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Crystallization and spectroscopic properties in Er^{3+} doped oxyfluorogermanate glass ceramics containing Na

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ABSTRACT

The Er^{3+} doped oxyfluorogermanate glasses, with a composition containing Na element, were synthesized by the conventional melting–quenching technique. When Na element was introduced into the composition of oxyfluorogermanate glass, the crystals behavior was investigated in details. Depending on the annealing procedure supplied, thermal annealing of precursor glasses in the system $GeO_2/BaF_2/AlF_3/Na_2O/NaF/ZnO/GdF_3/ErF_3$ led to the precipitation of different crystal phase nanocrystals. It was confirmed the nanocrystals in GC600 is orthorhombic $NaBaAlF_6$ which led to enhance obviously in the UC luminescence of Er^{3+}. However, the nanocrystals in G585 led to decrease in the UC luminescence, which indicated few Er ions enter into the lattice of this nanocrystal phase. The reason of the decrease in UC emission intensity of GC585 was analyzed.

1. Introduction

In recent decades, rare-earth (RE) doped frequency conversion luminescence materials have attracted much attention due to their potential applications in different areas such as solid state lasers, optical data storages, three-dimensional displays, solar cells and biomedical instruments [1–4]. Among various RE ions, Er^{3+} is one of the important active ions for luminescence, because it can offer not only infrared luminescence for optical amplification at the third communication window, which is the reason Er^{3+} is considered to be one of the most popular and efficient RE ions employed in the optical telecommunication systems, but also a favorable energy level structure in the near infrared spectral region with two transitions: $^4I_{15/2} \rightarrow {}^4I_{9/2}$ (at about 800 nm) and $^4I_{15/2} \rightarrow {}^4I_{11/2}$ (at about 980 nm), which can be efficiently excited, thereby yielding blue, green and red upconversion (UC) emission [5,6].

As host materials for use in RE-doped luminescence, oxyfluoride glass ceramics have drawn a lot of attention, as they combined the good chemical and physical stability of oxide glasses and the excellent spectral properties of fluoride crystal [7,8]. Many investigations have been carried out on the UC luminescence of Er^{3+} doped oxyfluoride glass ceramics containing BaF_2 nanocrystals due to alkaline-earth fluorides are important optical raw materials with high solubility of both sensitizer and activator RE ions, and have been used successfully as a crystal laser host [9–11]. The results confirmed the reason that Er^{3+} doped oxyfluoride glass ceramics have strong UC emission lies in the doped Er^{3+} ions preferentially incorporated into crystalline phases with lower phonon energy by substituting for Ba^{2+}.

Furthermore, it is pointed out that less symmetric crystal phases possess advantageous emission properties in comparison to more symmetric crystal phases. One example is the hexagonal β-phase of $NaYF_4$: Yb^{3+}, Er^{3+} displays an UC efficiency approximately one to two times higher than that of the corresponding cubic α-phase one [12]. So, to improve the emission properties of RE ions by preparing glass ceramics, the nanocrystals with optimal structure precipitated from precursor glasses are very essential. There are two major factors that affect the properties of crystal phases precipitated from host glasses: matrix composition and crystallization procedure. Thoma et al. [13] have obtained hexagonal and cubic phases depending on the Na/Ln molar ratio and the temperature by studying the phase diagrams of the $NaF–LnF_3$ systems (Ln = Y, La–Lu) in the temperature range of 700–1300 °C. In addition, sodium is one of the major elements to prepare sodium rare earth fluorides micro-crystallite, such as $NaInF_4$ [14–16]. Up to mow, however, little attention has been paid to oxyfluorogermanate glass ceramics containing sodium rare earth fluorides micro-crystallite, and for all we know, only Kamma et al. [17] reported $NaErF_4$ nanocrystals were successfully precipitated in the system $GeO_2/TeO_2/PbO/Na_2CO_3/ErF_3$. So, in this paper, the crystallization behavior and properties of crystal phases in Er^{3+}

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doped oxyfluorogermanate glass ceramics were investigated in details when Na element was introduced into the composition containing BaF_2 of precursor glass, and the effect of nanocrystals precipitated from precursor glass on the UC luminescence of Er^{3+} ions in oxyfluorogermanate glass ceramics was analyzed.

2. Experimental

The glass samples with molar composition of $45GeO_2$–$20BaF_2$–$10AlF_3$–$10Na_2O$–5NaF–8ZnO–$1GdF_3$–$1ErF_3$ were prepared by high temperature melting method. High pure reagents of GeO_2, BaF_2, AlF_3, NaF, GdF_3, ErF_3 and analytical pure reagents Na_2CO_3 were used as raw materials. Accurately weighed 10 g batches of raw materials were fully mixed and then melted in a covered corundum crucible at 1350 °C for 50 min. The melts were cast quickly into stainless steel plates which were kept around 350 °C. The obtained glasses were annealed in a furnace to release the internal stress. To obtain transparent glass ceramics, the precursor glasses were reheated respectively at 585 and 600 °C for 1 h (denoted as GC585 and GC600, respectively). The obtained glass and glass ceramics were polished for optical measurements.

