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N. Cherepy, J. Kuntz, Z. Seeley, S. Fisher, O. Drury, B. Sturm, T. Hurst, R. Sanner, J. Roberts, S. Payne

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Transparent Ceramic Scintillators for Gamma Spectroscopy and Radiography

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

ABSTRACT

Transparent ceramics combine the scintillation performance of single crystals with the ruggedness and processability of glass. We have developed a versatile, scaleable fabrication method, wherein nanoparticle feedstock is consolidated at temperatures well below melting to form inch-scale phase-pure transparent ceramics with optical scatter of α <0.1 cm^{-1}. We have fabricated Cerium-doped Gadolinium Garnets with light yields of ~50,000 Ph/MeV and energy resolution of <5% at 662 keV. We have also developed methods to form sheets of the high-Z ceramic scintillator, Europium-doped Lutetium Oxide Bixbyite, producing ~75,000 Ph/MeV for radiographic imaging applications.

Keywords: Scintillators, garnets, bixbyites, transparent ceramics, gamma ray spectrometers, radiography scintillators

1. INTRODUCTION

Transparent ceramics have become available in useful sizes for a variety of applications within the past 15 years due to improved understanding of sintering phenomena on the nanoscale.[1,2] While traditional ceramics may be comprised of single or multiple crystalline and amorphous mineral phases and are typically translucent or opaque to light, modern optically transparent ceramics are fully dense monoliths of micron-scale (or smaller) crystallites, in most cases formed from pure phase cubic crystal structures. Fabrication of transparent ceramics begins with high purity ceramic nanopowders, which are consolidated into a "green body" by pressing or casting. The "green body" is sintered to near full density and subsequently hot isostatic pressing may be used to remove remaining porosity. A few commercial transparent ceramics are "Lumicera" lenses (a barium-based oxide made by Murata Mfg.), laser gain media (neodymium-doped yttrium aluminum garnet, Nd:YAG, is available from Konoshima) and transparent armor (aluminum oxynitride, ALON, and spinel, $MgAl_2O_4$, are available from Surmet and other vendors). As the manufacturing processes for transparent ceramics become better understood, industrial optical uses for these transparent materials with excellent mechanical robustness are likely to expand.

At Lawrence Livermore National Laboratory, transparent ceramic oxide scintillators are being developed for gamma ray spectrometers and for high energy (MeV) radiographic imaging devices.[3,4] Scintillators are optical materials that emit pulses of visible photons when excited with high energy radiation. Gamma ray spectrometers providing high sensitivity and effective isotope identification require high energy resolution, high effective atomic number and scintillators that can be produced large sizes. The scintillators currently offering the best energy resolution for gamma spectroscopy are $LaBr_3$(Ce) and SrI_2(Eu), however these are available only as single crystals.[5-7] Among the garnets, the density and effective atomic number of YAG are too low, while lutetium-based garnets have excellent stopping power, but possess intrinsic radioactivity due to the presence of Lu-176, resulting in an undesirable background for low-rate counting. Garnet single crystals are typically grown by the Czochralski method, rendering production of large-sized optics expensive, therefore fabrication of garnet transparent ceramics is being pursued.[8-11] An additional feature of ceramics is their excellent mechanical and environmental robustness, enabling them to withstand harsh environments such as for monitoring nuclear fuel rods, oil well logging, and high energy physics experiments.

We are optimizing a Gadolinium-based garnet transparent ceramic for phase stability, uniformity and high light yield, in order to produce a low-cost, gamma scintillator material useful for radio-isotope identification applications. Gadolinium-based garnets offer good stopping power, for a high photofraction. Furthermore, the electronic structure of Gadolinium provides a means for improving light yield proportionality,[12] since the Gd^{3+} level just below the conduction band is capable of enhancing exciton migration.

