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High Energy Resolution Transparent Ceramic Garnet Scintillators

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ABSTRACT

Breakthrough energy resolution, $R(662\text{keV}) < 4\%$, has been achieved with an oxide scintillator, Cerium-doped Gadolinium Yttrium Gallium Aluminum Garnet, or GYGAG(Ce), by optimizing fabrication conditions. Transparent ceramic Cerium-doped Gadolinium Garnet, GYGAG(Ce), has a peak emission wavelength of 550 nm that is better matched to Silicon photodetectors than to standard PMTs. We have therefore designed a spectrometer based on pixelated GYGAG(Ce) on a Silicon photodiode array that can provide $R(662\text{ keV}) = 3.5\%$. In comparison, with large 1-2 in³ size GYGAG(Ce) ceramics we obtain $R(662\text{ keV}) = 4.6\%$ with PMT readout. We find that ceramic GYGAG(Ce) of a given stoichiometric chemical composition can exhibit very different scintillation properties, depending on sintering conditions and post-anneal treatments. Oxide scintillators tend to exhibit multiple scintillation decay components, including some very slow components, classified as “afterglow,” and related to shallow traps, thought to be predominantly due to oxygen vacancies. Among the characteristics of transparent ceramic garnet scintillators that can be controlled by fabrication conditions are: scintillation decay component amplitudes, intensity and duration of afterglow, thermoluminescence glow curve peak positions and amplitudes, integrated light yield, light yield non-proportionality, as measured in the Scintillator Light Yield Non-Proportionality Characterization Instrument (SLYNCl), and energy resolution for gamma spectroscopy. Garnet samples exhibiting a significant fraction of Cerium dopant in the tetravalent valence also exhibit: faster overall scintillation decay, very low afterglow, high light yield, but poor light yield proportionality and degraded energy resolution.

Keywords: scintillators, gamma ray detection, transparent ceramics, garnets

1. INTRODUCTION

Since 2006, we have been working to identify and develop a transparent ceramics scintillator for gamma ray spectroscopy. Since one of the first transparent ceramic materials to be demonstrated with excellent phase stability, as required for transparency, is Yttrium Aluminum Garnet, YAG [1, 2], we began our search with garnets, substituting Gadolinium for Yttrium, for higher gamma stopping. We found that Gadolinium Aluminum Garnet GAG, exhibits poor phase stability due to the non-ideal match of the ionic radii of Gd and Al to the required 8-fold (A), 6-fold (B) and 4-fold (C) coordinated sites of the formula $A_3B_2C_3O_{12}$. Table 1 shows the progression we made through a variety of garnet compositions employing the approach of “intersubstitutional ions” in which multiple cations are included that can substitute on a given coordinational site. Among the characteristics of the Cerium-doped Gadolinium Yttrium Gallium Aluminum Garnet, GYGAG(Ce), composition that we have narrowed our focus on are: (1) Increased light yield compared to YAG, due to ability for excitation to migrate on Gd^{3+} as a stoichiometric sensitizer for Ce^{3+} , (2) Green emission (for better PMT detection), as opposed to yellow emission of GSAG(Ce) and GYAG(Ce), (3) No intrinsic trap, as present in Sc-substituted garnets, that reduces the light yield, (4) Substitutional flexibility and subsequent compositional flexibility arising from the ability of Y to substitute on both the 8- and 6-fold sites and Ga to substitute on the 6- and 4-fold sites [3]. The GYGAG(Ce) ceramic scintillator offers: (1) high fast light yield of $>40,000\text{ Ph/MeV}$ and principal decay of $\sim 100\text{ ns}$, (2) photopeak

efficiency superior to NaI(Tl), (3) excellent light yield proportionality, (4) ease of uniform fabrication via ceramics processing due to the use intersubstitutional ions, and (5) no intrinsic radioactivity. In our reports on GYGAG(Ce) ceramics [4-10], we measured energy resolution at 662 keV of 4.9% with 1 in³ and PMT readout, 4.3% with 1 cm³ and PMT readout, and 4% with 0.05 cm³ and Silicon photodiode readout. Nanocerox, Inc. is now beginning production of GYGAG(Ce) of transparency and scintillation properties comparable to the ceramics fabricated at LLNL for commercial sale (Figure 1).

