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TECHNICAL REPORT

Strategy for Enhanced Light Output from Luminescent Nanoparticles

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HDTRA1-08-1-0015

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14. ABSTRACT The objective of this research program was to synthesize luminescent oxide or halide nanoparticles with improved brightness and scintillation efficiency under excitation by energetic X-ray and gamma radiation. Improved brightness and efficiency was achieved by growth of undoped and doped nanoparticles with a core/shell nanostructure. The nanoparticle properties characterized included photoluminescence-PL, crystallography, particle size distribution, quantum efficiency and nuclear spectroscopic responses.					
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CONVERSION TABLE

Conversion Factors for U.S. Customary to metric (SI) units of measurement.

MULTIPLY → BY → TO GET
TO GET ← BY ← DIVIDE

angstrom	1.000 000 x E -10	meters (m)
atmosphere (normal)	1.013 25 x E +2	kilo pascal (kPa)
bar	1.000 000 x E +2	kilo pascal (kPa)
barn	1.000 000 x E -28	meter ² (m ²)
British thermal unit (thermochemical)	1.054 350 x E +3	joule (J)
calorie (thermochemical)	4.184 000	joule (J)
cal (thermochemical/cm ²)	4.184 000 x E -2	mega joule/m ² (MJ/m ²)
curie	3.700 000 x E +1	*giga bacquerel (GBq)
degree (angle)	1.745 329 x E -2	radian (rad)
degree Fahrenheit	$t_k = (t^{\circ}f + 459.67)/1.8$	degree kelvin (K)
electron volt	1.602 19 x E -19	joule (J)
erg	1.000 000 x E -7	joule (J)
erg/second	1.000 000 x E -7	watt (W)
foot	3.048 000 x E -1	meter (m)
foot-pound-force	1.355 818	joule (J)
gallon (U.S. liquid)	3.785 412 x E -3	meter ³ (m ³)
inch	2.540 000 x E -2	meter (m)
jerk	1.000 000 x E +9	joule (J)
joule/kilogram (J/kg) radiation dose absorbed	1.000 000	Gray (Gy)
kilotons	4.183	terajoules
kip (1000 lbf)	4.448 222 x E +3	newton (N)
kip/inch ² (ksi)	6.894 757 x E +3	kilo pascal (kPa)
ktap	1.000 000 x E +2	newton-second/m ² (N-s/m ²)
micron	1.000 000 x E -6	meter (m)
mil	2.540 000 x E -5	meter (m)
mile (international)	1.609 344 x E +3	meter (m)
ounce	2.834 952 x E -2	kilogram (kg)
pound-force (lbs avoirdupois)	4.448 222	newton (N)
pound-force inch	1.129 848 x E -1	newton-meter (N-m)
pound-force/inch	1.751 268 x E +2	newton/meter (N/m)
pound-force/foot ²	4.788 026 x E -2	kilo pascal (kPa)
pound-force/inch ² (psi)	6.894 757	kilo pascal (kPa)
pound-mass (lbm avoirdupois)	4.535 924 x E -1	kilogram (kg)
pound-mass-foot ² (moment of inertia)	4.214 011 x E -2	kilogram-meter ² (kg-m ²)
pound-mass/foot ³	1.601 846 x E +1	kilogram-meter ³ (kg/m ³)
rad (radiation dose absorbed)	1.000 000 x E -2	**Gray (Gy)
roentgen	2.579 760 x E -4	coulomb/kilogram (C/kg)
shake	1.000 000 x E -8	second (s)
slug	1.459 390 x E +1	kilogram (kg)
torr (mm Hg, 0° C)	1.333 22 x E -1	kilo pascal (kPa)

*The bacquerel (Bq) is the SI unit of radioactivity; 1 Bq = 1 event/s.

**The Gray (GY) is the SI unit of absorbed radiation.

Objectives:

The objective of this research program was to synthesize luminescent oxide or halide nanoparticles with improved brightness and scintillation efficiency under excitation by energetic X-ray and gamma radiation. Improved brightness and efficiency was achieved by growth of undoped and doped nanoparticles with a core/shell nanostructure. The nanoparticle properties characterized included photoluminescence-PL, crystallography, particle size distribution, quantum efficiency and nuclear spectroscopic responses.

Status of effort:

Oxide Nanoparticles:

Luminescent core or core/shell nanocrystals of self-activated bismuth germinate (BGO) and gadolinium oxide (Gd_2O_3) activated with europium (Eu^{3+}) were studied for scintillation detection of radiological and nuclear materials. $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ core and shell nanocrystals were synthesized by an aqueous sol-gel method, by direct precipitation in a high-boiling point glycol, and by a non-hydrolytic hot-solution method. The $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ nanocrystal cores and shells exhibited strong red photoluminescence (PL) with quantum yields up to ~45%. Luminescent bismuth germinate (BGO) was synthesized by a sol-gel method to form nanospheres, nanoflower and nanocoral cubic $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ crystals in 30 min at ~85 °C. As-prepared and calcined BGO nanocrystals showed a broad PL emission peak (400 to 600 nm) with a quantum yield (QY) of ~56 % and ~80 %, respectively. Novel core/shell materials combinations, e.g. $\text{SiO}_2/\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$, $\text{Bi}_2\text{O}_3/\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ and $\text{Bi}_2\text{O}_3/\text{BGO}$, were synthesized and the data suggest that a high Z core and luminescent shell was promising for scintillator detectors.

Halide Nanoparticles:

Synthesis core/shell halide nanoparticles were prepared using a precipitation method taking advantage of ADDP (ammonium di-*n*-octadecyldithiophosphate) as ligand, and using metal nitrates and NH_4F as precursors, as shown in Fig. 1. The size of the nanoparticles was controlled by the addition of shells around the rare earth-doped cores.

Accomplishments/New Findings:

Research at the University of Florida has been focused on undoped and doped core/shell and core/multi-shell oxide nanoparticles, while research at Clemson University has been focused on halide core nanoparticles without and with shells. Both classes of materials are known to make excellent single-crystal scintillators, including $\text{Gd}_2\text{SiO}_5:\text{Ce}$ (GSO), $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ (BGO), $\text{CaF}_2:\text{Eu}$, and $\text{BaF}_2:\text{Ce}$.

