particular samples.

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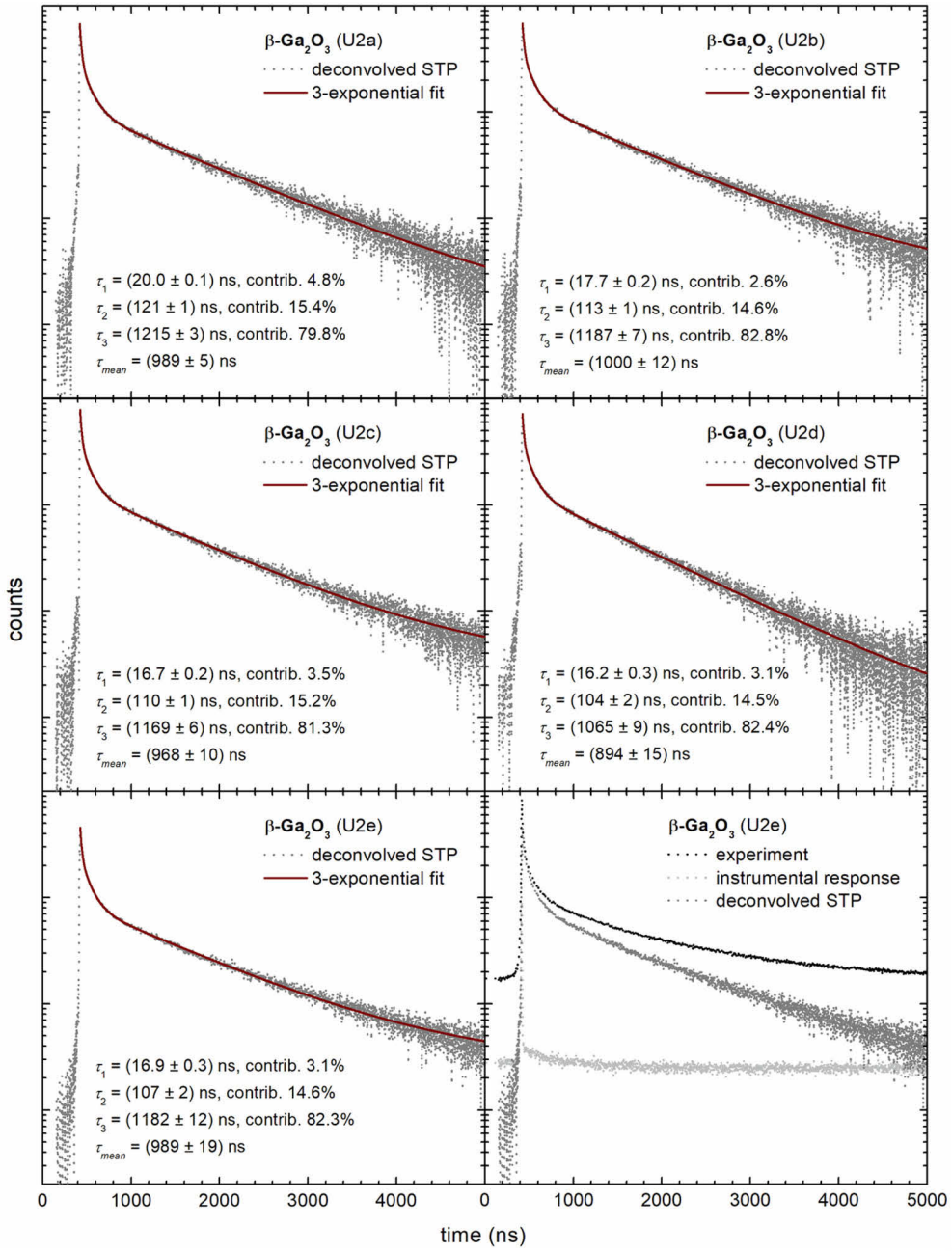

Fig. 3. Scintillation time profiles of β-Ga_2O_3 (samples: U2a,b,c,d,e; in addition, for the case of the U2e sample three curves have been shown to explain the way we analyze the scintillation time profiles).

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4. Conclusions

The present study confirms our previous findings that the scintillation yield of semiconducting β-Ga_2O_3 crystals is mainly driven by the free electron concentration. Adjusting the free electron concentration in a crystal grown by the Czochralski method without any intentional doping, we have obtained high values of yield close to 9000 ph/MeV, accompanied by energy resolutions of 10-11% (at 662 keV), and mean decay times below 1 μs. The scintillation yield proportionality has revealed a similar tendency to that of electrically insulating oxide scintillators. Further adjustments of the electrical properties of semiconducting β-Ga_2O_3 single crystals combined with yet higher chemical purity may bring a subsequent enhancement of their scintillation properties, the more that we are still far below a theoretical upper limit for the scintillation yield of β-Ga_2O_3, estimated by Mykhaylyk et al. [16] at about 40000 ph/MeV.

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Disclosures. The authors declare that there are no conflicts of interest related to this article.

