physica status solidi a
www.pss-a.com
applications and materials science

Scintillation properties of pure and Ca-doped $ZnWO_4$ crystals

F. A. Danevich[1], S. Henry[2], H. Kraus[2], R. McGowan[2], V. B. Mikhailik[2], O. G. Shkulkova[1], and J. Telfer[3]

[1] Institute for Nuclear Research, MSP 03680 Kyiv, Ukraine
[2] Department of Physics, University of Oxford, Oxford OX1 3RH, UK
[3] Hilger Crystals, Margate, Kent CT9 4JL, UK

Received 18 May 2007, revised 27 September 2007, accepted 2 October 2007
Published online 13 December 2007

PACS 29.40.Mc, 78.70.–g, 81.40.Tv

Following the investigations of the structure and scintillation properties of Ca-doped zinc tungstate powder [phys. stat. sol. (a) **204**, 730 (2007)] a single-crystal of $ZnWO_4$–Ca (0.5 mol%) was grown and characterised. The relative light output, energy resolution and decay characteristics were measured for pure and Ca-doped $ZnWO_4$ scintillators. An increase in the light yield of ~40% compared with the undoped crystal, and an energy resolution 9.6% (^{137}Cs) were obtained for Ca-doped $ZnWO_4$. The observed improvement is attributed to the reduction of self-absorption (bleaching) of the crystal. The cause of bleaching as well as the possible contribution of scattering is discussed.

phys. stat. sol. (a) **205**, No. 2, 335–339 (2008) / **DOI** 10.1002/pssa.200723205

phys. stat. sol. (a) **205**, No. 2, 335–339 (2008) / **DOI** 10.1002/pssa.200723205

physica status solidi a
www.pss-a.com
applications and materials science

Scintillation properties of pure and Ca-doped $ZnWO_4$ crystals

F. A. Danevich[1], S. Henry[2], H. Kraus[2], R. McGowan[2], V. B. Mikhailik[*,2], O. G. Shkulkova[1], and J. Telfer[3]

[1] Institute for Nuclear Research, MSP 03680 Kyiv, Ukraine
[2] Department of Physics, University of Oxford, Oxford OX1 3RH, UK
[3] Hilger Crystals, Margate, Kent CT9 4JL, UK

Received 18 May 2007, revised 27 September 2007, accepted 2 October 2007
Published online 13 December 2007

PACS 29.40.Mc, 78.70.–g, 81.40.Tv

[*] Corresponding author: e-mail vmikhai@hotmail.com, Phone: +44 (0)1865-273459, Fax: +44 (0)1865-273418

Following the investigations of the structure and scintillation properties of Ca-doped zinc tungstate powder [phys. stat. sol. (a) **204**, 730 (2007)] a single-crystal of $ZnWO_4$–Ca (0.5 mol%) was grown and characterised. The relative light output, energy resolution and decay characteristics were measured for pure and Ca-doped $ZnWO_4$ scintillators. An increase in the light yield of ~40% compared with the undoped crystal, and an energy resolution 9.6% (^{137}Cs) were obtained for Ca-doped $ZnWO_4$. The observed improvement is attributed to the reduction of self-absorption (bleaching) of the crystal. The cause of bleaching as well as the possible contribution of scattering is discussed.

1 Introduction Single crystalline $ZnWO_4$ is a well-known scintillation material, which has been used for decades in X-ray computer tomography due to its good stopping power, low afterglow and high scintillation light yield [1, 2]. It belongs to the class of scintillating materials exhibiting intrinsic emission: the regular oxyanion $(WO_6)^{6-}$ complex is responsible for the radiative transitions. Recently, $ZnWO_4$ has been identified as a promising cryogenic scintillation detector for experiments searching for double beta decay and weakly interacting massive particle (WIMP) dark matter [3–5]. This provides strong motivation for research aimed to improve the performance of this material.

Scintillation efficiency is a key parameter that determines the sensitivity of the scintillation detector in any application. Doping is an effective technique for changing the properties of crystals; it has helped to increase the light yield of lead tungstate scintillators [6]. Therefore we applied this approach towards improving the properties of zinc tungstate.

