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# Sensitization and deactivation effects to $Er^{3+}$ at ~2.7 μm mid-infrared emission by $Nd^{3+}$ ions in $Gd_{0.1}Y_{0.9}AlO_3$ crystal

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## A B S T R A C T

The use of $Nd^{3+}$ codoping for sensitizing the $Er^{3+}$ ion and enhancing the ~2.7 μm emission from transition of $Er^{3+}$:$^4I_{11/2} \rightarrow {}^4I_{13/2}$ were investigated in the Er/Nd codoped $Gd_{0.1}Y_{0.9}AlO_3$ (GYAP) crystal for the first time, to the best of our knowledge. The ~2.7 μm emission characteristics and the energy transfer mechanism of the as-grown crystals were investigated in details. On one hand, it is found that the codoped of $Nd^{3+}$ ion can act as an appropriate sensitizer for $Er^{3+}$ ion in GYAP crystal, making the Er/Nd:GYAP crystal can be pumped by commercialized 808 nm laser diodes (LD). On the other hand, the $Nd^{3+}$ ions can also act as a suitable deactivated ion for $Er^{3+}$ ions with efficient depopulation effect on the lower laser level $Er^{3+}$:$^4I_{13/2}$ for enhancing the ~2.7 μm fluorescence emission, while having little influence on the upper laser level of $Er^{3+}$:$^4I_{11/2}$. With these favorable properties, the Er/Nd:GYAP crystal may become an attractive host for developing solid state lasers at around 2.7 μm under a conventional 808 nm LD pump.

## 1. Introduction

In recent years, mid-infrared (MIR) solid-state lasers operating around 2.7–3.0 μm have attracted great attention for numerous applications in environmental protection, military fields, medical surgery, and remote sensors [1–5]. Besides, 2.7–3.0 μm lasers are suitable pump sources for achieving longer wavelength far-infrared lasers by the optical parametric oscillators [6,7].

It is well known that $Er^{3+}$ is a natural candidate for ~2.7 μm lasers owing to the $^4I_{11/2} \rightarrow {}^4I_{13/2}$ transition, and more recently, a lot of work about $Er^{3+}$ doped materials have been widely studied and demonstrated as effective ~2.7 μm laser sources, such as $Er^{3+}$ single doped ZBLAN fiber, $Y_2O_3$ ceramic, $Lu_2O_3$ ceramic, $CaF_2$ crystal, $SrF_2$ crystal, etc, [8–12]. However, the ~2.7 μm laser operation cannot be obtained efficiently because of the following two shortcomings of $Er^{3+}$: (i) the weak intensity and narrow bandwidth of the absorption bands with peaks around 980 or 800 nm, which would limit the absorption efficiency of laser diode (LD) pumping energy; (ii) the self-terminating "bottleneck" effect, which arises from the fluorescence lifetime of the upper $^4I_{11/2}$ level of $Er^{3+}$ is considerably shorter than that of the lower $^4I_{13/2}$ level, easy to cause the termination of ~2.7 μm laser [13]. In order to conquer these problems, on one hand, sensitized excitation with suitable rare earth ion co-doping having strong absorption at pump powers, such as $Yb^{3+}$, or $Nd^{3+}$ ions with strong and broad absorption bands around 980 nm or 808 nm, seems to be a good choice to improve the absorption efficiency [14–16]. On the other hand, high doping concentrations ($>30$ at.%) of $Er^{3+}$ can mitigate the self-termination effect by the well-known concentration dependent up-conversion process [$^4I_{13/2} + {}^4I_{13/2} \rightarrow {}^4I_{11/2} + {}^4I_{9/2}$]. However, the doping of too high concentration of $Er^{3+}$ may bring about a degeneration of the optical-quality and thermal properties of the crystal, limiting the laser output efficiency and beam quality. Another solution to restrain the self-termination effect is to co-dope with deactivation ions to reduce the lifetime of the lower level $^4I_{13/2}$ of $Er^{3+}$, leading to possible of population inversion. Up to now, the deactivation ion for $Er^{3+}$ ion, such as $Pr^{3+}$, $Ho^{3+}$, $Tm^{3+}$, $Dy^{3+}$, or $Nd^{3+}$, have been widely used in luminescent materials [17–24]. These ions can effectively reduce the populations of laser lower level, which would

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lower the laser threshold and increase the laser out efficiency. For example, recently, an improved 2.79 μm laser performance was demonstrated in Er,Pr:$CaF_2$ crystal, the slope efficiency was effectively improved from 8.% to 15.8% after the codoping of $Pr^{3+}$ in Er:$CaF_2$ crystal [18].

