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Characterization of GAGG:Ce scintillators with various Al-to-Ga ratio

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ABSTRACT

We have studied the scintillation properties of cerium doped gadolinium aluminum gallium garnet (GAGG:Ce) scintillators with various Al-to-Ga ratio. Having many advantages, like high density (6.63 g/cm^3), high light output, fair energy resolution and quite fast decay time, the scintillators are an excellent solution for gamma rays detection. In this paper performance of the GAGG:1%Ce crystals with different Al-to-Ga ratios is presented. The study covered measurements of emission spectra, light output, energy resolution and non-proportionality for each crystal. It was observed that the light output of the recently obtainable crystals varies from 40,000 to 55,000 ph/MeV. Maximum emission wavelength of about 520 nm promotes silicon based photodetectors for use with these scintillators. The best energy resolution of 3.7% at 662 keV, measured with Hamamatsu S8664-1010 APD, was obtained for the sample with the minimum gallium content. This result is close to these obtained with the group of scintillators retaining very good energy resolution, like $LaCl_3$ and $CeBr_3$.

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1. Introduction

Scintillation crystals with high density and high atomic number coupled with photodetectors are commonly used for efficient detection of X-ray, γ-ray and charged particles. There is continuous demand for new scintillator materials for such application as: X-ray radiography, X-ray computed tomography (CT), positron emission tomography (PET) and other medical imaging techniques, as well as in the nuclear and high energy physics. In the case of modern scintillators, apart from the high light yield, good energy resolution, high effective atomic number, fast scintillation response, chemical stability also ruggedness and capability of large crystal growth are very important parameters. The recent discovery of single crystal multicomponent garnet scintillators, based on YAG crystal with admixture of Ga and Gd, presented by Cherepy et al. [1] and Kamada et al. [2,3] provides new structures with high density and high atomic number. From the variety of heavy garnets, like LuAG-based compositions, the GAGG:Ce appeared to be the most attractive material from the point of view of light output, decay time, energy resolution, density and absence of intrinsic radioactivity [4].

In this study performance of 1% Cerium doped Gadolinium Aluminum Gallium Garnet (GAGG:Ce) scintillators with different ratio of Al and Ga was investigated. The scintillators, grown by Czochralski (CZ) method with radiofrequency heating system, were prepared in Ar + 30% CO_2 atmosphere in order to prevent evaporation of gallium oxide, then gradually cooled to room temperature [5]. The crystals chemical notations and their size are presented in Table 1.

In the previous study it was shown that standard non-annealed GAGG:Ce is an efficient scintillator, presenting high light output, linearity of response on the gamma quanta better than LSO:Ce, good energy resolution, comparable to NaI:Tl when coupled to PMT. The decay time is composed of two-components—first of about 130 ns and longer of about 500 ns, which slightly vary between the samples [2,6–8]. In this manuscript the emission spectra, light output, energy resolution and nonproportionality of the new generation of GAGG:Ce scintillators with various Al-to-Ga ratio are presented.

2. Experimental details

Emission spectra were measured using compact Digikrom CM-110 monochromator, synchronized in time with Ortec 994 counter [9]. Both units were connected to the same PC with RS-232 link and the

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Table 1
Chemical notations of the scintillators used in the present investigation.

No.	Scintillator chemical notation	Size (mm × mm × mm)
1	$Gd_3Al_2Ga_3O_{12}$:Ce (1%)	5 × 5 × 5
2	$Gd_3Al_{2.3}Ga_{2.7}O_{12}$:Ce (1%)	5 × 5 × 5
3	$Gd_3Al_{2.6}Ga_{2.4}O_{12}$:Ce (1%)	5 × 5 × 5

emission spectra were registered with dedicated software. The scintillator samples, placed on the entrance window of the monochromator, were irradiated with ^{241}Am source of 1.2 GBq. On the monochromator exit window, a calibrated Photonis XP2020Q photomultiplier (PMT) was mounted, which registered single photoelectron pulses generated by the emitted scintillation light.

