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Synthesis and Luminescence Properties of Transparent Nanocrystalline GdF₃:Tb Glass-Ceramic Scintillator

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Abstract

Transparent glass-ceramic containing rare-earth doped halide nanocrystals exhibits enhanced luminescence performance. In this study, a glass-ceramic with Tb doped gadolinium fluoride nanocrystals embedded in an aluminosilicate glass matrix is investigated for X-ray imaging applications. The nanocrystalline glass-ceramic scintillator was prepared by a melt-quench method followed by an anneal. The GdF₃:Tb nanocrystals precipitated within the oxide glass matrix during the processing and their luminescence and scintillation properties were investigated. In this nanocomposite scintillator system, the incorporation of high atomic number Gd compound into the glass matrix increases the X-ray stopping power of the glass scintillator, and effective energy transfer between Gd³⁺ and Tb³⁺ ions in the nanocrystals enhances the scintillation efficiency.

1. Introduction

Phosphor screens made from micron-sized phosphors such as Gd₂O₂S:Tb are efficient and bright X-ray converters and widely used in X-ray imaging. However, the micron-sized phosphor particles cause strong light scattering, which limits spatial resolution, and prevents light-propagation thus reducing efficiency in relatively thicker screens. There is ample theoretical and experimental argument to suggest that nanophosphors in a transparent polymer or glass matrix will exhibit significantly better spatial resolution than micron-sized phosphor particles.^{i,ii,iii,iv} In addition, the screen can be made much thicker for high stopping power without losing any light by scattering because nanophosphor-containing composite remains highly transparent due to the negligible scattering from nanoparticles.^{v,vi,vii,viii} With a glass as the matrix material for embedding the nanophosphors, the scintillator screen will be chemically and mechanically stable, and can be easily shaped into large-area plates for applications in adverse environments.^{ix}

Transparent glass ceramics containing rare-earth doped halide nanocrystals have been investigated in recently years mainly for applications in upconversion solid state lasers and optical amplification.^x Glass ceramics containing (Pb,Cd)F₂, LaF₃, GdF₃, BaF₂, BaCl₂, and CaF₂ nanocrystals have been well studied.^{iv,x,xi,xii,xiii,xiv,xv} Compared to rare-earth doped glass materials, the fluorescence of the dopant rare-earth ions in glass-ceramics was enhanced considerably as the crystal phase acted as a sink for the dopant. During the

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annealing process, the rare-earth ions are typically precipitated together with the nanocrystal phase to form a dopant inside the crystal. However, the use of transparent glass-ceramic for scintillation applications has been rarely reported. A few of these transparent glass-ceramic nanocomposite systems have been investigated for X-ray scintillation and imaging.^{iv,xv,xvi} For example, the application of $\text{BaCl}_2\text{:Eu}^{2+}$ nanocrystals embedded in a fluorozirconate-based halide glass-ceramic suggested the advantages of this nanocomposite for applications such as high resolution mammography imaging.^{iv,xvi} X-ray imaging tests showed that the resolution of these glass-ceramic plates exceeded that of commercial plates by about a factor of 10, and that their efficiency was higher than a single-crystal CdWO_4 scintillator. Fu *et al.* prepared a transparent glass-ceramic with $\text{CaF}_2\text{:Eu}^{2+}$ nanoparticles embedded within an oxyfluoride glass matrix.^{xv} The precursor glass showed little scintillation while the glass nanocomposite scintillated strongly with an efficiency up to 30% of that of a $\text{CaF}_2\text{:Eu}^{2+}$ single-crystal. The fluorescence of the dopant rare-earth ions in glass ceramics was enhanced considerably due to the movement of these rare-earth ions from the amorphous glass-matrix into a crystalline environment.

In this work $\text{GdF}_3\text{:Tb}$ nanocrystal-containing glass-ceramic was investigated for X-ray imaging applications. In a gadolinium compound based system, Gd^{3+} ion can act as a sensitizer to transfer energy to Tb^{3+} ion, which is desired to enhance the luminescence. Compared to blue-emitting Eu^{2+} , the green emission from Tb^{3+} matches the spectral sensitivity of conventional CCD detectors very well. The structural and optical properties of such nanocomposites were studied in this paper.

2. Experimental

The $\text{GdF}_3\text{:Tb}$ -containing glass-ceramics were prepared by a melt-quench method followed by an anneal. Robust aluminosilicate glass was selected as the matrix material to form the nanocrystalline glass-ceramic scintillator. To prepare the samples, high-purity SiO_2 , Al_2O_3 , NaF , GdF_3 , and TbF_3 powders were thoroughly mixed together. A series of glass-ceramic samples with varied compositions was synthesized. A typical composition of the glass-ceramic scintillator was $40\text{SiO}_2\text{-}26\text{Al}_2\text{O}_3\text{-}15\text{NaF-}16\text{GdF}_3\text{-}3\text{TbF}_3$ in mol ratios. The mixture was loaded into an alumina crucible and melted in a box furnace. The melt was kept at 1400°C for two hours, and then quenched into a 400°C preheated graphite mold to form a transparent glass sample. Subsequently, the sample was annealed in a furnace at different temperatures between $550\text{--}700^\circ\text{C}$ for 3 hours to precipitate $\text{GdF}_3\text{:Tb}$ nanocrystals in the glass matrix and create nanophosphor-embedded glass-ceramic scintillators.

