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Preparation and Upconversion Luminescence of Nd^{3+}/Yb^{3+} Co-doped La_2O_3-TiO_2-ZrO_2 Glass-ceramics

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Abstract: Nd^{3+}/Yb^{3+} co-doped La_2O_3-TiO_2-ZrO_2 glass-ceramic samples were prepared by heat treatment of precursor glasses fabricated *via* aerodynamic levitation method. The thermal stability of the precursor glass was studied by DTA. The glass-ceramic samples were characterized by photoluminescence spectra, TEM and EDS. The effects of heat treatment on the upconversion luminescence were studied. The DTA curve shows that the glass transition temperature and the onset temperature of crystallization are 799℃ and 880℃, respectively. Five emission bands centered at 497, 523, 545, 603 and 657 nm are obtained at the excitation of 980 nm laser. The emission intensity can be increased by heat treatment. The glass-ceramic samples heat-treated at 880℃ for 50 min perform the strongest upconversion luminescence with intensity (at 545 nm) as 11 times high as that of the precursor glasses, which can be ascribed to the dense columnar crystals embedded in the glass matrix and the enrichment of Nd^{3+} ions in the crystals.

Key words: glass-ceramics; aerodynamic levitation method; heat treatment; upconversion luminescence

Rare-earth-doped materials with upconversion luminescence have attracted increasing attention, driven by potential applications in fiber amplifier[1], and white light LED[2]. Host materials play an important role in obtaining strong upconversion luminescence. Recently, fluoride and oxyfluoride hosts have been researched extensively for their high upconversion luminescence efficiency[3-4]. However, the instability of fluorides and the toxicity of fluorine ions restrict their applications. Therefore, it's important to develop novel host materials.

In our previous study, TiO_2 based glass has been demonstrated to be the material with high refractive index of ~2.24 which can lead to high upconversion luminescence efficiency[5]. So it can be regarded as one of the most promising hosts. In this work, Nd^{3+} and Yb^{3+} (as a sensitizer) co-doped heavy-metal oxide La_2O_3-TiO_2-ZrO_2 (Nd^{3+}/Yb^{3+}: LTZ) is selected as the upconversion luminescence material. However, bulk LTZ glasses can't be fabricated by the conventional methods except adding "strong glass former"[6]. Aerodynamic levitation is one of the most widely used containerless methods which can prevent contamination of crucibles and preclude the source for heterogenous nucleation[7]. Deep undercooling for glass forming in the melt can be easily achieved. Hence, Aerodynamic Levitation Method (ALM) is ideal for the fabrication of Nd^{3+}/Yb^{3+}: LTZ bulk glass spheres. The upconversion luminescence can be improved by crystallization of the glasses[8-9]. To achieve more intense emission and study effects of heat treatment on the upconversion luminescence, Nd^{3+}/Yb^{3+}: LTZ glass-ceramic samples were prepared by heat treatment of the precursor glasses.

In this study, Nd^{3+}/Yb^{3+}: LTZ glass-ceramic samples were prepared by heat treatment of the precursor glasses fabricated in an Aerodynamic Levitation Furnace (ALF). The detailed description of ALF has been introduced elsewhere[10-11]. The upconversion luminescence has been improved by heat treatment which has been optimized. The enhancement mechanism of upconversion luminescence has been discussed after heat treatment of the precursor glasses.

1 Experimental

The compositions of Nd^{3+}/Yb^{3+}: LTZ oxide glasses are $(La_{0.95}Nd_{0.04}Yb_{0.01})(Ti_{0.95}Zr_{0.05})_{2.25}O_6$. High-purity La_2O_3, TiO_2, ZrO_2, Nd_2O_3 and Yb_2O_3 powders were mixed thoroughly, sintered, and then compressed into columnar rods. The spherical glasses with a diameter of ~3 mm were fab-

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ricated by melting the rods in an ALF. Subsequently, the glasses were polished to be 1.5 mm thickness wafers for the later measurements. The preparation method was similar to the description in the previous study[12].

