



Dysprosium in fluoroindate glass: a platform for mid-infrared laser development [Invited]

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Abstract: We report a comprehensive spectroscopic investigation of Dysprosium (Dy^{3+})-doped fluoroindate (InF_3 -based) glasses as a promising material platform for mid-infrared fiber lasers. Dy^{3+} ions exhibit a stimulated emission cross-section of $0.31 \times 10^{-20} \text{ cm}^2$ at 2924 nm for the ${}^6\text{H}_{13/2} \rightarrow {}^6\text{H}_{15/2}$ transition, with a gain bandwidth of $>500 \text{ nm}$. The associated Stokes multiphonon emission sideband further extends the emission up to at least $4 \mu\text{m}$. Transition probabilities of Dy^{3+} ions are analyzed using a modified Judd–Ofelt formalism incorporating configuration interaction effects. Concentration quenching of the ${}^6\text{H}_{13/2}$ excited-state lifetime is characterized, and anomalously strong multiphonon nonradiative relaxation is discussed. These properties are evaluated in comparison with other low-phonon-energy host matrices for Dy^{3+} doping. Energy transfer processes in $\text{Er}^{3+}, \text{Dy}^{3+}$ codoped glasses are quantified. Laser action is demonstrated in a bulk $\text{Er}^{3+}, \text{Dy}^{3+}:\text{InF}_3$ -based glass, with free-running emission spanning $2.7\text{--}3.4 \mu\text{m}$, and, in addition, a double-clad fiber laser diode-pumped at 976 nm delivers output power at the 100 mW level at $3.3 \mu\text{m}$. InF_3 -based glass fibers with optimized codoping concentrations emerge as promising candidates for broadly wavelength-tunable and ultrashort-pulse mid-infrared laser sources.

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1. Introduction

Mid-infrared (mid-IR) lasers operating in the $3\text{--}4 \mu\text{m}$ spectral region are of exceptional technological importance due to the presence of strong fundamental vibrational absorption bands of numerous molecular species. Hydrocarbons, water vapor, and various greenhouse gases (CH_4 , N_2O , O_3) exhibit intense absorption features in this window, making it attractive for environmental monitoring, industrial process control, and trace-gas sensing. This spectral range also coincides with an atmospheric transmission window, enabling free-space optical communication and remote sensing. Strong water absorption near $3 \mu\text{m}$ makes these lasers effective for precise surgical procedures and minimally invasive treatments. Consequently, the

development of efficient and broadband laser sources in the 3–4 μm region remains a central objective in mid-IR photonics research [1].

Mid-infrared fiber lasers have emerged as a highly promising platform for generating radiation in the 3–4 μm spectral region due to their inherent advantages in efficiency, beam quality, and thermal management [1,2]. The waveguiding geometry enables excellent heat dissipation and long interaction lengths, facilitating high gain and low lasing thresholds even for transitions and gain media with relatively weak stimulated-emission cross-sections. Fiber configurations also provide diffraction-limited beam quality, compactness, and robust alignment-free operation, which are critical for practical deployment outside laboratory. However, the sharply increasing material losses beyond 2 μm , as well as a high phonon energy of silica glass restricts efficient fiber laser operation to wavelengths below 2.2 μm (Tm^{3+} and Ho^{3+} -ion lasers) [3], necessitating alternative glass hosts for longer-wavelength emission. In this context, heavy-metal fluoride glasses, particularly ZBLAN and fluoroindate (InF_3 -based) glass fibers, have emerged as promising platforms [4].

Fluoride glasses are well-known laser host matrices for rare-earth doping [5,6]. They exhibit relatively low phonon energies (570 cm^{-1} for ZrF_4 -based glass – ZBLAN) allowing for laser operation up to $\sim 4 \mu\text{m}$ [7–9]. This is coupled with advantageous properties, such as i) broad range of transparency, ii) good thermal properties, iii) high solubility of rare-earth ions, iv) long luminescence lifetimes and v) low synthesis temperatures. In particular, the long luminescence lifetimes of rare-earth ions in fluoride glasses arise from their low phonon energy, weak crystal field strength, and low refractive index. The former feature suppresses multiphonon non-radiative relaxation, favoring radiative decay. Concurrently, the weak crystal field limits mixing between $4f$ states and opposite-parity configurations, so that $4f$ – $4f$ transitions remain weakly allowed (Laporte-forbidden), yielding low oscillator strengths and small spontaneous emission probabilities. Finally, the low refractive index reduces the local photonic density of states and, within Judd–Ofelt theory, the radiative transition rate, thereby further extending the radiative lifetimes. However, the elaboration of fluoride glasses requires precise control of the synthesis atmosphere to avoid any oxygen contamination. Fluoroindate (InF_3 -based) glasses are currently attracting attention for the development of rare-earth mid-infrared fiber lasers [8,10]. As compared to more widely used ZrF_4 -based fluoride glasses, their advantages include a lower phonon energy and a broader transparency range, while maintaining high solubilities of laser-active rare-earth ions under minimal clustering and a low risk of crystallization. InF_3 -based glasses can be drawn into fibers.

