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Heading for brighter and faster β-Ga_2O_3 scintillator crystals

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ABSTRACT

Czochralski-grown β-Ga_2O_3 and β-Ga_2O_3:Si crystals with the free electron concentrations between $2.5{\cdot}10^{16}$ and $4.3{\cdot}10^{18}$ cm^{-3} have been characterized by means of pulse height and scintillation time profile measurements in order to assess their basic scintillation properties. At room temperature, with increasing free electron concentration in the studied range, the scintillation yields decrease from 8920 to 1930 ph/MeV, while the mean scintillation decay times pare down from 989 to 61 ns. However, when the brightest β-Ga_2O_3 sample is cooled down below 100 K, its scintillation yield exceeds 20000 ph/MeV.

1. Introduction

Five years after the first report on promising scintillation properties of β-Ga_2O_3 crystals [[1]] a strongly increased interest in this field can easily be noticed. Research is carried on at several laboratories, in which diverse growth technologies are applied and various dopants are examined, mostly aimed at enhancement of the basic scintillation parameters, such as light yield, energy resolution and decay time constants [[1–9]]. Most importantly, at least some of these studies are not based on trials and errors, but focus on understanding the physics that stands behind the acquired data and observed correlations, providing an important feedback for subsequent growth procedures. In particular, the free electron concentration has already been pointed out as the most important factor determining both the scintillation yield and the scintillation decay times, regardless of the presence of any dopant [6–8].

In this Communication we present the sequel of our research on scintillation properties of Czochralski-grown β-Ga_2O_3 crystals [6,8]. With several new crystals (either undoped or doped with Si) characterized by free electron concentrations of 10^{17} $cm^{-3} < n_e < 10^{18}$ cm^{-3}, we fill the gap between lightly conductive crystals ($n_e < 10^{17}$ cm^{-3}) with higher yields but slower scintillation decays and highly conductive ones ($n_e > 10^{18}$ cm^{-3}) with lower yields but faster decays. The results of pulse height and scintillation time profile measurements confirm the dominant role of the free electron concentration for the scintillation properties of β-Ga_2O_3 crystals. Additionally, we show for the first time the thermal dependence of the scintillation yield investigated between 91 and 347 K. This experiment indicates that at temperatures marginally above liquid N_2 (LNT) the yield of β-Ga_2O_3 is more than two times higher than at room temperature (RT), although it seems that, for several reasons, such a high value (well over 20000 ph/MeV) cannot be maintained for higher temperatures.

2. Materials and experiment

High-quality bulk single crystals of β-Ga_2O_3 and β-Ga_2O_3:Si were grown by the Czochralski method along the <010> crystallographic direction as described in detail by Galazka et al. [[6,10]]. The crystals were either undoped or intentionally doped with Si by adding powdered SiO_2 at a pre-defined molar concentration (0.025 or 0.2 mol%) to the powdered Ga_2O_3 starting material. The undoped crystals showed the free electron concentration (n_e) between $2.5{\cdot}10^{16}$ and $1.9{\cdot}10^{17}$ cm^{-3}. The origin of the electrical conductivity in undoped crystals comes from residual impurities, mainly from Si and H [[10–12]]. The β-Ga_2O_3 crystals intentionally doped with very low level of Si (0.025 mol%) revealed $n_e = (5.9–8.9){\cdot}10^{17}$ cm^{-3}, while those doped with higher Si concentration (0.2 mol%) resulted in $n_e > 10^{18}$ cm^{-3}. The 5 × 5 × 0.5 mm^3 sized, (100) oriented samples for the pulse height and scintillation time profile measurements, as well as one thicker (5 × 5 × 2.5 mm^3)

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sample necessary for the temperature-dependent studies, were prepared by cleaving parallel to the easy cleavage plane {100}. We note that freshly cleaved surfaces have an advantage over polished ones due to the avoidance of any damage and contamination from polishing. The list of the investigated crystals with their free electron concentrations (determined by the Hall effect measurements) and basic scintillation properties is featured in Table 1.

