THERMAL NEUTRON MEASUREMENTS USING YAP:Ce POWDER

by

Lucie FISEROVA*[*] *and Jiri JANDA

NBC Defence Institute, University of Defence, Vyskov, Czech Republic

Scientific paper
https://doi.org/10.2298/NTRP180711012F

A YAP:Ce powder was used as a scintillator for the detection of thermal neutrons. For neutrons energy conversion, enriched LiF was used. The dependence of the concentration of the scintillator: LiF ratio on neutron detection efficiency was studied as well as the influence of areal density of layers and different YAP:Ce powder grains. The preamplifier pulse shape study of YAP:Ce was also provided in response to the dependence of shape of the amplitude spectrum on shaping the time setting. It was shown that based on the pulse shape from YAP:Ce, the neutron and gamma pulses can be clearly distinguished. The results were related to the reference mixture of ZnS:Ag/LiF which is commonly used in combination with thermal neutron detectors.

Key words: YAP:Ce, scintillation powders, thermal neutron detection

INTRODUCTION

The research and development of inorganic scintillators has considerably evolved in recent decades [1-8]. The advanced technology of crystal growth together with a closer understanding of the scintillation process and band model of solids led to the successful production of complex crystal structures consisting of rare earth elements. The most common and historically one of the best-known scintillators is zinc sulfide activated by a suitable activator, usually silver. Its' phosphorescence was first reported in 1866 and it is still widely used in many applications including thermal neutron detection in connection with Li-6 by the Li(n, α)H reaction since zinc sulfide is suitable for detection of charged particles. The main application of ZnS:Ag is in neutron monitors [9]. The sulfide is available only as a polycrystalline powder. There are several methods of scintillation powders production. One conceivable way is to crush a monocrystal and separate the individual fractions from each other by using particular sieves. Or it is possible to prepare powders by using one of the synthesis methods. This process is more accessible because there is no concern with the technology of crystal growth. In addition, with the use of synthesis methods, powders of various grain sizes can be produced, from micro-powders to nanopowders. This can be hardly feasible in the case of crushed monocrystals because the analytical sieves are not capable of separating particles smaller than 10 μm apart.

Cerium-doped yttrium aluminum perovskite (YAP:Ce) is a fast, mechanically and chemically resistant scintillation material with very low energy secondary X-ray emission, which is an advantage in imaging applications. The YAP:Ce detectors are used for gamma and X-ray counting, electron microscopy, electron and X-ray imaging screens, tomography systems and even for experimental neutron detection [10-14]. Selected physical and luminescence properties of YAP:Ce in comparison with ZnS:Ag are listed in tab. 1.

It was found that the YAP:Ce powder can clearly distinguish alpha events from beta and gamma events [15]. The ability to separate radiation in mixed neutron-gamma fields is one of the major parameters monitored by scintillators intended for the detection of neutrons.

Table 1. Comparison of properties of YAP:Ce and ZnS:Ag scintillation materials [11, 12]

Properties	ZnS:Ag	YAP:Ce
Density [gcm^{-1}]	4.09	5.37
Crystal structure	Polycrystalline	Rhombic
Hygroscopic	NO	NO
The wavelength of max. emission [nm]	450	370
Decay constant [ns]	110	25
Index of refraction	2.36	1.95
Light output (% of NaI:Tl)	130	40

---

[*] Corresponding author; e-mail: lucie.fiserova@nuvia.cz

EXPERIMENTAL

Devices and equipment

The measurement was performed in a light-tight chamber with an inbuilt 5.08 mm ET Enterprises photomultiplier (PMT) of the 9266KB type (Great Britain) which was connected to the NUVIA, Ltd. preamplifier base. Digital signal processing was performed by InSpector 2000, spectra acquisition was conducted by Genie 2000 (both Canberra, USA) and evaluated by GAMWIN SW (NUVIA, Czech Republic).

Chemicals

The ZnS:Ag,Cu of grain size less than 5 μm was manufactured and supplied by Leuchtstoffwerk Breitungen GmbH (Germany). The YAP:Ce scintillation crystal was grown, milled and sieved on different grain sizes by Crytur, Ltd (Czech Republic). The available fractions were 315-250 μm, 200-90 μm, 125-90 μm, 90-70 μm, 70-50 μm, and <50 μm.

The LiF enriched with more than 95 at. % of Li-6 was bought from Sigma Aldrich.

The ^{252}Cf isotope of 21 MBq activity with a cylindrical 7 kg paraffin moderator was used as a thermal neutron source. The Am-241 and Co-60 were used as a source of gamma radiation with the activity of 493 Bq and 354 kBq, respectively. Furthermore, the Am-241 was used as a source of alpha radiation.

