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Preparation and photoluminescence of Eu-doped oxyfluoride borosilicate glass ceramics

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Abstract: Eu-doped transparent oxyfluoride borosilicate glass ceramics containing Ba_2GdF_7 nanocrystals were prepared by controlling crystallization of melt-quenched glass fabricated under a reductive atmosphere. In the oxyfluoride borosilicate glass ceramics, the mean crystal size of Ba_2GdF_7 nanocrystals was about 30 nm, which could be observed by X-ray diffraction (XRD) and transmission electron microscopy analysis. The photoluminescence spectra of the samples excited at 392 nm showed that, besides the characteristic sharp emissions of Eu^{3+} ions, a very intense broadband emission of Eu^{2+} ions centered at 450 nm appeared. The photoluminescence intensity of Eu^{3+} and Eu^{2+} ions in the glass ceramics was much stronger than that in the as-made precursor. The long decay lifetimes of Eu^{3+} and Eu^{2+} ions evidenced the partitions of Eu^{3+} and Eu^{2+} ions into the Ba_2GdF_7 nanocrystals. The energy transfer from Gd^{3+} ions to Eu^{3+} and Eu^{2+} ions was confirmed by the excitation and emission spectra.

Keywords: optical materials and properties; photoluminescence; glass ceramics; rare earths

Rare earth (RE) ions-doped transparent oxyfloride glass ceramics containing fluoride crystalline phase have attracted much attention in the luminescent materials field, such as optical communication, scintillator, laser, three-dimensional solid-state display, white light emitting diodes (W-LEDs) and so on[1]. Such materials provide low phonon energy environment of fluoride glasses and maintain excellent chemical and thermal stability of oxide glasses[2]. Through controlling nucleation and crystallization of oxyfloride glasses, different sizes of fluoride nanocrystals could be obtained in the glass matrix. In order to develop highly efficient rare earth doped glass ceramics, the key factor depends on the partition of optically active RE ions into the precipitated fluoride nanocrystals. Solid solution MF_2-LnF_3 (M=alkaline earth and Ln=lanthanides) systems have been systematically investigated and may be used as good host matrix for many active ions[3]. By now, only a few kinds of solid solution MF_2-LnF_3 nanocrystals (such as Sr_2GdF_7[3], Ba_2LaF_7[4,5], Ba_2YF_7[6]) have been successfully precipitated among the glass matrix, and rare earth doped transparent glass ceramics containing these solid solutions exhibit excellent luminescence properties. Furthermore, solid solution MF_2-LnF_3 could provide two kinds of sites (M and Ln) and different metal ions may selectively participate into the solid solution MF_2-LnF_3 by substituting for M or Ln sites, respectively. However, as far as we know, few investigations on these have been carried out by now. In this work, the photoluminescence properties and fluorescence lifetime of Eu-doped transparent oxyfluoride borosilicate glass-ceramics containing Ba_2GdF_7 nanocrystals were investigated.

1 Experimental

The glass sample was prepared with the following composition in mol.% of $60SiO_2$-$15B_2O_3$-$10Na_2O$-$10BaF_2$-$5GdF_3$-$0.1EuF_3$. Carbon powder was introduced to create a reductive atmosphere in the covered corundum crucibles. After being melted at 1450 ºC for 60 min, the mixture was rapidly poured into a preheated copper plate and annealed at 500 °C for 2 h. In order to obtain transparent glass ceramics, the as-made precursor was cut and heat-treated at 650 °C (named as GC650), 670 °C (named as GC670) and 690 °C (named as GC690) for 2 h, respectively. X-ray diffraction (XRD) measurements were performed on a Rigaku D/max 2550V/PC with Cu Kα radiation (λ=0.154 nm) at 4 °C/min scanning rate. The microstructure of GC670 was analyzed by a transmission electron microscope (TEM, Philips-FEI-Tecnai G2 F30). The photoluminescence excitation and emission spectra of the samples were measured on a Jobin-Yvon Frolog3 fluorescence spectrophotometer with a Xe-lamp, and the fluorescence decay curves were obtained using excitation of microsecond and nanosecond flash lamps. All measurements were carried out at room temperature.

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2 Results and discussion

2.1 XRD analysis

The XRD patterns of the as-made precursor and glass ceramics heat-treated at different temperatures are shown in Fig. 1. For the as-made precursor, besides the amorphous diffuse humps, several weak diffraction peaks were obviously observed and assigned to orthorhombic Ba_2GdF_7 crystal[7]. With the increase of heat treatment temperature, diffraction peaks became obvious and sharp, which indicated the gradual formation of Ba_2GdF_7 nanocrystals. Based on the peak widths of XRD pattern, the crystallite size D was evaluated by Scherrer equation

$$D = \frac{0.9\lambda}{\beta \cos\theta} \tag{1}$$

Where λ is the X-ray wavelength, β is the full width at half-maximum of the peak, and θ is the diffraction angel. The calculated mean crystallite sizes are 22.2, 29.5 and 36.7 nm for GC650, GC670 and GC690 samples, respectively[8]. Due to its distortion of GC690 after heat treatment, GC670 was selected as the object of study.