RT pulse height spectra were collected under 662 keV gamma excitation from a ^{137}Cs source. The pulsed output signal from a Hamamatsu R878 photomultiplier tube (PMT) biased with 1250 V was processed by a Canberra 2005 integrating preamplifier, a Canberra 2022 spectroscopy amplifier working with a shaping time of 2 μs, and a TUKAN-8K-USB multichannel analyzer (MCA) [[13]]. The photoelectron yields, i.e. the numbers of photoelectrons released from the photocathode per 1 MeV of energy deposited in each sample, were evaluated based on the positions of so-called full-energy peaks in the spectra. Then, considering the spectral matching of the scintillation light emitted by the crystals to the characteristics of the PMT, these photoelectron yields were converted into the scintillation yields expressed in numbers of photons per 1 MeV (ph/MeV). To improve the light collection efficiency, the samples were coupled to the quartz window of the PMT with Viscasil grease and covered with several layers of Teflon tape, forming a "reflective umbrella".

A custom designed cryostat, manufactured at the National Centre for Nuclear Research, was used to record pulse height spectra at various temperatures between LNT and somewhat above RT. The scintillation light was collected by a Hamamatsu S13360-6050 PE silicon photomultiplier (SiPM). The signal from the photodetector was preamplified by a Cremat CR-113 unit, shaped using an Ortec 672 spectroscopy amplifier, and then analyzed by a TUKAN-8K-USB MCA (see [[14]] for a more detailed description of this setup and experimental procedure).

To acquire RT scintillation time profiles the delayed coincidence single photon counting method proposed by Bollinger and Thomas [[15]] was employed, making use of a ^{137}Cs source, two Hamamatsu PMTs (R1104 and R928 for "starts" and "stops", respectively), a Canberra 2145 time-to-amplitude converter, and again a TUKAN-8K-USB MCA.

Table 1
RT scintillation properties of the studied 0.5 mm thick samples of β-Ga_2O_3 and β-Ga_2O_3:Si (n_e - free electron concentration, Y - scintillation yield, R - energy resolution at 662 keV, τ_i - scintillation decay time constants, τ_{mean} - scintillation mean decay time).

material	n_e (cm^{-3})	Y (ph/MeV)	R (%)	τ_i (ns)	τ_{mean} (ns)
β-Ga_2O_3 (undoped)	$2.50\cdot10^{16}$	8920	10.7	16.9 (3.1%) 107 (14.6%) 1182 (82.3%)	989
	$4.66\cdot10^{16}$	7560	13.5	19.1 (4.9%) 127 (17.6%) 1032 (77.5%)	823
	$1.90\cdot10^{17}$	6270	12.6	17.1 (5.0%) 101 (19.6%) 574 (75.4%)	453
β-Ga_2O_3:Si (0.025 mol%)	$5.86\cdot10^{17}$	4920	14.3	13.3 (7.3%) 70.5 (24.8%) 255 (67.9%)	191
	$8.87\cdot10^{17}$	4540	14.4	14.0 (10.1%) 81.0 (39.5%) 235 (50.4%)	152
β-Ga_2O_3:Si (0.2 mol %)	$2.80\cdot10^{18}$	2760	21.3	13.9 (15.4%) 71.5 (59.2%) 235 (25.4%)	104
	$4.27\cdot10^{18}$	1930	21.5	12.9 (23.4%) 52.6 (67.8%) 249 (8.8%)	61

The Si concentrations are related to doping in the Ga_2O_3 starting material. The uncertainties of determination of Y, R and τ_i are below 5%, while of τ_{mean} below 10%.

3. Results and discussion

Two exemplary RT pulse height spectra, one of β-Ga_2O_3 and one of β-Ga_2O_3:Si (both from the current series of crystals), are presented in Fig. 1. They are characterized by a clearly resolved full energy peak (FEP), which makes it easy to determine the scintillation yield accurately. The values of yield and resolution for all the studied 0.5 mm thick samples are summarized in Table 1. We note that we deal with Si-doped β-Ga_2O_3 samples displaying such good yields for the first time: we achieve up to 4920 ph/MeV, while previously we could hardly exceed the level of 2000 ph/MeV [7]. This increase is related to the lower free electron concentrations in the present β-Ga_2O_3:Si crystals ($n_e < 10^{18}$ cm^{-3}) due to very low Si doping level (thus lower n_e values) compared to the previous ones with a higher Si doping level and higher corresponding n_e values. Such a conclusion is also supported by the present undoped β-Ga_2O_3 samples, the lower yields of which (compared to those investigated earlier [7]) go hand in hand with their higher free electron concentrations. It even seems that with respect to the scintillation yield there is no need to distinguish between undoped and Si-doped β-Ga_2O_3 crystals. The doping with Si is just a tool for preparing crystals with higher free electron concentrations, but the presence of Si has no other impact on the scintillation properties than this related to the value of n_e. An illustration is provided by Fig. 2, which leaves no doubts that the scintillation yield of β-Ga_2O_3 is controlled by a single factor, namely the free electron concentration.

