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Red emitting silicones for particles detection: coupling with APD

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Up to date, neutron detection has been relying on sophisticated and voluminous systems, employing toxic and awkward liquid scintillators and fragile expensive PMT. In order to overcome these main drawbacks, red emitting polysiloxane based solid scintillators have been developed and optimized for coupling with high responsivity APD, having higher External Quantum Efficiency (EQE) in the red region of the visible spectrum. Optical properties of phenyl substituted polysiloxane based matrices, doped with different amounts of three organic dyes (PPO, Basf Lumogen Violet® and Basf Lumogen Red®) have been investigated in order to optimize light output for detection with APD. Scintillation performances of these red emitting scintillators have been measured with alpha particles and gamma rays and compared with the previously developed blue emitting polysiloxane based scintillators, showing an improved scintillation light yield with APD detectors. The performances of this polysiloxane based materials in fast neutron detection have also been verified using time of flight (TOF) discrimination technique with a 2.32 MeV neutron beam. Finally, the possibility to achieve pulse shape discrimination with this innovative materials has been also explored, achieving very interesting preliminary results that pave the way to the use of polysiloxane based scintillators in a field where liquid scintillators have been so far the only competitor.

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1. Introduction

Up to now, neutron detection and especially fast neutron detection has been relying mainly in systems employing liquid scintillators due to their good efficiency and pulse shape discrimination capability [1]. However, these materials show some main drawbacks due to their toxicity, their flammability, their volatility and sensitivity to dissolved oxygen limiting the duration and the quality of the performances [2]. To avoid these issues, liquid scintillators need to be used in sealed containers with consequently worse handiness and increased costs.

Furthermore, scintillation light detection, traditionally, has been mainly performed by photomultiplier tubes, due to their high gain, low noise and quite good quantum efficiency. These devices are however bulky and fragile (PMT are vacuum based detectors), with high sensitivity to magnetic fields, high power consumption and can be easily damaged by high light intensities [1].

In order to meet new demands in medical diagnostic [3-5], nuclear [6]and high energy physics [7], radiation monitoring [8, 9] and in military fields [10, 11] there's the need to replace bulky and magnetic fields sensitive PMT with more compact detection systems. Avalanche Photodiodes are in the number of the most promising candidates given their higher quantum efficiency, compactness, insensitivity to magnetic fields, low power consumption, ruggedness and good energy resolution [12-15].

As regarding the replacement of awkward liquid scintillators, plastic scintillators have been so far the most used alternative, due to their fast response time, fair efficiency, low cost and ease of production [1,2]. On the other hand, plastic scintillators proved to have low radiation hardness and to overcome this issue, polysiloxane based scintillators have been

recently developed, where the traditional polystyrene or polyvinyltoluene matrix has been replaced by radiation harder phenyl-substituted polysiloxane matrix [16-18]. These newly developed scintillators, doped with boron, proved to be very efficient also in thermal neutron detection [19,20].

Coupling between APD detector and polysiloxane based scintillators would overcome some of the above listed main issues towards the development of a new compact radiation detector. Most of the commercially available APDs, however, show a higher responsivity in the red part of the visible spectrum and the maximization of the spectral matching factor between scintillator and detector would require a red emitting scintillator [21]. These considerations may be also useful in next years for the on-going development of 3D detectors with internal multiplication [22], widening the application fields of these new developing devices.

Another main disadvantage of plastic over liquid scintillators is that, so far, efficient pulse shape discrimination was performed only using the latter and no plastic material proved to be able to perform efficient neutron-gamma discrimination. This feature however is very important for neutron detection since it allows to rejects gamma ray induced events occurring during neutron detection, which most often can't be discriminated in other ways. The development of plastic scintillators with this feature would be the breakthrough towards the complete replacement of liquids and for this reason, Pulse Shape Discrimination (PSD) capability of polysiloxane based materials has been here also investigated.

In this work, red emitting polysiloxane based scintillators have been produced by dissolving a suitable amount of three different dyes (PPO, Basf Lumogen Violet® and Basf Lumogen Red®) into phenyl substituted polysiloxane matrix. In order to maximize the red light output and achieve the best performance when coupled with APD detectors, optical properties of these materials have been studied. The scintillation light yield, collected by both APD and PMT, has been compared with that from best commercially available plastic scintillator (EJ212 by Eljien Technologies ®). Response of these red emitting scintillators to fast neutrons has also been measured and the possibility to perform PSD has been investigated showing good preliminary results.

