

High-density scintillating glasses for a proton imaging detector



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ARTICLE INFO

Article history:

Received 23 September 2016

Received in revised form

5 October 2016

Accepted 7 October 2016

Available online 30 October 2016

Keywords:

Scintillating glass

Cerium

Terbium

High-density glass

Europium

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/cm³, 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.

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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/cm³ to have an adequate signal-to-noise ratio for imaging applications like X-CT [2]. Early scintillating glasses struggled to break 4 g/cm³ [3–5], but several glasses developed more recently have been able to get above 5 g/cm³ 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 Gd₂O₃ for glass and Gd₂SiO₅ 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 Ce³⁺-doped glass with a density greater than 5.0 g/cm³ 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 WO₃ (99%), Gd₂O₃

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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) $_2\text{HPO}_4$ (98%), Ga_2O_3 (99.99%), Tb_2O_3 (99.99%) CeCl_3 (99.9%), and Eu_2O_3 (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 \times 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 monochromators 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 .

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

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

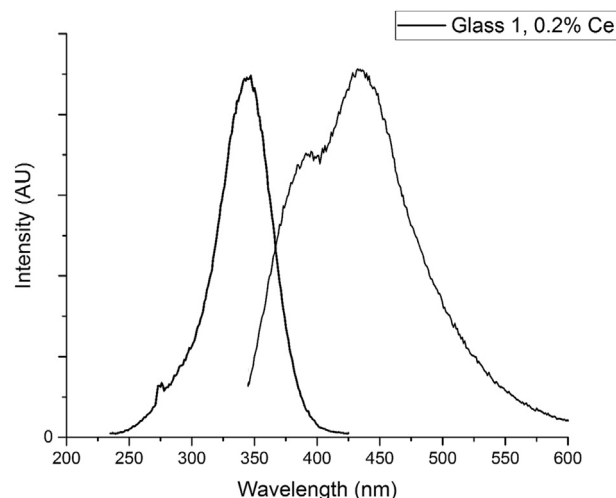


Fig. 1. Excitation (Solid) and Emission (Dashed) of Glass 1 doped with Ce^{3+} .

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	$0.3\text{Gd}_2\text{O}_3-0.35\text{SiO}_2-0.15(2\text{H}_3\text{BO}_3)-0.2\text{Al}_2\text{O}_3$	Ce, Eu
Glass 2	$0.38\text{Gd}_2\text{O}_3-0.15\text{SiO}_2-0.25(2\text{H}_3\text{BO}_3)-0.05(\text{NH}_4)_2\text{HPO}_4-0.15\text{Ga}_2\text{O}_3$	Tb
Glass 3	$0.15\text{La}_2\text{O}_3-0.20\text{Gd}_2\text{O}_3-0.05\text{ZrO}_2-0.15\text{WO}_3-0.25(2\text{H}_3\text{BO}_3)-0.1\text{SiO}_2-0.1\text{Al}_2\text{O}_3$	Ce, Eu, Tb
Glass 4	$0.25\text{Gd}_2\text{O}_3-0.55\text{WO}_3-0.2(2\text{H}_3\text{BO}_3)$	Eu
Glass 5	$0.25\text{Gd}_2\text{O}_3-0.35\text{WO}_3-0.4(2\text{H}_3\text{BO}_3)$	Ce, Eu, Tb

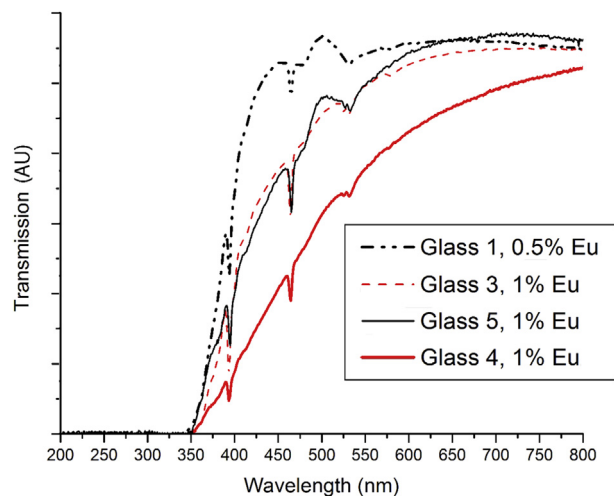


Fig. 2. Transparencies of Glass 1 (Black Dashed), 3 (Red Dashed), 4 (Red Solid), and 5 (Black Solid) when doped with Eu^{3+} . (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

