# Upconversion fluorescence in $Nd^{3+}/Yb^{3+}$ co-doped titanate glasses prepared by containerless method

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$Nd^{3+}/Yb^{3+}$ co-doped $TiO_2$–$La_2O_3$ glasses modified by $ZrO_2$ were fabricated by containerless method. Under the excitation of 980 nm lasers, three intense emissions centered at 521, 545, and 655 nm were observed, which are assigned to the $Nd^{3+}$: $^4G_{9/2} \rightarrow {}^4I_{9/2}$, $^4G_{7/2} \rightarrow {}^4I_{9/2}$, and $^4G_{7/2} \rightarrow {}^4I_{13/2}$ transitions, respectively. Besides, two very weak emission bands at 496 and 603 nm were also found due to the $Nd^{3+}$ transition of $^2G_{9/2} \rightarrow {}^4I_{9/2}$ and $^4G_{5/2}$ (or $^2G_{7/2}$) $\rightarrow {}^4I_{9/2}$, respectively. Pumping powder dependence of emission intensity suggests a two-photon adsorption process responsible for the upconversion luminescence. A combined phonon-assisted and cooperative sensitization mechanism is presented to interpret the energy transfer from $Yb^{3+}$ to $Nd^{3+}$ ions. In addition, the highest intensity of luminescence was found for the glass with 1.2 mol% $Nd^{3+}$, and the upconversion efficiency can be enhanced by increasing of $ZrO_2$ content.

## I. INTRODUCTION

Upconversion of light from infrared to visible wavelength in rare earth (RE) ions-doped glasses attracted much attention because of their potential use in infrared converters and upconversion short wavelength solid-state lasers.[1,2] The trivalent neodymium ion ($Nd^{3+}$) is one of the most important active ions in the RE family due to its favorable energy level structure. Spectroscopic results demonstrate that the $Nd^{3+}$ ions are good candidates for upconversion luminescence.[3,4]

Usually, host materials with low phonon energy are in favor of strong upconversion luminescence because it can reduce the nonradiative loss caused by the multiphonon relaxation. Recently, sincere attention has been focused on the development of $Nd^{3+}$-doped low phonon glasses (like antimonate, germanate, tellurite, and fluoride glasses), which display efficient upconversion of the infrared into visible light.[5–10] Titanium dioxide can be a good candidate for upconversion generation due to its low cutoff phonons of energy (~600–700 $cm^{-1}$).[11,12] However, to the best of our knowledge, there is no report dealing with the upconversion fluorescence characteristic of $Nd^{3+}$-doped $TiO_2$-based glasses, mainly due to the difficulty of titanate glass formation by traditional melt-quenching method.

In this article, we report the fabrication of $Nd^{3+}$-doped high titanium dioxide (~80 mol%) containing $La_2O_3$–$ZrO_2$–$TiO_2$ (LZT) glasses by containerless processing in an aerodynamic levitation furnace (ALF). The upconversion property sensitized by $Yb^{3+}$ ion is investigated with special emphasis. The purpose of this investigation is to develop a low phonon titanate glass, and understanding of the upconversion behavior of $Nd^{3+}$ in this glassy host predicting its potential laser properties.

## II. EXPERIMENTAL

The composition (mol%) of the base LZT oxide glass is $20La_2O_3$–$xZrO_2$–$(80 - x)TiO_2$, where $x$ varied as 1, 2, 3, and 4. Neodymium and ytterbium ions in the form of $Nd_2O_3$ and $Yb_2O_3$ were added in. The concentrations of $Yb^{3+}$ ion was fixed of 0.2 mol% while $Nd^{3+}$ concentration varied as 0.6, 1.2, 1.8, and 2.4 mol%, respectively. Raw materials were mixed in ethanol in stoichiometric composition. After sintering at 1073 K for 10 h, the mixed powder was compressed into rods each with a 2 mm diameter and a 3 mm length. Rod samples with a mass of about 150 mg were levitated in an ALF. A pyrometer was utilized to measure the temperature of the sample. A high-resolution charge-coupled device video camera equipped with a telephoto objective lens was used to obtain a magnified view of the sample. Laser power was used to carefully bring the sample to the desired temperature prior to quenching.

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After quenching at a cooling rate of about 300 K/s, 3-mm-diameter glass spheres could be obtained. Then, the sphere samples were polished to be 2-mm-thick wafers for the following measurements.