2.Experimental procedure

2.1 Samples preparation

Polysiloxanes samples have been prepared by mixing different amount of PPO (primary dye), BASF Lumogen Violet® (secondary dye) and BASF Lumogen Red® (tertiary dye) in vinyl-terminated A resin (polydimethyl-co-diphenyl siloxane, with 22-25% molar content of diphenyl siloxane groups) Hydride-terminated B resin (polymethylhydro-co-methylphenyl siloxane, with 45-50% of methylhydrosiloxane groups), in a weight ratio of 100:8, has been then added to perform cross-linking, together with Pt based catalyst and cure moderator.

Before curing, the mixture has been degassed in vacuum (0.1 mbar) in order to remove air bubbles and gasses. Then it was poured in an aluminium mould and kept in an oven at 60°C overnight to complete the cross-linking reaction. The cured samples have been easily extracted from the mould, providing tough and transparent scintillators as shown in Fig. 2. All the components for the synthesis of the matrix were purchased from ABCR GmbH® (Karlsruhe,

Germany), PPO (2,5-diphenyl oxazole) was supplied by Sigma--Aldrich® (Milano, Italy) while Lumogen Violet® (LV) and Lumogen Red® (LR) were kindly offered by Colorflex® (Mannheim, Germany). Samples prepared for PSD studies contained higher amounts of PPO (around 8%), 0.02% LV and no LR and after degassing they have been poured in a bigger aluminium mould (the final sample dimension is 8cm diameter and 2 cm thickness).

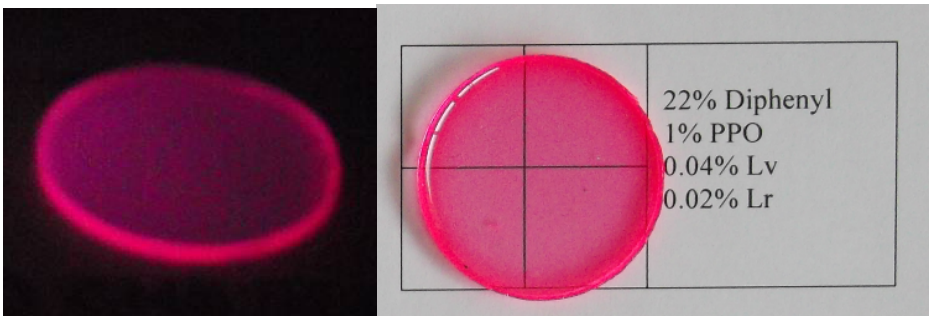

Fig. 1. Polysiloxane based red emitting scintillator irradiated by 380 nm UV light (left) and in daylight (right), the sample diameter is 3 cm and thickness is 1mm.

2.2 Sample characterization

Optical characterization of samples has been performed by means of fluorescence spectroscopy with a Jasco FP-6300 spectrofluorimeter, equipped with a 150 W Xe lamp, in transmission geometry.

Scintillation measurements have been made by irradiating the samples with ^{241}Am α source (5.48 MeV) and ^{60}Co γ source (1.33 MeV and 1.17 MeV).The scintillation light was recorded both by a PMT (Hamamatsu® R2228) and by an APD (Advanced Photonics Inc.® SD 630-70-72-500) photodetector. Optical coupling was achieved without optical grease: the smooth scintillator face, due to its rubbery nature, perfectly adhered to the PMT window or to the ADP surface. The sample was then wrapped with aluminium Mylar foil and Teflon and the whole system was closed into a scattering chamber and isolated from ambient light. Radioactive sources were set directly in contact with the scintillator, inside the chamber. For some measurements, in order to measure the contribution to the light yield of the red emission alone using the PMT, a long-pass filter (515 nm) by Thorlabs® (Newton, NJ, USA) was interposed between the PMT head and the sample. In this case a drop of A resin was spread between the filter and the PMT window in order to improve optical coupling.