* cherepy1@llnl.gov; phone 925 424-3492

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For MeV radiography, moderate light yield Tb-doped scintillating glass sheets, coupled to imaging cameras may be used.[13] An alternative is the General Electric radiography scintillator ceramic, "HiLight," a europium-doped bixbyite, $(Gd,Y)_2O_3$, with better light yield than scintillating glass.[14] We are developing fabrication methods for extremely low optical scatter Eu-doped Lu_2O_3 which offers considerably better stopping and higher light yield than HiLight.

2. EQUIPMENT AND METHODS

Transparent ceramics were formed using stoichiometric mixed metal oxide particles synthesized via flame spray pyrolysis (FSP), a nanoparticle production method developed by Pratsinis and co-workers[15] and Laine and co-workers.[16] Synthesis of FSP nanoparticles was carried out at LLNL, as well as by Nanocerox, Inc. The FSP nanoparticles are formed into a green body, vacuum sintered, then hot-isostatic pressed into optically transparent parts.[11]

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. The scintillation light produced by the samples under excitation with a ^{137}Cs source (662 keV gamma) was detected by a commercially available Hamamatsu R6231-100 PMT. The signals 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 have been fabricating and characterizing Gadolinium Yttrium Gallium Aluminum Garnet ceramics, using FSP nanoparticles to form green bodies that are vacuum sintered to near full density and finally pressed isostatically under Argon to remove residual porosity. Using the general formula $(Gd,Y,Ce)_3(Ga,Al)_5O_{12}$, we found that the ratio of the 8-fold coordinate ions to the other metal ions is a critical parameter to control in order to achieve phase stabilization and transparency. The intersubstitutional nature of the metal ions in a mixed garnet permit flexibility and thus promotes phase stability over a broader compositional range than for a simple garnet with only two metal ion constituents. Photographs of a stoichiometry series performed to optimize the composition are shown in Figure 1, the best composition (5th sample from left) has been scaled up to 1 in^3 (Figure 2).

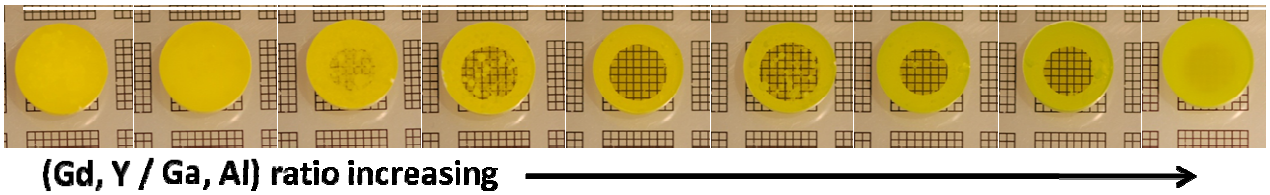

Figure 1. Photographs of a stoichiometry series for Cerium-doped Gadolinium Yttrium Gallium Aluminum Garnet, GYGAG(Ce), ceramics in which the metal ion concentrations were varied.

Figure 2. Photograph of a 3.2 cm diameter by 2 cm tall GYGAG(Ce) ceramic. This composition possesses the excellent phase stability required in order to avoid secondary phases that lead to deleterious scatter. This sample exhibits optical scatter $\alpha < 0.1$ cm^{-1}.