In this communication we present the results of a comparative study of pure $ZnWO_4$ and a $ZnWO_4$–Ca (0.5 mol%) scintillator. In a previous paper [7] we reported the effect of Ca-doping on zinc tungstate. $ZnWO_4$ and $CaWO_4$ tungstates exhibit different crystal structure (wolframite and scheelite, respectively). To verify the benefit of doping, the primary emphasis was to find how Ca-doping affects the structure of $ZnWO_4$. Initially, experiments were carried out using powder samples to establish there are no indications of deterioration of the important material properties. It was found that there is no mixing in $CaWO_4$–$ZnWO_4$ pseudo-binary systems and Ca-doping has no detrimental effect on the scintillation efficiency of powder samples [7]. With this finding the growth of Ca-doped single-crystalline zinc tungstate became feasible.

2 Experiment The crystals were grown by Hilger Crystals, Margate, UK, from raw materials of 4N purity, using the Czochralski technique. Two $10 \times 10 \times 5$ mm^3 samples with the large faces parallel to the cleavage plane (010) were cut from the ingots. The measurements of the scintillation characteristics were carried out at University of Oxford (test 1) using the multiphoton counting (MPC) technique [8, 9] and at the Institute for Nuclear Research, Kyiv (test 2) using the conventional technique of pulse height analysis, described elsewhere [3]. The set-up for the measurements was very similar for both techniques: the scintillator was positioned on the photomultiplier tube (PMT) and excited by ionising radiation or particles. The resulting scintillation light was then detected.

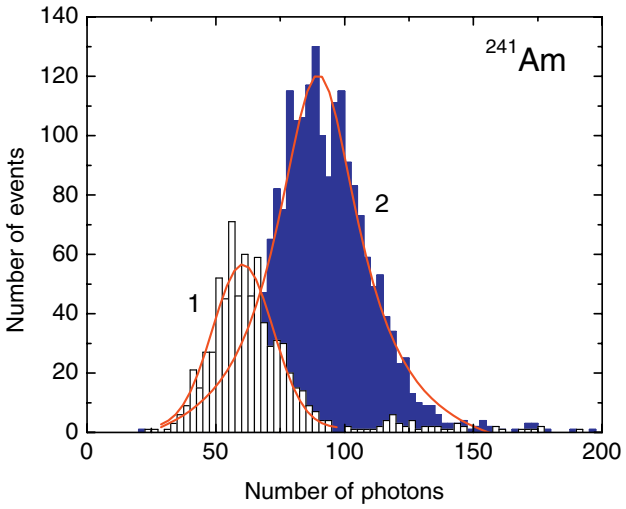

Figure 1 (online colour at: www.pss-a.com) Distribution of the number of photons per scintillation events detected from $ZnWO_4$ (1) and $ZnWO_4$–Ca (2) using MPC. Excitation was with 60 keV γ-quanta from an ^{241}Am source. The curves represent single Gaussians fitted to the histograms.

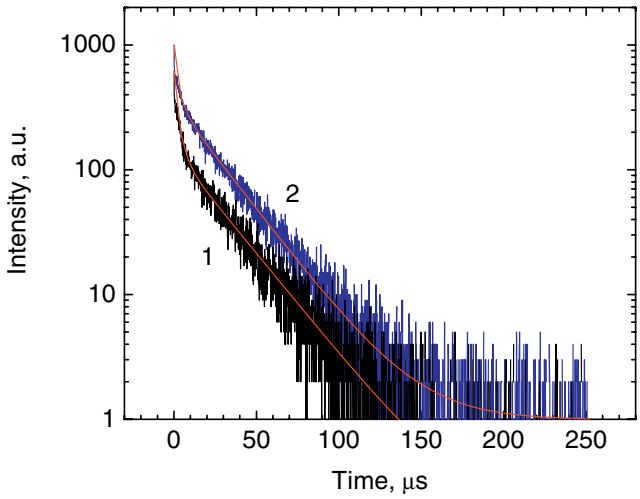

Figure 2 (online colour at: www.pss-a.com) Scintillation decay curves of $ZnWO_4$ (1) and $ZnWO_4$–Ca (2) crystals measured using MPC. Excitation with 60 keV γ-quanta from an ^{241}Am source. Lines show the fit to the data with three exponentials.

There were some differences in the optical coupling between the crystal and PMT (no coupling in test 1 and optical grease in test 2) and in the methods used to improve the light collection. In test 2 first the polished samples were measured and then the side surface of the crystals was roughened with polishing paper and wrapped in PTFE tape. We used 60 keV γ-quanta from an ^{241}Am-source in test 1, and γ-sources (^{137}Cs, 662 keV, ^{60}Co, 1173 keV and 1333 keV) and an α-source (^{241}Am, ~5.5 MeV) in test 2.