We are now focusing our scientific program on $Nd^{3+}$ ion, because $Nd^{3+}$ is the sole one ion not only be able to act as sensitized ion, but also as deactivated ion, for $Er^{3+}$ ion at the same time [25–28]. To this end, only few efforts have been paid to demonstrate the sensitization and deactivation effects to $Er^{3+}$ at ~2.7 μm emission by $Nd^{3+}$ in a few laser host materials, such as tellurite glass [25], chalcohalide glass [26], LuYSGG crystal [27], and $CaLaGa_3O_7$ crystal [28]. However, the glasses exhibit a poor thermal conductivity, which restrain their practical applications in ~2.7 μm lasers; the LuYSGG and $CaLaGa_3O_7$ crystals present a high phonon energy, which bring about a low ~2.7 μm fluorescence emission efficiency. Therefore, better crystal hosts are highly desirable to achieve both extensive practical applications and excellent optical properties.

In this works, we are now focusing our attentions on a new gain medium $Gd_{0.1}Y_{0.9}AlO_3$ (GYAP) crystal, which is a solid solution of two crystals, $YAlO_3$ (YAP) and $GdAlO_3$ (GdAP). GYAP crystal belongs to the oxide crystal, which has properties similar to YAP crystal, such as, the crystal can be grown into the form of large-size transparent single crystal with high optical quality by the Czochralski (CZ) method; furthermore, the crystal possesses good physicochemical and thermal properties; the most important, the phonon energy of the crystal is as low as in the range of 500–600 $cm^{-1}$ [29], which is beneficial for suppressing multi-phonon de-excitation processes and increasing the mid-infrared quantum luminescent efficiency. Up to now, to our knowledge, the observation of emission around 2.7 μm in $Er^{3+}$/$Nd^{3+}$ co-doped GYAP crystal (Er/Nd:GYAP) has not been successfully obtained. In this work, Er/Nd:GYAP crystal was successfully prepared. $Nd^{3+}$ ion was demonstrated to be a sensitized and deactivated ion of $Er^{3+}$ ion at the same time for achieving an efficient ~2.7 μm fluorescence emission in GYAP crystal for the first time, to the best of our knowledge. The spectroscopic properties around 2.7 μm of Er/Nd:GYAP crystal under a 808 nm LD pump are investigated for future application in MIR lasers.

## 2. Experimental procedures

In the $Er^{3+}$, $Nd^{3+}$ codoped system, if the concentration of $Nd^{3+}$ is too small, the absorption coefficient at around 808 nm would be greatly reduced, resulting in a lower pumping absorption efficiency. On the contrary, if the concentration of $Nd^{3+}$ is too large, the concentration quenching of $Nd^{3+}$ ions would appear, which would result in the fluorescence quenching [30]. A middle-ground approach was taken in our experiment, the concentration of $Nd^{3+}$ was chose as about 1.0 at. % in both the Nd:GYAP and Er/Nd:GYAP crystals. On the other hand, the concentration of $Er^{3+}$ was chose as about 15.0 at. % in both the Er:GYAP and Er/Nd:GYAP crystals.

The 15.0 at. % Er:GYAP, 1.0 at. % Nd:GYAP, and 15.0 at. % Er/1.0 at. %Nd:GYAP crystals were grown by the traditional Czochralski method in an atmosphere of $N_2$. The $Al_2O_3$, $Y_2O_3$, $Gd_2O_3$, $Er_2O_3$, and $Nd_2O_3$ (all had the same purity of 99.999%) were used as raw materials. The stoichiometric amounts of chemicals were weighed accurately according to the compositional formula $Er_x/Nd_y$: $Gd_{0.1-x/2-y/2}Y_{0.9-x/2-y/2}AlO_3$, where x and y are the concentrations of $Er^{3+}$ ions, and $Nd^{3+}$ ions, respectively. The mixture was completely mixed for 24 h to ensure homogeneity, and pressed into disks, followed by heating in air for 25 h at 1320 °C. The bulks were loaded into a 60 mm diameter iridium crucible for crystal growth. The crystal was grown by using [100] directed GYAP seed in a nitrogen gas environment. The pulling speed and rotation rate were 1.0–1.5 mm/h, and 10–15 rpm, respectively. After the growth was completed, the crystal was pulled out of the melt and cooled slowly to room temperature at a rate of 10–30 °C/h. Finally, the crystals were obtained.

