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Near infrared emission for erbium-doped calcium aluminum silicate glass

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Abstract

In this work, erbium-doped calcium aluminum silicate (CAS) glass has been synthesized by solid-state reaction. Intense emission at 1534 nm, corresponding to the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition of the Er^{3+} ion, was observed upon both 488 nm Ar^+ laser and 978 nm diode laser excitations at room temperature. The luminescence mechanisms in the glass are discussed. These results indicate this glass is a promising laser material with its high chemical durability and thermal stability. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

In recent years, Er^{3+} -doped glass has attracted much interest [1–5], since its first operation as a laser material in 1965 [6] for telemetry and laser ranging applications, due to the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition of the Er^{3+} ion at about 1.53 μm , which is an eye-safe wavelength.

More recently, with the development of the stained-layer InGaAs laser diodes emitting at 980 nm wavelength, laser physicists have in particular been actively considering continuous wave laser oscillators based on Er^{3+} -doped glasses and optical fibers. The successful operation of the Er-doped fiber amplifier pumped at 980 nm wavelength reported by Mears et al. [7] has stimulated this interest from the view point of

application. The oxide glasses have several advantages, such as being easy-made, scale-varied, easy-fibered and having adjustable host composition along with their high durability and thermal stability.

The purpose of this Letter is to report the near infrared emission properties of Er-doped calcium aluminum silicate (CAS) glass. Under the excitation of a 488 nm line of an Ar^+ laser or that of a 978 nm diode laser, an intense emission band with a peak at 1534 nm was recorded at room temperature. The luminescence mechanisms are also explained.

2. Experimental

The glass samples used in this work were synthesized by solid-state reaction. The starting materials were high purity CaO , Al_2O_3 , SiO_2 , which were mixed with the stoichiometric ratio

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$\text{Ca}_{2.97}\text{Er}_{0.03}\text{Al}_{2.03}\text{Si}_{2.97}\text{O}_{12}$. Er^{3+} was introduced as Er_2O_3 with 4 N purity. The erbium doping concentration in the prepared glass was 0.15 at.% ($1.05 \times 10^{20} \text{ cm}^{-3}$). The well-mixed batches were introduced into a furnace, and were fired at 850 and 1300 °C for 2–4 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 requirements for optical measurements. In addition, we found that this glass could be drawn into fibers easily.

The absorption spectrum of the sample was performed by a Perkin–Elmer Lambda 9 model spectrophotometer at room temperature. The infrared emission spectra were measured with a SPEX-1269 spectrophotometer at room temperature. A 488 nm Ar^+ laser (Spectra-Physics 171) with a power of 300 mW and a 978 nm diode laser with a power of 200 mW were used as the excitation sources. The excitation light was introduced at a 45° angle to avoid harming the grating of the monochromator and the Ge detector by the reflected laser. The emitted light was analyzed using a 1 m single grating monochromator and detected with a liquid-nitrogen-cooled Ge detector.

For a comparison of infrared emission intensity, a kind of laser material, multi-quantum-well material InGaAs/InGaAsP grown by metal–organic chemical vapor deposition, which emits near 1550 nm under 488 nm Ar^+ laser excitation, was measured under the same conditions as that of the CAS:Er glass.

3. Results and discussion

The absorption spectrum of Er^{3+} ions for a CAS glass sample at room temperature is shown in Figs. 1a and b. It consists of 12 absorption bands centered at 1532(1490), 978, 804, 650, 544, 520, 488, 451, 406, 377, 365 and 356 nm, corresponding to the absorptions from the ground state $^4\text{I}_{15/2}$ to the excited states $^4\text{I}_{13/2}$, $^4\text{I}_{11/2}$, $^4\text{I}_{9/2}$, $^4\text{F}_{9/2}$, $^4\text{S}_{3/2}$, $^2\text{H}_{11/2}$, $^4\text{F}_{7/2}$, $^4\text{F}_{5/2}$ ($^4\text{F}_{3/2}$), $^2\text{H}_{9/2}$, $^4\text{G}_{11/2}$, $^4\text{G}_{9/2}$ and $^2\text{K}_{15/2}$ ($^2\text{G}_{7/2}$), respectively. These results indicate

