ISSN 1062-8738, Bulletin of the Russian Academy of Sciences: Physics, 2009, Vol. 73, No. 10, pp. 1369–1373. © Allerton Press, Inc., 2009.
Original Russian Text © N.V. Klassen, V.N. Kurlov, S.N. Rossolenko, O.A. Krivko, A.D. Orlov, S.Z. Shmurak, 2009, published in Izvestiya Rossiiskoi Akademii Nauk. Seriya Fizicheskaya, 2009, Vol. 73, No. 10, pp. 1451–1456.

Scintillation Fibers and Nanoscintillators for Improving the Spatial, Spectrometric, and Time Resolution of Radiation Detectors

N. V. Klassen, V. N. Kurlov, S. N. Rossolenko, O. A. Krivko, A. D. Orlov, and S. Z. Shmurak

Institute of Solid State Physics, Russian Academy of Sciences, Chernogolovka, Moscow oblast, 142432 Russia
e-mail: klassen@issp.ac.ru; kurlov@issp.ac.ru

Abstract—Experimental examples demonstrate a significant improvement of the most important parameters (sensitivity; spatial, spectrometric, and time resolution; and radiation hardness) of radiation detectors with sensitive elements based on fiber and nanocrystalline scintillators instead of conventional bulk single crystals. This improvement is related to several specific features of the new scintillator types: improved homogeneity of activator distribution, larger soft X-ray component in the secondary emission due to the high frequency of hot electron collisions with the nanoparticle surface, formation of high-quality optical nanocavities, and enhanced annihilation of radiation defects at their rapid motion to the surface.

DOI: 10.3103/S1062873809100141

Scintillators are materials emitting light flashes (referred to as scintillations) as a result of absorption of ionizing radiation (X and γ rays, neutrons, electrons, etc.). The transformation of ionizing particle energy in crystals into light photons is a multistep process, whose study gives a rich information about the hot electron relaxation with production of phonons, secondary electrons, and X rays; the capture of electronic excitations by structural defects; and their radiative and nonradiative recombination. These studies, performed for more than 50 years, are primarily caused by the sharp need for increased scintillator efficiency in detection of ionizing radiations in nuclear physics, atomic power engineering, medical diagnostics, structural and chemical analysis, antiterrorist control, etc. However, despite the systematic work of very many research and technology groups, the progress in single-crystal detectors with high scintillation parameters is very slow. For example, since 1948 the coefficient of absorbed energy–light conversion has reached only 20%, and the time and spatial resolutions are currently not better than few nanoseconds and several tens of micrometers, respectively. However, the modern technique requires these characteristics to be at least several times higher.

The technical parameters of scintillation detectors can be significantly improved (with simultaneous essential decrease in their production cost) by replacing bulk single crystals with scintillators of new types: profiled (including fiber ones) and nanocrystalline. For example, the distributions of luminescence activators and dopants of other types can be controlled by both types of such scintillators in a much wider range and with a much higher accuracy in comparison with the single-crystal scintillators. In the profiled scintillators grown by the Stepanov method (edge-defined film-fed growth), the significant increase in the activator distribution homogeneity is provided by the small volume of melt meniscus that is in direct contact with the crystallization front. Due to this smallness, there is no significant redistribution of impurities between the melt and crystal, which generally leads to significantly inhomogeneous distribution of impurities in bulk crystals. This advantage of profiled scintillators results in significant improvement of their energy resolution in spectrometric measurements because the main reason for the light response spatial inhomogeneity is absent: their response is independent of the location of the point of high-energy particle absorption. The fiber scintillators are also characterized by much better amplitude homogeneity of the light signals supplied to photodetector. This is provided by the significant decrease in the light loss upon reflection from the scintillation element external faces due to the significant improvement of the growth surface at the atomic level. This improvement is obtained by computer control of profiled crystal growth based on specially developed algorithms [1] and special techniques; as a result, the optical smoothness of the growth surface approaches that of optically polished details. Moreover, the structural quality of the profiled crystal growth surface significantly exceeds that of optically polished faces of conventional scintillation elements: profiled scintillators do not contain an inactive (nonemitting) surface layer with a high content of structural defects and contaminations, introduced into crystals during mechanical treatment (abrasive polishing). In addition, a modification of the Stepanov method has been developed at the Institute of Solid State Physics, Russian Academy of Sciences (ISSP RAS) (Chernogolovka, Russia), which makes it possible to grow fibers with specified radial compositional gradient and properties

