LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

LLNL-PROC-406543

Transparent Ceramic Scintillator Fabrication, Properties and Applications

N. J. Cherepy, J. D. Kuntz, J. J. Roberts, T. A. Hurst, O. B. Drury, R. D. Sanner, T. M. Tillotson, S. A. Payne

August 25, 2008

SPIE- Hard X-Ray, Gamma-Ray, and Neutron Detector Physics X
San Diego, CA, United States
August 10, 2008 through August 14, 2008

Disclaimer

Transparent Ceramic Scintillator Fabrication, Properties and Applications

N.J. Cherepy*, J.D. Kuntz, J.J. Roberts, T.A. Hurst, O.B. Drury,
R.D. Sanner, T.M. Tillotson, S.A. Payne
Lawrence Livermore National Laboratory, 7000 East Ave, Livermore, CA 94550, USA

ABSTRACT

Transparent ceramics offer an alternative to single crystals for scintillator applications such as gamma ray spectroscopy and radiography. We have developed a versatile, scaleable fabrication method, using Flame Spray Pyrolysis (FSP) to produce feedstock which is readily converted into phase-pure transparent ceramics. We measure integral light yields in excess of 80,000 Ph/MeV with Cerium-doped Garnets, and excellent optical quality. Avalanche photodiode readout of Garnets provides resolution near 6%. For radiography applications, Lutetium Oxide offers a high performance metric and is formable by ceramics processing. Scatter in transparent ceramics due to secondary phases is the principal limitation to optical quality, and afterglow issues that affect the scintillation performance are presently being addressed.

Keywords: Scintillators, Garnets, transparent ceramics, gamma ray spectrometers, radiography scintillators

1. INTRODUCTION

Inorganic scintillators are used in radiation detectors for medical imaging, high energy physics, and environmental radiation monitoring applications. Currently, $LaBr_3$(Ce) and SrI_2(Eu) single crystal scintillators provide the best energy resolution, 2.6-2.7% at 662 keV [1-5]. Gamma ray spectrometers providing high sensitivity and effective isotope identification require high energy resolution, high Z and materials that are growable in large size. The family of Cerium-doped Gadolinium Garnet scintillators appears to meet these requirements. For MeV radiography, scintillating glasses and ceramics such as the GE ceramic, "HiLight,"$(Y,Gd)_2O_3$:Eu, are used. Radiography systems require materials with high light yield and stopping power, and one candidate of particular interest is Lu_2O_3(Eu). A summary of properties of scintillator materials is provided in Table 1, with a focus on ceramic scintillators.

Gadolinium Garnets feature high stopping power and high light yields, however the simple Gadolinium Aluminum Garnet phase is thermodynamically unstable, so ions such as Ytttium, Scandium and/or Gallium are used to stabilize the Garnet phase. Garnet single crystals are typically grown by the Czochralski method, rendering production of large-sized optics expensive. Transparent polycrystalline ceramics not only allow production costs to be reduced, but the activator concentration and uniformity can be enhanced. Cubic crystal phases are preferred for ceramics since scatter from the typical transparent ceramic grain size (~3 μm) can become deleterious for birefringent materials. Cubic oxides structures under development as transparent ceramics are shown in Table 2.

With bialkali photomultiplier tube (PMT) readout, Ce-doped Gadolinium Scandium Aluminum Garnet (GSAG) single crystals offer 12.5% resolution at 662 keV [6], while Yttrium Aluminium Garnet (YAG) ceramics provide ~7% resolution [7]. New photodetectors with improved green-red sensitivity are being explored to provide higher resolution readout of Garnet scintillators, including red-sensitive PMTs and silicon-based devices [8,9]. Additionally, slow luminescence components (afterglow) need to be mitigated for improved energy resolution.

*cherepy1@llnl.gov; 925-424-3492; MS-L181, Lawrence Livermore National Laboratory, Livermore, CA 94550

2. EQUIPMENT AND METHODS

The Garnet ceramics were formed using stoichiometric mixed metal oxide particles synthesized via flame spray pyrolysis. Fully dense, transparent polycrystalline ceramics were formed by cold pressing green bodies that were subsequently vacuum sintered, and residual porosity removed by hot isostatic pressing. Further details on ceramics fabrication are available in Kuntz et al. [10].

