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High-density scintillating glasses for a proton imaging detector

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ABSTRACT

High-density scintillating glasses are proposed for a novel proton-imaging device that can improve the accuracy of the hadron therapy. High-density scintillating glasses are needed to build a cost effective, compact calorimeter that can be attached to a gantry. This report summarizes the study on Europium, Terbium, and Cerium-doped scintillating glasses that were developed containing heavy elements such as Lanthanum, Gadolinium, and Tungsten. The density of the samples reach up to 5.9 g/cm^3, and their 300–600 nm emission overlaps perfectly with the peak cathode sensitivity of the commercial photo detectors. The developed glasses do not require any special quenching and can be poured easily, which makes them a good candidate for production in various geometries. Here, the glass making conditions, preliminary tests on optical and physical properties of these scintillating, high-density, oxide glasses developed for a novel medical imaging application are reported.

1. Introduction

High-density scintillating glass is a good alternative to the single crystal scintillators currently being used in radiation detectors. Glass is superior to the single crystals because it can be produced faster, cheaper, and can be molded easily [1]. This means that producing the detector will be more cost-effective. Ideally, the glass would be > 6.0 g/cm^3 to have an adequate signal-to-noise ratio for imaging applications like X-CT [2]. Early scintillating glasses struggled to break 4 g/cm^3 [3–5], but several glasses developed more recently have been able to get above 5 g/cm^3 while keeping acceptable transparency and light yield [6,7]. Our main objective in developing the high density glasses is to build a compact detector that can be attached to the gantry of proton therapy systems.

Using protons to kill diseased tissue, such as tumors, is superior to other treatments because most of a proton beam's energy (up to 250 MeV per proton) is deposited just before the particles comes to rest (The Bragg peak location). This means more precise radiation therapy and harm less healthy tissue. Naturally, this therapy technique requires prior imaging, which is conventionally done via x-rays, i.e. the fluence maps of the beam. However, unlike the x-ray images, proton radiographs provide absorbed proton range information. This would allow us to reduce the range uncertainties and improve the image quality. By designing a novel proton detector, we are introducing an alternative for the initial imaging which would lead to better tumor control.

The scintillating, high-density, oxide glasses are preferred over crystals due to their cost effectiveness [8] and flexibility to be molded into various geometries.

Most of the previous work done on scintillating glasses and crystals have focused on using rare earth cations, Cerium, Terbium, and Europium, as activators. They also include rare earth metals in oxide form, such as Gd_2O_3 for glass and Gd_2SiO_5 for single crystals, to increase density and promote fluorescence of the scintillator [9–11]. This work was focused on modifying pre-existing high density optical glasses by adding a rare earth activator. Specifically, activators were added to an aluminoborosilicate glass patented in 1978 [12] and a borate glass series developed in 2013 [13]. A Ce^{3+}-doped glass with a density greater than 5.0 g/cm^3 that was developed in 2003 [6] was also resynthesized and used for comparison purposes in this work. The goal of this project was to further develop one of these glasses to make it a suitable replacement for the single crystals currently being used in medical and particle physics applications.

2. Experimental methods

Glass samples were prepared using a melt-quench technique. The starting materials were reagent grade WO_3 (99%), Gd_2O_3

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(99.9%), H_3BO_3 (99.5%), La_2O_3 (99.99%), ZrO_2 (99%), SiO_2 (99%), Al_2O_3 (Activated, Neutral, Brockmann I) $(NH_4)_2HPO_4$ (98%), Ga_2O_3 (99.99%), Tb_2O_3 (99.99%) $CeCl_3$ (99.9%), and Eu2O3 (99.9%). Appropriate amounts of these materials were weighed in an alumina crucible and mixed by hand for at least five minutes. The mixture was then put into a furnace preheated to 1200–1500 °C depending on the glass and left for half an hour. This was enough time to melt the mixture and allow it to be poured onto a room temperature iron plate. The glasses cooled into round, domed samples that were not polished because some would crack under the stress of sanding.

Raman scans were done on a JASCO NRS 3100 micro-raman photospectrometer with a 785 nm laser. Runs were done with a 50× magnification lens and had 30 s exposures with 2 accumulations.

The machine used for UV/Vis scanning was a Perkin Elmer Lambda 900 UV/Vis/NIR spectrometer. All samples were scanned from 200 to 800 nm with a step size of 1 nm. Photoluminescence data was gathered with a Jobin Yvon Horiba Fluorolog 3 spectrophotometer equipped with double monochrometers for both excitation and emission. A 450 W Xenon arc lamp was used as an excitation source. The emission data was collected by scanning at that glass's peak excitation and the excitation data was collected while scanning at that glass's peak emission.

Once all optical testing was done, glass samples were crushed by hand with a mortar and pestle in order for them to fit inside the pycnometer and to get rid of as much of the air trapped inside the sample as possible. Density measurements were taken using Helium gas in a Quantachrome Micropycnometer. In order to ensure the data was accurate at least 0.5 g of each sample was used and was run fifteen times, averaging the runs out to get our recorded volumes. The mass of the measured samples were found using an analytical scale. The densities reported are accurate to 0.01 g/cm^3.

