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Tailoring the scintillation properties of β-Ga_2O_3 by doping with Ce and codoping with Si

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Abstract: Measurements of pulse height spectra and scintillation time profiles performed on Czochralski-grown β-Ga_2O_3, β-Ga_2O_3:Ce, and β-Ga_2O_3:Ce,Si crystals are reported. The highest value of scintillation yield, 7040 ph/MeV, was achieved for pure β-Ga_2O_3 at a low free electron concentration, nevertheless Ce-doped crystals could also approach high values thereof. Si-codoping, however, decreases the scintillation yield. The presence of Ce, and the more of Ce and Si, in β-Ga_2O_3 significantly increases the contribution of the fastest components in scintillation time profiles, which makes β-Ga_2O_3 a very fast scintillator under γ-excitation.

1. Introduction

Gallium oxide is known since the 19th century when de Boisbaudran [1] reported a newly discovered element Gallium and its compounds. After several tens of years in oblivion, it emerged about two decades ago as a promising ultrawide bandgap semiconductor for manifold applications [2,3]. Recently, another important feature of this material was pointed out by Yanagida et al. [4], who informed about fast and relatively efficient scintillation of β-Ga_2O_3 under γ-irradiation. Scintillation properties in semiconducting β-Ga_2O_3, which could potentially open the gate to some brand new electronic devices, were newly demonstrated for pure [5–7] and doped crystals [8–10] obtained with different growth techniques, i.a. OFZ (optical floating zone) [6–9], EFG (edge-defined film-fed growth) [6], and the Czochralski method [5,10].

In this Communication we present our systematic studies on scintillation properties of β-Ga_2O_3, including the effects of single doping with Ce and double doping with Ce and Si. Our initial results obtained for the first series of Czochralski-grown β-Ga_2O_3:Ce crystals [10] indicate that although no Ce^{3+} *d-f* luminescence is observed (scintillation of β-Ga_2O_3:Ce is associated with self-trapped exciton emission peaking at about 360 nm [11]; this issue was wrongly interpreted before by Usui et al. [9]) and the scintillation yield is mostly related to the free electron concentration, the presence of Ce is advantageous for speed and possibly also for efficiency. The scintillation time profiles are faster for β-Ga_2O_3:Ce than for pure β-Ga_2O_3, as well as a higher content of Ce enables to maintain the scintillation yield at a reasonably high level. The intention of codoping β-Ga_2O_3:Ce with Si was to significantly increase the free electron concentration, which cannot be achieved with undoped or Ce-doped crystals. Doping with Si or Sn, acting as shallow donors, is commonly practiced for β-Ga_2O_3 [12,13].

2. Materials and experiment

Nine high-quality bulk β-Ga_2O_3 single crystals, including one pure, four doped with Ce, and four doubly doped with Ce and Si, were grown by the Czochralski method along the <010> crystallographic direction as described by Galazka et al. [14]. All the crystals investigated

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here were obtained at very similar growth conditions to minimize an impact of any factors other than dopants on the scintillation performance. The dopant and free electron concentrations, as well as the basic scintillation properties of these crystals, are listed in Table 1. The dopant concentrations are those in the melt (in mol%), while the free electron densities were determined with the Hall effect measurements. To prepare plate samples necessary for pulse height spectra and scintillation time profiles, first (010)-oriented 5 mm thick slabs were cut from the bulk crystals, from which bars with 5×5 mm^2 cross-sections parallel to the (100) plane (which is an easy cleavage plane) were prepared. Then, (0.50 ± 0.05) mm thick (100)-oriented samples were cleaved from the bars. The advantage of freshly cleaved surfaces is the avoidance of any contamination and surface damage that could arise from polishing.

Table 1. Summary of properties of the studied β-Ga_2O_3 crystals (n - free electron concentration, 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)