Oxide Nanoparticles:

Scintillator crystals are currently single crystals made with complex, high temperature growth methods resulting in high cost and small crystal size. We have investigated alternative processing methods for the preparation of scintillation nanocomposite which offers the promise of low-cost processes for large area, mass produced ceramic scintillation materials. A variety of

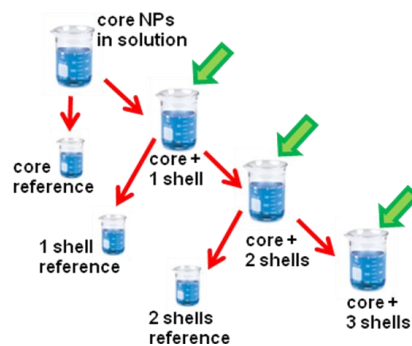


Fig. 1 Synthesis of core/shell fluoride nanoparticles.

ceramic scintillator oxide nanocomposites were synthesized using either non-hydrolytic hot solution route at 280°C or aqueous precipitation methods at low temperature of 90 °C in short reaction time of 30 min to 2 h.

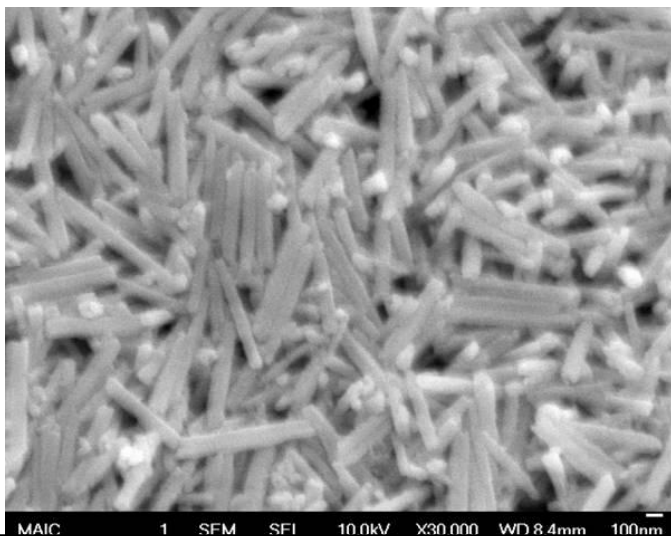


Fig. 2 SEM micrograph of $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ nanorods.

see Fig. 2) after growth for 2 h. The addition of polyethylene glycol 8000 (PEG-8000) to the reaction resulted in slower growth along the [001] direction, leading to shorter rod-like nanocrystals with a smaller aspect ratio of ~ 2 . The hexagonal $\text{Gd}(\text{OH})_3:\text{Eu}^{3+}$ were converted to cubic $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ while maintaining the nanorod geometry and dimensions by calcining in air at 800 °C for 2 h. The photoluminescence (PL) and radioluminescence (RL) emission spectra of

Nanoparticles of 20 nm flower-like and 10 nm spherical $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ were synthesized using a non-hydrolytic hot solution method. The effects of reaction procedure and temperature upon nanocrystal shape (hemisphere versus self assembled flower-like) were explained based on nucleation and growth of oxide nanocrystals. In addition, $\text{Gd}(\text{OH})_3:\text{Eu}^{3+}$ nanocrystals were synthesized through sol-gel precipitation method and evolved from nano-size spheres into 1-D rod-like nanocrystals ~ 800 nm long with a diameter of ~ 70 nm (aspect ratio: ~ 11 ; see Fig. 2) after growth for 2 h. The addition of polyethylene glycol 8000 (PEG-8000) to the reaction resulted in slower growth along the [001] direction, leading to shorter rod-like nanocrystals with a smaller aspect ratio of ~ 2 . The hexagonal $\text{Gd}(\text{OH})_3:\text{Eu}^{3+}$ were converted to cubic $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ while maintaining the nanorod geometry and dimensions by calcining in air at 800 °C for 2 h. The photoluminescence (PL) and radioluminescence (RL) emission spectra of these calcined $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ nanocrystals excited by 280 nm ultra-violet (UV) irradiation and 25 KeV X-ray, respectively, showed emission of red light from the dominant $^5\text{D}_0\text{-}^7\text{F}_2$ transition at 612 nm from Eu^{3+} .

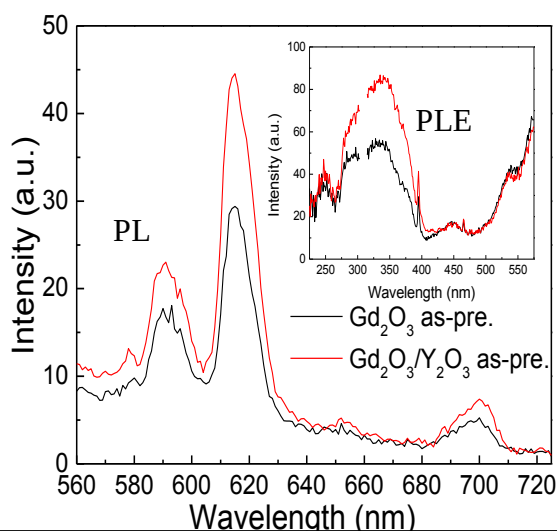


Fig. 3 PL and PLE spectra from $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ core and $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}/\text{Y}_2\text{O}_3$ core/shell nanoparticles prepared by the polyol method.

Nanoparticles of $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ ~ 20 nm in diameter were also synthesized at $\sim 180^\circ\text{C}$ using a facile high boiling-point alcohol (polyol) method. The Gd_2O_3 nanoparticles, doped with 5 mol% Eu, exhibited intense $^5\text{D}_0\text{-}^7\text{F}_2$ photoluminescence (PL) from Eu^{3+} after calcination at 600 °C for 2h in air. Photoluminescence excitation (PLE) data showed that while a small fraction of the emission resulted from direct excitation of Eu^{3+} , most of the excitation resulted from adsorption in the oxygen to europium

charge-transfer band between 225 and 275 nm. Transmission electron microscopy (TEM) showed that the $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ cores were slightly agglomerated, but TEM analysis could not detect the thin Y_2O_3 shell. X-ray photoelectron spectroscopy (XPS) was used to detect the thin Y_2O_3 shell around the $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ core. Drop-cast thin films of the $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}/\text{Y}_2\text{O}_3$ core/shell nanoparticles exhibited PL intensities (see Fig. 3) up to 40% larger than from bare $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ nanoparticles, which was attributed to reduced non-radiative recombination based on PL decay times.

