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Original Article

Transparent $Sr_{0.84}Lu_{0.16}F_{2.16}$: Yb^{3+}, Er^{3+} glass ceramics: Elaboration, structure, up-conversion properties and applications

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ABSTRACT

The development of optical temperature sensors is of fundamental and industrial importance for various applications. Despite the great advance in optical temperature-sensing techniques, challenges remain to search for novel sensing materials with low cost, easy fabrication and high sensitivity. Here, transparent glass ceramics (GC) embedded with cubic $Sr_{0.84}Lu_{0.16}F_{2.16}$:$Yb^{3+}$/$Er^{3+}$ nano-crystals were prepared via thermal annealing on the parent glass. The optical and structural properties were investigated. The enhanced emission intensity, obvious Stark splitting and prolonged lifetimes of Er^{3+} confirm the enrichment of Er^{3+} ions into formed $Sr_{0.84}Lu_{0.16}F_{2.16}$ nano-crystals. The temperature sensing performance of Yb^{3+}/Er^{3+} ions in $Sr_{0.84}Lu_{0.16}F_{2.16}$GC were investigated based on up-conversion intensity ratio (FIR) from thermally coupled emitting states of Er^{3+}. High energy difference (ΔE = 839 cm^{-1}) and high absolute sensitivity (27.4 × 10^{-4} K^{-1} at 606 K) are obtained. Our results reveal $Sr_{0.84}Lu_{0.16}F_{2.16}$GC are excellent host for rare earth ions doping and potential candidate for optical thermometry.

1. Introduction

Rare earth (RE) ions functionalized up-converting materials remain prosperous for their huge potential in photovoltaic devices, biomedical imaging, color displays and optical temperature sensors [1–6]. The highest efficiency of up-conversion luminescence is obtained in diverse materials doped with RE ions, especially, Tb^{3+}, Yb^{3+}, Tm^{3+} and Er^{3+}, which is because of their ladder-like energy level structures enabling photon absorption and subsequent energy transfer steps [7–11].

RE-doped fluoride nano-particles are essential for efficient up-conversion due to their low phonon energy [12,13]. However, the granular morphology and insufficient stability of nano-particles hinder their practical applications [14]. From the view of application, highly plastic glass is more suitable where bulk materials are required due to its low cost, excellent stability and easy shaping of elements. While glass with its inherent disordered structure suffers from lower up-conversion efficiency than fluoride nano-particles resulting from high phonon energy of glass [15].

Bulk fluoride glass-ceramics (GC), with homogeneously crystallized fluoride nano-crystals in oxide glasses, are one of the most perspective materials in the sense of application. They combine the advantages of bulk oxide glass and superior up-converting properties of RE ions in the formed nano-sized polycrystals [11,16–19]. Interestingly, RE ions preferentially gather into the formed nano-crystals after thermal treatment on parent glass [19–21].Then outstanding up-conversion behavior can be observed, based on the decreased non-radiative transition probability and further increased energy transfer (ET) benefiting from shortened distance of RE^{3+} ions [11,14].

Among these RE-doped oxyfluoride GC, Lu-based fluoride nano-crystals, for instance, $NaLuF_4$ [22,23], $BaLuF_5$ [24] $Ba_{1-x}Lu_xF_{2+x}$ [25] and KLu_2F_7 [19], have been attracting much attention for their excellent up-conversion behavior. Searching for novel Lu-based oxyfluoride bulk GC as excellent up-conversion materials bears great significance. Nevertheless, there are only few reports concerning Lu-based oxyfluoride GC [25].

Here, bulk Yb^{3+}/Er^{3+} co-doped oxyfluoride GC with cubic $Sr_{0.84}Lu_{0.16}F_{2.16}$ (SLF) nano-crystals were prepared via melt-quenching technique and thermal annealing on parent glass. All GC samples remain high transparence up to 85% in visible and near-infrared (VIS-NIR) region. Under 980 nm excitation, highly enhanced green up-conversion emissions were observed in annealed GC samples. Then the temperature-sensing performance based on the bright green up-conversion emissions of Er^{3+} ions in Yb^{3+} /Er^{3+} co-doped SLF GC were investigated via emission intensity ratio (FIR) method.

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2. Experimental procedure

Glass samples with molar composition $70SiO_2$-$7Al_2O_3$-$16SrF_2$-$6LuF_3$-$1YbF_3$-$0.2ErF_3$ were fabricated via conventional melting-quenching method. The parent glass was designed to contain high content silica to obtain good stability under current melting temperature. Silicate glass with high content silica often exhibit excellent structure properties including high mechanical strength, small thermal expansion coefficient, outstanding heat resistance and good chemical stability, on account of strong Si—O bonds (about 106 kcal/mol) in tetrahedral [SiO_4] unit. Analytical grade regents Al_2O_3, SrF_2, SiO_2 and high-pure LuF_3, YbF_3, ErF_3 were utilized as raw materials. The samples were mixed thoroughly in a mortar and then melted at 1560 °C for 50 min. The glass melt was cast on a copper plate and pressed by another cupper plate to speed up the cooling rate and prevent possible devitrification. The acquired sample was denoted as PG. PG were thermal annealed for 2 h at 750, 770 and 790 °C.The heat-treated samples were denoted to be GC750, GC770 and GC790, respectively. These samples were transparent and bubble-free, and then mechanically polished into suitable shapes and thickness (1.5 mm) for thermal annealing and further optical and structural measurements.