Laser emission at 3–4 μm is commonly achieved using Erbium (Er^{3+}) [11,12], Holmium (Ho^{3+}) [10] and Dysprosium (Dy^{3+}) ions [13–15]. Among them, Dy^{3+} offers i) the broadest emission and gain bandwidth related to the ${}^6\text{H}_{13/2} \rightarrow {}^6\text{H}_{15/2}$ quasi-3-level transition covering the range far beyond 3 μm , *i.e.*, being well detuned from the structured water vapor absorption in air, a property being essential for achieving femtosecond pulses from mode-locked oscillators, as well as broadband continuous tuning of the laser wavelength, ii) multiple absorption bands in the near-infrared, corresponding to spin-allowed (intense) transitions, and iii) unlike for Er^{3+} and Ho^{3+} , the 3- μm ${}^6\text{H}_{13/2} \rightarrow {}^6\text{H}_{15/2}$ Dy^{3+} transition is not of self-terminating nature, Fig. 1.

Figure 2 presents an overview of broadly tunable continuous-wave mid-infrared fiber lasers employing ZBLAN glass fibers doped with Er^{3+} , Ho^{3+} and Dy^{3+} ions [14–21].

Lasers based on Dy^{3+} :ZBLAN fibers have been extensively investigated, demonstrating output powers reaching the 10 W level at 3.24 μm in the monolithic configuration under resonant (in-band) pumping by an Er-fiber laser at 2.83 μm [13], as well as slope efficiencies as high as 77% with respect to the absorbed pump power (approaching the Stokes limit) at 3.15 μm [14]. Moreover, a broad tuning range of 573 nm (2.807–3.380 μm) [15] and sub-800 fs pulses at 3.1 μm in the mode-locked operation regime driven by the nonlinear polarization evolution technique in a ring laser cavity configuration [22] have been reported. In contrast, laser performance

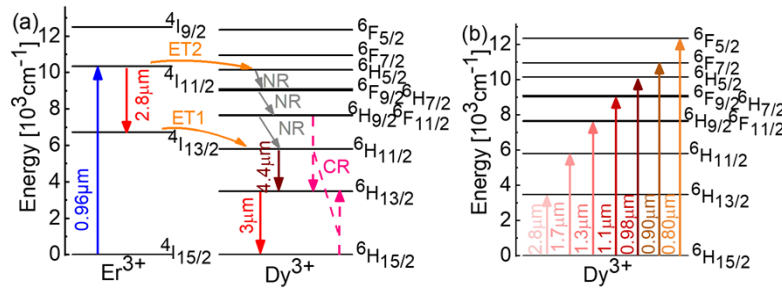


Fig. 1. (a) Energy-level scheme of Er³⁺ and Dy³⁺ ions showing pump and laser transitions in the mid-infrared region, ET – energy-transfer, NR – multiphonon nonradiative relaxation, CR – cross relaxation; (b) excitation paths of Dy³⁺ ions.

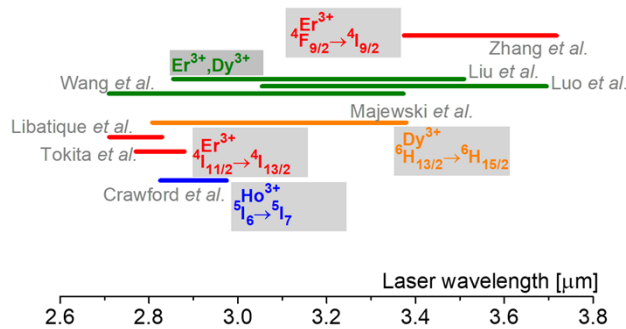


Fig. 2. Summary of broadly tunable continuous-wave fluoride fiber lasers based on Er³⁺, Ho³⁺, and Dy³⁺ ions reported so far [14–21].

in Dy³⁺-doped InF₃-based fibers remains comparatively less explored. Recently, Majewski *et al.* demonstrated continuous-wave lasing from a singly Dy³⁺-doped InF₃-based fiber laser at 2.95 μm with a slope efficiency of 14% and a laser threshold of only 0.39 W when pumping by a Raman-shifted fiber laser at 1.7 μm [7]. The authors also detected the 4.4-μm emission related to the ⁶H₁₁/₂ → ⁶H₁₃/₂ self-terminating transition. Ososkov *et al.* achieved high-efficient laser operation at 3.05 μm with a slope efficiency of 82% in the case of in-band pumping at 2.8 μm [23].

Furthermore, Er³⁺, Dy³⁺ codoping could be considered as a solution to access conventional pumping at 0.98 μm, and to broaden the overall gain bandwidth around 3 μm, Fig. 1. Watt-level laser output beyond 3.1 μm was achieved employing an Er³⁺, Dy³⁺:ZrF₄-based fiber as a gain medium pumped by a laser diode at 0.976 μm [24]. Owing to the spectral overlap of the stimulated-emission spectral profiles of both ions, significantly broader wavelength tuning ranges have been achieved in Er³⁺, Dy³⁺:ZrF₄ fiber lasers, spanning 675 nm (2.709–3.374 μm) and 656 nm (2.854–3.510 μm), compared to singly Dy³⁺-doped fiber lasers [16,17]. Luo *et al.* extended the longest achieved laser wavelength in the tunable operation regime to 3.696 μm and proposed an alternative pumping scheme employing red diodes at 639 nm [18]. Mode-locked and Q-switched operation regimes of such laser sources have also been demonstrated [25,26].