The main difference between tests 1 and 2 arises from the recording and processing of the PMT signal. The conventional technique uses the integrated signal from the PMT and the light yield is derived from the histogram of the scintillation pulse heights. The MPC technique is based on single-photon counting and employs fast sampling of the stream of PMT pulses following each scintillation event. The number of the pulses recorded per event is proportional to the light yield, and the distribution of the arrival times of pulses gives the decay characteristic of the scintillation process. The scintillation pulse shape in test 2 was studied using a transient digitiser as explained elsewhere [3]. All measurements where carried out at room temperature.

3 Results Figure 1 shows the distribution of the numbers of scintillation photons in individual scintillation events detected from pure and Ca-doped $ZnWO_4$ for excitation with a 60 keV ^{241}Am source. This distribution, measured using the MPC technique, is a direct measure of the energy deposited in the crystal, being the analogue of scintillation amplitude spectra. The histograms were fitted with single Gaussians and the centroid is taken as an estimate of the light output of the crystal. In this experiment it was found that on average $ZnWO_4$ with 0.5 mol% of Ca emits ~40% more photons than pure $ZnWO_4$ (see also Table 1).

The scintillation decay curves, measured in this experiment, are displayed in Fig. 2. The data were fitted using a sum of three exponentials and the deduced decay time constants are listed in Table 2. It is found that the value of the longest decay constant (τ_3) is shorter in Ca-doped $ZnWO_4$, compared with pure $ZnWO_4$. This is expected from the results obtained in our earlier measurements of powder samples [7]. This shortening is associated with a contribution to the decay process from the $CaWO_4$-related phase that exhibits a much faster decay time constant than $ZnWO_4$ (~9 μs according to [8]).

Table 1 Relative light output and energy resolution of pure and Ca-doped $ZnWO_4$ scintillators.

sample	relative light yield (%)			energy resolution (%)	
	^{241}Am polished*	^{137}Cs polished**	^{137}Cs roughened**	^{137}Cs polished	^{137}Cs roughened
$ZnWO_4$	59	61	78	15.5	15.0
$ZnWO_4$–Ca (0.5 mol%)	100	100	121	12.4	9.6

* Normalised to the light output of the polished $ZnWO_4$–Ca sample at excitation with 60 keV (^{241}Am).
** Normalised to the light output of the polished $ZnWO_4$–Ca sample at excitation with 662 keV (^{137}Cs).

Table 2 Decay time constants (for fit with three exponentials) of pure and Ca-doped $ZnWO_4$ scintillators measured for excitation with different sources.

sample	type of irradiation	τ_1 (μs)	τ_2 (μs)	τ_3 (μs)
$ZnWO_4$	γ, $^{241}Am^*$	0.1	3.5	26.6
	γ, $^{137}Cs^{**}$	0.9	5.9	26.7
	α, $^{241}Am^{**}$	0.9	6.0	26.0
$ZnWO_4$–Ca (0.5 mol%)	γ, $^{241}Am^*$	0.1	3.5	25.3
	γ, $^{137}Cs^{**}$	1.0	4.9	25.5
	α, $^{241}Am^{**}$	0.9	5.2	25.3

* test 1.
** test 2.

The scintillation amplitude spectrum obtained from Ca-doped $ZnWO_4$ scintillator, when irradiated with 662 keV γ-quanta from a ^{137}Cs source, is shown in Fig. 3. The measurements were carried out using the pulse height technique (test 2) and the light output obtained in this experiment is 39% higher compared with pure $ZnWO_4$, which correlates very well with the result obtained in the test 1. When the side surfaces of the samples were roughened the light output increased by ~20%, while the ratio showed no significant change (see Table 1). At the same time the roughening had a major effect on the energy resolution; the best resolution of 9.6% for 662 keV ^{137}Cs is obtained for roughened $ZnWO_4$–Ca.

Figure 4 shows the time profile of the scintillations produced by α-particles (^{241}Am) and γ-quanta (^{60}Co) in the Ca-doped $ZnWO_4$ crystal. This was obtained in test 2 by summing up a few hundred individual scintillation events. The fit to the experimental curves was done using a sum of three exponentials and the results are listed in the Table 2. One can see that the value of decay time constants τ_2 and τ_3 obtained for excitation with γ-quanta in tests 1 and 2 are

