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Room-temperature intense emission at 1534 nm in Er-doped $\text{Cd}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ glass

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In this work, a promising solid-state laser material, Er-doped cadmium aluminum silicate glass, has been synthesized by solid-state reaction. Very intense emission at 1534 nm, corresponding to the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition of Er^{3+} ions, was observed upon both 488 nm Ar^+ laser and 632.8 nm He–Ne laser excitations at room temperature. Possible cross-relaxation processes in the glass are discussed. © 2000 American Institute of Physics. [S0003-6951(00)04944-5]

In recent years, Er^{3+} -ion-doped polycrystal and glasses have caught much attention since the 1.53 μm emission of Er^{3+} is incorporated well with the minimum attenuation window of silica optical fiber and is eye safe.^{1–7} Spariosu *et al.* reported an $\text{Er}:\text{Ca}_5(\text{PO}_4)_3\text{F}$ saturable-absorber Q switch for the Er:glass laser at 1.53 μm .⁸ The erbium-doped phosphate glass waveguide on silicon with 4.1 dB/cm gain at 1.535 μm was reported by Yan *et al.*⁹ Therefore, Er^{3+} -doped glasses are promising materials in fiber telecommunications and other areas.

Compared with polycrystals, glasses have many advantageous applications, such as easy-made, scale-varied, easy to be optic fiber, and adjustable host composition. Gu *et al.* reported broadband excitation of Er^{3+} luminescence in chalcogenide glasses.¹⁰ On the other hand, from the viewpoint of application, the oxide glasses have several advantages over the chalcogenide glasses, including high durability and thermal stability.

This letter reports the near-infrared emission properties of Er-doped cadmium aluminum silicate glass ($\text{Cd}_3\text{Al}_2\text{Si}_3\text{O}_{12}$, hereafter called CAS). With the excitation of a 488 nm Ar^+ laser or 632.8 nm He–Ne laser, an intense infrared emission band with a peak at 1534 nm was recorded at room temperature.

The glass samples used in this work were synthesized by high-temperature solid-state reaction. The starting materials are high-purity CdO , Al_2O_3 , and SiO_2 , which are mixed with the stoichiometric ratio as $\text{Cd}_{2.97}\text{Er}_{0.03}\text{Al}_{2.03}\text{Si}_{2.97}\text{O}_{12}$. The Er^{3+} was introduced as Er_2O_3 with 4N purity. The erbium dopant concentration in the prepared glass is 1 at. %. 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 requirement for optical measurements. In addition, we find that this glass is easy to be fibered.

The transmission spectrum of the sample was performed by an UV-360 spectrophotometer (data not shown). 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 290 mW and a 632.8 nm He–Ne laser with a power of 30 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 Ge detector by the reflected laser. The emitted light was analyzed using a 1 m single-grating monochromator and detected with a cooled (77 K) Ge detector.

For 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 a 488 nm Ar^+ laser, was measured under the same conditions as that of the CAS:Er glass.

The transmission spectrum of the CAS:Er glass shows seven absorption subbands due to $4f-4f$ transitions of Er^{3+} ions in the glass. The results indicate that both 488 and 632.8 nm light can efficiently excite Er^{3+} ions in the glass. Figure 1 shows the emission spectra of CAS:Er³⁺ glass with excitation of a 488 nm Ar^+ laser at room temperature. In Fig. 1(a), the emission at 856 nm ($11\,682\text{ cm}^{-1}$) is due to the $^4S_{3/2} \rightarrow ^4I_{13/2}$ transition of Er^{3+} , while the emission near 982 nm ($10\,183\text{ cm}^{-1}$) is due to the $^4I_{11/2} \rightarrow ^4I_{15/2}$ transition of Er^{3+} . Figure 1(b) shows the very intense emission between 1400 and 1700 nm. This luminescence intensity has greatly exceeded the measurement range of the device.