Procedures

The scintillation powder, lithium fluoride, and 5 % water solution of polyvinyl alcohol (Sloviol R trademark) as an optical binder was mixed together in a ratio of 3:1:6 and then put into the ultrasonic bath in order to get a homogeneous mixture. Afterward, the mixture was applied to the surface of the cylindrical optical glass with dimensions of 50 mm in diameter and 1 mm of thickness. The sample thus prepared was placed in the desiccator for 24 hours to dry. The dry sample, fig. 1, was covered with a Teflon tape and black light-tight tape. Dow corning 4 was used as a sample – photomultiplier optical contact.

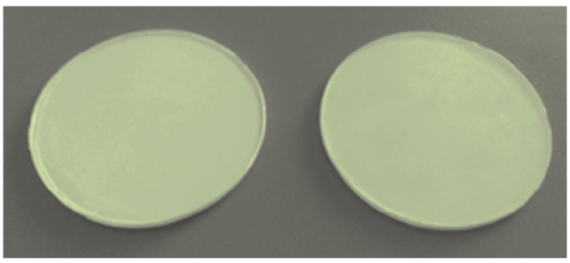

Figure 1. Prepared samples

The four samples of different scintillator: converter mass ratios were prepared in order to determine the best concentration proportion. Another three samples of each mass ratio but different thickness were prepared also to establish the dependence of detection efficiency on the aerial density of the detection layer. As a thermal neutron source, the paraffin moderated Cf-252 was used.

RESULTS AND DISCUSSION

The main aspect of the neutron detector based on the reaction of $n(\alpha)$ is the scintillator sensitivity to these reaction products. Thus, in the beginning, the sensitivity of both scintillation powders to alpha radiation was measured. The amplitude spectrum is shown in fig. 2. The shape of the alpha peak, as well as its position in the amplitude spectrum, was affected by the magnitude of the energy of the interacting alpha particle and by the grain size of the scintillation powder. The setting of multichannel analyzer remains the same for both the measurements. Due to the opacity of the ZnS:Ag the light output of the ZnS:Ag, contrary to the YAP:Ce fraction, was reduced, resulting in the shifting of counts in the lower part of the amplitude spectrum. This shift in the amplitude spectrum is undesirable when gamma/neutron radiation is measured due to the worse discrimination between gamma/neutron pulses. Unlike the ZnS:Ag with the grain size of about 5 μm, the YAP:Ce grain size ranged from 50 to 70 μm, thus ten times larger. The difference in grain sizes possibly led to decrease of photon collection efficiency due to reflections at grain boundaries.

Scanning electron microscope (SEM) analysis confirmed the high diversity among YAP:Ce grains due to crushing and regular shape of the ZnS:Ag powder. The reason is in different production methods of each scintillator – solid-state synthesis contrary to crystal growth and milling.

One of the common issues in neutron systems based on the scintillator/convertor mixture is that only

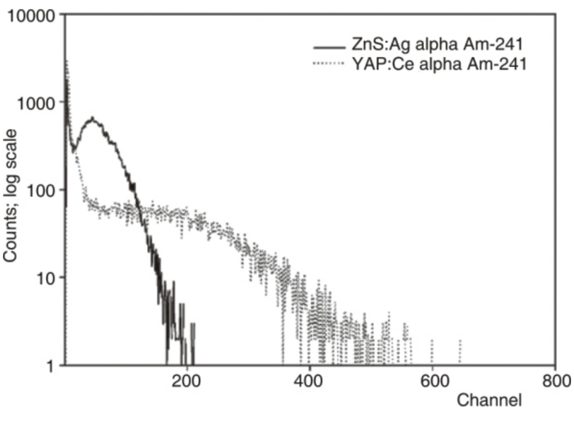

Figure 2. The response of scintillation powders to alpha Am-241 radiation

the layer thickness and mixture ratio are solved. To fully optimize the scintillator/converter system it is necessary to deal with the grain size of both scintillator and converter which has been shown to have a crucial influence on the efficiency of measurement. It was calculated that the range of alpha particles in lithium fluoride is ~6.6 μm, whereas the range of triton is ~28.1 μm [9]. This means that a part of the alpha particles and tritons energy is directly absorbed into the LiF itself. The SEM analysis showed that the particle size of enriched LiF was approximately ten times larger in comparison with LiF with natural abundance. One of the possible solutions to the problem with energy absorption is to employ the nano-sized converter.

Figure 3 shows the difference between the particle size of LiF with natural abundance and the enriched LiF. The enriched LiF particle size of 2 μm is unsuitable especially for small-grain scintillation powders. The use of lithium-6 chloride as a converter successfully solved this problem. Furthermore, there was also a significant increase in detection efficiency using the same molar concentration as in the case of the use of lithium fluoride. Another advantage of implementing lithium-6 chloride was the decrease in its weight in the mixture maintaining the same detection efficiency. This was probably caused due to a better distribution of the lithium atoms around the scintillation powder. On the contrary, the main disadvantage of lithium chloride that prevents its wider use is its hygroscopicity. This was the main reason why lithium fluoride was used in the following studies.

