New Radiation-Hard Wavelength Shifting Fibers

Burak Bilki, Yasar Onel, Emrah Tiras, James Wetzel and David Winn

***Abstract*—R&D on new radiation-hard wavelength shifting fibers is gaining crucial importance as the radiation conditions projected for the High Luminosity LHC and future hadron and lepton colliders reach unprecedented levels. We have identified materials with proven radiation resistance, long Stokes shifts to enable long self-absorption lengths, with decay constants $\sim$ 10 ns or less. Here we describe two strong candidates' Doped ZnO:Zn/Mg and 3HF (3-hydroxyflavone) properties along with other material options and report on basic performance characteristics of recent prototypes.**

I. Introduction

Unprecedented radiation conditions are projected for future circular and linear colliders [1], [2], [3] as well as the Large Hadron Collider in the High-Luminosity era [4]. In parallel with the effort of identifying radiation-hard scintillator materials, an R&D on radiation-hard wavelength shifting (WLS) fibers should also be carried out in order to facilitate a complete active medium for detectors under harsh radiation conditions.

In this context, we have identified materials with proven radiation resistance, long Stokes shifts to enable long self-absorption lengths, and with decay constants $\sim$ 10 ns or less. Their absorption is well-matched to the emission of the radiation-hard thin film scintillators such as quartz plates with pTerphenyl (pTp) or ZnO coatings. To absorb 90 % of the incident scintillation light, film thicknesses of $\sim$ 1-2 μm are needed (similar to the technique of WLS deposition on PMT for UV detection).

II. Thin Film Radiation-Hard and Fast Scintillators

Previously, we validated the principle with in-house methods of coating quartz fibers with pTp. We produced many coated fibers and formed ribbons of fibers to sandwich between quartz plates. Figure 1 (top) shows the semi-assembled coated fiber ribbons and the quartz plates. The assembly was tested in electromagnetic showers and the response is shown in Fig. 1 (bottom). The validation of the concept that a signal generation and propagation in such fibers would be possible was done with these results showing a clear difference of the setup when data was taken in the absence of the electromagnetic shower.

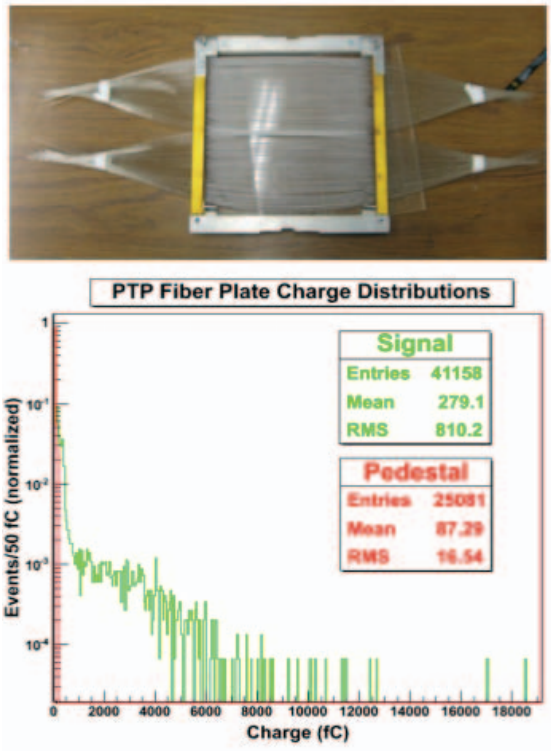

Fig. 1. Picture of the tile semi-assembled to bundles of pTp deposited quartz fibers (top) and the response of the tile to the electromagnetic shower maximum (bottom).

Among promising thin film scintillating fluors, ZnO:Ga (1 - 4 %) [5] and $CeBr_3$ [6] are outstanding scintillators for radiation-hard wavelength shifting fiber applications:

- **ZnO:Ga:** 390 nm peak, 0.4 ns decay time, 15,000 photons/MeV, dE/dx = 0.510 MeV/mm, 5.6 g/cc, when in microcrystalline form, is a CRT phosphor with 1 Grad resistance to 20 keV electrons.
- **$CeBr_3$:** 140 % light yield of LYSO, 4x brighter than plastic scintillators, 60,000 photons/MeV, 371 nm peak emission, 17 ns decay, n = 1.9, ρ = 5.33 g/cc, dE/dx=0.67 MeV/mm.

