

Gamma Ray Scintillators via BaF₂:Ce Nanopowders

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Abstract

Nano-scale BaF₂:Ce phosphor powders (“nanophosphors”) show great potential for improving the functioning of inorganic scintillators for gamma ray detectors. These particles may offer greater efficiency and ease of manufacture than most state-of-the-art single crystal scintillators currently in use. Chemical precipitation similar to that of LaF₃:Ce synthesis was used to prepare the BaF₂:Ce powders, while care was taken to optimize doping levels to prevent internal absorption while maximizing photon production. Select particle samples were then encapsulated in a polymer matrix in an attempt to improve mechanical robustness while maintaining photon yield. Results from photoluminescence excitation and emission measurements of samples of BaF₂:Ce powders doped from 1-30mol% suggest that the BaF₂:15mol%Ce sample exhibited the greatest photon production, but that a more UV transparent polymer must be found in order to maximize light transmission when the powder is encapsulated in a polymer matrix.

Keywords: Nanophosphor Synthesis, Characterization

1. Introduction

1.1 Motivation for Development

According to the Security and Accountability for Every Port Act (SAFE Port Act, H.R. 4954), all cargo entering the country must be scanned for threatening radioactive material¹. Current scintillator detectors are fragile, hygroscopic, and unable to classify the specific isotope emitting radiation. This research focuses on improving two main scintillator properties: photon yield and bulk density². Photon yield/production refers to the number of photons produced per MeV of gamma ray energy absorbed,³ while bulk density correlates to the atomic weight of the host/dopant material. Ideal scintillators will have a light yield of more than 5×10⁴ photons/MeV, and high bulk density (alkaline/actinide elements) for increased photon interaction³.

The best scintillators currently in use are single crystals of NaI, doped with less than 1mol% Tl. These scintillators have a photon yield of 4.1×10⁴ photons/MeV and a density² of 3.67 g/cm³. NaI(Tl) single crystals can be grown easily and economically, but are extremely fragile and hygroscopic, and so must be encased in a protective shell³. Large single crystals of BaF₂ have lower photon yields than NaI(Tl) crystals due to a higher concentration of defects arising from more sensitive crystal growth.³ Difficulty arises from the need to grow large single crystals of BaF₂, but if crystal size could be decreased, photon yield and energy resolution could increase.

1.2 Inorganic Phosphor Nanopowders

Nano-scale phosphor powders (nanophosphors) offer improved photon yields compared to single crystals by minimizing absorption and scattering due to impurities, which are a problem in large crystal growth^{4,5}. BaF₂:Ce nanophosphors in particular exhibit properties that suggest superior performance in scintillator technology. Energy deposited into the powder by lower energy radiation will not excite electrons in BaF₂, and thus the powder will only generate scintillation photons in the presence of high energy gamma-rays, thereby eliminating much noise from the energy spectrum⁶.

1.3 Direction of Work

This investigation seeks to improve scintillators by increasing scintillation material density, and increasing photon yield by decreasing defect concentration. Past studies have indicated that scintillator efficiency can be improved by doping a host crystal with rare earth elements³. Maintaining this assumption, BaF₂:Ce nanopowders will be synthesized using a method similar to the chemical precipitation synthesis⁷ of LaF₃:Ce. Goals include the creation of a nanophosphor with a high bulk density and increased photon production. Photoluminescence excitation (PLE) and emission (PL), and X-ray diffraction (XRD) measurements will be used to characterize all powders synthesized. Powders with high efficiency indicated by PL measurements will be encapsulated in a UV curable polymer, and

gamma ray measurements conducted to measure efficiency upon excitation by a radionuclide source. The results will be compared to single crystal NaI(Tl) scintillators, which are currently the most efficient.