In the present work, we investigate the mid-infrared emission characteristics and energy-transfer mechanisms in Er³⁺ and Dy³⁺ singly doped, as well as codoped low-phonon-energy fluorindate glasses, with the aim of developing ultrabroadband (3–4 μm) mid-infrared fiber laser sources.

2. Optical spectroscopy

2.1. Glass synthesis

Fluoroindate glasses, both singly doped and codoped with Er^{3+} and Dy^{3+} ions were fabricated by *Le Verre Fluoré*. The glasses were prepared by the melt-quenching technique [27]. High-purity fluoride starting materials were melted in platinum crucibles at $T > 800^\circ\text{C}$ under dry atmosphere. To prevent crystallization, the homogeneous melt was rapidly cooled by casting onto a metallic mold. The glass was annealed near the glass transition temperature to remove mechanical stress.

Two singly doped glasses were studied, containing 0.5 mol% Dy^{3+} and 1.1 mol% Er^{3+} . Two sets of codoped glasses were prepared. For the first set, the Er^{3+} content was fixed at 4 mol% and the Dy^{3+} one was varied in the range of 0.15–0.40 mol% with a step of 0.05 mol%. For the second set, the Dy/Er codoping ratio was fixed at 0.063, resulting in three glasses: 3 mol% Er^{3+} , 0.187 mol% Dy^{3+} , 4 mol% Er^{3+} , 0.25 mol% Dy^{3+} and 5 mol% Er^{3+} , 0.312 mol% Dy^{3+} .

The measured glass density ρ was 5.205 g/cm^3 . The differential scanning calorimetry measurement performed at a heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$ yielded the characteristic temperatures: the glass transition temperature T_g of 297°C , the onset of crystallization temperature T_x of 394°C , and the crystallization peak temperature T_c of 421°C ($\pm 1^\circ\text{C}$). The glass exhibits good thermal stability, with a relatively wide supercooled liquid region ($\Delta T = 97^\circ\text{C}$), making it reasonably resistant to crystallization during heating.

The glasses were prepared in the form of slabs having an aperture of $10 \times 10\text{ mm}^2$ and a thickness of 3.0 mm. They were polished on both sides to laser grade quality. The glasses were colorless (singly Dy^{3+} doped) and rose-colored (Er^{3+} -containing ones). The transmission spectra of two singly doped glasses are depicted in Fig. 3. The UV absorption edge of glasses was $0.22\text{ }\mu\text{m}$, and their IR transparency was up to 10–11 μm , depending on the glass composition. No noticeable absorption at $\sim 3\text{ }\mu\text{m}$ related to hydroxyl groups was detected.

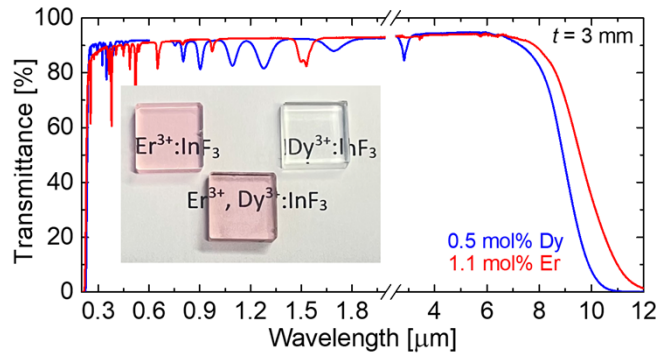


Fig. 3. Transmission spectra of Er^{3+} and Dy^{3+} singly doped InF_3 -based glasses, inset – photograph of laser-grade polished glasses with single Er^{3+} and Dy^{3+} doping and $\text{Er}^{3+}/\text{Dy}^{3+}$ codoping.

2.2. Optical absorption

The absorption spectra of InF_3 -based glasses singly doped with 1.1 mol% Er^{3+} and 0.5 mol% Dy^{3+} have been recorded using a Varian CARY 5000 spectrophotometer. The spectral resolution was 0.5–1.5 nm depending on the wavelength region. The observed absorption bands were attributed to the $4f - 4f$ electronic transitions of the activator ions, originating from their ground states $^4\text{I}_{15/2}(\text{Er}^{3+})$ and $^6\text{H}_{15/2}(\text{Dy}^{3+})$. The absorption cross-sections, $\sigma_{\text{abs}} = \alpha_{\text{abs}}/N_{\text{dop}}$, were then calculated, where α_{abs} and N_{dop} stand for the absorption coefficient and the ion density. The latter equal to $2.20 \times 10^{20}\text{ at/cm}^3$ (Er^{3+}) and $1.02 \times 10^{20}\text{ at/cm}^3$ (Dy^{3+}). Figure 4(a-d) shows the

σ_{abs} spectra of these two singly doped glasses. The electronic transitions of Er^{3+} and Dy^{3+} ions were assigned according to the energy-level scheme of the free ion reported by Carnall *et al.* [28]. The spectra exhibit broadband absorption features characteristics of glasses where strong inhomogeneous line broadening arises from the lack of long-range structural order.

