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Infrared and visible luminescence properties of Er^{3+} and Yb^{3+} ions codoped $Ca_3Al_2Ge_3O_{12}$ glass under 978 nm diode laser excitation

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Er^{3+} and Yb^{3+} ions codoped calcium aluminum germanate glass has been synthesized by solid-state reaction. An intense infrared emission at 1534 nm, which corresponds to the minimum losses of silica based fibers used in optical communications, and visible emissions at 416, 490, 525, 548, and 660 nm, corresponding to the $^4I_{13/2}\rightarrow{}^4I_{15/2}$, $^2H_{9/2}\rightarrow{}^4I_{15/2}$, $^4F_{7/2}\rightarrow{}^4I_{15/2}$, $^2H_{11/2}\rightarrow{}^4I_{15/2}$, $^4S_{3/2}\rightarrow{}^4I_{15/2}$, and $^4F_{9/2}\rightarrow{}^4I_{15/2}$ transitions of Er^{3+} ions, respectively, were simultaneously observed in this glass under the excitation of a 978 nm diode laser at room temperature. These emissions are mainly attributed to energy transfer from Yb^{3+} ions to Er^{3+} ions. The up-conversion processes involve a sequential two-photon absorption for the red (660 nm), the green emissions (525 and 548 nm) and the blue emission (490 nm), and a sequential three-photon absorption for the violet-bluish emission (416 nm). The up-conversion fluorescence of $Ca_3Al_2Ge_3O_{12}$:Er,Yb glass can be used to detect 980 nm infrared laser light. © *2001 American Institute of Physics.*
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I. INTRODUCTION

In recent years, Er^{3+} doped glasses have attracted much interest due to their important optical properties for use in lasers and devices for optical communications.[1–5] With the development of the 980 nm laser diodes, these interests have been stimulated from the view point of application,[6] since Mears *et al.*[7] reported the operation of the Er-doped fiber amplifier pumped at a 980 nm wavelength.

Since the spectral region of the $^2F_{7/2}\rightarrow{}^2F_{5/2}$ transition of the Yb^{3+} ion overlaps that of the $^4I_{15/2}\rightarrow{}^4I_{11/2}$ transition of the Er^{3+} ion, it is possible to achieve an effective Yb to Er transfer mechanism of the excitation energy.[8] In the last few years, many authors have demonstrated pulsed, as well as continuous, wave operation of Er and Yb codoped glass lasers.[9,10]

On the other hand, the up-conversion luminescence from Er^{3+}-doped glass has caught much attention for the purpose of developing infrared laser pumped solid state up-conversion lasers.[11,12] An efficient up-conversion laser at 540 nm when pumped with a laser diode at 800 nm has been realized and has shown a higher efficiency than harmonic generation techniques.[13] So far, most efforts have been paid to fluoride systems owing to their relatively lower phonon energy. But oxides are much more appropriate than fluorides as host materials for practical applications due to their ease of fabrication, high chemical durability, and thermal stability. Several up-conversion studies in oxide glass systems have shown efficient up-conversion even at room temperature.[14,15]

This article reports the up-conversion emissions and the Stokes emission of Er^{3+} and Yb^{3+} ions codoped calcium aluminum germanate glass ($Ca_3Al_2Ge_3O_{12}$, hereafter called CAG) under the excitation of a 978 nm diode laser at room temperature.

II. EXPERIMENT

The glass samples used in this work were synthesized by high-temperature solid-state reaction. The starting materials are high-purity CaO, Al_2O_3, and GeO_2, which are mixed with the stoichiometric ratio as $Ca_3Al_2Ge_3O_{12}$. Er^{3+} and Yb^{3+} ions were introduced as Er_2O_3 and Y_2O_3 with 4N purity. Er^{3+} and Yb^{3+} doping concentrations in the prepared glass are 0.4 at. % and 3.2 at. %, respectively. Well-mixed batches were introduced into a furnace, and were fired at 850 °C, 1300 °C, and 1520 °C for 2 h–4 h, respectively. Then, the heating product was cast into thin board. After annealing in air gradually from 600 °C to room temperature for 48 h, the glass samples were polished carefully in order to meet the requirement for optical measurements. In addition, we found that this glass can be drawn into fibers easily.