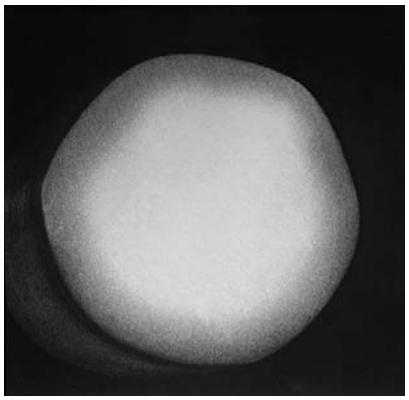

Fig. 1. Cross section of sapphire fiber with a Ti-doped central part, grown by the modified Stepanov method with a specified radial gradient of composition and optical properties.

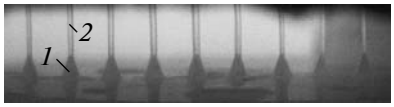

Fig. 2. Group growth of bismuth germanate scintillation fibers by the Stepanov method: (*1*) shaper and (*2*) crystal.

(Fig. 1) and improves the conditions for light collection (for example, due to the total internal reflection of scintillation light not directly from the external face but from the surface layer with a large refractive index gradient [2]. The improvement of light emission and collection homogeneity in profiled scintillators gives the latter significant advantages in spectrometric measurements: higher energy resolution of scintillation signals.

Along with the technical advantages, profiled (in particular, fiber) scintillators are also much less expensive. Exact control of the cross section of crystals grown makes unnecessary cutting, grinding, and polishing—operations that are inevitable for bulk crystals, thus decreasing the operating time and consumption of processing materials and expensive raw materials; eliminating ecologically harmful waste; etc. An important advantage of scintillators fabricated by the Stepanov method is the possibility of their group growth, when up to a hundred of fibers can be grown in a single process (Fig. 2). These advantage is especially essential in production of multielement detector matrices with a submillimeter spatial resolution, when the cross section of an individual scintillation element is less than a millimeter in size, and their total number exceeds a thousand.

The improvement of the parameters of radiation detectors based on profiled scintillators is quantitative. At the same time, nanocrystalline scintillation powders (with 100-nm or smaller particles) provide radical qualitative improvement of a number of detector characteristics. This is explained by the significant modification of the processes of electronic excitations by high-energy particles and subsequent relaxation of these excitations in nanocrystals, because the sizes of the latter are comparable with the characteristic spatial parameters of nonequilibrium electronic states, lattice oscillations, diffusion processes, and emitted photons. For example, the hot electrons formed as a result of X-ray absorption have initial velocities of 10^9 cm s^{-1} or more; hence, their collision rates with nanoparticles are also high (on the order of 10^{15} s^{-1} or more). In this case, the changes in the dipole moments of the electrons and the polarization charges induced by them in nanoparticles form inevitably electromagnetic fields of bremsstrahlung and transient types [3–5]. As simple estimates show, at the relaxation times of hot electrons to the bottom of the conduction band (the necessary value is 10^{-12} s) at such high collisions rates, a large part of the initial kinetic energy of excited electron can be transformed into bremsstrahlung and transient radiation. Thus, a qualitatively new mechanism of transformation of ionizing radiation energy into softer electromagnetic components arises in nanoparticles. This mechanism competes with the energy transformation into lattice vibrations, as a result of which the total energy yield of scintillations may increase and their kinetics can be significantly enhanced (because these new-type components are emitted for picosecond times). When measuring the scintillation kinetics in nanoparticles of lutetium and gadolinium borates, it was found that the scintillation leading edge is shorter by 0.1 ns, which can be explained in terms of the above-described mechanisms [6, 7]. Another reason for increasing the ionizing energy conversion efficiency into light is the possibility of optical resonance of emitted light waves at particles of corresponding sizes, which significantly increases the spontaneous emission probability due to the increase in the virtual photon density (Purcell effect [8–10]).

In the case of hot electron relaxation in bulk scintillators, a large part of the initial energy is re-emited in the form of characteristic X-ray photons with energies of about 10 keV or more, which have a large free path in solids (up to hundreds of micrometers [11]). For this reason, the regions initially excited by the absorbed high-energy particles reach several tens of micrometers in size, and specifically these regions determine the spatial detector resolution. In nanoscintillators, where softer bremsstrahlung and transient quanta with much smaller penetration depths play an active role, the excited region size can be reduced to several micrometers, which significantly improves the spatial resolution.

