Effect of OH⁻ on Fluorescence Lifetime and Laser Performance of Er³⁺ Glass

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ABSTRACT: A measurement apparatus for the lifetime of Er³⁺ ⁴I₁₃/₂ fluorescence using direct excitation of a 1.54nm laser was established. The absorption bands of OH⁻ in Er³⁺: phosphate glass at near IR region are derived. A linear relationship between the transition rate of ⁴I₁₃/₂ to ⁴I₁₅/₂ and the absorption coefficient at 2.2µm was determined. A large influence of lifetime on laser performance was indicated.

KEY WORDS Erbium glass laser, eye-safe laser

Introduction

Er³⁺ glass has been widely used as a laser material due to its eye-safe emission wavelength of 1.54µm. In addition, the atmosphere exhibits a high transparency in this region of the optical spectrum. Lasing of Er³⁺ in glass is produced by the resonant transition between the excited state of ⁴I₁₃/₂ and the ground state ⁴I₁₅/₂. Compared to the long lifetime of ⁴I₁₃/₂ fluorescence of the higher excited states of Er³⁺ in glass is quenched by nonradiative multiphonon relaxation at a relatively fast rate of between 10⁵ to 10⁷ s⁻¹. The long fluorescence lifetime is an important parameter for Er³⁺ laser glass. The quenching of the fluorescence from the ⁴I₁₃/₂ has a significant influence on the laser performance of Er³⁺ glass laser.

Since 1973, Kigre has been devoting to the investigation of Er³⁺ doped glass lasers for military, industrial and scientific applications. In recent years, Kigre has developed a number of new Er³⁺ glasses. These glasses are doped with different sensitizer ions and exhibit various thermal-optical properties [1,2]. In this paper, we summarized the measurement of lifetime, the effects of hydroxyl ion quenching on the Er³⁺ fluorescence lifetime, and the influence of lifetime on laser performance.

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2. Experiment
The experimental apparatus used for the measurement of fluorescence decay is shown schematically in Fig. 1. The 1.54 µm excitation beam from the Er\(^{3+}\) glass laser was targeted on the polished surface of the Er\(^{3+}\) glass samples. An EOT BP3000 Photodiode Receiver was placed perpendicular to the laser beam. Data processing was accomplished with a Tektronix Digitizing Signal Analyzer DSA601. The fluorescence decay was displayed with an exponential curve of fluorescence intensity versus time or with a straight line of logarithmic fluorescence intensity versus time. For low Er\(^{3+}\) concentration glasses, a relationship of ln(I) vs. t is linear until the second e-fold time. Fluorescence lifetime may be determined from the reciprocal of the slope of the straight line. In our experiment, the first e-fold fluorescence lifetime was determined using paired dot cursors showing an increment of natural logarithmic intensity equal to unity.

Two excitation sources were used. One was a Kigre QE7S free running Er\(^{3+}\) glass laser with 400mJ, 1ms output. The other was a Kigre Q-switched Er\(^{3+}\) glass laser with 5mJ, 30ns output. Typical fluorescence decay curves, the relationship between logarithmic fluorescence intensity and time, from these different excitation sources are shown in Fig. 2. The same slope was observed for the upper trace excited by the free running laser as the lower trace by Q-switched laser.

All of the glass samples used in this study were obtained from standard production melt composition of Cr\(^{3+}\), Yb\(^{3+}\) and Er\(^{3+}\) doped QE7S glass. High purity raw materials with total composition of transition metal contents of less than 3ppm, and 99.99% rare-earth oxides were used to minimize the influence of quenching from these impurities. Atmospheric and dry process controls were utilized in order to adjust the hydroxyl concentration. Standard QE7S production glass exhibits an absorption coefficient of less than lcm\(^{-1}\) at 3.4µm.

3. Results and discussion

(1) The Spectra of OH\(^-\) in Phosphate Glass

The presence of H\(_2\)O in oxide glass introduces a series of absorption bands throughout the NIR spectrum. It was identified the water bands as due to OH\(^-\). Most measurements showed a fundamental absorption band \(\nu_0\) at near 3.5µm for OH\(^-\) in phosphate glass. Many other overtone bands associated with it will occur. Since the OH\(^-\) ion sits in the glass matrix associated with PO\(_4\) tetrahedron, combination bands, will also
occur between $\nu_0$ and the fundamental P0$_4$ vibration $\nu_1$. Hydroxyl exhibits the fundamental absorption at 3.2µm (3125cm$^{-1}$) in phosphate glasses according to the IR spectrum measurement of Kigre erbium phosphate glass. P0$_4$ tetrahedron has fundamental stretching vibrations at 1100cm$^{-1}$ and 1300 cm$^{-1}$. The combination and overtone bands of $\nu_0 + \nu_1$ at 4425cm$^{-1}$ (2.26 µm), $\nu_0 + 2\nu_1$ at 5725cm$^{-1}$ (1.75 µm) and $2\nu_0$ at 6250cm$^{-1}$ (1.6 µm) will occur. Transparency of QE7S glass was measured with the same composition and very dry sample as reference to eliminate the influence of absorption from base glass. Fig. 3 shows the transmittance spectra of samples with different OH contents. The OH- content increases from sample a to c. There exist a very strong absorption band at 3.2µm, an absorption shoulder at 2.3µm and a continuous decreases of transmission from 1.6µm. The absorption band at the vicinity of 3.2 µm is complicated for high OH content glasses. Large absorption bands at 2.9 to 3.0µm and 3.1µm suggest that there are different sites of OH in the glass network. These OH are relatively easy to remove by dry processing. The absorption coefficient measurement at 2.2µm was chosen for OH concentration control in the phosphate glass. This control is due to the absence of other competing absorption bands of rare earth dopant at this wavelength.