The visible and near-infrared absorption spectra of the sample were measured at room temperature using a Perkin-Elmer Lambda 9 spectrophotometer over a spectral range of 300–1800 nm. The emission spectrum by direct excitation was performed at a Hitachi F-4500 fluorescence spectrophotometer. The up-conversion luminescence spectra were recorded by a Hitachi F-4000 fluorescence spectrometer. The infrared emission spectra were measured with a Spex-1269 spectrophotometer. A 978 nm diode laser with a maximum power of 1 W was used as the excitation sources in the aforementioned measurements. The excitation light was introduced at a 45° angle to avoid harming the grating of monochromator and the Ge detector by the reflected laser. The emitted near-infrared light was analyzed using a 1 m single grating monochromator and detected with a liquid-nitrogen-cooled Ge detector. All measurements were performed at room temperature.

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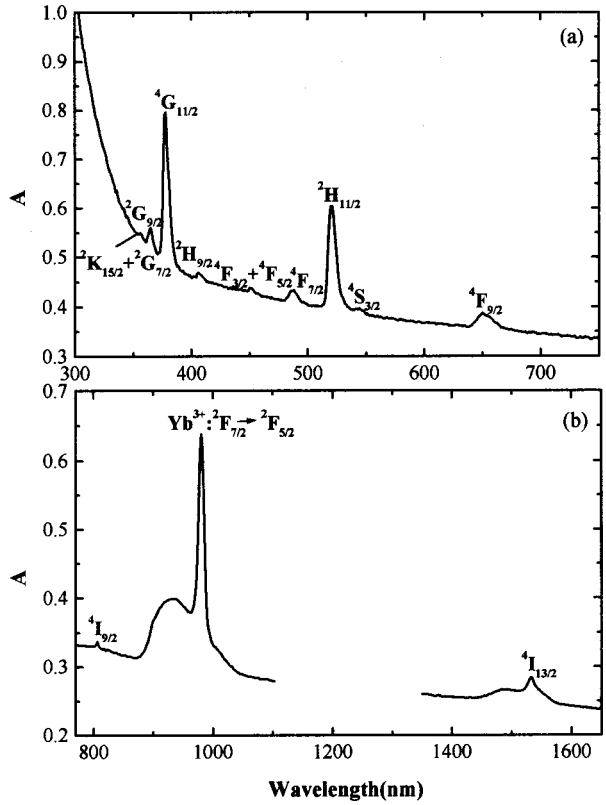

FIG. 1. Absorption spectra of Er^{3+} and Yb^{3+} ions in the range of (a) 300 to 750 nm and (b) 770 to 1100 nm and 1350 to 1650 nm for the CAG glass (thickness=1.98 mm) at room temperature. Absorption bands of Er^{3+} ions are all from the ground level $^4I_{15/2}$ to the level specified. A is the absorption $[^{-10}\log(I/I_0)]$.

III. RESULTS AND DISCUSSION

Figures 1(a) and 1(b) show the absorption spectra of Er^{3+} and Yb^{3+} ions for the CAG glass sample at room temperature. The absorption spectrum of Er^{3+} ion consists of 11 absorption bands centered at 1532(1490), 804, 650, 544, 520, 488, 451, 406, 377, 365, and 356 nm, corresponding to the absorptions from the ground state $^4I_{15/2}$ to the excited states $^4I_{13/2}$, $^4I_{9/2}$, $^4F_{9/2}$, $^4S_{3/2}$, $^2H_{11/2}$, $^4F_{7/2}$, $^4F_{5/2}+^4F_{3/2}$, $^2H_{9/2}$, $^4G_{11/2}$, $^2G_{9/2}$, and $^2K_{15/2}+^2G_{7/2}$, respectively. The absorption spectrum of Yb^{3+} ions shows an intense absorption band centered at 980 nm in the sample, due to the $^2F_{7/2}\rightarrow^2F_{5/2}$ transition of the Yb^{3+} ion. Certainly, the absorption band centered at 980 nm is also partially attributed to the absorption of Er^{3+} ion due to the $^4I_{15/2}\rightarrow^4I_{11/2}$ transition of the Er^{3+} ion. However, the 980 nm absorption of the Er^{3+} ion is much weaker than that of the Yb^{3+} ion. These results indicate that Yb^{3+} and Er^{3+} ions in the CAG glass can be excited by 978 nm light simultaneously.