Fig. 3 shows pulse height spectra of the brightest β-Ga_2O_3 crystal ($n_e = 2.5\cdot10^{16}$ cm^{-3}) recorded at various temperatures. With increasing temperature, the FEP demonstrably moves towards lower channels, indicating that the scintillation yield goes down. Based on the FEP positions, the dependence of the yield on temperature has been plotted in Fig. 4. Since 0.5 mm thick samples (regarded as standard for RT pulse height and scintillation time profile measurements) are too thin for the setup used for temperature-dependent investigations, a 2.5 mm thick sample has been cleaved from the same bulk crystal. Due to this difference in thicknesses its observed RT scintillation yield is somewhat lower than 8920 ph/MeV determined for the 0.5 mm thick sample (which is related to relatively large internal light losses in β-Ga_2O_3 [[16]]), nevertheless for clarity of presentation in Fig. 4 we take the value of 8920 ph/MeV as the reference level at RT. As we see, only 40% of the yield is preserved at RT compared to 90 K. To explain this large disparity we first remind here that the free electron concentration decreases towards lower temperatures, which is a typical semiconductor behavior. Since the temperature-dependent free electron concentration for Czochralski-grown β-Ga_2O_3 crystals has already been studied [11], in Fig. 4 we have incorporated such a characteristics, which can be directly compared with the temperature-dependent scintillation profile. The scintillation yield profile has an almost linear dependence in the measured thermal range (90–350 K). On the other hand, the free electron concentration profile is not linear, but it could be approximated by a segmented linear dependence in the ranges of 60–180 K, 180–230 K, and 230–350 K, with different slopes. Therefore, a direct correlation of the scintillation yield with free carrier concentration below room

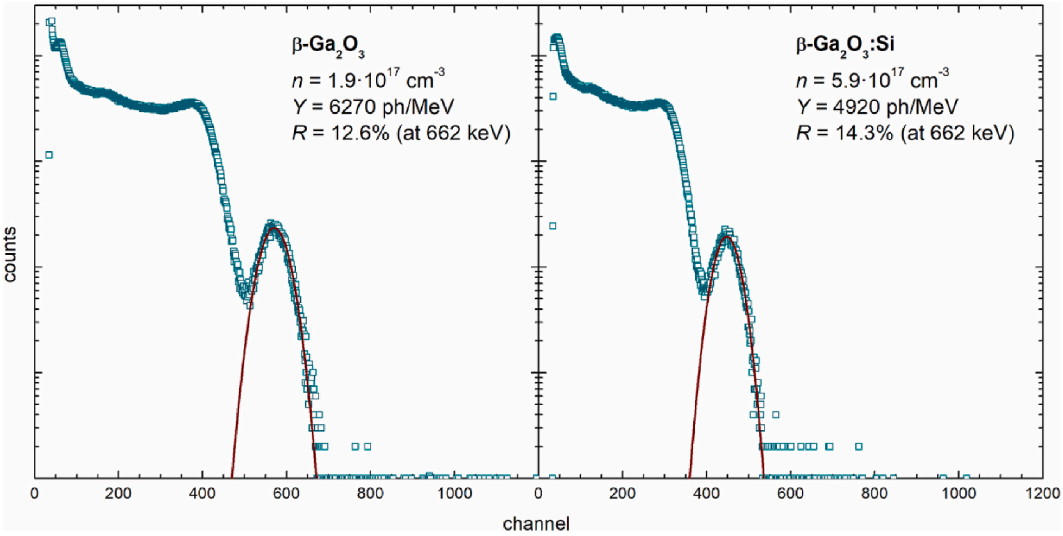

Fig. 1. Exemplary 662 keV pulse height spectra of β-Ga_2O_3 and β-Ga_2O_3:Si measured at RT.

