ISSN 2409-9066. Sci. innov. 2016, 12(6): 37—45 doi: https://doi.org/10.15407/scine12.06.037

Galkin, S.M., Rybalka, I.A.,
Tupitsyna, I.A., Zvereva, V.S., and Litichevskiy, V.A.

Institute for Scintillation Materials, the NAS of Ukraine, 60, Nauky Av., Kharkiv, 61001, Ukraine
Tel. +38 (057) 341-02-06, 340-93-99; Fax: +38 (057) 340-44-74, 340-93-41; info@isma.kharkov.ua

THE DEVELOPMENT OF FLEXIBLE SCINTILLATION PANELS BASED ON CHALCOGENIDE AND OXIDE PHOSPHORS FOR ADVANCED X-RAY SCANNERS AND TOMOGRAPHS

The technology of flexible panels and dispersed scintillation elements for X-rays registration with high uniformity of scintillation parameters (mean deviation no more than 2%) and low cost has been developed. Parameters of flexible scintillation panels have been optimized, which enable their obtaining with high spatial resolution. The panels can be used as intensifying screens in medical and industrial radiography. Options for the operation of dual energy X-ray detectors working effectively in X-ray energy band (from 20 to 100 keV) have been proposed. Their possible applications are multienergy scanners and medical computer tomography.

Keywords: composite, scintillation panel, fine crystalline scintillator, detector, radiographic scanner, and ionizing radiation.

Given globally increasing threat of terrorist attacks, in order to keep public safety, the X-ray luggage screening at the airports and ground transport facilities, as well as at the post offices becomes more and more important. For reliable detection of explosives as compared with other materials it is necessary to register the difference in materials density within ± 5%. This requirement can be met using multi-energy scanning of objects by energy selective detectors. Visualization of the internal structure of objects with energy selective scintillation detectors is a key to improving detective ability of X-ray scanners, with parameters of detectors largely effecting the quality of shadow images.

Most commonly, the detectors of X-ray scanning systems are based on the use of scintillation crystals, composite scintillators or ceramic [1—3]. The intensity of their luminescence depends on scintillator quantum yield, thickness of the absorbing layer and scintillator transparency to its own luminescent radiation.

Zinc selenide (ZnSe) as scintillator crystal was developed and prototyped at the Institute for Scintillation Materials (ISMA) of the National Academy of Sciences of Ukraine. It has an extremely high light output (70 thousand photons/MeV) and a low afterglow (<0.05% in 10 ms) [4, 5]. Zinc tungstate ZnWO4 (the technology for which production was developed in ISMA) has satisfactory scintillation properties and ability to absorb high-energy X-rays due to high atomic number.

These scintillators can be used in 2-energy detector, ZnSe in the low energy path and $ZnWO_4$ in the high energy path.

The composite flexible scintillation panels have significant advantages over the single crystalline materials:

- No limitations of linear dimensions of composite panels;
- High homogeneity of scintillation parameters due to keeping high homogenization of powdered crystals while manufacturing the scintillation panels;
- Controllable output optical and scintillation parameters of composite scintillators while manufacturing;
- Capacity variability within a wide range of scintillation and optical properties of composite scintillators by making multicomponent systems (based on two or more scintillation materials);
- improved mechanical and structural properties as compared with the single crystalline counterparts, which makes it possible to manufacture detectors of arbitrary shapes.

Design of flowchart for manufacture of flexible composite scintillators is an important and urgent task for the development of advanced radiation instrumentation.

The aim of this research is to develop a technology for manufacturing flexible dispersion scintillation panels and elements for X-rays record. The panels have a high uniformity of scintillation parameters (a mean deviation of less than 2%) and low cost (as compared with single crystals). In the future, high-tech production of a new class of flexible scintillation panels based on chalcogenide and oxide phosphors for advanced scanners and X-ray scanners is expected.

DESIGN OF FLOWCHART FOR MANUFACTURE OF COMPOSITE SCINTILLATION PANELS

Previously, zinc sulfide or calcium tungstate phosphors were used for making the intensifying screens for X-ray films. These phosphors are not suitable for composite scintillators because of poor kinetic parameters [6—8]. To get fast scintillation composite panels has become possible due to the use of powdered scintillators based on milled crystal or crystalline oxide phosphors obtained by solid-phase synthesis.

