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Energy-transfer enhanced mid-infrared luminescence at 2.75µm of Er^{3+}/Pr^{3+} co-doped ZBLAY glass

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ABSTRACT: *The 2.7 µm mid-infrared luminescence of Er^{3+} has broad development prospects in many fields. The lifetime of the $^4I_{11/2}$ level of Er^{3+} is lower than that of the $^4I_{13/2}$ level, which is not conducive to 2.7 µm laser generation. The lifetime of the $^4I_{13/2}$ level of Er^{3+} can be reduced by Pr^{3+} ion co-doping. Herein, this work reports on the Er^{3+}/Pr^{3+} co-doped ZBLAY glass, which can emit a mid-infrared luminescence located at 2.75 µm. When Pr^{3+} ions are added, the energy of Er^{3+}: $^4I_{13/2}$ level can be transferred to Pr^{3+}: $^3F_3$ level, so the 2.75µm emission is enhanced and the 1.55µm emission is weakened. The addition of Er^{3+} and Pr^{3+} ions does not change the structure of ZBLAY glass.*

KEYWORDS -*Er^{3+} ions, Fluoride glass, Infrared luminescence, Pr^{3+} ions, Rare earth ions*

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I. INTRODUCTION

Mid-infrared emission in the wavelength ranges of two transmission windows of the atmosphere (1–3 µm, 3–5 µm) covers the distinctive spectra of a large number of significant atmospheric molecules.[1] It can be widely used in fields such as optical detection,[2] interdisciplinary research,[3] environmental pollution detection, and material processing.[4]The medical community has recently focused a lot of attention on the 3 µm emission, which has a particularly unique position among infrared band light sources due to its fortunate overlap with the water absorption band.[5] When used as a surgical scalpel, the 3µm laser is especially appealing. In comparison to 2µm lasers, its precision is also higher. A lot of research has been done on rare earth ion doped glass materials due to their superior photon emission capabilities.[6]Among the several rare earth ions, Er^{3+} is a natural contender for a 3µm laser due to the $^4I_{11/2}\rightarrow{}^4I_{13/2}$ transition. The near 2.75 µm emission in various kinds of Er^{3+}-doped crystals and glasses has been extensively studied.[7] The 2.7µm mid-infrared luminescence of Er^{3+} has broad development prospects in the fields of medicine,[8] sensing,[9] optical fiber communication,[10] and laser.[11]The $^4I_{11/2}$ level lifetime of Er^{3+} is lower than the $^4I_{13/2}$ level lifetime of Er^{3+}, which is not conducive to the generation of 2.7µm luminescence. Reducing the $^4I_{13/2}$ level lifetime of Er^{3+} can change this situation. Pr^{3+} has a rich energy level structure, and the $^3H_5$ level of Pr^{3+} is lower than the $^4I_{13/2}$ level of Er^{3+}.[12] This provides the possibility of reducing the energy level lifetime of Er^{3+}: $^4I_{13/2}$. Some studies on energy transfer in Er^{3+}/Pr^{3+} co-doped glasses or crystals have been reported.[13] These studies mostly use oxide glass with high phonon energy or fluoride single crystal as the matrix. Therefore, it is difficult to apply to efficient fiber lasers and large volume solid-state lasers. Fluoride glass has many advantages as a rare earth ion doped matrix. Fluoride glass is easy to process and has low phonon energy. Fluoride glass has a wide transmission region in which light in the range of 300-6600 nm can be transmitted with lower phonon energy, which can block the radiation-free leap channel of mid-infrared emission.[14] Fluoride glasses have high rare earth solubility and are suitable as mid-infrared laser gain media.[15] However, there are few reports on Er^{3+}/Pr^{3+} co-doped ZBLAY glass.

In this contribution, a Er^{3+}/Pr^{3+} co-doped system in ZBLAY fluoride glass is fabricated, and the 2.75 µm luminescence property under 980 nm laser excitation is reported. The crystal structures of the Er^{3+}/Pr^{3+} co-doped ZBLAY glasses are studied by XRD. The absorption and fluorescence spectra of each sample are measured. The luminescence mechanism and energy transfers between Er^{3+} and Pr^{3+} ions are studied in detail. The effect of co-doped ions on mid-infrared luminescence is discussed in terms of fluorescence spectroscopy and fluorescence lifetime.

