Enhancement of up-conversion luminescence properties in $Yb^{3+}/Tm^{3+}/Er^{3+}$ tri-doped transparent oxyfluoride tellurite glass ceramics

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Optically transparent $Er^{3+}/Tm^{3+}/Yb^{3+}$ tri-doped oxyfluoride tellurite based nano-crystallized glass ceramics with the batching composition of $73TeO_2$-15ZnO-$7ZnF_2$-$3YF_3$-$1.5YbF_3$-$0.3ErF_3$-$0.2TmF_3$ (mol%) is prepared by a conventional melting quenching and the subsequent heat treatment processes. The sizes of grown nano-crystals in glass matrix appear to be smaller than 100 nm from the scanning electron microscope measurement. Visible up-conversion luminescence of the as melted glass and glass ceramics is investigated. The three-color up-conversion luminescence intensities by 980-nm pumping are increased significantly due to the heat treatment, and the blue intensity increases with a higher magnitude than other wavelengths after heat treatment.

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Over the past decades, there has been significant interest in the production of new vitreous materials for multicolor displays. A new technique for solid-state color displays has been developed based on the infrared to visible frequency up-conversion in lanthanide-doped materials[1]. Oxyfluoride glass ceramics is one of the most attractive materials for near-infrared to visible up-conversion, because it combines the advantages of rare earth doped fluoride crystals and oxide glasses[2,3]. Considerable efforts have been made in order to obtain rare-earth-doped glass-ceramic materials with active ions embedded in the crystalline phase[2,4–7]. Most researchers paid attention to prepare rare earth ions doped oxyfluoride silicate glass ceramics[8,9], however, only a few articles were reported on preparing tellurite glass ceramics[10,11]. TeO_2-based glass, as one kind of the heavy metal glasses, possesses relative low photon energy ($\sim$750 cm^{-1}) compared with other oxide that reduces the multi-phonon loss which is critical in determining the up-conversion efficiency[12]. Recently, we succeeded in fabricating transparent Er^{3+} singly doped tellurite glass ceramics and transparent oxyfluoride tellurite one[13]. In this letter, we investigate the multicolor visible up-conversion luminescence properties of $Yb^{3+}/Tm^{3+}/Er^{3+}$ tri-doped transparent oxyfluoride tellurite glass ceramics excited by the 980-nm laser diode (LD).

Precursor glass $73TeO_2$-15ZnO-$7ZnF_2$-$3YF_3$-$1.5YbF_3$-$0.3ErF_3$-$0.2TmF_3$ (mol%) were melted with commercial purity (usually 99.9%) oxides and fluorides in platinum crucible. About 30-g batches of the well-mixed raw materials were melted at 950 °C for 30 min under air atmosphere. In order to prevent the vaporization loss of the fluoride components, the crucibles were covered with an alumina plate. The glass was cast into a heated copper mold, and then annealed for 300 min in a muffle. The glass-ceramic samples were obtained by traditional two-step heat treatment based on the differential scanning (DSC) result. The samples were polished with 1.5-mm thickness. The glass transition temperature (T_g) and onset crystallization temperature (T_x) were decided with different thermal analysis DSC. The DSC was performed with a NETZSCH STA 409 PC/PG apparatus under Ar atmosphere at a heating rare of 10 K/min. The up-conversion luminescence spectra in the range of 400 – 700 nm were measured with JOBIN-YVON TRIAX550 fluorescence spectrometer upon the excitation at 980 nm. In order to compare the intensity of the luminescence of all samples as accurate as possible, the position and power of the pumping beam and the width (0.2 mm) of the slit to collect the luminescence signal were fixed under the same conditions. All the measurements were carried out at room temperature.

Figure 1 shows the DSC curve of the oxyfluoride tellurite glass with a heating rate of 10 K/min. The glass transition temperature is about 329 °C, and the onset crystallization temperature is 392 °C. Based on the characteristic temperatures, the precursor glass (PG) samples were heated by using the following schedules: 345 °C for 10 h and 375 °C for 2 h (glass ceramics sample A (GCA)), 345 °C for 10 h and 375 °C for 3 h (glass ceramics sample B (GCB)), respectively.

It can be seen from Fig. 2(a), after heat treatment, transparent glass ceramics were successfully prepared. Based on the X-ray diffraction (XRD) measurements, the possible phase identified in the patterns is $Y_2Te_6O_{15}$ cubic phase. As can be seen from scanning electron microscope (SEM) result depicted in Fig. 2(b), the average size of crystalline phase is smaller than 100 nm.

