Study on optical properties and luminescence of Er\(^{3+}/\)Yb\(^{3+}\) co-doped La\(_2\)O\(_3\)-Nb\(_2\)O\(_5\)-Ta\(_2\)O\(_5\) glasses prepared by aerodynamic levitation

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Abstract

Aerodynamic levitation method has been successfully used to prepare new Er\(^{3+}/\)Yb\(^{3+}\) co-doped La\(_2\)O\(_3\)-Nb\(_2\)O\(_5\)-Ta\(_2\)O\(_5\) glasses. 980 nm laser can be used to excite the glass for strong absorption of Yb\(^{3+}\) ions. The glass show high infrared transmittance of \(\sim 80\%\). Moreover, the OH\(^-\) concentration is very low with the value of \(\sim 7\) ppm, indicating excellent infrared transmission. The glass performs good optical properties with refractive index of near 2.3. The plane sweeping of EDS reveals that Er\(^{3+}\) and Yb\(^{3+}\) ions are distributed homogeneously in the glass. Strong down-conversion luminescence centered at 1530 nm has been achieved from the glass excited at 980 nm. The near-infrared emission is due to the transition of \(^4I_{13/2} \rightarrow ^4I_{15/2}\) in Er\(^{3+}\) ions. After fitting the decay curve, the lifetime of the near-infrared emission can be decided to be \(\sim 5.517\) ms. Such long lifetime is very helpful for rare earth ions to achieve strong emission.

1. Introduction

Efficient near-infrared photo-luminescence has attracted more and more attention for the promising applications in optical fiber communication [1], remote sensor [2], biological imaging [3], and laser guide stars [4], etc. So these laser materials have become study focus [5–7]. Moreover, low OH\(^-\) concentration is favorable for infrared properties. Therefore, materials with high transparency in infrared range and low OH\(^-\) concentration would be more important in infrared fields. Among rare earth ions, Er\(^{3+}\) ions are often used to generate near- and mid-infrared emissions [8, 9]. Moreover, Er\(^{3+}\) ions can be excited by 980 nm pump laser which matches the intrinsic absorption of Er\(^{3+}\) ions and is commercialized well. Yb\(^{3+}\) ions can also absorb 980 nm incident laser efficiently, which can obviously improve the use of incident energy. Near-infrared emissions from Er\(^{3+}\)/Yb\(^{3+}\) ions can be applied in deep tissue imaging [10], light detection and ranging [11], optical amplifiers [12]. Therefore, Er\(^{3+}\)/Yb\(^{3+}\) system can be employed to obtain promising near-infrared lasers at the excitation of 980 nm laser.

Matrix is very important for the applications and good luminescence properties. Compared with crystals and ceramics, glasses can be fabricated easily and formed in fine shapes. Er\(^{3+}/\)Yb\(^{3+}\) co-doped glasses could become promising near-infrared materials which are favorable to improve the applications. So it’s very important to find a glass which has high transparency in infrared range and low OH\(^-\) concentration. Novel heavy-metal Nb\(_2\)O\(_5\)-based glasses show high density, broad optical transparency from the visible to infrared regions, high thermal stability, and good mechanical properties. It’s expectable to achieve strong infrared emissions from Er\(^{3+}/\)Yb\(^{3+}\) co-doped Nb\(_2\)O\(_5\)-based glasses at the excitation of 980 nm laser. However, it’s difficult to prepare bulk heavy-metal oxide glasses by conventional techniques. Containerless processing methods can constrain...
heterogeneous nucleation, obtain deep undercooling, and achieve fast solidification [13, 14]. It’s very favorable to fabricate new glasses which can’t be obtained by conventional methods. As one of containerless processing methods, aerodynamic levitation has been used to prepare some types of novel glasses successfully [15, 16]. Moreover, new glass materials containing Nb₂O₅ prepared by aerodynamic levitation method are begun to be researched in the view of optical properties, luminescence, etc [17–19].

In this work, Er³⁺/Yb³⁺ co-doped La₂O₃-Nb₂O₅-Ta₂O₅ glasses have been prepared by aerodynamic levitation. Ta₂O₅ can be helpful to achieve high refractive index and low dispersion. The addition of Ta₂O₅ is favorable to reduce the dispersion of optical glasses. The transparent properties have been studied. The optical refractive index has been analyzed. The composition distribution has been characterized. The down-conversion spectrum has been researched at the excitation of 980 nm laser. The emission mechanism has been discussed.

2. Experimental

The composition of this glass in molar ratio is 0.65Nb₂O₅-0.25La₂O₃-0.01Er₂O₃-0.04Yb₂O₃-0.05Ta₂O₅. High-purity Nb₂O₅ (4 N), La₂O₃ (4 N), Ta₂O₅ (4 N), Er₂O₃ (3 N), and Yb₂O₃ (4 N) powders were used as raw materials. The powders were weighed and then mixed with each other in ethanol. After complete mixture, the powder materials were pressed into plate shape. The plate samples were put into furnace and heated at 1200 °C for 8 h. This could increase the density and strength of the samples. Small masses were cut from the plate samples. Here, aerodynamic levitation equipment was used. The small mass was thrown into the nozzle which is the key part of the equipment and suspended by O₂ flow. The CO₂ laser at 10.6 μm was employed to heat and melt the mass. After melt, the sample would be shaped into a sphere by itself. And then the laser would be closed and the melt could be quenched into glass. The detail of the glass preparation has also been introduced in the previous research [18]. Finally, bulk glass spheres with ~3 mm diameter were successfully prepared.

