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Synthesis and luminescence properties of transparent nanocrystalline GdF_3:Tb glass-ceramic scintillator

Gyuhyon Lee [a,b], Nicholas Savage [a,b], Brent Wagner [a], Yuelan Zhang [b], Benjamin Jacobs [a], Hisham Menkara [a], Christopher Summers [b], Zhitao Kang [a,b,*]

[a] Electro-Optical Systems Laboratory, Georgia Tech Research Institute, Georgia Institute of Technology, Atlanta, GA 30332, United States
[b] School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332, United States

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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 GdF_3: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 Gd^{3+} and Tb^{3+} ions in the nanocrystals enhances the scintillation efficiency.

1. Introduction

Phosphor screens made from micron-sized phosphors such as Gd_2O_2S: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. [1–4] 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 [5–8]. 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 [9].

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 [10]. Glass ceramics containing $(Pb,Cd)F_2$, LaF_3, GdF_3, BaF_2, $BaCl_2$, and CaF_2 nanocrystals have been well studied.[4,10–15], 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 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 [4,15,16]. For example, the application of $BaCl_2$: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 [4,16]. 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 CaF_2:Eu^{2+} nanoparticles embedded within an oxyfluoride glass matrix [15]. The precursor glass showed little scintillation while the glass nanocomposite scintillated strongly with an efficiency up to 30% of that of a CaF_2: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 GdF_3:Tb nanocrystal-containing glass-ceramic was investigated for X-ray imaging applications. In a gadolinium

* Corresponding author at: Electro-Optical Systems Laboratory, Georgia Tech Research Institute, Georgia Institute of Technology, Atlanta, GA 30332, United States. Tel.: +1 4044 076 109.
E-mail address: zhitao.kang@gtri.gatech.edu (Z. Kang).

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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 GdF_3: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 $40SiO_2$–$26Al_2O_3$–15NaF–$16GdF_3$–$3TbF_3$ 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 2 h, 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 and 700 °C for 3 h to precipitate GdF_3: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 150 W 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 355 nm tripled YAG:Nd 10 ns 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 60 kV 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. Fig. 1(a) shows the photoluminescence spectra of the synthesized GdF_3: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. [17] 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 and $^8S_{7/2}$ levels within Gd^{3+}. The broad emission band from 350 to 450 nm is probably also due to emissions from gadolinium complexes which can be efficiently excited at 278 nm.

Fig. 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 [18]. The 278 nm excitation peak is due to the excitation in Gd^{3+} from $^8S_{7/2}$ to ^6I_J levels. As seen from Fig. 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 Fig. 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.

Fig. 2 shows the PL and PLE spectra of the synthesized GdF_3 glass-ceramic sample without any Tb doping. The PL spectrum

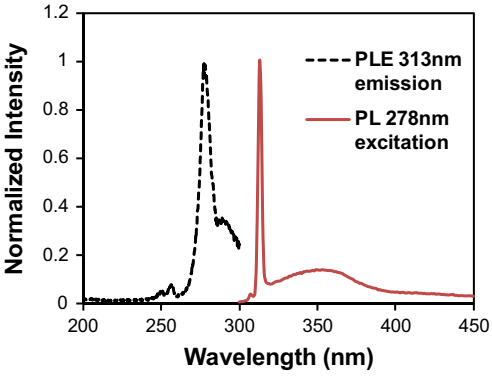

Fig. 2. PL and PLE spectra of undoped GdF_3 glass-ceramic sample.

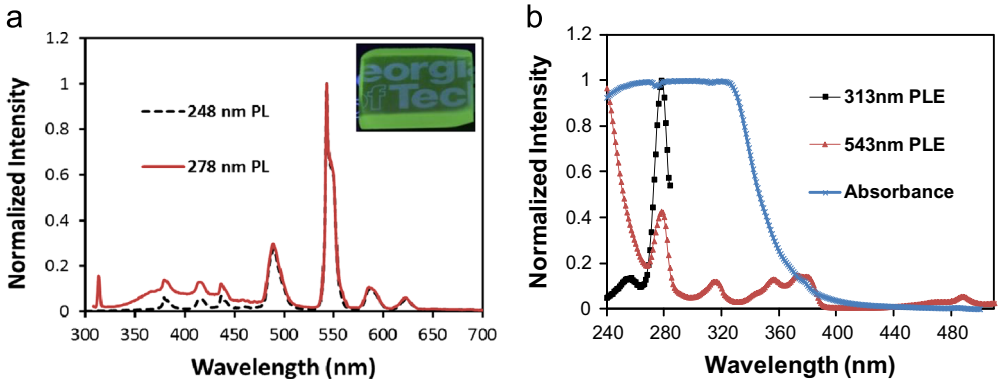

Fig. 1. (a) PL spectra of a 700 °C annealed GdF_3:Tb glass-ceramic at different excitation wavelengths; inset picture is the sample under a UV lamp; (b) PLE spectra at different monitoring wavelengths together with the absorption spectrum of the glass-ceramic sample.