A flowchart for the manufacture of composite scintillation panels and elements has been designed and optimized. It comprises the following steps:

1) Preparation of raw material;
2) Milling of raw material;
3) Grading of raw material;
4) Manufacture of scintillation panels and elements.

The preparation of initial raw material depends on specific scintillator (ZnSe, $ZnWO_4$ or other) and can consist of solid-phase synthesis of powder or ceramic or growth of crystal with its further grinding. The crystals are powdered by mill up to particles of specified size. Having been graded by sieving the scintillation powder is mixed with silicone composite Sylgard, with the mix poured into mold to get a composite of given thickness and dimensions. After polymerization, a reflector is stuck to the scintillator that is cut into elements of specified dimension, with a deviation of linear size less than 0.1 mm, by a cutting plotter.

EFFECT OF ZnSe SCINTILLATOR PARTICLE SIZE AND COMPOSITE ELEMENT THICKNESS ON RELATIVE LIGHT YIELD OF SCINTILLATION PANELS

To elaborate flowcharts for manufacture of scintillation panels with optimal functional parameters the dependence of element's light yield on size of ZnSe scintillator particles and panel thickness has been determined (Fig. 1 and Fig. 2).

The dependence of ZnSe light yield on particle size distribution is defined by X-ray absorption by luminescent particles. The larger the particle, the bigger is percentage of absorbed X rays. Therefore, intensity of luminescence grows as size of crystalline scintillator particles in the composite increases. According to Fig. 1, the highest intensity in the case of irradiation by X-ray tube with tungsten anode having a voltage of 120 kV is reported for the particles with a size distribution 200—600 μm. As the particle size decreases, the luminescence intensity weakens. It should be noted that as the size reaches a certain value (about 30 μm), luminescence goes down substantially. This is explained by the fact that if free path of excited electron in given material is larger than size of particles, only a small part of X rays induces luminescence. The dissipative properties of composite scintillator environment (scattering and reabsorption of luminescence quanta) also lead to weakening luminescence as particle size decreases.

The optimal thickness of scintillation panel samples for reaching the maximum quantum yield is 1—1.5 mm for a size distribution 40—120 μm, 1.3—1.8 mm for 120—200 μm, and 1.5—2 mm for 200—600 μm. If the panel thickness exceeds the optimal one, X rays are absorbed inside the sample and its luminescence intensity is low, with luminescence quanta from upper layers not reaching the photo receiver and emitted as heat in the composite. If the panel thickness is less than the optimal one, the amount of scintillation material in the sample is not sufficient for absorbing X ray quanta and for reaching maximum luminescence. For the panel samples of more fine-graded material, the optimum thickness decreases (Fig. 2) and reaches 0.3—0.6 mm for particle size 25—40 μm.

Relative light yield of crystalline and dispersive samples of scintillators based on ZnSe is given on Fig 3.

The scintillation panels made of more coarse-graded ZnSe powder (200—600 μm) have a light yield close to that of the crystalline samples (up to 95% of light yield of crystal). As particle size decreases the light yield goes down as explained above. It amounts to nearly 80% for a particle size within 120—200 μm, 55% for 40—120 μm, and 30% for 25—40 μm. Particles with the least size distribution are not practically used because of very low light yield (about 10%). The