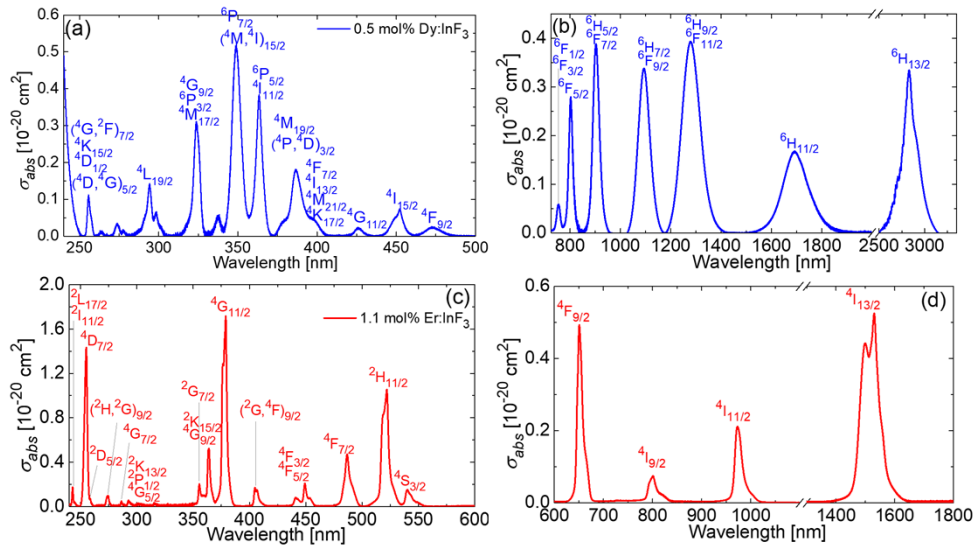


Fig. 4. (a-d) Absorption spectra of (a,b) Dy^{3+} and (c,d) Er^{3+} singly doped InF_3 -based glasses. The assignment of electronic transitions is according to Carnall *et al.* [28].

Dy³⁺ ion offers several absorption transitions from its ground state (⁶H_{15/2}) falling into the near-infrared spectral range with prominent bands centered around 0.80 μm (⁶F_{5/2}), 0.90 μm (⁶H_{5/2} + ⁶F_{7/2}), 1.09 μm (⁶H_{7/2} + ⁶F_{9/2}), 1.28 μm (⁶H_{9/2} + ⁶F_{11/2}), 1.69 μm (⁶H_{11/2}) and 2.83 μm (⁶H_{13/2}). All these transitions can be used for building excited-state population leading to mid-infrared emission: moving to shorter wavelengths generally enables the use of more accessible diode lasers at the expense of increased quantum defect. Meanwhile, Dy³⁺ suffers from intrinsically weak absorption, measuring $\sigma_{abs} = 0.17 \times 10^{-20}$ cm² at 1692 nm (bandwidth, FWHM: 115 nm) and 0.33×10^{-20} cm² at 2828 nm (bandwidth, FWHM: 175 nm). Significant increase of Dy³⁺ doping level is not possible due to the fast quenching of its luminescence lifetimes via energy migration and cross-relaxation.

To mitigate this issue, the $\text{Er}^{3+}, \text{Dy}^{3+}$ codoping scheme is exploited since Er^{3+} can be efficiently pumped at ~ 980 nm by high-power, fiber-coupled spatially multimode InGaAs diode lasers corresponding to the $^4\text{I}_{15/2} \rightarrow ^4\text{I}_{11/2}$ transition. Heavy Er^{3+} doping levels do not deteriorate the emission properties of fluoride glasses in the mid-infrared. For Er^{3+} ions in the studied InF_3 -based glass, the maximum σ_{abs} reaches $0.21 \times 10^{-20} \text{ cm}^2$ at 973 nm corresponding to an absorption bandwidth of 16.5 nm.

2.3. Judd-Ofelt analysis

The theory of $4f-4f$ transition intensities of rare-earth ions was applied to describe the transition probabilities of Er^{3+} and Dy^{3+} ions in InF_3 -based glasses. In addition to the standard Judd–Ofelt (J-O) formalism [29,30], modified approaches incorporating configuration interaction were employed to improve the agreement between calculated and experimental absorption oscillator strengths, as well as to ensure consistency with the luminescence lifetimes of excited states exhibiting almost negligible non-radiative relaxation, which serve as benchmarks for validating

the fitting procedure. In the most general approach implemented in this work, namely the intermediate configuration interaction (ICI) approximation, the electric dipole (ED) line strengths S are expressed as [31,32]:

$$S_{\text{calc}}^{\text{ED}}(JJ') = \sum_{k=2,4,6} U^{(k)} \tilde{\Omega}_k, \quad (1)$$

where:

$$\tilde{\Omega}_k = \Omega_k [1 + 2R_k(E_J + E_{J'} - 2E_f^0)], \quad (2a)$$

$$U^{(k)} = \langle (4f^n)SLJ || U^{(k)} || (4f^n)S'L'J' \rangle^2. \quad (2b)$$

Here, $U^{(k)}$ are the squared reduced matrix elements of the transitions calculated in the present work using the free-ion parameters reported by Carnall *et al.* [28], and R_k ($k = 2, 4, 6$) are parameters describing the effects of configuration interaction. Within the ICI model, the intensity parameters $\tilde{\Omega}_k$ are linear functions of the energies of the two multiplets involved in the transition, E_J and $E_{J'}$, while E_f^0 denotes the mean energy of the $4f^n$ ground configuration. Consequently, the model involves six free parameters, namely Ω_k and R_k . If only the opposite-parity excited configuration $4f^{n-1}5d^1$ contributes to the configuration interaction, then $R_2 = R_4 = R_6 = \alpha$. This parameter α accounts for two physical mechanisms: covalency effects and admixture of opposite-parity excited configurations. Under this assumption, the expression for line strengths is simplified, yielding the weak configuration interaction approximation, also known as the modified Judd–Ofelt (mJ-O) theory with four free parameters (Ω_k and α) [33]:

$$\tilde{\Omega}_k = \Omega_k [1 + 2\alpha(E_J + E_{J'} - 2E_f^0)]. \quad (3)$$

In the limiting case where the opposite-parity excited configurations lie at much higher energies ($\alpha \rightarrow 0$), the expression for the line strengths reduces to that of the standard Judd–Ofelt (J-O) model, which involves three free intensity parameters (Ω_k).

