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Effect of crystalline fraction on upconversion luminescence in Er^{3+}/Yb^{3+} Co-doped $NaYF_4$ oxyfluoride glass-ceramics

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ABSTRACT

The crystalline fraction were adjusted MgO concentration and the corresponding effect on upconversion (UC) luminescence in Er^{3+}/Yb^{3+} co-doped $NaYF_4$ oxyfluorode glass-ceramics was investigated. With increase of MgO and the content of Na_2O reduced, the internal network structure of the glass became compact, which made the size of $NaYF_4$ nanocrystals unchanged, while the average distance between the nanocrystals increased significantly. Crystal growth is limited with the glass network, keeping the crystal size not changed. SNM-1 glass ceramics samples show a predominant red up-conversion emission under near infrared excitation at 980 nm, while a predominant green emission is observed in the SNM-3 samples. In this paper, it was indicated that it changed the effect of glass network modifier MgO in the glass structure. The possible mechanism responsible for the color variation of UC in Er^{3+}/Yb^{3+} co-doped was discussed.

1. Introduction

The lanthanide-doped micro-crystal materials have attracted considerable attentions in the field of optical fibers, solid laser, three-dimensional display and W-LED illumination and so on [1–3]. Fluoride glasses are ideal for rare-earth doped substrate, on account of their high transparency, rare earth ions solubility and the low phonon energy. However, the fluoride glass is expensive and toxic expensive and it is toxic, susceptible to corrosion and of poor stability which hinder their applications in many fields [4]. Lanthanide-doped oxides glass possesses excellent chemical and mechanical stability, but it shows high phonon energy, resulting in poor upconversion emission. Oxyfluoride glass-ceramics taking into account of the high mechanical strength of the oxides glass matrix and good upconversion efficiency of the fluoride crystals, thus become a research hotspot a hot research and get some interesting results have been reported [5].

Conversion luminescent material has excellent prospects, but the conversion efficiency is not high luminous and restricts its actually use, so how to improve the luminous efficiency has become the focus of research. According to the previous research, glass up-conversion luminescence intensity is mainly determined by the maximum phonon energy of the glass, and the most important factor is the glass body, which determines the maximum phonon energy. Oxyfluoride glass ceramics show a low phonon energy, which can improve the luminous efficiency of rare earth ions. Meanwhile, glass matrix has better physical and chemical stability and high mechanical strength. In order to pursue higher up-conversion efficiency, fluoride glass ceramics with low phonon energy arouse wide concerns. Many rare-earth doped fluoride-based phosphors possess the UC ability for their low phonon energy. Among them, $NaYF_4$ crystal doped with Er^{3+}/Yb^{3+} is known as one of the most efficient NIR-to-visible UC hosts. Previous investigations have shown that the UC luminescence in RE doped $NaYF_4$ strongly depends on the phase and particle size [5–7]. It is known that crystallization species, crystal sizes, crystal shapes and the distances among the nanoparticles precipitated in the glass matrix are strongly related to the network structure of glass, i.e., glass former, network intermediate and network modifier will affect the crystallization behavior, Imanieh et al. has demonstrated that alumina content had significant effect on phase separation and viscosity of the glass [8]. In addition, the solubility of rare earth ions in different crystallization species or crystal size is quite different, in other words, different crystallization behavior will lead to diverse the luminescence properties of rare earth ions. Furthermore, MgO

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and Na_2O, as the glass network modifier, show different impact on breaking and linking degree in glass network, for which there were significant differences between the valence states and ionic radius.

In the present work, $NaYF_4$ nanocrystals were precipitated in the glass matrix by thermal treatment, and the crystalline fraction has been controlled by replacing glass network modifier composition Na_2O to MgO, and the relationship between glass structure and Er^{3+}/Yb^{3+} upconversion properties has been discussed.

2. Experiment

The precursor glass samples were prepared with the composition in mol% of $40SiO_2$-$20Al_2O_3$-(20-x)Na_2O-xMgO-10NaF-$10YF_3$-$0{\cdot}5ErF_3$-$1{\cdot}0YbF_3$ (x = 0,5,10). The samples were named as SNM-1, SNM-2, SNM-3, respectively. For each batch, about 10 g of original material was fully mixed and melted in covered Alumina crucible in air atmosphere at 1500 °C for 45 min, and cast into a brass mold, followed by annealing at 450 °C to relinquish in inner stress, where it was slowly cooled down to room temperature. All Precursor glasses were heat-treated for 2 h at 573 °C to form transparent glass ceramics. All samples were cut and polished for subsequent use.

The differential thermal analysis(DTA) measure was carried out in a DTG-60AH differential thermal analyzer in a temperature range from room temperature to 1000 °C with the 10 $Kmin^{-1}$ heating rate under an air atmosphere for the purpose of confirm the glass transition temperature (T_g) and the crystallization peak temperature (T_{c1}). To characterize the crystallization phase, X-ray diffraction (XRD, Rigaku D/MAX2200PC) with Cu-Kα diffraction at 10°.min^{-1} scanning rate, 40kv tube voltage and 20-mA tube current. The transmission electron microscopy (TEM, JEM-2100, equipped with an energy dispersive x-ray spectroscopy system) observation were carried out with an accelerate voltage of 200KV. The UC emission spectra in a wavelength range from 450 to 750 nm were recorded with a HITACHI F-7000 fluorescence spectrophotometer under 980 nm excitation with various powers. The infrared spectra (IR-TENSOR27, Bruker, Germany) scan range from 400 to 1400 cm^{-1} with spectral resolution of 4 cm^{-1}. A Raman spectrum measurement was performed on (invia, RENISHAW, England) using the 514 nm line of a solid-state laser as the excitation source with the resolution of 1 cm^{-1}. All the measurements were carried out at room temperature.