The dependence of the measured count rate per areal density and the concentration of the mixture is shown in fig. 4. The vertical axis represents measured

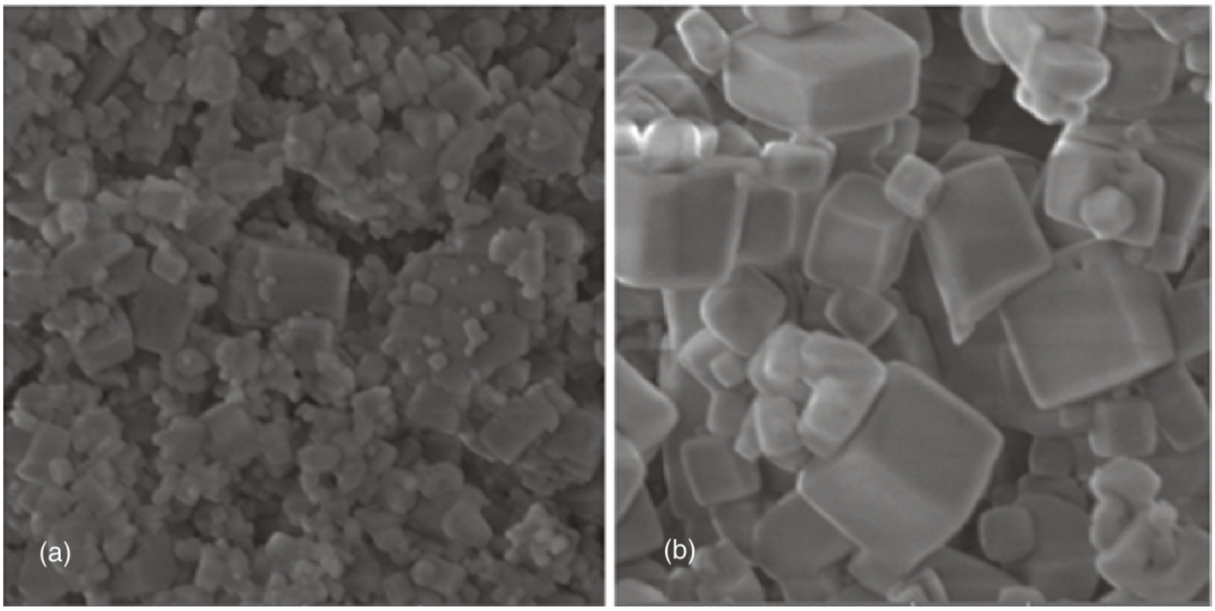

Figure 3. The SEM analysis of the LiF particle size; (a) LiF with natural abundance, (b) LiF enriched 95 at. 95 % of Li-6. Measured by VEGA3 TESCAN, HV 5.0 kV, 2 μm scale

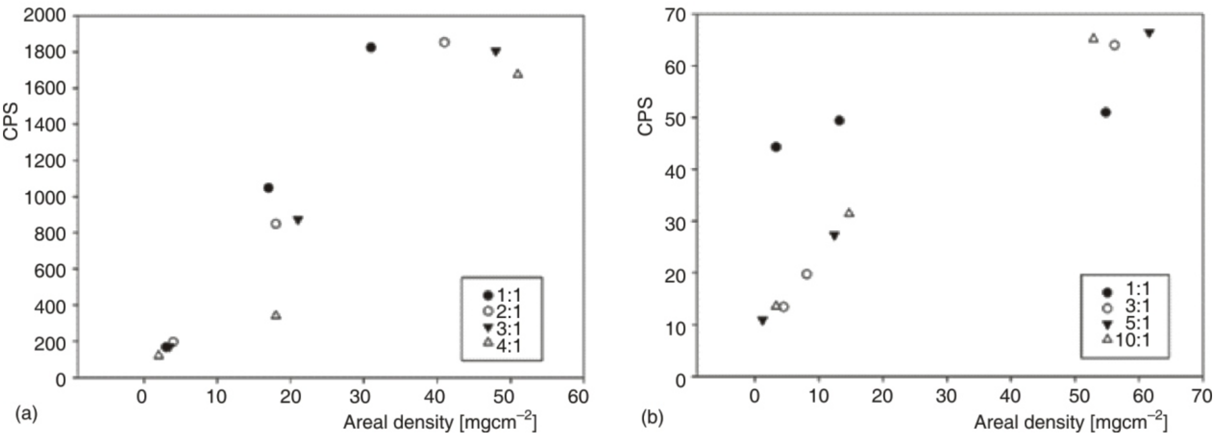

Figure 4. The dependency of measured counts per areal density and concentration of the mixture of ZnS:Ag/LiF (a) and YAP:Ce/LiF (b)

CPS (counts per second) of the complete amplitude spectrum. The detection efficiency of ZnS can be largely maintained up to a 4: 1 for the scintillator to the converter mass ratios, in the case of YAP:Ce even up to a ratio of 10: 1. In this case, however, the larger particle size of the YAP:Ce scintillation powder plays an important role. For subsequent measurements, the 3 : 1 of the scintillator : converter ratio was used for the case of lithium fluoride. This conclusion is consistent with the results achieved in former studies [16-21]. The importance of the proper choice of the concentration and grain size in the mixture and their effect on detection efficiency is explained in [5].