ID	dopants	n (cm^{-3})	Y (ph/MeV)	R (%)	τ_i (ns)	τ_{mean} (ns)
U1	-	$2.5 \cdot 10^{16}$	7040	9.20	4.92 (2.4%) 28.7 (6.1%) 148 (15.9%) 1198 (76.5%)	922
C1	Ce (0.1%)	$3.3 \cdot 10^{16}$	6580	10.5	5.57 (2.6%) 35.8 (7.7%) 181 (19.5%) 1000 (70.2%)	741
S1	Ce (0.1%), Si (0.2%)	$4.9 \cdot 10^{18}$	2040	17.3	4.84 (15.7%) 23.0 (29.3%) 71.4 (42.9%) 467 (12.1%)	94.5
C2	Ce (0.25%)	$7.0 \cdot 10^{15}$	3700	13.7	5.62 (5.4%) 35.5 (12.8%) 171 (27.5%) 967 (54.3%)	577
S2	Ce (0.25%), Si (0.5%)	$4.1 \cdot 10^{18}$	970	27.4	3.45 (18.1%) 13.6 (42.6%) 38.1 (20.3%) 459 (19.0%)	101
C3	Ce (0.5%)	$3.9 \cdot 10^{16}$	4640	13.5	4.28 (5.1%) 27.5 (9.2%) 150 (23.7%) 916 (62.0%)	605
S3	Ce (0.5%), Si (0.2%)	$3.8 \cdot 10^{18}$	1610	22.2	4.04 (19.8%) 17.7 (28.5%) 51.2 (37.7%) 470 (14.0%)	91.0
C4	Ce (1.0%)	$2.9 \cdot 10^{17}$	5470	10.8	3.86 (8.4%) 22.0 (8.2%) 110 (20.4%) 479 (63.0%)	327
S4	Ce (1.0%), Si (0.2%)	$5.3 \cdot 10^{18}$	1330	21.4	3.12 (10.7%) 13.7 (28.1%) 41.7 (43.9%) 551 (17.3%)	118

The uncertainties of determination of Y, R, and τ_i are below 5%.

Pulse height spectra were recorded at room temperature under 662 keV γ-excitation from a ^{137}Cs source (210 kBq). The output signal from a Hamamatsu R878 PMT biased with 1250 V was processed by a Canberra 2005 integrating preamplifier, a Canberra 2022 spectroscopy amplifier

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(2 μs shaping time), and a TUKAN-8K-USB multichannel analyzer. To avoid potential light losses, a small amount of optical grease was always injected between the sample and the PMT window. Moreover, the sample was covered with several layers of Teflon tape. To provide the most accurate values of the photoelectron yield, single photoelectron spectra were measured before and after examination of each sample. The photoelectron yields (in phe/MeV) were next converted into the scintillation yields (in ph/MeV), taking into account the spectral matching of the β-Ga_2O_3 scintillation light to the characteristics of the PMT.

We note that we had at our disposal at least two plate samples of each of the crystals specified in Table 1. To improve the data accuracy, pulse height spectra of each plate were measured twice (i.e. sticking both sides of the plate to the PMT window). In this way for each crystal we arrived at no less than 4 pairs of values of scintillation yield and energy resolution. Since the highest obtained value of yield indicates the real potential of the crystal, for convenience sake in Table 1 we single out the highest yields and lowest energy resolutions observed for each crystal.

The delayed coincidence single photon counting method originally proposed by Bollinger and Thomas [15] was used for scintillation time profile measurements. The same ^{137}Cs source, two Hamamatsu PMTs (R1104 for "starts", R928 for "stops"), a Canberra 2145 time-to-amplitude converter, and a TUKAN-8K-USB multichannel analyzer were employed.

3. Results and discussion

3.1. Scintillation yield and energy resolution

Pulse height spectra of the brightest sample of each kind (β-Ga_2O_3, β-Ga_2O_3:Ce, and β-Ga_2O_3:Ce,Si) are presented in Fig. 1. Compared to our previous studies [10] we achieved significantly higher scintillation yields: 7040 ph/MeV (this work) vs. 4510 ph/MeV [10] for β-Ga_2O_3 and 6580 ph/MeV (this work) vs. 4760 ph/MeV for β-Ga_2O_3:Ce (in all cases the dimensions of the samples were the same, $5 \times 5 \times 0.5$ mm^3). The improvement also comprises energy resolutions (at 662 keV), which are now closer to the level of 10% (or even better for pure β-Ga_2O_3).