At the same time, when nanoscintillators are used in radiation detectors, a serious problem of supplying light from individual nanoemitters to photodetectors arises, because, due to light scattering from numerous boundaries between nanoparticles, nanoparticle layers

more than 0.5 mm thick become opaque. To solve this problem, we approved two methods. The first implies deposition of nanoscintillator layers no more than 0.5 mm thick on the lateral surfaces of optical fibers collecting emitted light and supplying it to photodetectors located at the fiber end faces. The other method of supplying light from nanoscintillators to photodetector, which was approved at ISSP RAS, is their introduction into a microcapillary matrix with optically transparent walls, which should operate as optical fibers in the above-mentioned scheme.

The operation of such a design based on yttrium oxysulfide nanoscintillators embedded in a glass microcapillary matrix is demonstrated in Fig. 3. A planar photodetector is located at the matrix end face perpendicularly to the capillaries. A matrix assembly of nanoscintillation elements allows one to improve the light collection and detector sensitivity by choosing the period between microcapillaries such as to make this matrix form a photonic crystal for emitted light in the cross section; this crystal prevents light propagation across the capillary axis due to intercapillary interference [12, 13]. In this case, light must be emitted mainly along the axis, i.e., toward the photodetector. Appropriate glass matrices are produced by the OOO Nanotekhnologii Stekla (Saratov) [13].

The small sizes of nanoscintillators are advantageous not only in the electronic phenomena but also for the atomic structure. For example, the ability of nanoscintillators to withstand large radiation dose without significant changes in their properties exceeds many times that of single crystals of similar composition. The reason is that the diffusion times τ to the surface for point defects generated in a nanoparticle by high-energy quanta are fairly short in comparison with the time interval between two subsequent events of ionizing quantum penetration into this nanoparticle:

$$\tau \approx \frac{L^2}{D}; \quad \Delta t \sim \frac{1}{I\alpha L^3},$$

where L is the particle size, D is the diffusivity, I is the radiation flux intensity, and α is the radiation absorption probability.

Equating these two times shows that the limiting flux radiation intensity at which the nanoscintillator parameters remain stable is inversely proportional to the fifth power of its radius and directly proportional to the radiation defect diffusivity. Bulk single crystals of similar compositions lack such an efficient stabilizing factor as the diffusive transfer of radiation defects to the nanoparticle surface; therefore, their radiation hardness is much lower.

Note that several low-budget techniques for fabricating nanoscintillators of controlled composition and size have been developed at ISSP RAS: synthesis from aqueous solutions and fluxes, thermal-diffusion synthesis, laser synthesis, and laser grinding [6, 7, 10, 14]. A new method for preparing heavy fast scintillators from compositions of inorganic nanoparticles and organic phosphors was found to be rather promising [15].

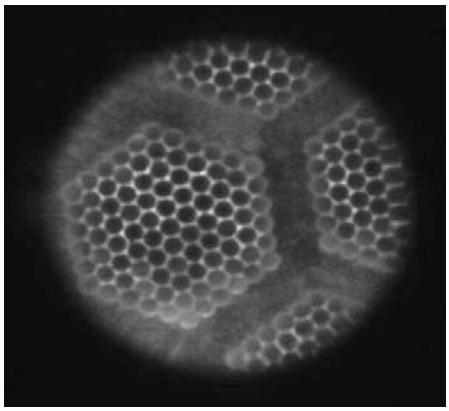

Fig. 3. Emergence of light emitted by nanoscintillators collected into a microcapillary matrix through transparent intercapillary walls.

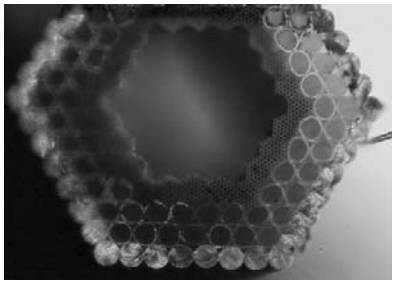

Fig. 4. Micrograph of the cross section of an optical fiber with hollow core, whose capillary shell forms a photonic crystal.