2. Procedure

2.1 $BaF_2:Ce$ Nanophosphor Synthesis

$BaF_2:Ce$ with doping levels from 1-30mol% were synthesized. The molar amount of $Ba(NO_3)_2$ powder was held at a constant 18.89mmol while the amount of $Ce(NO_3)_3$ powder was varied from 0.2-8.09mmol to achieve the desired doping level. These powders were mixed in 80mL of deionized (DI) water in a round bottomed flask, and the mixture stirred mechanically. In a separate flask, 1.6g NaF was mixed into 100mL of DI water with a solution of 3.6g of oleic acid in 100mL of ethanol. This solution was heated to 78°C using a heating mantle. The $Ba(NO_3)_2$ solution was then added drop-wise under a nitrogen gas purge to the NaF solution, and the final mixture held and stirred at 78°C for one hour. The solution was then centrifuged at 3000 rpm for 15 minutes, then the liquid decanted and 200mL of ethanol added to each flask. The $BaF_2:Ce$ powders were mechanically agitated and a sample of the suspension was taken and placed into a scintillation vial for photoluminescence tests. The powder was then dried in air overnight.

2.2 $BaF_2:Ce$ Nanophosphor Characterization

Photoluminescence excitation (PLE) measurements were conducted using a Cary Eclipse Fluorescence Spectrometer with a monitor wavelength of 353nm to find the optimal excitation wavelength for the $BaF_2:Ce$ powders. The sample was excited with wavelengths ranging from 200nm to 340nm. Photoluminescence emission (PL) measurements were conducted using a 288nm excitation beam (determined from the PLE measurements) scanning a wavelength range from 300nm to 480nm.

Transmission electron microscopy (TEM) was used to confirm that the nanophosphors were composed of individual particles, while X-ray diffraction (XRD) was used to determine $BaF_2:Ce$ crystallite size. TEM analysis was conducted using a JEOL 100CX TEM operating at 100kV. Particle size analysis was conducted with an X'Pert Pro α -1 diffractometer equipped with a Cu $K\alpha$ X-ray tube emitting at 1.54Å scanning a 2θ range from 20-70°.

2.3 Scintillator Fabrication

To match the refractive indices (RI) of the powder and polymer matrix, commercially available liquids with known RI at 589nm from Cargille Labs Inc. (Cedar Grove, NJ) were used in conjunction with a Leica M165C optical microscope and a 400nm LED. Two drops of RI matching liquid were added to 10mg of $BaF_2:Ce$ powder on a glass slide. An optical microscope was used to determine the visibility of the powder agglomerates under each RI liquid, which was the criterion for determining the RI of the powder. After a matching liquid was found, a disper-

sion curve for the specific liquid was acquired from the manufacturer, and the RI of the powder estimated via a polynomial fit to the data.

A UV curable (OptiClad) polymer with a RI of 1.485 at 389nm was acquired from Ovation Polymers (Medina, OH) and used to encapsulate the $BaF_2:Ce$ nanophosphors. The custom made polymer was a mixture of several different monomers that imparted the specific physical and optical properties needed for this investigation. $BaF_2:Ce$ was placed into 10mL of the OptiClad polymer in a standard 40mm diameter by 30mm deep mold. The suspension was homogenized using a Fisher Scientific 550 sonic dismembrator probe to disperse the powder uniformly in the polymer, and then cured using a Lesco Rocket Cure SuperSpot Mk II UV lamp operating with a 100W DC mercury vapor short-arc.

2.4 Gamma Ray Measurements

Gamma ray measurements were conducted using a radionuclide source placed on top of the cylindrical scintillator sample. The sample and source were placed on a photomultiplier tube (PMT) and the entire apparatus encased in a shield to block excess light. Photons generated by the scintillator-gamma-ray interactions were recorded by the PMT, and assigned a "channel number" ranging from 1-12keV depending on the energy of the photon emitted. In this test, 1040 channels between 1keV and 12keV were used, with a total counting time of 6×10^4 s.

3. Results and Discussion

3.1 $BaF_2:Ce$ Synthesis

The total mass of the finished $BaF_2:Ce$ powder was kept below 5g because it was found that extensive agglomeration would occur when the batch size exceeded 8g. Drying the finished powder in air also introduced error because BaF_2 is hygroscopic, causing the powder to absorb moisture during the drying process. This was problematic during encapsulation, when excess moisture had an adverse effect on the polymer curing process; and therefore, data collected.