The gamma spectrometry of tested scintillators was performed with three different types of photodetector, developed by Hamamatsu: R6231-100 PMT, S3590-18 PiN diode and S8664-1010 avalanche photodiode (APD). Also additional measurements with Hamamatsu 6 × 6 mm^2 MPPC array, used previously in [6,10], were also conducted. Each crystal was coupled to the photodetector with silicone grease in order to improve the light collection. When the PMT was used, anode signal was fed the Canberra 2005 preamplifier. In the case of PiN and APD, a Cremat CR-110 low-noise preamplifier was applied. Signals from photodetectors were shaped by Ortec 672 Spectroscopy Amplifier. The shaped pulses were analyzed and recorded by Tukan 8k Multi-Channel Analyzer [11].

3. Results

3.1. Emission spectra

It is known from the previous study that the GAGG:Ce scintillator maximum emission wavelength of about 520 nm the maximum wavelength of about 520 nm is due to the 5d–4f radiative transition of Ce3+ [6]. In Fig. 1 the emission spectra of the GAGG:Ce scintillators with different Al-to-Ga ratio are presented. Minor shift towards red emission range can be seen when Ga content decreases to 2.4. It is likely that the shift is due to lower probability of dodecahedral structure distortion in the crystal lattice with lowering the Ga content; this fact will be discussed in Section 3.4. The emission spectra shown below were not corrected for the PMT quantum efficiency because of its low efficiency above 500 nm.

3.2. Decay time

The decay time for each scintillator was measured with Tektronix DPO7254 digital oscilloscope recording 10,000 averaged waveforms from fast timing PMT, Hamamatsu R5320. The plots of decay time for each tested scintillator are presented Fig. 2. The samples with Ga content of 3.0 and 2.7 shows almost identical two-exponential decay time of 150 ns and 490 ns, comparable to that observed in [6]. However, lowering the Ga content to 2.4 causes significant change of the pulse shape. In this case, three decay components can be observed, with the longest one of 6.7 ± 0.5 μs and a relative intensity of 27%. The short and moderate components are 126 ± 20 ns and 622 ± 50 ns with intensity of 42% and 31%, respectively.

3.3. Light output

The light outputs of the new GAGG:Ce samples were measured using Hamamatsu S3590-18 Si-PIN photodiode [12]. The light yield was obtained by comparing the 661.7 keV peak position in ^{137}Cs scintillation light spectrum to the position, of 59.5 keV peak in ^{241}Am spectrum directly detected in the photodiode after crystal removing. Both spectra are shown in Fig. 3. This measurement provides the best precision of the light output estimation, much better than that measured with modern PMTs. This fact was introduced in [13], where it was shown that modern PMTs contribute an excess value to the measured photoelectrons. Moreover, estimation of the PMT quantum efficiency is loaded with significant error, up to 10%. Additionally, as opposed to the PMT, the QE of the PIN diode is practically flat at the range of 500–600 nm, thus the measured light output is weakly affected by an accuracy of emission spectrum.

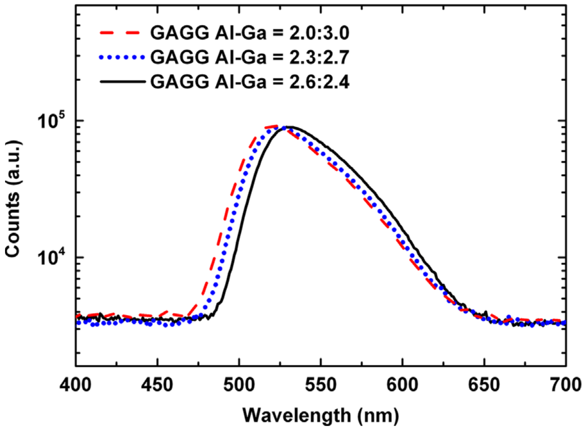

Fig. 1. Emission spectra of the GAGG:Ce scintillators.