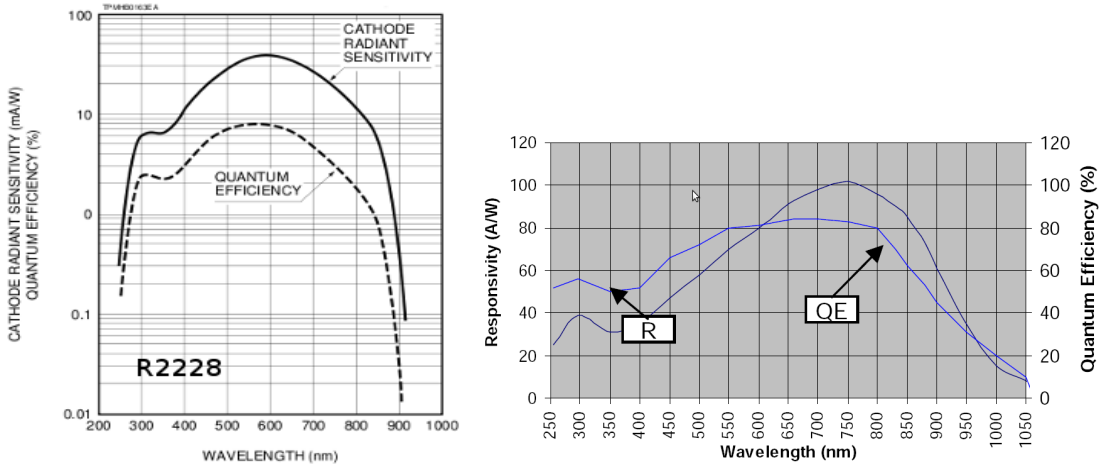

Fig. 2.QE and responsivity curves as a function o detected light wavelength for the PMT and the APD detectors used in this work.Data are supplied by the manufacturers.

The signal from the photo-detector has been amplified with a Canberra® 2021 Spectroscopy Amplifier giving Gaussian signals whose amplitude is the integral of the incoming pulse. In all these measurements the amplifier was set with a fixed shaping time of 0.25 μs and a gain of 30. The light yield of the samples was compared with that of one of the best commercially available plastic scintillators, EJ-212 with the same dimensions of the samples.

PMT was fed with a bias of -1200 V supplied by a CAEN® High Voltage Power Supply mod.126.

Regarding the measurements with the APD, the signal from the photo-diode was pre-amplified in order to extract the signal without compromising the signal to noise ratio and after this stage it was sent to the same amplifier used with the PMT. The device was fed with a +1830 V bias supplied by an ORTEC® High Voltage Power Supply.

Neutron detection measurements have been performed at CN 7MV Van Der Graaf Accelerator at Legnaro National Laboratories (Padova, Italy), with a LiF target irradiated by 4 MeV pulsed proton beam in order to produce a 2.32 MeV pulsed neutron beam. Scintillators coupled to Hamamatsu R2228 PMT were placed at a distance of about 60 cm from the LiF target. Signals produced by the detector have been acquired by a CAEN® digital system. For TOF measurements, a proton current sensitive pick-up was used to set the reference time. In this way it is possible to register signal variations as a function of time and thus discriminate neutrons from gammas due to their different speed and thus different arrival time.

3. Results and discussion

3.1 Optical characterization

Both efficiency and radiation hardness of silicone-based scintillators, employing PPO and LV as primary and secondary solutes, had already been proved [18,19]. A light yield as high as 60% of EJ-212 has been achieved by careful choice of the dyes concentration for samples 6 mm thick, while the radiation stability has been tested under exposure to heavy doses of ^{60}Co gamma

rays and only negligible light losses have been evidenced up to irradiation doses as high as 54 kGy [23]. LR was chosen as ternary red emitting dye because of its very high quantum yield, very good solubility in different matrices, good photo-stability even when exposed to UV light [24] and good radiation hardness [25]. Furthermore, the main absorption peak of this dye, located at about 560 nm is accompanied by a minor component at about 450 nm, well matching LV emission range.

In order to optimize energy transfer between LV and LR, transmission mode fluorescence emission spectra have been collected for different LR concentrations (Fig. 3).