Furthermore, it was shown that increasing the areal density up to 50 mgcm^{-2} resulted in maintaining the detection efficiency, thus expected losses due to absorption of radiation in the deposited layer were not observed.

The dependence of different YAP:Ce grain sizes on detection efficiency is shown in fig. 5. The results were corrected on the uniform areal density of 42 mgcm^{-2} and scintillator : converter ratio of 3:1. According to the results, the significant difference in the measurements of various scintillator powder grains was obtained in the case of 70-50 μm grain size. At a confidence level of 95 %, it was statistically verified that the measured value for the 70-50 μm grain size powder is statistically significant and exhibited the highest detection efficiency compared to others. The lowest detection efficiency was calculated for the scintillator powder with the smallest grains. This was probably caused by energy loss due to refraction and reflection of light on a large number of small grains as mentioned above. The amplitude spectrum of grain size below 50 μm was shifted towards lower channels confirming the fact that light yield was significantly affected by the grain size as in the case of ZnS:Ag.

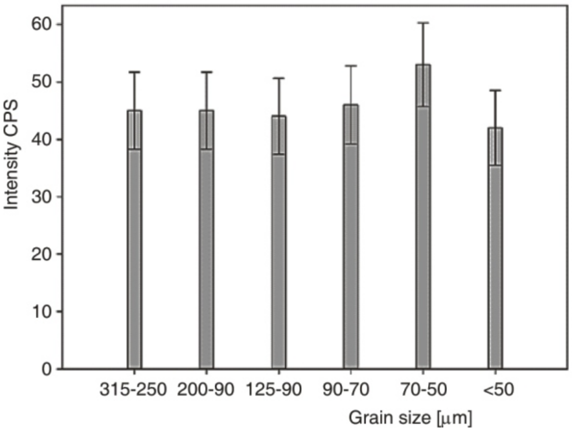

Figure 5. The dependence of different grain sizes on detection efficiency

Additionally, the signal output from the preamplifier was also analyzed. All types of radiation interact with matter in a different way, resulting in differences in height and time characteristics of preamplifier pulses [21]. Figure 6 shows preamplifier pulse shapes from both YAP:Ce (1-A, B) and ZnS:Ag (2-A, B) scintillation powders. In both cases, the analysis showed that the pulse height from the alpha pulse (hundreds of millivolts) is approximately 10 times higher than pulse height from gamma pulses (tens of millivolts).

The previous studies [22] reported that ZnS:Ag phosphor has two types of decay, one is exponential and another hyperbolic. The exponential decay has a shorter decay constant, 10^{-7}-10^{-9} sec and is caused almost by the single excitation by γ-rays and β-rays. The hyperbolic decay has a longer decay mode of ZnS