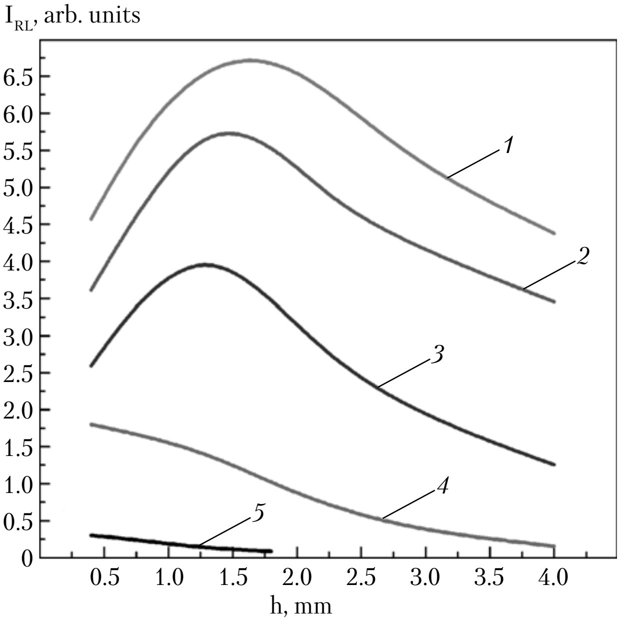


Fig. 1. Dependence of light yield of ZnSe based scintillation panels on particle size and sample thickness. The curves correspond to the panel samples with particle size range: *1* — 200—600 μm; *2* — 120—200 μm; *3* — 40—120 μm; *4* — 25—40 μm; *5* — 1—25 μm

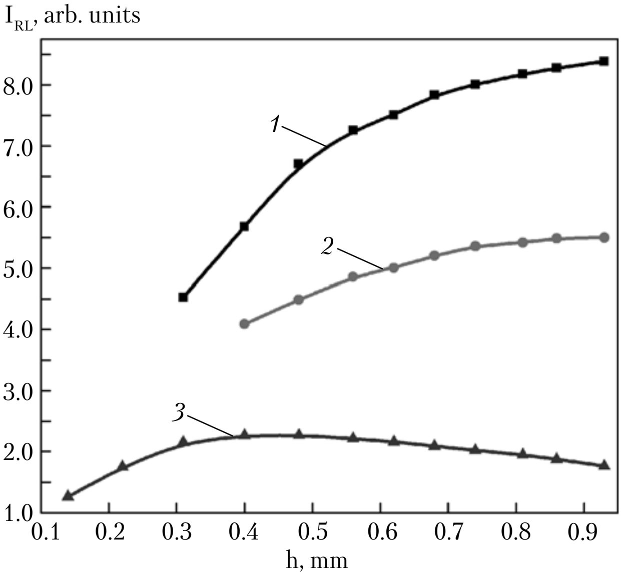


Fig. 2. Dependence of light yield of ZnSe based scintillation panels on particle size and sample thickness. The curves correspond to the panel samples with particle size range: *1* — 120—200 μm; *2* — 40—120 μm; *3* —25—40 μm

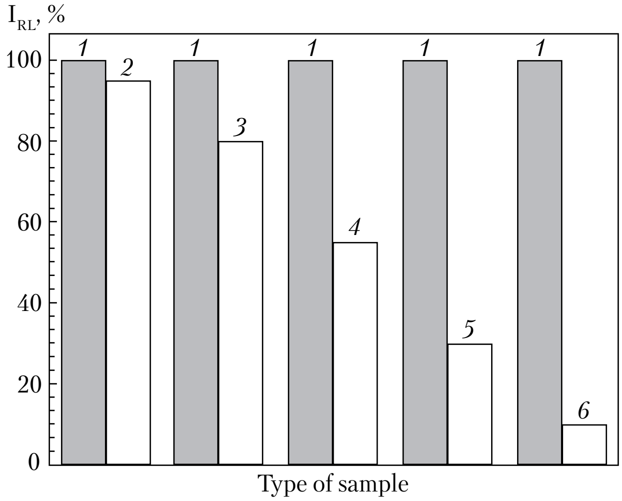


Fig. 3. Comparison of relative light yield of composite and single crystalline scintillators of the same type and size based on ZnSe: *1* — single crystalline ZnSe scintillator; *2—6* — composite scintillators with ZnSe powder particle size 200—600, 120—200, 40—120, 25—40, and 1—25 μm, respectively

light yield is compared for the crystalline samples having the same type and size as the scintillation panels.

The intensity of light yield of the samples was measured using well-known method with the help of device for recording light yield and afterglow of scintillator samples under the action of pulsed radiation. For the scintillation panels based on oxide scintillators $ZnWO_4$, $CdWO_4$, $LuGdSiO_5$(Ce), and Gd_2SiO_5(Ce) the general trend of light yield dependence on panel thickness and particle size corresponds to that showed for ZnSe.