The transmittance spectrum was recorded by ultraviolet spectrophotometer (Varian Cary 5000). The glass spheres with ~3 mm diameter were polished by two sides. After that, 1.5 mm thick glass wafers can be obtained. And then the refractive index value of the glass was measured and fitted by spectroscopic ellipsometer (Uvisel 2) with the wavelength from 300 to 1000 nm. EDS about the composition distribution was carried out by SEM (SU8220). The down-conversion spectrum and the excited state lifetime of Er³⁺ ions were tested by a spectrofluorometer (Edinburgh Instruments FLSP920) with 980 nm laser excitation.

3. Results and discussion

The transmittance spectrum of Er³⁺/Yb³⁺ co-doped La₂O₃-Nb₂O₅-Ta₂O₅ glass with a thickness of 1.5 mm was recorded. Figure 1 presents the results. The labeled absorption peaks are ascribed to the electronic transitions from ground states to excited states in Er³⁺ and Yb³⁺ ions. The absorption around 980 nm is mainly due to Yb³⁺ ions which have simple energy level structure. Other absorption peaks are caused by Er³⁺ ions. From the results, it can be revealed that the transmittance in infrared range reaches as high as ~80%. The glass is transparent until as long as 3 μm, indicating low phonon energy. The photo of the glass is inserted in figure 1, confirming the good transparency. It can be seen in figure 1 that the absorption of OH⁻ groups occurs at ~2.8 μm which locates in range of the important infrared laser. So it’s a key factor to reduce the OH⁻ contents to obtain excellent infrared laser glasses. Based on the transmittance spectrum, the OH⁻ concentration can be calculated by the following equation [20–22]: [OH⁻] (ppm) = (1000/d)log(To/T). Here, d is the thickness of the glass in millimeters, T₀ is the transmittance at the baseline (~2.5 μm), and T is the transmittance at the maximum absorption of the OH⁻ band (~2.8 μm). It can be estimated to be ~7 ppm in Er³⁺/Yb³⁺ co-doped La₂O₃-Nb₂O₅-Ta₂O₅ glasses, which is much lower than germinate glass (50–420 ppm) [20] and fluorophosphates glass (26.4 ppm) [23]. Low OH⁻ concentration indicates excellent infrared properties, especially for mid-infrared range. So this heavy-metal oxide glass is a good infrared material.

Besides the transparency, refractive properties are another important aspect for optical glasses. The refractive curve of Er³⁺/Yb³⁺ co-doped La₂O₃-Nb₂O₅-Ta₂O₅ glass was measured and fitted. The results are presented in figure 2. With the incident wavelength, the refractive index value decreases gradually. Some characteristic values such as n₁, n₂, and n₃ which are the refractive index values at 587.56, 486.10, and 656.30 nm can be obtained according to the curve. The values of n₁, n₂, and n₃ can be decided to be 2.285, 2.327, and 2.266, respectively. Here, n₂ is often used to evaluate the refractive performance of optical materials. The value of n₄ is near 2.3, which is much higher than borate glasses [24], and silicate glasses [25]. It can be concluded that Er³⁺/Yb³⁺ co-doped La₂O₃-Nb₂O₅-Ta₂O₅ glass shows a very high refractive index. Optical wavelength dispersion is another key factor for glasses. Abbe number (ν₄) can evaluate the wavelength dispersion ability. Small dispersion means large Abbe number. According to the three characteristic values, Abbe number can be calculated by the following the equation ν₄ = (n₄-1)/(n₃-n₁). After calculation, ν₄ of Er³⁺/Yb³⁺ co-doped
La$_2$O$_3$-Nb$_2$O$_5$-Ta$_2$O$_5$ glass can be decided to be $\sim 21$. The value of $v_d$ is not very high. Therefore, Er$^{3+}$/Yb$^{3+}$ co-doped La$_2$O$_3$-Nb$_2$O$_5$-Ta$_2$O$_5$ glass performs high refractive index, while the wavelength dispersion is not very good.

To reveal the composition distribution of the glass, plane sweeping of EDS has been employed in SEM. The results are presented in figure 3. Figure 3(a) shows the SEM image of the glass. No crystals can be found in the image, indicating the amorphous state of the materials. Figure 3(b) presents the distribution of Er$^{3+}$ ions in the glass, while figure 3(c) indicating the distribution of Yb$^{3+}$ ions. It can be concluded that rare earth ions are homogeneously incorporated in the glass. The EDS spectrum (figure 3(d)) shows the signal of all the elements of the new glass. Therefore, glasses with homogeneous composition can be prepared by aerodynamic levitation.

