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Luminescence Characteristics and Energy Transfer of Tm^{3+}-Doped Calcium Fluoroborate Glasses for Fiber Amplifiers

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Abstract: *The conventional melt quenching method was employed to fabricate calcium fluoroborate glasses doped with Tm_2O_3 (CFBTm). Optical absorption and photoluminescence spectra were recorded in the UV, Vis, and NIR wavelength ranges. Judd-Ofelt (J-O) and free-ion parameters were computed based on the absorption band intensities and energy level positions. Utilizing the J-O parameters, various radiative parameters were determined for distinct excited states of Tm^{3+} ions in CFB glasses. Stimulated emission cross-sections (se) and effective bandwidths (Dleff) were calculated for the observed emission bands. The increase in Tm_2O_3 concentration resulted in an augmentation of emission peak intensities in the visible range, followed by a decline at higher concentrations. The quenching of emission intensities was attributed to energy transfer through cross-relaxation mechanisms. The NIR emission spectrum, excited by an 808 nm laser diode (LD), exhibited a peak at 1.47 mm corresponding to the 3H4-3F4 transition, with the intensity of the NIR emission peak increasing with the concentration of Tm_2O_3. Furthermore, Beer-Lambert and McCumber theories were applied to assess the absorption and emission cross-sections for the prominent 3F4–3H6 transition at the 1.82 mm emission wavelength.*

Keywords: *NIR emission, laser diode, Beer-Lambert theory, Mc Cumber theory.*

1. Introduction

Contemporary demands for optical data storage and multicolor laser displays have propelled the exploration of solid-state laser materials infused with trivalent rare earth (RE^{3+}) ions [1]. Among the RE^{3+} ions, Tm^{3+}-doped glasses and crystals have garnered significant technical interest due to their potential applications as laser active media, optical reading materials, and atmospheric sensors, offering emissions across both visible and infrared spectra. The versatile applications of Tm^{3+}-doped materials extend to medical diagnostics, optical radar systems, remote control technologies, molecular spectrum analysis, and fiber amplifiers [2].The primary focus of Tm^{3+} ion research has centered on its four meta-stable excited multiplets: $^3F_4$, $^3H_4$, $^1G_4$, and $^1D_2$. The lower excited levels, $^3F_4$ and $^3H_4$, emit in the near-infrared (NIR) region, while the upper excited levels, $^1G_4$ and $^1D_2$, predominantly emit in the visible spectrum. A notable emission of Tm^{3+} ions in the near-infrared spectrum is the $^3H_4$-$^3F_4$ transition, occurring at 1.47 mm. This emission band can be observed by exciting the ground-state Tm^{3+} ions to the $^3H_4$ level, ideally utilizing an 808 nm diode laser. The generation of broad-band near-infrared (NIR) emission is primarily influenced by the host materials, with Tm^{3+}-doped glasses, especially borate glasses [4,5], playing a crucial role. Borate glasses are considered optimal among suitable glass hosts for investigating the spectral characteristics of RE^{3+} ions. Their superiority arises from high mechanical stability and a broad transmission range (350 nm–5 mm), distinguishing them from silicate and tellurite glasses [6]. In communication networks, the full width at half maximum (FWHM) of the emission transition and the phonon energy of the glass host play a crucial role in determining the transmission window capacity of S-band amplifiers. Tm^{3+}-doped borate glasses, given the distinctive properties of borate glasses such as transmission range, mechanical stability, and rare earth ion solubility, emerge as more suitable hosts for obtaining NIR emission.Hence, this study presents an exploration of the absorption, emission, and the influence of Tm^{3+} ion concentration on emission characteristics, emphasizing their relevance for near-infrared (NIR) communication networks.