DETERMINATION OF HOMOGENEITY OF SCINTILLATION PARAMETERS OF PANELS BASED ON ZnSe, $ZnWO_4$, $CdWO_4$, LGSO(Ce), and GSO(Ce)

Homogeneity of parameters is an important property of scintillation panels. The homogeneity of characteristics of panels based on ZnSe, $ZnWO_4$, $CdWO_4$, $LuGdSiO_5$(Ce), and Gd_2SiO_5(Ce) was measured by 2D scanning of composite scintillators.

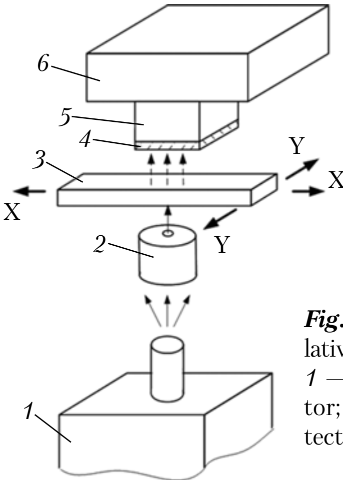


Fig. 4. Stand for measuring relative light yield of scintillators: *1* — X-ray tube; *2* — collimator; *3* — scintillator; *4* — protective filter; *5* — photo receiver; *6* — amplifier

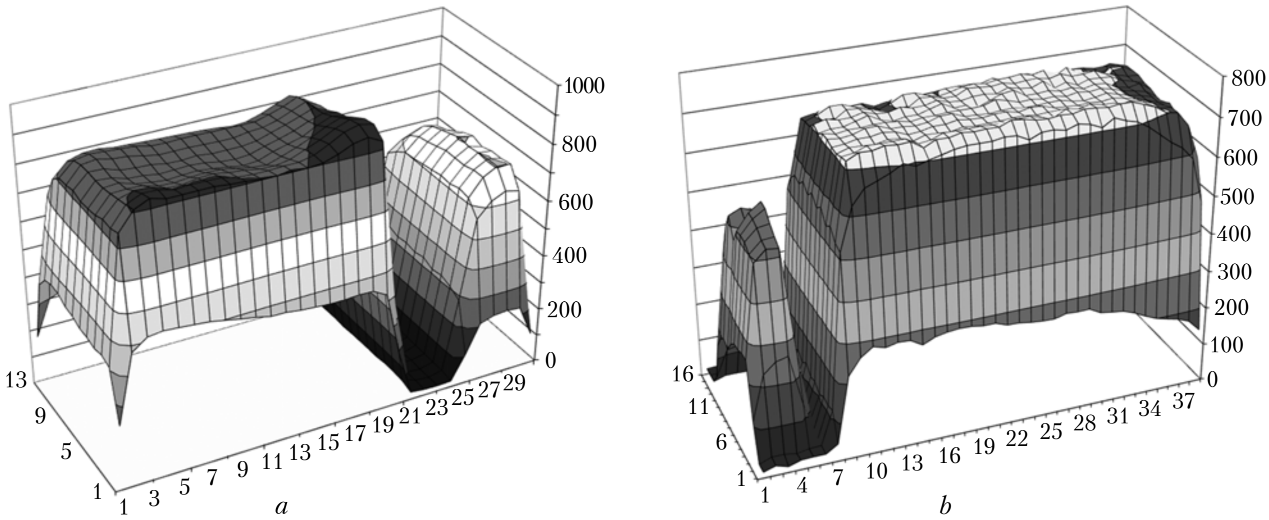
Basic parameters of measuring installation are as follows:

X-ray source	X-ray machine RAP-150 with W-anode;
Voltage on emitter's anode, kV	60—140
Collimator diameter, mm	1—4
Size of photo receiver active area, mm	5 × 5
Thickness of studied sample, mm	0.5—15
Size of sample displacement field, mm	200 × 200
Step size, mm	0.1

The source of exciting radiation and the recording photo receiver were located on different sides of the studied sample (Fig. 4). The displacement system enabled 2D displacement of scintillator with respect to source of radiation and photo receiver. Step of displacement along both axes was 0.1 mm; size of scanned area was 200 × 200 мм.

To protect receiver's photodiode from direct action X-ray beam, a filter that absorbs X-ray radiation but is transparent within the optical band of spectrum was used. A silicon photodiode with 5 × 5 mm photosensitive window was used as photo receiver.