Since the Ce^{+3} ion is intrinsic to $CeBr_3$, rather than doped into it, we expect the radiation damage resistance of $CeBr_3$ to be at least as good as CeF_3 or better (i.e. 50 Mrad) [7], [8]. CeF_3 could be considered, but its light yield is about 5x less, its decay time is 30 ns, its emission is quite short (340 nm), and its physical vapour deposition (PVD) temperature is around 1500 °C compared to 725 °C of $CeBr_3$. Table I summarizes the specifications of interest of these materials.

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TABLE I
SUMMARY OF SCINTILLATION PROPERTIES OF ZNO:GA AND $CeBr_3$.

	ZnO:Ga	**$CeBr_3$**
Light yield (γ/MeV)	15,000	60,000 - 65,000
Decay (ns)	0.4 - 0.5	17
T_{melt} (°C)	1980	722
dE/dx (MeV/cm)	5.1	6.7
Peak λ (nm)	375	371
Index n	1.85	1.91
Density (g/cc)	5.6	5.33

III. QUARTZ CAPILLARIES WITH ORGANIC WLS CORES

Soft WLS materials fill capillary cores via vacuum melt imbibition, such as pTerphenyl and Stilbene admixtures (long Stokes shift; $\sim$ 200 °C), bisMSB, POPOP, 3HF+naphthalene (radiation-hard; 85 °C) or others. The quartz capillaries available commercially are cladded with fluorine-doped quartz, and then buffered with a thin ($\sim$ 10 micron) UV transparent polymide buffer. Inner diameters are up to 750 microns and the capillaries are flexible with 5 cm radius.

We constructed demonstrative quartz capillaries with anthracene and placed a bunch of 7 fibers into an 80 GeV electron beam. A picture of the capillary tubes filed with Anthracene and a typical pulse shape obtained with a finger photomultiplier tube attached to one end of the fibers is shown in Fig. 2 top and bottom respectively. The typical observed pulse was 8-9 photoelectrons.

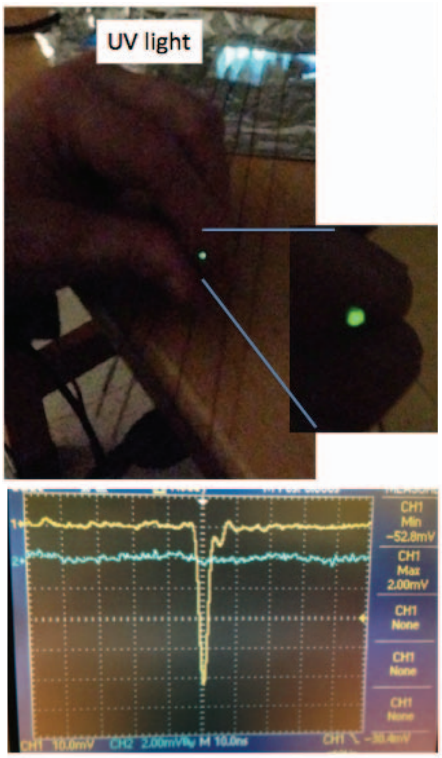

Fig. 2. Pictures of capillary tubes filled with anthracene (top) and the pulse observed on the scope at the electromagnetic shower maximum (bottom).

We then performed preliminary studies of capillaries filled with 3HF [9]. Figure 3 (top) shows pictures of the constructed fibers along with the finger scintillator tile they are coupled with. The capillaries were 100 μm core, 360 μm outer diameter with UV transparent buffer. They constituted less than 1/25 of usual WLS fibers such as those of CMS Hadron Endcap Calorimeter wavelength shifting fiber core volume [10]. Only 3 of such capillaries were tested. For realistic tests, larger capillaries would be needed. Figure 3 (bottom) shows the response of a finger tile read out with the 3HF capillaries at the electromagnetic shower maximum. Despite the fractional dimension compared to a realistic WLS fiber, the results indicate that the 3HF filled capilarries can be successfully utilized in future implementations.