The magnetic dipole (MD, $\Delta J = 0, \pm 1$) contributions to transition intensities were calculated separately using the Russell–Saunders approximation applied to the Er^{3+} and Dy^{3+} wavefunctions, assuming a free-ion model. A refractive index $n \approx 1.52$ was used in the calculations.

Table 1 presents the analysis of the Dy^{3+} absorption transitions. Here, the experimental absorption oscillator strengths are calculated as:

$$f_{\text{calc}}^{\Sigma}(JJ') = \frac{m_e c^2}{\pi e^2 N_{\text{dop}} <\lambda_{\text{abs}}>^2} \Gamma(JJ') \quad (4)$$

where m_e and e are the electron mass and charge, respectively, c is the speed of light, $\langle \Gamma(JJ') \rangle$ is the integrated absorption coefficient and $\langle \lambda_{\text{abs}} \rangle$ is the “center of gravity” of the absorption band. The expression for calculated absorption oscillator strength is:

$$f_{\text{calc}}^{\Sigma}(JJ') = \frac{8}{3h(2J+1) <\lambda_{\text{abs}}>} \frac{(<n>^2 + 2)^2}{9 <n>} S_{\text{calc}}^{\text{ED}}(JJ') + f_{\text{calc}}^{\text{MD}}(JJ'). \quad (5)$$

Here, h is the Planck constant and $\langle n \rangle$ is the mean refractive index at $\langle \lambda_{\text{abs}} \rangle$. By applying the more advanced ICI model, which includes additional free parameters, the root mean square (r.m.s.) deviation between the experimental (f_{exp}) and calculated (f_{calc}) absorption oscillator strengths,

$$RMS = \sqrt{\sum_{i=1}^N \frac{[f_{\text{exp}}(i) - f_{\text{calc}}(i)]^2}{N - p}}, \quad (6)$$

is reduced from 0.539 to 0.415. Using the luminescence lifetime of the $^4\text{F}_{9/2}$ visible-emitting manifold as a reference, $\tau_{\text{lum}} = 1.38$ ms, for which negligible non-radiative relaxation is expected

according to the energy gap law ($\Delta E/h\nu_{ph} \gg 5$), the choice between the standard Judd–Ofelt and ICI models becomes clearer. The ICI model yields a radiative lifetime ($\tau_{rad} = 1.32$ ms) that is in much better agreement with the experimental value than that obtained from the standard model (1.77 ms), confirming the improved reliability of the ICI approach.

Table 1. Absorption Oscillator Strengths^a for Dy³⁺ Ions in InF₃-based Glass

${}^6H_{15/2} \rightarrow$ $2S + {}^1L_J$	$\langle E \rangle$, cm ⁻¹	Γ , cm ⁻¹ × nm	f_{exp} , 10 ⁻⁶	f_{calc} , J-O 10 ⁻⁶	f_{calc} , ICI 10 ⁻⁶
${}^6H_{13/2}$	3461.2	108.6	1.499	1.028 ^{ED} + 0.336 ^{MD}	0.824 ^{ED} + 0.336 ^{MD}
${}^6H_{11/2}$	5897.3	28.04	1.080	0.958 ^{ED}	1.126 ^{ED}
${}^6H_{9/2} + {}^6F_{11/2}$	7802.6	43.72	2.952	3.021 ^{ED}	2.983 ^{ED}
${}^6F_{9/2} + {}^6H_{7/2}$	9146.7	24.80	2.294	3.021 ^{ED}	2.983 ^{ED}
${}^6H_{5/2} + {}^6F_{7/2}$	11070	16.60	2.249	2.371 ^{ED}	2.382 ^{ED}
${}^6F_{5/2}$	12461	8.42	1.451	1.035 ^{ED}	1.250 ^{ED}
${}^6F_{3/2} + {}^6F_{1/2}$	13270	2.91	0.543	0.197 ^{ED}	0.239 ^{ED}
${}^4F_{9/2}$	21126	0.594	0.294	0.179 ^{ED}	0.216 ^{ED}
${}^4I_{15/2}$	22204	0.784	0.427	0.356 ^{ED} + 0.089 ^{MD}	0.498 ^{ED} + 0.089 ^{MD}
${}^4G_{11/2}$	23459	0.255	0.155	0.114 ^{ED}	0.091 ^{ED}
${}^4F_{7/2} + {}^4I_{13/2} + {}^4M_{21/2} + {}^4K_{17/2}$	25828	2.76	2.031	2.204 ^{ED} + 0.007 ^{MD}	2.690 ^{ED} + 0.007 ^{MD}
${}^6P_{5/2} + {}^4I_{11/2} + {}^6P_{7/2} + {}^4M_{15/2} + {}^4D_{5/2} + {}^4I_{9/2}$	28618	7.17	6.347	6.011 ^{ED} + 0.011 ^{MD}	6.281 ^{ED} + 0.011 ^{MD}
${}^4G_{9/2} + {}^6P_{3/2} + {}^4M_{17/2}$	30809	1.75	2.162	0.950 ^{ED}	1.386 ^{ED}
${}^2K_{13/2} + {}^4F_{3/2} + {}^4K_{13/2} + {}^4D_{7/2} + {}^4H_{11/2} + {}^4H_{9/2} + {}^4F_{5/2}$	33751	1.14	1.447	1.017 ^{ED} + 0.015 ^{MD}	1.264 ^{ED} + 0.015 ^{MD}
r.m.s. dev.				0.539	0.415

