3D Printing Neutron Detectors using BN/ZnS Resin

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ABSTRACT: In this paper we demonstrate that it is possible to produce low cost neutron-sensitive detectors using stereo-lithography additive manufacturing. A curable scintillating resin is made by mixing BN:ZnS with a commercially available UV resin. This resin is used to print several small area neutron detectors made of arrays of BN:ZnS cones that can be directly coupled to a photo-multiplier tube.

KEYWORDS: 3D Printing; Neutron Detection; Radiation Detection.
1. Introduction

Helium 3 detectors are considered the “gold standard” for neutron detection due to their high efficiency and insensitivity to gamma radiation. Driven by shortages of Helium-3 in recent years however, there has been rapid development in alternatives to this technology using solid state detectors or scintillating materials. Li:ZnS composite materials are one such alternative that are sensitive to thermal neutrons. A neutron capture by Li results in a long characteristic decay time of the ZnS scintillator pulse which can be easily identified using pulse shape discrimination techniques. Since Li:ZnS is opaque, the sensitivity of a detector is governed by the total active surface area coupled to a photo-detector. Several designs have made use of rippled structures, or light guides to effectively increase the total sensitive area of these detectors with a minimal number of photo-detectors [1][2]. In [3], it was shown that unenriched hexagonal BN mixed with ZnS was a suitable lower cost alternative to Li:ZnS provided large area, low cost detectors could be constructed using wavelength shifting light guides for readout.

Recently, with rapid advances in the availability and reduction in cost of 3D printing, there have been several studies on the development of 3D printing plastic scintillator [4][5][6]. In [5], scintillating dopants are mixed with a photopolymer resin to produce a solution that can be cured (solidified) using 385 nm light. This makes it possible to use StereoLithography (SL) to produce 3D objects by curing multiple 2D images from the resin and stacking them on top of one another as shown in Figure 1. A high efficiency scintillator resin that can be 3D printed using SL has the potential to radically transform the radiation detector field, making it possible to prototype complex structures that are not feasible using standard manufacturing techniques.

Figure 1. Stereolithography 3D printing method. Objects are “sliced” into multiple 2D layers which are cured by a UV screen projected into the resin container. 3D objects are constructed by curing many different 2D layers on top of one another, moving the print bed up slightly after each layer.
In this paper we demonstrate that it is possible to 3D print complex, neutron-sensitive geometries by mixing unenriched BN:ZnS with a UV curing resin. Since only the top surface layers of a BN:ZnS or Li:ZnS detector are sensitive to neutrons due to the material’s opaqueness, it is feasible to mix these compounds into commercially available UV curing resins to produce sensitive detector prototypes at low cost. This paper is organised as follows; in section 2 the scintillating resin mixture and curing procedures are discussed, in section 3 the scintillator testing method is described, in section 4 the pulse discrimination performance for three differing geometries is evaluated, before finally section 5 discusses the conclusions and potential uses for this technique.

2. UV Cured BN/ZnS Scintillator

To produce a neutron sensitive scintillating resin, BN and ZnS powders were mixed into a commercially available clear UV resin from AnyCubic Photon Ltd [7] with a weight ratio of 1 BN : 5 ZnS : 5 Clear Resin.

In [3], ratios greater than 1:3 of BN to ZnS were shown to satisfy the condition that each BN molecule is sufficiently surrounded by ZnS that the neutron capture products lead to a strong scintillation signal. A slightly larger conservative fraction of ZnS was chosen in this work to ensure this was still the case in the UV curable resin mixture. To ensure adequate mixing of the BN:ZnS compound, these were first mixed dry inside a black container. The resulting powder was then placed in a slow magnetic stirrer as UV resin was poured in to produce an opaque white resin. The scintillating resin was slowly stirred for two hours to ensure a good solution with no air bubbles. Finally, this resin was stored in a blacked out container to ensure no curing of the resin occurred on the outside of the jar before being used for 3D printing.

Ideally, the ratio of BN:ZnS to resin should be as high as possible as the resin is insensitive to neutron interactions, however initial tests found that mixtures with a ratio much higher than 1:1...
began to behave as a non-Newtonian fluid that made it incredibly difficult to produce a well-mixed solution of BN:ZnS:resin that could be printed with.

An AnyCubic Photon SL printer was used to construct 3D objects from this new resin, curing it with a 405 nm UV screen [8] with a voxel resolution of ~10µm. When trying to print with the scintillating resin using the standard curing settings suggested for the original clear resin, many prints failed as the resin tended to cure directly to the UV screen instead of the print bed. This was determined to be due to poor UV light transport through the opaque resin; since insufficient light could pass through, the first few layers the resin was only slightly cured far away from the UV screen. This problem was solved by printing the first few layers of disposable support structures using a clear UV resin before filling the resin container with BN:ZnS:resin mixture once a stable base on the print bed had been formed.