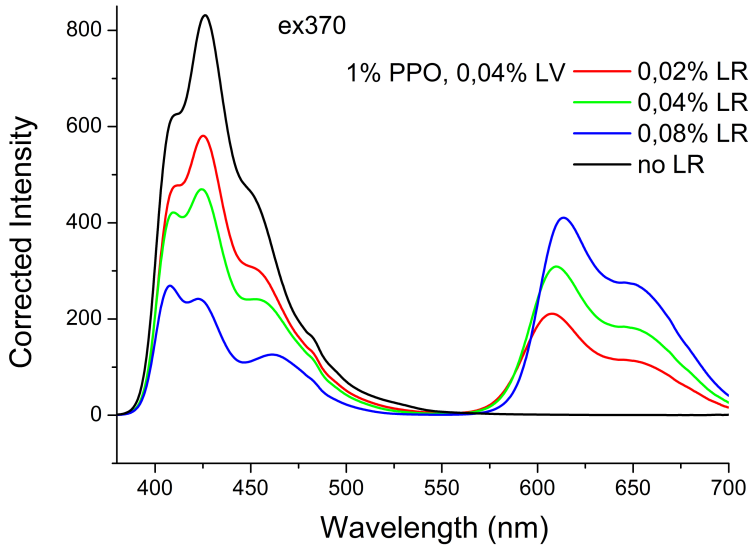

Fig. 3. Transmission mode fluorescence emission spectra for samples with different LR concentrations, for LV direct excitation (370 nm).

As clearly visible, LV emission band, ranging from 400 nm to 500 nm, decreases for higher LR concentrations while LR emission intensity around 610 nm increases, as a result of the improved energy transfer from LV to LR.

3.2 Scintillation measurements

In order to confirm the results achieved from optical characterization on energy transfer, scintillation light yield measurements have been performed using a Hamamatsu R2228 red enhanced PMT detector and ^{241}Am alpha source. Analysis has been done by comparing direct measurements with scintillation light yields achieved interposing a 515 nm long-pass optical filter between the sample and the detector in order to register the only LR contribution. Results of these former measurements are shown in Fig. 4

As it can be observed, measured red light yield indeed steadily increases for LR concentration ranging from 0.01% to 0.08%, but the intensity enhancement is more important from 0.01% to 0.02% LR. On the other hand, light yield measured without optical filter slightly decreases for higher solute concentrations. This effect can be related to the decrease of the LV contribution to the overall light yield, which can be detected by the PMT thanks to its sensitivity over a wide wavelength interval.

On these bases, scintillation light yield for samples irradiated with ^{241}Am alpha source and ^{60}Co gamma source has been recorder coupling the red emitting polysiloxane based scintillators to Advanced Photonix SD 630-70-72-500 APD. Best results have been achieved for the sample

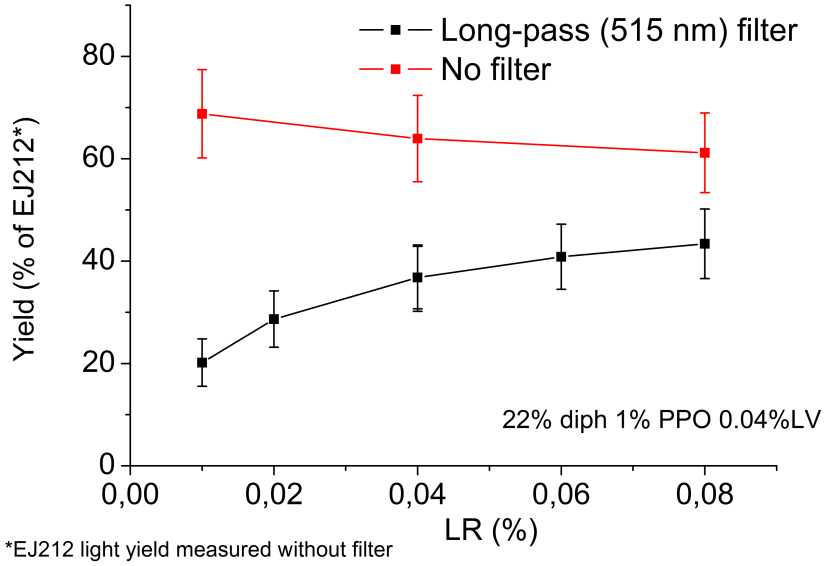

Fig. 4. Scintillation light yields recorded by red enhanced PMT detector with a ^{241}Am alpha source. Analysis has been done comparing mesurements achieved with and without 515 nm long-pass filter.

with 0.02% LR concentration, being the best compromise between spectral matching factor and overall light emission. With this sample, a 40% improvement has been recorded with respect to a previously developed blue emitting polysiloxane based scintillator (Fig. 5), containing 1% PPO and 0.02% LV.

