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Tuning into blue and red luminescence in dual-phase nano-glass-ceramics



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ABSTRACT

A series of γ -Ga₂O₃ and β -YF₃ nanocrystals embedded dual-phase glass ceramics co-doped with rare earth (Eu³⁺ or Tm³⁺) and transition metal (Cr³⁺) activators were successfully prepared by high-temperature melt-quenching to explore blue/red luminescent materials for potential application in photosynthesis of green plants. It is experimentally verified that Eu³⁺ (or Tm³⁺) ions partitioned into the crystallized orthorhombic YF₃ nanophases, while Cr³⁺ ones entered into the precipitated cubic Ga₂O₃ nanocrystals after glass crystallization. Such spatial separation of the different active ions in the dual-phase glass ceramics can effectively suppress adverse energy transfers between rare earth and transition metal ions, resulting in their independent and efficient luminescence. As an example, it is experimentally demonstrated that both intense Tm³⁺ blue and Cr³⁺ deep-red emissions are easily achieved in the Tm³⁺/Cr³⁺ co-doped dual-phase glass ceramics.

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1. Introduction

Photosynthesis is the process of converting light energy to chemical energy and storing it in the bonds of sugar, which usually occurs in plants and some algae [1]. Plants need only light energy, CO₂, and H₂O to make sugar, and the photosynthesis takes place in the chloroplasts, specifically using chlorophylls [2]. Chlorophylls look green because it mainly absorbs blue and red light, meaning that the energy from the absorbed blue and red light is, thereby, able to be used to realize photosynthesis [3,4]. In the solar spectrum, the energy percentages of the ultraviolet (UV), visible, and infrared (IR) light are 7%, 50%, and 43%, respectively [5,6]. The lights absorbed by green plants for photosynthesis are only a very small part in the whole solar spectrum. It will be a desirable work to improve the utilization of solar via spectral modification strategy, i.e., converting a photon, which cannot be efficiently absorbed by green plants for photosynthesis, into another photon, which can be efficiently absorbed by chlorophylls for photosynthesis.

Rare earth (RE) and transition metal (TM) ions have ample energy levels due to their special 4fⁿ and 5dⁿ electronic configurations respectively, enabling them to absorb and emit photons from UV to IR when doped into the appropriate hosts [7–15]. To

simultaneously realize efficient blue and red luminescence for photosynthesis, doping two different emitting centers such as RE and TM into a sole host is an ideal choice. Unfortunately, unwanted energy transfers between RE and TM usually occur ascribing to the energy level matching between them, which subsequently leads to the emission quenching for both active ions [16–20].

Herein, RE (Eu³⁺ or Tm³⁺) and TM (Cr³⁺) co-doped oxyfluoride glasses with special designed glass compositions (SiO₂–Al₂O₃–LiF–YF₃–Ga₂O₃) were successfully fabricated by a melt-quenching route. To suppress adverse energy transfers between Eu³⁺/Tm³⁺ and Cr³⁺, crystallization strategy was successfully applied to convert the precursor glasses into nano-glass-ceramics containing YF₃ and Ga₂O₃ dual-crystalline-phases. As a consequence, RE ions were evidenced to incorporate into the precipitated orthorhombic YF₃ nanoparticle, while Cr³⁺ ones entered into the cubic Ga₂O₃ nanoparticles. Such spatial separation of the different active ions can effectively suppress unwanted energy transfers between Tm³⁺ and Cr³⁺, leading to both intense blue and red luminescence in the nano-glass-ceramics.

