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Infrared to ultraviolet upconversion luminescence in Nd^{3+} doped nano-glass-ceramic

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Abstract: Nd^{3+} doped transparent oxyfluoride glass ceramic containing β-YF_3 nanocrystals was prepared and the upconversion luminescence behaviors of Nd^{3+} in the precursor glass and glass ceramic were investigated. Under 796 nm laser excitation, ultraviolet upconversion emissions of Nd^{3+} ions at 354 nm ($^4D_{3/2}\rightarrow{}^4I_{9/2}$) and 382 nm ($^4D_{3/2}\rightarrow{}^4I_{11/2}$) were observed at room temperature. Power dependence analysis demonstrated that three-photon upconversion processes populated the $^4D_{3/2}$ excited state. In comparison with those of the precursor glass, the ultraviolet emissions were enhanced by a factor of 500 in the glass ceramic, which was attributed to the change in the ligand field of Nd^{3+} ions and the decrease in phonon energy because of the partition of Nd^{3+} ions into the β-YF_3 nanocrystals after crystallization.

Keywords: upconversion; ultraviolet; nanocrystal; glass ceramic; rare earths

Short wavelength solid-state lasers in the ultraviolet (UV) to green spectral range have attracted much attention in recent years because of a wide range of applications including optical data storage, color display, infrared sensor, and so on. In upconversion (UC) processes, an emission photon with a wavelength shorter than that of an excitation photon is obtained as a result of multiphoton processes involving two or more excitation photons. The phenomena and mechanisms of upconversion luminescence have been studied, with rare earth ions, in various hosts during the past two decades[1–4]. However, efficient infrared to UV UC emissions at room temperature have been rarely reported[5,6].

Nd^{3+} has been recognized as one of the most efficient rare earth ions for solid-state lasers in various hosts because of its intense emission at about 1.06 um. Recent spectroscopic results demonstrate that the Nd^{3+} ions are also good candidates for upconversion luminescence and lasers[7,8]. These upconversion emissions act as losses for the 1.06 μm IR emissions, however, if they are efficient enough, they can be used as high frequency coherent light sources pumped by commercially available and inexpensive laser diodes. For this purpose, it is necessary to decrease multiphoton relaxation rates to increase the lifetimes of the Nd^{3+} excited levels lying in the visible (VIS) and UV range. Investigating in new stable hosts with low energy phonon is thus a promising way to develop efficient infrared (IR) pumped UV and VIS upconversion emission devices.

Oxyfluoride glass ceramics are currently being intensively investigated as suitable hosts for upconversion luminescence[9–15]. These nanocomposites may combine the favorable properties from both fluoride crystals and oxide glass matrices, that is, low phonon energy and high mechanical and chemical stabilities. The nano-structured transparent glass ceramic is achieved by controlled crystallization of the precursor glass with appropriate chemical compositions, and the key factor for efficient luminescence is the partition of the optically active ions into precipitated fluoride nanocrystals. Ultraviolet and visible upconversion emissions in Nd^{3+} doped glass ceramic containing $Pb_xCd_{1-x}F_2$ nanocrystals have been reported in recent times[16]. However, lead and cadmium in this glass ceramic are toxic substances and cannot be used extensively on account of environment issues. In the present article, the authors report intense infrared to ultraviolet and visible upconversion emissions from a glass ceramic containing β-YF_3 nanocrystals doped with Nd^{3+}.

1 Experimental

The $44SiO_2$-$28Al_2O_3$-17LiF-$11YF_3$-$0.1NdF_3$ (mol.%) precursor glass was prepared by melting a mixture of reagent grade chemical compositions in a platinum crucible at 1400 °C for 30 min in an ambient atmosphere. The melt was poured

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into a 300 °C preheated copper mold and then cooled down to room temperature naturally. The obtained precursor glass was then cut into 3 mm^2 coupons and heat-treated for 2 h at a temperature of 620 °C, determined by differential thermal analysis (DTA) measurements, to form glass ceramic through crystallization. To identify the crystallization phase and determine the mean size of the crystallites, X-ray diffraction (XRD) analysis was carried out with a powder diffractometer (DMAX2500 RIGAKU) using Cu Kα radiation (λ=0.154 nm). The microstructures of the samples were studied using a transmission electron microscope (TEM, JEM-2010) equipped with an energy dispersive X-ray (EDX) spectroscopy system. The absorption spectra in the range of 350 to 1100 nm were recorded on a spectrophotometer (Lambda900, Perkin-Elmer) with a resolution of 0.5 nm. Room temperature upconversion signals were recorded with the InP/InGaAS photomultiplier tubes (PMT, R928) under 796 nm Ti sapphire laser excitation.

