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## Gd-based oxyfluoride glass ceramics: Phase transformation, optical spectroscopy and upconverting temperature sensing

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## ABSTRACT

A series of precursor glasses with compositions of SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-AlF<sub>3</sub>-Na<sub>2</sub>O- NaF-Gd<sub>2</sub>O<sub>3</sub>/GdF<sub>3</sub>-YbF<sub>3</sub>-ErF<sub>3</sub> were prepared and their crystallization behaviors were investigated. For the samples with high F content, meta-stable hexagonal GdF<sub>3</sub> nanocrystals were preferentially precipitated from glass matrix and decreasing F/O ratio induced phase transformation to cubic NaGdF<sub>4</sub> and finally to hexagonal NaGdF<sub>4</sub>. Benefited from its multiple active sites, significant enhanced upconversion luminescence was achieved for Yb/Er co-doped glass ceramic containing hexagonal NaGdF<sub>4</sub> nanocrystals. Importantly, significant temperature-sensitive upconversion fluorescence intensity ratio between Er<sup>3+</sup>: <sup>2</sup>H<sub>11/2</sub> → <sup>4</sup>I<sub>15/2</sub> transition (520 nm) and <sup>4</sup>S<sub>3/2</sub> → <sup>4</sup>I<sub>15/2</sub> one (540 nm) was detected owing to the competitive radiation transitions from these two thermally coupled emitting-states. Furthermore, linear temperature-dependent fluorescence intensity ratio between Er<sup>3+</sup>: <sup>4</sup>F<sub>9/2</sub> → <sup>4</sup>I<sub>15/2</sub> transition (650 nm) to <sup>4</sup>S<sub>3/2</sub> → <sup>4</sup>I<sub>15/2</sub> one (540 nm) was achieved, showing the advantages of high sensitivity, superior signal discriminability as well as excellent thermal stability for temperature determination.

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## 1. Introduction

Recently, upconversion (UC) materials with excellent ability of converting low-energy near-infrared (NIR) photons into high-energy visible or ultraviolet (UV) one through a multi-photon absorption process have been extensively investigated for promising applications in different fields, such as solid-state lasers, solar cells, bioimages, sensors and others [1–10]. Currently, lanthanide (Ln<sup>3+</sup>, such as Er<sup>3+</sup>, Ho<sup>3+</sup> and Tm<sup>3+</sup>) doped products have been demonstrated to exhibit high UC efficiency related to other materials [11]. Notably, the host is one of the most important factors to determine UC efficiency since the phonon energy of host has a significant impact on the probability of non-radiative transitions for the incorporated Ln<sup>3+</sup> dopants [12]. Hence, exploring a kind of applicable material with low phonon energy and superior physical/chemical stability is highly desired.

Crystal, ceramics and glass are the most common bulk hosts for Ln<sup>3+</sup> doping to achieve the related luminescence [13–16]. Unfortu-

nately, the fabrication of single crystal and ceramics is extremely complicated and time-consuming. For instance, some materials may not be readily grown as bulk single crystal owing to the occurrence of phase transformation [17]; several challenges, including complex procedures to avoid porosity, limited compositions, segregation of doping agents, etc, remain to achieve transparent ceramics [18]. On the other hand, oxide glass is easily fabricated but usually suffers from poor UC property for Ln<sup>3+</sup> dopants owing to its high phonon energy. As an alternative, transparent oxyfluoride glass ceramic (GC) nanocomposite, combining the merits of oxide glasses and fluoride crystals, emerged as required. GCs are generally achieved via controlling crystallization of the specially designed glasses with appropriate chemical compositions [19,20]. And the partition of the optically active Ln<sup>3+</sup> ions into the precipitated fluoride lattice plays a key role to improve optical performance [21–31]. In order to achieve highly efficient UC luminescence in the oxyfluoride GCs, the crystalline phase is expected to have low phonon energy and high solubility of Ln<sup>3+</sup> ions. Therefore, controlling fluoride crystallization and understanding phase transformation in glass matrix are highly important to design oxyfluoride GCs with optimized Ln<sup>3+</sup> UC properties. However, as far as we know, there is rarely investigation on phase-structure tunability in glass and the related optical spectroscopy so far.

