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Enhanced emissions in Tb^{3+}-doped oxyfluoride scintillating glass ceramics containing BaF_2 nanocrystals

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ABSTRACT

Transparent Tb^{3+}-doped glass ceramics containing BaF_2 nanocrystals were prepared by melt-quenching method with subsequent heat treatment. The XRD and EDS results showed the precipitated crystalline phase in the glass matrix was BaF_2. Under 376 nm light, Tb^{3+} doped oxyfluoride glass ceramics containing BaF_2 nanocrystals showed more intense green emission than the as-made glass, and the emission intensity increased with increasing heat treatment temperature and time. The lifetimes of 541 nm emission of Tb^{3+} doped oxyfluoride glass ceramics were longer than that of as-made glass, which are in the range from 3.00 ms to 3.55 ms. Under X-ray excitation, the green emission was enhanced in the glass ceramics compared to the as-made glass. The results indicate Tb^{3+} doped oxyfluoride glass ceramics containing BaF_2 nanocrystals could be a material candidate for X-ray glass scintillator for slow event detection.

1. Introduction

Rare earth (RE) doped optical materials have attracted much attention due to their unique optical behavior and potential applications such as lasers, three dimensional displays, light converters, optical fibers and amplifiers [1–3]. Among them, RE doped glasses have been attractive materials due to their low production cost, easy shaping of elements, possibility to incorporate activator ions at high concentrations and the ease of manufacture in different sizes and shapes [4]. Glass ceramic, is a kind of composite materials which possess glasses and crystals, and have the advantages of both materials. For oxyfluoride glass ceramics, such materials combined the low phonon energy of fluoride crystals and the high chemical and mechanical stability of oxide glasses and have widely been investigated [5–8]. The earliest oxyfluoride glass ceramics contain CdF_2 and PbF_2. However, they are poisonous so that they could not be used extensively in view of the environment issue. Therefore, some researchers have developed glass ceramics containing LaF_3, CaF_2 or SrF_2 nanocrystals [6,9–11]. The alkaline-earth fluorides have high solubility of both sensitizer and activator RE^{3+} ions and their lattice consists of a body-centered cubic structure. The F^- ions form a cubic cage with the alkaline-earth cation and trivalent RE ions can be substituted for the divalent alkaline-earth cations [12,13], which makes it possible to prepare transparent glass ceramics containing MF_2: RE^{3+}($M=Mg^{2+}$, Ca^{2+}, Sr^{2+}, Ba^{2+}) nanocrystals. Further studies should be conducted to master the controllable growth of fluoride nanocrystals and evaluate the potential applications of these materials for optical devices. In this work, we developed transparent Tb^{3+}-doped oxyfluoride scintillating glass ceramics containing BaF_2 nanocrystals. The aluminosilicate glass was fabricated, and the corresponding glass ceramics were obtained by appropriate heat treatment on the as-made glass. X-ray diffraction (XRD), optical transmission, photoluminescence (PL), X-ray excited luminescence (XEL), and fluorescence decay properties of the as-made glass and glass ceramics were investigated.

2. Experimental

The oxyfluoride glasses with the composition of $40SiO_2$–$10Al_2O_3$–$10Na_2O$–20 BaO–$(20-x)BaF_2$–$xTbF_3$ ($x=1$, 4, 6, 8, 10) (mol%) were prepared from high purity (99.99%) SiO_2, Al_2O_3, Na_2CO_3, $BaCO_3$, BaF_2, TbF_3. These chemicals were mixed thoroughly and melted in a covered alumina crucible at 1500 °C for 30 min in an electric furnace in the ambient atmosphere. The melt was poured onto a preheated steel plate and pressed by another steel plate, and then slowly cooled down to room temperature. Differential thermal analysis (DTA) measurements were carried out on a Netzsch DTA 404PC at the rate of 10 K/min. The glass samples with a regular size of 15 mm × 15 mm × 1.5 mm were

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finally obtained after cutting and polishing. 1 mol%, 4 mol%, 6 mol% Tb^{3+} doped oxyfluoride glass samples were then heat-treated for 1 h at 640 °C to induce crystallization and form transparent oxyfluoride glass ceramics, and were denoted as 1 mol% Tb^{3+} GC, 4 mol% Tb^{3+} GC, and 6 mol% Tb^{3+} GC, respectively. Meanwhile, 8 mol% Tb^{3+} doped oxyfluoride glass samples were heat-treated at 640 °C for 1 h, 640 °C for 2 h and at 650 °C 2 h to induce crystallization and form transparent oxyfluoride glass ceramics, and were denoted as GC6401h, GC6402h and GC6502h, respectively.