Experimentation

Using the melt quenching technique, a series of calcium fluoroborate (CFB) glasses with varying Tm_2O_3 concentrations (0.05, 0.1, 0.5, 1.0, 2.0, and 4.0 mol%) were synthesized. Approximately 10 g batches of pre-weighed chemicals were meticulously ground in an agate mortar to ensure homogeneity. The mixture was then melted in a platinum crucible using an electric furnace for one hour at temperatures ranging from 1050 to 1075°C. The molten material was swiftly poured into a pre-heated and polished brass mold, undergoing rapid quenching. To alleviate thermal stresses, the samples were annealed at 420°C for 12 hours. Following this, the samples were cut into rectangular shapes, polished, and subjected to measurements of optical and physical characteristics.For ease of reference, the CFB glasses doped with Tm_2O_3 concentrations of 0.05, 0.1, 0.5, 1.0, 2.0, and 4.0 mol% were designated as CFBTm005, CFBTm01, CFBTm05, CFBTm10, CFBTm20, and CFBTm40, respectively. The refractive index (1.604) of CFBTm10 glass, doped with 1.0 mol% Tm_2O_3, was determined using an Abbe-refractometer. Density (3.278 g/cc) was calculated through the Archimedes principle and immersion technique. The Tm^{3+} ion concentration in CFBTm10 was measured at 3.379 × 10^20 ions/cc, and the glass thickness was found to be 0.443 cm. The absorption spectra, covering the range of 340–2000 nm, were recorded using a Perkin Elmer Lambda 950 UV-vis-NIR spectrophotometer. Visible emission spectra and decay profiles of CFBTm glasses were obtained by exciting the samples with a xenon lamp, utilizing a Horba Jobin-Yvon Fluorolog-3 spectrofluorimeter.The NIR photoluminescence spectra (1300–1600 nm) of all CFBTm glasses were acquired by exciting the samples with an 808 nm diode laser. This was done using an integrated setup comprising a DongwooOptron monochromator equipped with an NIR detector and an electronic data storage assembly.

2. Results and discussion

Energy levels of absorption and J-O analysis

Figure 1(a) display the UV-vis and NIR absorption spectra of CFBTm10 glass in the wavelength range of 340–2000 nm as shown figure 1. The absorption spectra reveal seven distinct bands corresponding to transitions from the $^3H_6$ ground level to various excited levels: $^3F_4$, $^3H_5$, $^3H_4$, $^3F_3$, $^3F_2$, $^1G_4$, and $^1D_2$.Centered at 1669, 1209, 791, 685, 659, 468, and 357 nm, the absorption bands in CFBTm10 glass exhibit notable strength. The robust absorption bands at 685 and 791 nm suggest that 685 and 808 nm diode lasers could effectively excite these glasses.The determination of experimental oscillator strengths (f_{exp}) for each absorption transition involves measuring the areas under the absorption bands [10–12]. Employing the least-square fit method [15], these measured experimental oscillator strengths (f_{exp}) have been employed to calculate the Judd-Ofelt (J-O) [13, 14] intensity parameters (Ol).

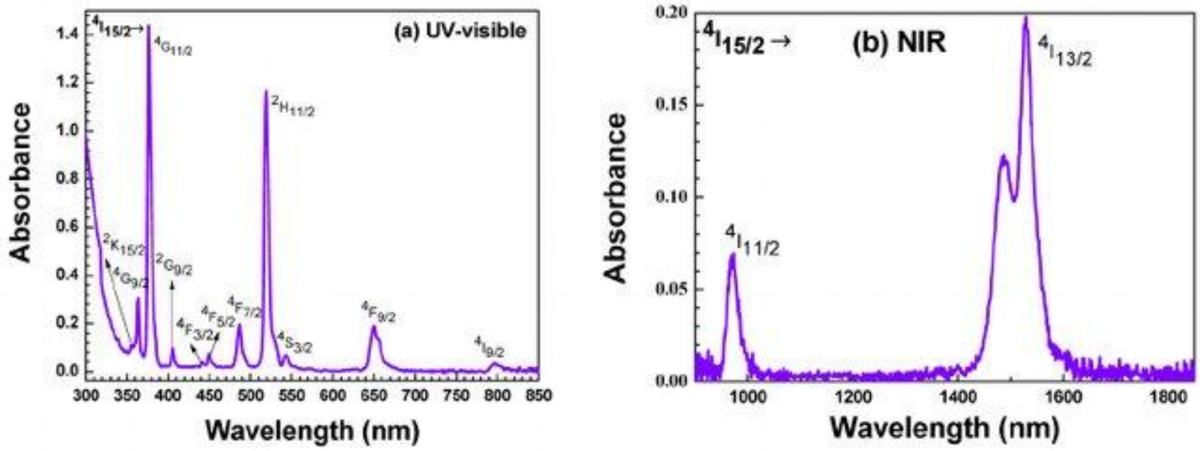

FIGURE 1. Absorption spectra in the (a) UV-visible and (b) NIR ranges [3]