Herein, phase evolution from hexagonal GdF<sub>3</sub> to cubic NaGdF<sub>4</sub> and finally to hexagonal NaGdF<sub>4</sub> in the glass matrix was realized in

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a specially designed glass via controlling crystallization and modifying F/O ratio. Further experiments were carried out by using  $\text{GdF}_3$  instead of  $\text{Gd}_2\text{O}_3$  to investigate the influence of F content on the phase transformation. X-ray diffraction, transmission electron microscopy, high-angle annular dark-field scanning transmission electron microscopy, elemental mapping as well as steady state and time-resolved upconversion emission spectra were used to study microstructure evolution after glass crystallization. Additionally, the phase-structure dependent UC performance in the Yb/Er co-doped GC samples was systematically investigated. Finally, to explore their possible application in optical thermometry, the influence of temperature on  $\text{Er}^{3+}$  green UC emissions originated from thermally coupled  ${}^2\text{H}_{11/2}$  and  ${}^4\text{S}_{3/2}$  emitting states and both the red and green ones ascribed to  ${}^4\text{F}_{9/2}$  and  ${}^2\text{H}_{11/2}/{}^4\text{S}_{3/2}$  emitting ones was examined.

## 2. Experimental

The precursor glasses (PGs) were prepared with the compositions (in mol%) of  $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-AlF}_3\text{-Na}_2\text{O-NaF-GdF}_3/\text{Gd}_2\text{O}_3$ . The  $\text{Ln}^{3+}$  activators were introduced into glasses by addition of  $\text{YbF}_3$  and  $\text{ErF}_3$  compounds with fixed contents of 1 mol% and 0.1 mol%, respectively. For each batch, about 15 g raw materials were drastically mixed and melted in a covered alumina crucible at  $1590^\circ\text{C}$  for 1 h in the air atmosphere to achieve a homogeneous melting, then were cast into a  $300^\circ\text{C}$  preheated brass mold to cool down to room temperature. Then the samples were cut into  $5\text{ mm}^2$  square coupons and were crystallized by heat-treating at 650, 675, 700, 725 and  $750^\circ\text{C}$  for 2 h to form GCs.

To characterize the crystallization phase and determine the mean size of the crystallites, X-ray diffraction (XRD) analysis was performed with a powder diffractometer (Rigaku, MiniFlex600) using  $\text{CuK}\alpha$  radiation ( $\lambda = 0.154\text{ nm}$ ). Transmission electron microscope (TEM, JEM-2010) equipped with selected area electron diffraction (SAED) was used to study the microstructures of samples. High resolution TEM (HRTEM) image was recorded to observe atomic plane inside the crystalline lattice. Scanning transmission electron microscopy (STEM) observation in the high-angle annular dark-field (HAADF) mode, being sensitive to atomic number ( $Z$ ) of the sample (proportionally scaling to  $\sim Z^2$ ) [32], was performed on an FEI aberration-corrected Titan Cubed S-Twin transmission electron microscope operated at 200 kV. The samples were ground into a very fine powder that was placed onto a carbon coated copper grid and introduced into the microscope. UC emission spectra of PG and GC samples were detected using the Hamamatsu R943-02 photomultiplier tube and the Spex 1000 M monochromator with an adjustable laser diode (980 nm) as the excitation source. Visible UC decay curves were measured with a customized UV to mid-infrared steady-state and phosphorescence lifetime spectrometer (FSP920-C, Edinburgh) equipped with a digital oscilloscope (TDS3052B, Tektronix) and a tunable mid-band OPO pulse laser (410–2400 nm, 10 Hz, pulse width  $\leq 5\text{ ns}$ , Vibrant 3551I, OPOTEK) as the excitation source. The UC lifetime values were determined via the equation of  $\tau = \int I(t)dt/I_0$ , where  $I(t)$  was the time-related luminescence intensity and  $I_0$  was the peak intensity. Temperature-dependent UC emission spectra were recorded on an Edinburgh Instruments FS5 spectrofluorometer equipped with a homemade temperature controlling stage and a 980 nm laser diode.

## Results and discussion

XRD patterns of GC samples with different F/O ratios are shown in Fig. 1a. With replacement of NaF by  $\text{Na}_2\text{O}$ , i.e., with gradual decrease of F/O ratio, the main crystallization phase in glass matrix converts from hexagonal  $\text{GdF}_3$  (GC1 and GC2) to cubic  $\alpha\text{-NaGdF}_4$