The crystalline phases in the as-made glass and glass ceramics were identified by X-ray diffraction (XRD) measurements using a Bruker D2 PHASER Diffractometer with Cu-$K\alpha$ radiation (λ=0.154 nm). The microstructure of oxyfluoride glass ceramics was analyzed by a transmission electron microscope (TEM, JEM-2100) equipped with the energy dispersive X-ray spectroscopy (EDX). The transmittance spectra of the oxyfluoride glass ceramics were recorded with a Shimadzu UV-3600 spectrophotometer in the range of 280–900 nm. Photoluminescence (PL) spectra and luminescence decay curves were recorded on a Jobin-Yvon Fluorolog3 fluorescence spectrophotometer using Xe lamp as an excitation source. X-ray excited luminescence (XEL) spectra were performed by a X-ray excited spectrometer, where an F-30 X-ray tube (W anticathode target) was the X-ray source, operated under 70 kV and 6 mA.

3. Results and discussions

Fig. 1 shows the DTA curve of the as-made 8 mol% Tb^{3+} doped oxyfluoride glass. The glass transition (T_g) temperature is around 570 °C. Two exothermic peaks are observed with the values at 650 °C (T_{x1}) and 815 °C (T_{x2}). XRD analysis shows the former peak is due to the precipitation of BaF_2 and the latter is due to the crystallization of the glass. The large difference up to 145 °C between T_{x1} and T_{x2} indicates that it is easy to precipitate the BaF_2 phase from the glass matrix.

The XRD patterns of oxyfluoride glass and glass ceramics with different concentrations of Tb^{3+} are shown in Fig. 2. Sharp diffraction peaks are observed for the glass ceramics while the as-made glass is completely amorphous with no crystalline diffraction peaks. For 1 mol% and 4 mol% Tb^{3+} doped GC, the diffraction peaks can be easily assigned to cubic BaF_2 (JCPDS 04-0452) and no other diffraction peaks were detected. For 6 mol% and 8 mol% Tb^{3+} doped GC, the diffraction peaks shift larger angle gradually and regularly. It probably dues to vast Tb^{3+} ions enter into the BaF_2 nanocrystals and lead to lattice distortion, which is similar to the phenomenon of trivalent

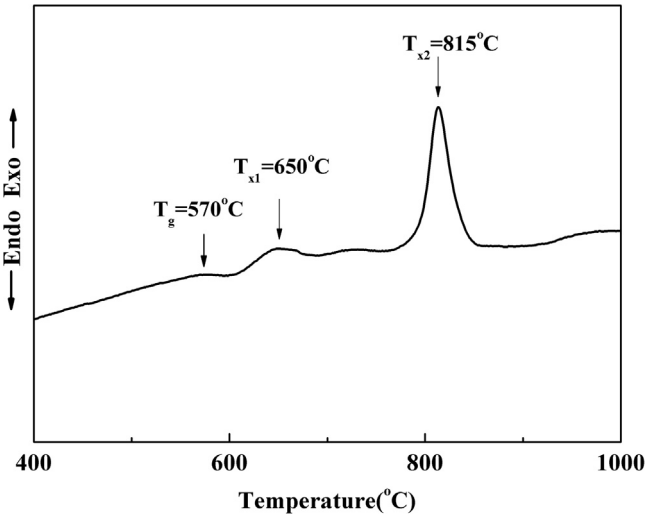

Fig. 1. DTA curve of 8 mol% Tb^{3+} doped oxyfluoride glass.