II. EXPERIMENT AND CHARACTERIZATION

Er^{3+}/Pr^{3+} co-doped ZBLAY glasses were prepared by melt-quenching, and the ratio was $50ZrF_4$-$33BaF_2$-$2LaF_3$-$5AlF_3$-$10YF_3$-$4ErF_3$-(y/6) Pr_6O_{11}(mol%)(x=0.5,1,2,3,4). All drugs were evenly mixed and placed in an agate mortar, fully ground for 40 minutes. The milled drug was placed in a sealed crucible and melted at

820℃ for 30 minutes in a reducing atmosphere. The crucible was transferred to a muffle furnace preheated to 210 ℃ and annealed for 8 hours. Turn off the annealing furnace and wait for natural cooling to remove glass stress. The samples were polished for optical testing. Sandpapers of different thicknesses are used to polish glass sheets for various optical tests.

A D/max-2500/PC diffractometer was used to measure an X-ray diffraction (XRD) pattern with a 2θ range of 10° to 60° and Cu-Ka radiation. The UV-Vis (UV-4100) spectrometer was used to measure steady-state absorption spectra. The MIR luminescence spectroscopy of the materials was measured using a Princeton Instruments Acton Advanced SP2500A spectrometer equipped with a liquid nitrogen cool SbIn detector.

III. IRESULTS AND DISCUSSION

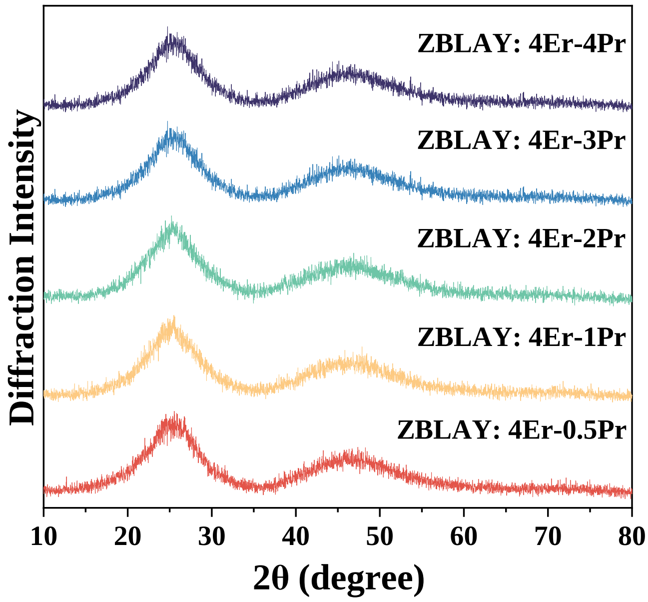

Fig.1 XRD patterns for Er^{3+}/ Pr^{3+} co-doped ZBLAY glass

X-ray diffraction (XRD) analysis results for Er^{3+}/Pr^{3+} co-doped ZBLAY fluoride glasses are compared in Fig.1. The XRD patterns in Fig.1show thatEr^{3+}/Pr^{3+} co-doped ZBLAY fluoride glasses have two amorphous peaks at 26° and 47°, respectively. The phases of all glass samples are typical glass phases. No sharp diffraction peak appeared, indicating that no crystal phase appeared in the glasses. Lakshminarayana et al. reached this conclusion based on the prepared Er^{3+}/Pr^{3+} co-doped borotellurite glass.[16] When the content of Er^{3+}/Pr^{3+} co-doped reaches 8 mol%, the glass sample does not crystallize. The ZBLAY glass matrix has a high solubility of rare earth ions, which reduces the ion spacing and improves the energy transfer efficiency.