Data availability. Data underlying the results presented in this paper are not publicly available at this time but may be obtained from the authors upon reasonable request.

References

1. Z. Galazka, "β-Ga_2O_3 for wide-bandgap electronics and optoelectronics," Semicond. Sci. Technol. **33**(11), 113001 (2018).
2. T. Yanagida, G. Okada, T. Kato, D. Nakauchi, and S. Yanagida, "Fast and high light yield scintillation in the Ga_2O_3 semiconductor material," Appl. Phys. Express **9**(4), 042601 (2016).
3. D. Szalkai, Z. Galazka, K. Irmscher, P. Tutto, A. Klix, and D. Gehre, "β-Ga_2O_3 solid state devices for fast neutron detection," IEEE Trans. Nucl. Sci. **64**(6), 1574–1579 (2017).
4. N. He, H. Tang, B. Liu, Z. Zhu, Q. Li, C. Guo, M. Gu, J. Xu, J. Liu, M. Xu, L. Chen, and X. Ouyang, "Ultra-fast scintillation properties of β-Ga2O3 single crystals grown by floating zone method," Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment **888**, 9–12 (2018).
5. Y. Usui, T. Kato, N. Kawano, G. Okada, N. Kawaguchi, and T. Yanagida, "Comparative study of scintillation properties of Ga_2O_3 single crystals and ceramics," J. Lumin. **200**, 81–86 (2018).
6. Y. Usui, T. Oya, G. Okada, N. Kawaguchi, and T. Yanagida, "Ce-doped Ga_2O_3 single crystalline semiconductor showing scintillation features," Optik **143**, 150–157 (2017).
7. W. Drozdowski, M. Makowski, M. E. Witkowski, A. J. Wojtowicz, Z. Galazka, K. Irmscher, and R. Schewski, "β-Ga_2O_3:Ce as a fast scintillator: An unclear role of cerium," Radiat. Meas. **121**, 49–53 (2019).
8. M. Makowski, W. Drozdowski, M. E. Witkowski, A. J. Wojtowicz, K. Irmscher, R. Schewski, and Z. Galazka, "Tailoring the scintillation properties of β-Ga_2O_3 by doping with Ce and codoping with Si," Opt. Mater. Express **9**(9), 3738–3743 (2019).
9. W. Drozdowski, M. Makowski, M. E. Witkowski, A. J. Wojtowicz, R. Schewski, K. Irmscher, and Z. Galazka, "Semiconductor scintillator development: pure and doped β-Ga_2O_3," Opt. Mater. **105**, 109856 (2020).
10. Z. Galazka, R. Schewski, K. Irmscher, W. Drozdowski, M. E. Witkowski, M. Makowski, A. J. Wojtowicz, I. M. Hanke, M. Pietsch, T. Schulz, D. Klimm, S. Ganschow, A. Dittmar, A. Fiedler, T. Schroeder, and M. Bickermann, "Bulk β-Ga_2O_3 single crystals doped with Ce, Ce + Si, Ce + Al, and Ce + Al + Si for detection of nuclear radiation," Journal of Alloys and Compounds **818**, 152842 (2020).
11. Z. Galazka, K. Irmscher, R. Schewski, I. M. Hanke, M. Pietsch, S. Ganschow, D. Klimm, A. Dittmar, A. Fiedler, T. Schroeder, and M. Bickermann, "Czochralski-grown bulk β-Ga_2O_3 single crystals doped with mono-, di-, tri-, and tetravalent ions," J. Cryst. Growth **529**, 125297 (2020).
12. L. M. Bollinger and G. E. Thomas, "Measurement of the time dependence of scintillation intensity by a delayed-coincidence method," Review of Scientific Instruments **32**(9), 1044–1050 (1961).
13. W. Drozdowski, P. Dorenbos, A. J. J. Bos, G. Bizarri, A. Owens, and F. G. A. Quarati, "$CeBr_3$ scintillator development for possible use in space missions," IEEE Trans. Nucl. Sci. **55**(3), 1391–1396 (2008).
14. M. Kapusta, P. Szupryczynski, C. L. Melcher, M. Moszynski, M. Balcerzyk, A. A. Carey, W. Czarnacki, M. A. Spurrier, and A. Syntfeld, "Non-proportionality and thermoluminescence of LSO:Ce," IEEE Trans. Nucl. Sci. **52**(4), 1098–1104 (2005).
15. W. Drozdowski, P. Dorenbos, J. T. M. de Haas, R. Drozdowska, A. Owens, K. Kamada, K. Tsutsumi, Y. Usuki, T. Yanagida, and A. Yoshikawa, "Scintillation properties of praseodymium activated $Lu_3Al_5O_{12}$ single crystals," IEEE Trans. Nucl. Sci. **55**(4), 2420–2424 (2008).
16. V.B. Mykhaylyk, H. Kraus, V. Kapustianyk, and M. Rudko, "Low Temperature Scintillation Properties of Ga_2O_3," Appl. Phys. Lett. **115**(8), 081103–5 (2019).