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Synthesis and luminescence properties of Tb doped LaBGeO₅ and GdBGeO₅ glass scintillators

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Abstract

Borogermanate glasses show promise as scintillators due to their ability to incorporate high levels of heavy metal oxides without excessive loss of luminescent output intensity. Heavy metal oxide scintillating glasses of 50GeO₂-25B₂O₃-(25-x)La₂O₃/Gd₂O₃-xTb₂O₃ (x=1,2,3,4) with the same stoichiometric composition of crystalline Tb doped LaBGeO₅/GdBGeO₅ were synthesized via the melt-quench method. Three times of higher light output under gamma ray excitation was observed from Tb doped GdBGeO₅ based glass compared to LaBGeO₅ glass due to efficient energy transfer between Gd-Tb pairs and higher luminescence efficiency in the GdBGeO₅ glasses. The potential to form LaBGeO₅/GdBGeO₅ glass ceramic scintillators was also discussed and preliminarily investigated.

Keywords

ceramics; optical materials; optical properties

1. Introduction

Tb doped LaBGeO₅ and GdBGeO₅ based glasses, prepared in the same stoichiometric composition as their crystalline counterparts, are explored in this study for potential low cost scintillator applications. Glass and glass ceramic scintillators doped with rare-earth elements are promising to replace single crystal scintillators for certain application areas in medical and industrial imaging, and homeland security fields with significant concerns on material and fabrication cost, large volume/custom shaped products, and high resistance to environment, moisture and impacts.[1–4] The issue of glass scintillators is the low light output due to the amorphous structure. A glass ceramic with scintillating crystals embedded in a stable glass matrix may enhance its luminosity performance, especially if the crystal volume can be dramatically increased to near 100% like single crystal or transparent ceramic scintillators. However, such glass systems are rarely investigated for scintillator applications.

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Glasses with a stoichiometric composition that closely matches their crystalline form may be prepared as glass ceramics with a very high crystalline volume while causing little to no change in the transparency of the sample due to perfect refractive index matching.[5–9] For example, $\text{Ba}_2\text{TiSi}_2\text{O}_8$ glass ceramics have been prepared with a crystalline ratio of 71% $\text{Ba}_2\text{TiSi}_2\text{O}_8$ phase while high transparency still remained and luminescence enhancement was observed from Dy^{3+} doped $\text{Ba}_2\text{TiSi}_2\text{O}_8$ glass ceramic compared to the counterpart glass.[6, 8–9] Samples of highly transparent KNbGeO_5 glass ceramic have achieved 80% crystalline volume with a $\text{K}_{3.8}\text{Nb}_5\text{Ge}_3\text{O}_{20.4}$ phase.[10] Berthier's study of $\text{Na}_2\text{Ca}_2\text{Si}_3\text{O}_9$ glass ceramic samples shows that up to 97% crystal volume and large grain size cause little change in the transparency of the sample due to excellent refractive index matching between the glass and the crystalline phases.[5] Unfortunately, these glass/glass ceramic systems are not highly efficient light emitting materials for scintillating applications. Therefore, other potential stoichiometric glass systems need to be pursued. In this study, we chose to explore LaBGeO_5 and GdBGeO_5 glasses which share their composition with their crystalline phases, to characterize their scintillation performances and preliminarily investigate their potential to be prepared as a transparent glass ceramic scintillator.

Lanthanum borogermanate and gadolinium borogermanate glasses are of interest as both glasses support addition of large amounts of germanium and lanthanum group elements, giving the germanate glasses a much higher density than their counterpart silicate glasses which is advantageous for scintillator applications. The higher density allows the glasses to better stop and absorb x-rays and gamma rays. Heavy metal oxide glasses are also valuable since they possess high radiation hardness.[11] In addition, germanate glasses have smaller maximum vibrational frequencies than silicate, phosphate, and borate glasses which increases the quantum efficiency of the rare-earth ions they are doped with; this gives the germanate glass potential to be a more efficient medium for optical lasers and fiber optical amplifiers.[12] Glass-based active dielectrics of LaBGeO_5 and nanocrystal embedded LaBGeO_5 glass ceramic are looking to replicate many favorable characteristics of single crystal such as ferroelectricity, high electrical resistivity, low dielectric constant, and low dielectric losses, but they are rarely studied for scintillator applications.[13] However, crystalline form LaBGeO_5 has been proven to be a successful host matrix for efficient light emission from Eu^{3+} , Tb^{3+} , and Tm^{3+} . [14] As for GdBGeO_5 , its crystalline form was also reported as effective host material for rare-earth doping and efficient emissions from Eu^{3+} or Tb^{3+} doped GdBGeO_5 crystals were reported.[15] Luminescent properties of Eu^{3+} or Tb^{3+} doped GdBGeO_5 glass were also investigated and recently borogermanate glasses with high Gd content were reported for scintillator applications.[4,15,16] However, a focus on the investigation of stoichiometric compositions and comparison between LaBGeO_5 and GdBGeO_5 based glasses are not reported. Tb^{3+} exhibits a slow decay time of a few milliseconds compared to the fast Ce^{3+} decay time of $\sim 100\text{ns}$, which is not applicable for gamma spectroscopy needed in many homeland security applications. However, Tb^{3+} doped scintillators and phosphors have been well used in medical and industrial X-ray imaging inspection systems.[3] Efficient Tb doped glass scintillators may also find applications in portal imaging at MeV energies.