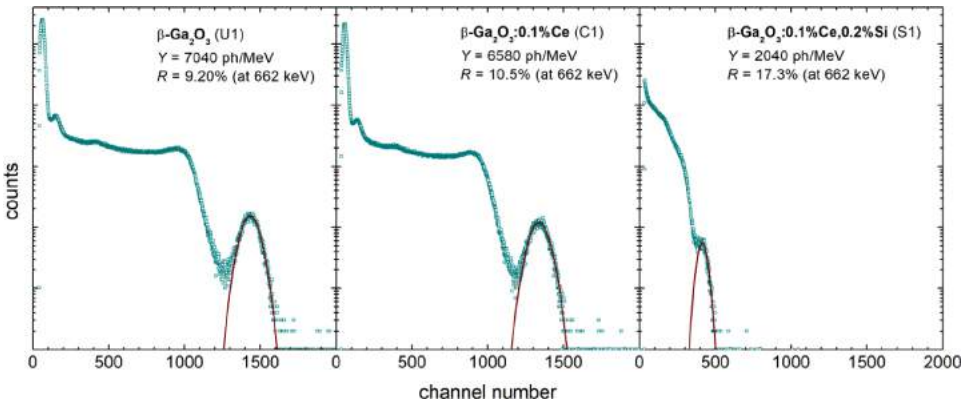

Fig. 1. Representative pulse height spectra of β-Ga_2O_3, β-Ga_2O_3:Ce, and β-Ga_2O_3:Ce,Si.

To compare all the studied crystals with each other and to find potential correlations, in Fig. 2 we plot the scintillation yields of the samples against their free electron concentrations. Such a presentation let us divide the samples into three groups:

(a) the samples with the highest yields (above 6500 ph/MeV) and moderate free electron concentrations (~$3 \cdot 10^{16}$ cm^{-3}): β-Ga_2O_3 pure (U1) and lightly doped with Ce (C1);

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(b) the β-Ga_2O_3:Ce samples (C2-C4) with middle yields (~3500–5500 ph/MeV), showing a distinct enhancement of yield with increasing concentration of free electrons, conceivably also related to the content of Ce, however this issue is not clear;

(c) the β-Ga_2O_3:Ce,Si samples (S1-S4) with relatively low yields (below 2100 ph/MeV) in spite of the highest free electron concentrations ((3.8–5.3)·10^{18} cm^{-3}).

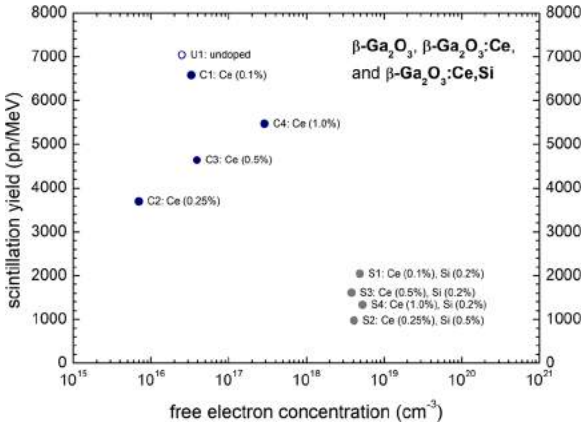

Fig. 2. Scintillation yield of β-Ga_2O_3, β-Ga_2O_3:Ce, and β-Ga_2O_3:Ce,Si as a function of free electron concentration.

We note that due to a very low segregation coefficient of Ce in β-Ga_2O_3 [14], Ce concentrations are at very low levels (several to tens of wt. ppm only) and such crystals may behave as undoped ones. This could explain why the lightly Ce-doped crystal (C1) displays the highest scintillation yield together with the undoped one (U1), both at moderate free electron concentrations. In contrast, high concentrations of free electrons (above 10^{18} cm^{-3}) in all the Si-codoped samples (S1-S4) significantly decrease the scintillation yield.

3.2. Scintillation time profiles

Scintillation time profiles (often referred to as scintillation decays) of β-Ga_2O_3, β-Ga_2O_3:Ce, and β-Ga_2O_3:Ce,Si (the same samples as in Fig. 1) are illustrated in Fig. 3. The experimental points are not distorted with afterpulses and may be regarded as a reliable base for determination of decay time constants. For all the investigated crystals, this task is accomplished by fitting 4-exponential decay curves, which are the least component curves providing an acceptable agreement between experimental and fitted profiles. The derived decay time constants with their contributions are summarized in Table 1. To simplify any comparisons we extend the number of parameters with a so-called mean decay time, herein defined as:

$$\tau_{mean} = \frac{\sum_{i=1}^{4} A_i \tau_i^2}{\sum_{i=1}^{4} A_i \tau_i}$$

where A_i and τ_i are amplitudes and decay time constants of each decay component, respectively.