The structures of the samples were identified by x-ray diffraction (XRD) measurements. Upconversion luminescence spectra were recorded by a spectrofluorometer. A 980-nm continuous wave diode laser was used as the excitation source.

## III. RESULTS AND DISCUSSION

The $Nd^{3+}/Yb^{3+}$ co-doped LZT samples prepared by levitation method are spheres with diameter of about 3 mm. Figure 1 shows the typical XRD pattern of the LZT sample (for the sample of 1.2 mol% $Nd^{3+}$ and 1 mol% $ZrO_2$). The broad peak near 30° followed by other broad peaks of lesser intensities is characteristic for the amorphous structure. The inset in Fig. 1 is a photo of the polished sample. It is obvious that the $Nd^{3+}/Yb^{3+}$ co-doped LZT glass performs high transparency in the region of visible light.

The upconversion emission spectra of $Nd^{3+}/Yb^{3+}$ co-doped LZT glasses have been recorded using 980 nm excitations. Figure 2 shows the upconversion spectra of RE-doped LZT glasses for different $ZrO_2$ contents with a fixed $Nd^{3+}$ concentration of 1.2 mol%.

All the spectra show similar features except for an increase in intensities of the upconversion bands. Three intense upconverted bands are observed centered at 521, 545, and 655 nm, respectively. By going over many emission spectra of $Nd^{3+}$ ions, these upconversion bands are assigned to be $^4G_{9/2}\rightarrow{}^4I_{9/2}$, $^4G_{7/2}\rightarrow{}^4I_{9/2}$, and $^4G_{7/2}\rightarrow{}^4I_{13/2}$ transitions of $Nd^{3+}$ ions, respectively.[8,13,14]

It is apparent that the green emission at 545 nm has the highest peak intensity irrespective of the $ZrO_2$ concentrations. The red emission at 655 nm is much weaker than the green emission at 545 nm but is almost the same as the green emission at 521 nm. In addition to these three intense bands, two very weak emission bands also appear at 496 nm (green or blue) and 603 nm (orange) originated from the $Nd^{3+}$: $^2G_{9/2}\rightarrow{}^4I_{9/2}$ and $^4G_{5/2}$ (or $^2G_{7/2}$)$\rightarrow{}^4I_{9/2}$ transitions, respectively.[15,16]

From Fig. 2, one can also clearly see that the intensities of the intense upconversion emissions increase with the increasing of $ZrO_2$ concentration. This owes mainly to the lower phonon energy of $ZrO_2$ (cutoff phonon energy of $\sim$470 $cm^{-1}$)[17] than that of $TiO_2$. And thus the nonradiative loss by the multiphonon relaxation can be effectively reduced. However, too much $ZrO_2$ added in may reduce the glass-forming ability. As a result, glass samples with amorphous structure are difficult to be obtained even by containerless processing method. In our present experiments, the maximum of $ZrO_2$ concentration for glass sample is only 4 mol% or so. For the sample with $ZrO_2$ concentration of $\sim$5 mol%, it is translucent. When $ZrO_2$ concentration gets even larger, the as-prepared sample becomes opaque and thus no glass is obtained.

To get more insight into the upconversion mechanism, the dependence of the upconversion emission intensity $I$ was studied as a function of the incident pump power $P$. The emission intensity $I$ varies with the $m^{\text{th}}$ power of the pump power $P$ according to the relation $I \propto P^m$,[18] where $m$ is the number of pump photons absorbed per upconverted photon emitted. Figure 3 shows the typical lines of log $I$–log $P$ plot for the RE-doped LZT glasses. The plot of log $I$ versus log $P$ yields a straight line with slope $m$. The values of the slope $m$ for 496, 521,545, 603, and 655 nm upconverted emissions are 1.68, 1.75, 1.68, 2.10, and 1.64,