2. Methods

Tb doped LaBGeO₅ and GdBGeO₅ glass samples, hereafter abbreviated as LBGT and GBGT, were prepared with the melt-quench method. The glass samples were synthesized according to stoichiometric compositions of 50GeO₂-25B₂O₃-(25-x)La₂O₃/Gd₂O₃-(x)Tb₂O₃ (x=1, 2, 3, 4) in mole ratios. In the actual experiment, (x/2)Tb₄O₇ was used instead of xTb₂O₃. Powder materials utilized were GeO₂ (Acros Organics, 99.999%), B₂O₃ (Alfa Aesar, 99.98%), La₂O₃ (Cerao, 99.99%), Gd₂O₃ (Alfa Aesar, 99.9%), and Tb₄O₇ (Alfa Aesar, 99.9%). The powders of raw materials were thoroughly mixed together into an alumina crucible and loaded into a box furnace. The samples were melted at 1250°C for 2.5 hours in an argon atmosphere. The melted glass was quenched by pouring into a graphite mold which was pre-heated to 400°C and then slowly cooled down to room temperature in a furnace. Bulk samples were annealed at 500°C to remove thermal stress before polishing for further analyses. Pieces of samples were annealed at 600–900°C for various times to investigate the crystallization behavior of the glasses.

Glass density was measured via Archimedes' principle in water. For annealed samples, they were crushed into powders and analyzed by X-ray Diffraction using an X'pert PRO Alpha-1 system at a scanning speed of 175–190 seconds per step. Photoluminescence (PL) and photoluminescence excitation (PLE) spectra of bulk samples were obtained with a Spex1000M spectrometer which used a 150W Xe lamp/monochromator combination as the excitation source. Luminescence decay measurements were made using a 355 nm tripled YAG:Nd 10ns pulsed laser as the excitation source and a Tektronix DSA 602A oscilloscope to collect the decay signal. A Hamamatsu R943-02 GaAs photomultiplier tube (PMT) was used as the light detector. Gamma ray excited brightness was measured by wrapping the sample with reflecting Teflon tape on its sides and on the face that would be exposed to the radiation source, applying optical grease to the exposed face and placing onto a PMT. The PMT is a 2 inch diameter Hamamatsu R669 with extended detection wavelength in the red, which was connected to a current meter to directly read the relative light output signal from the excited sample. The radioactive isotope point sources used for the gamma ray tests were 1μCi Cobalt-60 and 5μCi Manganese-54. Emission under X-ray excitation was performed in transmission mode using a 60kV source and the emitted light was imaged using a CCD camera and a 45 degree mirror. All measurements were performed at room temperature.

3. Results and discussion

Photoluminescence spectra of Tb doped LaBGeO₅ and GdBGeO₅ glass samples under 274 nm excitation are shown in Figure 1(a) and Figure 1(b) respectively. The inset graphs show an expanded view of the 350–450 nm range and the inset pictures show the green emitting samples under 365 nm UV lamp excitation. The results are consistent with typical green emission lines associated with the f-f internal orbital transitions observed from Tb³⁺ doped materials.[17] For both LBGT and GBGT samples, the 4 main peaks at 489, 543, 585, and 622 nm which correspond to the ⁵D₄-⁷F_J (J=6,5,4,3) optical transitions are clearly visible. [4,18–19] The brightness of this green emission is shown to increase with an increase in the concentration of Tb³⁺. The inset enlarged graph in Figure 1(a) shows three small peaks in the 350–450 nm range corresponding to the ⁵D₃-⁷F_J (J=5,4,3) transitions in the Tb³⁺ doped