Concerning the individual decay time constants, the longest ones are observed for pure β-Ga_2O_3. The presence of Ce makes the scintillation faster, which agrees with our previous report [10]. The addition of Si speeds up the scintillation even more. The contribution from particular time constants into the time profiles is quite complex, but apparently codoping with Si increases the contribution from the two shortest components and decreases that from the longest one. The contribution from the fastest decay (3–6 ns) is about 3%, below 8%, and up to about

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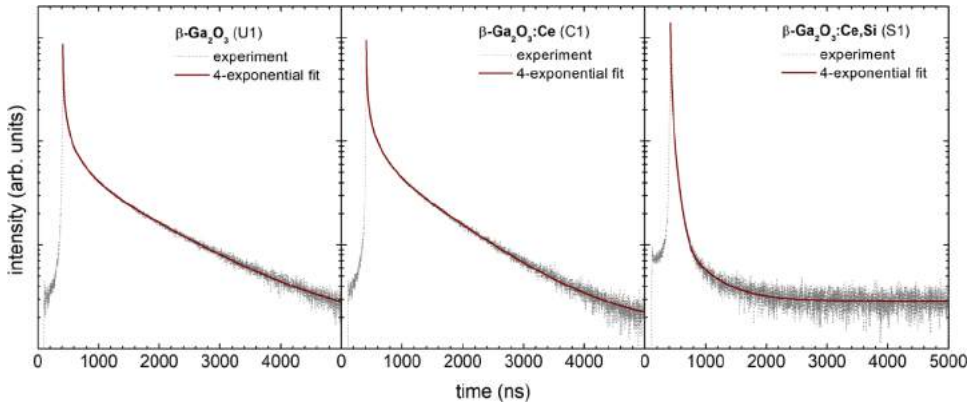

Fig. 3. Representative scintillation time profiles of β-Ga_2O_3, β-Ga_2O_3:Ce, and β-Ga_2O_3:Ce,Si.

20% for undoped, Ce-doped, and Ce,Si-doped crystals, respectively. Considering the second fastest decay (13–36 ns), its contribution is about 6%, 8–13%, and 28–43% for the same order of crystals, respectively.

In Fig. 4 we show the dependence of the scintillation mean decay time on the free electron concentration. It can easily be noticed that with the exception of one β-Ga_2O_3:Ce sample (C2) the mean decay time shortens significantly with increasing concentration of free electrons. Unfortunately, this uncorrelates with the scintillation yield, since the "faster" β-Ga_2O_3:Ce,Si crystals offer much lower yields than the "slower" β-Ga_2O_3 and β-Ga_2O_3:Ce ones.

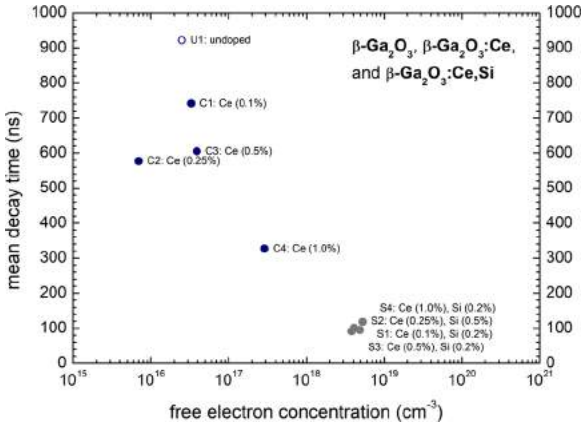

Fig. 4. Scintillation mean decay time of β-Ga_2O_3, β-Ga_2O_3:Ce, and β-Ga_2O_3:Ce,Si as a function of free electron concentration.

4. Conclusions

Heading towards the highest possible scintillation yield from Czochralski-grown pure or doped β-Ga_2O_3 crystals, we just exceed the threshold of 7000 ph/MeV with an energy resolution of about 10%, which makes up a substantial step forward per se. The value of 7040 ph/MeV is achieved, against expectations, for pure β-Ga_2O_3, although some of the Ce-doped samples are also close to this result. The codoping with Si, introduced to increase the free electron concentration, has alas a negative impact on the scintillation yield of β-Ga_2O_3. On the other hand,

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in terms of scintillation time profiles the samples of β-Ga_2O_3:Ce are better than pure β-Ga_2O_3, while the samples of β-Ga_2O_3:Ce,Si are the prominent ones, offering the fastest scintillation with relatively high contributions (> 50%) from the two shortest decay components (3–6 and 13–36 ns). Unfortunately, these promising timing properties of β-Ga_2O_3:Ce,Si crystals do not go hand in hand with their scintillation yields, which are relatively low. Therefore, a high scintillation yield can be achieved at the expense of a lower contribution from the fastest decays, and vice-versa. Thus any further research activities should be aimed at combining the strongest points of the already examined crystals to find a compromise providing both fast and efficient scintillation.

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