Amplified analogue signal is fed to the board of 12-bit ADC computer. The computer controls 2D table and X-ray beam source. The installation enables measuring relative light yield as compared with reference sample. The reference sam-



a *b*

Fig. 5. Radio-luminescence topograms: *a* —ZnSe crystal wafer (size is 24 × 30 × 1 mm³); *b* — ZnSe based scintillation panel, particle size 120—200 μm (panel's size is 24 × 30 × 1 mm³)

ple is chosen depending on specific task of measurement (the same thickness with respect to scintillation panels).

Fig. 5 shows luminescence topograms of single crystal sample and ZnSe scintillation panel of the same size as compared with the reference sample. One can see that the scintillation panel has a more homogeneous light yield of X-ray luminescence. Dispersion of light yield on the sample area for ZnSe panels does not exceed 2% of mean value.

For the scintillation panels based on oxide scintillators $ZnWO_4$, $CdWO_4$, $LuGdSiO_5$(Ce), and Gd_2SiO_5(Ce), dispersion of light yield on the sample area does not exceed 2% of mean value as well.

TESTING OF PILOT SAMPLES OF SCINTILLATION PANELS BASED ON ZnSe, $ZnWO_4$, $CdWO_4$, LGSO(Ce), and GSO(Ce)

X-ray luminescence spectra of the studied scintillation materials were obtained using spectrometric system KSVU-23 and X-ray apparatus REIS-I at a X-ray tube voltage of 40 kV and a current of 30 mA. The scintillation signal was recorded by FEP-100 with a spectral sensitivity range 200—800 nm.

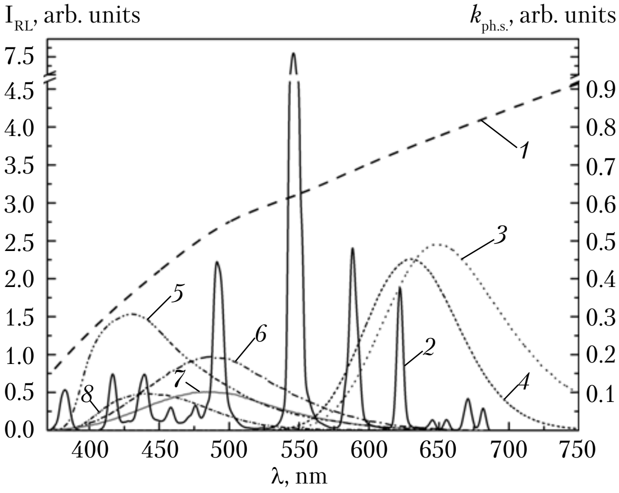


Fig. 6. Radio-luminescence spectra of scintillation panels based on: curve *3* —ZnSe(Te); *4* — ZnSe(Al); *5* — $LuGdSiO_5$(Ce); *6* — $CdWO_4$; *7* — $ZnWO_4$; 8 — Gd_2SiO_5(Ce). Curve *1* corresponds to region of silicon photodiode photosensitivity (Hamamatsu S3590); $k_{ph.s.}$ is photosensitivity coefficient of photodiode; curve *2* is radio luminescence spectrum of industrial intensifying screen RENEKS EFG-G-2V based on Gd_2O_2S(Tb)

The present-fay photodetectors have maximum of spectral sensitivity in the red region (curve *2* Fig. 6). By this parameter they mainly correlate with the sensitivity spectrum of silicon photo receiver of ZnSe based panel (curves *3* and *4* Fig. 6).

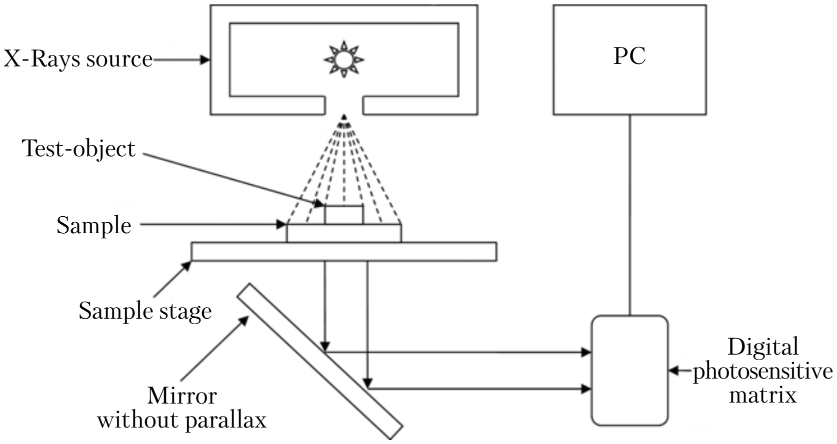


Fig. 7. Flowchart of installation for determining spatial resolution of scintillation panels