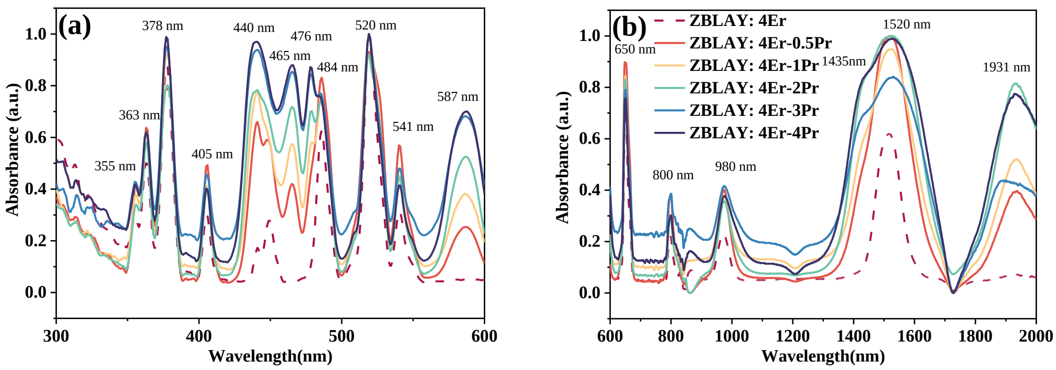

Fig.2 Absorption spectra of Er^{3+}/ Pr^{3+} co-doped ZBLAY glasses (a)absorption spectra in the range of 300-600 nm (b) absorption spectra in the range of 600-2000 nm

The normalized absorption spectra of the glass samples are shown in Fig.2. All intrinsic Er^{3+} and Pr^{3+} absorption transitions in the range of 300 to 2000 nm are observed in these absorption spectra. The ten absorption peaks with central wavelengths of 1520, 980, 800, 650, 541, 520, 484, 450, 405, and 378 nm correspond to the absorption bands of the transitions of $Er^{3+}$from the $^4I_{15/2}$ground level to excited energy levels$^4I_{13/2}$, $^4I_{11/2}$, $^4I_{9/2}$, $^4F_{9/2}$, $^4S_{3/2}$, $^2H_{11/2}$, $^4F_{7/2}$,$^4F_{5/2}$, $^4F_{3/2}$,and $^4G_{11/2}$.The eight absorption peaks with central wavelengths of 1931, 1600, 1435, 1000, 587, 476, 465, and 440 nm correspond to the absorption bands of the transitions of $Pr^{3+}$from the $^3H_4$ground level to excited energy levels$^3F_2$, $^3F_3$, $^3F_4$, $^1G_4$, $^1D_2$, $^3P_0$, $^3P_1$, and $^3P_2$.The shape and position of each absorption peak of the Er^{3+}/Pr^{3+} co-doped ZBLAY glass samples obtained in this experiment are very similar to those of other Er^{3+}/Pr^{3+} co-doped glasses.[17] The samples can be efficiently pumped by the 980 nm laser, as indicated by the absorption peak at 980 nm caused by the $^4I_{15/2}$ to $^4I_{11/2}$ transition. The addition of Pr^{3+} enhanced the absorption intensity of Er^{3+} at 980 nm.

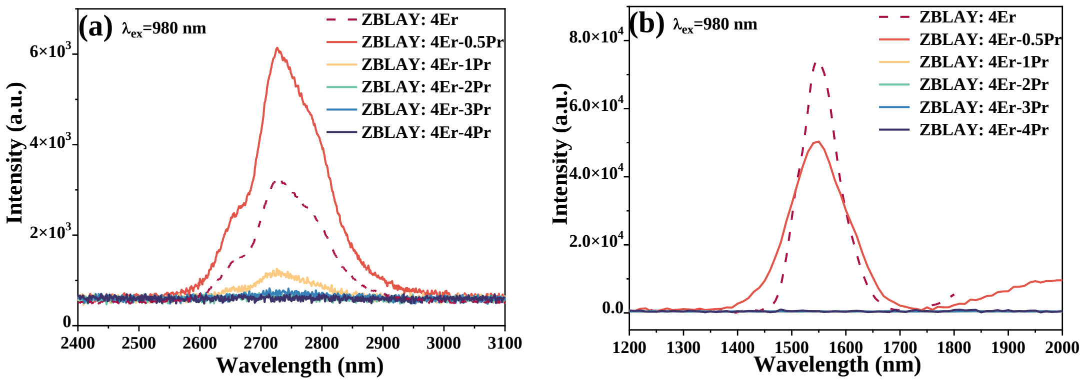

Fig.3(a)Mid-infrared emission spectra of Er^{3+}/Pr^{3+} co-doped ZBLAY glass, (b)Near-infrared emission spectra of Er^{3+}/Pr^{3+} co-doped ZBLAY glass