Differential Thermal Analysis (DTA) was carried out to characterize the thermal stability of the glasses. The DTA curves were obtained by NETZSCH STA 449C at a heating rate of 10 ℃/min. The glass samples were heat-treated in air at 860, 870, 880, 890, 900, 920℃ and at 880℃ for 40, 50, 60 min to prepare glass-ceramics. The upconversion luminescence spectra were measured by a spectrofluorometer (Fluorolog-3, Jobin Yvon, France) equipped with Hamamatsu R928 photomultiplier tube. A wavelength of 980 nm continuous-wave diode laser was used as the excitation source. While measuring spectra of the samples whose luminescence should be compared, the samples were placed at the same position in the spectrofluorometer, and the position and power of the pump beam and the width of the slit were set at the same condition. X-ray diffraction (XRD) patterns were recorded with D8 ADVANCE X-ray diffractometer. The powder samples were dispersed into ethanol for Transmission Electron Microscope (TEM) measurement. TEM micrographs and Energy Disperse Spectroscopy (EDS) spectra were taken by JEM-2100F field emission TEM.

2 Results and discussion

2.1 Characterization of thermal property

The DTA curve (Fig. 1) of Nd^{3+}/Yb^{3+}: LTZ glass has a single glass transition and a single crystallization peak. The results show that the glass transition temperature T_g and the onset temperature of crystallization T_o can be determined to be 799℃ and 880℃, respectively. This indicates that the LTZ glass performs much higher thermal stability than ZBLAN glass which is a fluoride system with high upconversion luminescence efficiency[13]. So the upconversion luminescence devices made of LTZ materials can be used in technological applications more widely. Furthermore, the difference $\triangle T$ between the onset temperature of crystallization and the glass transition temperature is an important parameter to characterize the glass forming ability[14]. $\triangle T$ of the present LTZ glass can be calculated to be ~81℃, which is much lower than that of most traditional oxide glasses, such as silicate and borate glass systems[15-16]. This indicates that LTZ glasses show a comparatively poor glass forming ability, leading to much difficulty to obtain bulk glasses by conventional melt-quenching methods. Thus, ALM is introduced for the fabrication of LTZ glasses. Moreover, the heat treatment temperatures can be determined based on the DTA curve.

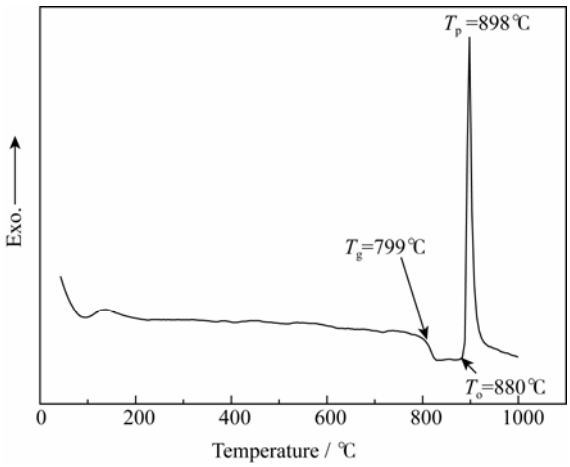

Fig. 1　DTA curve of Nd^{3+}/Yb^{3+}: LTZ

2.2 Upconversion luminescence

To enhance the upconversion luminescence, LTZ glasses were heated at different temperatures holding for different times with a heating rate of 10 ℃/min. The upconversion luminescence spectra of the resulting samples were recorded in Fig. 2. There are five emission bands in the curves corresponding to energy transitions among energy levels in Nd^{3+} ions. One blue emission band centered at 497 nm is observed, owing to the $^2G_{9/2}\rightarrow{}^4I_{9/2}$ transition[17]. Two green emissions, at 523 and 545 nm, are attributed to the transitions from Nd^{3+}: $^4G_{9/2}$ and $^4G_{7/2}$ levels to the ground state $^4I_{9/2}$, respectively[18-19]. Again two emission bands are observed at 603 and 657 nm originated from the Nd^{3+}: $^4G_{7/2}\rightarrow{}^4I_{11/2}$ and $^4G_{7/2}\rightarrow{}^4I_{13/2}$ transitions, respectively[18, 20]. The $^2G_{9/2}$, $^4G_{9/2}$, $^4G_{7/2}$ states of Nd^{3+} ions in LTZ samples are populated *via* a two-photon process, which has been discussed by Pan, *et al*[21]. Excited-State Absorption (ESA) and Energy Transfer Upconversion (ETU) are two possible mechanisms which are responsible for the observed emission bands in Nd^{3+}/Yb^{3+}: LTZ samples. Nd^{3+} ions can't absorb the 980 nm photons directly due to the nonexistence of a matching energy level. But Yb^{3+} ions, with a huge absorption coefficient (at 980 nm), can act as efficient sensitizers to transfer the absorbed energy from Yb^{3+} ions to neighboring Nd^{3+} ions. Therefore, the main upconversion luminescence mechanism can be considered as ETU.