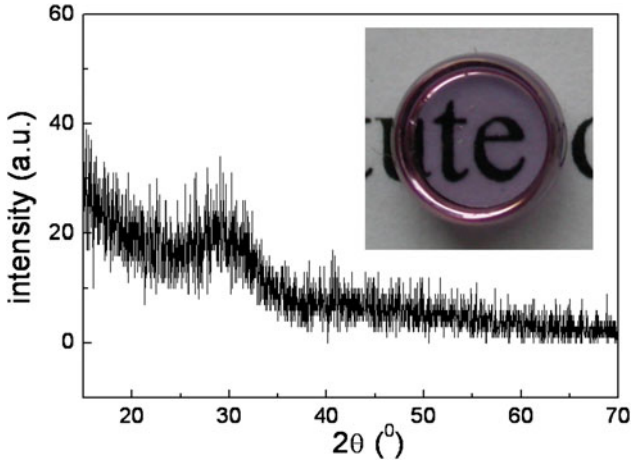



FIG. 1. Typical x-ray pattern for the $Nd^{3+}/Yb^{3+}$ co-doped $La_2O_3$–$ZrO_2$–$TiO_2$ (LZT) sample. Inset shows the photo of the LZT wafer with both sides well polished (1.2 mol% $Nd^{3+}$ and 1 mol% $ZrO_2$ sample).

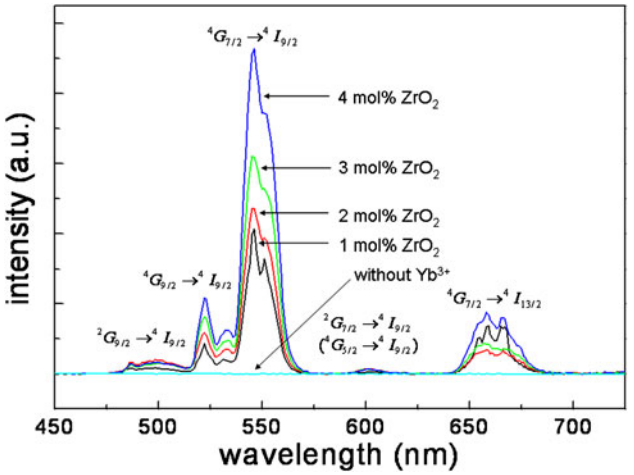



FIG. 2. Upconversion emission spectra of $Nd^{3+}/Yb^{3+}$ co-doped LZT glasses with varied $ZrO_2$ content upon excitation at 980 nm, where the concentrations of $Nd^{3+}$ is fixed of 1.2 mol%. The bottom curve shows the upconversion emission spectrum of $Nd^{3+}$-doped LZT glass without $Yb^{3+}$ ion.

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respectively. This indicates that two photons are involved for all the upconversion processes.

Disregarding the presence of avalanche upconversion, two possible mechanisms could be responsible for the observed luminescence: excited-state absorption (ESA) and energy transfer (ET). In general, $Nd^{3+}$ ions cannot absorb the 980 nm photons directly due to the nonexistence of a matching energy level. However, $Yb^{3+}$ ions adsorb this infrared radiation efficiently. So ET process plays an important role for the upconversion emissions in the $Nd^{3+}/Yb^{3+}$ co-doped LZT glasses. To demonstrate the role of $Yb^{3+}$ in the upconversion emissions, the upconversion spectrum of $Nd^{3+}$-doped LZT glass without $Yb^{3+}$ is also illustrated in Fig. 2 by the bottom curve. It is clear that no significant upconversion bands are observed without $Yb^{3+}$ ion as sensitization dopant. So, it can be concluded that ET process from $Yb^{3+}$ to $Nd^{3+}$ ions must be the predominant process responsible for the upconversion emissions in the $Nd^{3+}/Yb^{3+}$ co-doped LZT glasses. Based on the energy matching conditions and the quadratic dependence on excitation power, the following possible upconversion mechanisms are achieved and sketched in Fig. 4.

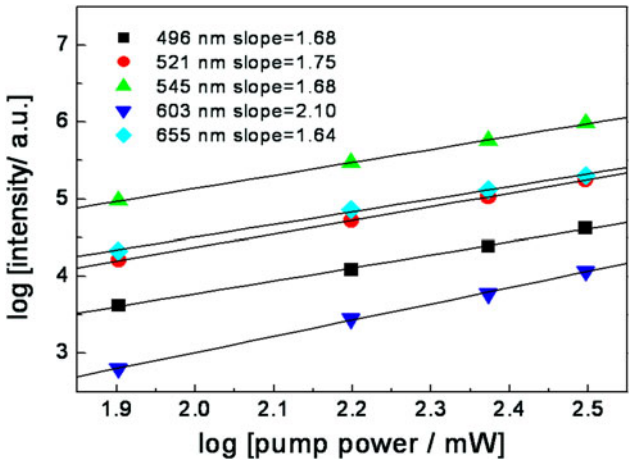



FIG. 3. Dependence of upconversion fluorescence intensities on excitation power at 980 nm excitation for $Nd^{3+}/Yb^{3+}$ co-doped LZT glass (1.2 mol% $Nd^{3+}$ and 1 mol% $ZrO_2$).