Radiative characteristics and visible emission spectrum

The emission spectra of CFBTm glasses, recorded by varying the concentration of Tm^{3+} ions under 357 nm illuminations, were observed in the 440–500 nm spectral range. The energy level diagram of Tm3+ ions, along with the emission and excitation channels and potential relaxation processes, includes computed radiative transition probabilities (A_R), branching ratios (β_R), total radiative transition probabilities (A_T), and radiative lifetimes (τ_R) for various excited levels of Tm^{3+} ions in CFBTm glasses. Upon excitation with 357 nm light, it is apparent that the Tm^{3+} ions are excited to the $^1D_2$ level. As per the Judd-Ofelt (J-O) parameters, the theoretical lifetime of the $^1D_2$ level (38 ms) is shorter than that of the $^1G_4$ level (438 ms). Consequently, a significant proportion of Tm^{3+} ions from the $^1D_2$ level will promptly engage in the radiative emission process to the $^3F_4$ level, resulting in emission at 453 nm, corresponding to the transition between the $^1D_2$and $^3F_4$ levels.

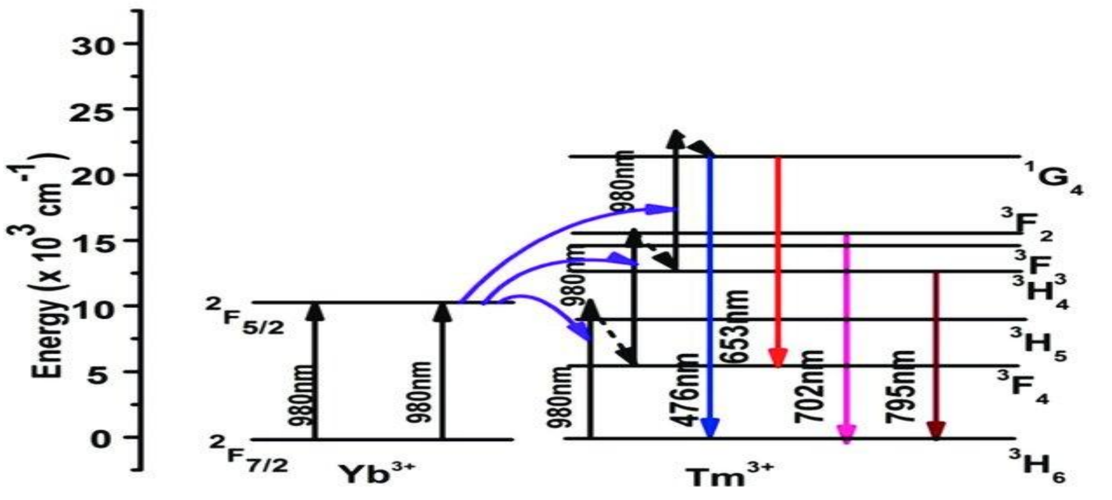

FIGURE 2. The energy levels and the energy transfer process for Tm $^{3+}$ [4]

Non-radiative multiphonon relaxation is anticipated primarily from the $^3F_2$, $^3F_3$, and $^3H_5$ levels, with a lesser contribution from the $^3H_4$ level, based on the Tm^{3+} ion's energy level positions in CFB glass [23]. As indicatedthe energy differences between $^3F_3$–$^3H_4$, $^3F_2$–$^3F_3$, and $^3H_5$–$^3F_4$ are approximately 2850, 570, and 2280 cm^{-1} as shown figure 2, respectively, while the highest phonon energy is roughly 1380 cm^{-1} [24]. Given the narrower energy gaps between the three levels$^3F_3$, $^3F_2$, and $^3H_5$there is a high likelihood of multiphonon relaxation.