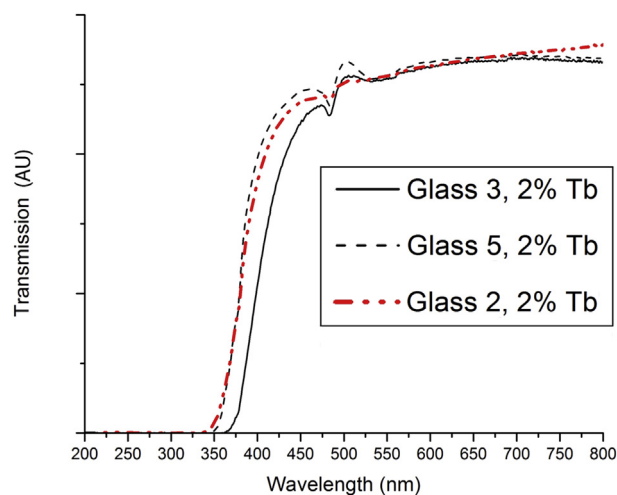


Fig. 3. Transparencies of Glass 2 (Red Dashed), 3 (Solid), and 5 (Black Dashed) when doped with Tb^{3+} . (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

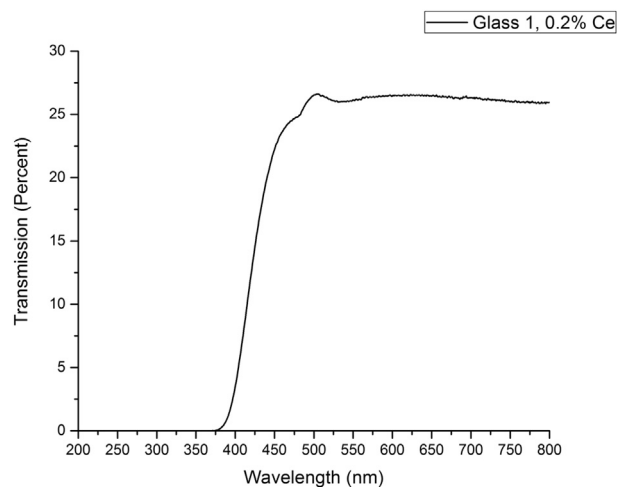


Fig. 4. Transparency of Glass 1 when doped with Ce^{3+} .

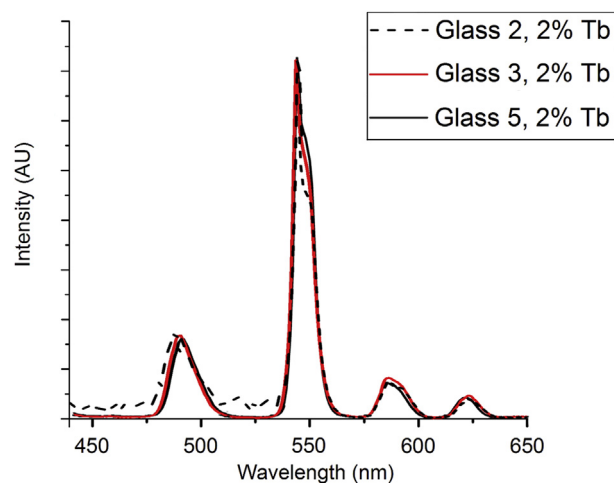


Fig. 5. Emission of Glass 2 (Black Dashed), 3 (Red Solid), and 5 (Black Solid) when doped with Tb^{3+} . (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

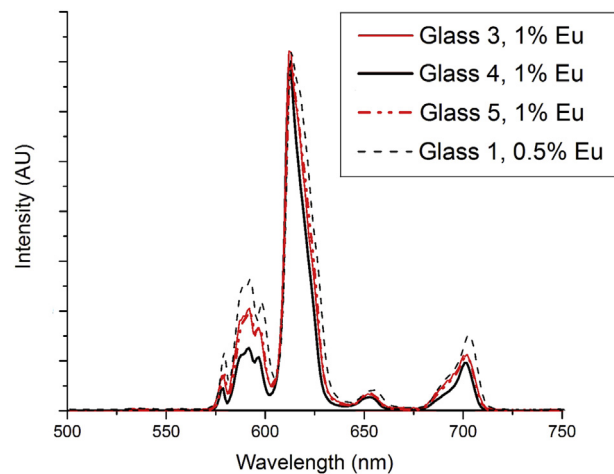


Fig. 6. Emission of Glass 1 (Black Dashed), 3 (Red Solid), 4 (Black Solid), and 5 (Red Dashed) when doped with Eu^{3+} . (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