This dual resin method allowed 3D objects to be formed with the UV resin, however as shown in Figure 2, it was still not possible to produce high quality objects due to the print bed developing a skew over the course of a print. This problem was found to only occur when using vertical layer sizes < 50 µm. It is believed this is a result of the slightly non-newtonian behaviour of the resin when mixed at a 6:5 powder to resin ratio. This behaviour leads to a minimum compression thickness below which excess pressure is applied to the print bed that leads to a small skew after each layer is cured. This results in failed print parts with noticeable warping.

Changing to a minimum vertical layer size of 50 µm still allowed complex prints to be successfully produced from the resin. Figure 2 shows a successfully printed neutron detector made of an array of 3 mm radius BN:ZnS cones that can be directly mounted onto the face of Photo-Multiplier Tube (PMT) for readout. This cone structure makes it possible to couple a larger surface area to a PMT compared to a flat BN:ZnS sheet simply by changing the geometry of the printed part. Since the minimum compression thickness is believed to be a function of the powder to resin ratio, it is possible that reduced mixing ratios could be used to produce parts with a much finer vertical resolution in the future albeit with lower detection efficiency.

![Diagram of neutron detector setup](image)

Figure 3. Photo-multiplier test stand layout. A neutron capture on the BN:ZnS cone detector results in a long scintillator pulse in the PMT which is tagged during offline analysis of the DT5740 digitiser data.

### 3. Scintillator Testing

To evaluate the neutron discrimination power of this 3D printed cone detector, a test stand was setup inside a dark box as shown in Figure 3. The neutron detector was mounted directly onto the front face of an ET-Enterprises 9902B PMT. The PMT was supplied with a 1.2kV High Voltage (HV) bias using an ET-HV3820AN base. The output pulse from the PMT was fed into a CAEN DT5740 Digitiser, which digitised the signal into 12 ADC-bits at a rate of
62.5MHz. Since this digitiser does not have a Pulse Shape Discrimination (PSD) trigger built in, a fixed threshold discriminator set at 3mV was used to trigger the digitisation of a full pulse which was saved for further processing offline. It is expected that a setup with dedicated PSD could improve the efficiencies of these detectors by removing dead time due to low amplitude background noise, however a low hardware threshold on DT5740 was found to be sufficient to demonstrate the neutron sensitivity of these detectors, provided long exposure times were considered, whilst allowing the level of smearing between neutron events and background at very small pulse amplitudes to also be evaluated.

In early tests it was noted that the ZnS was easily activated by UV light, therefore each 3D print was left for several days in a dark box after printing. In each test, the BN:ZnS detector was removed from storage and mounted inside the test stand before being left for one hour extra for any stray activation of the ZnS during its installation to decay. Following this installation period, a 24 hour data taking period was started on the digitiser. To provide an optional source of neutrons, a Cf-252 source (1.92kBq) was placed inside the dark box surrounded by a HDPE moderator, approximately 20cm away from the detector. As expected, neutrons from the Cf-252 source were found to produce extremely long pulses in the BN:ZnS mixture, of the order of several microseconds. Example pulses from a characteristic neutron and background pulse can be seen in Figure 4.

Using the digitised pulses collected over each 24 hour period, a Pulse Shape Discrimination (PSD) algorithm was applied to the pulses offline. A PSD metric was defined as the ratio of “short” and “long” integrals. Given a trigger time, $T_0$, the “short” integral was defined as the total pulse area from $T_0-48$ ns to $T_0+48$ ns, and “long” was the total area from $T_0-48$ ns to $T_0+2000$ ns. A width of 96 ns ($\pm 3$ time samples) for the short integral was chosen based on studies of PMT background noise without any neutron-detector installed in the test-stand. Plotting this distribution as a function of the pulse amplitude in Figure 4 shows a distribution between $0 < \text{PSD} < 1.5$ due to single background pulses. When a Cf-252 source was placed inside the dark box, a clear excess of events with long decaying pulses appears at high pulse amplitudes in the $1.5 < \text{PSD} < 10$ region. The large amount of noise due to background pulses extends to high PSD values at low peak amplitude when pulse pileup leads to a higher than normal “long” integral. This background rate was found to slowly decay over the 24 hour period. Due to the long activation times of ZnS it is expected that a longer waiting period of more than 72 hours following opening of the dark box would improve the detector response at lower peak amplitudes.