In Table 2 the measured light yield of the new GAGG:Ce crystals is presented. In the case of the PIN diode, the shaping time in the spectroscopy amplifier was set to unipolar 2 μs—this value was sufficient to fully integrate the light pulse and allows for the lowest contribution of the PiN diode noise. The samples with Al:Ga ratio of 2.3:2.7 and 2.0:3.0 show an excellent light output, with the highest value of 56,500 ± 5600 ph/MeV, significantly higher than that obtained with the previously tested 10 × 10 × 5 mm^3 samples in [6]. Measurements of the centroid position at 661.7 keV for the new 10 × 10 × 5 mm^3 and 5 × 5 × 5 mm^3 GAGG:Ce scintillators with Al–Ga ratio of 2.0–3.0 were conducted in order to estimate the light loss on the edges of the PiN diode. The light loss was estimated to be about 6%, being in good agreement with the measurements conducted in [14]. Thus, the light output of the recent crystals was improved in comparison with previously measured 10 × 10 × 5 mm^3 samples. From the set of tested crystals, the $Al_{2.6}Ga_{2.4}$ sample shows the smallest value of the light output. Such similar tendency of the light output variations was reported in [5], however, the measured light output values with the Hamamatsu APD was misrepresented due to discrepancy between the gain for X-rays and light, as reported in [15], [16]. This is caused by distortion of electric field distribution in the avalanche region. During characterization of the $Al_{2.6}Ga_{2.4}$ sample, setting the shaping time to 10 μs let to integrate about 9% more light in comparison with the measurement done with 2 μs.

3.4. Energy resolution and non-proportionality

The studies of the energy resolution and nonproportionality of response to gamma rays were done with use of Hamamatsu S8664-1010 APD. For the purpose of comparison, the energy resolution was also measured with the scintillator coupled to the Hamamatsu R6231-100 PMT. The shaping time of 1 μs was used in measurements to minimize noise contribution of an APD. A set of radioactive sources emitting X and gamma radiation in the energy range between 16 and 1408 keV was used to fully characterize the response of scintillators. The results of energy resolution obtained