2 Results and discussion

The crystallization and structural evolution of Nd^{3+} doped oxyfluoride glass ceramic containing β-YF_3 nanocrystals have been reported and discussed previously[17]. X-ray diffraction (XRD) and transmission electron microscopy (TEM) analyses evidenced the amorphous structure of the precursor glass, and the spherical YF_3 nanocrystals, with a mean size of 25 nm, homogeneously embedded among the glassy matrix, after crystallization.

Fig.1 shows the absorption spectra calculated for the PG and gas chromatography (GC) samples at room temperature. The crystal-like absorption bands appear as a consequence of the crystallization because of the partition of Nd^{3+} into the precipitated YF_3 nanocrystals in the glass matrix. The absorption cross-section at 796 nm is increased up to 400% after crystallization, which favors the pumping of glass ceramic by a common high-power laser diode.

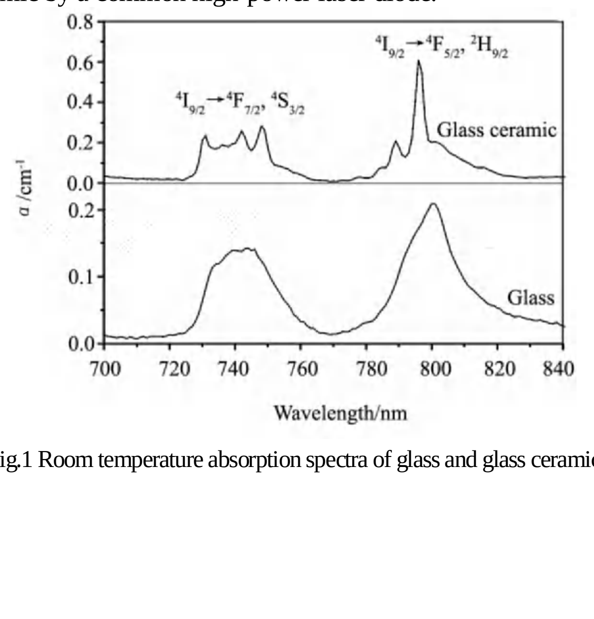

Fig.1 Room temperature absorption spectra of glass and glass ceramic

The upconversion emission spectra for the precursor glass and glass ceramic samples are portrayed in Figs.2 and 3, when the laser wavelength was tuned to 796 nm, in resonance with the transitions $^4I_{9/2}\rightarrow{}^4F_{5/2}$, $^2H_{9/2}$. Two peaks at 354 and 382 nm are observed and attributed to the Nd^{3+} $^4D_{3/2}\rightarrow{}^4I_{9/2}$ and $^4D_{3/2}\rightarrow{}^4I_{11/2}$ transitions, respectively. In comparison with the upconversion of the precursor glass, the ultraviolet emissions are greatly enhanced by about 500-fold in the glass ceramic. The nearly cubic dependence of both lines on the pump power as presented in the inset of Fig.2 has been obtained and indicates that three laser photons participate in the UV upconversion processes. Other visible upconversion emissions have also been detected at 414, 450, 523, 587, and 655 nm and the corresponding transitions of Nd^{3+} are indicated in Fig.3. It is interesting to mention that the intensity ratios of I_{587}/I_{523} and I_{655}/I_{523} obviously decrease in the glass ceramic when compared with those in the precursor glass. The visible fluorescence is very strong and can

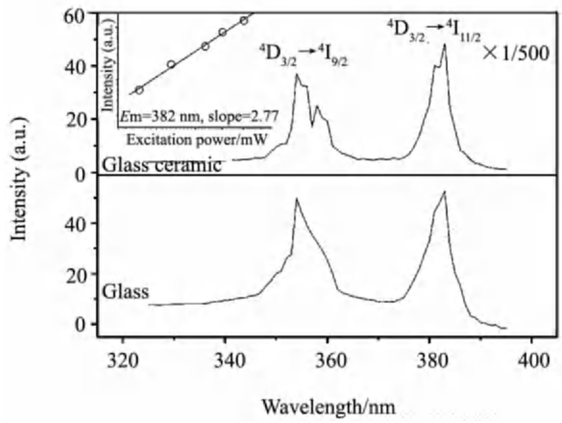

Fig.2 Room temperature upconversion emission spectra of the precursor glass and glass ceramic in the wavelength range of 320–400 nm, the inset shows the logarithmic plot of upconversion intensity versus excitation power