The emission spectra of Er^{3+} ions for an Er^{3+} and Yb^{3+} codoped CAG glass sample in the range of 520 to 700 nm under the direct excitation at 490 nm (excited in the $^4F_{7/2}$ level) and 520 nm (excited in the $^2H_{11/2}$ level) at room temperature are shown in Fig. 2. Under 490 nm excitation (solid line), there are two emission subbands centered around 530 and 546 nm, corresponding to the $^2H_{11/2}\rightarrow^4I_{15/2}$ and $^4S_{3/2}\rightarrow^4I_{15/2}$ transition of Er^{3+} ion, respectively. However, only one emission band peaking at 546 nm due to the transition

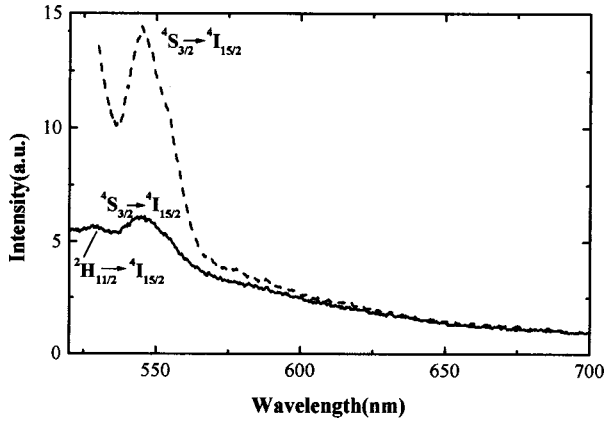

FIG. 2. Emission spectra of Er^{3+} ions for the Er^{3+} and Yb^{3+} codoped CAG glass under 490 (solid line) and 520 nm (dashed line) excitation at room temperature.

from $^4S_{3/2}$ level to the ground-state $^4I_{5/2}$ level was observed upon the excitation of 520 nm light (dashed line). There is no evidence that emission (due to the $^4F_{9/2}\rightarrow^4I_{15/2}$ transition of Er^{3+} ion around 660 nm) is recorded under the two aforementioned excitations. These results indicate that the $^4F_{9/2}$ level is not populated by relaxation or any other processes from the $^4F_{7/2}$ level in the sample. On the other hand, relaxation or any other process from the upper $^4F_{7/2}$ level can populate the $^2H_{11/2}$ level and $^4S_{3/2}$ level.

Figure 3 shows the up-conversion emission spectra of Er^{3+} ions in the range of 400 to 700 nm for the Er^{3+} and Yb^{3+} ions codoped CAG glass sample under the excitation of a 978 nm diode laser at room temperature. The up-conversion emission bands centered at 416, 490, 525, 548, and 660 nm are attributed to the transitions from the excited states $^2H_{9/2}$, $^4F_{7/2}$, $^2H_{11/2}$, $^4S_{3/2}$, and $^4F_{9/2}$ to the ground-state $^4I_{15/2}$ of Er^{3+} ion, respectively. However, the emissions centered at 416 and 490 nm are much weaker than the other emissions. In addition, the up-conversion fluorescence is too weak to be recorded in Er^{3+} single-doped CAG glass (erbium concentration is 0.4 at. %) under the same excitation conditions. This confirms that there exists an effective Yb to

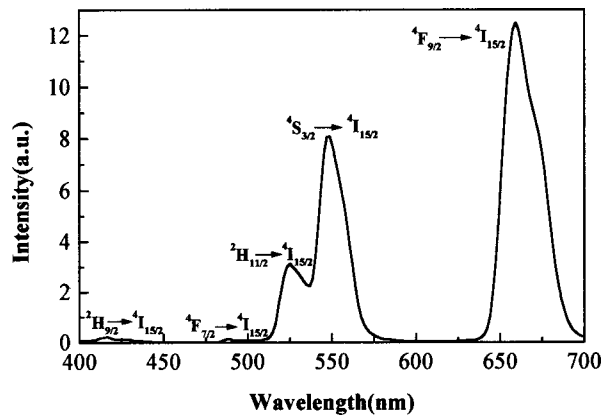

FIG. 3. Up-conversion emission spectra of Er^{3+} ions for the Er^{3+} 3m and Yb^{3+} codoped CAG glass under the excitation of a 978 nm diode laser at room temperature.