Table 1. Progression of the LLNL effort to identification of GYGAG(Ce) as offering a robust combination of chemical composition and scintillation properties for production as a transparent ceramic scintillator for gamma ray spectroscopy.

	2006-2007		2007-2008		2008-2009		2009-present
Composition	GAG: Gd ₃ Al ₅ O ₁₂	GYAG: Gd _{1.5} Y _{1.5} Al ₅ O ₁₂	GGG: Gd ₃ Ga ₅ O ₁₂	GSAG: Gd ₃ Sc ₃ Al ₂ O ₁₂	GYSAG: Gd _{1.5} Y _{1.5} Sc ₃ Al ₂ O ₁₂	GGAG: Gd ₃ Ga _{2.5} Al _{2.5} O ₁₂	GYGAG: Gd _{1.5} Y _{1.5} Ga _{2.5} Al _{2.5} O ₁₂
Phase Stability	Poor	Moderate	Excellent	Excellent	Excellent	Moderate	Excellent
γ-LY(Ph/MeV)	—	40,000	—	25,000	30,000	50,000	50,000
En. Res. (662 keV)	—	11%	—	11%	10%	4-7%	3-5%

Since we identified GYGAG(Ce) as a scintillator capable of $R(662\text{ keV}) < 5\%$, a breakthrough performance for oxide scintillators, many efforts have been directed toward Gd-based garnets, most studying single crystal growth, powder synthesis and/or computational techniques, and are aimed at identifying high light yield compositions [11-15]. So far, single crystal growth has not produced large-size scintillators with $R(662\text{ keV}) < 5\%$, likely due to Ce-doping gradients that while quite significant in single crystals [14], are negligible in transparent ceramics due to their small grain sizes of 1-10 μm. Transparent ceramics are polycrystalline, monolithic, fully-dense optics that offer advantages in increased doping levels that can be obtained, as well as avoiding macroscopic doping gradients. Ce-doping gradients in single crystal garnets are significant, due to the poor match in ionic radius between Ce³⁺ (103 pm) and that of the substitutional sites of e.g. Gd³⁺ (94 pm) and Y³⁺ (88 pm), resulting in a segregation coefficient of Ce in GGAG and YAG of 0.36 and 0.082, respectively [15, 16]. Therefore, although high light yields and good energy resolution in small single crystal samples have been obtained for Ce-doped Gd-garnets, the unavoidable Ce-doping gradients in large single crystals result in light yield non-uniformity, degrading achievable energy resolution with large single crystals for gamma spectroscopy. In contrast, transparent ceramic GYGAG(Ce) in the largest sizes produced so far, 5.6 in³ (Figure 2), provides good energy resolution, as described below. To take advantage of the ruggedness of silicon photodiode arrays, the garnet ceramics offer excellent mechanical toughness and are easily cut into small cuboids matched to the small photodiodes required for minimal dark current. Gamma spectroscopy presented below for large size GYGAG(Ce) using PMT readout and small GYGAG(Ce) with photodiode readout indicate both approaches can provide gamma spectroscopy superior to that of Thallium-doped Sodium Iodide, NaI(Tl), the most commonly employed gamma spectroscopy scintillator.

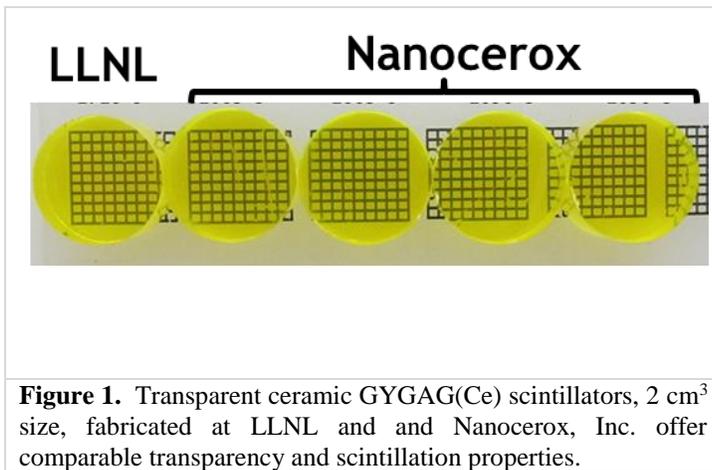


Figure 1. Transparent ceramic GYGAG(Ce) scintillators, 2 cm³ size, fabricated at LLNL and and Nanocerox, Inc. offer comparable transparency and scintillation properties.