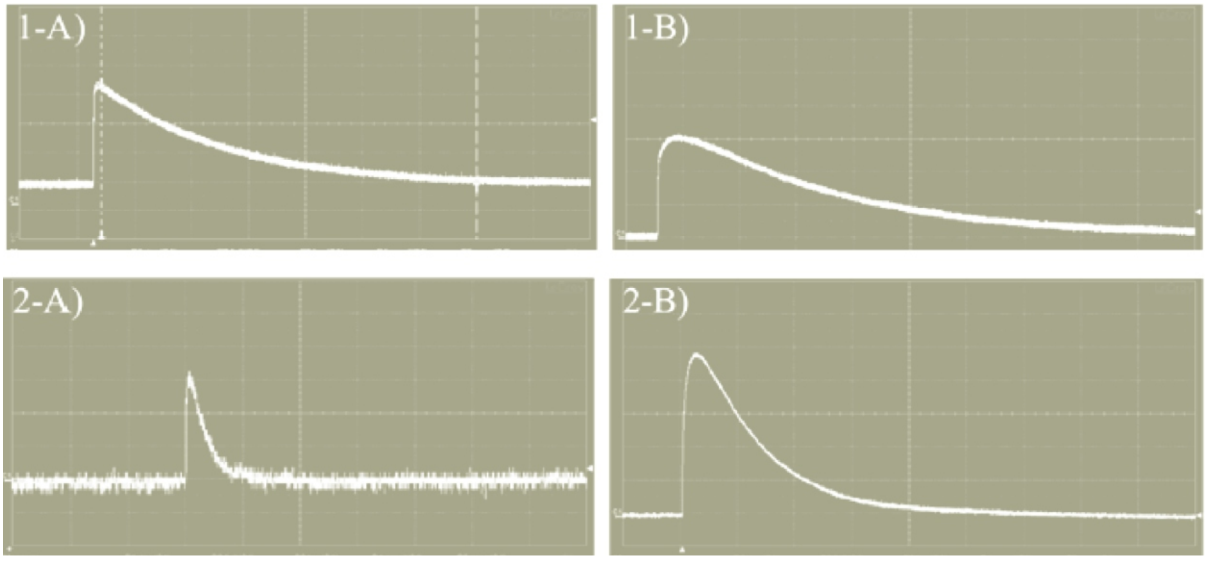

Figure 6. Pulse shapes from YAP:Ce (1) and ZnS:Ag (2), where gamma pulses (A) and alpha pulses (B). Parameter settings: 1-A) voltage/div = 50 mV, time/div = 20 μs, 1-B) voltage/div = 500 mV, time/div = 20 μs, 2-A) voltage/div = 100 mV, time/div = 200 μs, 2-B) voltage/div = 1 V, time/div = 50 μs

$\sim 10^{-5}$ sec which always exists in addition to the exponential decay and is caused by α-particles.

The time distributions of the light pulses of YAP:Ce were also reported for γ-rays and α-particles [23]. A very intense fast component with a decay time constant of 27 ns, followed by a slow component with the decay time constant of 150 ns were measured for γ-ray excitation. The light pulse due to α-particles showed the fast component of 25 ns and the slow component with the decay time constant of 100 ns. While a fast component of γ and α pulses is almost the same, the decay time constant of the slow component under α-particle excitation was faster by about 30 %. The contribution of the slow component depended on different mixtures of trapping centers associated with the quality of tested materials.

In response to the previous facts, the dependency of the pulse-height distribution on shaping time (ST) was studied. The results are shown in fig. 7. The ST was set from 0.4 µs to 4.6 µs with variable values of rise time (RT) and flattop time (FT). The rise time of the pulse is defined as the time interval from 0.1 to 0.9 of the pulse maximum. It is not possible to ignore the role of the decay time of each scintillator. Scintillators which have longer decay time need more time to let the photons fully contribute to the signal creation. To ensure complete collection of light, it is necessary to set the shaping time to be longer than the decay time of the scintillator. Incomplete photon collection gives rise to a proportion of pulses rather smaller than what they should be and would lead to tailing at the low-energy side of the spectrum. All of them are related as is shown in fig. 8

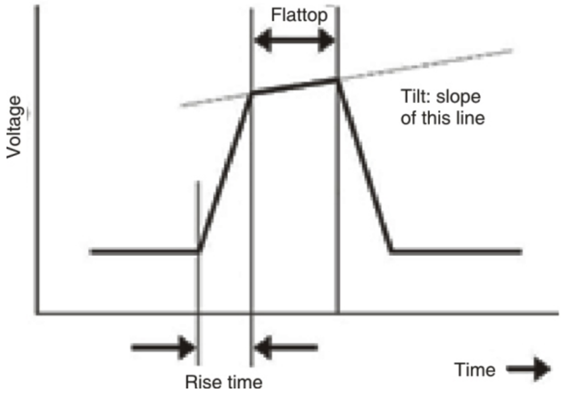

Figure 7. Rise time and flattop definition [24]

According to the results, the shape of the amplitude spectrum significantly changed in the case of ZnS:Ag/LiF. The different process of interaction of gamma and alpha radiation in the scintillator itself leads to a different shape of the output signal from the preamplifier [15]. The gamma pulse has generally a steeper leading edge whereas the pulse generated from alpha radiation is more gradual and its height is several times higher so that it takes more time for the pulse shaper to process it. Therefore, the pulse shaper has to be set so that both pulses can be processed properly and their real height is correctly determined for both. In this case, the improper setting of shaping time can lead to shifting of the alpha signal amplitude histogram to the left part of the spectrum because the height of the alpha pulse is not correctly determined, and then into the loss of alpha pulses and worsening of alpha/gamma discrimination.

Finally, the amplitude spectrum analysis and comparison were performed. According to the results shown in fig. 9, the ZnS:Ag exhibited better gamma-neutron pulse height discrimination measured with 0.6 µs RT and 0.3 µs FT which was probably caused due to a combination of higher density, particle size, and shape of the YAP:Ce powder. The scintillator