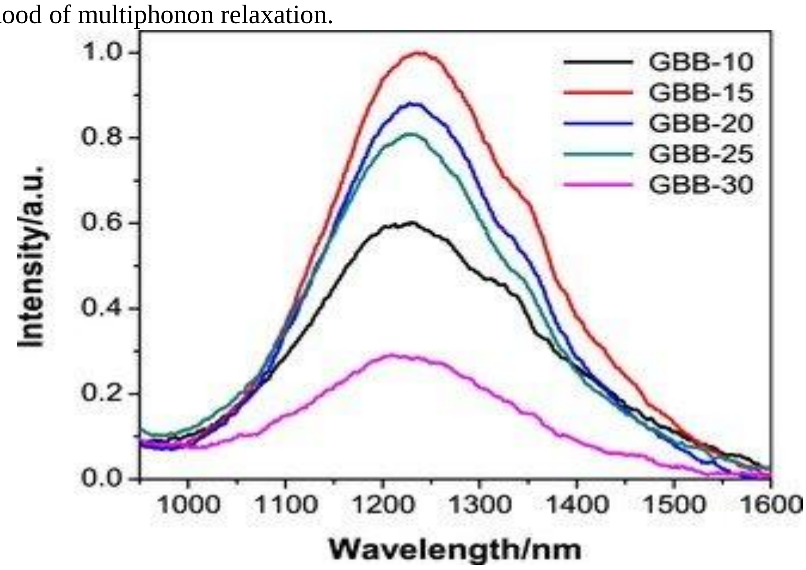

FIGURE 3. NIR emission spectra when being stimulated [5]

The lifetime of the $^1G_4$ level is more than 10 times greater than that of the $^1D_2$ level's radiative lifetime (t_R).The product of the stimulated emission cross-section and the radiative lifetime ($s_e \times t_R$) is a crucial parameter for achieving high optical gain in the CFBTm glasses, especially for the $^1D_2$–$^3F_4$ transition [25].

NIR discharge

The infrared emission spectra of various CFBTm glasses with distinct Tm^{3+} ion concentrations under 808 nm laser excitation are presented in Fig. 3, spanning the spectral range of 1.3–1.6 mm. In all CFBTm glasses, a prominent emission peak centered at 1.47 mm is observed, corresponding to the $^3H_4$-$^3F_4$ transition.The NIR region at 1.82 mm, associated with the 3F4-3H6 transition, is an additional noteworthy emission for the Tm^{3+} ion, potentially extending the transmission capacity into the 1.6-1.9 mm atmospheric window [28].The substantial optical gain parameter value for CFBTm10 glass indicates that the $^3F_4$–$^3H_6$ transition is favorable for optical amplification in the near-infrared spectrum.

Analysis of the decay curve

Decay curves for the $^1D_2$ level of Tm3ξ ions stimulated at 357 nm and observed at 453 nm were recorded for all concentrations of Tm_2O_3-doped CFB glasses to understand the experimental lifetimes (τ_{exp}). The experimental lifespan (τ_{exp}) of an emitting level can be determined by considering the initial e-folding times of the decay curves. In another theoretical expression, τ_{exp} can be stated.The experimental lifespan, t_{exp}, is determined using J-O theory, while the estimated lifetime, t_R, is derived from decay curves. The non-radiative relaxation rate, WNR, encompasses various non-radiative processes, including energy transfer through cross-relaxation (WCR), multi-phonon relaxation (WMP), and others. The equation yields the quantum efficiency (Z) of an excited state.

Our findings reveal the non-radiative relaxation rates (W_{NR}), quantum efficiencies (Z), and experimental durations (τ_{exp}) for the $^1D_2$ level in CFBTm glasses. With the increase in Tm_2O_3 concentration in CFB glasses from 0.05 to 4.0 mol%, the non-radiative relaxation rates escalate from 4934 to 98,684 s-1, while the quantum efficiencies decline from 84% to 21%. The observed increase in non-radiative relaxation rates and decrease in quantum efficiencies at the $^1D_2$ level suggest energy transfer between dopant ions through cross-relaxation processes.

3. Conclusions

Tm2O3-doped calcium fluoroborate glasses (CFBTm) were prepared using the conventional melt quenching method. Both visible and near-infrared optical absorption and photoluminescence spectra were recorded. The energy level positions and absorption band intensities were employed to calculate the free-ion and Judd–Ofelt (J–O) parameters. Several radiative parameters were then computed using the J–O parameters. The emission spectra suggest that the 1.0 mol% Tm_2O_3 doped CFB glasses have significant potential for optical amplification at the 453 nm wavelength. The quenching of emission peak intensities has been attributed to energy transfer via cross-relaxation mechanisms. In the NIR spectra of the CBTm10 glasses, the $^3H_4$-$^3F_4$ transition emerged as the prominent peak at 1.47 mm.The Beer-Lambert and Mc Cumber theories were applied to evaluate the absorption and emission cross-sections for the established NIR emission transition 3F4-3H6 at 1.82 mm. The results indicate that Tm3+-doped CFB glasses hold promise for applications in fiber amplifiers.

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