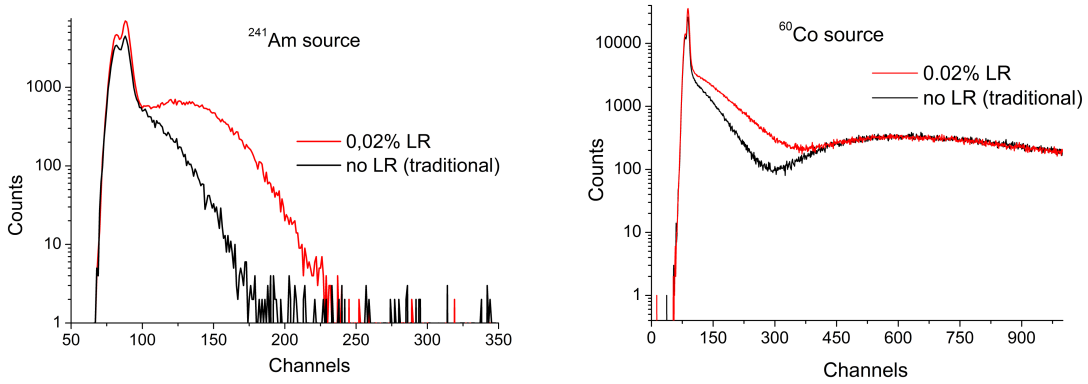

Fig. 5. Scintillation spectra recorded wit APD for alpha particles (left) and gamma rays (right). Comparison between polysiloxane based scintillators with and without 0.02% LR is shown.

3.3 Neutron detection

The response of red emitting polysiloxane based scintillators to 2.32 MeV fast neutrons has been tested at CN accelerator at INFN Legnaro National Laboratories. TOF technique was used in order to discriminate between gamma rays and neutrons and the related counts vs. time spectrum is shown in

Fig. *6* for the sample with 0.02% LR concentration. The reported spectrum clearly shows how this material is capable of fast neutron detection. Neutron detection efficiency comparable to that of the commercially available plastic scintillators has been estimated.

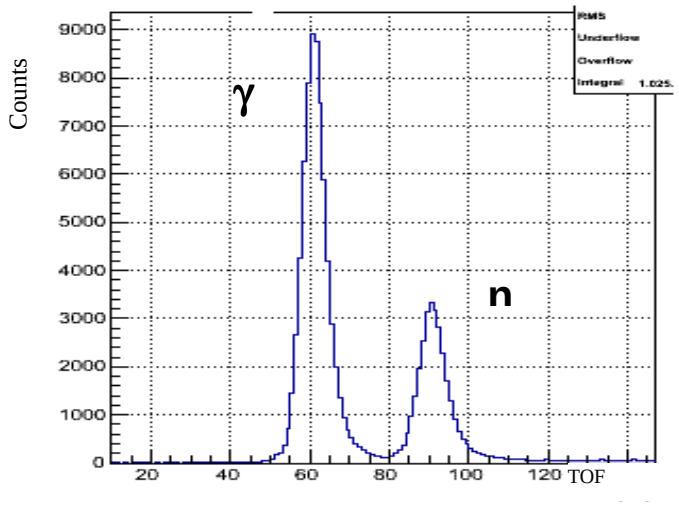

Fig. 6. TOF spectrum of a red emitting polysiloxane based scintillator with 0.02% LR. The peak on the left corresponds to the gamma ray signal while the one on the right is the neutron peak.

3.4 Preliminary results on pulse shape discrimination

A preliminary analysis has been carried out on the possibility to perform neutron-gamma discrimination on the basis of pulse shape discrimination (PSD). Up to date, good results with this technique have been achieved only with liquid scintillators and this was one of the reasons for their widespread use in neutron detection.

Fig. 7 shows the normalized average pulse shapes for gamma rays from different sources and for 2.32 MeV neutrons from CN accelerator for polysiloxane based scintillator with 8% PPO and 0.02% LV. Reported shapes are the average over 1000 pulses.