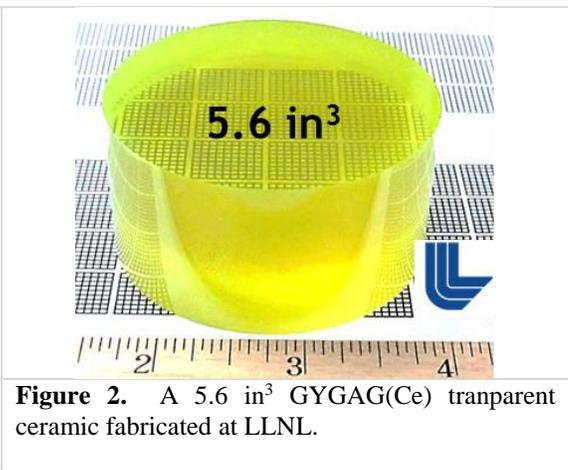


Figure 2. A 5.6 in³ GYGAG(Ce) transparent ceramic fabricated at LLNL.

2. EQUIPMENT AND METHODS

Transparent ceramic garnet scintillators were fabricated at LLNL using stoichiometric mixed metal oxide particles synthesized via flame spray pyrolysis (FSP), a nanoparticle production method developed by Pratsinis and co-workers [17] and by Laine and co-workers [18]. The nanoparticles are formed into a green body, vacuum sintered, then hot-isostatic pressed into optically transparent optics [3].

Gamma spectra were acquired with scintillators were optically coupled to a Hamamatsu R6231-100 PMT, which was connected to an Ortec 113 preamplifier, the signals shaped with a Tennelec TC 244 spectroscopy amplifier (shaping time of 4 μ s) and then recorded with an Amptek MCA8000-A multi-channel analyzer. Spectra were analyzed off-line by non-linear least squares fitting to a Gaussian in order to estimate the energy resolution. Light yields were measured by comparison to a standard YAG(Ce) ceramic from Baikowski. For photodiode measurements, we employed a Digirad gamma camera platform described in [9], and 2.8 x 2.8 x 6 mm scintillator cuboids coupled to the photodiode array. Decay times of scintillator materials were obtained by capturing and averaging scintillation traces under ^{137}Cs gamma excitation with a PMT coupled to an oscilloscope. The Scintillator Light Yield Non-proportionality Characterization Instrument (SLYNCI), located at LLNL, is based on the Compton Coincidence technique. Details of the instrumentation and use of the data to obtain intrinsic energy resolution estimates may be found in Refs. 19-21. Optical absorption and thermoluminescence measurements were performed with the arrangement described in Ref. 22.

3. RESULTS AND DISCUSSION

3.1 Gamma Ray Spectroscopy with GYGAG(Ce)

Scintillator-based gamma ray spectrometers provide large volumes for high sensitivity, permitting detection of weak sources, and therefore very large size scintillators providing high energy resolution gamma spectroscopy are desired. Figure 3 shows the pulse height spectra with ^{137}Cs acquired with 2 in³ and 0.1 in³ size GYGAG(Ce), using PMT readout, obtaining $R(662 \text{ keV}) = 4.3\%$ and 4.6% , respectively. With Silicon photodiode readout, a single pixel of 0.05 cm³ size can provide $R(662 \text{ keV}) = 3.6\%$. It is expected that when co-adding the full array of 1024 pixels that energy resolution will be slightly degraded, but early results indicate that $R(662 \text{ keV}) < 4\%$ for a 1024 pixel array populated with a total GYGAG(Ce) volume of 3.4 in³ is achievable.