The down-conversion luminescence spectrum of Er$^{3+}$/Yb$^{3+}$ co-doped La$_2$O$_3$-Nb$_2$O$_5$-Ta$_2$O$_5$ glass is presented in figure 4(a). A strong and broad emission band centered at 1530 nm is obtained. This emission is ascribed to the energy transition of $^4I_{13/2} \rightarrow ^4I_{15/2}$ in Er$^{3+}$ ions. So the near-infrared emission has been achieved.
by pumping the glass with cheap 980 nm laser. The excited state lifetime of Er$^{3+}$ ions in the glass was measured. The temporal evolution of $^4I_{13/2} \rightarrow ^4I_{15/2}$ (near-infrared emission) is presented in figure 4(b). Generally, all of the decay curves can be fitted by solving the rate equations [26]. Hence, a single exponential function has been employed to fit the decay part of the lifetime curve to get the value of the lifetime for the near-infrared emission. According to figure 4(b), the decay curve is well fitted. The lifetime of 1530 nm emission for Er$^{3+}$/Yb$^{3+}$ co-doped La$_2$O$_3$-Nb$_2$O$_5$-Ta$_2$O$_5$ glass can be calculated to be 5.517 ms. The lifetime is higher than $\sim 3.3$ ms of fluoroapatite materials [27] and 0.52 ms of phosphate glasses [28]. Therefore, long lifetime can be achieved for Er$^{3+}$ ions in La$_2$O$_3$-Nb$_2$O$_5$-Ta$_2$O$_5$ glass. It can be concluded that new heavy-metal oxide glasses can provide an excellent environment for rare earth ions to generate emissions. Strong near-infrared luminescence can be obtained from this type of glasses, which agrees well with the results of down-conversion luminescence spectrum.

According to the energy level structure of Er$^{3+}$ and Yb$^{3+}$ ions [29], the luminescence mechanism has been analyzed. The result is presented in figure 5. 980 nm laser has been employed to excite the glass. Yb$^{3+}$ ions in ground state absorb 980 nm photons efficiently and then are excited to $^2F_{5/2}$ states. Yb$^{3+}$ ions in excited state would transfer energy to neighboring Er$^{3+}$ ions in $^4I_{15/2}$ ground state. The Er$^{3+}$ ions can be excited from $^4I_{15/2}$ to
Er$^{3+}$ ions in $^4I_{11/2}$ intermediate states will transit to $^4I_{13/2}$ states by multi-phonon relaxation. There is no lower energy level near $^4I_{13/2}$ state except the ground state. Therefore, it’s not easy to form non-radiative relaxation by multi-phonon process for $^4I_{13/2}$ state. In this case, long lifetime can be achieved. The excited Er$^{3+}$ ions will radiate emission centered at 1530 nm by the transition of $^4I_{13/2} \rightarrow ^0F_{15/2}$. In this way, infrared emission is generated from Er$^{3+}$/Yb$^{3+}$ co-doped La$_2$O$_3$-Nb$_2$O$_5$-Ta$_2$O$_5$ glass at the excitation of 980 nm laser.

4. Conclusions

Er$^{3+}$/Yb$^{3+}$ co-doped La$_2$O$_3$-Nb$_2$O$_5$-Ta$_2$O$_5$ glasses have been successfully prepared by aerodynamic levitation method. Several absorption peaks appear in the transmittance spectrum. Yb$^{3+}$ ions make the major contribution to the absorption of $\sim$980 nm. Other absorption bands are due to Er$^{3+}$ ions. So, commercial and cheap 980 nm laser can be used to excite the glass samples effectively. Moreover, the transmittance of the glass in infrared range can reach as high as $\sim$80%. According to the results of the transmittance spectrum, OH$^-$ concentration can be calculated to be $\sim$7 ppm, which is much lower than some often-studied luminescence glasses. This heavy-metal oxide glass with low OH$^-$ content is very helpful to achieve high infrared transmission properties. The glass shows excellent optical properties, which may be favorable for the applications of this down-luminescence glass. The refractive index value can be evaluated to be near 2.3, while Abbe number is calculated to be $\sim$21. The glass has very high refractive index, indicating promising commercialization. SEM image indicates that no crystals appear in the sample. The EDS results of Er$^{3+}$ and Yb$^{3+}$ show that rare earth ions distribute homogeneously in the glass samples. Aerodynamic levitation method can be employed to prepare homogeneous glasses. Strong near-infrared emission has been obtained from Er$^{3+}$/Yb$^{3+}$ co-doped La$_2$O$_3$-Nb$_2$O$_5$-Ta$_2$O$_5$ glasses at the excitation of 980 nm laser. The emission is originated from the transition of $^4I_{13/2} \rightarrow ^4I_{15/2}$. A single exponential function has been employed to fit the decay curve. Finally, the lifetime of near-infrared emission can be calculated to be $\sim$5.517 ms. This glass has long lifetime which is very favorable to achieve strong down-conversion luminescence. Er$^{3+}$/Yb$^{3+}$ co-doped La$_2$O$_3$-Nb$_2$O$_5$-Ta$_2$O$_5$ glasses with high transparency, low OH$^-$ concentration and good optical properties show potential applications in infrared fields such as biomedical imaging, sensors, lasers, etc.

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