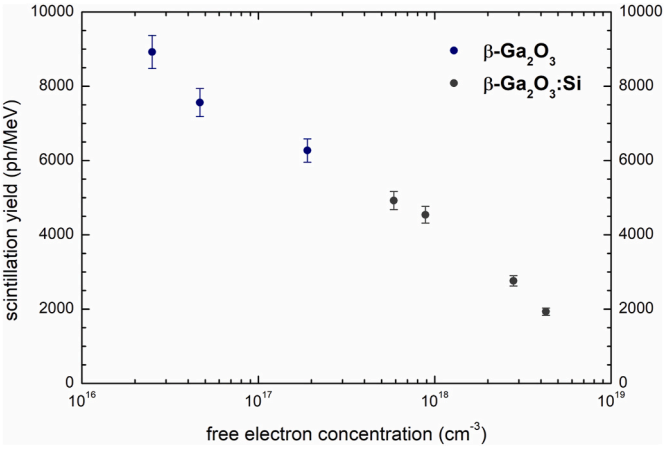

Fig. 2. Scintillation yield of β-Ga_2O_3 and β-Ga_2O_3:Si as a function of free electron concentration.

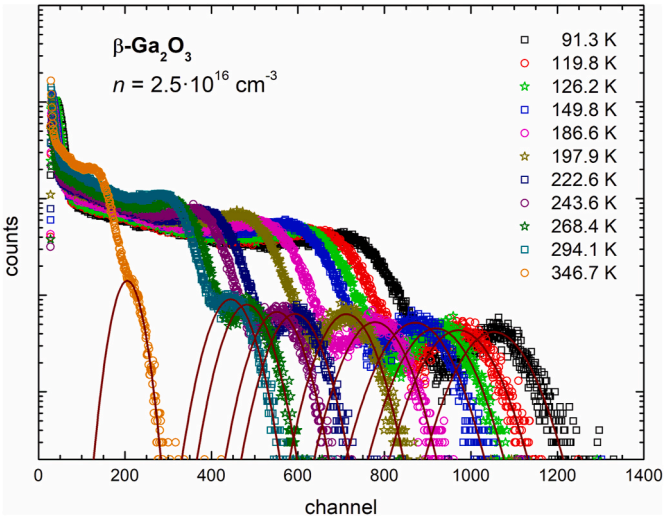

Fig. 3. 662 keV pulse height spectra of β-Ga_2O_3 measured at various temperatures between 91.3 and 346.7 K.

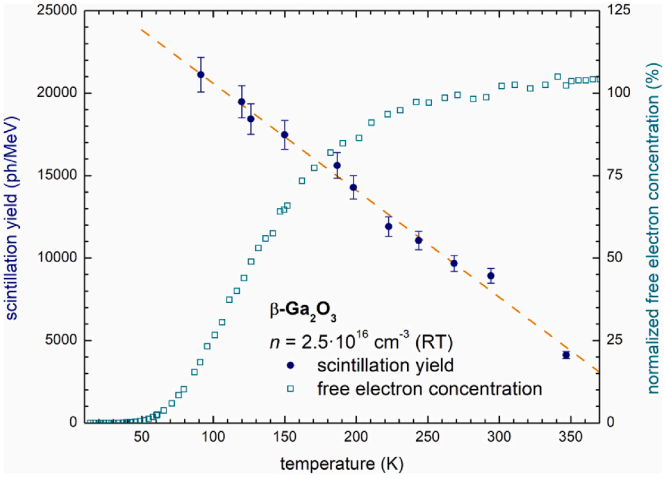

Fig. 4. Scintillation yield as a function of temperature compared to a temperature-dependent free electron concentration profile of β-Ga_2O_3.

temperature becomes complex, which is a result of gradual ionization of shallow donors with rising temperature, and also excitation of deeper electron traps [11]. Still, approximating the scintillation yield to 60 K, where the free electron concentration substantially vanishes, we get a value of about 23000 ph/MeV, which seems to be a "semi-empirical limit" for β-Ga_2O_3. We note that besides the dependence of the free electron concentration on temperature, some thermal quenching mechanisms, possibly due to a thermal activation of non-radiative recombination processes at Fe impurities [[17]], with a contribution from the so-called Auger quenching [[18,19]], may contribute to the decrease of yield with temperature.