3.2 PL and PLE Trends

PLE data monitored at 353nm (see Figures 1 and 2), yielded a peak at 288nm, indicating that this wavelength would most efficiently excite the $BaF_2:Ce$ powders. A wavelength of 353nm was chosen for PLE measurements from peak locations in a PL spectra.

After the optimal 288nm excitation wavelength was determined, PL scans were conducted on samples of each doping concentration. It was found that the $BaF_2:15\%$ Ce powder sample showed the greatest light intensity between 300-480nm. Reduced photon production (concentration quenching) occurred at 15mol% Ce doping, a much higher level than in large crystals (usually less than 1mol%). One possible explanation for this discrepancy is that energy transfer may be regulated to the nanometer region, thus

the energy loss due to dopant-dopant transitions is less widespread; therefore, less serious of a problem⁸.

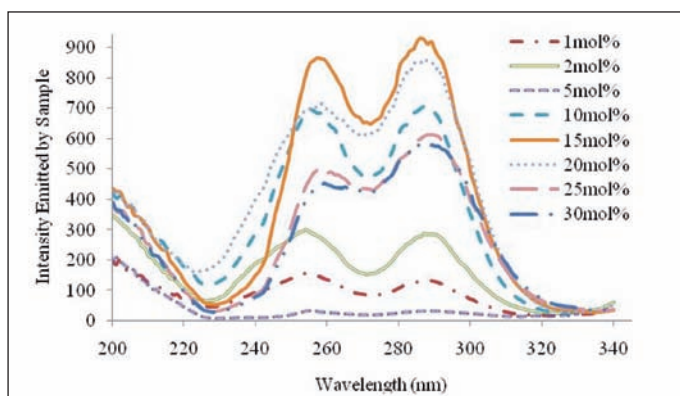


Figure 1. PLE data ($\lambda=353\text{nm}$) for $\text{BaF}_2:\text{Ce}$ powders with dopant levels 1-30mol% (see legend).

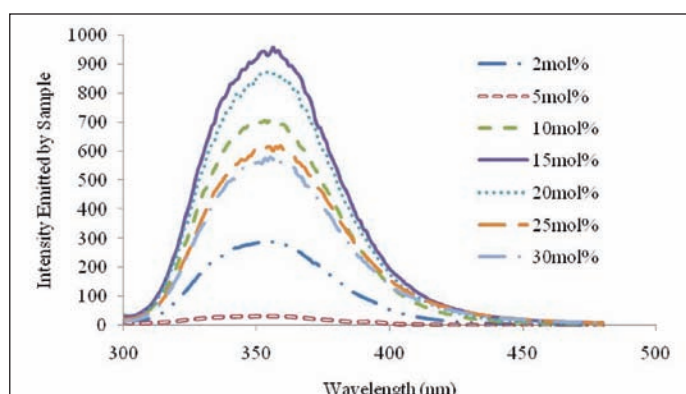


Figure 2. PL data ($\lambda=288\text{nm}$) for $\text{BaF}_2:\text{Ce}$ powders with dopant levels 1-30mol% (see legend).