Beta radioluminescence employed $^{90}Sr/^{90}Y$ source (~1 MeV average beta energy). Radioluminescence spectra were collected with a Princeton Instruments/Acton Spec 10 spectrograph coupled to a thermoelectrically cooled CCD camera. A Golden Engineering XR-200 pulsed x-ray source, producing 50 ns FWHM pulses was used to acquire luminescence decays. Luminescence is collected with a PMT and read out by an oscilloscope.

The scintillation light produced by the samples under excitation with a ^{137}Cs source (662 keV gamma) was detected by a commercially available Hamamatsu R329EGP PMT, quantum efficiency at 550 nm of 15% [11]. Additional experiments employed an Avalanche Photodiode (APD) from Radiation Monitoring Devices (RMD) configured with a preamplifier from Cremat. The signals from the photodetectors were shaped with a Tennelec TC 244 spectroscopy amplifier and recorded with an Amptek MCA8000-A multi-channel analyzer for offline analysis.

3. RESULTS AND DISCUSSION

We fabricated and characterized a series of Gadolinium Garnet ceramics, and found that the addition of Scandium facilitates phase stabilization and transparency. Photographs of several of the ceramics characterized in this report are shown in Figure 1. Figure 2 shows a Europium-doped Lutetium Oxide, $Lu_2O_3(Eu)$, ceramic with promising transparency under visible and UV excitation.

3.1 Radioluminescence Spectra and Decay Times

Under steady-state beta excitation, the emission spectra recorded represent the integral luminescence over all timescales. In Figure 3, the beta excited luminescence of three Gadolinium Garnet ceramics are shown. While the measured integral light yield is very high for GYAG(Ce) (~100,000 Photons/MeV), some long decay components do not contribute to the scintillation light pulse measured in the pulse height spectra, and furthermore it offers only limited transparency, due to the presence of small amounts of a secondary phase, Gadolinium Aluminum Perovskite ($GdAlO_3$). In contrast, GSAG(Ce) offers a modest light yield (~20,000 Photons/MeV), but is stable and transparent. Intermediate light yield and good transparency can be achieved with GYSAG(Ce) ceramics. The amplitudes of the slower decay components can be reduced by increasing the Ce doping level, as shown in Figure 4. The light yield for the $Lu_2O_3(Eu)$ ceramic (shown in Figure 1) under beta excitation was measured to be 48,000 Ph/MeV.

3.2 Pulse Height Spectra

Gamma ray pulse-height spectra at 662 keV were acquired with the Gadolinium Garnets and with a YAG ceramic. The total absorption peaks were processed with a Gaussian fit procedure to evaluate the peak position and full width at half maximum, in order to estimate the scintillation light yield and the energy resolution, respectively. In Figure 5, the pulse-height spectrum of YAG(Ce) acquired with a thermoelectrically cooled APD (250 ns shaping time) was found to be 6.6%. The measured gamma light yields, using the R329EGP PMT and a shaping time of 8 μs of GSAG(Ce), YAG(Ce) and GYSAG(Ce) are found to be 11,000 Ph/MeV, 32,000 Ph/MeV and 41,000 Ph/MeV respectively.

3.3 Optical Scatter in Transparent Ceramics

Figure 6 offers a simple assessment as to the acceptable amount of secondary phase induced scatter in ceramics, where we take the secondary phase component to have an index difference of 0.2. The Raleigh and Mie scattering region are calculated, while the upper limit of acceptability (also drawn) is taken as 0.1 cm^{-1} for a 10 cm optic. Moreover, the emergence of forward-type scatter is accounted for in terms of the rise in the upper limit of acceptability for larger particles. From these plots we see that on the order of 0.2% second phase material is permissible for a typical domain size of 3 μm, a fairly stringent criterion. [12]