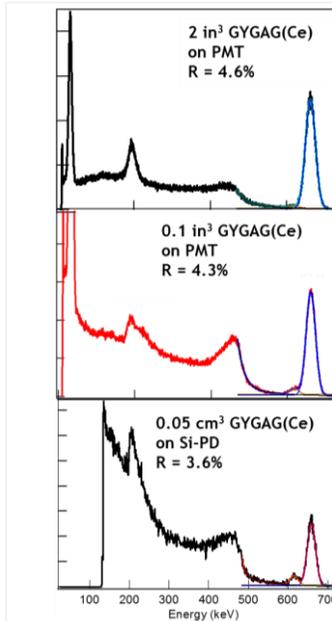


Figure 3. Cs-137 spectra with different sized GYGAG(Ce), all providing $R(662 \text{ keV}) < 5\%$.

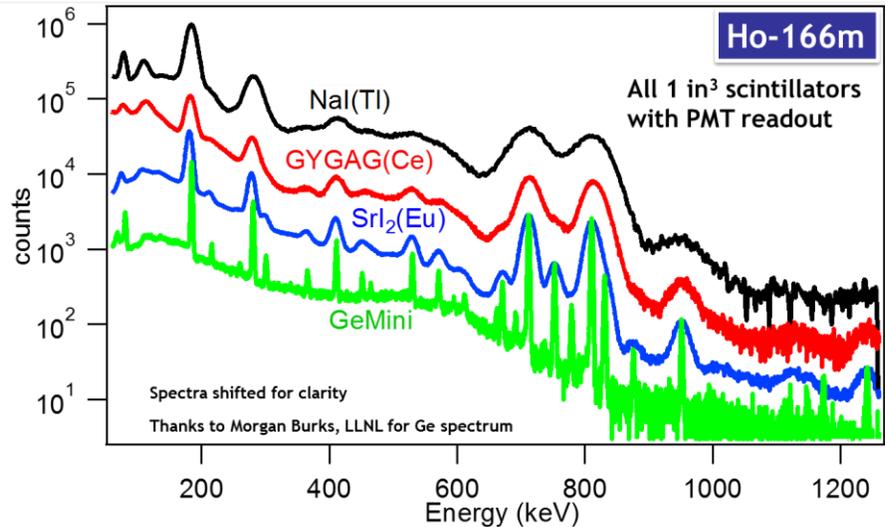


Figure 4. Gamma spectra obtained with $^{166\text{m}}\text{Ho}$ show improved resolution for GYGAG(Ce) compared to NaI(Tl).

Comparative gamma spectroscopy obtained with three 1 in³ scintillators, compared to a Germanium semiconductor detector, using a ^{166m}Ho source is shown in Figure 4. The energy resolution obtained with GYGAG(Ce) is considerably better than that of NaI(Tl), but is surpassed by single crystal Europium-doped Strontium Iodide, SrI₂(Eu). However, GYGAG(Ce) is not hygroscopic and offers excellent fracture toughness, surpassing both NaI(Tl) and SrI₂(Eu) in mechanical properties, and is thus expected to be more rugged for field use.

3.2 Scintillation Mechanism Dependence on Fabrication Conditions

In order to optimize the performance of the GYGAG(Ce) ceramic scintillator, we fabricated a series of samples using a single batch of GYGAG(Ce) nanopowder; it must be noted that the composition used for these studies is not the preferred composition used to fabricate the samples providing the gamma spectra shown in Figures 3-4, but a composition with a different ratio of Gd/Y and Ga/Al, that results in somewhat poorer energy resolution, even for the best samples. Each sample was prepared in exactly the same way, except that three samples were vacuum sintered and three were oxygen sintered. After sintering, the samples all attained equivalent transparency and were indistinguishable by eye. Next, one each of the vacuum and oxygen sintered samples were vacuum annealed at 1600 °C, and one each was air annealed at 1600 °C. The series of samples thus prepared are shown in Figure 5, top row. The second row shows the same samples, after brief illumination with a 254 nm mercury lamp, the photo acquired in the dark in order to show the differential afterglow, 1 second after turning off the lamp. It is notable that the air annealed samples do not show afterglow, while the vacuum anneal increase afterglow for the vacuum sintered sample and decreases afterglow for the oxygen sintered sample.