Nanocomposites consisting of mono-dispersed 220 nm SiO_2 cores capped with a 13 nm $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ shell, sometimes followed by an undoped SiO_2 or Gd_2O_3 shell, were prepared via a urea precipitation method. The PL quantum yield (QY) from $\text{SiO}_2/\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ core/shell nanoparticles excited at 280 nm decreased from 25% to 16% with addition of a SiO_2 shell to form a $\text{SiO}_2/\text{Gd}_2\text{O}_3:\text{Eu}^{3+}/\text{SiO}_2$ nanostructure. However, the QY increased to 32% from a $\text{SiO}_2/\text{Gd}_2\text{O}_3:\text{Eu}^{3+}/\text{Gd}_2\text{O}_3$ nanostructure. Moreover, for a $\text{SiO}_2:\text{Eu}^{3+}$ core, addition of a Gd_2O_3 capping layer increased the QY by four times. This enhancement was attributed to the crystalline Gd_2O_3 layer acting as an antenna for energy transfer to the Eu^{3+} . Surprisingly, this core/shell/shell structure led to a 16x increase of the 612 nm Eu^{3+} emission excited by 25 keV X-rays from a silver source. The reason for this increase is not obvious, but may result from the antenna effects discussed above.

Three dimensional (3D) self-assembled hierarchical Bi_2O_3 architectures were prepared via a solution precipitation synthesis at 85 °C in 45 min with the aid of PEG-8000 as a surfactant capping agent. With an increased concentration of PEG, the morphology and structural phase evolved from monoclinic α -phase micro-rods into cubic γ -phase flower-like crystals. For flower-like Bi_2O_3 crystals, the morphology change from 60 nm nano-spheres, to self assembled sub-micron clusters, to 3D self-assembled crystals. Deposition of $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ on this hierarchical Bi_2O_3 resulted in red luminescence from the core/shell composite under UV irradiation after calcining at 500 °C for 2 h in air.

Self-activated $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ (BGO) crystals were synthesized at a low reaction temperature (<90 °C) in short reaction times (<30 min) from aqueous solutions. Flower- and coral-like BGO crystals obtained by using NaOH versus NH_4OH precipitation agents exhibited QYs of 28% and 80%, respectively, when excited at 280 nm after calcination at 600 °C for 2 h. Calcined coral-like BGO crystals (see Fig. 4(a)) showed a scintillation response when excited by ^{241}Am and ^{137}Cs irradiation sources. Moreover, $\text{Bi}_2\text{O}_3/\text{BGO}$ core/shell scintillation composites were synthesized with a one-pot solution precipitation method. The BGO shell nucleated heterogeneously as islands on the Bi_2O_3 microrod cores, and was followed by diffusion-limited lateral growth into a continuous shell with a dendrite-like morphology. Under the 60 keV gamma-ray irradiation from a ^{241}Am source, differential pulse height distribution measurements yielded a broad scintillation photopeak from the calcined core/shell composite. When excited at 280 nm, these self-activated BGO crystals had a broad photoluminescent emission band from 350 to 700 nm with the peak at 530 nm assigned to the $^3\text{P}_1 \rightarrow ^1\text{S}_0$ transition of Bi^{3+} (see Fig. 4(b)).

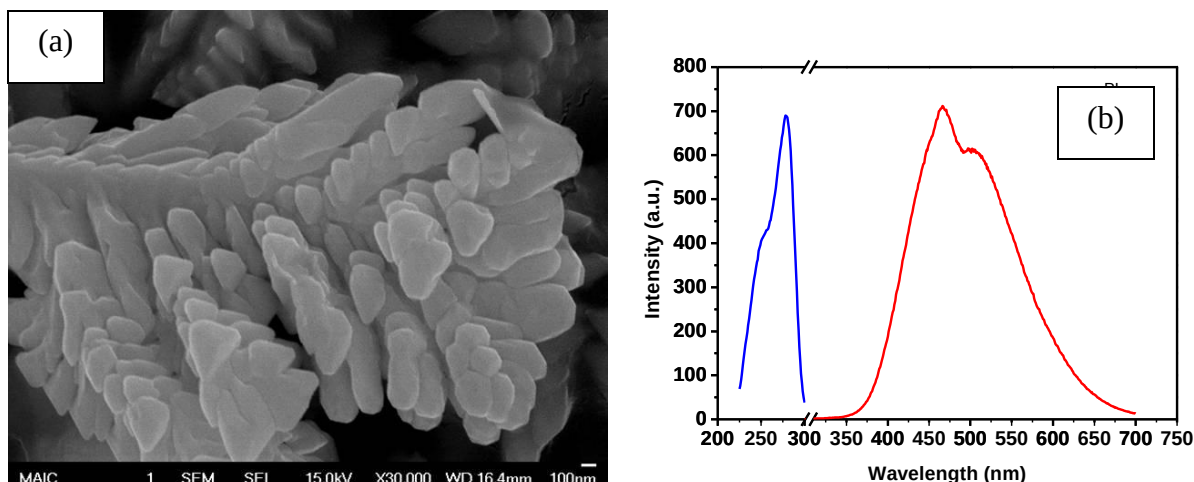


Fig. 4 (a) SEM of coral-like BGO, and (b) PL and PLE from coral-like BGO.

Self-assembled, almond-shaped colloidal $\text{GdVO}_4:\text{Eu}^{3+}$ nanocrystals ~ 60 nm long and ~ 10 nm wide were synthesized in aqueous solutions. The as-prepared nanocrystals were crystallized in short growth time (~ 3 min) with no post-growth heat treatment. The PL emission spectra showed strong, sharp peaks near 617 nm associated with the characteristic $^5\text{D}_0\text{-}^7\text{F}_2$ transitions from Eu^{3+} . For excitation at 347 nm and with 2 mol% co-doped Bi^{3+} and 10 mol% Eu^{3+} concentration, the QY was 2.5 times more than that from singly doped $\text{GdVO}_4:\text{Eu}^{3+}$ nanocrystals. This enhancement was attributed to additional absorption from the Bi-O charge transfer band due to codoping.

Representative samples of selected oxide nanoparticles were tested for X-ray luminescence on a beam line at the Advanced Photon Source at Argonne National Laboratory. The beam line allowed irradiation of thin films of the nano powders by monochromatic X-rays over a range of energy. The luminance was measured by a power meter which allowed conversion to number of photons per unit energy. The results are shown in Fig. 5 for X-rays with energies between 17 and 26 keV. Note that the highest photon yield at 26 keV is approximately 3000 photons/MeV, which begins to approach the single crystal GSO (~ 8000 photons/MeV). Nano powders of $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ with surfaces passivated by oleate-complex from the hot solution growth method, or passivated by inorganic Y_2O_3 shells gave high photon yields, by more than a factor of 10 when compared to bare $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ cores from the polyol method. Similarly, the photon yield from an estimated BGO was a factor of 10 higher than that from BGO grown by the precipitation method. The photon yields a passivated gadolinia and BGO nanoparticles were comparable to the yield from commercial BGO powder. We attribute the lower photon yields from commercial BGO as compared to single crystal BGO to optical scattering and absorption. Apparently all of the nano powders grown by the low-temperature precipitation method require surface passivation by an inorganic shell in order to improve their photon yield. The photon yields from bismuth oxide/BGO core/shell structures are low due to the large size of the bismuth oxide core, consistent with the low photoluminescent yields for this nano composite. Finally, the very low photon yields for gadolinia nanorods is again consistent with low PL intensities from these nano materials. Based upon previous results, we believe this low intensity results from low

incorporation rate of the europium dopant. These data clearly show that surface passivation leads to increased light output from nanoparticles used for scintillation detectors.