The possible ETU mechanisms which can explain the above upconversion emissions are shown in Fig. 3. Yb^{3+} ions are efficiently excited to $^2F_{5/2}$ states at the excitation of 980 nm laser. Subsequently, ETU processes from Yb^{3+} ions to Nd^{3+} ions populate $^2G_{9/2}$ levels through cooperative sensitization and Phonon Assisted ETU (PAETU)[22-24]. Then Nd^{3+} ions in $^2G_{9/2}$ states decay to $^4G_{9/2}$ and $^4G_{7/2}$ states via nonradiative relaxation. Moreover, the $^4G_{7/2}$ levels can be populated by ETU among neighboring Nd^{3+} ions through the following channel: ($^4F_{3/2}$, $^4F_{3/2}$)→($^4G_{7/2}$,

$^4I_{13/2}$). Finally, upconversion emissions centered at 497, 523, 545, 603 and 657 nm are obtained by corresponding transitions as indicated in Fig. 2(a).

2.3 Effects of heat treatment

In Fig. 2(a), the emission intensity increases and then decreases as the temperature increases. In Fig. 2(b), the intensity increases and then decreases at 880℃ as the holding time prolongs. It can be indicated that the optimal heat treatment is at 880℃ for 50 min. The glass-ceramic samples heat-treated at 880℃ for 50 min perform the best luminescence property with intensity (at 545 nm) as 11 times high as that of the precursor glasses. The XRD result (Fig. 4) shows the precipitation of $La_4Ti_9O_{24}$ crystals in the LTZ glass matrix.

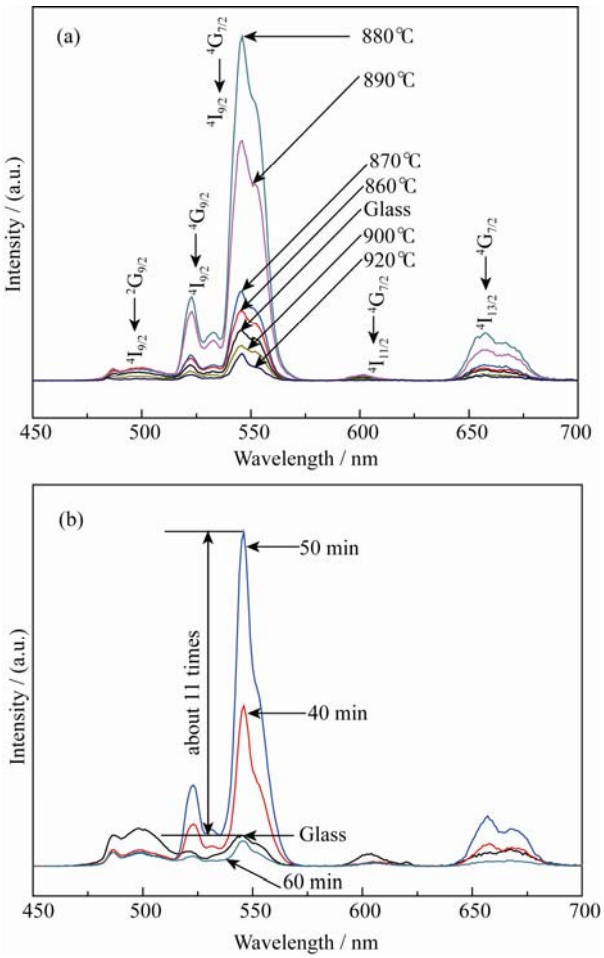

Fig. 2 Upconversion emission spectra of Nd^{3+}/Yb^{3+}: LTZ samples heat-treated (a) at different temperatures and (b) at 880℃ for different holding times under 980 nm excitation with 313.9 mW power