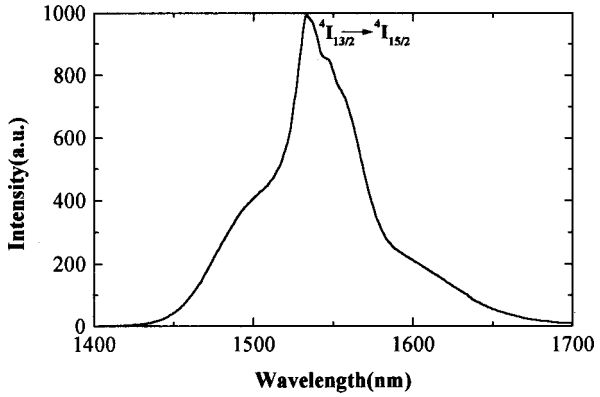

FIG. 4. Infrared emission spectra of Er^{3+} ions for the CAG glass under the excitation of a 978 nm diode laser at room temperature in the range of 1300–1700 nm.

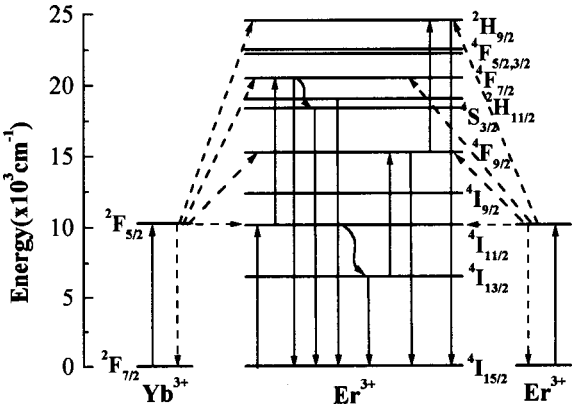

FIG. 6. Energy level diagram of Er^{3+} and Yb^{3+} ions and luminescence mechanisms of Er^{3+} and Yb^{3+} ions codoped CAG glass under a 978 nm diode laser excitation at room temperature. The solid lines stand for the absorption and emission transitions for Er^{3+} and Yb^{3+} ions. The dashed lines stand for energy transfer from Yb^{3+} and Er^{3+} ions. The curves represent the nonradiative relaxations.

Er transfer mechanism of the excitation energy. The up-conversion fluorescence of CAG:Er,Yb glass can be used to detect a 980 nm laser light.

A near-infrared emission spectrum of Er^{3+} emission in the range of 1400 to 1700 for the Er and Yb codoped CAG glass under the excitation of a 978 nm diode laser at room temperature is recorded, as shown in Fig. 4. There is an intense emission centered at 1534 nm with the full width at half maximum is about 54 nm, corresponding to the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+} ion, which corresponds to the minimum losses of silica based fibers used in optical communications.