In order to verify that the intense emission is due to Er^{3+} luminescence, not the signal from the excitation source, a laser excitation monochromator was used in the following experiments. The emission spectrum for the CAS:Er glass in the near-infrared region is shown in Fig. 2(a). The intense emission peak is located at 1534 nm and the full width at half maximum is $\sim 45\text{ nm}$, corresponding to the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition. According to Figs. 1 and 2(a), the emission intensity at 1534 nm in Fig. 1 is about 1.07×10^5 (a.u.), while that at 982 and 856 nm are about 500 and 260 (a.u.), respectively. Therefore, the intensity ratio of the emission at 1534 nm to the emission at 982 nm (due to the $^4I_{11/2} \rightarrow ^4I_{15/2}$ transition) is about 214:1, while that of the emission at 1534 nm to the emission at 856 nm (due to the $^4S_{3/2} \rightarrow ^4I_{13/2}$ transition) is 412:1. These results indicate that the

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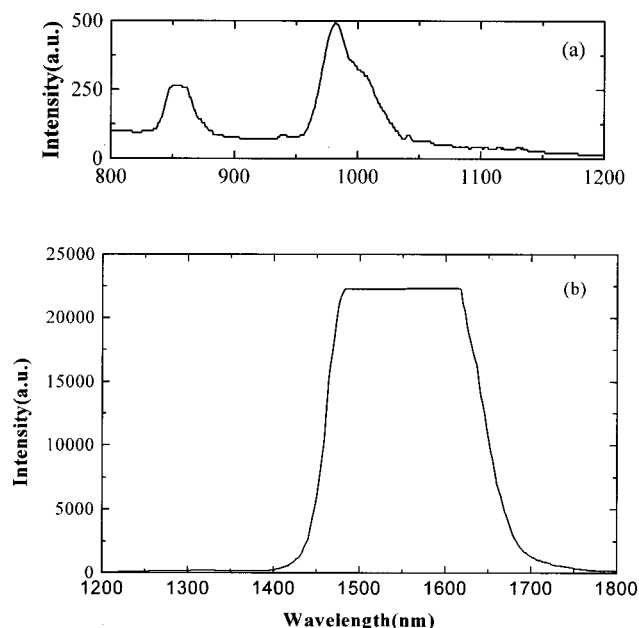


FIG. 1. Emission spectra of CAS:Er³⁺ glass excited by 488 nm Ar⁺ at room temperature in the near-infrared region: (a) 800–1200 nm; (b) 1200–1800 nm.

emission at 1534 nm of Er³⁺ in CAS glass is very intense emission at the range of 800–1800 nm.

Figure 2(b) shows the emission spectrum of the InGaAs/InGaAsP material under the same condition. 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 Er³⁺ in CAS glass to the 1552 nm emission of InGaAs/InGaAsP material is about 70. This result also indicates that the emission at 1534 nm of Er³⁺ in CAS glass is very intense.

The intense emission at 1534 nm of Er³⁺ was also observed when excited by the 632.8 nm laser (produced by the He–Ne laser). The spectrum in the range from 800 to 1800 nm is similar to that excited by the 488 nm laser. This result confirms the intense emission at 1.534 μm is due to Er³⁺ luminescence in this glass.

The intense emission at 1534 nm of Er³⁺ in CAS:Er glass is attributed to the energy transfer effect of the Er³⁺

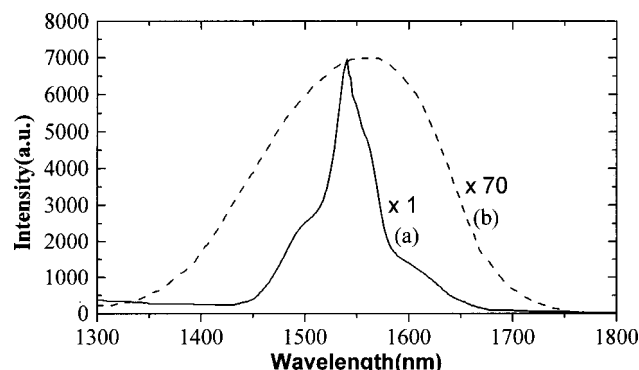


FIG. 2. Emission spectra of two kinds of materials with excitation of a 488 nm Ar⁺ laser at room temperature: (a) CAS:Er³⁺ glass, emission peak at 1534 nm (solid line); (b) InGaAs/InGaAsP material (multiplied by 70), emission peak at 1552 nm (dashed line). The intensity ratio of (a) to (b) is about 70.