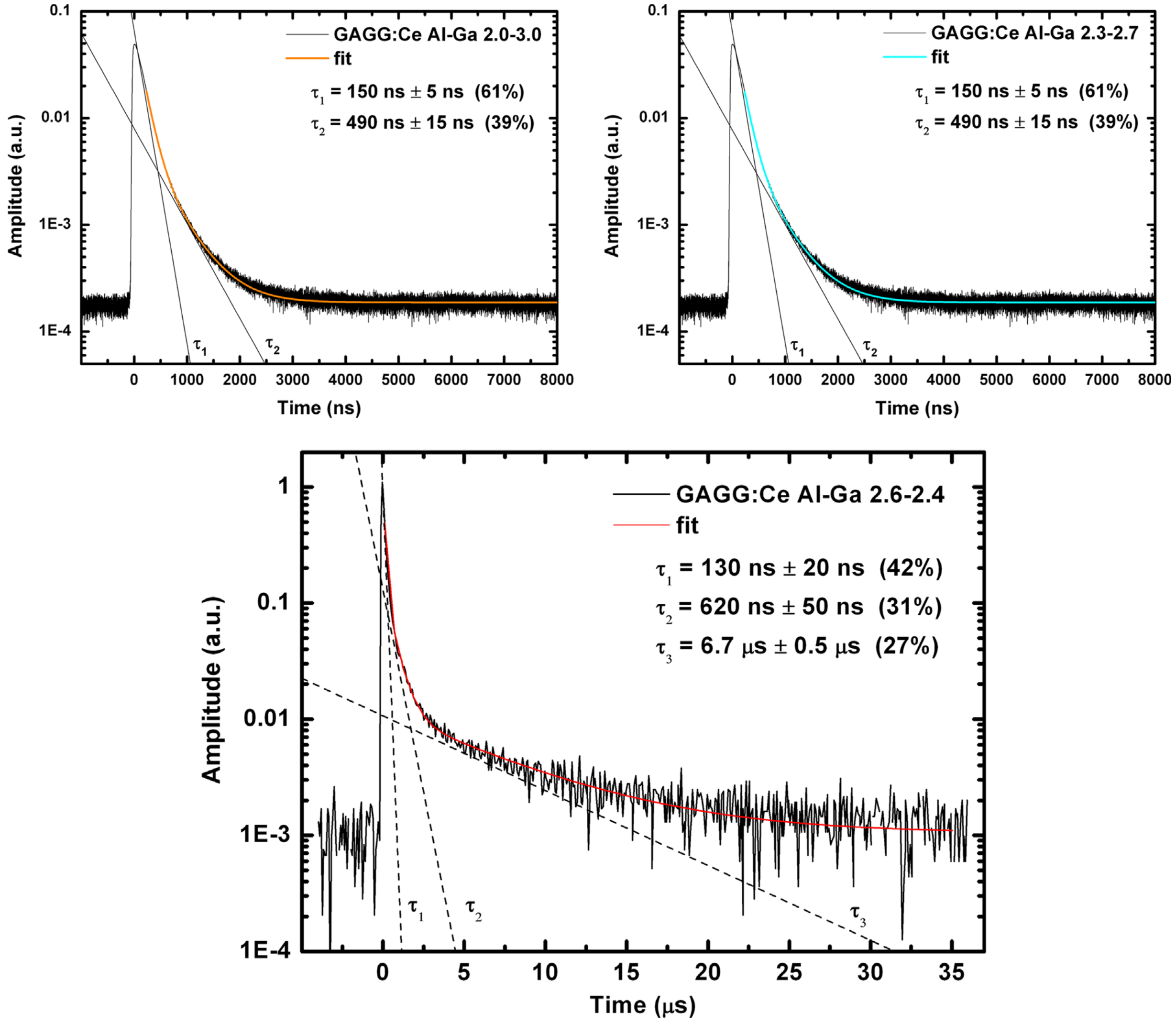

Fig. 2. The decay time for each tested GAGG:Ce scintillator. The long component in case of sample with Al–Ga = 2.6–2.4 is clearly seen.

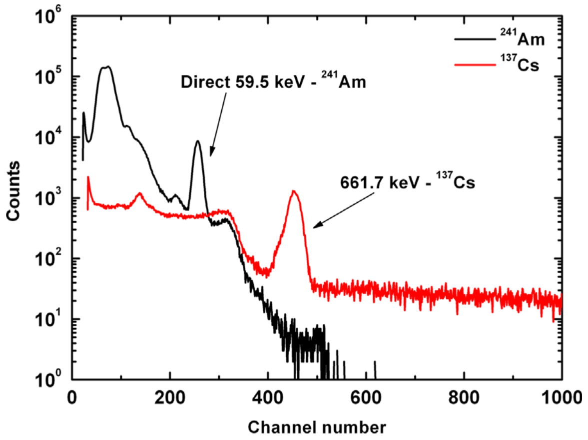

Fig. 3. Spectra of ^{241}Am, recorded by the direct illumination of the S3590-18 Si-PIN photodiode, and ^{137}Cs detected by the GAGG:Ce scintillator with Al:Ga ratio of 2.3:2.7. The γ rays of 59.5 keV and 661.7 keV were emitted from the ^{241}Am and ^{137}Cs source, respectively.

Table 2
The light output of the new GAGG:Ce scintillators measured with S3590-18 PIN photodiode.

Scintillator	No.	N_{e-h} pairs (N_{e-h}/MeV)	Light output (ph/MeV)
$Gd_3Al_2Ga_3O_{12}$	1	49,700 ± 2500	56,500 ± 5600
$Gd_3Al_{2.3}Ga_{2.7}O_{12}$	1	48,900 ± 2400	55,600 ± 5600
$Gd_3Al_{2.6}Ga_{2.4}O_{12}$	1	39,200 ± 2000	44,600 ± 4400
Prev. $G_3Al_2Ga_3O_{12}$ [6]	–	29,400 ± 1500	33,100 ± 3000

for 662 keV photons in ^{137}Cs spectra are presented in Table 3. It can be seen that the performance of the novel GAGG:Ce scintillators was notably improved in comparison with the older sample. This fact can be confirmed by the fact that the same energy resolution was obtained with the previous GAGG:Ce 2.0–3.0 sample measured with Photonis XP5500B PMT and the new GAGG:Ce 2.0–3.0 sample measured with commercially available Hamamatsu R6231-100, although the QE the Hamamatsu PMT is significantly lower at 550 nm. The best achieved result is 3.7% ± 0.1% for the samples with Al-to-Ga ratio of 2.6:2.4 measured with APD (see Fig. 4) is far better than that recorded previously in [3] and comparable to that obtained with $LaCl_3$ and $CeBr_3$ coupled to PMTs [16,17]. The values of measured energy resolution for the set of samples in wide energy range are presented in Fig. 5. The non-proportionality of response on gamma-rays energy for each crystal is presented in Fig. 6. Characteristics of 10 × 10 × 5 mm^3 $LaBr_3$:Ce scintillator tested on PMT are also included. It can be seen that the non-proportionality plot of the GAGG:Ce scintillator with the least Ga content is very similar to that for $LaBr_3$:Ce.