LaBGeO₅ samples. The decrease in these peak intensities with increase of Tb doping is due to cross-relaxation in Tb³⁺ ions.[20–22] These peaks can also be observed from the Tb doped GdBGeO₅ samples as shown in the inset graph of Figure 1(b). However, they are overlapped with a broad emission band which is likely due to emissions from Gd³⁺. [23] This broad emission band is highest at low Tb₂O₃ doping concentration of 1% because not enough Tb³⁺ ions available for energy transfer from Gd³⁺ to Tb³⁺. With increase of Tb concentration, energy transfer rate increases and the intensity of the broad Gd³⁺ emission band decreases. The Tb³⁺ emission peaks in the 350–450 nm range are well-resolved at 2% Tb₂O₃ doping but quenched at higher doping concentrations.

The relative brightness of photoluminescence from each sample under 365 nm excitation is compared in Figure 2. The brightness of both sets of samples increases with increasing Tb³⁺ content which suggests we have not yet reached the critical point of concentration quenching for the green emission from Tb³⁺. Additionally it is shown that for equal concentrations of Tb³⁺ the GBGT samples produce more luminescence than their LBGT counterparts. As the emission was originated directly from Tb³⁺ excitation at 365 nm according to the excitation spectra discussed later, it is suggested that the GBGT samples exhibit less non-radiative defects and thus a higher PL efficiency.

Figure 3 shows examples of PLE spectra conducted by monitoring the emission wavelength at 544nm for the LaBGeO₅:Tb and GdBGeO₅:Tb glass samples. All of the samples exhibit the highest excitation peak at 372nm due to the ⁷F₆ – ⁵D₃ transition in Tb³⁺ and lower intensity peaks at 352 and 490 nm attributed to the ⁷F₆–⁵L₉ and ⁷F₆ – ⁵D₄ excitation in Tb³⁺ respectively which were reported from crystalline materials and are consistent with the absorption measurements shown in Figure 4(a).[19,24–25] There is also a peak from the LBGT sample at 315 nm which corresponds to the ⁷F₆–⁵D₁ transition in Tb³⁺ which is supported by the absorption measurements.[26] However, these observed peaks are less sharp due to the glass environment of Tb³⁺ ions. The PLE measurements show distinct peaks in the GBGT sample at 274 nm and 313 nm that are not present in the LBGT sample, which are due to transitions in Gd³⁺ and indicating the energy transfer between Gd³⁺ and Tb³⁺. The peak at 274 nm is attributed to the characteristic transition ⁸S_{7/2}–⁶I_j in Gd³⁺ while the peak at 313 nm corresponds to the ⁸S_{7/2} – ⁶P_{7/2} transition in Gd³⁺. [4,16,22,27] The lack of overlap in the excitation and emission spectra seem to suggest there should be very little self-absorption in the material which will be advantageous for scintillation application.[23]

The absorption measurements of the LBGT samples in Figure 4 show a small peak at 485 nm with several other peaks in the 380 nm to 315 nm range. The peak at 485 nm is assigned to the ⁷F₆→⁵D₄ transition in the Tb³⁺ ion.[28] The peaks at 378, 371, 350, 338, and 315 nm correspond respectively to the ⁵G₆+⁵D₃, ⁵L₁₀, ⁵L₉, ⁵D₀, and ⁵D₁ transitions from ⁷F₆ in Tb³⁺. [19,26–28] The same Tb absorption peaks are visible in the GBGT samples at 485, 378, 371, 350, and 338 nm, as well as a peak at 313 nm from the ⁸S_{7/2}–⁶P_{7/2} transition in Gd³⁺. [19,23,27] The absorbance for the undoped LaBGeO₅ glass itself does not exhibit any peaks, only a slow, nearly exponential, growth as it heads towards the UV side of the spectrum.[29] This confirms that the peaks in our absorbance graph are due to the Tb³⁺ ion.