The up-conversion luminescence spectra of the Er^{3+}-doped oxyfluoride tellurite glasses before PG and after GCA and GCB heat treatments at room temperature

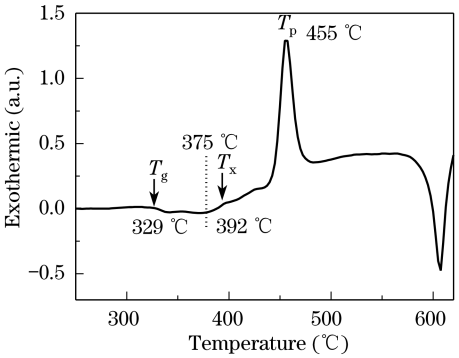

Fig. 1. DSC curve of the oxyfluoride tellurite glass.

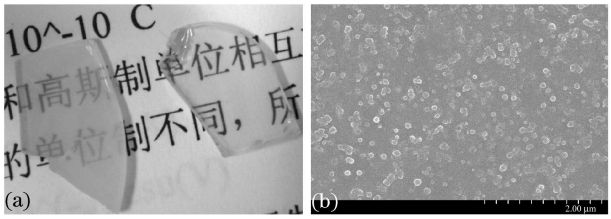

Fig. 2. (a) Photos of glass before (right) and after heat treatment (left) by camera; (b) SEM of glass ceramic.

are shown in Fig. 3(a). In the $Er^{3+}/Tm^{3+}/Yb^{3+}$ tri-doped glass, all the three fundamental colors (red, green, and blue) were obtained simultaneously. The up-conversion mechanism[14] is that blue emission originating from $^1G_4 \rightarrow {}^3H_6$ transition of Tm^{3+}, green emission originating from $^2H_{11/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+}, and red emission mainly related with $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+}. The luminescence intensities for glass ceramic samples are much stronger than that in the base glass, which indicates that the rare earth ions have been incorporated into the crystalline phase. In order to understand the effects of ceramic processing on the local environment of rare earth ions, the normalized up-conversion luminescence spectra of Fig. 3(a) by the intensity of 545 nm was made as shown in Fig. 3(b). It is interesting that the enhancement magnitude of luminescence intensities with different wavelengths are different. Because of the heat treatment, one of the most obvious changes is observed that the blue intensitity increases with higher magnitude than other wavelengths. Associated with the previous work[14], in $Er^{3+}/Tm^{3+}/Yb^{3+}$ tri-doped glass the output color can be modulated with Er^{3+}, Tm^{3+}, and Yb^{3+} doping concentration changes. So one of the possible reasons for higher enhancement magnitude of blue emission is that three different rare earth ions with different dissolved abilities in the precipitated crystalline phase are mainly ascribed to the different ionic radii, which leads the relative concentration ratio of three ions changed from batching composition. In other words, the ceramic processing can modulate the relative doping concentration ratio of rare earth ions in glass ceramics, which can be used to modulate the output color by changing the ceramic processing time.

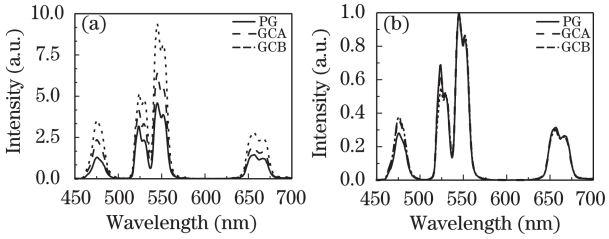

Fig. 3. Up-conversion fluorescence spectra of glass samples (a) before and (b) after normalized.

In conclusion, we have prepared the transparent Er^{3+}-/Tm^{3+}-/Yb^{3+}-doped oxyfluoride tellurite based nanocrystallized glass ceramics with the batching composition of $73TeO_2$-15ZnO-$7ZnF_2$-$3YF_3$-$1.5YbF_3$-$0.3ErF_3$-$0.2TmF_3$ (mol%). The three-color up-conversion emission intensity around the visible wavelength in the glass ceramics can be much stronger than that in the base glass, and the most obvious change is observed that the blue intensity increases with higher magnitude than other wavelengths after heat treatment. Hence, the ceramic processing can be used to modulate the relative doping concentration ratio of rare earth ions in glass ceramics.

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