^a f_{exp} and f_{calc} – experimental and calculated absorption oscillator strengths, respectively, Γ – integrated absorption coefficient, ED – electric dipole, MD – magnetic dipole.

The intensity parameters parameters for both ions (Er³⁺ and Dy³⁺) obtained using the standard parametrization scheme (J-O theory – Ω_k), as well as its modifications (mJ-O – Ω_k and α , and ICI – Ω_k and R_k , all for $k = 2, 4, 6$), are listed in Table 2. Here, we provide the values for the standard J-O theory as a reference for adequate comparison with the previous studies.

Table 2. Intensity Parameters of Er³⁺ and Dy³⁺ Ions in InF₃-based Glasses

Ion	Model	Ω_2 , 10 ⁻²⁰ cm ²	Ω_4 , 10 ⁻²⁰ cm ²	Ω_6 , 10 ⁻²⁰ cm ²	α , 10 ⁻⁴ cm	R_2 , 10 ⁻⁴ cm	R_4 , 10 ⁻⁴ cm	R_6 , 10 ⁻⁴ cm
Er ³⁺	J-O	1.950	2.006	1.338	–	–	–	–
	mJ-O	1.894	1.979	1.357	0.016	–	–	–
Dy ³⁺	J-O	0.139	3.669	2.612	–	–	–	–
	ICI	1.509	3.063	3.601	–	-0.215	0.228	0.049

The probabilities of spontaneous radiative transitions are calculated as following:

$$A_{\Sigma}^{calc}(JJ') = \frac{64\pi^4 e^2}{3h(2J' + 1) < \lambda_{em} >^3} n \left(\frac{n^2 + 2}{3} \right)^2 S_{ED}^{calc}(JJ') + A_{MD}(JJ'). \quad (7)$$

Here, the line strengths were determined using the intensity parameters (mJ-O theory for Er³⁺ and ICI theory for Dy³⁺), based on the corresponding reduced squared matrix elements $U^{(k)}$ for transitions in emission. The MD contributions were calculated separately, as described above.

The mean emission wavelength for each $J \rightarrow J'$ transition, $\langle \lambda_{em} \rangle$, was estimated from the barycenters of absorption bands. Using the calculated spontaneous emission probabilities for the individual transitions, we determined the total radiative probability A_{tot}^{calc} , the radiative lifetimes of the excited states τ_{rad} , and the luminescence branching ratios $\beta_{JJ'}$ for the individual emission channels $J \rightarrow J'$:

$$\tau_{rad} = \frac{1}{A_{tot}^{calc}}, \text{ where } A_{tot}^{calc} = \sum_{JJ'} A_{\Sigma}^{calc}(JJ'), \quad (8a)$$

$$\beta_{JJ'} = \frac{A_{\Sigma}^{calc}(JJ')}{\sum_{JJ'} A_{\Sigma}^{calc}(JJ')}. \quad (8b)$$

Table 3 summarizes selected probabilities of spontaneous radiative transitions for Er^{3+} and Dy^{3+} ions in InF_3 -based glass relevant for laser development. Regarding emission around $3 \mu\text{m}$, the radiative lifetimes of the $^4\text{I}_{11/2}(\text{Er}^{3+})$ and $^4\text{I}_{13/2}(\text{Er}^{3+})$ manifolds amount to 7.63 ms and 7.98 ms, and the luminescence branching ratio for the $^4\text{I}_{11/2} \rightarrow ^4\text{I}_{13/2}$ Er^{3+} transition is relatively high, 20.8%. For Dy^{3+} ions, the two lowest lying excited states exhibit radiative lifetimes of 43.35 ms ($^6\text{H}_{13/2}$) and 12.02 ms ($^6\text{H}_{11/2}$), and $\beta(^6\text{H}_{11/2} \rightarrow ^6\text{H}_{13/2})$ reaches 8.3%.