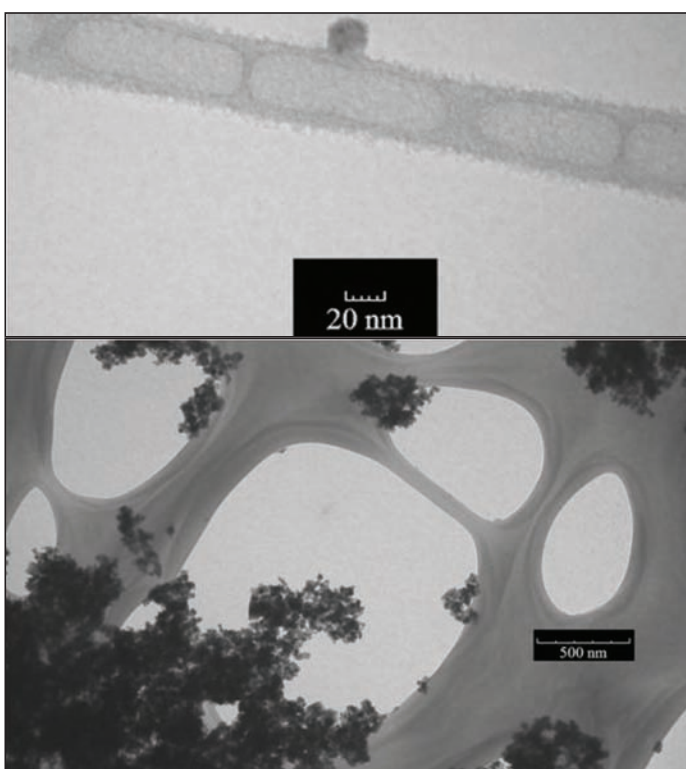


Figure 3. TEM images of $\text{BaF}_2:15\%\text{Ce}$ particle.

Via TEM observation (see Figure 3), it was concluded that the powder synthesized was composed of individual particles. Results from the XRD analysis are shown in Figure 4, and particle size was estimated to be between 40nm and 50nm using Debye-Scherrer analysis.

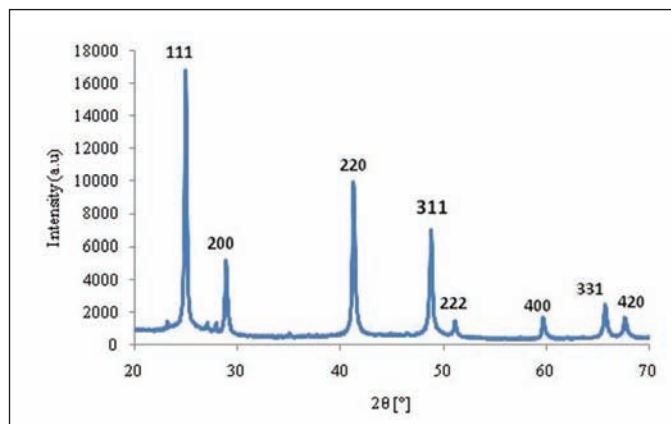


Figure 4. XRD pattern of $\text{BaF}_2:1\%\text{Ce}$ nanopowder.

3.3 Nanopowder/ Polymer Composite

Using RI matching liquids, it was found that the $\text{BaF}_2:\text{Ce}$ powder should have a RI of 1.485 at 389nm. The puck of $\text{BaF}_2:\text{Ce}$ encapsulated in the OptiClad polymer was exposed to an Am-241 radionuclide source. The counts for each channel number were summed and normalized to counting time to generate an energy spectrum (Figure 5) from photons generated by gamma-ray excitation of the phosphors.

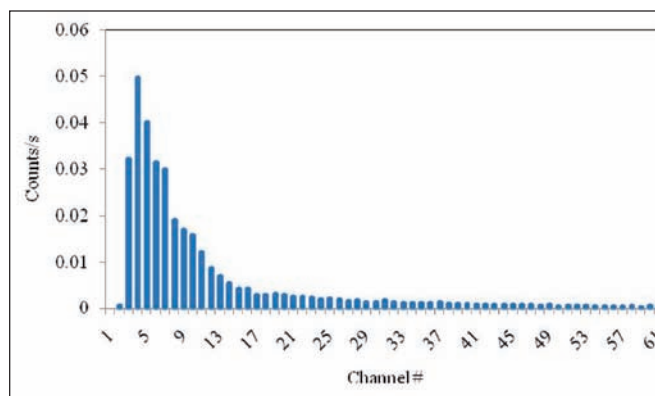


Figure 5. Gamma ray data (energy spectrum) generated by $\text{BaF}_2:\text{Ce}$ encapsulated in UV curable matrix (50vol% solids loading), measured over $6 \times 10^4\text{s}$ under an Am-241 radionuclide source.