The graph of the luminescence decay curves for the 543nm Tb³⁺ emission exhibits exponential decay portions for intensity levels above 1% which were used to determine the decay time for our samples. The exponential section of the decay was fit with a line of the form:

$$I(t) = I_0 e^{-\frac{t}{\tau}} \quad (1)$$

where I_0 is the initial intensity, t is the time, and τ is the decay time.[30–31] In the process of fitting the above equation trendlines were used that gave information in the form:

$$y = C e^{-bx} \quad (2)$$

where C and b are constants. It was then easy to determine the value of τ by taking the inverse of b . The decay times of LBGT1, LBGT2, LBGT3, and LBGT4 were 1.93, 1.94, 1.87, and 1.91 ms respectively and the decay times for GBGT1, GBGT2, GBGT3, and GBGT4 were 1.88, 1.94, 1.97, and 1.97 ms respectively. The decay time of the LBGT samples appears to not change much or slightly decrease with an increase in doping, whereas the decay time of the GBGT samples appears to increase slightly with increased doping. The decrease in decay time of the LBGT series at relatively higher concentrations is most likely due to cross relaxation between the ⁵D₃ and ⁵D₄ states in Tb³⁺ as described by Weg et al.[20] Considering the higher PL efficiency observed in GBGT samples over the LBGT samples, the longer decay time in GBGT at higher concentrations could indicate a higher radiative relaxation rate due to fewer defects.[20–21] It should be noted the difference is too small to concretely decide.

Gamma ray excitation measurements were gathered using radioactive sources of Cobalt-60 and Manganese-54 with decay energies of 1.17/1.33 MeV and 0.835 MeV respectively. The data gathered in Fig. 7 shows the GBGT series to be greatly more efficient than the LBGT series at the energies tested with nearly every sample of the GBGT series performing better by 2–3 times than sample LBGT4, the most heavily doped LaBGeO₅ sample. The high light output observed from GBGT samples can be attributed to three reasons: 1. The high PL efficiency observed from GBGT compared to LBGT samples indicates less non-radiative defects existed in the GBGT samples; 2. The energy directly absorbed by the Gd³⁺ ions due to gamma ray excitation is easily transferred to the Tb³⁺ ions and contributes to light output in the GBGT samples, while the LBGT samples are greatly relying on the glass matrix to absorb the energy where there is a greater chance of the energy becoming trapped in defects in the sample instead of transferring to a Tb³⁺ ion; 3. The samples of the GBGT series are denser than their LBGT counterparts as shown in Table 1, which allows the GBGT samples to absorb more gamma rays and thus emit more light per unit volume than the LBGT samples.[4,16] Since the light output of the scintillator is one of the main performance factors in a radiation detection or imaging system the GdBGeO₅ sample appears better suited for this purpose. A CsI:Tl single crystal scintillator of comparable size was also measured under Co-60 gamma excitation and a relative light output of ~4318 was obtained as noted in Table 1, indicating that the light yield of GBGT4 sample is about 6.9% of CsI:Tl.

Further improvement in light yield is required for these glass scintillators. A glass-ceramic approach is the main objective for this study to improve light yield performance. Although they are not comparable to single crystal scintillators, economic glass or glass ceramic scintillators may find practical applications in large-area X-ray imaging detectors when cost is a concern.

X-ray imaging measurements were also performed on the Tb doped LaBGeO₅ and GdBGeO₅ samples. As is clearly visible in Fig. 7 the GBGT4 sample scintillates at over 2.5 times the intensity of the LBGT4 sample under x-ray excitation, which is consistent with the gamma ray scintillation results. It should be noted that this number should be higher because a saturation of detector to the GBGT4 emission intensity is noticed. The weaker intensity of the LBGT samples is most likely due to the lack of energy transfer as seen in the Gd-Tb pairs in GBGT samples as well as a higher non-radiative defect level as implied by the lower PL efficiency and faster decay time.