2. Experimental section

The materials were prepared with the following composition (in mol%): 40SiO₂–20Al₂O₃–15LiF–(15–x)YF₃–(10–y)Ga₂O₃–xREF₃–yCr₂O₃ (RE = Eu³⁺ or Tm³⁺; x = 0–1.5, y = 0–0.1). The chemicals were mixed thoroughly and melted in a covered Pt crucible at 1450 °C for 1 h in the air. The melt was poured into a

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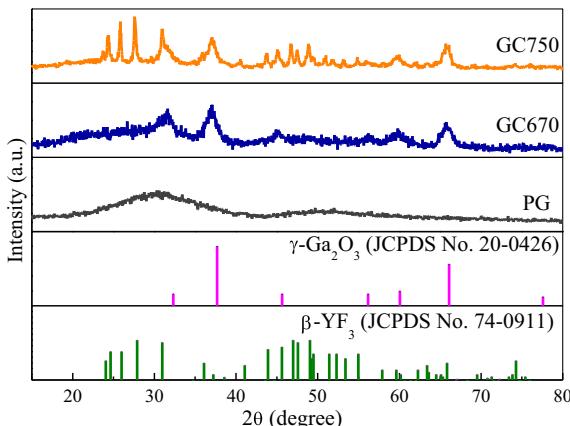


Fig. 1. XRD patterns of PG, GC670 and GC750. The standard cubic Ga_2O_3 (JCPDS No. 20-0426) and orthorhombic YF_3 diffraction data are also provided (JCPDS No. 74-0911).

450 °C pre-heated copper mold to form the precursor glass (denoted as PG). The as-quenched glass was annealed at 550 °C for 2 h and then cooled down naturally to room temperature to relinquish the inner stress. Afterwards, the precursor glass was then heat-treated to 670 °C or 750 °C with a heating rate of 10 K/min, and hold for 2 h to form glass ceramic (denoted as GC670 and GC750 respectively) through glass crystallization.

To identify the crystallization phase and determine the mean size of crystallites, X-ray diffraction (XRD) analysis was carried out with a powder diffractometer (DMAX2500 RIGAKU) using Cu K α radiation ($\lambda = 0.154 \text{ nm}$). The microstructure of GC was studied using a transmission electron microscopy (TEM, JEM-2010) equipped with an energy dispersive X-ray (EDX) spectroscopy and the selected area electron diffraction (SAED). TEM specimen was prepared by directly drying a drop of a dilute ethanol dispersion solution of glass pieces on the surface of a carbon coated copper grid. The emission, excitation spectra and decay curves of PG and GCs were recorded on an Edinburgh Instruments FS5 spectrophotofluorometer equipped with both continuous (150 W) and pulsed xenon lamps.

3. Results and discussion

XRD patterns of the PG, GC670 and GC750 samples are presented in Fig. 1. The precursor glass is amorphous without any sharp signals. After crystallization at 670 °C, the XRD pattern of GC670 shows intense diffraction peaks assigned to the cubic $\gamma\text{-}\text{Ga}_2\text{O}_3$ crystal (JCPDS No. 20-0426). Further increasing crystallization temperature to 750 °C will induce the precipitation of the orthorhombic $\beta\text{-}\text{YF}_3$ crystal (JCPDS No. 74-0911) together with $\gamma\text{-}\text{Ga}_2\text{O}_3$ one in the GC750 sample. Based on the Scherrer formula, the mean sizes of the $\beta\text{-}\text{YF}_3$ and $\gamma\text{-}\text{Ga}_2\text{O}_3$ crystals were calculated to be about 5 and 25 nm respectively. TEM image of the GC670

sample (Fig. 2a) demonstrates that nanoparticles sized 3–6 nm distribute homogeneously among the glass matrix with their SAED rings well indexed to the cubic Ga_2O_3 . TEM observation on GC750 sample (Fig. 2b) clearly evidences the existence of two types of crystals, i.e., YF_3 with large size of 20–30 nm and Ga_2O_3 with small size of 3–6 nm, in the glass matrix. High-resolution TEM (HRTEM) images of the Ga_2O_3 (Fig. 2c) and YF_3 (Fig. 2d) nanocrystals exhibit clear-cut crystalline lattice structures with measured inter-planar spacing to be 0.21 nm and 0.32 nm, respectively, which are matching well with the (400) plane of Ga_2O_3 and the (111) plane of YF_3 .