These values would ideally generate energy peaks characteristic of Am-241, which is more accurately shown in the energy spectrum produced by a NaI(Tl) single crystal scintillator (Figure 6). It is theorized that the low photon production and poor energy resolution were caused by adverse polymer-phosphor chemical interactions, which induced photon scattering rather than transmission, causing the puck to appear a cloudy shade of yellow instead of the desired clear⁹. The opacity may also have been caused by overheating during the polymerization process, which

is exothermic, thus creating difficulty in stabilizing the sample temperature as polymer thickness increased. The high and unstable temperatures may have caused monomer burn off, thus altering the optical properties of the cured polymer. The overheating problem could be solved by placing the mold in an ice bath during curing, or chilling the sample in a refrigerator or freezer prior to curing.

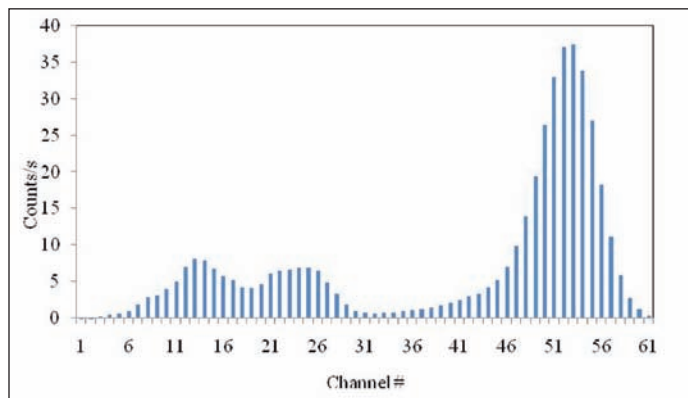


Figure 6. Gamma-ray data (energy spectrum) generated by NaI(Tl) single crystal, measured over 6×10^4 s under an Am-241 radionuclide source.

Low resolution in the energy spectrum may also be due to a lower density of scintillating material in the composite scintillator compared to a single crystal, thus resulting in a lower light yield. The NaI(Tl) single crystal is composed entirely of scintillating material, whereas the composite scintillator was only loaded with 50vol% scintillating particles, reducing the probability of incident gamma-rays striking and interacting with scintillating material. This problem could be mitigated by encapsulating a higher concentration of particles, or pressing a pellet of $\text{BaF}_2:\text{Ce}$ particles and using the polymer as a binder. Although 1024 channels were available during the scans, no relevant peaks were generated above channel #61, and so channels above this value are omitted from the spectra. Removing the superfluous channels simplified analysis of the peaks that were generated by the scintillators under Am-241 excitation.

4. Conclusion

While $\text{BaF}_2:15\text{mol}\%\text{Ce}$ showed the greatest efficiency of the powders synthesized, if polymer encapsulation remains the preferred method of fabricating the nanophosphor scintillators, a polymer with a more controllable polymerization process will need to be procured. Alternatively, particles may be pressed into a pellet and the polymer used as a protective binder rather than an encapsulant in order to maximize density of scintillating material.

Future Work

Future work in nanophosphor synthesis will include doping BaF_2 with other lanthanide series ions such as Eu^{2+} that have the potential to further increase photon produc-

tion. Doping with this ion is desirable because it exhibits greater fluorescence on the blue side of the light spectrum, allowing the light to pass through the polymer matrix (which absorbs light close to UV energy).

Acknowledgements

The author gratefully acknowledges Dr. Jason H. Nadler and Dr. Zhitao Kang of the Georgia Tech Research Institute at the Georgia Institute of Technology for their supervision and guidance. Research was conducted as part of an initiative by the Domestic Nuclear Detection Office (DNDO) in response to the SAFE Port Act.

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About the Author



Brooke Barta is a fourth year undergraduate student majoring in Materials Science & Engineering at the Georgia Institute of Technology. She has been working at the Georgia Tech Research Institute since May 2008. After graduation in May 2010, she hopes to pursue a master's degree in the same field.