Table 3
Energy resolution of the new GAGG:Ce scintillators measured with Hamamatsu R6231-100 PMT and S8664-1010 APD.

Scintillator	No.	dE/E@662keV (%) PMT	dE/E@662keV (%) APD
$Gd_3Al_2Ga_3O_{12}$	1	6.1 ± 0.2	5.1 ± 0.2
$Gd_3Al_{2.3}Ga_{2.7}O_{12}$	1	5.7 ± 0.2	4.5 ± 0.2
$Gd_3Al_{2.6}Ga_{2.4}O_{12}$	1	5.6 ± 0.2	3.7 ± 0.1
$Gd_3Al_2Ga_3O_{12}$ [a][6]	–	6.1 ± 0.2	–
$Gd_3Al_2Ga_3O_{12}$ [b][5]	–	–	5.2

[a] Measured with Photonis XP5500B PMT.
[b] Measured with Hamamatsu S8664-55 APD.

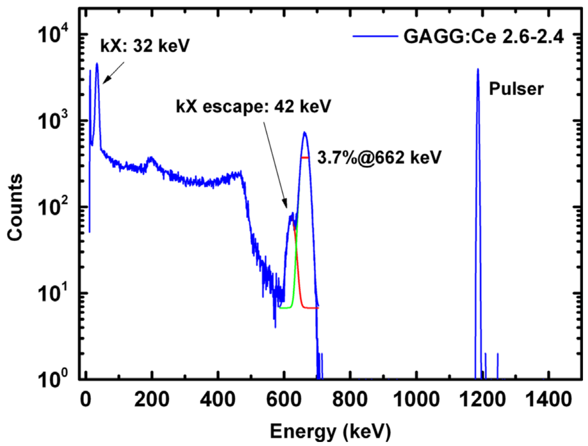

Fig. 4. Energy resolution of the GAGG:Ce sample with Al–Ga ratio of 2.6–2.4 irradiated with ^{137}Cs source. Scintillator was coupled to Hamamatsu S8664-1010 APD.

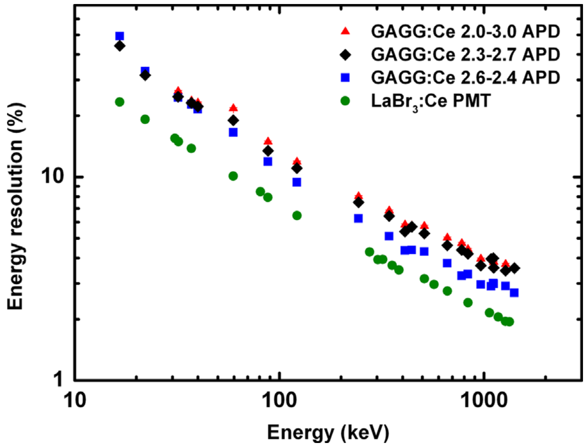

Fig. 5. Energy resolution of the tested scintillators. Error bars are within the size of the points.

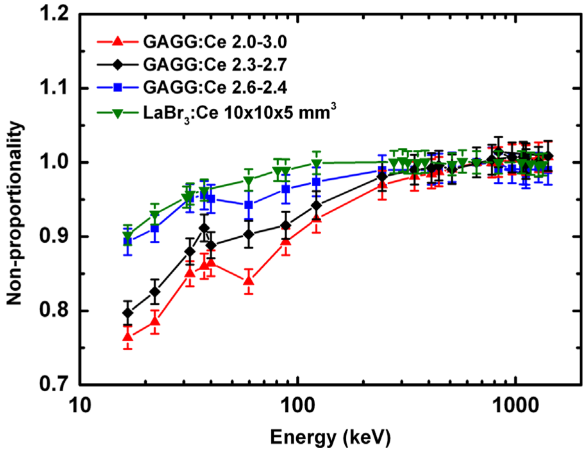

Fig. 6. Nonproportionality of the tested scintillators. Characteristics for 10 × 10 × 5 mm^3 LaBr$_3$:Ce was included as a reference.

Table 4
Main parameters of the MPPC array used in the present study.