To investigate whether a transparent glass ceramic can be formed in these systems, both LaBGeO₅ and GdBGeO₅ samples are annealed at different temperatures for crystallization. LaBGeO₅ samples were annealed at 670 °C for 6h, 745 °C for 3h, and 765 °C for 6h as was suggested in the work done by Gupta et al for nanocrystal nucleation and growth in LaBGeO₅ glass to form transparent glass ceramics.[32] After the 670 °C anneal no changes are visible in the samples. After the 745 °C anneal the 1%, 2%, and 4% Tb₂O₃ doped samples show visible opaque surface crystallization while all samples exhibit softening. After the 765 °C anneal all LaBGeO₅ samples show significant surface crystallization and have changed shape due to softening. However, crystalline phase was not able to be identified by XRD for the 765 °C annealed sample probably due to the low crystal volume which only occurred on the surface. By increasing the anneal temperature to 850 °C for 6 hours, diffraction peaks were observed by XRD indicating a mixture of crystalline phases including LaBGeO₅ and LaGe₂O₇ phases along with some other unidentified phases. As suggested by Sigaev's reports, alumina content coming from the crucibles may be inhibiting the growth of stillwellite LaBGeO₅ as well as causing the growth of the pyrogermanate LaGe₂O₇ phase and other impurity phases.[29,33–34] Samples of GdBGeO₅ were also annealed at 800 °C and 850 °C for 6h to develop crystallites. At 800 °C crystallization was visible on the surface of the samples. At 850 °C the samples became opaque due to crystallization and exhibited softening similar to the LaBGeO₅ samples but crystalline phases was not able to be identified by XRD. For samples annealed at 900 °C for 6 hours, peaks representing GdBO₃, Gd₂GeO₅ and other phases were observed. It is determined that the alumina content in the crucibles may also inhibit the growth of GdBGeO₅ nanocrystals. [29,33] A platinum crucible will be needed to avoid Al₂O₃ contamination and prepare LaBGeO₅ and GdBGeO₅ glass ceramics in future studies.

4. Conclusion

Tb doped LaBGeO₅ and GdBGeO₅ glasses both show promise as potential scintillation glasses with GdBGeO₅ providing up to three times of better light output under gamma ray excitation. The efficient energy transfer between Gd³⁺ and Tb³⁺ ions and the higher photoluminescence efficiency observed in the GdBGeO₅ samples play important roles in the

higher scintillation performance compared to the LaBGeO₅ samples. The higher density of GdBGeO₅ glass is also advantageous for providing higher stopping power to gamma rays. To further improve the light output, a glass ceramic with high crystal volume ratio is desired. However, transparent LaBGeO₅ and GdBGeO₅ glass ceramics were not able to form in this study probably due to the use of alumina crucible during glass preparation. An investigation into the optical properties of the annealed LaBGeO₅ and GdBGeO₅ glass ceramics prepared in platinum or zirconia crucibles and pursuit of other luminescent activators will follow.

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- Tb doped stoichiometric composition LaBGeO₅/GdBGeO₅ glasses were synthesized
- Gamma ray and X-ray excited scintillation properties were investigated
- GdBGeO₅:Tb scintillator shows threefold higher light yield than LaBGeO₅:Tb
- The potential to form LaBGeO₅/GdBGeO₅ glass ceramic scintillators was investigated

Figure 1.

PL spectra of (a) LaBGeO₅:Tb and (b) GdBGeO₅:Tb glass samples excited at 274 nm; the inset graphs show an expanded view of the 350 nm to 450 nm region; inset pictures show samples stimulated by a 365 nm UV lamp.

Figure 2.
Comparison of relative intensity of the 543nm emission of the LBGT and GBGT series by exciting at 365 nm UV; All intensities were normalized to that of sample LBGT4.

Figure 3.
PLE spectra for the 2% Tb doped LBGT and GBGT samples by monitoring the emission wavelength at 544 nm.

Fig. 4. Absorption spectra of the (a) LBGT samples and (b) GBGT samples; the spectra were manually adjusted in vertical direction for display clarity.

Figure 5. Decay curves of the 543 nm emission peaks for (a) LBGT and (b) GBGT samples with an exponential decay fitting.

Figure 6.

Graph representation of the gamma ray excited light output measurements normalized to LBGT4 using (a) Mn-54 source and (b) Co-60 source.

Figure 7.

X-ray image and light output intensity profile of a comparison between LBG T4(left) and GBGT4(right) samples excited at 60 kVp.

Table 1

Light output of LBGT and GBGT samples under gamma ray excitation with Mn-54 and Co-60 point sources, normalized to a percentage comparison to sample LBGT4.

Sample	Weight (g)	Volume (cm ³)	Density (g/cm ³)	Mn-54/g	Co-60/g	Mn-54/cm ³	Co-60/cm ³
LBGT4	17.9	3.7	4.81	100	100	100	100
LBGT3	17.3	3.6	4.77	89	96	88	95
LBGT2	16.9	3.6	4.76	61	57	60	57
LBGT1	15.2	3.3	4.61	69	65	66	63
GBGT4	17.8	3.5	5.05	288	284	303	298 [*]
GBGT3	13.6	2.7	5.06	263	252	277	265
GBGT2	17.2	3.3	5.18	208	239	224	257
GBGT1	18.7	3.6	5.14	185	211	197	225

* The relative light output of a CsI:Tl scintillator of comparable size was measured to be ~4318.