(GC3) and finally to hexagonal  $\beta\text{-NaGdF}_4$  (GC4). Notably, since XRD data of hexagonal  $\text{GdF}_3$  have not been reported, we indexed this phase with the help of isostructural  $\text{EuF}_3$  (JPCDS No. 32-0373). To better investigate the influence of F/O ratio on the phase transformation, as tabulated in Table 1,  $\text{GdF}_3$  (3 mol%) compound was used to substitute  $\text{Gd}_2\text{O}_3$  (1.5 mol%) in GC4 sample. Evidently, increase of F/O ratio will indeed induce the precipitation of hexagonal  $\text{GdF}_3$  particles among glass matrix. Further increasing  $\text{GdF}_3$  content from 3 mol% to 15 mol% will not modify the crystallized phase structure (Fig. 1b, Table 1). Additionally, the broadened diffraction peaks and the enhanced diffraction intensity of crystalline phase related to amorphous glass hump (Fig. 1b) indicate that the mean size of precipitated particles decreases and their crystallized fraction increases with increase of  $\text{GdF}_3$  doping content. Meanwhile, it is well-known that crystallization temperature is also a key factor for controlling phase structure. Taking GC7 sample as a typical example, XRD patterns of the corresponding GCs obtained by heat-treatment at various temperatures were recorded, as shown in Fig. 1c. It exhibits a typical amorphous structure in the precursor glass. With increase of heating temperature, several diffraction peaks corresponding to hexagonal  $\text{GdF}_3$  appear and tend to be sharper. And further increasing temperature ( $725\text{--}750^\circ\text{C}$ ) results in partial conversion of hexagonal  $\text{GdF}_3$  into orthorhombic  $\text{GdF}_3$  crystals (JPCDS No. 12-0788). As demonstrated in Fig. 1d, all the GC5–GC9 samples exhibit both hexagonal and orthorhombic  $\text{GdF}_3$  crystals in glass matrix after heat-treated at  $750^\circ\text{C}$ . Therefore, it is concluded that the meta-stable hexagonal  $\text{GdF}_3$  easily nucleates from the glass matrix for GC samples with high F/O ratio while the orthorhombic one is thermodynamically stable and occurs with elevation of crystallization temperature.

The microstructures of GC samples were studied by electron microscopy. TEM bright field image of GC1 sample (Fig. 2a) shows that nearly spherical hexagonal  $\text{GdF}_3$  NCs with size of 20–30 nm homogeneously precipitate from the glass matrix. And the corresponding SAED pattern exhibits discrete polycrystalline diffraction rings, confirming the precipitation of hexagonal  $\text{GdF}_3$  particles after glass crystallization. TEM observations on GC3 and GC4 samples (Fig. 2b,c) demonstrate that cubic  $\text{NaGdF}_4$  nanoparticles sized 15–20 nm and hexagonal  $\text{NaGdF}_4$  ones sized 10–15 nm homogeneously distribute among the glass matrix, respectively. HRTEM image for an individual hexagonal  $\text{NaGdF}_4$  NC (Fig. 2d) verifies its single-crystalline nature with high-crystallinity. Furthermore, TEM micrographs of the 3 mol% and 15 mol%  $\text{GdF}_3$  doped samples (GC5, GC9) after heat-treated at  $650^\circ\text{C}$  are presented in Fig. 2e and f. As expected, the size of spherical hexagonal  $\text{GdF}_3$  NCs in glass matrix reduces from 10 to 20 nm to 5–10 nm and the crystal fraction remarkably enhances with increase of  $\text{GdF}_3$  doping content, being consistent with XRD result (Fig. 1b).

Additionally, STEM operated in HAADF mode, which is sensitive to the atomic number ( $Z$ ) of sample (proportionally scaling to  $\sim Z^2$ ) [32], is adopted to further study microstructure of GC4. Contrary to previous TEM ones (Fig. 2),  $\text{NaGdF}_4$  NCs in STEM-HAADF micrograph appear with a brighter contrast than the aluminosilicate glass matrix (Fig. 3a) owing to much higher atomic number of Gd ( $Z = 64$ ) staying in  $\text{NaGdF}_4$  particles than those of Si/Al ( $Z = 14/13$ ) distributing in glass matrix. The Na, Gd, F, Yb and Er elemental mappings for the GC4 sample (Fig. 3b–f) confirm the segregation of Na, Gd, Yb and Er in the  $\text{NaGdF}_4$  NCs, whereas the equal presence of F in the particles and the glass matrix. These results indicate the successful incorporation of  $\text{Yb}^{3+}$  and  $\text{Er}^{3+}$  activators into  $\text{NaGdF}_4$  crystalline lattice after glass crystallization. Owing to their similar ionic radius and electron configurations,  $\text{Yb}^{3+}$  and  $\text{Er}^{3+}$  ions are expected to substitute  $\text{Gd}^{3+}$  cations in the  $\text{NaGdF}_4$  lattice.

Generally,  $[\text{AlO}_4]$  tetrahedra will partially replace  $[\text{SiO}_4]$  ones in aluminosilicate glass network, and charge compensation by network modifying ions is required owing to valence difference

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