Manufacturer	Hamamatsu
Number of channels	4 (2 × 2 ch)
Active area/channel	3 × 3 mm^2
Total active area	6 × 6 mm^2
Number of pixels/channel	14,400
Pixel size	25 × 25 μm^2
Fill factor	30.8
Gain (at 72.80 V)	2.75×10^5
Spectral range	320–900 nm (maximum sensitivity at 440 nm)
Recommended voltage	72.8 V
Dark count/channel	0.3 Mcps (at 72.8 V)
Capacitance/channel	320 pF
Total number of pixels	57,600

The tendency of improving the nonproportionality curve with lowering of gallium in the crystal structure is noticeable. According to Kamada et al. [5], the improvement of the nonproportionality can be explained by a change of lattice structure. In the case of the scintillators with Al–Ga ratio of 2.0–3.0 and 2.3–2.7 a biased occupancy of Ga can be observed in octahedral (perovskite) structures. In this case, dodecahedral (garnet) structure is often distorted. It is guessed that distorted dodecahedral structures generate defects in band structure of GAGG scintillators, which increase the light output. However, with lowering the Ga content, the garnet structure in the crystal lattice becomes more dominant and it reflects in decreasing of the light output, but on the other hand, improvement the energy resolution.

We also measured the energy resolution of the 2.6–2.4 GAGG:Ce sample coupled to the MPPC array and compared to the results obtained with the PMT and APD. Main parameters of the MPPC array are presented in Table 4. We can see that the performance of GAGG:Ce scintillator is similar while measured with the standard PMT and MPPC. However, due to 30% fill factor (FF) of the MPPC, the measured energy resolution for GAGG:Ce 2.6–2.4 sample is worse than that obtained with the same scintillator coupled to APD. The spectrum of ^{137}Cs obtained with MPPC coupled to GAGG:Ce 2.6–2.4 is presented in Fig. 7 showing the energy resolution of 5.5% at 662 keV full energy peak.

3.5. *Intrinsic resolution*

The intrinsic resolution is a factor, which describes the scintillator quality in terms of its response on gamma rays and is mainly associated with the scintillator nonproportional response. For given crystal it can be evaluated on the basis of measured light output, nonproportionality and energy resolution [18,19].

The intrinsic resolution of the scintillator δ_{sc} coupled to a photodetector is evaluated from the measured energy resolution corrected by statistical contribution of the primary photoelectrons (PMT) or electron–hole pairs (APD, PiN diodes) and statistical fluctuations of photodetector gain, ascribed as δ_{st}, and electronic

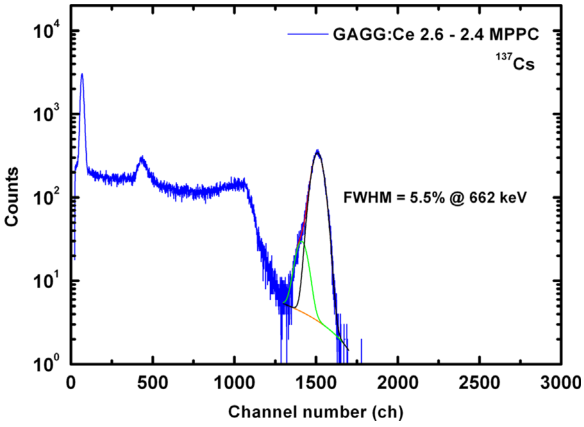

Fig. 7. Energy resolution for the GAGG:Ce sample with Al-to-Ga ratio of 2.6–2.4, exposed on ^{137}Cs source, measured with 6 × 6 mm^2 Hamamatsu MPPC.

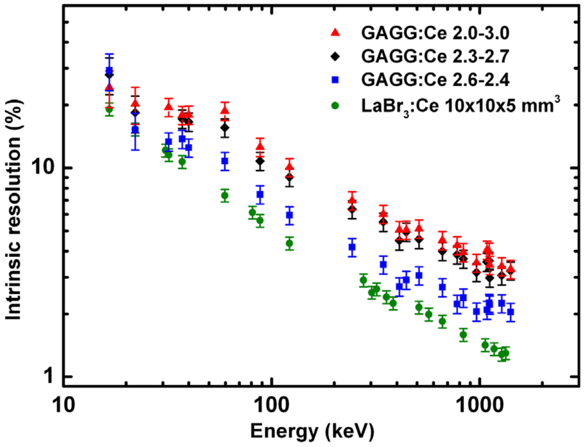

Fig. 8. Intrinsic resolution of the tested crystals.