Table 2
Density measurements of the glass samples.

Base and dopant	Density (g/cm^3)
Glass 1 with 0.2% Ce	4.74
Glass 1 with 0.5% Eu	4.52
Glass 2 with 2% Tb	4.19
Glass 3 with 0.2% Ce	4.97
Glass 3 with 1% Eu	5.68
Glass 3 with 2% Tb	5.12
Glass 4 with 1% Eu	5.84
Glass 5 with 1% Eu	4.92
Glass 5 with 2% Tb	4.48
Glass 5 with 0.2% Ce	5.00

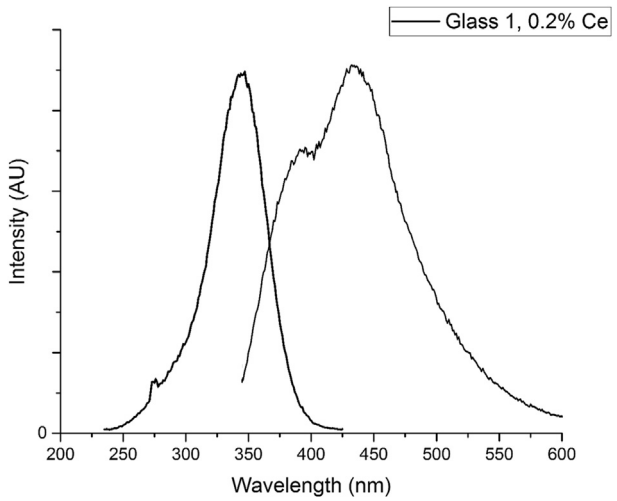

Fig. 1. Excitation (Solid) and Emission (Dashed) of Glass 1 doped with Ce^{3+}.

3. Results

The properties of three different base glasses were studied, each having either zero or one rare earth dopant at a time to induce scintillation. Table 1 shows all of the samples that were synthesized and tested along with their labels that will be used for the remainder of this paper. Glass 1 and Glass 2 are existing compositions [6,14] that were used as relative markers to compare our glasses to. Glass 3 has the aluminaborosilicate composition [12] and Glass 4 and Glass 5 use the high density borate glasses [13] as the base composition. Table 2 shows the densities of each sample that data will be reported for.

Fig. 1 shows the emission and excitation of Glass 1 doped with 0.2% Ce. No luminescence data could be recorded from any other glass with Cerium due to Ce^{3+} oxidizing into Ce^{4+} when melted in an oxygen-rich atmosphere, which causes loss of transparency, and light production.

Figs. 2–4 shows the transparencies of glasses doped with Europium, Terbium, and Cerium, respectively.

Figs. 5 and 6 show the emission spectra for all samples doped with Terbium and Europium, respectively. All glasses doped with Terbium share peaks at 542 nm, 585 nm, and 621 nm. All glasses except for Glass 2 also have a shoulder at 545 nm. All samples doped with Europium show emission bands at 580 nm, 612 nm, 655 nm, and about 700 nm.

Figs. 7 and 8 show the excitation spectra of all samples doped with Terbium and Europium, respectively. All samples doped with Terbium share the same peaks, though intensities of the peaks relative to the max are varied and the two largest peaks show a general trend of being inversely proportional. The Europium samples also share the same peaks between glasses and show some variation in peak intensities relative to the max.

Figs. 9–11 show the Raman spectra for Glasses 1, 3, and 5, respectively, when doped with Europium.

According to [13], the peaks near 350 and 950 cm^{-1} are due to WO_4 tetrahedra forming, which is why that peak is not present in the raman shift plot of Glass 1.

4. Discussion

The activators added to these glasses separately were Ce^{3+}, Eu^{3+}, and Tb^{3+}. Cerium was the primary candidate as, although it is

Table 1
The compositions of the glass samples.

Sample name	Base composition	Activators added
Glass 1	$0.3Gd_2O_3$-$0.35SiO_2$-$0.15(2H_3BO_3)$-$0.2Al_2O_3$	Ce, Eu
Glass 2	$0.38Gd_2O_3$-$0.15SiO_2$-$0.25(2H_3BO_3)$-$0.05(NH_4)2HPO_4$-$0.15Ga_2O_3$	Tb
Glass 3	$0.15La_2O_3$-$0.20Gd_2O_3$-$0.05ZrO_2$-$0.15WO_3$- $0.25(2H_3BO_3)$-$0.1SiO_2$-$0.1Al_2O_3$	Ce, Eu, Tb
Glass 4	$0.25Gd_2O_3$-$0.55WO_3$-$0.2(2H_3BO_3)$	Eu
Glass 5	$0.25Gd_2O_3$-$0.35WO_3$-$0.4(2H_3BO_3)$	Ce, Eu, Tb

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