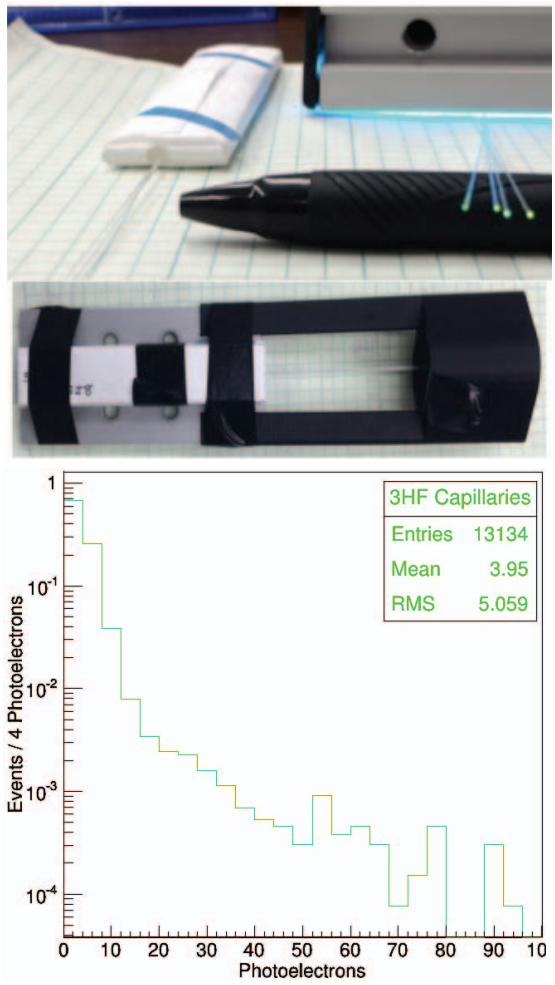

Fig. 3. Picture of the 100 μm 3HF core quartz capillaries (top) and the response of the finger tile read out with the capillaries to the electromagnetic shower maximum (bottom).

To assemble and protect these materials, especially for WLS fibers, transparent elastomers and gels exist which are radiation-resistant. Among these are silicone elastomers (Sylgard 184 - retain $\sim$ 90 % transparency at $\sim$ 100 Mrad), as do high purity polyurethane potting compounds (50 Mrad), and PolyVinyl Alcohol (PVA) gels. Teflon-AF readily dissoves in perfluorocarbon liquids (fluorinerts FC-75 and similar). These materials, when used to convey WLS materials, do not need to share their ionization energy with the fluor, as necessary in a high quality scintillator; rather, there only needs to be enough of the WLS fluor uniformly conveyed in the transparent matrix

to absorb the incident shorter wavelength light. Figure 4 shows the picture of Teflon-AF (top) and Sylgard 184 transmission after 0 - 91 Mrad of gamma dose (bottom) [11].

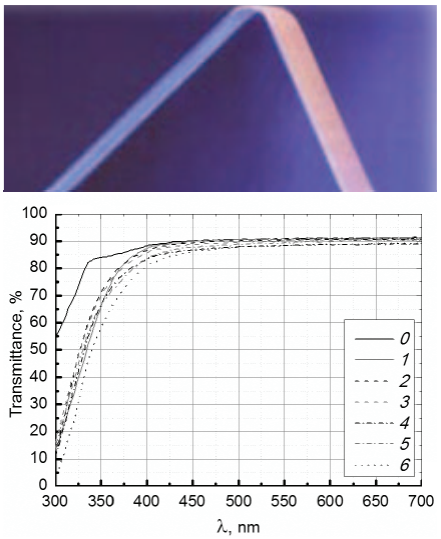

Fig. 4. Teflon-AF - as a cladding at least 10 Mrad resistant (not tested beyond 10 MRad) (top). Sylgard 184 transmission after 0 - 91 Mrad of gamma dose (bottom).

We have investigated adding 3HF (3-hydroxyflavone) and nanodots of scintillating/shifting diamond and have produced the first samples. Figure 5 shows pictures of CdSeZnO nanodots in Sylgard 184 injected into capillaries Teflon - AF Quartz (top) and raw CdSeZnO nanodots in Sylgard 184 for hot injection into capillaries (bottom).