The crystallization of the sample was confirmed by X-ray diffraction (XRD, Philips X'Pert PRO SUPER X-ray diffraction apparatus (Cu Kα radiation, $\lambda = 0.154056$ nm)) at room temperature. The micro-structure of GC sample is detected by TEM and HRTEM (JEM-2010, JOEL Ltd.)).Transmittance was evaluated by U-3900 UV–VIS spectrophotometer (Hitachi).Up-conversion emission spectra as well as decay curves were analyzed with a FS920 spectrofluorometer equipped with a 980 nm LD. Temperature dependent up-conversion emission spectra were obtained via a system combining a temperature-controlling device (FOTEK MT48-V-E) and a thermocouple. The emission spectra on temperature were recorded by a Jobin-Yvon HRD-1 double monochromator with a Hamamatsu R928 Photomultiplier. The signal was analyzed by an EG&G 7265 DSP lock-in amplifier.

3. Results and discussions

3.1. Analyses of the structure

Fig. 1(a) shows the XRD patterns of PG and GC samples together with cubic $Sr_{0.84}Lu_{0.16}F_{2.16}$ (SLF) (JCPDS card No. 82-0640). Clearly, XRD patterns of PG show no evidence of crystallization. After thermal treatment, sharp diffraction peaks attributed to SLF emerged, indicating the crystallization of SLF nano-crystals in GC samples. Based on the following Scherrer's equation [18], the size of SLF nano-crystals obtained is 29, 34 and 38 nm for GC750, GC770 and GC790, respectively,

$$D = k\lambda/\beta\cos\theta \quad (1)$$

where $k = 0.89$, $\lambda = 0.154056$ nm, β is the corrected half width of diffraction peak and θ represents Bragg angle.

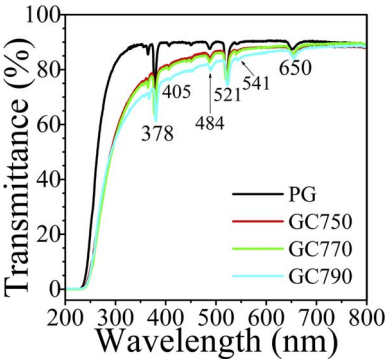

Fig. 2. Transmittance spectra.

Fig. 1(b) displays the XRD pattern of sample GC790 and results of Rietveld refinement. The crystalline phase can be confirmed to be $Sr_{0.84}Lu_{0.16}F_{2.16}$ with space group of Fm-3m[225] by the low Bragg R-factor ($R_b = 6.193\%$) and the goodness of fit parameter $Chi^2 = 2.48$. The lattice constant is calculated to be 0.5709 nm, which is close to the standard value (0.5711 nm).

The size of crystallized SLF nano-crystals is smaller compared to the corresponding wavelength of VIS-NIR light, all heat-treated samples remain high transparence up to 85% (Fig. 2). Furthermore, the absorption peaks 378,405, 484, 521, 541 and 650 nm are corresponding to transitions of Er^{3+} from $^4I_{15/2}$ level to $^4G_{11/2}$, $^2K_{15/2}$, $^4F_{7/2}$, $^2H_{11/2}$, $^4S_{3/2}$ and $^4F_{9/2}$ excited levels, respectively [14].

Fig. 3(a) plots the TEM micrograph of GC790. SLF nano-crystals with size of 26–35 nm are homogeneously embedded in aluminosilicate glass matrix. The inset of Fig. 1(c) is the corresponding size distribution plot, which reveals that the $Sr_{0.84}Lu_{0.16}F_{2.16}$ nano-crystals present a narrow size distribution. The size of nano-crystals from TEM consists with the data obtained via the above Scherrer's equation. As presented in the HRTEM image for GC790 sample (Fig. 3(b)), regular lattice image can be seen clearly, which indicating SLF nano-crystals bear good crystallinity [11]. The obtained interplanar spacing d from HRTEM image is 0.329 nm and corresponding to the (111) crystal plane of SLF crystals ($d_{(111)} = 0.328$ nm). Fig. 3(b) exhibits the selected area electron diffraction (SAED) patterns, which reveals that GC are composite materials containing nano-crystals and amorphous glass [26].

3.2. Up-conversion luminescence properties and mechanism

The room temperature up-conversion emission spectra are exhibited in Fig. 4. Under the excitation of 980 nm, intense up-conversion emission bands located at 408, 525, 550 and 660 nm emerged and can be assigned to transitions from $^2H_{9/2}$, $^2H_{11/2}$, $^4S_{3/2}$ and $^4F_{9/2}$ levels to $^4I_{15/2}$ level of Er^{3+}, respectively [11]. Correspondingly, as presented in the

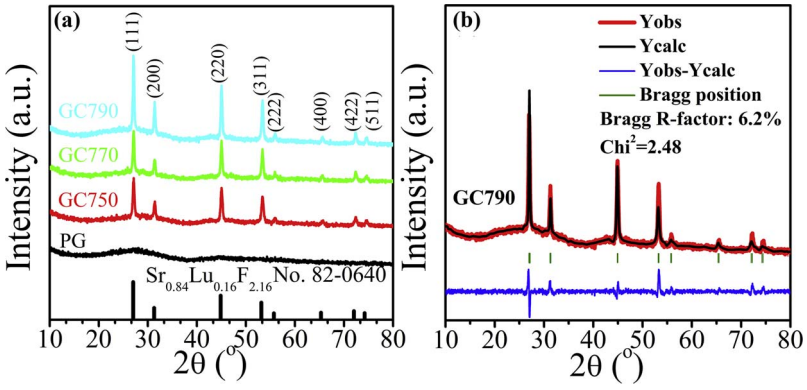

Fig. 1. (a) XRD patterns of PG, GC samples and $Sr_{0.84}Lu_{0.16}F_{2.16}$ (JCPDS card No. 82-0640); (b) the XRD pattern of sample GC790 and results of Rietveld refinement.