Initially, the first incident photon induces the $Yb^{3+}$: ${}^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition. Then, an ET process occurs from the ${}^2F_{5/2}$ level of $Yb^{3+}$ to the ${}^4F_{3/2}$ level of $Nd^{3+}$. Since there is an energy gap of approximately 1000 $cm^{-1}$ between the $Nd^{3+}$: ${}^4F_{3/2}$ and $Yb^{3+}$: ${}^2F_{5/2}$ metastable excited states, ET between these trivalent neodymium and ytterbium ions, therefore performs by a phonon-assisted process. Such phonon-assisted ET (PAET) or migration from a lower level to an upper level has also been found in other matrix.[19–21] Then, a second photon is adsorbed, involving the excitation of $Nd^{3+}$ in ${}^4F_{3/2}$ level to ${}^2G_{9/2}$ level by means of ESA: ${}^4F_{3/2}(Nd^{3+})$ + photon $\rightarrow {}^2G_{9/2}(Nd^{3+})$. The level of ${}^2G_{9/2}(Nd^{3+})$ can also be populated by ET from two excited $Yb^{3+}$ ions through the cooperative sensitization. Cooperative excitation of RE ions has been reported in many cases in the presence of $Yb^{3+}$ as a codopant.[1,22] During this process, a pair of excited $Yb^{3+}$ ions in the ${}^2F_{5/2}$ level transfer their energy to one nearby $Nd^{3+}$ ion, exciting $Nd^{3+}$ to ${}^2G_{9/2}$ state from the ground state. This process can be described as: ${}^2F_{5/2}(Yb^{3+})$ + ${}^2F_{5/2}(Yb^{3+})$ + ${}^4I_{9/2}(Nd^{3+}) \rightarrow {}^2F_{7/2}(Yb^{3+})$ + ${}^2F_{7/2}(Yb^{3+})$ + ${}^2G_{9/2}(Nd^{3+})$. The radiative decay from ${}^2G_{9/2}(Nd^{3+})$ level to the ground state then occurs producing the ${}^2G_{9/2} \rightarrow {}^4I_{9/2}$ emissions centered at 496 nm.

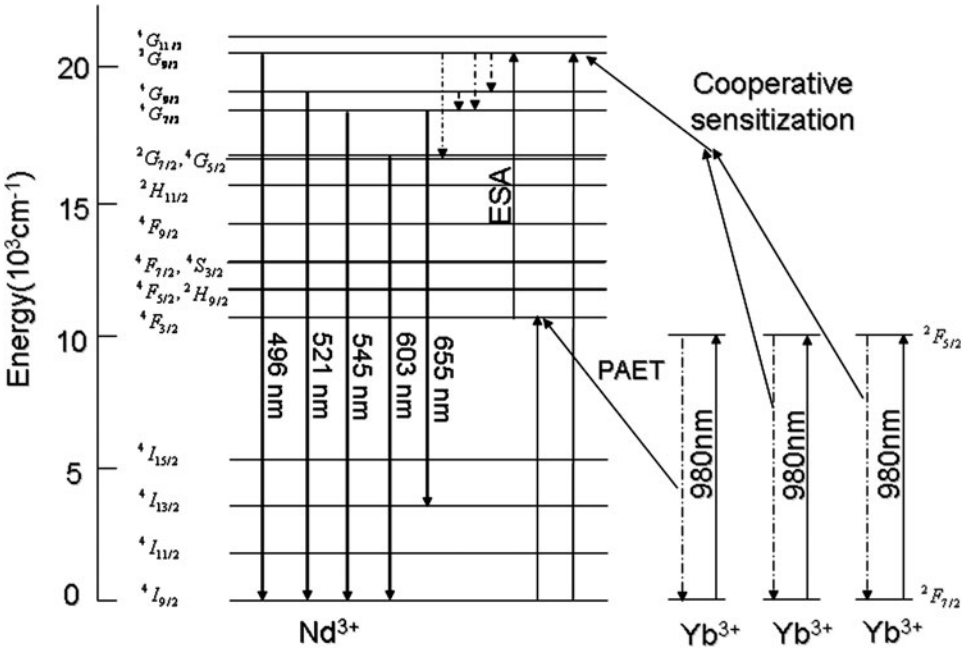



FIG. 4. Energy level diagram of $Nd^{3+}$ and $Yb^{3+}$ in LZT glasses and possible mechanisms for upconverted emissions upon 980 nm excitation.