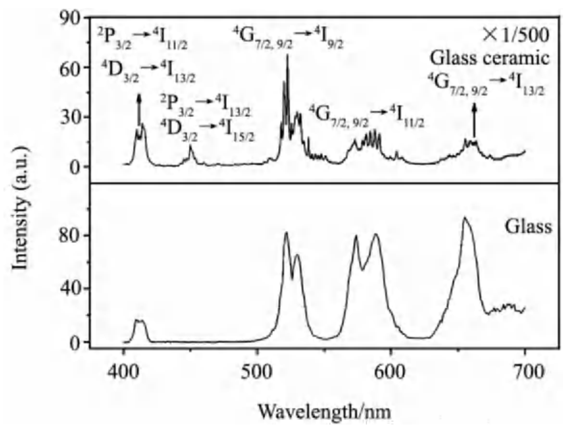

Fig.3 Room temperature upconversion emission spectra of the precursor glass and glass ceramic in the wavelength range of 400–700 nm

be seen with the naked eyes, which indicates that UV upconversion emissions are intense, as they are comparable with the visible ones.

The possible upconversion mechanisms are proposed in Fig.4. The excited $^4G_{7/2,\,9/2}$ states can be populated by two possible mechanisms, excited state absorption (ESA) and energy transfer upconversion (ETU). In the first process, one Nd^{3+} ion, initially in the ground state, is excited to the $^4F_{5/2}$, $^2H_{9/2}$ states by ground state absorption (GSA) from where the $^4F_{3/2}$ state is populated by fast nonradiative relaxation. This is followed by absorption of a second IR photon from the $^4F_{3/2}$ excited state to the $^2P_{1/2}$ state, from which it can decay nonradiatively to the $^4G_{7/2,\,9/2}$ states. In the case of ETU, the emitting level can be populated by means of an interaction between two ions. From the energy levels of Nd^{3+}, the most probable resonant energy transfer process to populate the $^4G_{7/2,\,9/2}$ states are $^4F_{3/2}+^4F_{3/2}\rightarrow^4I_{13/2}+^4G_{7/2,9/2}$ (ETU1) and $^4F_{3/2}+^4F_{3/2}\rightarrow^4I_{11/2}+^2G_{9/2}$ (ETU2). With the population of $^4G_{7/2,9/2}$ states, the $^4D_{3/2}$ state can be populated by another resonant energy transfer process (ETU3): $^4F_{3/2}+^4G_{7/2,\,9/2}\rightarrow^4I_{11/2}+^4G_{3/2}$, from which the two intense UV emissions can be obtained. Similar upconversion mechanisms are also proposed for the Nd^{3+} doped glass ceramic containing $Pb_xCd_{1-x}F_2$ nanocrystals[16] and the Nd^{3+}:LaF_3 layer on CaF_2 substrate[18].

To analyze the change of optical properties in the precursor glass and the glass ceramic, the authors undertook the Judd-Ofelt analysis[19,20]. Generally, the intensity parameter Ω_2 is sensitive to the environmental configuration symmetry of rare earth ions, and it decreases with the host changing from oxides to fluorides[21–24]. On the other hand, Ω_6 increases usually with the covalence decreasing between rare earth ions and the surrounding elements[25]. From the precursor glass to the glass ceramic, the decrease of Ω_2 and the increase of Ω_6, presented in Table 1, suggest that some Nd^{3+} ions had been incorporated into YF_3 nanocrystals after crystallization, which are well known in other RE doped oxyfluoride glass ceramics[13–15]. With the help of the set of three Judd-Ofelt intensity parameters Ω_i, the radiative transition probability between state J and J' can be written as[19–20]

$$A_{JJ'}=\frac{64\pi^4e^2}{3h(2J+1)\lambda^3}\frac{n(n^2+2)^2}{9}\sum_{i=2,4,6}\Omega_iU^i_{JJ'}$$

where $U^i_{JJ'}$ are the reduced matrix elements of the rank i unit tensor between J and J'. The reduced matrix elements of Nd^{3+} for J=$^4G_{7/2,\,9/2}$ and J'=$^4I_{13/2}$, $^4I_{11/2}$, and $^4I_{9/2}$ are listed in Table 1. It can be seen that the $^4G_{7/2,\,9/2}\rightarrow^4I_{13/2}$ and $^4G_{7/2,\,9/2}\rightarrow^4I_{11/2}$ transitions of the Nd^{3+} ions largely depend on Ω_2, as they have large reduced matrix elements of U^2. In this case, after crystallization, the decrease of the intensity ratios of I_{587}/I_{523} and I_{655}/I_{523} also demonstrate the decrease of the Judd-Ofelt parameter Ω_2.