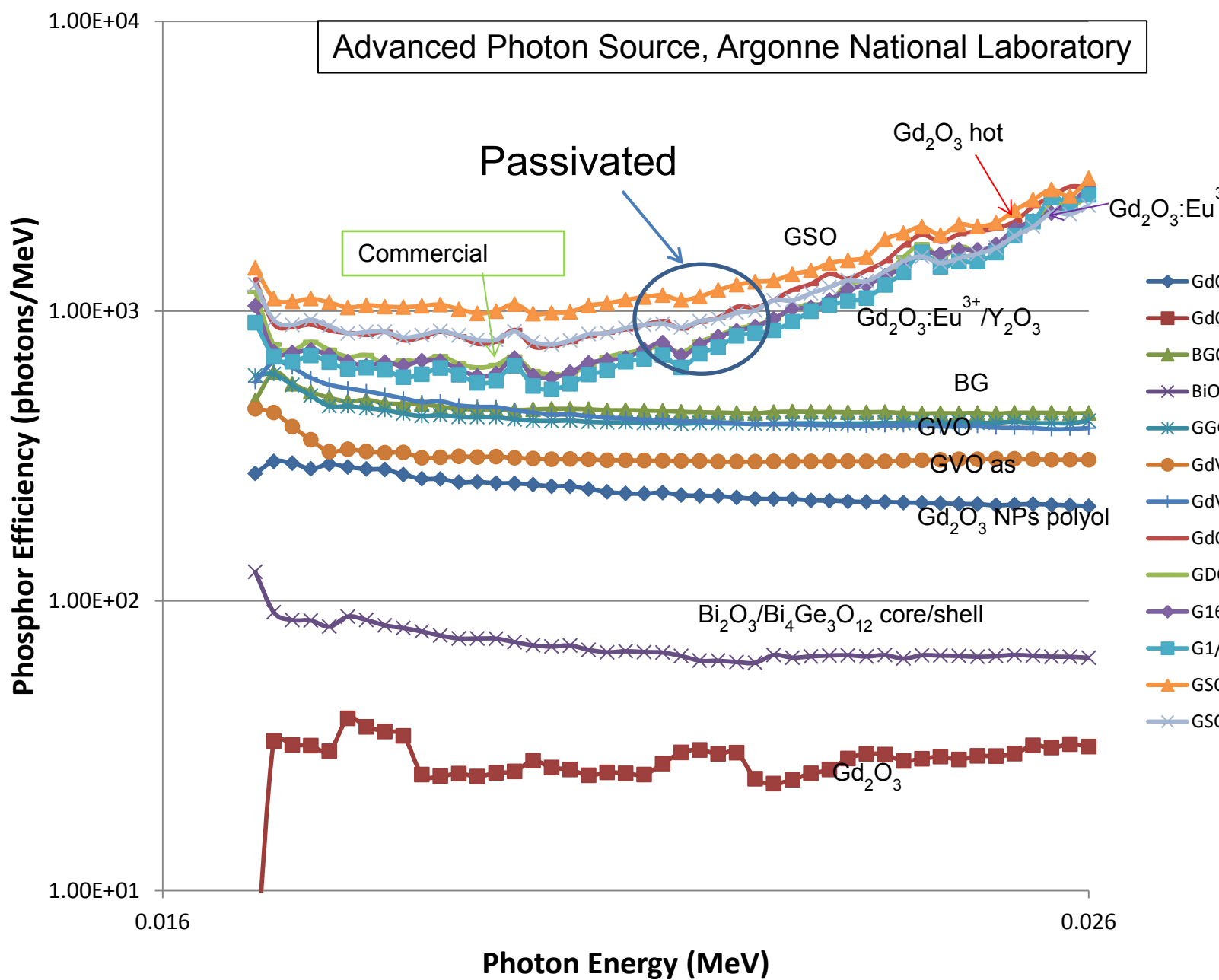


Fig. 5 X-ray luminescence from a variety of oxide nanocrystals with and without surface passivation for excitation by energies ranging from 17 keV to 26 keV. Note that the maximum yield at 26 keV is approximately 3000 photons per MeV. The best photon yield is from nanoparticles whose surfaces are passivated by a surfactant or inorganic shell.

Halide Nanoparticles:

Scintillators are luminescent materials that are used in the detection of ionizing radiation, and some of the most frequently used scintillators are fluorides, including $\text{CaF}_2\text{:Eu}$, CeF_3 , and $\text{BaF}_2\text{:Ce}$. Scintillation corresponds to the emission of light upon excitation due to ionizing radiation, and scintillation efficiency, η , can be described by the combination of three processes: conversion, β , transfer, Q , and luminescence, S , summarized in the relation, $\eta = \beta SQ$.

The first process corresponds to how efficiently the energy of the incoming radiation is used to produce electron-hole ($e-h$) pairs. For gamma-rays, β is commonly estimated by dividing the energy of the gamma-ray by 2 to 2.5 times the value of the bandgap energy. Once created, free electrons and holes migrate through the lattice of the scintillator material. Once below the ionization threshold, these free electrons and holes lose enough energy to strongly interact with the vibrations of the lattice (electron-phonon interactions) and thermalize, moving to the bottom of the conduction band and to the top of the valence band, respectively. Eventually, they bond, forming excitons. Typically, $e-h$ pairs have diffusion length in the range of several tens to about 100 nm in ionic crystals, and during this migration through the lattice, a fraction of the $e-h$ pairs is lost, either trapped or recombined non-radiatively at quenching centers, resulting in a decrease in the number of pairs available to produce luminescence. Only those pairs that reach the luminescent centers contribute to scintillation, and the efficiency of the migration process is given by S . The remaining $e-h$ pairs that recombine at the luminescence centers generate scintillation, and the intrinsic efficiency of the radiative recombination at the luminescent center is quantified by Q .