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The populated $^2G_{9/2}$ level of $Nd^{3+}$ can relax rapidly and nonradiatively to the next lower $^4G_{9/2}$ and $^4G_{7/2}$ levels due to the small energy gap between them. In fact, the rate of multiphonon relaxation from $^2G_{9/2}$ level is so high that every electron is expected to immediately relax to $^4G_{9/2}$ or $^4G_{7/2}$ level. This is the reason why the emission at 496 nm is very weak. The above processes then produce the $^4G_{9/2} \rightarrow {}^4I_{9/2}$, $^4G_{7/2} \rightarrow {}^4I_{9/2}$, and $^4G_{7/2} \rightarrow {}^4I_{13/2}$ emissions centered at 521, 545, and 655 nm, respectively. $Nd^{3+}$ ions at the $^4G_{9/2}$ level can also decay to $^4G_{7/2}$ level by means of multiphonon relaxation process because of that the estimated energy gap between the $^4G_{9/2}$ level and the next lower $^4G_{7/2}$ level is only about 400 $cm^{-1}$. It decreases the 521 nm emission intensity. Since the ground state $^4I_{9/2}$ is more stable than the exited state $^4I_{13/2}$, more $Nd^{3+}$ ions would radiatively decay from $^4G_{7/2}$ level to $^4I_{9/2}$ level than those to $^4I_{13/2}$ level. As a result, the intensity of 545 nm emission is higher than that of 655 nm emission. As to the emission at 603 nm, its intensity is very weak mainly due to the possible fact that only a few $Nd^{3+}$ ions can decay from $^2G_{9/2}$ to $^4G_{5/2}$ (or $^2G_{7/2}$) level because nonradiative multiphonon relaxation is less likely to occur from this level due to the large energy gap.

The effect of the $Nd^{3+}$ ion on the upconversion emission intensity of LZT glass was also presented. Figure 5 shows the concentration dependence of upconversion emission intensity on $Nd^{3+}$ concentration. It can be found that the doped $Nd^{3+}$ ions enhance the emission intensity because ET process becomes efficient by concentration increasing of $Nd^{3+}$ ions due to the shortened distance between RE ions.[23] The highest intensities are found to be at the concentration of 1.2 mol% $Nd^{3+}$ ions. Beyond this concentration, intensities of the bands are seen to decrease due to the increase in nonradiative processes, indicating the occurrence of concentration quenching.

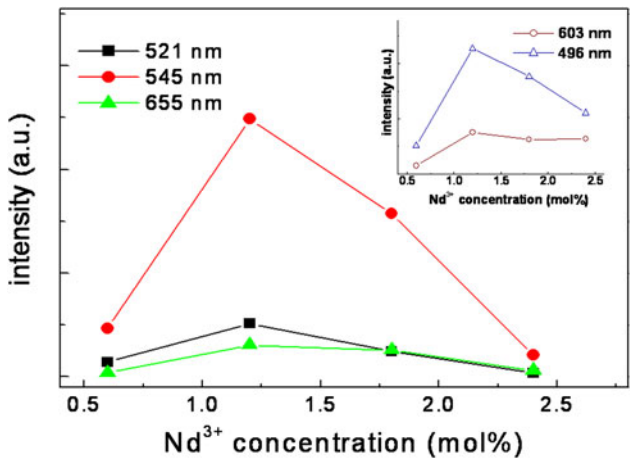



FIG. 5. Upconversion emission intensity as a function of $Nd^{3+}$ ion concentration in $Nd^{3+}/Yb^{3+}$ co-doped LZT glasses, where $ZrO_2$ content is fixed of 1 mol%.

## IV. CONCLUSIONS

$Nd^{3+}$-doped LZT glasses were successfully fabricated by containerless method with incorporated $Yb^{3+}$ ions as sensitizers for the first time. Upon 980 nm excitation, three intense emissions centered at 521, 545, and 655 nm and two weak emissions at 496 and 603 nm were observed in these titanate glasses. The highest intensity of luminescence was found for glasses with 1.2 mol% $Nd^{3+}$. The intensities of upconversion luminescence are enhanced by increasing concentration of $ZrO_2$.

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