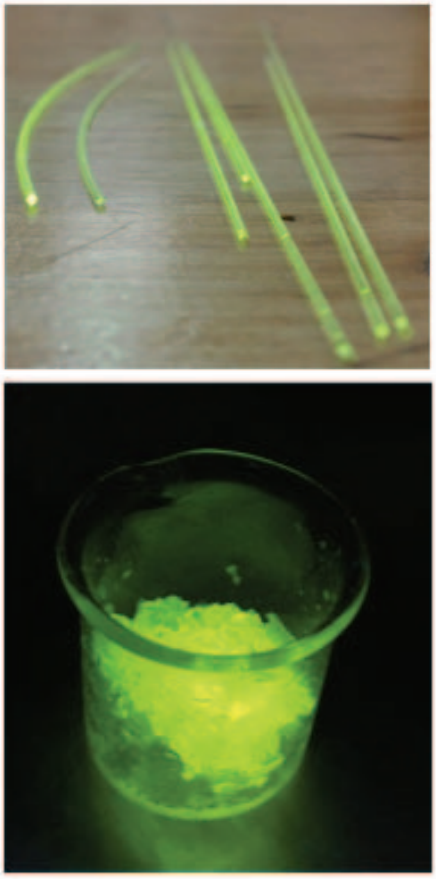

Fig. 5. Pictures of CdSeZnO nanodots in Sylgard 184 injected into capillaries Teflon - AF Quartz (top) and raw CdSeZnO nanodots in Sylgard 184 for hot injection into capillaries (bottom).

IV. Scintillating Glasses

Another area of investigation in terms of scintillating fibers is based on Cerium and/or Boron doped scintillating glasses. In collaboration with Coe College, Iowa, we developed special glasses with several implementations so far.

^{10}B-based glass scintillators were first studied with a focus on glasses containing Boron, Sodium, Aluminum, and Cerium as the scintillator. In a separate study, it was also shown that glasses with Boron content increase in efficiency with higher Boron concentration in glass. This shows that Cerium-doped Borosilicate glasses, even with natural Boron, can be effectively used as scintillators.

In a recent study, a soda-lime borosilicate glass was chosen due to its well-studied features, such as low refractive index and high transparency that make it a good candidate for adding a cerium dopant. The glass-forming conditions of Boron oxide are well studied. This investigation focused on maximizing the Boron content, while yielding the most light out of Cerium scintillation. Initially, scintillating glasses with 70 % B_2O_3 content were successfully made. These glasses were found to be highly hygroscopic, drastically decreasing their optical clarity.

In order to make the samples more stable, the Boron content was reduced and glass samples were made with SiO_2 ranging from (molar %) 42.7 % - 72.7 %, B_2O_3 ranging from 0 % - 30 %, 14 % Na_2O, 9 % CaO, 4 % MgO, .15 % Al_2O_3, .1 % Fe_2O_3, .03 % K_2O, .02 % TiO_2 and Ce dopant ranging from 0 - 5 %. The composition of the final glass sample was $62.7SiO_2$-$14Na_2$0- $10B_2O_3$-9CaO-4MgO-.$15Al_2O_3$-.$1Fe_2O_3$-.$03K_2O$-.$02TiO_2$ + .01Ce (molar %), using the precursors $CeCl_3$, Na_2CO_3, $2H_3BO_3$, SiO_2, Al_2O_3, CaO, MgO, K_2CO_3, TiO_2 and Fe_2O_3, all of at least 99 % purity. Samples with both ^{10}B and natural Boron were prepared for tests. The components were individually weighed in a glass beaker, zeroing the scale after each component was added. Chemicals were added in order of least to most contribution to the total mass. The Cerium, which came in small pellets, needed to be thoroughly crushed with a mortar and pestle before adding and weighing it. After all the components were added. The powder was mixed for ten minutes with a stirrer, then three small platinum crucibles were filled with a portion of the mix. The crucibles were heated in the same furnace for 15 minutes at 1550 °C. After the first three batches were heated and cooled sufficiently, more powder was added to each crucible and the crucibles were heated again in the same manner until no powder remained. Immediately after the last heating all the crucibles were simultaneously poured into a 5 cm x 5 cm x 1 cm steel mold pre-heated to 300 °C. The steel mold was then annealed on a hot plate at 300 °C for 30 minutes. The

resulting plates of glass were tested for structural integrity. The protruding parts were sanded away and polished.

Ideally, the emission peak of the glass would be in a region of high transmission. Cerium is known to have host-dependent scintillation properties due to its valance electron energy variation. The final sample was found to have light emission wavelengths from 325 nm to 500 nm with peak at 392 nm. Tests using the UV-VIS-NIR spectrometer revealed the light transmission of the sample to be $\sim$ 50 % at this peak emission wavelength. Although it is not the optimal transmission, this much light emission should be enough for particle detectors using high quantum efficiency photomultiplier tubes. The most important aspect of these scintillating glasses is that they can be drawn into fibers ending up with radiation-hard WLS fibers. Figure 6 shows pictures of Cerium doped scintillating glasses (top) and transmittance and emission properties of these glasses (bottom).