On the basis of the above-mentioned results, it is reasonable to consider that the reason for the great enhancement of the Nd^{3+} upconversion emission intensities, after crystallization, is because of the changes in the ligand field, around the rare earth ions, upon heat treatment. According to the Miyakawa-Dexter theory, a nonradiative decay rate because of a multiphonon relaxation process is governed by the phonon energy around the rare earth ions[26]. In the precursor glass, Nd^{3+} ions are readily coupled with the nonbridging oxygen on the strong O-Si and/or O-Al bonds[10]. Such coupling causes an increase in the nonradiative decay rate because of multiphonon relaxation and substantially reduces the lifetimes of excited levels in upconversion processes. Therefore, similar to most oxide glasses, oxyfluoride glass is also not effective for upconversion. On the other hand, as the Nd^{3+} ions are incorporated into the YF_3 nanocrystals after crystallization, the rare earth ions reside in the low phonon energy environments with highly efficient upconversion.

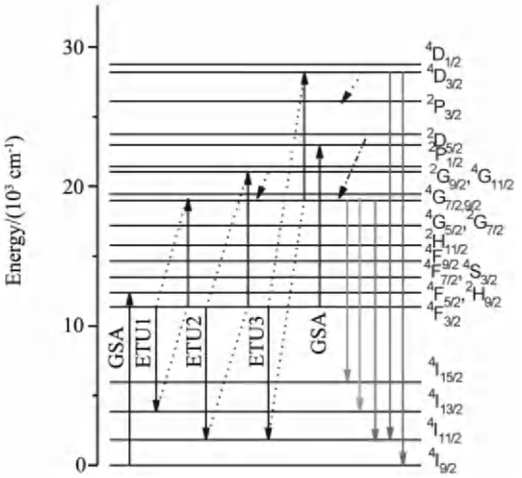

Fig.4 Energy level diagram of Nd^{3+} ions and possible upconversion mechanisms under excitation at 796 nm involving two or three photons by means of energy transfer upconversion (ETU) or excited state absorption (ESA)

Table 1 Reduced matrix elements of specified transitions of Nd^{3+} and calculated Judd-Ofelt parameters of Nd^{3+} in the precursor glass and glass ceramic

Transitions of Nd^{3+}	U^2	U^4	U^6
$^4G_{7/2,9/2}\rightarrow^4I_{13/2}$	0.9950	0.6186	0.0699
$^4G_{7/2,9/2}\rightarrow^4I_{11/2}$	0.6761	0.4536	0.0672
$^4G_{7/2,9/2}\rightarrow^4I_{9/2}$	0.0596	0.2180	0.0959
	Glass	Glass ceramic	
Judd-Ofelt parameters/ 10^{-16} m^{-2}	Ω_2=3.58	Ω_2=2.61	
	Ω_4=4.31	Ω_4=3.95	
	Ω_6=5.69	Ω_6=6.64	

3 Conclusion

The Nd^{3+} doped transparent SiO_2-Al_2O_3-LiF-YF_3 glass ceramic embedding β-YF_3 nanocrystals were developed. Intense infrared to ultraviolet upconversion emissions of Nd^{3+} $^4D_{3/2}\rightarrow{}^4I_{9/2}$ (354 nm) and $^4D_{3/2}\rightarrow{}^4I_{11/2}$ (382 nm) were obtained. The results of Tm^{3+} as a probe of the structure indicated that the Judd-Ofelt parameter Ω_2 became small after crystallization because of the incorporation of some Nd^{3+} ions into the YF_3 nanocrystals with low phonon energy, which could also be confirmed by the change of visible upconversion emission intensity ratios. The high efficiency of the upconversion processes in this glass ceramic made it a good candidate for ultraviolet and green solid-state laser or fiber laser.

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