Fig. 5 presents the scintillation time profiles of the two samples (one β-Ga_2O_3 and one β-Ga_2O_3:Si) chosen theretofore as exemplary for the purpose of Fig. 1. The values of scintillation decay constants with their contributions for all the investigated samples are specified in Table 1. We observe that with increasing free electron concentration: *i)* the contribution of the prompt (~13–19 ns) component increases (from ~3% to ~23%), *ii)* the middle component becomes shorter (from above 100 ns to ~50 ns) and its contribution goes up (from ~15% to ~68%), *iii)* the slow component also pares down (from ~1.2 μs to below 250 ns) and its contribution is strongly reduced (from ~82% to ~9%). Consistently, the mean scintillation decay time defined as:

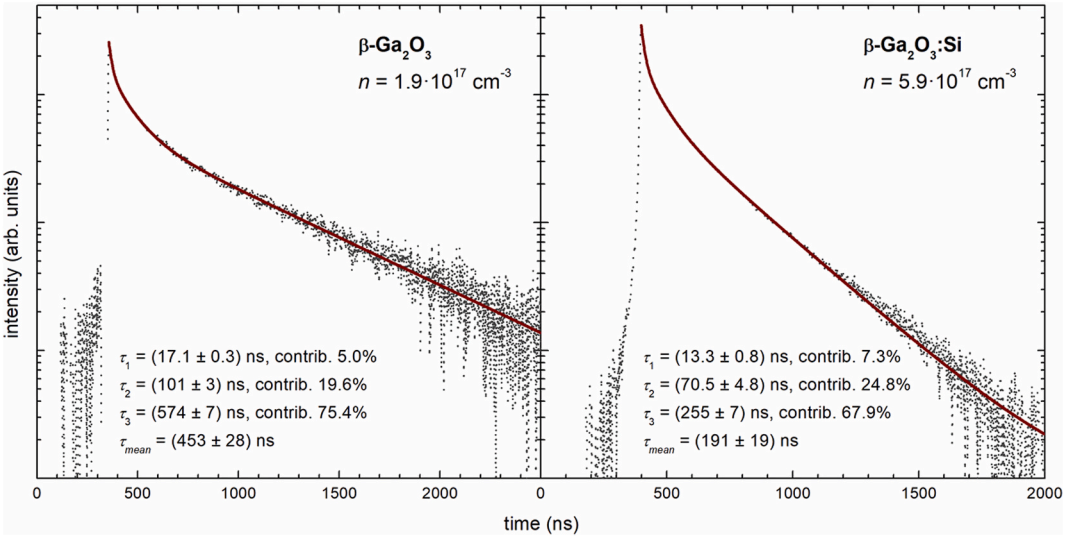

Fig. 5. Exemplary scintillation time profiles of β-Ga_2O_3 and β-Ga_2O_3:Si measured at RT.

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

(A_i and τ_i - amplitudes and decay time constants of each decay component, respectively) decreases from ~1 μs to ~60 ns in the range from $n_e = 2.5{\cdot}10^{16}$ cm^{-3} to $n_e = 4.3{\cdot}10^{18}$ cm^{-3} (Fig. 6), which confirms the occurrence of a strong free and/or bound electron Auger quenching [18,19] (also responsible for lower yields of the highly conductive samples). Furthermore, similarly like for the scintillation yield, after considering the obvious increase of the free electron concentration we recognize no additional effect of Si-doping on the time profiles, hence the β-Ga_2O_3 and β-Ga_2O_3:Si samples may be treated equivalently as belonging to the same family, merely differing by the value of n_e.

Since it is now absolutely clear that the two important scintillation parameters of β-Ga_2O_3 (no matter if undoped or Si-doped), i.e. the scintillation yield Y and the mean scintillation decay time τ_{mean}, depend (primarily or solely) on the free electron concentration, it would be very useful to establish a direct link between Y and τ_{mean}. To do this, in Fig. 7 we show the values of Y plotted against the values of τ_{mean}, measured at RT for all the samples listed in Table 1. Each point in this figure represents one sample for which these two parameters have been determined. The dashed line has been calculated from a simple arbitrary formula typical for phenomena displaying saturation effect [[20]]:

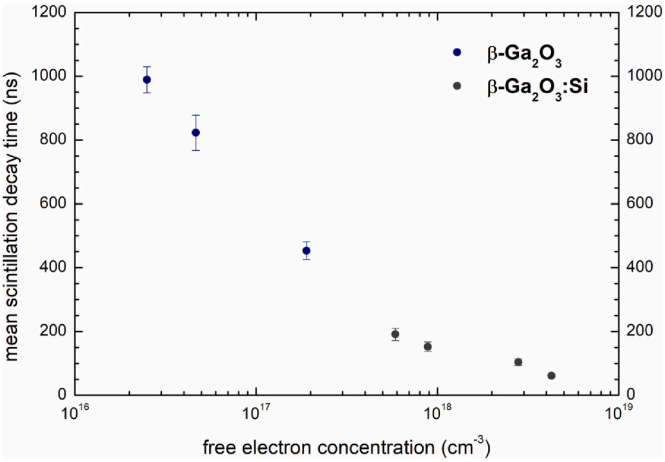

Fig. 6. Mean scintillation decay time of β-Ga_2O_3 and β-Ga_2O_3:Si as a function of free electron concentration.

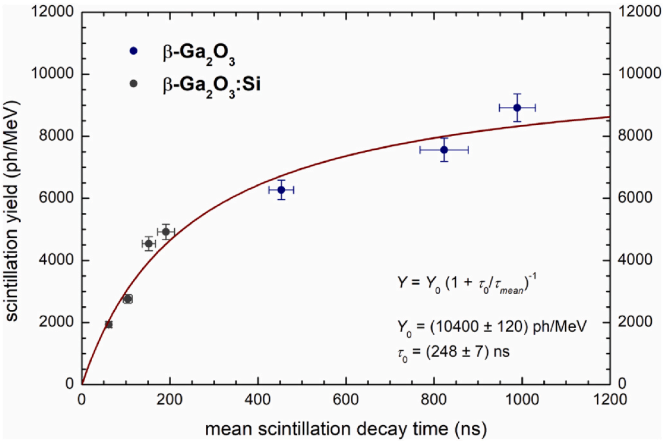

Fig. 7. Scintillation yield of β-Ga_2O_3 and β-Ga_2O_3:Si as a function of mean scintillation decay time.

$$Y = Y_0 \left(1 + \frac{\tau_0}{\tau_{mean}}\right)^{-1} \quad (2)$$

Although a physical interpretation of τ_0 is ambiguous, this formula let us estimate the scintillation yield of any hypothetical β-Ga_2O_3 crystal of a known mean scintillation decay time. It also provides a way to extrapolate the scintillation yield and evaluate its upper RT limit Y_0 as about 10400 ph/MeV, however we suspect that such a value - as associated with a very long decay - would not be observable in practice.

4. Conclusions

Based on the present crystals samples and measurements we have confirmed our previous conclusions on the dominant role of the free electron concentration for the scintillation properties of β-Ga_2O_3 [6–8]. For high quality Czochralski-grown crystals, the RT values of the scintillation yield and the mean scintillation decay time seem to be driven by one parameter: the free electron concentration. Unfortunately, as it has been characterized quantitatively by Eq. (2) and explained by the presence of the Auger quenching [18,19], it is impossible to combine both a high yield and a fast scintillation decay in one β-Ga_2O_3 crystal, at least at RT, at which the highest theoretically available yield is limited by a value not much exceeding 10000 ph/MeV, i.e. twice lower than

already observed at LNT. Nevertheless, while the Auger mechanism is quite well understood and this effect is rather not reducible at RT, less is known about the other possible processes responsible for the decrease of the scintillation yield with increasing temperature [17]. A full understanding of these processes, as well as finding a way to control them, might result in a new generation of much brighter β-Ga_2O_3 crystals for RT applications.

CRediT authorship contribution statement

Winicjusz Drozdowski: Conceptualization, Project administration, Investigation, Methodology, Writing – original draft, Writing – review & editing, Visualization. **Michał Makowski:** Investigation, Formal analysis, Software, Visualization. **Abdellah Bachiri:** Investigation, Formal analysis, Software, Visualization. **Marcin E. Witkowski:** Investigation, Formal analysis, Software, Visualization. **Andrzej J. Wojtowicz:** Methodology, Writing – review & editing. **Lukasz Swiderski:** Investigation, Methodology, Writing – review & editing. **Klaus Irmscher:** Resources, Methodology, Writing – review & editing. **Robert Schewski:** Resources, Investigation. **Zbigniew Galazka:** Conceptualization, Project administration, Resources, Methodology, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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