Table 3. Selected Probabilities^a of Spontaneous Radiative Transitions of Er^{3+} and Dy^{3+} Ions in InF_3 -based Glasses Relevant for Infrared Emission

Ion	Emitting state	Terminal state	$\langle \lambda_{em} \rangle$, μm	A_{rad} , s^{-1}	$\beta_{JJ'}$, %	τ_{rad} , ms
Er^{3+} (mJ-O)	$^4\text{I}_{13/2} \rightarrow$	$^4\text{I}_{15/2}$	1.51	$91.3^{\text{ED}} + 34.0^{\text{MD}}$	100	7.98
	$^4\text{I}_{11/2} \rightarrow$	$^4\text{I}_{13/2}$	2.74	$15.5^{\text{ED}} + 7.3^{\text{MD}}$	20.8	7.63
		$^4\text{I}_{15/2}$	0.975	108.2^{ED}	76.2	
	$^4\text{I}_{9/2} \rightarrow$	$^4\text{I}_{15/2}$	0.810	138.2^{ED}	78.5	5.60
	$^4\text{F}_{9/2} \rightarrow$	$^4\text{I}_{9/2}$	3.45	$1.5^{\text{ED}} + 2.5^{\text{MD}}$	0.3	0.732
		$^4\text{I}_{15/2}$	0.656	1248.7^{ED}	91.0	
	$^4\text{S}_{3/2} + ^2\text{H}_{11/2} \rightarrow$	$^4\text{I}_{15/2}$	0.527	3958.2^{ED}	82.3	0.208
Dy^{3+} (ICI)	$^6\text{H}_{13/2} \rightarrow$	$^6\text{H}_{15/2}$	2.89	$16.4^{\text{ED}} + 6.7^{\text{MD}}$	100	43.35
	$^6\text{H}_{11/2} \rightarrow$	$^6\text{H}_{13/2}$	4.11	$2.9^{\text{ED}} + 4.0^{\text{MD}}$	8.3	12.02
		$^6\text{H}_{15/2}$	1.69	76.3^{ED}	91.7	
	$^6\text{H}_{9/2} + ^6\text{F}_{11/2} \rightarrow$	$^6\text{H}_{11/2}$	5.25	$5.3^{\text{ED}} + 2.0^{\text{MD}}$	1.6	2.20
		$^6\text{H}_{13/2}$	2.30	$76.2^{\text{ED}} + 0.9^{\text{MD}}$	17.0	
		$^6\text{H}_{15/2}$	1.28	369.6^{ED}	81.4	

^a A_{rad} – probability of radiative spontaneous transition, τ_{rad} – radiative lifetime, $\beta_{JJ'}$ – luminescence branching ratio, $\langle \lambda_{em} \rangle$ – mean emission wavelength.

It is worth comparing the radiative transition probabilities with other fluoride compounds with a close phonon spectrum. Fleischman *et al.* estimated the radiative lifetime for the $^6\text{H}_{13/2}$ manifold for the $\text{Dy}^{3+}:\text{BaF}_2$ crystal with a glassy like spectral properties using an independent method of calculating the SE cross-sections at $3 \mu\text{m}$ by a combination of McCumber equation and Füchtbauer-Ladenburg (F-L) formula yielding $\tau_{rad} = 45.9$ ms being in agreement with our analysis [34]. Normani *et al.* applied the standard J-O theory to $\text{Er}^{3+}:\text{BaF}_2$ crystal giving $\tau_{rad} = 7.11$ ms ($^4\text{I}_{11/2}$) and 7.52 ms ($^4\text{I}_{13/2}$) which again well matches our results [35].

2.4. Stimulated-emission cross-sections and phonon sideband

The luminescence spectra around $3 \mu\text{m}$ were measured using an optical spectrum analyzer (OSA, Yokogawa AQ6377E) operating at 2 nm spectral resolution. A 960 nm diode laser served as excitation source. The emitted light was gathered with an uncoated CaF_2 lens and directed

straight into the OSA purged with N₂ gas. Calibration of the measurement setup was performed using a SiC globar lamp (ARCLIGHT-MIR, Arcoptix).

The stimulated-emission (SE), σ_{SE} , cross-sections for the $^4I_{11/2} \rightarrow ^4I_{13/2}$ Er³⁺ and $^6H_{13/2} \rightarrow ^6H_{15/2}$ Dy³⁺ transitions were derived using the F-L formula [36]:

$$\sigma_{SE}(\lambda) = \frac{\lambda^5}{8\pi n^2 \tau_{rad} c} \times \frac{\beta(JJ')I(\lambda)}{\int \lambda I(\lambda) d\lambda}, \quad (9)$$

where λ is the wavelength of light, n is the refractive index of the host glass at the mean emission wavelength, c is the speed of light, τ_{rad} is the radiative lifetime of the emitting state ($^4I_{11/2}$ Er³⁺ and $^6H_{13/2}$ Dy³⁺), $\beta_{JJ'}$ is the luminescence branching ratio, and $I(\lambda)$ is the measured luminescence spectral profile of the transition under consideration, calibrated for the instrument response function and corrected for structured water vapor absorption lines.

Figure 5(a) displays the σ_{SE} spectra of singly doped glasses around 3 μ m. The SE cross-sections reach 0.74×10^{-20} cm² at 2712 nm and 0.31×10^{-20} cm² at 2924 nm for Er³⁺ and Dy³⁺ ions, respectively. Dy³⁺ exhibits much broader emission bandwidth at the expense of lower SE cross-sections. Physically, this is related to larger terminal level splitting for this ion (as compared to the $^4I_{13/2}$ Er³⁺ manifold), as well as significantly longer radiative lifetime for the Dy³⁺ emitting state. On the same figure, we display the structured water vapor absorption lines (in grey). Er³⁺ luminescence strongly overlaps with this absorption, whereas Dy³⁺ emission, extending far beyond 3 μ m, is only weakly affected by water vapor in air. This suggests significantly better prospects for these ions in broadband laser wavelength tuning when employing hybrid cavities incorporating a free-space optical path.