Figure 4. Characteristic difference in pulse decay times for neutrons and gamma/dark-noise events for a BN/ZnS scintillating mixture. The long decay time of neutron events are used in their characterisation. The original PMT pulses have been inverted for legibility.
4. PSD Performance Evaluation

This novel development in 3D printed structures makes it possible to investigate alternative ways to print optimised structures. In this section we briefly investigate the possible effect cone size could have when producing a neutron detector similar to that shown in the previous section. By printing narrower conical structures with the same height, the active area coupled directly to the PMT should be effectively increased. To investigate the effect this could have on discrimination power, two alternative conical geometries were investigated. Conical radii of 2 mm (small), 3 mm (medium), and 4 mm (large) were considered as shown in Figure 6. The approximate increase in surface area compared to a flat disk when neglecting the sensitive surface of one cone being blocked by another, is 401% (small), 273% (medium), and 211% (large) respectively.

For each geometry study, the analysis procedure described in Section 3 was repeated. Digitiser pulses were recorded for a 24 hour period, with and without a Cf-252 source inserted into the PMT test stand, before being analysed offline. As can be seen in Figure 6, the addition of the Cf-252 source produces a clear excess of events around PSD ~ 3–4 for peak pulse amplitudes greater than 15 mV due to neutron interactions in the BN:ZnS. No significant difference in the shape or position of this distribution was observed in these limited statistic samples, observing 613 (small), 603 (medium), 610 (large) neutron candidate events for each geometry.

One possible reason for this is due to the voxelised nature of the 3D printed cone arrays. When considering perfectly smooth cones there is a large effective increase in area with reducing cone diameter. In a voxelised geometry however, all surfaces are either directly parallel or perpendicular to the PMT face when imaged at a 10 µm scale. Therefore the increase in effective area is likely to be significantly reduced. Despite this lack of improvement in discrimination power, these studies have demonstrated that the UV curing resin produced in this paper can be used to produce extremely fine scale features without further degradation of the detector sensitivity.

Figure 5. Pulse shape discrimination results for a UV-cured neutron detector with (left) and without (right) a Cf-252 source placed inside the test stand. The ray dashed line indicates a PSD cut boundary. A clear excess with a large “long” integral is seen in the presence of a neutron source.
5. Conclusions

This work has demonstrated that it is feasible to produce novel neutron detectors using additive manufacturing by mixing BN:ZnS compounds into commercially available UV resin. This makes it possible to produce complex structures that could be used to optimise detector sensitivity. Whilst changes in total surface area in a printed cone array geometry were found to not significantly improve the pulse shape discrimination power of the detectors, alternative geometries produced on printers with finer resolution could improve this in the future.

The use of low cost clear resin to print support structures was found to not only aid in print stability but also reduce the total cost of the prints. Custom built 3D printers could build on this in the future by using in-situ resin mixing to produce complex structures with varying levels of scintillator doping across a part. This could potentially provide positional information, or sensitivity to mixed radiation fields.

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Figure 6. PSD comparisons for neutron detectors with variable cone dimensions for pulse amplitudes > 15mV. All pieces were found to be sensitive to a Cf-252 source, but showed no significant variation in pulse height or discrimination power. (top-right) Small cone geometry, (bottom-left) medium cone geometry, (bottom-right) large cone geometry.
References

1. Thermal Neutron Detector EJ-420, Eljen Technology (2016) (datasheet): http://www.eljentechnology.com/images/products/data_sheets/EJ-420.pdf,

2. J. Barton, A Novel Neutron Multiplicity Detector Employing ZnS:LiF, J Phys G:Nuc 17 (1991).

3. E. J. Marsden, Large area thermal neutron detectors for security applications, Doctoral dissertation, University of Sheffield (2013).

4. Fargher, et Al. The use of 3D printing in the development of gaseous radiation detectors in EPJ Web of Conferences (Vol. 170, p. 01016 2018)

5. J. Son, et Al. (2018). Improved 3D printing plastic scintillator fabrication. Journal of the Korean Physical Society, 73(7), 887-892.

6. Y. Mishnayot, et Al. 3D Printing of Scintillating Materials. arXiv:1406.4817. (2014).

7. Anycubic Photon Resin, ANyCubic (2019) datasheet: https://fepfilm.eu/pobieranie/msds_anycubic_resin.pdf

8. Anycubic Photon Printer, AnyCubic (2019) datasheet: https://www.anycubic.com/products/anycubic-photon-3d-printer