To investigate the infrared luminescence properties of Er^{3+}/Pr^{3+} co-doped ZBLAY glasses, the samples are pumped with a 980 nm laser. As seen in Fig.3(a), the $^4I_{11/2}\rightarrow^4I_{13/2}$ transitions of Er^{3+} can be clearly ascribed to the emission peaks at roughly 2.75 μm under the excitation of a 980 nm laser. The test results are consistent with the Er^{3+}/Pr^{3+} co-doped oxyfluorotellurite glass prepared by Bai et al.[18] Compared with ZBLAY: 4Er glass, only ZBLAY: 4Er-0.5Pr glass shows enhanced mid-infrared fluorescence intensity. With the increase of Pr^{3+}, the mid-infrared luminescence intensity decreases rapidly. More than 2 mol% Pr^{3+} completely quenched the 2.7 μm mid-infrared luminescence intensity. The results show that Pr^{3+} can enhance the mid-infrared luminescence intensity of Er^{3+}, but the doping concentration should not be too high. Therefore, in order to obtain better mid-infrared luminescence, the content of Pr^{3+} should not exceed 1 mol%.

As seen in Fig.3(b), the $^4I_{13/2}\rightarrow^4I_{15/2}$ transitions of Er^{3+} can be clearly ascribed to the emission peaks at roughly 1.55 μm under the excitation of a 980 nm laser. The test results are consistent with the Er^{3+}/Pr^{3+} co-doped fluorotellurite glass prepared by Zhan et al.[19]0.5 mol% Pr^{3+} doping leads to a decrease and broadening of the emission peak intensity, and a wide infrared fluorescence peak with a center position of about 2 μm appears after 1.8μm. With the increase in Pr^{3+} concentration, the peaks at 1.55 μm and 2 μm disappeared. Pr^{3+} has a quenching effect on the 1.55 μm luminescence. The low content of Pr^{3+} can absorb the 1.55 μm luminescence energy of Er^{3+} and enhance the 2 μm luminescence of Pr^{3+} itself. The high content of Pr^{3+} makes it susceptible to self-quenching.

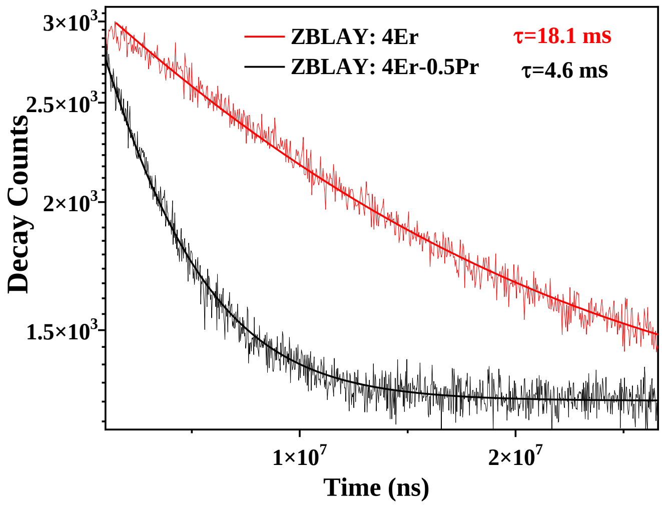

Fig.4 Life time of $^4I_{11/2}$ state from Er^{3+}

As shown in Fig.4,the fluorescence lifetime of the Er^{3+}: $^4I_{11/2}$ energy level in ZBLAY: 4Er glass is 18.1 ms, which decreases to 4.6 ms after 0.5 mol% Pr^{3+} co-doping. The test results are consistent with the Er^{3+}/Pr^{3+} co-doped glass prepared by Ding et al.[20] The Pr^{3+} ion provides a non-radiative decay channel for the electrons of the $^4I_{11/2}$ level of Er^{3+}, and the energy of the $^4I_{11/2}$ level is transferred to the excited state of Pr^{3+}. The energy transfer efficiency can be figured out by the equation(1):

$$\eta = 1 - \frac{\tau_D}{\tau_D^0} \quad (1)$$

The energy transfer efficiency is 74.58 %. Pr^{3+} can effectively reduce the lifetime of the $^4I_{11/2}$ energy level of Er^{3+}, which means that the conditions for realizing population inversion are easier and the laser pump threshold is reduced.