However, this scintillator is used basically in low-frequency paths of X-ray introscopes. For medium energies, due to higher effective atomic number, it is better to use $ZnWO_4$ and $CdWO_4$ (curves *6* and *7* Fig. 6). For the high-energy path, it is advisable to use scintillators with the highest effective atomic number, $LuGdSiO_5$(Ce) and Gd_2SiO_5(Ce) (curves *5* and *8* Fig. 6). The scintillation elements based on Gd_2SiO_5(Ce) unlike those on $LuGdSiO_5$(Ce) have a low factor of relative light yield, therefore their application is not expedient. Serially manufactured scintillation element RENEKS EFG-G-2V based on Gd_2O_2S(Tb) (curve *2* Fig. 6) also has a high effectiveness of absorption of medium- and high energy X-ray radiation, but much worse kinetic characteristics than $ZnWO_4$, $CdWO_4$, $LuGdSiO_5$(Ce), and Gd_2SiO_5(Ce) [13].

OPTIMIZATION OF ENERGY BAND OF SENSITIVITY AND SPATIAL RESOLUTION OF SCINTILLATION PANELS OF VARIOUS CONFIGURATIONS

For successful use in radiation instrumentation the scintillation panel shall have a certain contrast sensitivity and spatial resolution within a wide dynamic range. Depending on type of X-ray system, the spatial resolution can vary within the range: up to 20 line pairs/mm for the conventional film X-ray diffraction, about 10 line pairs/mm for the *intensifying screen — film system* and from 0.7 to 4—5 line pairs/mm for digital X-ray diffraction.

Dependences of spatial resolution on particle size of powder of scintillation panels of the three size distribution ranges 40—60 μm, 80—100 μm, and 140—160 μm were measured for the scintillator samples based on ZnSe, $ZnWO_4$, $CdWO_4$, $LuGdSiO_5$(Ce), and Gd_2SiO_5(Ce).

Spatial resolution of scintillation panels was determined using a customized stand for recording shadow image of radio luminescence (Fig. 7). ISOVOLT Titan E X-ray Generator 160 was used as X-ray source, the spatial resolution was measured with the help of standard test object EN 462-5 Duplex IQI.

The measurement method was as follows: the sample was placed on the position table at a distance of 1 m from the emitter. Test object EN 462-5 Duplex IQI that enables determining the panel

Spatial Resolution of Scintillation Panels Based on ZnSe, $ZnWO_4$, $CdWO_4$, LGSO(Ce), and GSO(Ce)

Scintillator powder particle size, μm	Thickness of sample, mm	Spatial resolution, line pairs/mm
40—60	0.1—0.3	6—7
80—100	0.3—0.5	4—5
140—160	0.5—1.5	2—3

spatial resolution by number of distinguished line pairs per 1 mm was put on the sample. Under the action of X-rays the scintillation signal was recorded in digital form by a photo camera.

The highest spatial resolution, about 6—7 line pairs/mm was reported for the panel based on powder of the first range of size distribution. This spatial resolution was reached due to a little thickness of samples (0.1—0.3 mm) and relatively small size of scintillator particles (40—60 μm) that form a dense scintillation layer. Light absorption in dispersive environment hampers light spread along the sample. The ZnSe-based panels with a particle size of 80—100 μm have lower spatial resolution, 4—5 line pairs/mm, while those with a particle size of 140—160 μm have 2—3 line pairs/mm (see Table).

Worsening spatial resolution of scintillation panels when the powder particle size grows is explained by an increase in panel transparency caused by reducing number of scattering centers and light absorbing surface in the *scintillator powder — immersive environment* system. As panel transparency increases the scattering cone of scintillation flashes widens. The obtained values of resolution correspond to optimized parameters of X-ray radiation.