3.1 Gamma Ray Spectroscopy with the Gadolinium Garnet Ceramic Scintillator

Gamma ray pulse-height spectra at 662 keV acquired with a 3.7 cm^3 Gadolinium Garnet and with a Europium-doped Strontium Iodide crystal acquired using a Hamamatsu R6231-100 PMT are shown in Figure 3. 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. With a shaping time of 8 μs, GYGAG(Ce) ceramic produces 48,000 Ph/MeV and 4.8% resolution at 662 keV, while the $SrI_2(Eu)$ crystal yields 85,000 Ph/MeV and 2.8% resolution at 662 keV. Additional experiments using an Avalanche Photodiode photodetector from Radiation Monitoring Devices, cooled to -40°C produced resolution of 4.0% at 662 keV with a 0.1 cm^3 GYGAG(Ce) ceramic. It is notable that GYGAG(Ce) ceramics provide energy resolution with PMT readout that does not vary significantly with size, instead, optimization of stoichiometry is key. Among the samples in Figure 1, one composition provides the combination of phase purity and light yield required for <5% resolution at 662 keV. A comparison of the energy resolution as a function of gamma ray energy of GYGAG(Ce) with $SrI_2(Eu)$ as well as the well-known scintillators, Thallium-doped Sodium Iodide, NaI(Tl) and Cerium-doped Lanthanum Bromide, $LaBr_3(Ce)$ is shown in Figure 4. Measurements were acquired with optimal shaping times, particular to each scintillator.

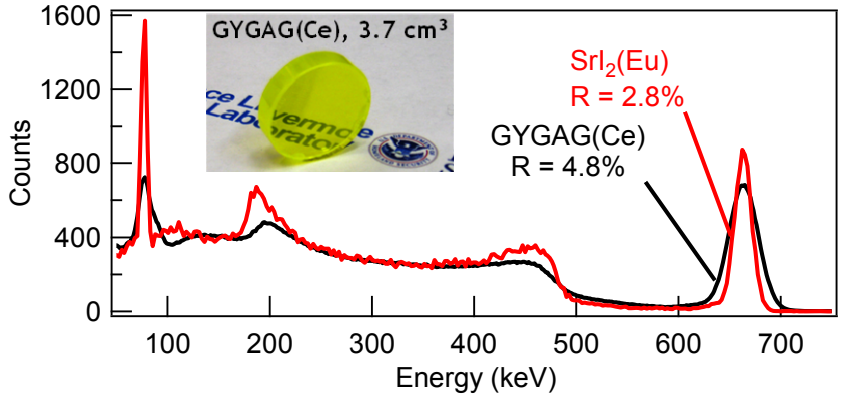

Figure 3. Pulse height spectra acquired with a Cs-137 source of a 3.7 cm^3 GYGAG(Ce) ceramic compared to a 1 cm^3 $SrI_2(Eu)$ single crystal. The energy resolution of GYGAG(Ce) is 4.9% at 662 keV, compared to 2.8% for $SrI_2(Eu)$. (inset) Photograph of the GYGAG(Ce) ceramic sample used for this measurement.

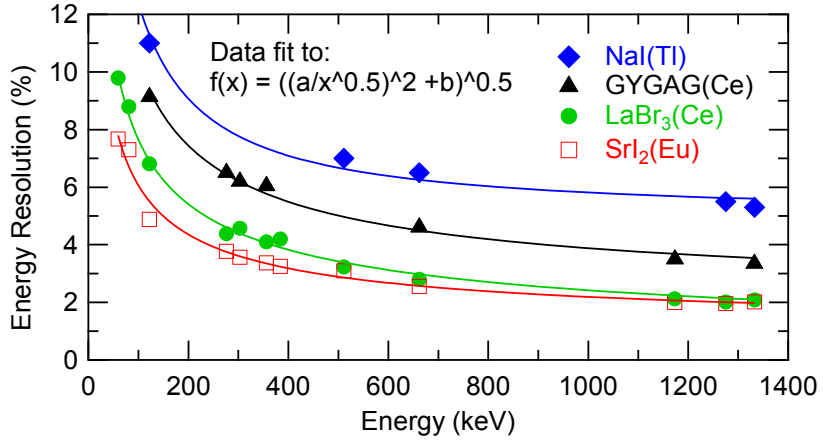

Figure 4. Energy resolution as a function of energy for several scintillators indicates that GYGAG(Ce) with PMT readout offers considerably superior gamma spectroscopy capability to NaI(Tl). Energy resolution with a higher QE photodetector, such as a Si photodiode, is further improved for GYGAG(Ce) (data not shown).