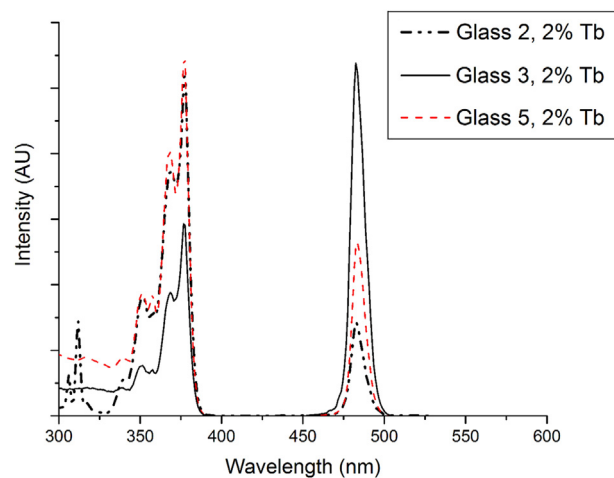


Fig. 7. Excitation of Glass 2 (Black Dashed), 3 (Black Solid), and 5 (Red Dashed) when doped with Tb^{3+} . (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

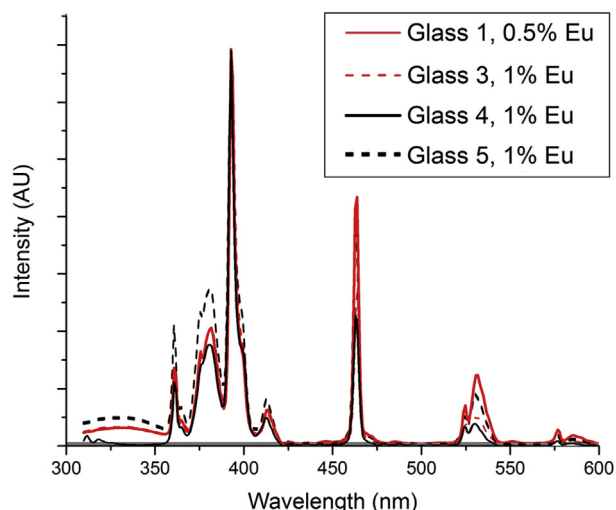


Fig. 8. Excitation of Glass 1 (Red Solid), 3 (Red Dashed), 4 (Black Solid), and 5 (Black Dashed) when doped with Eu^{3+} . (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

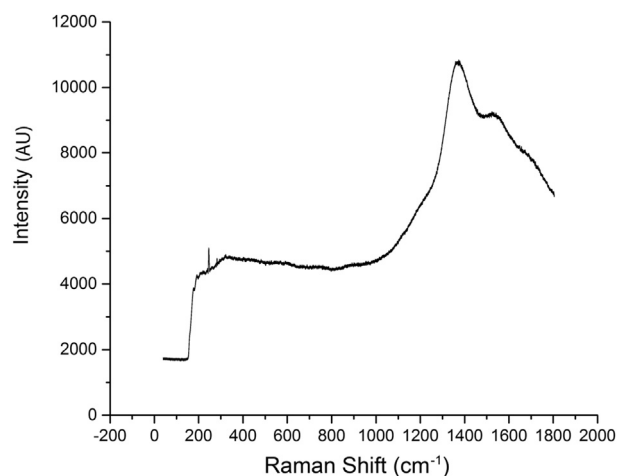


Fig. 9. Raman spectroscopy of Glass 1 when doped with 0.5% Eu^{3+} .

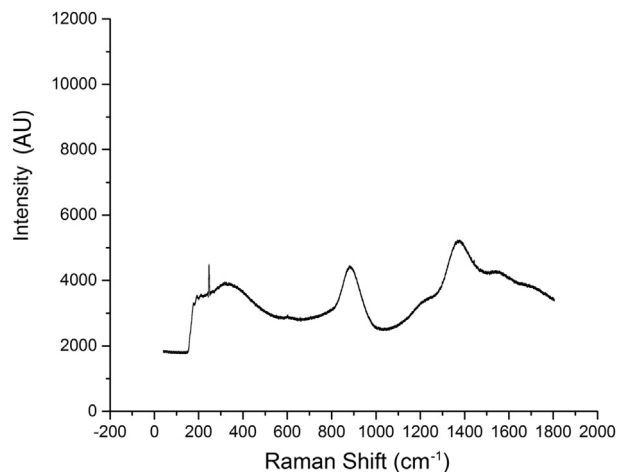


Fig. 10. Raman spectroscopy of Glass 3 when doped with 1% Eu^{3+} .