dark noise δ_n, as shown in Eq. (1).

$$\delta_{sc} = \sqrt{\left(\frac{dE}{E}\right)^2 - (\delta_{st})^2 - (\delta_n)^2} \qquad (1)$$

The intrinsic resolution of the scintillators was measured with APD, thus, the number of electron holes – a value included in the statistical contribution – was corrected by the factor of 0.8. This correction factor is the ratio of APD gain realized in direct detection of 5.9 keV X-rays from ^{55}Fe to the APD gain in detection of optical scintillation photons.

The measured intrinsic resolution characteristics of the GAGG:Ce scintillators are presented in Fig. 8. As expected from the improvement of the nonproportionality with lowering of the Ga content, the GAGG:Ce sample with Al–Ga of 2.6–2.4 presents the best intrinsic resolution of 2.7 ± 0.3% at 662 keV, significantly better than those obtained with other tested samples. In Table 5 results of the intrinsic resolution are presented and compared with the sample measured previously [20]. The intrinsic resolution of LaBr$_3$:Ce measured as a reference is in very good agreement with that presented in [20].

Table 5
Energy and intrinsic resolution of the new GAGG:Ce scintillators no 1 series measured with S8664-1010 APD. Data were compared with the previously measured sample.

Scintillator	No. APD	dE/E@662keV (%)	Intrinsic resolution @662keV (%)
$Gd_3Al_2Ga_3O_{12}$	1	5.1 ± 0.2	4.5 ± 0.3
$Gd_3Al_{2.3}Ga_{2.7}O_{12}$	1	4.5 ± 0.2	4.0 ± 0.3
$Gd_3Al_{2.6}Ga_{2.4}O_{12}$	1	3.7 ± 0.1	3.0 ± 0.2
Prev. $Gd_3Al_2Ga_3O_{12}$ [a][6]	–	6.1 ± 0.2[a]	5.2 ± 0.1
$LaBr_3$:Ce PMT	–	2.8 ± 0.1	1.8 ± 0.1

[a] Measured with Photonis XP5500B PMT.

Table 6
Main parameters of the tested GAGG:Ce scintillators. The FWHM was measured with use of Hamamatsu S8664-1010 APD.

Sample	Light output (ph/MeV)	λ_{max} (nm)	FWHM @662 keV
$Al_{2.0}Ga_{3.0}$	56,500 ± 5600	520	5.1 ± 0.2
$Al_{2.3}Ga_{2.7}$	55,600 ± 5600	525	4.5 ± 0.2
$Al_{2.6}Ga_{2.4}$	44,600 ± 4400	530	3.7 ± 0.1

4. Summary

The results presented above show an important improvement in the performance of the GAGG:Ce scintillators. The main properties of the investigated scintillators are summarized in Table 6. Particularly, the better energy resolution can be obtained with lowering the Ga content, however, the emission maximum shifts towards the longer wavelength and light output decreases. The scintillators response on gamma quanta becomes definitely more linear at the Al-to-Ga ratio of 2.6–2.4. In general, this is rather uncommon behavior due to the fact that only internal crystal structure is modified and the dopant level of 1% Ce is the same for each sample. Particularly, the better proportionality of the crystal response on γ quanta reflects in better intrinsic resolution of the scintillator, as observed for the $Gd_3Al_{2.6}Ga_{2.4}O_{12}$ scintillator. In general, many effects, like Compton scattering, photoelectric effect, resulting in event to event variation in produced amount of light as well as δ-rays emission by energetic electron and Landau fluctuations along the electron track, can be responsible for the degradation of energy resolution and non-proportionality [21–24]. Unfortunately, understanding of these effects on non-proportionality and energy resolution characteristics is still lacking. It is known that it depends on dopants, doping level, temperature and – as showed in the present paper – crystal structure, but not in a coherent or predictable way.

On the basis of these measurements a question arises: will further improvement of the energy resolution be observed if the amount of Ga in the crystal structure becomes even lower? This field of the study will be a part of further optimization of the GAGG:Ce scintillators, which come to be very promising material for gamma spectroscopy, especially when coupled to silicon photodetectors.

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