To investigate the partition behaviors of the RE and TM dopants, photoluminescence (PL), photoluminescence excitation (PLE) spectra, and decay curves of Eu^{3+} or Cr^{3+} single-doped PG, GC670 and GC750 were recorded. As evidenced in Fig. 3a, for Eu^{3+} single-doped PG sample, the excitation spectrum for the 611 nm emission of Eu^{3+} : $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition consists of several characteristic Eu^{3+} excitation peaks corresponding to the transitions from the $^7\text{F}_0$ ground state to the indexed excited states and a broad excitation band at 240 nm assigning to the $\text{O}^{2-}\text{-}\text{Eu}^{3+}$ charge transfer (CT). Similar result is found in the GC670 sample, indicating that Eu^{3+} ions are not incorporated into the precipitated Ga_2O_3 nanocrystals. This is well understood since the radius of Eu^{3+} ($r = 0.095 \text{ nm}$, CN = 6) is far larger than that of Ga^{3+} ($r = 0.062 \text{ nm}$, CN = 6). Interestingly, the CT band in the GC750 sample is much weaker than those of the PG and GC670. Under 393 nm excitation, the emission spectra of the PG, GC670 and GC750 mainly show the Eu^{3+} : $^5\text{D}_0 \rightarrow ^7\text{F}_j$ transitions. Compared to those of PG and GC670, these emission bands in GC750 become remarkably structured in a way similar to the case of Eu^{3+} doped YF_3 crystal [21]. In addition, the luminescence originated from the $^5\text{D}_{1,2,3}$ higher excited states appears in the GC750. All these results suggest the partition of Eu^{3+} ions in low-phonon-energy YF_3 crystalline environment instead of Ga_2O_3 one after 750 °C crystallization treatment, owing to the similar radii between Eu^{3+} ($r = 0.095 \text{ nm}$, CN = 6) and Y^{3+} ($r = 0.090 \text{ nm}$, CN = 6). This can be further confirmed by the much slower decay of Eu^{3+} in GC750 than in PG, as shown in Fig. 3b. The intensity ratio of $^5\text{D}_0 \rightarrow ^7\text{F}_2$ and $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transitions is determined by the symmetry of the crystal sites in which Eu^{3+} ions are located. From the emission spectra, the ratio is evaluated to be 1.78 and 0.81 for PG and GC750 respectively. The intensity of the magnetic dipolar $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition does not depend on the ligand field of Eu^{3+} , while the electric dipolar $^5\text{D}_0 \rightarrow ^7\text{F}_2$ one is known to be forbidden in the centrosymmetric environment [22]. Therefore, the decrease of the ratio value after 750 °C crystallization is related to the increase in the symmetry of the ligand field for Eu^{3+} incorporated in YF_3 host by substituting Y^{3+} .

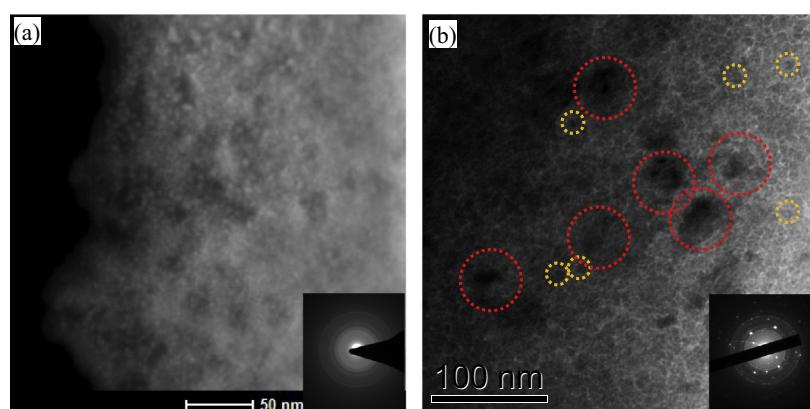


Fig. 2. TEM micrographs of (a) GC670 and (b) GC750, insets are the corresponding SAED patterns; HRTEM images of (c) $\gamma\text{-}\text{Ga}_2\text{O}_3$ and (d) $\beta\text{-}\text{YF}_3$ nanoparticles, insets are the corresponding fast Fourier transform (FFT) patterns.

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