not crucial for medical applications, it is the only option with a fast enough decay time (~ 10 ns) [8,15] appropriate for a possible particle physics application. Ce^{3+} oxidizes into Ce^{4+} whenever the glass mix was melted in an air atmosphere, a well-documented

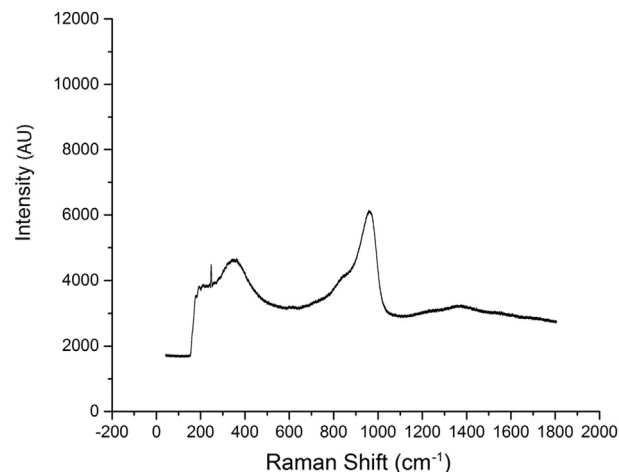


Fig. 11. Raman spectroscopy of Glass 5 when doped with 1% Eu^{3+} .

phenomenon that decreases light yield and transparency [16]. The most common way to avoid oxidation is to melt samples in an inert atmosphere. However doing so would drastically increase the cost of production so Tb^{3+} was tried next. Terbium did not oxidize when melted under a normal atmosphere and did not drastically affect our glasses' transmission properties. Although, as seen in Table 1, the use of Tb_2O_3 drops some of our glasses' respective densities by about 0.5 g/cm^3 . This is a major issue that, coupled with its millisecond decay time, moved the research towards Eu^{3+} . Even though Eu^{3+} also has microsecond decay times like Tb^{3+} , it does not have a major effect on density and also does not oxidize when exposed to a normal atmosphere. It also has the best light yield out of the three activators used and its signal is fast enough for medical applications.

The two glasses from Refs. [6,14], Glass 1 and Glass 2, were used as examples for us to compare our glasses to. Glass 1 is the only sample synthesized that was able to scintillate with Ce^{3+} , though its density lacked behind Glass 3 and 4 by about 1 g/cm^3 as shown in Table 1. Glass 2 was originally doped with Tb^{3+} and so it was used as a reference for our glasses doped with Tb^{3+} . Glass 3 and Glass 5 scintillate better (according to visual inspection) than Glass 2 when doped with 2% Tb_2O_3 . Glass 2 also crystallizes on the outside layer, meaning it must be polished to have similar transparency to Glass 3 or 5.

The first of the glasses that was modified, Glass 3, got its density from the Lanthanum, Gadolinium, Tungsten, and Zirconium that made up most of its mass and molar composition. Though it is not as dense as Glass 4, it is cost-efficient and vitrifies more consistently than Glass 4. This is mostly due to the fact that it does not gain much internal stress through the standard melt quenching and pouring technique, while Glass 4 does. When doped with Eu_2O_3 it has a noticeably higher light yield than any other glass that was synthesized and similar transparencies to Glass 5, which was the most transparent.

Glasses 4 and 5 are from Ref. [13] and are borate glasses that get their density from Tungsten and Gadolinium. They come from the series $25\text{Gd}_2\text{O}_3\text{-}x\text{WO}_3\text{-(}75-x\text{)B}_2\text{O}_3$ with $x = 55$ and $x = 35$, respectively. Those values of x were chosen because they exhibited the best density while maintaining optical transparency. Glass 4 has a density well above that of Glass 5 and, while it may not be as transparent as Glass 5, it passes enough scintillated light through for detector applications. They both have a slightly lower cost/cm³ when considering raw materials, though they are the only glasses that require annealing to not crack at small sample sizes. Also, when compared to Glass 1, 2, and 3 they do not consistently vitrify completely.

All synthesized glasses have a transmission cutoff below 375 nm, so Eu^{3+} and Tb^{3+} -doping will result in little to no loss in scintillated light [17–19].

Acknowledgements

This work was funded by NSF-DMR 1407404, NSF-REU 1358968, NSF DMR 1207080, and R.J McElroy Trust Student/Faculty Research Fund. The authors are thankful to Clemson University COMSET and Dr. Dongxu Wang of University of Iowa Hospitals and Clinics for their support on this project.

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