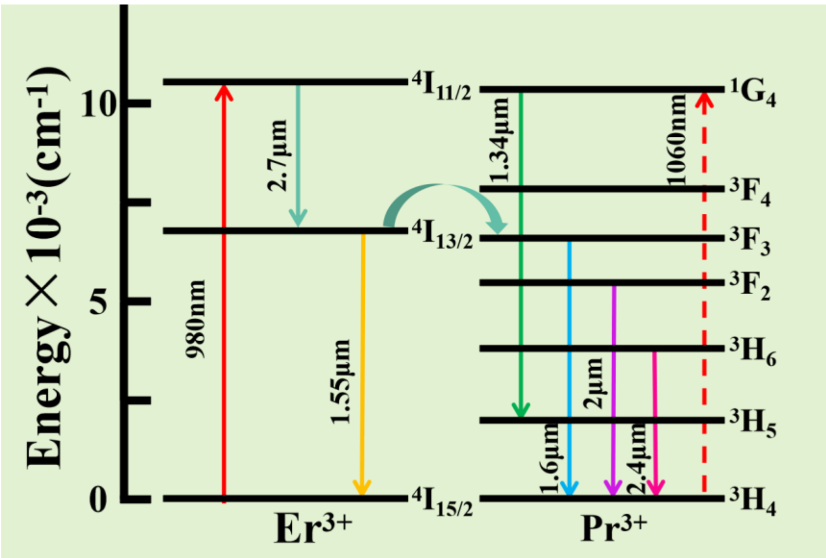

Fig.5 Energy level diagram for energy transfer process.

The schematic representation of energy level transition shown in Fig.5 can be used to understand the observed photoluminescence phenomenon. Under the excitation of a 980 nm laser, Er^{3+} ions are excited from the ground state $^4I_{15/2}$ to the upper level $^4I_{11/2}$. After that, the $^4I_{11/2}\rightarrow{}^4I_{13/2}$ transition of Er^{3+} ions in the $^4I_{11/2}$ level and the $^4I_{13/2}\rightarrow{}^4I_{15/2}$ transition of part of the Er^{3+} ions in the $^4I_{13/2}$ level produce infrared emissions in the 2.75 μm and 1.55 μm bands, respectively. The $^3F_3$ level of Pr^{3+} is close to the $^4I_{13/2}$ level of Er^{3+}. The $^4I_{13/2}$ level of Er^{3+} has a long lifetime and is easy to accumulate energy. The process of energy transfer from Er^{3+}: $^4I_{13/2}$ level to Pr^{3+}: $^3F_3$ level is easy to occur. Therefore, Pr^{3+} produces long-wave infrared light, such as 1.6 μm (Pr^{3+}: $^3F_3\rightarrow{}^3H_4$), 2 μm (Pr^{3+}: $^3F_2\rightarrow{}^3H_4$) and so on. These energy transfers together with the respective transitions of Er^{3+} and Pr^{3+} ions both determine the observed luminescent properties. The rich energy level structure of Pr^{3+}make it very easy to cause self-quenching, so Pr^{3+} must be controlled at an appropriate concentration.[21]

IV. CONCLUSION

In conclusion, a series of Er^{3+}/Pr^{3+} co-doped ZBLAY glasses are successfully prepared via the melt-quenching method. The XRD patterns show that the Er^{3+}/Pr^{3+} co-doped ZBLAY glasses have typical amorphous properties. When excited by a 980 nm laser, the Er^{3+}/Pr^{3+} co-doped ZBLAY glasses can emit light at 1.55 μm and 2.75 μm. The energy transfer process between Er^{3+} and Pr^{3+} is discussed by analyzing the absorption spectra and fluorescence lifetimes of the samples. The decrease of fluorescence lifetime confirms the occurrence of energy transfer from Er^{3+}:$^4I_{13/2}$ level to Pr^{3+}:$^3F_3$ level, which leads to the enhancement of luminescence at 2.7 μm and the decrease of luminescence at 1.55μm. Er^{3+}/Pr^{3+} co-doped ZBLAY glasses have good mid-infrared response prospects.

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