3. Results and discussion

In the part of introduction, we know that glass network structure is the main factor to the crystallization behavior. In this work, glass network modifier composition Na_2O is replaced to MgO, and the crystal size and distance of precipitated nanoparticle are investigated by DTA measurement firstly. Fig. 1(a) shows the variation of DTA thermographs curve of the as-made glass of SNM-1, SNM-2 and SNM-3 composition and the first crystallization temperatures of oxide matrix, T_{c1}, were estimated to be 573 °C, 574 °C and 572 °C, respectively. The result shows that it basically has no effect on the first crystallization peak temperature of the glass after using MgO instead of Na_2O. It provides an indispensable precondition for comparison after the heat treatment in the same temperature. Fig. 1(b) shows the crystallization peak of SNM-1, SNM-2 and SNM-3 glass samples, the crystallization intensity represents the enhancements of the crystallization. Here we used "*I*" to express the intensity of the first crystallization peak of glass DTA curve, so as to compare the difference of crystallization capacity among SNM-1, SNM-2 and SNM-3 more conveniently. It can be seen that the Tc_1 crystallization peak gradually decreased ($I_{SNM-1} > I_{SNM-2} > I_{SNM-3}$), indicating the glass network modifier MgO content may reduce the oxyfluoride glass crystallization ability. In the non-isothermal transition, the T_{c1} of the exothermic peak is affected by the heating rate. There is sufficient time for the transition from the glass to the crystalline at low heating rate, resulting in lower T_{c1} value, lower transition rate and smooth exothermic signal. When it is heated at higher heating rate, the transition is lagged, leading to higher T_{c1} value, higher transition rate, and sharp exothermic signal. Based on the above results and JMA (Johnson-Mehl-Avramic) equation, we could further investigate the dynamics and corresponding parameters of the glass crystallization. Based on thermal analysis theory and *JMA* equation, *JMA Ozawa* has proposed the following equation [9–11]:

$$\ln\beta = -\frac{E}{RTc1} + C1 \tag{1}$$

where is the temperature, corresponding to the exothermal peak and C_1 is a constant. Thus the activation energy *E* could be easily calculated. Experiment of the DTA analysis using the heating rate of 5 $Kmin^{-1}$, 10 $Kmin^{-1}$, 15 $Kmin^{-1}$, 20 $Kmin^{-1}$. As Fig. 1(c) shows, through calculation, we find that the crystallization activation energy is gradually increased in the range of sample SNM-1 to SNM-3 ($E_{SNM-1} = 507.84KJ/mol$, $E_{SNM-2} = 592.23KJ/mol$ and $E_{SNM-3} = 697.16KJ/mol$) Which is in accordance with the experimental results. Sufficient crystallization activation energy is desired so as to overcome the energy barrier of the rearrangement of structural motifs in the process of crystallization of the glass. And the energy barrier is in an inverse proportion to the ability of crystallization [12–14]. XRD patterns of glass and heat-treated at 573 °C (T_{c1}) at 2 h of transparent glass ceramics are shown in Fig. 1(d). Tow humps in XRD curve of glass signify its amorphous structure. After the heat treatment, some intensity diffraction peaks correspond to cubic $NaYF_4$ nanocrystals (JCPDS no. 06-0342) emerge. The mean crystallite size D can be evaluated by *Scherer's* equation [15]:

$$D_{hkl} = \frac{K\lambda}{\beta\cos\theta} \tag{2}$$

where $K = 0.89$, λ (=0.154056 nm) represents the wavelength of CuKα radiation, θ is the Bragg angle of X-ray diffraction peak and β represents the corrected half width of diffraction peak. The mean crystalline sizes are estimated to be about 10.9 nm, 11.4 nm and 11.2 nm for SNM-1, SNM-2 and SNM-3, respectively.

The TEM micrograph images of the SNM-2 glass ceramics are presented in Fig. 2(a), which reveal the homogeneous distribution of abundant spherical α-$NaYF_4$ nanocrystals, sized 10–11 nm, among the glass matrix, which is consistent with the XRD result. The crystalline size distribution in Fig. 2(b) falls in a narrow range with an average crystallize size of 11 nm, which agrees well with the result estimated from the XRD results. In Fig. 2(c) a high resolution TEM (HRTEM) image of a single droplet of the sample SNM-2 annealed at 574 °C for 2 h shown. The calculated d-spacing value is 0.318 nm, which could be ascribed to (111) plane of cubic $NaYF_4$ crystals ($d_{(111)} = 0.318$ nm). In order to detect the element distribution, the EDX spectra taken from the one selected nanoparticle and glass phase are shown in Fig. 2(d) and (e). The appearance of Cu signal is attributed to the carbon coated copper grid used in the TEM measurement. The spectrum taken from glass phase shows strong signals from O, F, Si, Al and Y elements and there is no signal of Er and Yb elements. In contrast, there are strong signals of F, Na, Yb and Er element in the EDX spectrum of nanoparticle, which indicates that Yb^{3+} and Er^{3+} ions mainly concentrate in $NaYF_4$ nanocrystals. In order to confirm that all samples of glass-ceramics have reasonably good crystalline properties with on obvious changes of crystal diameter, and the concentration of Er^{3+} and Yb^{3+} in the nanocrystals of different samples, only have minor difference, the HRTEM and EDX were used. Results presented in Fig. 3. HRTEM images of the glass-ceramics sample and EDX spectra are presented in (a)-(c) and (d)-(f). The HRTEM images of SNM-1, SNM-2 and SNM-3 glass-ceramics sample were performed and are presented in Fig. 3(a)–(c).