The possibility of studying inner structure of engineering and biological objects has been tested (Fig. 8). The best resolution was obtained using a scintillation powder panel with a particle size of 25—40 μm.

The logical conclusion from the above said is existing contradiction in parameters of spatial resolution and candlepower of scintillation panels. The larger the scintillator particle size, the higher is candlepower and the lower is spatial resolution and vice versa.

MANUFACTURE OF PILOT BATCH OF FLEXIBLE SCINTILLATION PANELS FOR FOREIGN CUSTOMER

Using the developed technique scintillation panels have been manufactured for *Beijing DT Electronic Technology Co.*, Ltd (Beijing, China). Fig. 9 shows pictures of a batch of scintillation panels. The scin-

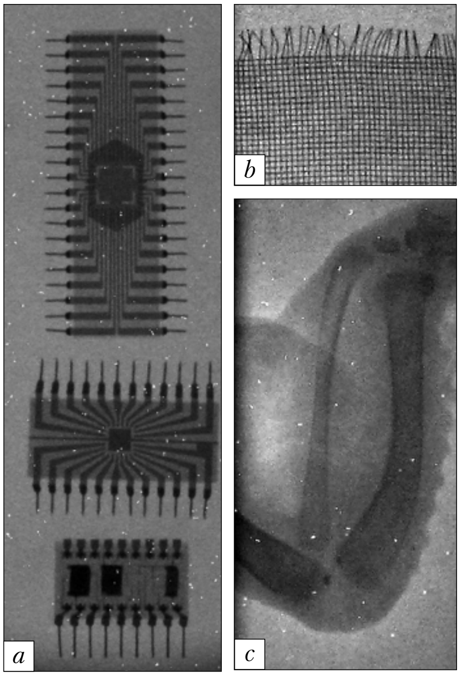


Fig. 8. Shadow X-ray images of electronic chip — *a*; metallic mesh — *b*; frozen chicken wings — *c*. Size of ZnSe scintillator particles ranges within 25—40 μm

Fig. 9. Trial batch of scintillation panels prepared for supply to the customer

tillators have passed comprehensive tests and put into application in serial X-ray scanners.

Currently, technical specifications for these products and conditions for further supplies of scintillators to the customer are discussed.

CONCLUSIONS

Within the framework of R&D project *Development of Highly Effective Scintillators for Detecting the Ionizing Radiation* the following works have been done:

1. Parameters of flexible scintillation panel have been optimized, which enables obtaining panels with a high spatial resolution (up to 7 line pairs/mm). Due to this fact these panels can be used as intensifying screens in medical and industrial X-ray analysis.

2. A technique for obtaining flexible scintillation panels and elements for X-ray radiation record having a high homogeneity of scintillation parameters (the mean deviation does not exceed 2%) and low cost of production (as compared with single crystals) has been elaborated.

3. Conditions for obtaining and manufacturing pilot samples of flexible scintillation panels based on fine crystalline chalcogenide and oxide luminescent materials have been optimized.

4. Pilot samples of flexible scintillation panels have been tested for X-ray sensitivity, energy range, and spatial resolution.

5. Process control documents and laboratory procedure for manufacturing the scintillation panels based on X-ray chalcogenide and oxide scintillators have been elaborated.

REFERENCES

1. Riudiger Y.G. O primenenii siney i zelenoy system vizualizacii izobrasheniia v rentgenographii. *Medicinskaja technika*. 2004, 6: 40—45 [in Russian].
2. Gurvich A.M. *Rentgenoluminophory i rentgenovskie ekrany*. Moskva: Atomizdat, 1976. 63 s. [in Russian].
3. Carel W E van Eijk. Inorganic scintillators in medical imaging. *Physics in medicine and biology*. 2002, 47: 85—88.
4. Ryzhikov V.D. *Scintilliazionnye kristally poluprovodnikovych soedinenii $A^{II}B^{IV}$. Poluchenie, svoistva, primenenie.* Moskva: NIITECHIM, 1989. 127 s. [in Russian].
5. Atroshenko L.V., Burachas S.F., Halchynetskyi L.P., Grinev B.V., Ryzhikov V.D., Starzhynskyi N.H. *Kristally scintillatorov i detectory ionoziruiushchich izlucheniy na ich osnove*. Kyiv: Naukova dumka, 1998. 310 s. [in Russian].
6. Derenzo S.E., Bourret-Courchesne E., Weber M.J., Klintenberg M.K. Scintillation studies of CdS(In): effects of various semiconductor doping strategies. *Nuclear Instruments and Methods in Physics Research*. 2005. V. 537. P. 261—265.
7. Nikl M. Scintillation detectors for X-rays. *Measurements science and technology*. 2006 17: R37 — R54.
8. Moses W.W. *Scintillation requirements for medical imaging*. Proceedings of the Fifth International Conference on Inorganic Scintillators and their Applications, Moscow State University, 2000, pp. 11—21.