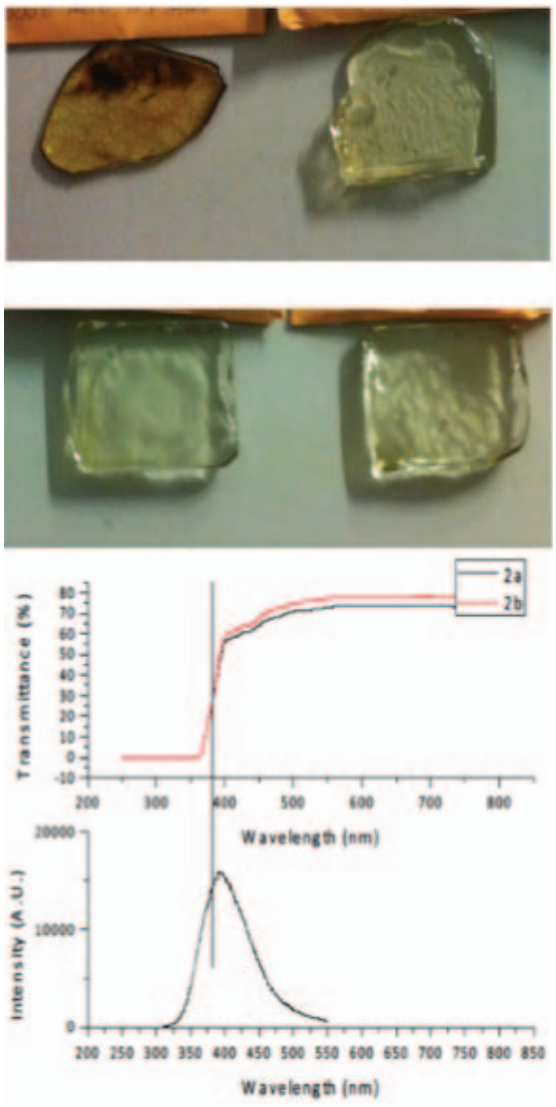

Fig. 6. Pictures of Cerium doped scintillating glasses (top) and transmittance and emission properties of the glasses (bottom).

V. Conclusions

Any future High Energy Physics implementation that requires radiation-hard scintillators will also potentially be in need of radiation-hard wavelength shifting (WLS) fibers. Although direct coupling of the photodetectors to the scintillating tiles is on the rising trend, there are particularly high radiation environments where the photodetectors as well as the readout electronics cannot be placed inside the detector.

In this context, we have identified materials with proven radiation resistance, long Stokes shifts and with decay constants at the order of 10 ns.

WLS materials to deposit as thin films on quartz fibers or in or on quartz capillaries include:

- **Doped ZnO:Zn/Mg:** It is a long shift WLS material with exceptional radiation resistance and has a long Stokes shift from the near UV to the blue-green.
- **3HF (3-hydroxyflavone):** $<$ 10 ns decay; long Stokes shift 180 nm, near UV to green 490 nm, T_{melt} = 170 °C, n = 1.68 - tested to 100 Mrad with no observable change. It is easily deposited with thermal evaporation, yet has a high enough melting temperature that it can be overcoated with silica or alumina films.

To assemble and protect these materials, especially for WLS fibers, transparent elastomers and gels exist which are radiation-resistant. Among these are silicone elastomers (Sylgard 184), as do high purity polyurethane potting compounds, and PolyVinyl Alcohol (PVA) gels. Teflon-AF readily dissoves in perfluorocarbon liquids (fluorinerts FC-75 and similar). We have investigated adding 3HF (3-hydroxyflavone) and nanodots of scintillating/shifting diamond and have produced the first samples.

Several small-scale samples of capillaries filled with WLS cores (Anthracene, 3HF) and thin film deposited quartz fibers (pTerphenyl) have been produced. Preliminary beam test results indicate that realistically-sized samples will provide radiation-hard, efficient wavelength shifting fibers.

We have also produced Cerium and/or Boron doped scintillating glasses of which the performance parameters can be fine tuned by adjusting the concentration of the ingredients and can also be drawn into fibers.

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