3.4 Conclusions

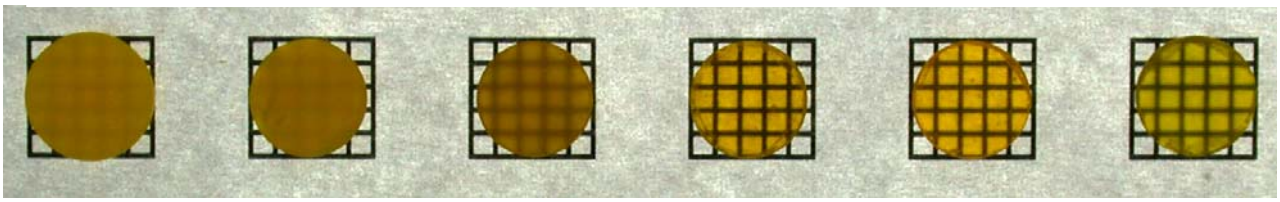
The use of Scandium for phase stabilization of the Gadolinium Garnets, combined with the incorporation of high Cerium doping to suppress afterglow may provide a pathway to a useful transparent ceramic scintillator for gamma ray spectroscopy. Advancement of APD technology and system integration should allow realization of energy resolution in the 3-5% range at 662 keV with Garnet scintillators. Europium-doped Lutetium Oxide is a formable ceramic scintillator that should offer a figure of merit for MeV radiography of about 4x better than standard scintillators, due to its high stopping power and light yield.

Table 1. Scintillator materials for gamma ray spectroscopy and MeV radiography. References 4 and 13 provide more details.

Scintillator	Z_{eff}	Density (g/cm^3)	λ_{max} (nm)	Principal Decay Time	Light Yield LY (Ph/MeV)	FOM = $\rho * Z_{eff}^4 * LY$	Energy Res. at 662 keV
$LaBr_3(Ce)$	44	5.07	360	20 ns	63,000	1.2	2.6%
$SrI_2(Eu)$	49	4.55	410	1300 ns	>70,000	2.9	2.7%
$Bi_4Ge_3O_{12}$	75	7.13	480	300 ns	9000	2.0	7.8%
$Y_3Al_5O_{12}(Ce)$	32	4.55	550	70 ns	30,000	0.2	7.3%
$Lu_3Al_5O_{12}(Ce)$	61	6.73	550	70 ns	30,000	2.8	8.6%
$Tb_3(Al,Sc)_5O_{12}(Ce)$	>50	≥6.4	570	1500 ns	>50,000	2.0	10.6%
$(Gd,Y)_3(Al,Sc)_5O_{12}(Ce)$	>40	≥5.5	570	100 ns	>50,000	0.7	10.8%
$SrHfO_3(Ce)$	50	7.4	400	20 ns	~10,000	0.5	17%
$Gd_3Ga_5O_{12}(Eu)$	52	7.1	611	3 ms	uncertain	2.6	N.A.
$La_2Hf_2O_7(Pr)$	51	7.9	600	10 ms	~15,000	0.8	N.A.
$Lu_2O_3(Eu)$	69	8.4	611	3 ms	50,000	9.5	N.A.

Table 2. Cubic oxides considered for development as transparent ceramics.

Structure type	Illustrative Material	Optical properties	Activates with Ce?	Activates with Eu?
Garnet	$Gd_3Sc_2Al_3O_{12}$	High transparency	Good LY	Good LY
Perovskite	$SrHfO_3$	High transparency	Modest LY	unknown
Bixbyite	Lu_2O_3	Moderate transparency so far	no	Good LY
Pyrochlore	$La_2Hf_2O_7$	Moderate transparency so far	no	Modest LY
Defect Fluorite	Y_3TaO_7	Unknown	no	unknown
Defect Fluorite	HfO_2-Y_2O_3	Unknown	no	Low LY
Simple Cubic	BaO	Hygroscopic	--	--



GYAG GYSAG → → → → increasing Sc GSAG

Fig. 1. Photographs of (left) a Gadolinium Yttrium Aluminum Garnet, $Gd_{1.485}Y_{1.485}Al_5O_{12}(Ce_{0.03})$, ceramic, (middle) Gadolinium Yttrium Scandium Aluminum Garnets ceramics, and (right) Gadolinium Scandium Aluminum Garnet, $Gd_{2.98}Sc_2Al_3O_{12}(Ce_{0.02})$ ceramic.