The concentration of $Er^{3+}$, and $Nd^{3+}$ ions in the as-grown crystals were measured by the inductively coupled plasma atomic emission spectrometry analysis (ICP-AES). The doping concentrations of $Er^{3+}$ and $Nd^{3+}$ in the Er/Nd:GYAP crystal were measured to be 15.1 at. % ($2.81 \times 10^{21}$ ions/$cm^3$) and 0.8 at. % ($1.93 \times 10^{20}$ ions/$cm^3$), respectively. The doping concentration of $Er^{3+}$ the Er:GYAP crystal was 15.1 at. % ($2.82 \times 10^{21}$ ions/$cm^3$), while the doping concentration of $Nd^{3+}$ in the Nd:GYAP crystal was 0.8 at. % ($1.94 \times 10^{20}$ ions/$cm^3$). The effective segregation coefficient of $Er^{3+}$ and $Nd^{3+}$ in the Er/Nd:GYAP crystal were calculated to be 1.00, and 0.80, respectively. In GYAP crystal, trivalent rare earth ions usually occupy the $Gd^{3+}$ and $Y^{3+}$ sites [31]. The ionic radius of $Gd^{3+}$(0.0938 nm), and $Y^{3+}$(0.088 nm) are smaller than that of $Nd^{3+}$(0.0995 nm), resulting in the segregator coefficients of $Nd^{3+}$ is smaller than 1.0. On the contrary, the segregator coefficients of $Er^{3+}$ is near 1.0 because of the small ionic radius ratio between $Er^{3+}$(0.0881 nm) and $Y^{3+}$.

Crystal structure identification was undertaken on a D/max2550 X-ray diffraction (XRD)using Cu $K_\alpha$ radiation. The absorption spectrum were measured by Perkin-Elmer UV-VIS-NIR spectrometer (Lambda 900). The Edinburgh Instruments FLS920 and FSP920 spectrophotometers were used to measure the fluorescence spectra and the fluorescence decay curves. All measurements were done at room temperature.

## 3. Results and discussion

Fig. 1 shows the XRD patterns of the as grown crystals and the YAP crystal from the JCPDS cards (nos. 70–1677). It can be seen that the diffraction peaks of the as grown crystals are strong and no second phase diffraction peak is found, indicating that the impurities do not change the essential structure of YAP. Therefore, we confirm that the as-grown crystals with the perovskite structure, which also indicates that no phase transition occur during the cooling process after crystal growth. The inset of Fig. 1 shows the pictures of the as grown crystals. It is easy to see that the crystals are of high quality with free from crack, inclusion, and bubbles.

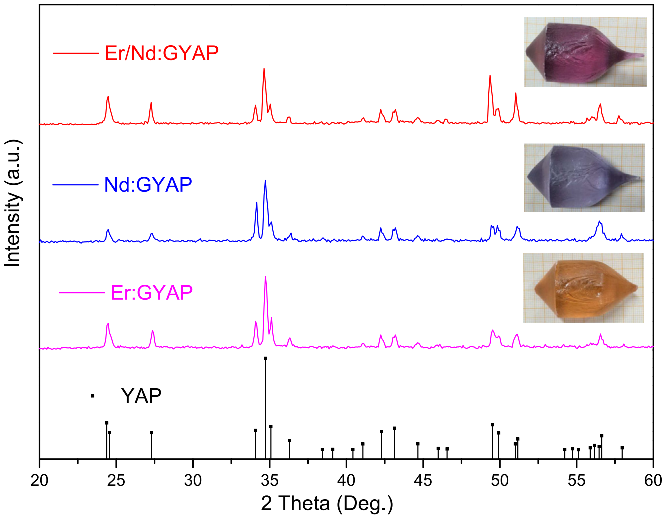

**Fig. 1.** XRD patterns of the Er:GYAP, Nd:GYAP, Er/Nd:GYAP, and YAP crystals. The inset shows the pictures of the as grown Er:GYAP, Nd:GYAP, and Er/Nd:GYAP crystals.