Photoluminescence (PL) and photoluminescence excitation (PLE) spectra of bulk or powdered glass samples were obtained with a Spex1000M spectrometer using a 150W Xe lamp/monochromator combination as the excitation source. X-ray diffractions were performed on powdered samples with an X'pert PRO Alpha-1 to verify GdF_3 nanocrystal precipitation and particle size. Luminescence decay measurements were carried out using a 355nm tripled YAG:Nd 10ns pulsed laser as the excitation source and a Tektronix DSA 602A oscilloscope to collect the transient decay signal. 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 conducted at room temperature.

3. Results and discussion

Transparent Tb^{3+} doped GdF_3 -containing glass-ceramic scintillators were successfully prepared. Figure 1(a) shows the photoluminescence spectra of the synthesized $\text{GdF}_3\text{:Tb}$ glass-ceramic sample excited at 248 nm and 278 nm. The four main emission peaks located

at 491, 543, 586, 623 nm can be observed in the visible range. These are attributed to the 5D_4 to 7F_J ($J = 6, 5, 4, 3$) energy transitions in Tb^{3+} ions.^{xvii} The emission occurring at 543 nm is the most intense, and thus accounts for the vibrant green color under an ultraviolet light. Also, three other peaks observed from 375 to 450 nm range are a result of the energy transitions of the Tb^{3+} ions from the 5D_3 to 7F_J levels. For 278 nm excitation, an additional emission peak at 313 nm and a broad emission band from 350–450 nm are found which are not observed for 248 nm excitation. The 313 nm peak is attributed to the well-documented energy transition between the 6P_J to $^8S_{7/2}$ levels within Gd^{3+} . The broad emission band from 350–450 nm is probably also due to emissions from gadolinium complexes which can be efficiently excited at 278 nm.

Figure 1(b) shows the photoluminescence excitation and absorption measurements of the $GdF_3:Tb$ glass-ceramic samples. The 278 nm excitation peak is clearly observed by monitoring both the intense 543 nm Tb^{3+} emission line and the 313 nm Gd^{3+} emission line, which suggests the efficient energy transfer between the Gd^{3+} and Tb^{3+} ions. Such effect was also reported from Gd^{3+} and Ce^{3+} containing scintillator materials.^{xviii} The 278 nm excitation peak is due to the excitation in Gd^{3+} from $^8S_{7/2}$ to 6I_J levels. As seen from Figure 1(b), by monitoring at 313 nm, only the 278 nm peak and a much weaker band at 255 nm are observed, which are due to transitions in Gd^{3+} and confirm that the 313 nm PL emission peak is from Gd^{3+} . By monitoring at 543 nm, the excitation bands observed around 315, 356 and 375 nm are due to the 4f transitions in Tb^{3+} , which contribute to the main visible Tb^{3+} emissions peaks, while the 278 nm excitation peak is due to Gd^{3+} - Tb^{3+} energy transfer. As shown from the absorbance curve in Figure 1(b), the absorption edge also starts at about 375 nm and rises continuously to the shorter wavelength direction, confirming the efficient 4f transitions in Tb^{3+} ions.

Figure 2 shows the PL and PLE spectra of the synthesized GdF_3 glass-ceramic sample without any Tb doping. The PL spectrum shows that there is a main peak at 313 nm and a broad emission band from 350–450 nm at the excitation wavelength of 278 nm. As discussed previously, the main 313 nm peak is due to well-documented energy transition between the 6P_J to $^8S_{7/2}$ levels within Gd^{3+} . As expected, peaks resulting from the energy transitions of the Tb^{3+} ions are not observed and thus the sample does not show any green color emission under a UV light. Also, the PLE spectrum confirms the 278 nm Gd^{3+} excitation peak when monitoring emission light at 313 nm.