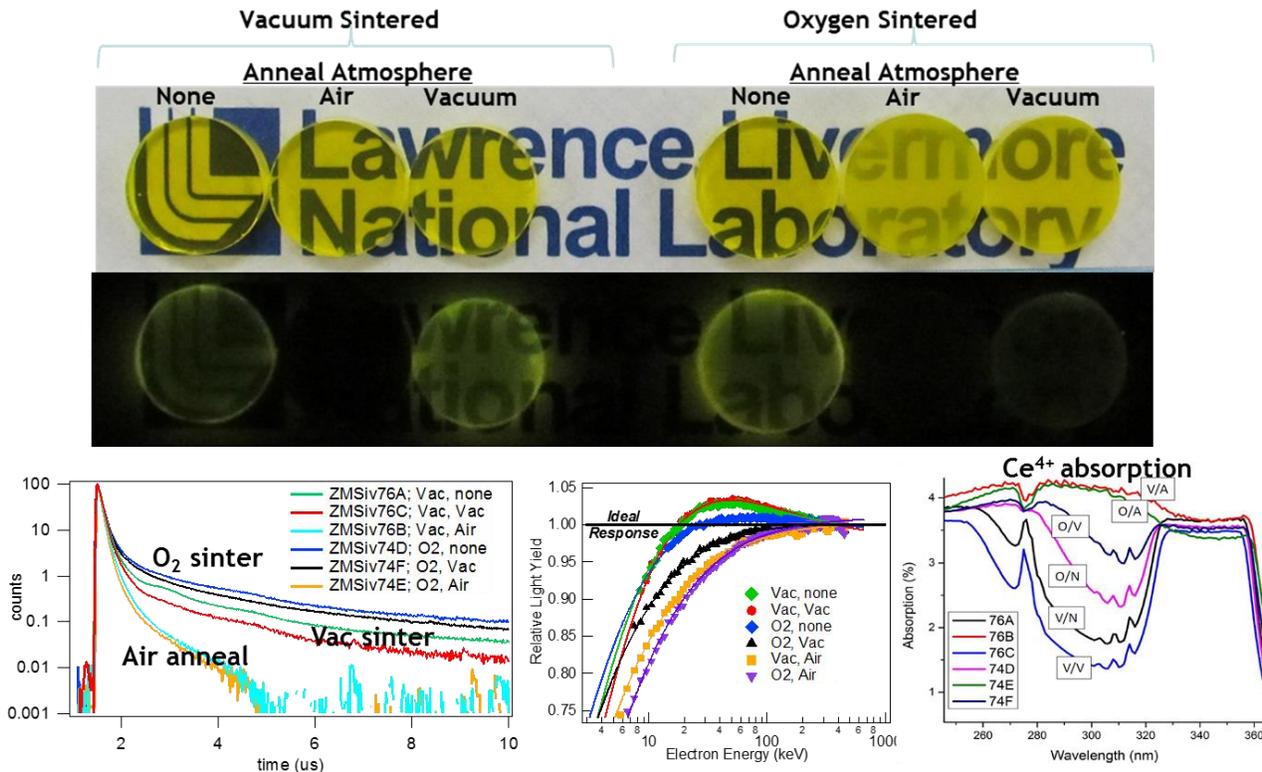


Figure 5. (top) Six GYGAG(Ce) ceramics were fabricated from the same starting powder, but processed either via vacuum sintering or oxygen sintering, then subjected to either no anneal, an air anneal or a vacuum anneal. The first row shows the samples in room lights. The second row shows the same samples, photo taken in the dark a few seconds after turning off UV illumination; the two air annealed samples exhibit no afterglow. **(bottom left)** Decay traces acquired with Cs-137 gamma excitation. **(bottom middle)** SLYNCI curves obtained for the same six samples. **(bottom right)** Optical absorption spectra of the samples showing significant Ce⁴⁺ absorbance in the air annealed samples.