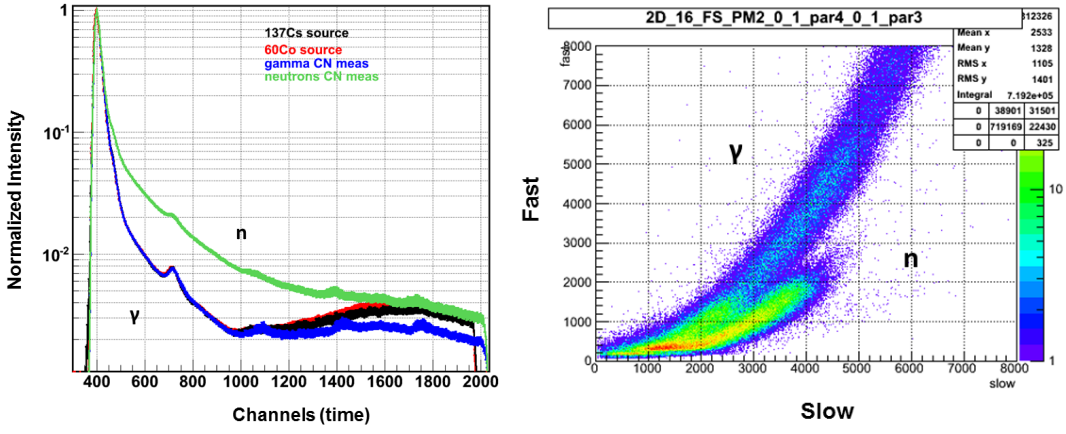

Fig. 7. Normalized pulse shape spectra of gamma rays from different source and neutrons. A clearly longer tale can be seen for neutrons signal (left). Fast vs. slow plot showing a different behaviour between neutron and gamma rays (right). Values reported on the fast axis (ordinate) are achieved upon signal integration over a 30 ns time interval, for the slow axis (abscissa) a time interval around 500ns has been used.

A clear difference can be noticed between neutrons and gammas as regarding the signal shape, while gamma rays from various sources have the same pulse shape. This feature could allow the performance of an efficient neutron-gamma discrimination, as clearly visible from the fast vs. slow graph (Fig. 7) achieved integrating the pulses over a time interval of about 30 ns (ordinate axis) and 500 ns (abscissa axis). On this graph, the different behaviour of neutrons and gamma rays is highlighted. Integration time intervals were chosen on the basis of the decay time spectra for preliminary investigations, further optimization of the PSD algorithm has however to be done. Secondary peaks appearing on the fluorescence decay spectra are instrumental effects due to after-pulses produced inside the PMT by electron reflections on the dynodes.

4.Conclusions

In this work, new red emitting polysiloxane based scintillators have been developed in order to optimize spectral matching with APD detector having higher response in the red part of visible spectrum. With this aim, optical properties of samples with different LR concentrations have been studied using fluorescence emission spectroscopy. The energy transfer between dyes has been further studied by measuring the scintillation light yield to alpha particles using a red enhanced PMT with or without long-pass optical filter and the results were in good agreement with optical characterizations.

On this bases, the scintillation light yield of the best performing sample with 1% PPO, 0.04% LV and 0.02% LR concentration has been measured with an APD detector for both ^{241}Am alpha particles and ^{60}Co gamma rays and results have been compared with scintillation yield achieved from a previously studied blue emitting polysiloxane based sample and an excellent 40% light yield improvement was recorded for both radiations.

This result paves the way to the development of a new compact radiation detection system employing compact, rugged and magnetic field insensitive APD detectors instead of the traditionally used PMT, with a great possible reduction in system volumes and also in production costs.

Red emitting polysiloxane based scintillator was also tested as fast neutron detector with 2.32 MeV neutron beam and results achieved from TOF measurements proved this material to be also efficient in fast neutron detection. The most promising preliminary result on polysiloxane based scintillators comes from the possibility to perform efficient pulse shape discrimination between neutrons and gamma rays. This technique was efficiently performed so far only using awkward and toxic liquid scintillators and these preliminary results open the door to their replacement with more compact, handy and cheap polysiloxane based scintillators.

Acknowledgments

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