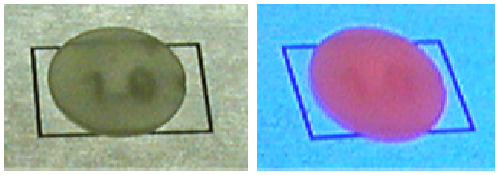


Fig. 2. Photographs of (left) a Europium-doped Lutetium Oxide ceramic under white light illumination and (right) the same ceramic under 254 nm excitation.

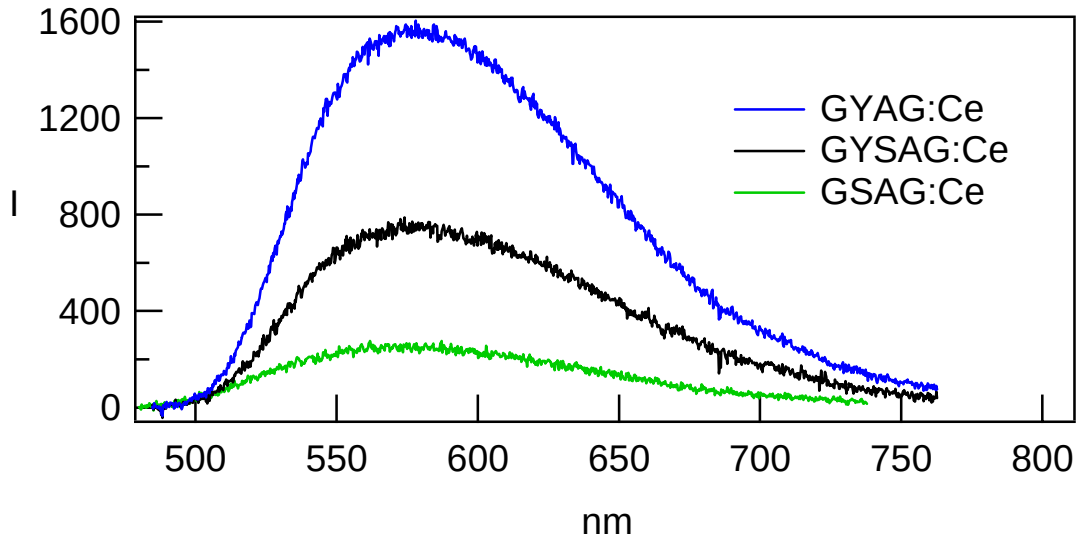


Fig. 3. Beta-excited radioluminescence spectra acquired of Ce-doped Gadolinium Garnets.

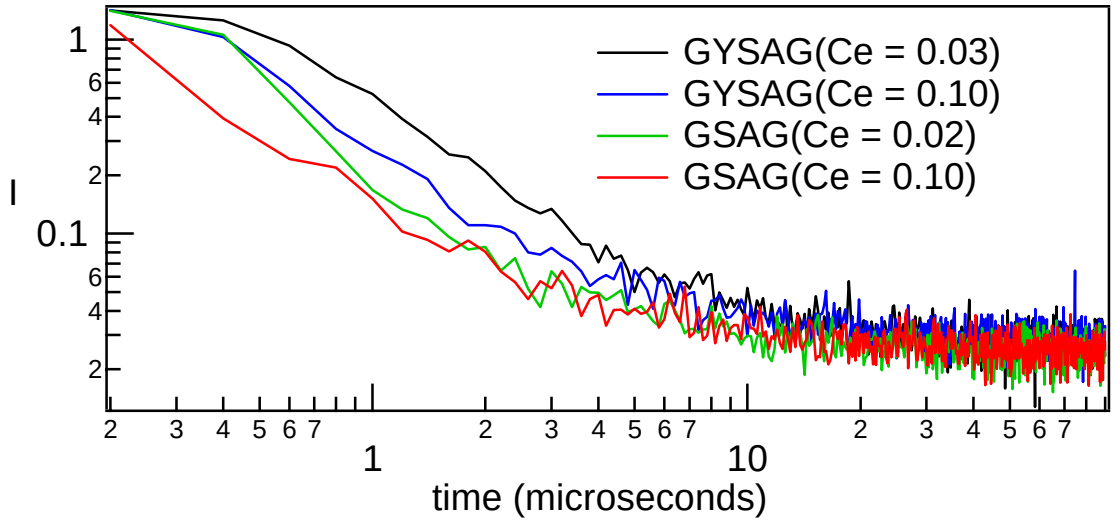


Fig. 4. Time-resolved luminescence decays acquired by excitation with 50 ns x-ray pulses. Delayed luminescence diminishes with higher Ce-doping.