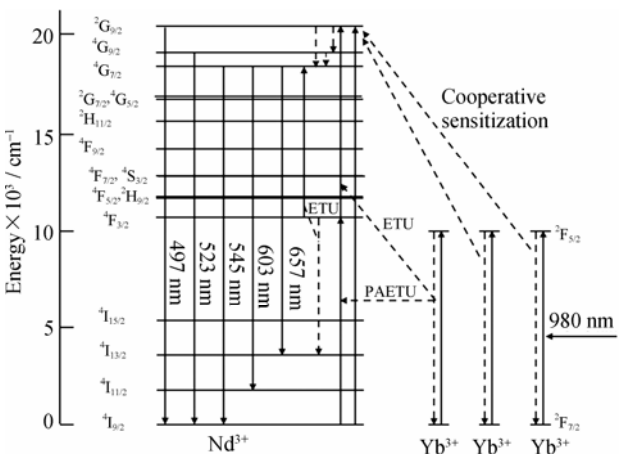

Fig. 3 Schematic illustration of the upconversion luminescence mechanism of Nd^{3+}/Yb^{3+}: LTZ

In order to discuss the enhancement of upconversion luminescence of glass-ceramic samples compared with the precursor glasses, Nd^{3+}/Yb^{3+}: LTZ samples were heated at 880℃ for 40, 50 and 60 min. TEM image and the selected-area electron diffraction pattern in Fig. 5(a) show that the crystals in the glass-ceramics fabricated at 880℃ for 40 min grown incompletely and are rare in the glass matrix. According to Fig. 5(b), columnar crystals with ~100 nm diameter and various lengths are obtained after heat treatment at 880℃ for 50 min. The sharp spots of the selected-area electron diffraction pattern indicate the single-crystalline nature of the crystals with a good single crystallinity. The crystals in Fig. 5(c) are obtained after heat treatment at 880℃ for 60 min. In Fig. 5(a,c), two kinds of crystals are not the optimal environment for the rare earth ions to gain high upconversion luminescence efficiency. Therefore, heat treatment at 880℃ for 50 min gives the best result that the columnar crystals can obviously improve upconversion luminescence properties, which is in good agreement with the results of upconversion emission spectra (Fig. 2).

The crystals in the samples heated at 880℃ for 50 min show good single crystallinity. So the local environment of active rare earth ions has dense lattice fields and strong partitions caused by the crystals. Then the mutual nonradiative relaxation rate among Nd^{3+} ions can be intensively decreased, which results in increased upconversion emission

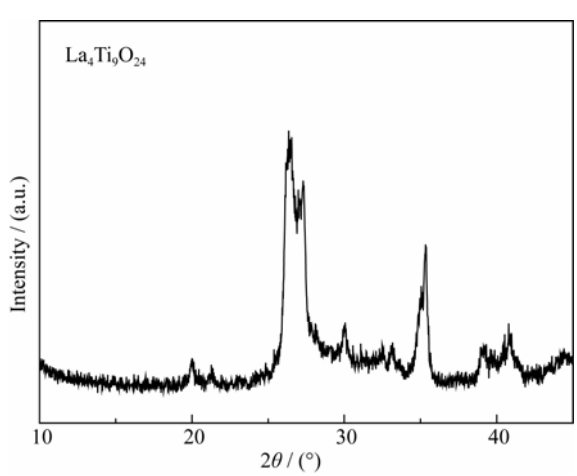

Fig. 4 XRD pattern of the Nd^{3+}/Yb^{3+}: LTZ heat-treated at 880℃ for 50 min

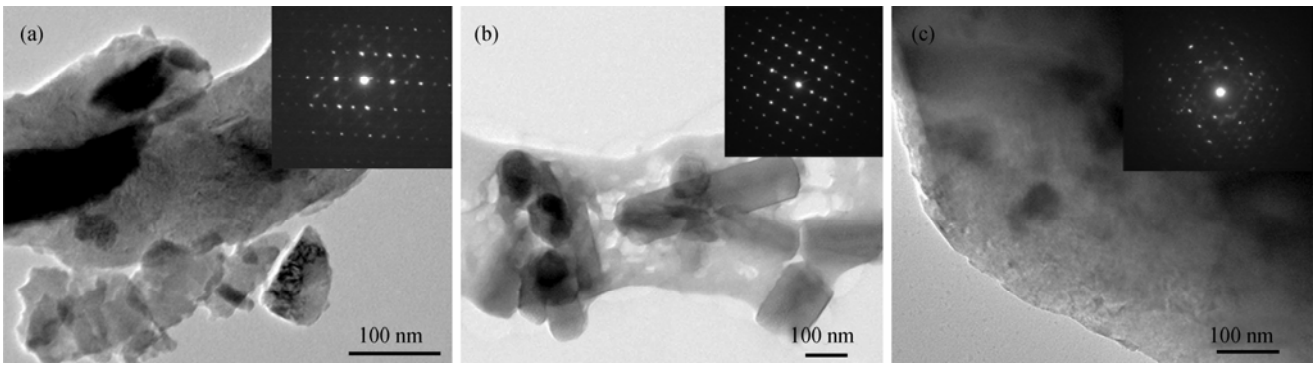

Fig. 5　TEM images and SAED patterns of Nd^{3+}/Yb^{3+}: LTZ samples heat-treated at 880℃ for (a) 40 min; (b) 50 min; (c) 60 min