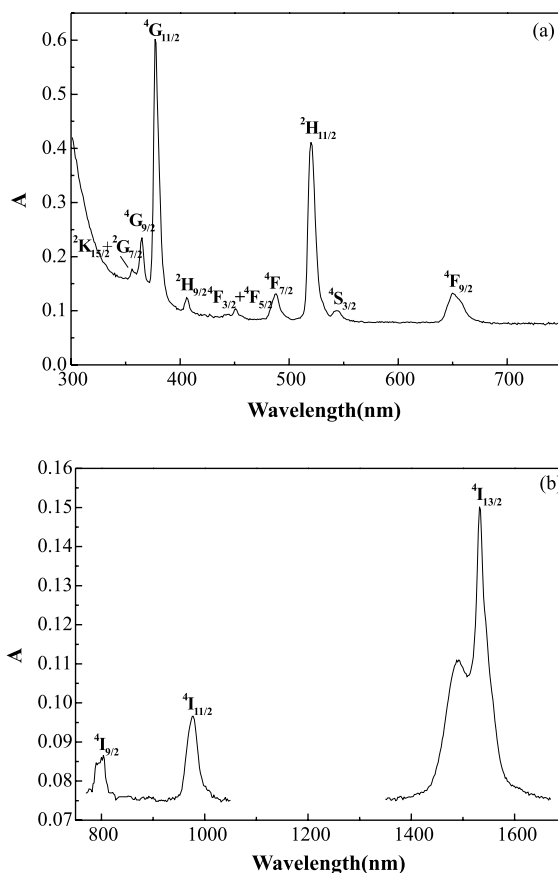


Fig. 1. Absorption spectrum of Er^{3+} ions in the range (a) 300–750 nm, (b) 770–1050 nm and 1350–1650 nm, for the CAS glass (thickness = 2.68 mm) at room temperature. Absorption bands of Er^{3+} ions are all from the ground level $^4\text{I}_{15/2}$ to the level specified. A is the absorption ($-\log(I/I_0)$).

that both 488 and 978 nm light can efficiently excite Er^{3+} ions in the CAS glass.

Fig. 2a represents the near infrared emission spectrum of Er^{3+} ions for CAS glass with the excitation of a 488 nm Ar^+ laser at room temperature. The spectrum consists of three subbands peaked at 852, 981 and about 1550 nm, respectively, corresponding to $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{13/2}$, $^4\text{I}_{11/2} \rightarrow ^4\text{I}_{15/2}$ and $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ transitions of Er^{3+} , respectively. Obviously, the intensity of the sub-band peaked at about 1550 nm is much more intense than that of 852 and 981 nm. The very intense emission between 1300 and 1800 nm is shown as a solid line in Fig. 2b. The intense

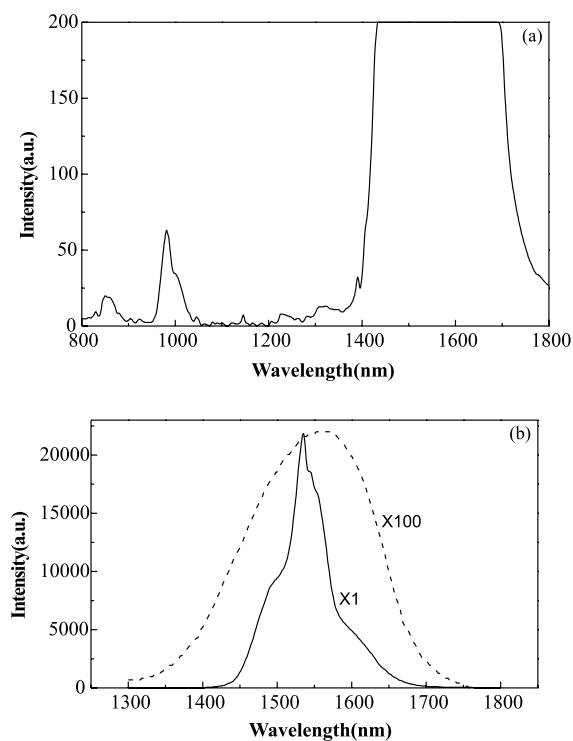


Fig. 2. Emission spectra of Er^{3+} ion for CAS glass (a) and (b) (solid line), and InGaAs/InGaAsP material (multiplied by 100) (b) (dashed line) with the excitation of a 488 nm Ar^+ laser at room temperature in the near infrared region.

emission peak is located at 1534 nm, and the full width at half-maximum is ~ 50 nm, corresponding to the ${}^4\text{I}_{13/2} \rightarrow {}^4\text{I}_{15/2}$ transition of the Er^{3+} ion. According to Figs. 2a and b, the intensity ratio of the emission at 1534 nm to the emission at 981 nm is 345:1, while that of the emission at 1534 nm to the emission at 852 nm is 1037:1. These results indicate that the emission at 1534 nm of Er^{3+} in CAS glass is very intense emission in the range 800–1800 nm, much more intense than the other two.

For a comparison of infrared emission intensity, the emission spectrum of the InGaAs/InGaAsP material under the same conditions is shown as a dashed line in Fig. 2b. The spectrum consists of a wide band with a peak at 1552 nm, but the intensity of the emission is much weaker than that of the 1534 nm emission in CAS:Er glass. The intensity ratio of the 1534 nm emission of Er^{3+} in

CAS glass to the 1552 nm emission of InGaAs/InGaAsP material is around 100:1. This result also indicates that the emission at 1534 nm of Er^{3+} in CAS glass is very intense.

The intense emission at 1534 nm of Er^{3+} was also observed and is shown in Fig. 3 when excited by a 978 nm diode laser. The spectrum of Er^{3+} in the range 1300–1800 nm is very similar to that excited by the 488 nm laser as shown in Fig. 2b, however, the full width at half-maximum is ~ 40 nm, narrower than that excited by the 488 nm laser. This result confirms that the intense emission at 1534 nm is due to Er^{3+} luminescence in this glass.