The above-mentioned advantages of profiled and nanocrystalline scintillators allow designing various radiation detectors with record characteristics.The calculations based on the above considerations and experimentally determined diffusivities and ionizing radiation absorption cross sections for different scintillation materials show that most inorganic nanoscintillators of oxide and halide compositions with particle sizes of about 50 nm can stably operate in neutron and γ-ray fluxes with intensities of 10^{12}–10^{14} particles cm^{-2} s^{-1}, which corresponds to the radiation intensity in nuclear reactor core. Scintillation signals can be extracted from the active zone to photodetectors using the radiation-resistant optical fibers from profiled sapphire or glass microcapillary structures with hollow cores, where luminous flux is retained at the core axis via total reflection from the lateral microcapillart system, forming a photonic crystal in the cross section [12, 13, 16] (Fig. 4). In the former case nanoscintillators are located on the lateral surface of sapphire optical fiber and in the hollow core in the latter case. The microcapillary fiber parameters are radiation stable because luminous flux propagates through the hollow core, whose transmission obviously does not degrade under

radiation. The application of radiation-resistant nanoscintillator detectors and the corresponding optical fibers for automatic monitoring radiation fluxes in the nuclear reactor active zones can improve significantly the monitoring reliability and operational speed, increase the efficiency of nuclear fuel use, and decrease the amount of radioactive waste subjected to disposal. The main arguments in favor of such detectors is that their operating speed greatly exceeds that of ionization and thermoelectric sensors used for in-core monitoring. The characteristic response times of such sensors are on the order of 10 s, whereas the response times of scintillation detectors are from several milliseconds to several nanoseconds; i.e., they are faster by a factor of more than 1000. Such a significant increase in the operational speed of core automatic monitoring and control system is especially urgent because atomic power engineering is to be intensively developed in most industrial countries.

Profiled sapphire single crystals are characterized by not only high radiation hardness (10^8 rad) but also high thermal stability. Hence, they can be used as transparent substrates (in the form of both plates and tubes [17]) for high-temperature synthesis of nanoscintillator layers from flux or by thermal diffusion. A high-speed wide-angle visualizer of fast neutron escape from a neutron generator for activation analysis of the chemical composition of materials inaccessible for direct inspection has been developed on this basis [18]. 14-MeV neutrons are formed in a tritium target bombarded by electrostatically accelerated deuterons. This deuteron–tritium reaction yields, along with neutrons, α particles, which escape in the directions strictly opposite to those of neutrons. When a tritium target is placed in a transparent sapphire tube with a thin layer of fast nanoscintillator on its inner surface, the coordinates and time of scintillation flashes from collisions of α particles with the tube wall allow one to exactly determine the directions and instants of neutron escape. The spatial and temporal detection of scintillations is performed by a multipixel photodetector located beyond the sapphire tube. A fast neutron, interacting with the nuclei inside the volume analyzed, excites characteristic γ rays. The γ quanta are recorded by a fast position-sensitive scintillation detector, which determines their energies, momenta, and absorption points. With a nanoscintillator time resolution of 0.1 ns (record for today), the path length from the point of neutron escape to the point of γ-quantum absorption is determined with an error of 3 cm. Using the known neutron exit direction and the coordinates of the γ-quantum absorption point, one can calculate (with the same accuracy) the coordinates of the parent nucleus of this characteristic quantum. A few-minute computer analysis of the data obtained forms a pattern of chemical material distribution in the volume examined. As a result, the volume images and chemical compositions of the subjects hidden in closed volumes are formed. For example, explosives, poisons, drugs, and other hazardous materials in closed volumes (containers, cars, motor-cars, etc.) can be found for relatively short (few minutes) times.

Scintillation fibers and nanoscintillators, deposited on optical fibers or embedded into microcapillary matrices, are an effective basis for three-dimensional radiation detectors, which can determine the spatial arrangement of radiation sources or X-ray scattering and absorption points at X-ray analysis of medical and other objects [7, 19–22]. Microcapillary matrices with multipixel silicon photodetectors mounted at their end faces are assembled into stacks. A computer comparative analysis of the spatial intensity distributions recorded by each matrix makes it possible to determine the directions to the ionizing radiation emission or scattering sources and their location (from the direction intersections). The accuracy in determining the object location depends on the size of microcapillary matrix cells, total stack thickness, and the distance to the object. For example, at a size of scintillation matrix cells of several micrometers and total stack thickness of 50 cm, an X-ray examination of patients in a system comparable with a standard fluorography system can form a volume image of inner human organs with a resolution of about 10 μm, which corresponds to the characteristic sizes of blood microvessels, neurons, and biological cells. Such possibilities of X-ray analysis make it possible to improve qualitatively the informativeness of rapid medical diagnostics. When a three-dimensional detector is formed of fiber scintillators, they are assembled into rows, which, in turn, are collected into stacks so that to make the fiber directions in neighboring series mutually perpendicular. The entrance point of X-ray photon is determined by the coincidence of signals from mutually perpendicular neighboring fibers. This scheme allows one to significantly reduce the number of photodetectors, because they are located only at the scintillation fiber end faces and the number of necessary detectors is much smaller than that of sensitive points.