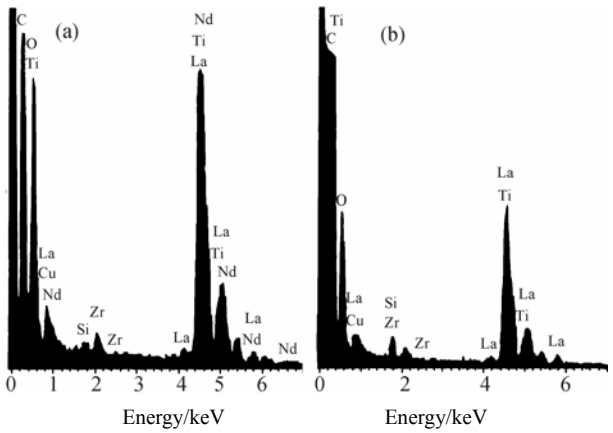

Fig. 6　EDS pattern of (a) crystal and (b) glass matrix in the sample heat-treated at 880℃ for 50 min

intensity. The distributions of Nd^{3+} ions in the glass-ceramic samples have been detected by EDS. The patterns (Fig. 6) show the enrichment of active Nd^{3+} ions in crystals. It has been reported that rare earth ions can concentrate mainly in the crystals of the glass-ceramics[25-26]. More Nd^{3+} ions can locate in the crystals which can efficiently reduce the energy losses caused by the mutual interactions among rare earth ions. In this way, the upconversion luminescence can be improved obviously after heat treatment. Hence, crystals with a good single crystallinity are helpful for active rare earth ions to achieve high upconversion luminescence efficiency.

3　Conclusions

Nd^{3+}/Yb^{3+}: LTZ bulk glasses with high thermal stability were fabricated by ALM. The well crystallized glasses were obtained by heat treatment to increase the emission intensity. From the results of the upconversion luminescence spectra, heat treatment is optimized. The glass-ceramic samples heat-treated at 880℃ for 50 min perform the best emission property with intensity (at 545 nm) as 11 times high as times that of the precursor glasses. Glass- ceramics comprising dense columnar crystals with a good single crystallinity and a diameter of ~100 nm are obtained. The EDS patterns indicate that Nd^{3+} ions are enriched in the crystals which are embedded in the glass matrix. The crystals and the rare earth ion distribution can be used to interpret that the glass-ceramics present much better upconversion properties than the precursor glasses. Nd^{3+}/Yb^{3+}: LTZ samples have potential applications in solid-state laser and LED.

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Nd^{3+}/Yb^{3+}共掺 La_2O_3-TiO_2-ZrO_2 微晶玻璃的制备及上转换发光研究

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摘 要: 利用气悬浮方法制备了 Nd^{3+}/Yb^{3+}共掺 La_2O_3-TiO_2-ZrO_2 前驱体玻璃, 通过热处理获得了微晶玻璃。通过 DTA 对前驱体玻璃的热稳定性进行了研究。利用光致发光谱, TEM 和 EDS 对微晶玻璃进行了表征分析, 并研究了热处理对上转换发光的影响。结果表明: 玻璃转变温度和析晶起始温度分别为 799℃和 880℃. 在 980 nm 激光激发下, 样品发射出中心位于 497, 523, 545, 603 和 657 nm 处的五条发光带。热处理后样品上转换发光强度提高, 经过 880℃保温 50 min 热处理的微晶玻璃显示了最强的上转换发光, 在 545 nm 处的发光强度是前驱体玻璃的 11 倍, 这是由于在微晶玻璃基质中存在致密柱状晶和 Nd^{3+}离子在晶体中富集造成的。

关 键 词: 微晶玻璃; 气悬浮方法; 热处理; 上转换发光

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