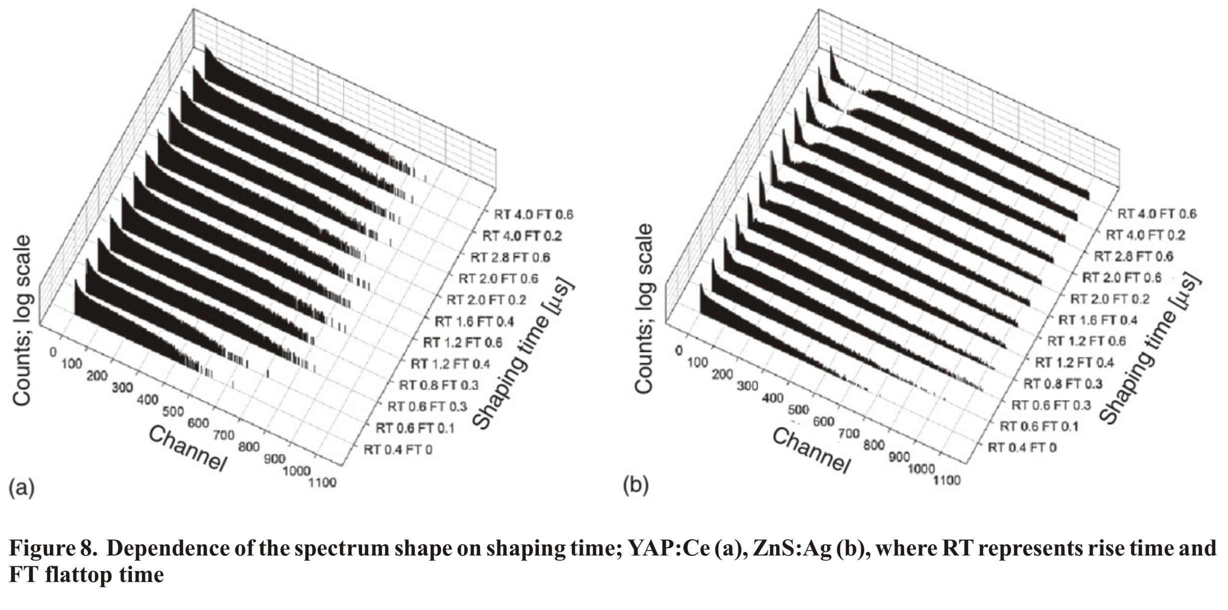

Figure 8. Dependence of the spectrum shape on shaping time; YAP:Ce (a), ZnS:Ag (b), where RT represents rise time and FT flattop time

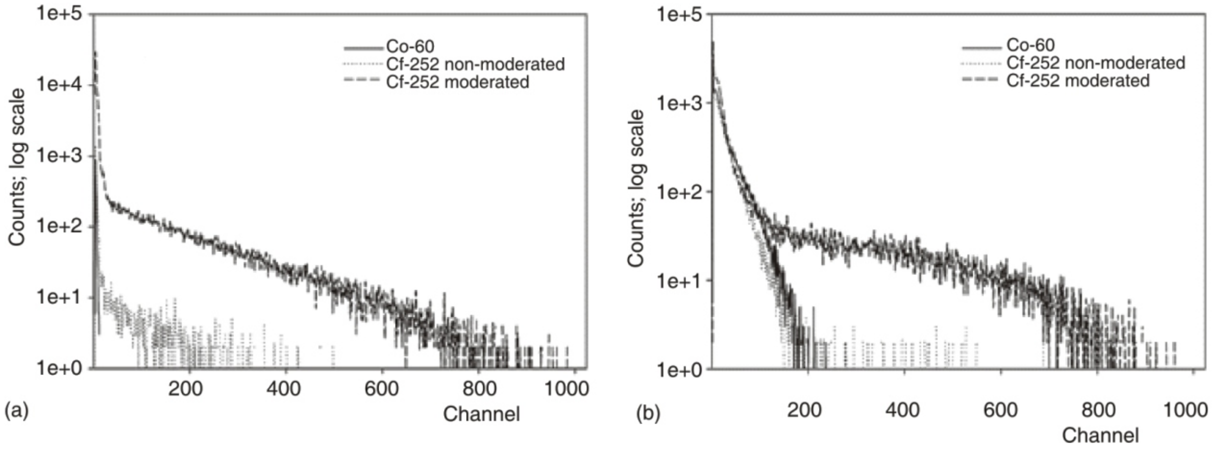

Figure 9. The amplitude spectra from ZnS:Ag (a) and YAP:Ce (b) scintillation powders

response to gamma radiation might be partially decreased by applying a thinner scintillation layer. This caused the decrease of the gamma photon detection efficiency and the reduction of the gamma pulse amplitude. The amplitude height of alpha or triton pulses was not influenced since their penetration depth is very short. Nevertheless, the alpha/triton detection efficiency was partly decreased as well since the likelihood of nuclear reaction of a neutron on Li-6 nuclei decreases with the thinning of the layer.

A significant increase of the count rate in the higher amplitude region when measuring the moderated Cf-252 source was apparent in both ZnS:Ag/LiF and YAP:Ce/LiF scintillation mixtures. The energy of alpha particles and tritons is transferred on a very short path due to their high LET. Therefore, even a very small thickness of the scintillation layer ensures complete absorption of alpha and triton energy. Large volumes and thick layers of thermal-neutron active layers are generally unnecessary and mostly undesirable because of self-absorption of scintillation photons which leads to lower photon collection efficiency. In the case of thermal neutron detection systems, the largest volume is usually occupied by a moderator. The Co-60 gamma amplitude spectrum is added to the neutron spectra to compare the sensitivity of each powder to gamma radiation. Most of the common neutron sources are also strong emitters of gamma radiation which is clearly visible in the increased count rate in the low amplitude range of the spectrum. This is more evident in the case of YAP:Ce which is shown to be more gamma-sensitive. Therefore, the contribution of the counts in the low amplitude part of the thermal neutron spectrum was partly due to the gamma radiation emitted from the Cf-252 neutron source.