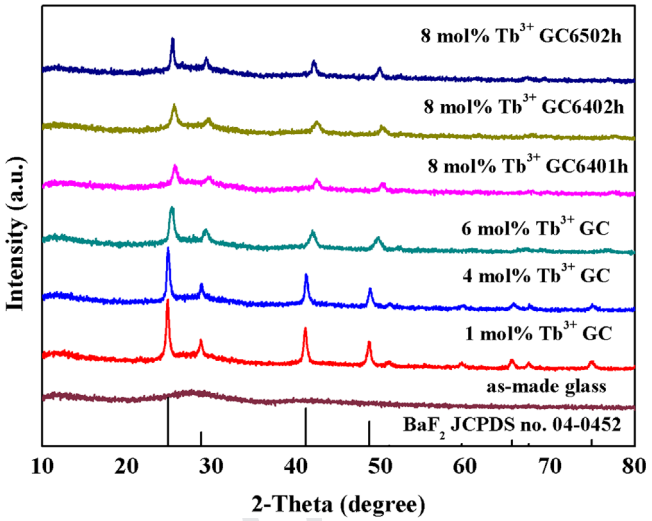

Fig. 2. XRD patterns of x mol% Tb^{3+} (x=1, 4, 6) doped glass ceramics and 8 mol% Tb^{3+} doped glass ceramics after heat-treated at for 640 °C 1 h, 640 °C 2 h, and 650 °C for 2 h.

rare-earth ions entering into fluorites and causing lattice distortions [14,15]. The size of BaF_2 nanocrystals in the glass ceramic can be calculated from the XRD pattern using the Scherrer equation [16]. The calculated sizes of BaF_2 nanocrystals were 12.5 nm, 13.6 nm, and 21.5 nm for the glass ceramics GC6401h, GC6402h, and GC6502h, respectively. The results indicate the crystal size in the glass ceramics increases with the increment of heat treatment temperature and time. The fractions of crystalline phase in the glass ceramics were calculated to be The fractions of crystallized material were calculated to be 47.5%, 42.3%, 38.8%, 36.3%, 38.8%, 39.2% for 1 mol% Tb^{3+} GC, 4 mol% Tb^{3+} GC, 6 mol% Tb^{3+} GC, 8 mol% Tb^{3+} doped GC6401h, GC6402h and GC6502h, respectively.

The TEM image of 8 mol% Tb^{3+} doped glass ceramic heat-treated at 640 °C for 2 h (GC6402h) is shown in Fig. 3(a). It demonstrates that spherical BaF_2 nanocrystals are distributed homogeneously in the glass matrix and the crystal size is approximately 10–15 nm, which is consistent with the value (13.6 nm) calculated using the Scherrer equation based XRD pattern. In order to detect the element distribution, the EDX spectra with nanosized probe of an individual BaF_2 nanocrystal and the glass matrix in 8 mol% Tb^{3+} doped glass ceramic (GC6402h) were recorded, as shown in Fig. 3(b). The appearance of a Cu signal could be attributed to the carbon coated copper grid used in the TEM measurement. In comparison with the EDX spectrum of the glass matrix, the spectrum of an individual BaF_2 nanocrystals exhibits relatively stronger Ba, Tb signals and the proportion of the atomic ratio of Ba to Tb ions is nearly 4:1. All the results indicate that the BaF_2 nanocrystals have formed in the glass matrix after heat treatment.

Fig. 4 shows the transmittance spectra of 8 mol% Tb^{3+} doped as-made glass and glass ceramics with the thickness of 1.50 ± 0.02 mm. It can be seen that the as-made glass and the glass ceramics have good transmittance in the visible spectrum region and the UV cut-off wavelength is around 300 nm. As-made glass has the highest transparency. The transparency of glass ceramics becomes lower with the increase of heat treatment temperature and time. The faster nucleation and growth rate of BaF_2 nanocrystals in oxyfluoride glass ceramics can be ascribed to the elevated heat treatment temperature and time, which would result in the larger size and higher crystallization fraction [17]. However, the glass ceramics still remain good transparency due to that the size of BaF_2 nanocrystal is much smaller than the wavelength of the visible light [10,18]. The absorption bands of Tb^{3+} ions centered at 351, 367, 377, 484 nm can be observed in the spectra as well, which are attributed to the transitions from the ground state $^7F_6$ to the higher ^5D states of Tb^{3+}. It can be observed

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