The characteristic temperatures (T_g glass transition temperature and T_c crystallization temperature) were measured using a differential thermal analysis (DTA) unit (SDT Q600 V8.2 build 100) with a rate of 10 K/min in an Ar atmosphere. X-ray diffraction (XRD) measurements were performed in a D8ADVANCE diffractometer with Cu Kα radiation at 0.1° min^{-1} scanning rate, tube voltage and tube current of 40 kV and 40 mA. The UV/VIS/NIR absorption spectra were recorded in the wavelength range from 330 to 700 nm using with a Model U-4100 Spectrophotometer. The UC luminescence spectra were measured by exciting the samples with the 980 nm LD, and recorded by using a HITACHI F-7000 Fluorescence spectrophotometer. The micro-morphology of nanocrystals was observed by a JEM-2100 transmission electron microscope (TEM) equipped with EDS system with accelerating voltage at 200 kV. All the measurements were taken at room temperature.

3. Results and discussion

Fig. 1 shows the DTA curve of the precursor glass. As seen from Fig. 1, two crystallization peaks (T_{c1}, T_{c2}) are observed in the DTA thermograph. Derived from this DTA curve, the values of T_{c1} and T_{c2} are 559 and 646 °C, respectively, and the melting point temperature is 505 °C. It is well known, large temperature difference between T_g and T_c can effectively prevent the growing up quickly of crystal nucleus. However, the ΔT ($T_{c1} - T_g$) of the precursor glass is 54 °C, which indicates the crystalline phase corresponding to the crystallization peak is very easy to crystallize. Compared with our previous study (the precursor glass composition without Na element) reported in Ref. [8], the performance against nucleation and crystallization of the precursor glass studied in this work become weak. In fact, the DTA curve indicates a new crystalline phase could precipitate from precursor glass due to the introduction of Na element in the glass composition. It was found that the sample became opaque when it was heated over 600 °C. Therefore, to obtain transparent glass ceramics, the heat treatment temperature was selected to be 585 and 600 °C.

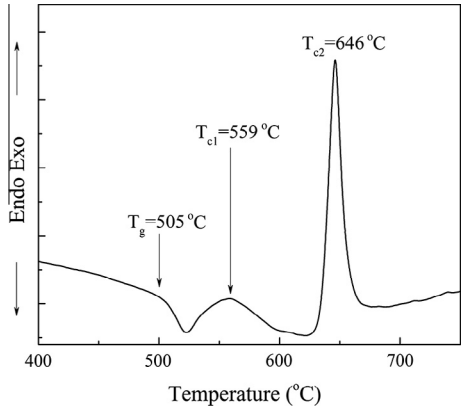

Fig. 1. DTA curve of Er^{3+} doped oxyfluorogermanate glass.

Fig. 2 shows the XRD patterns of the precursor glass and glass ceramics obtained by heat treatment at 585 and 600 °C for 1 h, respectively. As seen from Fig. 2, the precursor glass sample presents a broad diffraction curve characteristic of the amorphous state, while in the patterns of glass ceramics, several diffraction peaks are clearly observed, indicating that crystallites were successfully precipitated during thermal treatment. An average crystal diameter was calculated from XRD patterns by using the Debye-Scherrer equation [8] expressed by:

$$D_{hkl} = \frac{0.9\lambda \times 57.3}{\beta_{1/2} \cos\theta} \quad (1)$$

where D_{hkl} is the crystal radius, λ (=0.15418 nm) is the X-ray wavelength, $\beta_{1/2}$ is the full-width at half-maximum (FWHM) of the diffraction peak, θ is the diffraction angle, 57.3 is a factor used to convert $\beta_{1/2}$ in degree to $\beta_{1/2}$ in radian. The obtained mean crystal sizes are about 12 and 25 nm for the glass ceramics GC585 and GC600, respectively.

Furthermore, it is found, compared with the X-ray diffraction peak at $2\theta = 27°$, the intensity of the peak observed at $2\theta = 26°$ became stronger gradually with the increase of annealing temperature. This result indicates the structure and characteristic of the crystal phases depreciated from previous glass could take place the fundamental change with the increase of annealing temperature. Compared with the standard JCPDS 42-1151 card, the crystal phase identified in the pattern of GC600 sample is orthorhombic $NaBaAlF_6$. However, the XRD patterns of others samples cannot index to any reported standard XRD data of rare fluorides. On the other, it is noticeable that peaks are very similar to the diffraction data of above-mentioned orthorhombic $NaBaAlF_6$. The most visible difference lies solely in the relative intensity between peaks (2θ at 26° and 27°). Therefore, the glass ceramic samples GC585 are supposed to crystallize in another crystal phase of $NaBaAlF_6$, whose XRD data has not been reported yet.

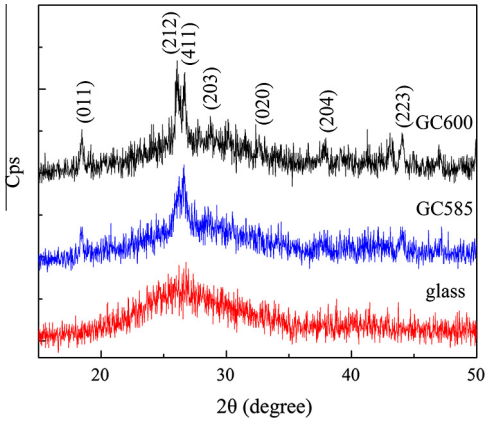

Fig. 2. XRD patterns of the Er^{3+} doped oxyfluorogermanate glass and glass ceramics obtained by heat treatment at 585 and 600 °C for 1 h, respectively.