CONCLUSIONS

Silver activated zinc sulfide powder has been used for a long time as one of the most efficient scintillators, especially for α counting, because of its high scintillation efficiency. However, it is unsuitable for the measurements at a high-count rate and for use as a fast component since its scintillation-decay time is relatively slow. In addition, it is not always an appropriate material, for example, if it is used in a chemically corrosive environment. The biggest advantage of the YAP:Ce powder is its shorter decay time. The comparison between YAP:Ce and ZnS:Ag scintillation powders for the detection of neutrons was performed. The crucial influence on the photon collection efficiency was essentially the particle size of the used powders and the composition of the converter material. Due to the difference in these dimensions, it was ideal to use the scintillation powder of grain size of m in connection with the conversion nano-powder.

The pulse shape differences between ZnS:Ag and YAP:Ce powders were also studied. The output light pulse from ZnS:Ag was initially rapid but has a slow afterglow with $\sim 10^{-5}$ sec decay time. Furthermore, ZnS:Ag had a greater tendency to glow in the dark after preceding daylight exposure.

The correct determination of the shaping time is an important part of the process of the detection system optimization. It was proved that in case of scintillators with longer decay time such as ZnS:Ag the loss of pulse height occurred at short shaping times since the scintillation light does not fully contribute to the signal and the amplitudes were therefore significantly lower compared to those measured at longer shaping constants.

On the other hand, ZnS:Ag showed better detection efficiency for charged particles in comparison with YAP:Ce. This was caused because of higher light yield since ZnS:Ag belongs to the group of sulfides, which have the smallest band gap and therefore the highest light outputs are reported [1].

The choice of the proper scintillation powder for the detection of thermal neutrons is therefore strongly dependent on the particular application and the environment in which the detector will operate.

ACKNOWLEDGMENT

The authors would like to express their gratitude to Crytur Ltd. for the preparation of the YAP:Ce scintillation powder, which has allowed us to conduct this study and the Brno University of Technology for the kind performance of scanning electron microscope analysis.

AUTHORS' CONTRIBUTIONS

The idea for this study was put forward by L. Fiserova. The measurements, theoretical calculations, and data evaluation were carried out by L. Fiserova and J. Janda.

REFERENCES

[1] Dorenbos, P., Scintillators for the Detection of X-Rays, Gamma Rays, and Thermal Neutrons. Collegediktaat, National Institute for Subatomic Physics, (2008), [On line], Available: https:// www.nikhef.nl/čd90/ collegediktaat/scintillators.pdf.

[2] Azinheiro, R. G. New Scintillators for Nuclear Medicine. Ph.D. Dissertation, University of Lisbon, 2013, [On line], Available: http://repositorio.ul.pt/bitstream/10451/10704/1/ulfc106046_tm_Rui_Azinheiro.pdf.

[3] Van, Eijk, C. W. E., Inorganic-Scintillator Development, *Nucl. Instruments Methods Phys. Res. Sect. A Accel. Spectrometers, Detect. Assoc. Equip., 460* (2001), pp. 1-14

[4] Derenzo, S. E., *et al*., The Quest for the Ideal Inorganic Scintillator, *Nuclear Instruments and Methods in Physics Research, Section A: Accelerators, Spectrometers, Detectors and Associated Equipment, 505* (2003), 1-2, pp. 111-117

[5] Weber, M. J., Scintillation: Mechanisms and New Crystals, *Nuclear Instruments and Methods in Physics Research, Section A: Accelerators, Spectrometers, Detectors and Associated Equipment, 527* (2004), 1-2, pp. 9-14

[6] Rodnyi, P. A., Progress in Fast Scintillators, *Radiation Measurements, 33* (2001), 5, pp. 605-614

[7] Lecoq, P., *et al*., Inorganic Scintillators for Detector Systems: Physical Principles and Crystal Engineering, Springer-Verlag Berlin, Heidelberg, 2006

[8] Janda, J., Ticha, J., An Experimental Approach to the Determination of the Gross Activity of Uranium, Plutonium, Americium and Strontium in Human Biological Samples Using Solid-State Scintillation, Scientific Publications of the State University of Novi Pazar Series A: Applied Mathematics, *Informatics and Mechanics, 10* (2018), 1, pp. 25-32

[9] Schooneveld, E., ZnS Neutron Detectors, International Neutron Scattering Instrumentation School, Frascati, Italy (2012), [On line], Available: http://info.ornl.gov/sites/insis/ Presentations/ ZnS%20neutron_detectors_Schooneveld.pdf.