Once the scintillator material is chosen, the band gap and the intrinsic efficiency of the luminescent center are determined. Because of that, the most unique aspect of scintillation in nanoparticles is related the migration process, and the fraction of the cascade generated by the incoming radiation is contained in the nanoparticle. In order to investigate these effects, we explored our unique synthesis capability to grow shells around core nanoparticles in a number of fluoride scintillators, namely: $\text{CaF}_2\text{:Eu}$, $\text{BaF}_2\text{:Ce}$, $\text{LaF}_3\text{:Ce}$, and $\text{LaF}_3\text{:Eu}$. Synthesis was based on the precipitation method taking advantage of ADDP as a ligand, and uses metal nitrates and NH_4F precursors, as shown in Fig. 1. The size of the nanoparticles was controlled by the addition of shells around the rare earth-doped cores. We also carried out preliminary investigation on the non-hepitaaxial growth of LaF_3 on CeF_3 nanoparticles using DEG to simultaneously serve as solvent and ligand.

All the fluoride nanoparticles were characterized on their structure, morphology, and photoluminescence by means of X-ray diffraction, TEM, and luminescence spectroscopy, respectively. The diffraction spectra were matched with data from the JCPDF database. Photoluminescence showed evidence of the $3+$ state of the rare earth.

The response of these scintillators was characterized by means of radioluminescence, when excited with X-rays, or through differential pulse height distribution measurements using a ^{241}Am source. These results are presented in the Figs. 6-8 below, for each of the scintillators investigated.

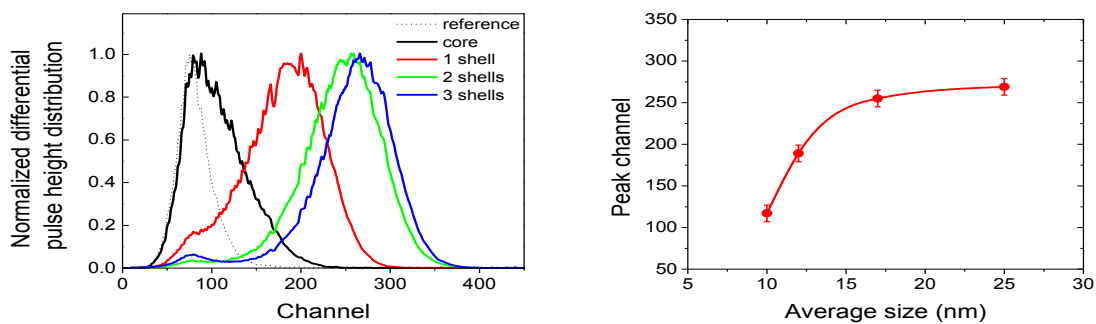


Fig. 6 Left: Differential pulse height distribution measurements of CaF₂:Eu/CaF₂ core/multi-shell nanoparticles irradiated with ²⁴¹Am source. Right: Photopeak position versus average

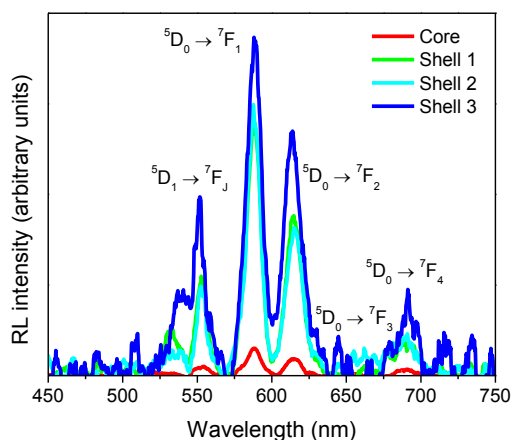


Fig. 7 Radioluminescence spectra of LaF₃:Eu/LaF₃ core/multi-shell nanoparticles showing multi-fold enhancement of scintillation response due to shelling

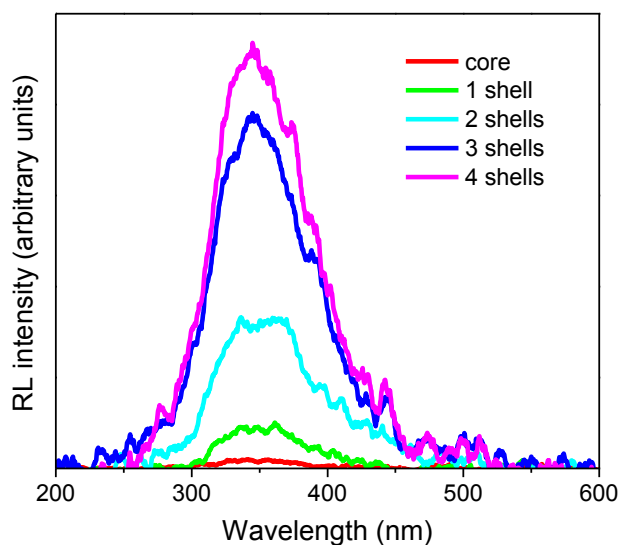


Fig. 8 Radioluminescence spectra of BaF₂:Ce/BaF₂ core/multi-shell nanoparticles showing scintillation enhancement after shelling.

In summary, our results show that three factors make larger nanoparticle sizes beneficial to the scintillation efficiency. The growth of the first shell passivates the surface and activates the luminescence centers on the surface of the core nanoparticle, enhancing luminescence output as seen from PL. Furthermore, the increase of the volume contains larger fractions of the irradiation cascade within the nanoparticle, and thus larger numbers of $e-h$ pairs become available for radiative recombination. Also, as the nanoparticle size increases, its dimensions approach the mean length for $e-h$ pair recombination and higher rates of radiative recombination are expected since less $e-h$ pairs recombine at the surface. These results are expected to impact radiation sensing technologies that make use of nanoparticles. Since they were obtained under alpha particle and x-ray irradiation, and from several fluoride host materials with two different RE dopants involving $4f-4f$ and $4f-5d$ transitions, they are expected to reflect a general aspect of the scintillation process in nanoparticles.