The pump power dependence of the aforementioned three up-conversion signals was analyzed and the results are depicted in log–log plots of Fig. 5. According to Fig. 5, the fluorescence emissions intensities presented a quadratic dependence upon excitation intensity at 978 nm. This behavior indicates the participation of two 978 nm excitation phonons to populate the emitting $^2H_{11/2}$, $^4S_{3/2}$, and $^4F_{9/2}$ excited-state levels. According to the energy matching conditions and the quadratic dependence on 978 nm pump intensity, the up-conversion mechanism in this system under 978 nm excitation could be explained as illustrated in Fig. 6. Firstly, the Er^{3+} ion was excited from the ground state $^4I_{15/2}$ to the excited state $^4I_{11/2}$ by one of the three processes: ground state absorption, phonon-assisted energy transfer from the Yb^{3+} $^2F_{5/2}$ level, and energy transfer from the $^4I_{11/2}$ level of an adjacent Er^{3+} ion. Among the three processes, the phonon-assisted energy transfer from an Yb^{3+} ion is the main one, since the Yb^{3+} ion has a larger absorption cross section than the Er^{3+} ion around 978 nm in the CAG glass host [see Fig. 1(b)] and the up-conversion fluorescence in Er^{3+} singly doped CAG glass under the same excitation conditions is very weak. Secondly, the populated $^4I_{11/2}$ level was excited to the $^4F_{7/2}$ level by the same three processes: excited state absorption, phonon-assisted energy transfer from a Yb^{3+} ion, and energy transfer from an adjacent Er^{3+} ion. The populated $^4F_{7/2}$ level may mostly nonradiatively relax to two lower levels: $^2H_{11/2}$ and $^4S_{3/2}$, which produce the two green up-conversion emission (525 and 548 nm), however, it seldom relaxes radiatively to the ground state $^4I_{15/2}$, producing very weak emission at 490 nm. On the other hand, the Er^{3+} ion populated $^4I_{11/2}$ level mostly relaxes nonradiatively to the long-living $^4I_{13/2}$ level. The populated $^4I_{13/2}$ level may be excited to the $^4F_{9/2}$ level by the same three processes. On one hand, the populated $^4F_{9/2}$ level of the Er^{3+} ion mostly relaxes radiatively to the ground-state $^4I_{15/2}$ level, which causes emission around 660 nm. On the other hand, it may be excited to the $^2H_{9/2}$ level by a third phonon absorption by the same three processes, producing weak blue emission at 416 nm. In addition, the red intense emission at 660 nm can readily be seen by the naked eye, for pump powers lower than 150 mW.

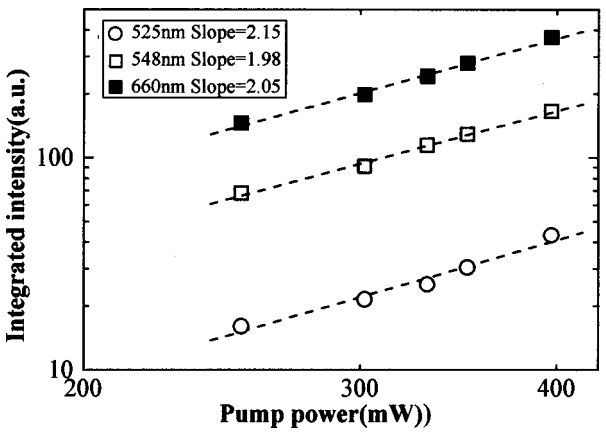

FIG. 5. Log–log plot of up-conversion fluorescence emission intensity as a function of pump intensity at 978 nm.

As mentioned, the populated $^4I_{13/2}$ mostly relaxes to the ground state, producing 1534 nm emission, because of the high multiphonon decay rate of the excited Er^{3+} $^4I_{11/2}$ manifold into the $^4I_{13/2}$ level due to the high effective phonon energies of the germanate glass host.

IV. CONCLUSION

Er^{3+} and Yb^{3+} ions codoped CAG glass has been synthesized by solid-state reaction. An intense infrared emission

at 1534 nm, which corresponds to the minimum losses of silica based fibers used in optical communications, and visible emissions at 416, 490, 525, 548, and 660 nm, corresponding to the $^4I_{13/2} \rightarrow {}^4I_{15/2}$, $^2H_{9/2} \rightarrow {}^4I_{15/2}$, $^4F_{7/2} \rightarrow {}^4I_{15/2}$, $^2H_{11/2} \rightarrow {}^4I_{15/2}$, $^4S_{3/2} \rightarrow {}^4I_{15/2}$, and $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transitions of Er^{3+} ions, respectively, were simultaneously observed in this glass under the excitation of a 978 nm diode laser at room temperature. These emissions are mainly attributed to phonon-assisted energy transfer from Yb^{3+} to Er^{3+}. The up-conversion processes involve a sequential two-photon absorption for the red emission (660 nm), the green emissions (525 and 548 nm) and the blue emission (490 nm), and a sequential three-photon absorption for the violet-bluish emission (416 nm). The up-conversion fluorescence of CAG:Er,Yb glass can efficiently detect a 980 nm infrared laser light.

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