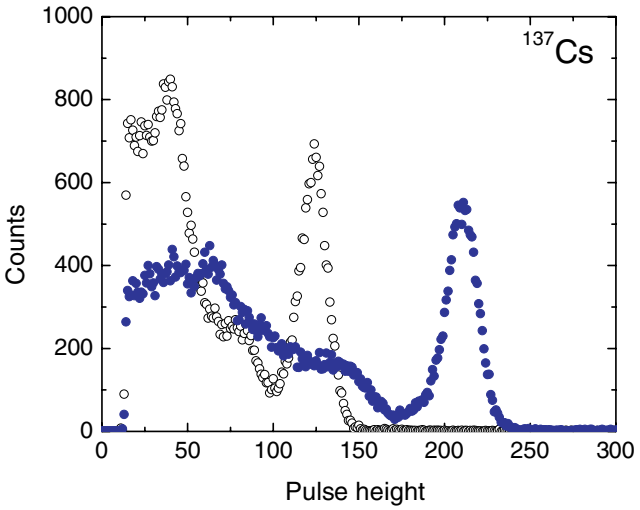

Figure 3 (online colour at: www.pss-a.com) Amplitude spectra of 662 keV γ-quanta from ^{137}Cs source measured for $ZnWO_4$ (empty circles) and $ZnWO_4$–Ca (solid circles).

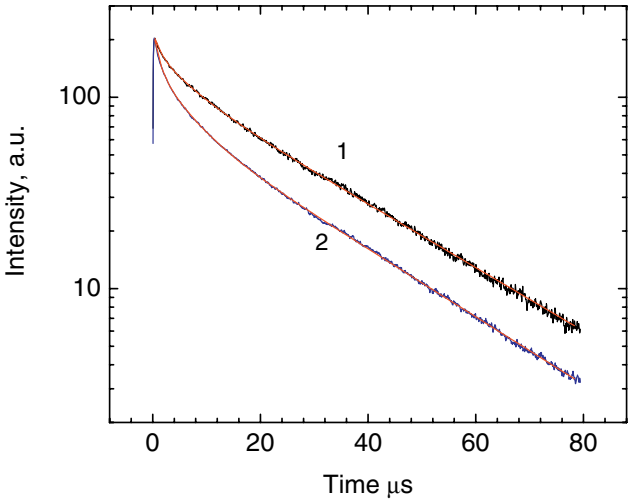

Figure 4 (online colour at: www.pss-a.com) Scintillation decay curves recorded for $ZnWO_4$–Ca crystal under excitation with γ-quanta from ^{137}Cs (1) and α-particles from ^{241}Am source (2). Lines show the fit of three exponentials to the curves.

almost identical. The difference in the shortest decay time constant τ_1 can be understood easily as being due to the different time resolutions of the experimental setup in the test 1 and 2 (5 ns and 20 ns respectively).

An obvious divergence in the shape of the decay curves at different excitation is clearly visible in Fig. 4, with α-particles producing noticeably faster scintillation response. This difference is due to the dissimilarity in the intensities of different decay components and it is widely used in pulse-shape analysis techniques to distinguish β- and γ-events from those induced by α-particles [3]. For this purpose the optimal filter method proposed by Gatti and de Martini [10] is used. The method was tested for the zinc tungstate crystals under study. A numerical parameter called shape indicator (SI) was calculated for each scintillation pulse as follows:

$$\mathrm{SI} = \sum f(t_k)\, P(t_k) / \sum f(t_k)\,. \tag{1}$$

The summation was made over the time bins starting from the pulse origin up to 90 μs; $f(t_k)$ is the digitised amplitude at the time t_k. The weight function $P(t)$ is defined here as:

$$P(t) = [f_\alpha(t) - f_\gamma(t)]/[f_\alpha(t) + f_\gamma(t)]\,, \tag{2}$$

where $f_\alpha(t)$ and $f_\gamma(t)$ are the reference pulse shapes for α-particle and γ-quanta.

Figure 5 shows the SI distribution obtained for the crystals excited with α-particles (^{241}Am) and γ-quanta (^{60}Co). Provided the α/β ratio for $ZnWO_4$ is ~0.2 [3], the electron equivalent energy of α-particles emitted by ^{241}Am (~1.1 MeV) is very close to the energy of the γ-quanta of ^{60}Co. The SI distributions obtained for α- and γ-events are sufficiently well separated demonstrating that event type discrimination in $ZnWO_4$ crystals is possible.