Reduced Optical Scattering in Nanoparticle-Polymer Composites

We have shown above that single passivation shells on luminescent cores can improve the PL brightness. Below we show that multiple shells on the surface of luminescent cores or inner shells can be used to reduce scattering. Light scattering is reduced when the outer shell matches the index of refraction of the matrix in which the nanoparticles reside. This discovery has resulted in a patent application entitled "Index of Refraction Matched Nanoparticles and Methods of Use", with the following inventors: Paul H. Holloway, Luiz Jacobsohn, Jihun Choi and Teng-Kuan Tseng. The application was assigned the US Provisional Patent Serial No. 61/685,245, was filed May 12, 2011 (University of Florida disclosure # 13541 dated July 29, 2010). The results of optical index matching are shown in Figs. 9 and 10 below. Even though the nanoparticles are small (i.e. the nanoparticles diameter, d_{NP} , is much less than the wavelength of light), scattering may still occur as shown in Figs. 9 and 10. However, if multiple shells are grown on the surface of the nanoparticles, with the last shell being index matched to the matrix in which the nanoparticles reside, scattering is reduced leading to improved energy resolution and radiation detection.

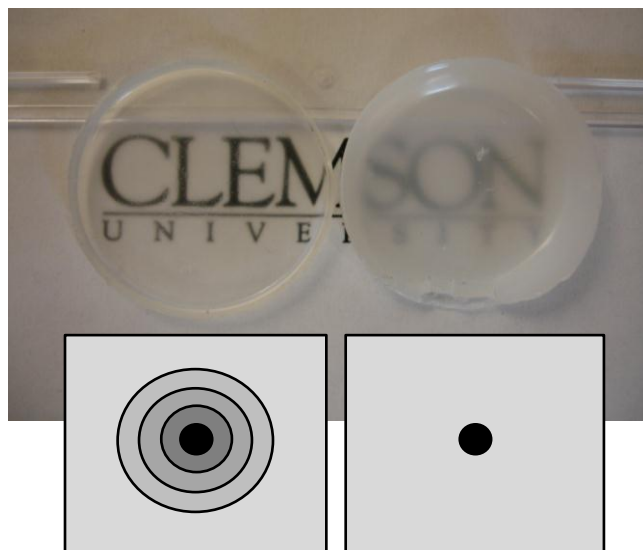


Fig. 9 Nanocomposite of $\text{CaF}_2:\text{Eu}$ (3mol%) core with (left) or without (right) a $\text{CaF}_2:\text{Pr}$ (11mol%) shell indexed matched to the PMMA matrix. Note the optical scattering without the index matching for ~20 vol% loading.

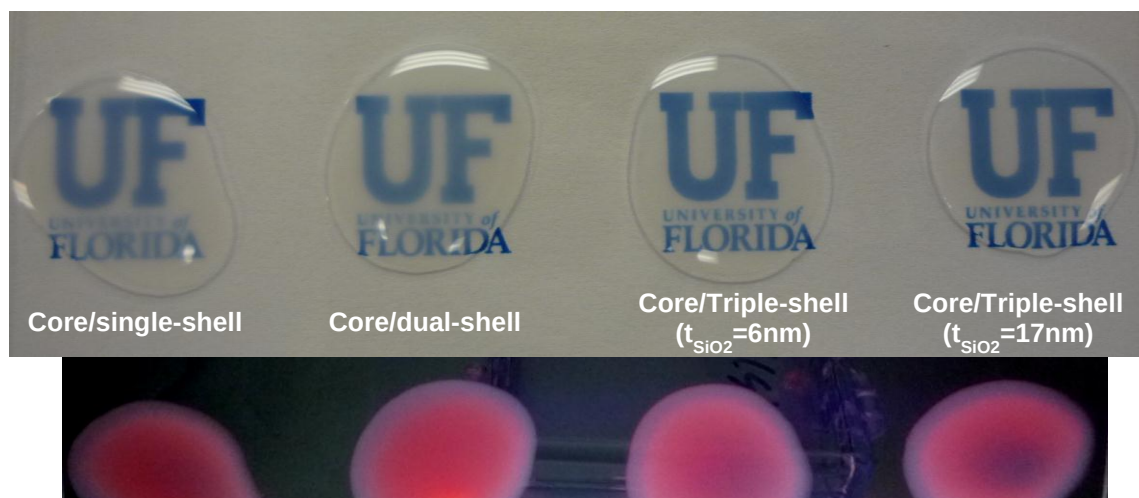


Fig. 10 Nanocomposites (1 vol%) consisting of a silica core with a $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ luminescent single shell, with a dual $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}/\text{Y}_2\text{O}_3$ shell, or with a triple shell structure of $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}/\text{Y}_2\text{O}_3/\text{SiO}_2$ where the silica index of refraction (1.47) matches the index of the PMMA (1.48).

Contribution to the Workforce

Finally and of equal important to the research results, undergraduate and graduates students have been trained and become proficient in the synthesis of scintillating materials and their characterization with techniques such as transmission electron microscopy, X-ray diffraction, luminescence spectroscopy, and differential pulse height distribution measurements.

Summary:

We have demonstrated that a surface shell on nanoparticles increased the PL brightness as well as the X-ray luminance. To accomplish this, we demonstrated synthesis of a number of potential scintillator nanoparticles, including Eu doped Gd_2O_3 , GSO, GVO, and BGO ($\text{Bi}_4\text{Ge}_3\text{O}_{12}$) with PL quantum yields between 56 and 80%. We demonstrated a factor of four increase in scintillation output from $\text{CaF}_2:\text{Eu}/\text{CaF}_2$ core/shell nanoparticles as compared to uncapped $\text{CaF}_2:\text{Eu}$ cores. We demonstrated reduced optical scattering in nanoparticles composites when the last shell matched the index of refraction of the polymer host. The matched index shells were grown using the same synthesis techniques as were used to grow the nanoparticles. This intellectual property was protected by filing a provisional patent. We graduated two Ph.Ds., trained two graduate and three undergraduate students in the area of nanoscintillators.

Personnel Supported:

University of Florida:

Paul H. Holloway, Distinguished Professor

Mark R. Davidson, Associate Research Professor
Teng-Kuan Tseng, Graduate Research Assistant (Graduated with Ph.D. August, 2010)
Jihun Choi, Graduate Research Assistant (Graduated with Ph.D. August, 2011)

Clemson University:

Luiz G. Jacobsohn, Research Associate Professor
Kevin Sprinkle, Undergraduate Research Assistant
Steven Roberts, Undergraduate student Research Assistant
Cameron McPherson, Undergraduate student Research Assistant

Ph.D. Dissertations:

Teng-Kuan Tseng, “Luminescent Oxide Nanocomposites: Synthesis, Characterization and Scintillation Applications”, PhD dissertation, University of Florida, August 2010.

Jihun Choi, “Enhanced Light Output from Luminescent Oxide Nanoparticles: Synthesis, Characterization and Scintillation Application, PhD Dissertation, University of Florida, August 2011.