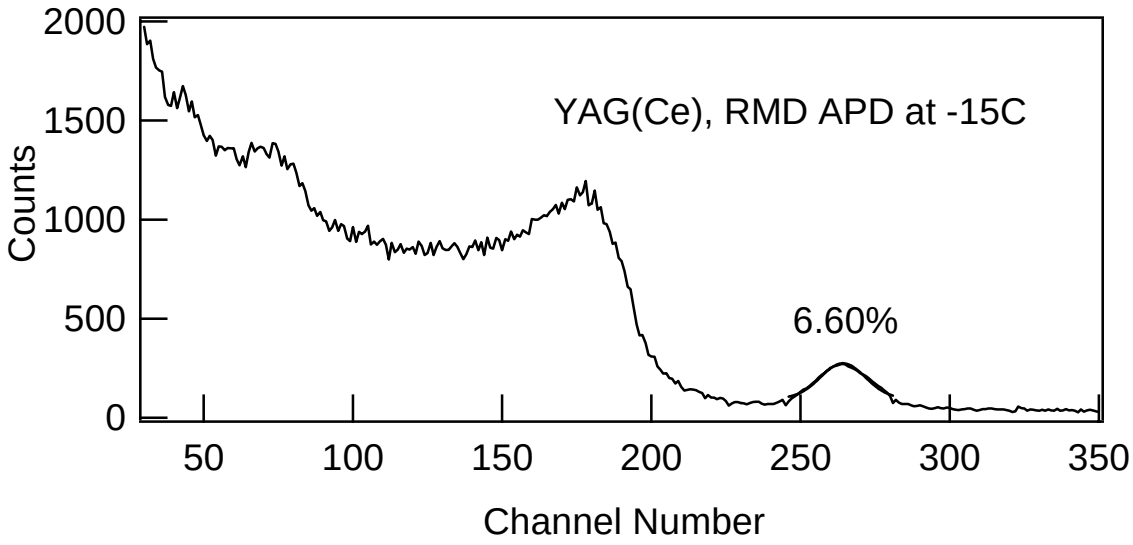


Fig. 5. Pulse height spectrum acquired at 662 keV of a Ce-doped Yttrium Aluminum Garnet ceramic, using Avalanche Photodiode readout, cooled to -15°C.

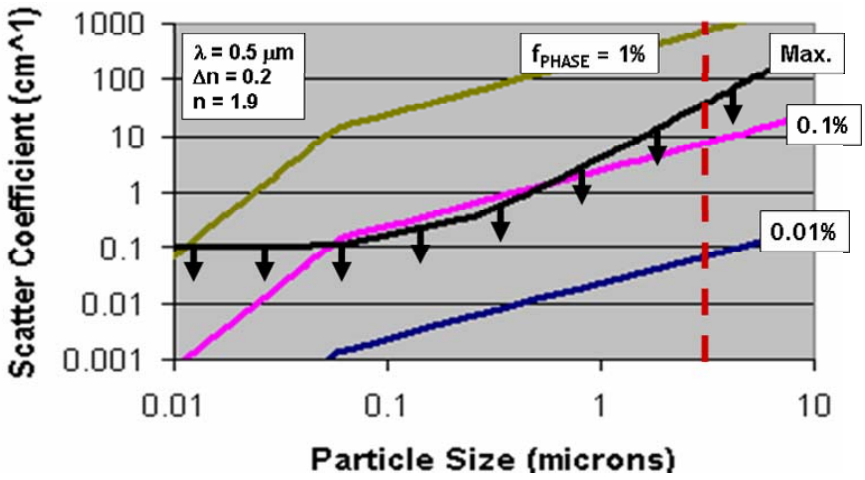


Fig. 6. Calculated scatter for a cubic crystalline material containing secondary phase (refractive index 0.2 different from primary phase) inclusions as a function of secondary phase particle size. The black line (maximum tolerable scatter for acceptable light collection) reveals that for larger particle sizes, the dominance of forward scatter permits a higher tolerable amount of scatter. Nevertheless, at a typical grain size of 3 μm, indicated by red dashed line, the amount of secondary phase inclusions should be held to <0.2%.