(2) The influence of OH- Concentration on the Fluorescence Lifetime of Er$^{3+}$ Ion

Effect of OH$^-$ on Fluorescence Lifetime and laser performance of Er$^{3+}$ Glass

A previous investigation of the effect of OH$^-$ concentration on the fluorescence lifetime of Nd$^{3+}$ in glass showed a direct energy transfer from excited Nd$^{3+}$ to the hydroxyl ion$^{[3]}$. The energy transfer rate from Nd$^{3+}$ to OH$^-$ is reported to be larger than the rate between neodymium ions$^{[4]}$. The most effective quencher in Er$^{3+}$ glass is also OH$^-$$^{[5]}$. A relationship between the fluorescence lifetime and the internal absorption coefficient at 2.2µm for QE7S laser glass with an Er$^{3+}$ concentration of 1 X 10$^{19}$ ions/cc is shown in Fig. 4. The OH$^-$ concentration in the samples used to produce Fig. 4 was estimated to vary between 1 X 10$^{19}$ to 6 X 10$^{20}$ ions/cc.

The energy transfer from donors to acceptors can be approximated for electric dipole–dipole interaction. Many authors employed and extended the Forster-Dexter theory for rare-earth energy transfer in crystals and glass material$^{[6]}$. The energy transfer rate $W_{DA}$ from a donor D to an acceptor A is briefly given by

$$W_{DA} = \frac{9X^2}{128\pi^4 N_A n^4 \epsilon_0^2 \mu_0^4 R_{DA}^6} \int g_D(\nu) K_A(\nu)^{-1} d\nu$$

Where the X is a factor relative to the orientational averaging of dipole, $N_A$ is the acceptor concentration, n is the
refractive index, $R_{DA}$ is the donor-acceptor distance, $\tau_0$ is the donor radiative lifetime, $g_D(v)$ is the shape factor of the fluorescence band, $K_A(v)$ is the absorption coefficient of the acceptor and $v$ is the frequency.

For low Er$^{3+}$ concentration glass, the $R_{DA}$ is mainly dependent on the OH$^-$ concentration and will be inversely proportional to the cube-root of OH$^-$ concentration. Fig. 5 depicts a linear relationship for the Er$^{3+}$ transition rate ($1/\tau$) from the measured fluorescence lifetime and the absorption coefficient at 2.2$\mu$m. A similar result was found for the energy transfer from neodymium to transition metal impurities in phosphate and silicate glasses\[7\].

The calculated influence of OH$^-$ absorption at 3.5$\mu$m on the Er$^{3+}$ glass transition rate is $6s^{-1}/cm^{-1}$. This is much less than the value of $69s^{-1}/cm^{-1}$ for Nd$^{3+}$-in phosphate glass\[8\].

(3) The Influence of Lifetime on Laser Output
An increase in nonradiation transfer will decrease laser efficiency as a result of low quantum efficiency. Fig. 6 shows the results of input-output curves generated by two 6mm dia. X 75mm long QE7S laser rods with 0.3ms lifetime difference. These rods were tested in a Kigre FCM63K Pump Chamber and Resonator Assembly. The fluorescence lifetime was found to exert a large influence on laser performance. This situation was especially amplified at or near the laser’s threshold.

4. Conclusion

A measurement apparatus was used for gathering Er$^{3+}$ $^4I_{13/2}$ fluorescence lifetime data via excitation from 1.534$\mu$m Er$^{3+}$ glass laser. The fluorescence lifetime was measured for various samples with different OH$^-$ contents. A linear relationship was determined between the Er$^{3+}$ $^4I_{13/2}$ transition rate and 2.2$\mu$m absorption coefficient resulted from the existence of OH$^-$ ions. The overall lasing efficiency for two Er$^{3+}$ glass rods with different lifetime (7.7ms and 8.0ms) was compared. A large difference in laser performance was observed. This was found to be most pronounced near the threshold region. This data has been found to be useful for both understanding production and experimental applications of Er$^{3+}$ glass laser materials.

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Biography

Jiang Yasi is a professor of Shanghai Institute of Optics and Fine Mechanics, Academia Sinica. After graduation from Inorganic Chemical Engineering Department of East China Institute of Chemical Technology he served for Changchun Institute of Optics and Fine Mechanics, Academia Sinica from 1958 to 1964 conducting researches on optical glass and colour glass for optics. Since 1964, he has been working at Shanghai Institute of Optics and Fine Mechanics, Academia Sinica on the area of laser materials. He was with Kigre Inc. at the United States for 2 years in 1990 and 1993 separately as a visiting scholar doing R&D n glasses for Faraday rotator, neodymium glass laser, eye-safe laser and laser protection. He authored and co-authored 6 works and 60 research papers. Seeing the research and development on the laser glasses, their technologies and production for high-power laser project, industrial and military applications, he won 6 National Progress Prizes f Science and Technology and Scientific and Technological Progress Prizes of Academia Sinica. His current interests are glasses for laser fusion, eye-safe lasers and photonics.