2.2 TEM analysis

The microstructure of the sample GC670 is shown in Fig. 2. It demonstrated that the size of Ba_2GdF_7 nanocrystals in the glass ceramics was about 25–35 nm, which was consistent with the previous calculated result.

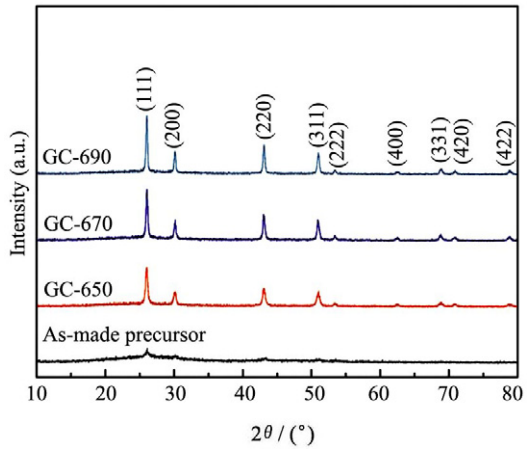

Fig. 1 XRD patterns of as-made precursor and glass ceramics

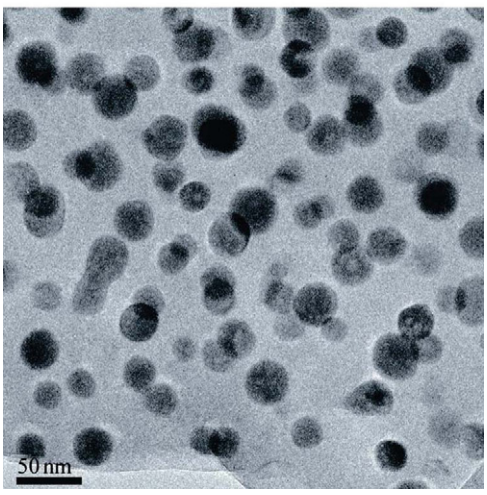

Fig. 2 TEM micrograph of GC670

2.3 Photoluminescence excitation and emission spectra

Fig. 3(a) and (b) show the photoluminescence excitation (monitored at 589 nm) and emission (excited at 392 nm) spectra of the as-made precursor and GC670, respectively. As shown in Fig. 3(a), the intensity of excitation spectra increased after heat treatment. The characteristic excitation peaks of Eu^{3+} ions occurred, which corresponded to the transitions of Eu^{3+} ions from the ground state $^7F_0$ to the excited states $^5D_4$ (360 nm), $^5G_3$ (381 nm), $^5L_6$ (392 nm), $^5D_3$ (414 nm), respectively. The excitation peaks at 274 and 310 nm originated from the transitions from the ground state $^8S_{7/2}$ to the excited state ^6I_J and ^6P_J of Gd^{3+} ions, respectively. This indicated the existence of energy transfer from Gd^{3+} to Eu^{3+} [9].

As shown in Fig. 3(b), two groups of emission signals appeared in the emission spectra. One was made of several characteristic emission peaks owing to $^5D_{0,1,2} \rightarrow {}^7F_J$ (J=0,1,2, 3, 4) transition of Eu^{3+} ions. The other consisted of a broad emission band from 400 to 550 nm, which was ascribed to 5d→4f transition of Eu^{2+} ions and was similar to the photoluminescence of Eu^{2+} doped oxyfluoride glass ceramics containing CaF_2[2], SrF_2[10] or BaF_2[11] nanocrystals. The photoluminescence intensity of Eu^{3+} and Eu^{2+} ions in GC670 was several times stronger than that in the as-made precursor.

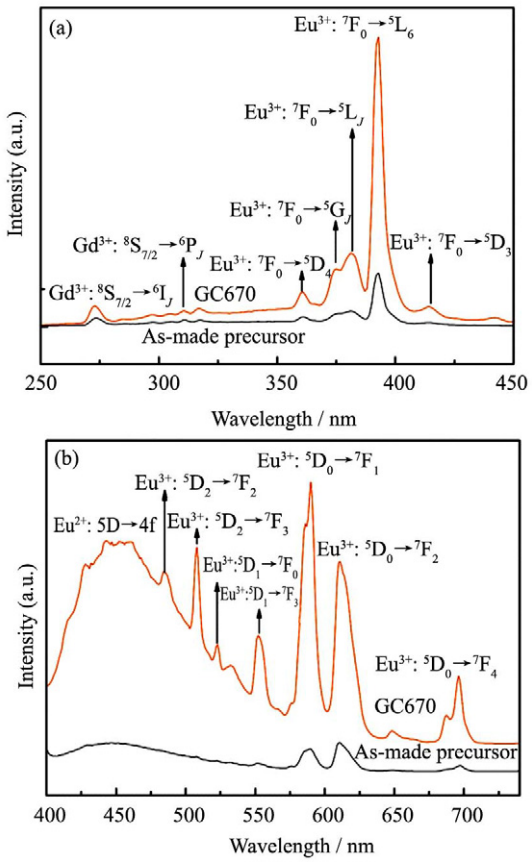

Fig. 3 Photoluminescence excitation spectra of 0.1 mol.% EuF_3 doped as-made precursor and GC670 monitored at 589 nm (a) and photoluminescence emission spectra of 0.1 mol.% EuF_3 doped as-made precursor and GC670 excitated at 392 nm (b)