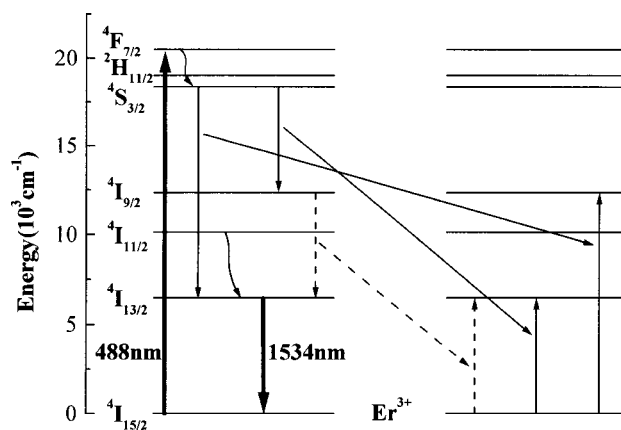


FIG. 3. Diagram of the mechanism of fluorescence and cross-relaxation processes from Er³⁺:⁴S_{3/2} (thin solid line) and ⁴I_{9/2} (dashed line). The bold solid lines stand for the absorption and emission transitions for the Er³⁺ ions. The curves represent the nonradiative relaxations.

ions. The dominant energy transfers are described as follows: the pump laser excites electrons from the ground state to the ⁴F_{7/2} excited state, then the excited electrons relax to the lower level by a nonradiative process, and finally to populate the ⁴S_{3/2} level. When the ⁴S_{3/2} level is populated, the following possible cross-relaxation processes may occur:^{11,12}

$$\text{Er}^{3+}:\text{}^4\text{I}_{15/2}, \quad \text{Er}^{3+}:\text{}^4\text{S}_{3/2} \rightarrow \text{Er}^{3+}:\text{}^4\text{I}_{9/2}, \quad \text{Er}^{3+}:\text{}^4\text{I}_{11/2},$$

$$\text{Er}^{3+}:\text{}^4\text{I}_{15/2}, \quad \text{Er}^{3+}:\text{}^4\text{S}_{3/2} \rightarrow \text{Er}^{3+}:\text{}^4\text{I}_{13/2}, \quad \text{Er}^{3+}:\text{}^4\text{I}_{9/2},$$

Both are shown as thin solid lines in Fig. 3. Furthermore, the successive process that depopulates the ⁴I_{9/2} level and populates the ⁴I_{13/2} level is as follows:

$$\text{Er}^{3+}:\text{}^4\text{I}_{9/2}, \quad \text{Er}^{3+}:\text{}^4\text{I}_{15/2} \rightarrow \text{Er}^{3+}:\text{}^4\text{I}_{13/2}, \quad \text{Er}^{3+}:\text{}^4\text{I}_{13/2}$$

This process is indicated as dashed lines in Fig. 3. These three kinds of cross-relaxation processes diminish the lifetime of the Er³⁺:⁴S_{3/2} level and make the lifetime of the Er³⁺:⁴I_{13/2} level in CAS:Er³⁺ glass increase. Therefore, the population distributed in the ⁴I_{13/2} level becomes very large, the ratio of the ⁴I_{13/2}→⁴I_{15/2} transitions is very high, and very intense emission occurs.

In summary, a promising solid-state laser material, Er-doped cadmium aluminum silicate glass, has been synthesized using solid-state reaction. Very intense emission at 1534 nm of Er³⁺ in CAS:Er glass excited by 488 and 632.8 nm laser was observed at room temperature. This emission is due to the ⁴I_{13/2}→⁴I_{15/2} transition of Er³⁺ in the glass. These results indicate that Er-doped CAS glass is a promising laser material in fiber communications along with its high chemical durability and thermal stability.

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