ACKNOWLEDGEMENTS

This work was supported by the Domestic Nuclear Detection Office of the Department of Homeland Security and LLNL internal funding. It was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

REFERENCES

1. E.V.D. van Loef, P. Dorenbos, C.W.E. van Eijk, K. Krämer, H.U. Güdel, "High-energy-resolution scintillator: Ce^{3+} activated $LaBr_3$", *Appl. Phys. Lett*, vol. 79, p. 1573, 2001.
2. K.S. Shah, J. Glodo, M. Klugerman, W.M. Higgins, T. Gupta, P. Wong, *IEEE Trans. Nucl. Sci.* vol. 51, p. 2395, 2004.
3. C. Fiorini, A. Gola, M. Zanchi, A. Longoni, P. Lechner, H. Soltau, L. Strüder, *IEEE Trans. Nucl. Sci.* vol. 53, p. 2392, 2006.
4. N.J. Cherepy, S.A. Payne, S.J. Asztalos, G. Hull, J.D. Kuntz, T. Niedermayr, S. Pimputkar, J.J. Roberts, R.D. Sanner, T.M. Tillotson, E. van Loef, C.M. Wilson, K.S. Shah, U.N. Roy, R. Hawrami, A. Burger, L.A. Boatner, W.-S. Choong, W.W. Moses, "Scintillators with Potential to Supersede Lanthanum Bromide" *IEEE Trans. Nucl. Sci.* (in press), 2008.
5. R. Hawrami, M. Groza,Y.Cui, A. Burger, M.D Aggarwal, N. Cherepy and S.A. Payne, "SrI_2, a Novel Scintillator Crystal for Nuclear Isotope Identifiers", *Proc. SPIE* (these proceedings). 2008.
6. A. Kling et al., "Scintillation properties of cerium-doped gadolinium-scandium-aluminum Garnets", *Nucl. Instr. & Meth. A* 346, 205-212 (1994).
7. T.Yanagida, H. Takahashi, T. Ito, D. Kasama, T. Enoto, M. Sato, Sh. Hirakuri, M. Kokubun, K. Makishima, T. Yanagitani, H. Yagi, T. Shigeta, T. Ito "Evaluation of Properties of YAG (Ce) Ceramic Scintillators," *IEEE Trans. Nucl. Sci*., vol. 52, p. 1836, 2005.
8. G. Hull, J.J. Roberts, J.D. Kuntz, S.E. Fisher, R.D. Sanner, T.M. Tillotson, A.D. Drobshoff, S.A. Payne, and N.J. Cherepy, "Ce-doped single crystal and ceramic Garnets for γ ray detection" *Proc. SPIE* vol. 6706, p. 670617, 2007.
9. N. Cherepy, J. Kuntz, T. Tillotson, D. Speaks, S.A. Payne, B. Chai, "Single Crystal and Transparent Ceramic Lutetium Aluminum Garnet Scintillators," *Nucl. Instr. Meth. A*, vol. 579, p. 38, 2007.
10. J.D. Kuntz, J.J. Roberts, M. Hough, N.J. Cherepy "Multiple Synthesis Routes to Transparent Ceramic Lutetium Aluminum Garnet," *Scripta Mat*., vol. 57, p. 960, 2007.
11. H.Y. Yoshida et al., "Development of a new PMT with high sensitivity for a wavelength-shifter fiber read-out", *Nucl. Instr. & Meth. A* 522, 477-486 (2004).
12. H. C. van de Hulst, Light scattering by small particles, Courier Dover Publications, 1981.
13. T. Martin and A. Koch, "Recent developments in X-ray imaging with micrometer spatial resolution", *J. Synchrotron Rad*., 13, 180–194, 2006.