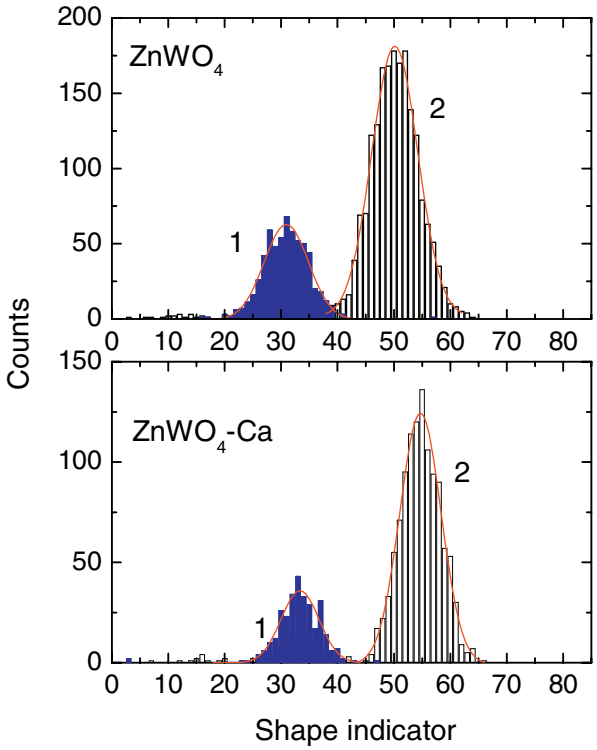

Figure 5 (online colour at: www.pss-a.com) Shape indicator distributions measured for pure and Ca-doped $ZnWO_4$ scintillators using γ-quanta (1) and α-particles (2). Lines show the single Gaussian fitting of the distributions.

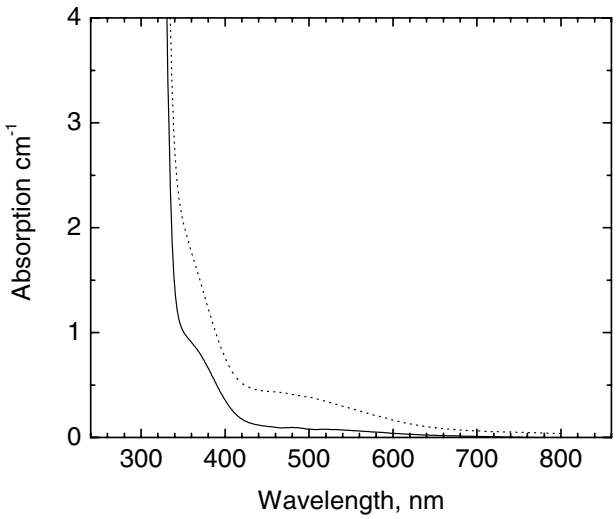

Figure 6 Absorption spectra of $ZnWO_4$–Ca (line) and $ZnWO_4$ (dots) crystals. Spectra are corrected for reflection losses using the refractivity data [15].

4 Discussion The results of our earlier studies [7] indicated that the scintillation light yield of the powder samples changes little with Ca-doping. However, when single-crystal scintillators are used, as it is in the majority of scintillator applications, the absorption of the bulk material is of importance. When noticeable it can significantly reduce the amount of light leaving the crystal. Self-absorption of the scintillation light is an issue for $ZnWO_4$ that usually exhibits a visible pink colour. There is no consensus on the origin of this coloration. Though it is usually attributed to the impurities of Cr^{3+} or Fe^{2+} ions [11–13] but the possible role of intrinsic defects similar to what has been found in tungstates with sheelite structure [14] is not excluded. It has to be noted that the concentration of Cr and Fe impurities in the pure $ZnWO_4$ used in this study does not exceed 1 ppm [4] while the coloration of the sample is notable. The measured absorption coefficient α is equal to 0.43 cm^{-1} at 460 nm (Fig. 6).

Notwithstanding the exact origin, the self-absorption of $ZnWO_4$ has an adverse effect on the scintillation efficiency. It has been shown that the light output increases with the decrease of the absorption coefficient [12]. This is very consistent with our observations. As shown in Fig. 6 the Ca-doped $ZnWO_4$ shows significantly improved transmittance ($\alpha = 0.10$ cm^{-1} at 460 nm) compared to the pure $ZnWO_4$.

Furthermore, taking the data from Fig. 4 in Ref. [12] one can estimate that for the given absorption coefficients the ratio of the scintillation efficiency of the two samples under test should be ca. 70%. This figure is not very dissimilar from what is measured in this study. Given the results of the examination of powder samples we suppose that the observed increase of the scintillation efficiency is mainly the result of the reduction of self-absorption (bleaching) of the $ZnWO_4$, crystal caused by Ca-doping.