[10] Stave, S., *et al*., LiF/ZnS Neutron Multiplicity Counter, *Nucl. Instruments Methods Phys. Res. Sect. A Accel, Spectrometers, Detect. Assoc. Equip., 784* (2015), pp. 208-212

[11] ***, YAP:Ce, Material Datasheet, CRYTUR, (2018), [On line], Available: http://www.crytur.cz/ Materials/yap-ce/

[12] ***, ZnS(Ag), Zinc Sulfide Scintillation Material Data Sheet, Saint-Gobain Crystals & Detectors, (2018), [On line], Available: http://www.hep.ph.ic.ac.uk/fets/pepperpot/ docs+papers/zns_602.pdf

[13] Lieberwirth, A., *et al*., Response from Inorganic Scintillation Screens Induced by High Energetic Ions, *Nucl Instruments Methods Phys Res Sect. B Beam Interact. with Mater., Atoms 365* (2015), December, pp. 533-539

[14] Fiserova, L., *et al*., Neutron Detection Using Conversion Layers and YAP:Ce and YAG:Ce Crystals, *Nucl Technol Radiat, 30* (2015), 3, pp. 198-202

[15] Yasuda, K., *et al*., Properties of a YAP powder scintillator as Alpha-Ray Detector, *Appl Radiat Isotopes, 52* (2000), 3, pp. 365-368

[16] Wu, C., *et al*., A Study of ZnS(Ag)/6LiF with Different Mass Ratios, *Radiat. Meas., 58* (2013), November, pp. 128-132

[17] Kiff, S. D., *et al*., Neutron Detection and Identification Using ZnS:Ag/6LiF in Segmented Antineutrino Detectors, *Nucl Instruments Methods Phys Res Sect A: Accelerators, Spectrometers, Detectors and Associated Equipment, 652* (2011), 1, pp. 412-416

[18] Yehuda-Zada, Y., *et al*., Monte Carlo Simulation for Optimizing 6LiF:ZnS(Ag) based Neutron Detector Configuration, Radiation Detectors Conference 2014

[19] Koontz, P. G., *et al*., ZnS(Ag) Phosphor Mixtures for Neutron Scintillation Counting, *Rev. Sci. Instrum., 26* (1955), 352, pp. 352-356

[20] Mason, T. E., Neutron Detectors for Materials Research. Oak Ridge National Laboratory, Technical Report (2000), [On line], Available: https://www.google.com/url?sa=t&rct=j&q=&esrc=s&source=web&cd=6&ved=2ahUKEwim-J_W5u_gAhUHyKQKHegYBMAQFjAFegQIAhAC&url=http%3A%2F%2Fwww.hep.ucl.ac.uk%2Fčsaakyan%2FProtonTherapy%2Fnxns_aug_00_detectors.ppt&usg=AOvVaw3-WDIDRzDGUX2064D0cYCU

[21] Janda, J., Hohnova, S., The Comparison of Detection Parameters of Selected Photomultipliers Depending on the Shape of the Scintillator, *Nucl Technol Radiat, 33* (2018), 1, pp. 61-67

[22] Asada, T., *et al*., Decay Properties of ZnS(Ag) Phosphors, *J. Phys. Soc., Japan, 14* (1959), 12, pp. 1766-1770

[23] Moszynski, M., *et al*., Properties of the YAP: Ce Scintillator, *Nucl. Instruments Methods Phys. Res. Sect. A Accel. Spectrometers, Detect. Assoc. Equip., 404* (1998), 1, pp. 157-165

[24] Keyser, R. M., T. R. Twomey, Optimization of Pulse Processing Parameters for HPGe Gamma-Ray Spectroscopy Systems Used in Extreme Count Rate Conditions and Wide Count Rate Ranges, *Journal of Radioanalytical and Nuclear Chemistry, 296* (2013), 1, pp. 503-508

Received on July 11, 2018
Accepted on March 6, 2019

Луција ФИШЕРОВА, Јиржи ЈАНДА

МЕРЕЊА ТЕРМИЧКИХ НЕУТРОНА ПРИМЕНОМ YAP:Ce ПРАХА

Приказана је употреба YAP:Ce праха као сцинтилатора за детекцију термичких неутрона. За конверзију енергије неутрона искоришћен је обогаћени LiF. Испитана је зависност односа концентрације сцинтилатора и LiF на ефикасност детекције неутрона, као и утицај површинске густине слоја и различите врсте зрна YAP:Ce праха. Приказано је и испитивање облика импулса претпојачавача YAP:Ce као одговор на зависност облика амплитудског спектра од подешавања времена обликовања. Показано је да се у зависности од облика импулса YAP:Ce могу јасно раздвојити неутронски и гама импулси. Резултати су упоређени са референтном смешом ZnS:Ag/LiF која се уобичајено користи у комбинацији са детекторима термичких неутрона.

Кључне речи: YAP:Ce, сцинтилациони прах, детекција термичких неутрона