Publications: Peer Reviewed Journal Papers

1. L. G. Jacobsohn, C. L. McPherson, K. B. Sprinkle, E. G. Yukihiro, T. A. DeVol and J. Ballato, “Scintillation of Rare Earth Doped Fluoride Nanoparticles”, *Applied Physics Letters* 99 (2011) 113111 (3 pages)
2. T. K. Tseng, J. Choi, M. Davidson, P. H. Holloway, “Synthesis and Luminescent Characteristic of Europium Dopants in SiO₂/Gd₂O₃ Core/Shell Scintillating Nanoparticles,” *Journal of Materials Chemistry*, 20 (2010) 6111
3. T. K. Tseng, J. Choi, Doh-Won Jung, M. Davidson, P. H. Holloway, “Three-Dimensional Self-Assembled Hierarchical Architectures of Gamma-Phase Flowerlike Bismuth Oxide,” *ACS Applied Materials & Interfaces*, 2 (2010) 943
4. T. K. Tseng, J. Choi, M. Davidson, P. H. Holloway, “Ceramic Nanoscintillator: Synthesis, Characterization and Detection Applications,” *American Ceramic Society Bulletin*, 89 (2010) 34
5. T. K. Tseng, J. Choi, L. G. Jacobsohn, E. G. Yukihiro, M. Davidson, P. H. Holloway, “Synthesis and Luminescent Characteristics of One-Dimensional Europium Doped Gd₂O₃ Phosphors,” *Applied Physics A: Materials Science and Processing* 100 (2010) 1137-1142
6. J. Choi, T. K. Tseng, M. Davidson, P. H. Holloway, “Enhanced photoluminescence from Gd₂O₃:Eu³⁺ nanocores with a Y₂O₃ thin shell,” *J. Materials Chem*, **21** (2011) 3113-3118;
7. D. Bera, L. Qian, T. K. Tseng, P. H. Holloway, “Quantum Dots and Their Multimodal Applications: A Review,” *Materials*, 3 (2010) 2260
8. L. Qian, D. Bera, T. K. Tseng, P. H. Holloway, “High Efficiency Photoluminescent from Silica-coated CdSe Quantum Dots,” *Appl. Phys. Lett.*, 94 (2009) 073112
9. L.G. Jacobsohn, S. Tornga, B. Bennett, R. Muenchausen, O. Ugurlu, T. K. Tseng, J. Choi, P. H. Holloway, “Annealing Effects on the Photoluminescence Yield of Gd₂O₃:Eu Nanoparticles Produced by Solution Combustion Synthesis,” *Radiation Measurements*, 45 (2010) 611

10. L.G. Jacobsohn, T.L. James, C.J. Kucera, K. Sprinkle, J. DiMaio, B. Kokuoz, B. Yazgan-Kukouze, and J. Ballato, "Rare Earth Doped Fluoride Nanoparticles", Invited review paper for a special issue on "Luminescent Materials" for *Materials* **3** (2010) 2053-2068
11. L.G. Jacobsohn, K.B. Sprinkle, C.J. Kucera, T.L. James, S.A. Roberts, H. Qian, E.G. Yukihara, T.A. DeVol and J. Ballato, "Synthesis, Luminescence and Scintillation of Rare Earth Doped Lanthanum Fluoride Nanoparticles", *Optical Materials* **33** (2010) 136-140
12. L.G. Jacobsohn, K.B. Sprinkle, S.A. Roberts, C.J. Kucera, T.L. James, E.G. Yukihara, T.A. DeVol and J. Ballato, "Fluoride Nanoscintillators", contribution to the special issue "Nanocrystals-Related Synthesis, Assembly, and Energy Applications", *Journal of Nanomaterials* **2011** (2011) article ID 523638 (6 pages), doi:10.1155/2011/523638
13. J. Choi, T. K. Tseng, M. Davidson and P. H. Holloway, *X-Ray and photo-luminescence from Gd₂SiO₅:Ce³⁺ nanoparticles synthesized by solution based methods*, Journal of Alloys and Compounds, submitted (2011)

Peer Reviewed Proceedings Papers:

1. T. K. Tseng, J. Choi, M. Davidson, P. H. Holloway, "Core/Shell Composite of Self-assembled Hierarchical Bismuth Oxide/Europium Doped Gadolinium Oxide for Scintillating Detection," *Mat. Res. Soc. Symp. Proc. Colloidal Nanoparticles for Electronic Applications-Light Emission, Detection, Photovoltaics and Transport*, 1207E (2009) 25
2. T. K. Tseng, J. Choi, M. Davidson, P. H. Holloway, "Structure and Luminescence of Europium-Doped Gadolinia-Based Core/Multi-Shell Scintillation Nanoparticles," *Mat. Res. Soc. Symp. Proc. Nuclear Radiation Detection Materials*, 1164L (2009) 01

Non-refereed Publications:

Teng-Kuan Tseng, Jihun Choi, Mark Davidson and Paul H. Holloway, "Ceramic nanoscintillator: Synthesis, characterization and detection applications", *Amer. Ceram. Soc. Bull.* **89**, 32-33 (2010).

L.G. Jacobsohn, C.J. Kucera, K.B. Sprinkle, S.A. Roberts, E.G. Yukihara, T.A. DeVol and J. Ballato, "Scintillation of nanoparticles: case study of rare earth doped fluorides", *IEEE Nuclear Science Symposium and Medical Imaging Conference Record*, N53-3, 1600-1602 (2010)

Interactions/Transitions:

a) Participation/presentations at meetings, conferences, seminars, etc.

1. P. Holloway, T. K. Tseng, J. Choi, M. Plaisant, L. Qian, D. Bera, "Nanophosphor for Light Emission & Radiation Detection" *Phosphor Global Summit*, March 23-25, San Diego, CA, 2010; Invited Talk
2. T. K. Tseng, J. Choi, M. Davidson, L. G. Jacobsohn, J. Ballato, T. DeVol, P. Holloway, "Nanoparticles for Scintillation Detection of Nuclear Radiation" *CAARI 2010*, August 8-13, Fort Worth TX, 2010; Invited Talk
3. L.G. Jacobsohn, "Nanophosphors", Faculty of Chemistry Seminar Series, University of Wroclaw, July, 6-10, 2009, Wroclaw, Poland. Invited Seminar