С.М. Галкін, І.А. Рибалка, І.А. Тупіцина,
В.С. Звєрєва, В.О. Літічевський

Інститут сцинтиляційних матеріалів НАН України,
пр. Науки, 60, Харків, 61001, Україна
Тел. (057) 341-02-06, 340-93-99;
факс: (057) 340-44-74, 340-93-41; info@isma.kharkov.ua

РОЗРОБЛЕННЯ ГНУЧКИХ СЦИНТИЛЯЦІЙНИХ ПАНЕЛЕЙ НА ОСНОВІ ХАЛЬКОГЕНІДНИХ ТА ОКСИДНИХ ЛЮМІНОФОРІВ ДЛЯ СУЧАСНИХ РЕНТГЕНІВСЬКИХ СКАНЕРІВ ТА ТОМОГРАФІВ

Для реєстрації рентгенівського випромінювання розроблено технологію одержання гнучких дисперсних сцинтиляційних панелей та елементів з високою рівномірністю сцинтиляційних параметрів (середнє відхилення показників не більше 2 %) і низькою собівартістю. Оптимізовано параметри гнучких сцинтиляційних панелей, що дало можливість отримувати їх з високим просторовим розрізненням. Дані панелі можна застосовувати як підсилюючі екрани в медичній та промисловоі рентгенографії. Запропоновано варіанти реалізації 2-енергетичних детекторів рентгенівського випромінювання, які ефективно працюють в діапазонах енергій рентгенівського випромінювання (від 20 до 100 кеВ). Можливе їх застосування — в мультиенергетичних сканерах і в медичних комп’ютерних томографах.

Ключові слова: композит, сцинтиляційна панель, дрібнокристалічний сцинтилятор, детектор, радіографічний сканер, іонізуюче випромінення.

С.Н. Галкин, И.А. Рибалка, И.А. Тупицына,
В.С. Зверева, В.А. Литичевский

Институт сцинтилляционных материалов НАН Украины,
пр. Науки, 60, Харков, 61001, Украина
Тел. (057) 341-02-06, 340-93-99;
факс: (057) 340-44-74, 340-93-41; info@isma.kharkov.ua

РАЗРАБОТКА ГИБКИХ СЦИНТИЛЛЯЦИОННЫХ ПАНЕЛЕЙ НА ОСНОВЕ ХАЛЬКОГЕНИДНЫХ И ОКСИДНЫХ ЛЮМИНОФОРОВ ДЛЯ СОВРЕМЕННЫХ РЕНТГЕНОВСКИХ СКАНЕРОВ И ТОМОГРАФОВ

Для регистрации рентгеновского излучения разработана технология получения гибких дисперсных сцинтилляционных панелей и элементов с высокой равномерностью сцинтилляционных параметров (среднее отклонение показателей не больше 2 %) и низкой себестоимостью. Оптимизированы параметры гибких сцинтилляционных панелей, что дало возможность получать их с высоким пространственным разрешением. Данные панели можно применять в качестве усиливающих экранов в медицинской и промышленной рентгенографии. Предложены варианты реализации двухэнергетических детекторов рентгеновского излучения, эффективно работающих в диапазонах энергий рентгеновского излучения (от 20 до 100 кэВ). Возможные направления их применения — в мультиэнергетических сканерах и в медицинских компьютерных томографах.

Ключевые слова: композит, сцинтилляционная панель, мелкокристаллический сцинтиллятор, детектор, радиографический сканер, ионизирующее излучение.

Received 29.07.16