3.2 Lutetium Oxide Bixbyite Radiography Scintillator Ceramic

Lutetium Oxide is a refractory oxide with a density of 9.42 g/cm^3 and effective atomic number of 69, resulting in high stopping power for gamma radiation, however its melting point of 2490°C renders it difficult and costly to produce as a single crystal. Transparent ceramics fabrication utilizing FSP nanoparticles, vacuum sintering and hot isostatic pressing permits fabrication of fully dense sheets of pure Bixbyite phase Lu_2O_3(5%Eu) with low optical scatter and high purity, minimizing contamination with optically absorptive species typically found in samples prepared by the usual method of graphite die hot pressing. In Figure 5, the light yields of a IQI scintillating glass and a Lu_2O_3(Eu) ceramic scintillator fabricated at LLNL are compared, at 20,000 and 75,000 Photons/MeV, respectively. Compared to the standard glass used for high energy scanning radiography, Lu_2O_3(Eu) offers a potential improvement in throughput of about 10x, where the figure of merit (FOM) is based on the product of the gamma attenuation and the light yield, as shown in Table 1.

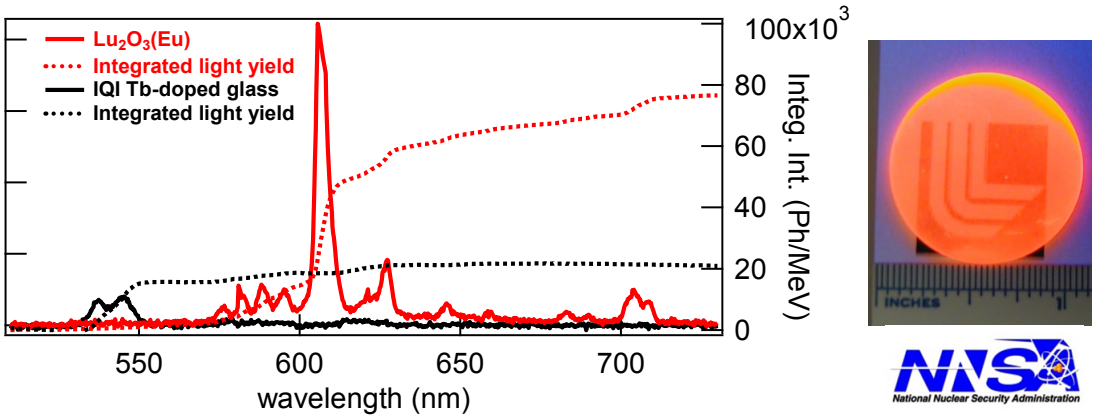

Figure 5. (left) Beta radioluminescence spectra of transparent ceramic 5% Eu-doped Lu_2O_3 compared with Tb-doped glass scintillator are shown, along with their integral light yields. (right) A photograph of a 2.5 cm diameter by 0.2 cm thick Eu-doped Lu_2O_3 radiography ceramic under UV illumination.

Table 1. Properties of several optically transparent scintillators used for high energy radiography.

Scintillator	Density (g/cm^3)	α, Attenuation, 9 MeV (cm^{-1})	LY (Ph/MeV)	FOM
IQI glass(Tb)	3.75	0.10	20,000	1
GE HiLight $(Gd,Y)_2O_3$(Eu)	5.95	0.25	40,000	5
Y_2O_3(Eu)	5.01	0.16	50,000	4
Lu_2O_3(Eu)	9.42	0.41	75,000	10

4. CONCLUSIONS

Transparent ceramics are a promising class of polycrystalline materials for scintillator and other optical materials applications where single crystal performance accompanied by robust mechanical properties is desirable. We have demonstrated high light yields and excellent phase stability for a new gamma spectroscopy scintillator, GYGAG(Ce) and the radiography scintillator Lu_2O_3(Eu). We are now optimizing annealing procedures to minimize afterglow and developing ceramics processing methods for scaling up to larger sizes.

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