4. Paul H. Holloway, "Luminescent Nanoparticles" 3rd Conference on Photonic Materials. Mabula Game Lodge, South Africa, March 23-27, 2009. Plenary Lecture
5. Jihun Choi, T.-K. Tseng, M. R. Davidson and Paul H. Holloway, "Enhanced photoluminescence from $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ based core/multi-shell nanoparticles", AVS 58th International Symposium, Nashville, TN, October 30- November 4, 2011.
6. L.G. Jacobsohn, C.L. McPherson, C.J. Kucera, H. Qian, R.S. Meltzer and J. Ballato, "Size effects on the scintillation of $\text{BaF}_2:\text{Ce}/\text{BaF}_2$ core/multi-shell nanoparticles", 16th International Conference on Luminescence & Optical Spectroscopy of Condensed Matter, Ann Arbor, MI, June 27- July 1, **2011**
7. L.G. Jacobsohn, K. Serivalsatit, S.A. Roberts, E.G. Yukihiro, T.A. DeVol and J. Ballato, "Fabrication and scintillation response of rare earth doped transparent ceramics", 2010 Glass & Optical Materials Division Annual Meeting of the American Ceramic Society, Savannah, GA, May 15-19, **2011**
8. L.G. Jacobsohn, K.B. Sprinkle, C.J. Kucera, T.L. James, T.A. DeVol and J. Ballato, "Synthesis, Luminescence and Scintillation of rare Earth Doped Fluoride Nanoparticles," 3rd International Workshop on Photoluminescence in Rare Earths: Photonic Materials and Devices, Florence, Italy, April 28-30, 2010.
9. L.G. Jacobsohn, K.B. Sprinkle, C.J. Kucera, T.L. James, T.A. DeVol and J. Ballato, "Fluoride Nanoscintillators", 2010 Glass & Optical Materials Division Annual Meeting of the American Ceramic Society, Corning, NY, May 16-20, 2010.
10. L.G. Jacobsohn, C.J. Kucera, K.B. Sprinkle, S.A. Roberts, E.G. Yukihiro, T.A. DeVol and J. Ballato, "Scintillation of Nanoparticles: Case Study of Rare Earth Doped Fluorides", 2010 Nuclear Science Symposium and Medical Imaging Conference and the 17th Room Temperature Semiconductor Detector Workshop, Knoxville, TN, 30 October- 6 November.
11. L.G. Jacobsohn, S.C. Tornga, B.L. Bennett, R.E. Muenchausen, O. Ugurlu, T.-K. Tseng, J. Choi and P.H. Holloway, "Annealing effects on the photoluminescence yield of $\text{Gd}_2\text{O}_3:\text{Eu}$ nanoparticles produced by solution combustion synthesis", 7th International Conference on Luminescent Detectors and Transformers of Ionizing Radiation, July 2009, Krakow, Poland.
12. T. K. Tseng, J. Choi, M. Davidson, P. Holloway, "Enhanced Photoluminescence from Europium-Doped Gadolinium-Based Nanocrystal Scintillators" *American Vacuum Society 57th International Symposium & Exhibition 2010*, October 17-22, Albuquerque NM, 2010
13. J. Choi, T. K. Tseng, M. Davidson, P. Holloway, "Enhanced Photoluminescence of $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ Nanoparticles by Encapsulation with Y_2O_3 ," *Annual Joint Symposium Florida Chapter of the AVS Science and Technology society and the Florida Society for Microscopy*, March 7-10, Orlando FL, 2010
14. T. K. Tseng, J. Choi, P. Holloway, "Properties of $\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ Nanoparticles and $\text{SiO}_2/\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ Core/Shell Nanoparticles for Scintillation Detectors," *IEEE Nuclear Science Symposium*, October 25-31, Orlando FL, 2009
15. T. K. Tseng, J. Choi, P. Holloway, "Synthesis and Characterization of $\text{SiO}_2/\text{Gd}_2\text{O}_3:\text{Eu}^{3+}$ Core/Shell Scintillation Nanoparticles," *Materials Research Society 2009 Spring Meeting*, April 13-17, San Francisco CA, 2009

Consultative and advisory functions to other laboratories and agencies and other DoD laboratories.

Received a single crystal BGO sample from Dr. Marc S. Litz, Army Research Laboratory, Adelphi, Maryland, and measured the minimum external quantum yield for photoluminescence

Transitions.

Mr. Scott Walker, Sandia National Laboratories, Albuquerque, will evaluate the benefits of using gadolinium oxide nanoparticles doped with europium to produce scintillation from neutron capture.

New discoveries, inventions, or patent disclosures:

Patent Disclosure: "Index Matching of Nanoparticles with the Matrix to Reduce Optical Scattering", University of Florida disclosure # 13541, filed July 29, 2010; Inventors-Paul H. Holloway, Luiz Jacobsohn, Jihun Choi, Mark Davidson, Teng-Kuan Tseng.

Honors/Awards:

1. Kevin Sprinkle, "The Undergraduate Award" Clemson University Chapter of MRS and OSA, Annual Poster Competition, "Fluoride Nanoscintillators", March 9, 2010
2. T. K. Tseng, J. Choi, M. Davidson, P. Holloway "Luminescence and Structure Characteristics of Self-Activated Bismuth Germinate Scintillation Nanocrystals," Annual Joint Symposium Florida Chapter of the AVS Science and Technology society and the Florida Society for Microscopy, March 7-10, Orlando FL, 2010; (First Place Poster Award)
3. J. Choi, T. K. Tseng, M. Davidson, P. Holloway, "Photoluminescence from $Gd_2O_3:Eu^{3+}$ Nanoparticles Synthesized by Hot Solution Method," *Annual Joint Symposium Florida Chapter of the AVS Science and Technology society and the Florida Society for Microscopy*, March 8-12, Orlando FL, 2009; Honorable mention poster award
4. T. K. Tseng, J. Choi, P. Holloway, "Structure and Luminescence of Europium-Doped Gadolinia-Based Core/Multi-Shell Scintillation Nanoparticles," *Annual Joint Symposium Florida Chapter of the AVS Science and Technology society and the Florida Society for Microscopy*, March 8-12, Orlando FL, 2009; Selected for Young Leader Oral Presentation Session
5. T. K. Tseng, J. Choi, M. Davidson, P. Holloway, "Synthesis of Flower-like $Gd_2O_3:Eu^{3+}$ Scintillation Nanocrystals via a One-pot Non-hydrolytic Method," *Annual Nanoscience Technology Symposium, NanoFlorida2008*, Sep. 26-27, Orlando FL, 2008; Certificate of Excellence for the Oral Presentation
5. Paul H Holloway. "Lifetime Achievement Award for Outstanding Research and Advancement of Science of Luminescent Materials", awarded at the 15th International Workshop on Organic and Inorganic Electroluminescence (EL 2010) September 27 - October 1, 2010, St. Petersburg, Russia.

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