Characterization of the time-resolved scintillation decays, acquired with Cs-137 gamma excitation, of the sample series is provided in Figure 5, bottom left. The fastest decays correspond to the air annealed samples. The decays consist of several components, a fast component with decay of ~100 ns, assigned to the Ce³⁺ decay, a medium component of ~500 ns assigned to energy migration via Gd³⁺, and a slow component of 1-5 μs, thought to be due to shallow traps that can be accessed via hopping to and from the conduction band. This third component is missing from the decays acquired for the air annealed samples. The effective decay, defined as the time to 1% of initial intensity, is listed in Table 2. The fastest decays correspond to the air annealed samples, however, the best energy resolution is obtained for the vacuum sintered samples, with either no anneal or a vacuum anneal. These latter samples offer the best overall properties, good energy resolution and fast decay.

The Scintillator Light Yield Non-proportionality Characterization Instrument (SLYNCI) [19-21] provides valuable feedback to compare scintillators and identify the best ceramics processing methods for GYGAG(Ce). The same six garnets samples were characterized to determine the impact of fabrication steps on light yield proportionality, data shown in Figure 5, bottom center. Notably, the air annealed samples have the lowest “free electron hole fraction,” while the vacuum sintered (no anneal or vacuum anneal) samples exhibit the highest “free electron hole fraction,” which corresponds to carriers that migrate within the scintillator via hopping prior to combining at a Ce³⁺ site forming scintillation photons.

Fitting of the SLYNCI data to the model described in Refs. 19-21 indicates that the best resolution should be obtained with the oxygen sintered samples, and worst with the vacuum sintered samples, contradictory to the experimental pulse height spectra. To better understand this, the optical absorption spectra of the six samples, shown in Figure 5, bottom right, reveal a significant presence of Ce⁴⁺ in the air annealed samples, and to a lesser extent, in the oxygen sintered samples. If Ce⁴⁺ acts as a deep trap, and its distribution is inhomogeneous through the sample, degradation of energy resolution, as observed, would result. Additionally, thermoluminescence curves obtained for the samples indicates that the dominant shallow trap differs between the vacuum sintered and oxygen sintered samples, at 0.17 and 0.3 eV, respectively. A more detailed analysis will be presented in a future publication.

Table 2. Analysis of the scintillation decays, the SLYNCI data, pulse height spectra, optical absorption spectra, and thermoluminescence curves reveal substantive differences in scintillation mechanisms, based on fabrication conditions.

Sinter / Anneal	Vac / Vac	Vac / None	Vac / Air	Ox / Vac	Ox / None	Ox / Air
(dE/dx) _{Birks} ^a	377	435	400	450	420	330
Free e/h fraction ^b	0.26	0.23	0.12	0.12	0.15	0.12
Afterglow	High	High	Low	Medium	High	Low
Ce ⁴⁺ observed? ^c	None	None	High	Low	Low	High
Decay to 1% (us)	0.60	0.75	0.49	1.5	1.2	0.49
Res. (% , 662 keV)	5.2	5.4	8.6	6.4	6.0	7.5
Calc'd Res. (% , 662 keV) ^d	3.6	3.2	2.9	2.5	2.4	3.3
Dominant trap (eV) ^e	0.17	0.17	0.17	0.3	0.3	0.3

^a For Debye dE/dx = 15

^b For (dE/dx)_{ONS} = 36 MeV/cm

^c From optical absorption spectra

^d From fitting of SLYNCI data

^e From thermoluminescence curves

4. CONCLUSIONS

Transparent ceramic GYGAG(Ce) offers high light yield and gamma spectroscopy with better resolution than NaI(Tl). It can be instrumented with PMT or Silicon photodiode readout, providing energy resolution R(662 keV) < 5%. We are optimizing the fabrication methods to achieve the best energy resolution, calculated to be <3%, by studying a series of ceramic GYGAG(Ce) samples. While vacuum sintering produces samples with the best experimental energy resolution, the SLYNCI data suggest that oxygen sintering should produce better light yield proportionality. We are continuing to optimize fabrication procedures and scaling up to larger sizes.

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