ACKNOWLEDGMENTS

This study was supported by the Federal Agency for Science and Innovations (state contract 2008-3-1.3-26-03); the programs “Support of Innovations and Development” and “Quantum Macrophysics” of the Russian Academy of Sciences; and the Russian Foundation for Basic Research, project nos. 08-02-01360, 08-02-12157-ofi and 09-04-13823-ofi-ts.

REFERENCES

1. Kurlov, V.N. and Rossolenko, S.N., *J. Cryst. Growth*, 1997, vol. 173, p. 417.

2. Kurlov, V.N., Rossolenko, S.N., and Belenko, S.V., *J. Cryst. Growth*, 1998, vol. 191/3, p. 520.

3. Akhiezer, A.I. and Shul'ga, N.F., *Elektrodinamika vysokikh energii v veshchestve* (Electrodynamics of High Energies in Matter), Moscow: Nauka, 1993.
4. Landau, L.D. and Lifshitz, E.M., *Elektrodinamika sploshnykh sred* (Electrodynamics of Continuous Media), Moscow: Nauka, 1992.
5. Ginzburg, V.L. and Tsitovich, V.L., *Usp. Fiz. Nauk*, 1978, vol. 126, no. 4, p. 553.
6. Klassen, N.V., Shmurak, S.Z., Shmyt'ko, I.M., et al., *Nucl. Instrum. Methods Phys. Res. A*, 2005, vol. 537, p. 144.
7. Klassen, N.V., Kedrov, V.V., Osipyan, Yu.A., et al., *IEEE Transact. Nanobiosci.*, vol. 8, no. 1, 2009, p. 20.
8. Purcell, E., *Phys. Rev.,* 1946, vol. 69, p. 681.
9. Reithmaier, J.P., Keldysh, L., Kulakovskii, V., et al., *Nature,* 2004, vol. 432, p. 197.
10. Klassen, N.V., Kedrov, V.V., and Kurlov, V.N., *IEEE Transact. Nucl. Sci.*, 2008, vol. 55, no. 3, p. 1536.
11. Vasil'ev, A.N., *Proc. 5th Int. Conf. on Inorganic Scintillators and their Applications*, Moscow State Univ., 2000, p. 43.
12. Zheltikov, A.M., *Usp. Fiz. Nauk*, 2009, vol. 178, no. 3, p. 619.
13. Skibina, Yu.S., Fedotov, A.B., Melnikov, L.A., and Beloglazov, V.I., *Laser Phys.,* 2000, vol. 10, p. 723.
14. Klassen, N.V., Krivko, O.A., and Kedrov, V.V., *Abstr. 10th Int. Conf. on Nanoscintillators and their Industrial Applications, SCINT 2009, Korea, 2009*, p. 176.
15. Klassen, N.V., Kedrov, V.V., Shmurak, S.Z., et al., *Abst. 10th Int. Conf. on Nanoscintillators and their Industrial Applications, SCINT 2009, Korea, 2009*, p. 128.
16. Beloglazov, V.I., Kedrov, V.V., Klassen, N.V., et al., RF patent on Application no. 2008151843, December 2008.
17. Kurlov, V.N. and Epelbaum, B.M., *J. Cryst. Growth,* 1998, vol. 187, p. 107.
18. Dunin, V.B., Kedrov, V.V., Kiselev, A.P., et al., RF Invention Application no. 2008151841, December 2008.
19. Krivko, O.A., Klassen, N.V., Loschenov, V.B., et al., *IEEE Medical Imaging Conf., Dresden, 2008*, p. 479.
20. Krivko, O.A., Klassen, N.V., Kedrov, V.V., et al., *Al'manakh klin. med.,* 2008, vol. 17, no. 2, p. 344.
21. Klassen, N., Krivko, O.A., Kedrov, V.V., et al., *Abstr. 10th Int. Conf. on Nanoscintillators and Their Industrial Applications, SCINT 2009, Korea, 2009*, p. 69.
22. Klassen, N.V., Kedrov, V.V., Kurlov, V.N., et al., *Ross. Bioterapevt. J.,* 2008, no. 1, p. 29.