The intense emission at 1534 nm of Er^{3+} ions in CAS glass under the excitation of a 488 nm Ar^+ laser is attributed to the energy transfer effect of the Er^{3+} ions. The dominant energy transfers are described as follows: firstly, the pump laser (488 nm laser) excites electrons from the ground state to the ${}^4\text{F}_{7/2}$ excited state, then the excited electrons relax to the lower level by a non-radiative process, and finally to populate the ${}^4\text{S}_{3/2}$ level. When the ${}^4\text{S}_{3/2}$ level is populated, the following possible cross-relaxation processes may occur [8,9]:

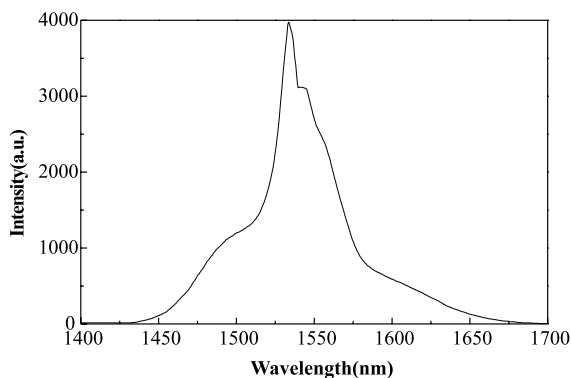
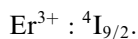
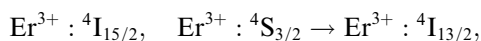
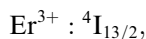
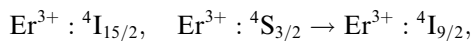


Fig. 3. Near infrared emission spectrum of CAS:Er³⁺ glass excited by a 978 nm laser diode at room temperature.

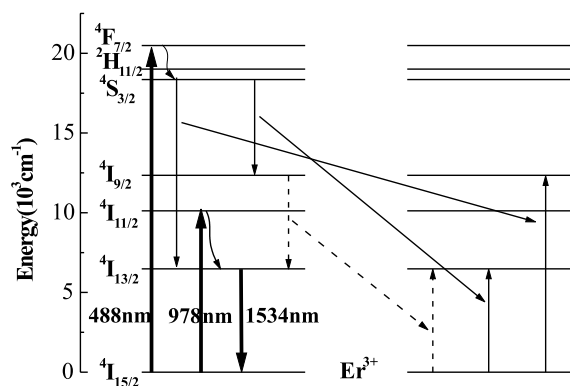
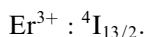
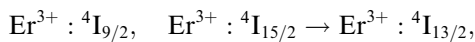


Fig. 4. Diagram of mechanism of fluorescence and cross-relaxation processes from Er^{3+} : $^4\text{S}_{3/2}$ (thin solid line) and $^4\text{I}_{9/2}$ (dashed line). The bold solid lines stand for the absorption and emission transitions for the Er^{3+} ions. The curves represent the non-radiative relaxations.

Both are shown as thin solid lines in Fig. 4. Furthermore, the successive process that depopulates the $^4\text{I}_{9/2}$ level and populates the $^4\text{I}_{13/2}$ level is as follows:



This process is indicated as dashed lines in Fig. 4. These three kinds of cross-relaxation processes diminish the lifetime of the $\text{Er}^{3+} : ^4\text{S}_{3/2}$ level and make the lifetime of the $\text{Er}^{3+} : ^4\text{I}_{13/2}$ level in $\text{CAS}:\text{Er}^{3+}$ glass increase. Therefore, the population distributed in the $^4\text{I}_{13/2}$ level is very large, the ratio of the $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ transitions is very high, and very intense emission occurs.

On the other hand, when the $^4\text{I}_{11/2}$ level of the Er^{3+} ion is directly excited by a 978 nm diode laser as shown in Fig. 4, the excited energy stored in the $^4\text{I}_{11/2}$ level rapidly non-radiatively relaxes to the $^4\text{I}_{13/2}$ level due to the high-energy phonons of the silicate glass host. Therefore, it induces the large population of the $^4\text{I}_{13/2}$ level and causes very

intense emission of the transition from the excited state $^4\text{I}_{13/2}$ to the ground state $^4\text{I}_{15/2}$ of Er^{3+} ions.

4. Conclusions

In summary, a promising solid-state laser material, erbium-doped calcium aluminum silicate glass, has been synthesized using solid-state reaction. Very intense emission at 1534 nm of Er^{3+} in CAS glass excited by a 488 nm Ar^+ laser or a 978 nm diode laser was observed at room temperature. This emission is due to the $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ transition of Er^{3+} in the glass. These results indicate that the Er-doped CAS glass is a promising laser material in fiber communication along with its high chemical durability and thermal stability.

Acknowledgements

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