The XRD patterns of the $GdF_3:Tb$ glass and glass-ceramic samples are shown in Figure 3. No well-defined diffraction peaks were observed from the as-cast glass sample except two broad humps between 20–35° and 40–50°, indicating that the sample was mostly amorphous. Other samples were annealed for 3 hours at their respective temperatures. The XRD results of all annealed samples clearly show the characteristic hexagonal GdF_3 peaks indicating that the GdF_3 nanoparticles are embedded within the glass matrix. The particle size of the nanocrystal was estimated using Scherrer equation and found to be increasing from about 13 nm to 30 nm with increasing the anneal temperature from 550 to 700°C. Also, the volume fraction of the GdF_3 nanoparticles was estimated from the XRD pattern based on the ratio of integrated peak intensity to the amorphous background. For the 700°C annealed sample, it was found to be 19.2%. The volume fraction is an important factor for high stopping power and light output. A thinner sample with large volume fraction of active nanoparticles is also preferred for higher spatial resolution. In our experiments, the glass-ceramic samples remained high transparency but volume fraction of GdF_3 nanoparticles needs to be further increased for X-ray imaging.

The decay time spectrum of a $GdF_3:Tb$ glass-ceramic sample is shown in Figure 4. It shows an exponential decay and the estimated decay time at $1/e$ relative intensity is found to be

2.85ms at 543nm, which is slower than the 0.47 ms decay time of conventional $\text{Gd}_2\text{O}_3\text{:Tb}$ X-ray phosphor.^{xix} Sayed et al. reported a 2.95ms decay time from $\text{GdF}_3\text{:15mol\%Tb}$ nanoparticles prepared by colloidal synthesis,^{xx} which is close to the result from our samples.

Preliminary X-ray imaging measurements were conducted on the $\text{GdF}_3\text{:Tb}$ glass-ceramic sample and compared to a commercial phosphor screen. From Figure 5, it is clearly visible that under X-ray excitation, the round-shaped $\text{GdF}_3\text{:Tb}$ glass-ceramic scintillates at a comparable intensity to a standard 640nm emitting ZnSe:Cu,Cl phosphor screen. The green Tb^{3+} emission is well matched to the spectral sensitivity of conventional CCD detectors for imaging applications. The X-ray excited image of a synthesized $\text{LaF}_3\text{:Ce,Tb}$ glass-ceramic sample is also shown in Figure 5. LaF_3 sample's weaker scintillation intensity may due to low transparency of the sample and the lack of efficient energy transfer between Gd-Tb pairs as in $\text{GdF}_3\text{:Tb}$. It should be also noted that the brightness of various samples depends on many factors such as sample thickness, light diffusion and emission wavelength. The $\text{GdF}_3\text{:Tb}$ sample was about 4 mm in thickness but the ZnSe:Cu,Cl screen was limited to ~200 μm due to its opaque feature resulted from strong light scattering. For future studies, Ce and Tb co-doping in GdF_3 and increase of GdF_3 nanocrystal loading in the glass-ceramics will be studied for X-ray imaging.

4. Conclusions

$\text{GdF}_3\text{:Tb}$ glass-ceramics were synthesized by a melt-quench method followed by annealing to precipitate nanophosphors in the oxide glass matrix. XRD studies confirmed that GdF_3 nanocrystals formed in the glass matrix. By incorporating $\text{GdF}_3\text{:Tb}$ into the glass matrix, the stopping power of the scintillator increased and the energy transfer between Gd^{3+} and Tb^{3+} ions is desired to enhance the scintillation efficiency. Preliminary X-ray scintillation results indicated that this material is promising for X-ray imaging applications. With negligible light scattering from nanoparticles, the transparent glass-ceramic nanocomposite X-ray converter can potentially exhibit higher spatial resolution than screens made of micron-sized particles. In addition, such Gd-based scintillators may have application in neutron detections due to Gd's high thermal neutron capture cross-section.

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Research Highlights

- Glass-ceramics containing Tb doped GdF_3 nanocrystals were synthesized.
- High transparency is due to negligible light scattering from nanocrystals.
- Effective energy transfer between Gd^{3+} and Tb^{3+} ions in the nanocrystals enhances the scintillation efficiency.
- $\text{GdF}_3\text{:Tb}$ glass-ceramic nanocomposite is promising for X-ray imaging applications.

Figure 1.

(a) PL spectra of a 700°C annealed GdF₃:Tb glass-ceramic at different excitation wavelengths; inset picture is the sample under a UV lamp; (b) PLE spectra at different monitoring wavelengths together with the absorption spectrum of the glass-ceramic sample

Figure 2.
PL and PLE spectra of undoped GdF_3 glass-ceramic sample

Figure 3.
XRD patterns of $\text{GdF}_3\text{:Tb}$ glass and glass-ceramic samples annealed at different temperatures

Figure 4. Decay curve of a 700°C annealed $\text{GdF}_3\text{:Tb}$ glass-ceramic sample shows an exponential decay and an $1/e$ decay time of 2.85 ms

Figure 5.

Image of a 700°C annealed GdF₃:Tb glass-ceramic scintillator under X-ray excitation with a comparison to a commercial ZnSe:Cu,Cl phosphor screen; a LaF₃:Ce,Tb glass-ceramic sample is also shown for comparison.