The bleaching of $ZnWO_4$ through Sb^{5+} has been already reported, although the mechanism of the process is not fully understood [12]. It is argued that Sb^{5+} and Fe^{3+} form charge compensating pairs that facilitate the oxidation process $Fe^{2+} \rightarrow Fe^{3+}$ and eliminate adverse visible absorption [11]. The essential point is that the excess of the local positive charge in the crystal lattice can create favourable conditions for bleaching. This concept can be used to explain the observed improvement of the transmittance of Ca-doped $ZnWO_4$. The results of our studies [7] evidenced that Ca-doping leads to the formation of a $CaWO_4$ sheelite phase in the framework of the wolframite $ZnWO_4$ structure. This effectively means that the regular $(WO_4)^{2-}$ tetrahedra of $CaWO_4$ phase formed at the boundary of two phases carry the surplus of positive charge with respect to the charge of the regular $ZnWO_4$ lattice comprising the $(WO_6)^{6-}$ octahedral complex. This excess of local positive charge can basically cause the same bleaching effect as Sb^{5+} ions.

Though the reduced self-absorption seems to provide a very convenient explanation for the observed effect we would like to comment that the doping also creates scattering centres in the bulk of the crystal. It was recently shown that scattering plays a very important role in the light collection of the crystals since it provides a chance for trapped light to escape the crystal [16]. The effect is more pro-

nounced, when the refraction index of the crystal is higher, as is the case for $ZnWO_4$. Taking into account that Ca-doping leads to the formation of inherent clusters with sheelite structure this should cause an increase of scattering and increase the light output of the crystal. Hence it is likely that the observed improvement of the scintillation light output might be the result of joint effect of reduced self-absorption and increased scattering.

Finally it has to be noted that the use of Ca for bleaching of a $ZnWO_4$ scintillator is preferable in rare events searches, as unlike many elements (such as antimony) calcium does not increase the intrinsic radioactivity of the target [5]. The problem that remains so far unsolved is the tendency of zinc tungstate to cleavage, something that needs to be addressed in future.

References

[1] T. Oi, K. Takagi, and T. Fukazawa, Appl. Phys. Lett. **36**, 278 (1980).
[2] M. Ishi and M. Kobayashi, Prog. Cryst. Growth Charact. **23**, 245 (1991).
[3] F. A. Danevich, V. V. Kobychev, S. S. Nagorny, D. V. Poda, V. I. Tretyak, S. S. Yurchenko, and Yu. G. Zdesenko, Nucl. Instrum. Methods A **544**, 553 (2005).
[4] H. Kraus, V. B. Mikhailik, Y. Ramachers, D. Day, K. B. Hutton, and J. Telfer, Phys. Lett. B **610**, 37 (2005).
[5] V. B. Mikhailik and H. Kraus, J. Phys. D, Appl. Phys. **39**, 1181 (2006).
[6] M. Kobayashi, Y. Usuki, M. Ishii, M. Itoh, and M. Nikl, Nucl. Instrum. Methods Phys. Res. A **540**, 381 (2005).
[7] H. Kraus, V. B. Mikhailik, L. Vasylechko, D. Day, K. B. Hutton, J. Telfer, and Yu. Prots, phys. stat. sol. (a) **204**, 730 (2007).
[8] H. Kraus, V. B. Mykhaylyk, and D. Wahl, Nucl. Instrum. Methods Phys. Res. A **553**, 522 (2005).
[9] H. Kraus, V. B. Mikhailik, and D. Wahl, Radiat. Meas. **42**, 921 (2007).
[10] E. Gatti and F. de Martini, Nuclear Electronics, Vol. 2 (IAEA, Vienna, 1962), p. 265.
[11] A. Watterich, O. R. Gilliam, and L. A. Kappers, Solid State Commun. **88**, 619 (1993).
[12] I. Földvari, A. Peter, S. Keszthelyi-Landori, R. Capelletti, I. Kravero, and F. Schmidt, J. Cryst. Growth **79**, 714 (1986).
[13] L. Grigorjeva, D. Millers, S. Chernov, V. Pankratov, and A. Watterich, Radiat. Meas. **33**, 645 (2001).
[14] A. A. Annenkov, M. V. Korzhik, and P. Lecoq, Nucl. Instrum. Methods Phys. Res. A **490**, 30 (2002).
[15] C. J. Spengler and S. O'Hara, Appl. Opt. **3**, 1084 (1964).
[16] D. Wahl, V. B. Mikhailik, and H. Kraus, Nucl. Instrum. Methods Phys. Res. A **570**, 529 (2007).