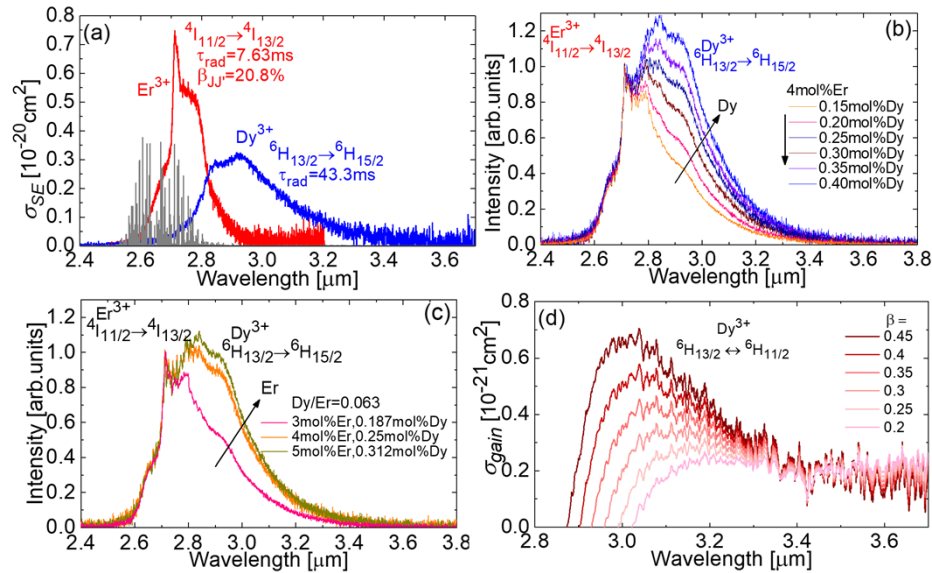


Fig. 5. Mid-infrared emission properties of Er³⁺ and Dy³⁺ ions in InF₃-based glasses: (a) stimulated emission (SE), σ_{SE} , cross-sections for the $^6H_{13/2} \rightarrow ^6H_{15/2}$ transition of Dy³⁺ and $^4I_{11/2} \rightarrow ^4I_{13/2}$ transition of Er³⁺, grey lines – water vapor absorption in air (arb. units); (b,c) emission spectra of codoped glasses under excitation at 0.96 μ m, normalized to Er³⁺ emission at 2.71 μ m: (b) fixed Er³⁺ content, varied Dy³⁺: 4 mol% Er³⁺, x mol% Dy³⁺ codoped glasses ($x = 0.15$ – 0.4), (c) constant Dy³⁺/Er³⁺ codoping ratio: y mol% Er³⁺, z mol% Dy³⁺ codoped glasses ($z/y = 0.063$); (d) gain spectral profiles of Dy³⁺ ions, σ_{gain} , for various population inversion ratios β .

Regarding the $\text{Er}^{3+}, \text{Dy}^{3+}$ -codoped InF_3 -based glasses, we first studied those with a fixed Er^{3+} content of 4 mol% and a varying content of Dy^{3+} (ranging from 0.15 to 0.40 mol%). By exciting glasses using an InGaAs laser diode at 960 nm (to the $^4\text{I}_{11/2}(\text{Er}^{3+})$ state), broadband emission around 3 μm originating from both ions was observed, as shown in the Fig. 5(b). In this figure, the spectra are normalized to Er^{3+} emission at 2.71 μm . The Dy^{3+} ions in the codoped glasses are excited via two phonon-assisted energy-transfer (ET) processes, cf. Figure 1(a), ET1: $^4\text{I}_{13/2}(\text{Er}^{3+}) \rightarrow ^6\text{H}_{11/2}(\text{Dy}^{3+})$ and ET2: $^4\text{I}_{11/2}(\text{Er}^{3+}) \rightarrow ^6\text{H}_{5/2}(\text{Dy}^{3+})$. By progressively increasing the Dy^{3+} content, the relative intensity of its emission was enhanced. The broadest emission profile was observed for the 4 mol% Er^{3+} , 0.4 mol% Dy^{3+} codoped glass, exhibiting a bandwidth (FWHM) of 328 nm owing to the efficient energy-transfer from Er^{3+} to Dy^{3+} .

For the second set of glasses with a fixed Dy/Er codoping ratio (0.063) and varying Er^{3+} concentrations of 3 to 5 mol%, the luminescence spectra are shown in Fig. 5(c). The sample with the highest Er^{3+} concentration (5 mol%) exhibits the strongest overall emission intensity. Note that the luminescence intensities and spectral profiles of the 4 mol% and 5 mol% Er^{3+} doped glasses are comparable. Therefore, the luminescence dynamics must be examined to further clarify the differences between these glass compositions, in relation to concentration quenching effects.

The $^6\text{H}_{13/2} \rightarrow ^6\text{H}_{15/2}$ transition of Dy^{3+} ions is of quasi-3-level nature with reabsorption from the ground state and thus gain cross-sections, $\sigma_{\text{gain}} = \beta\sigma_{\text{SE}} - (1 - \beta)\sigma_{\text{abs}}$, have been calculated for various inversion ratios $\beta = N_2(^6\text{H}_{13/2})/N_{\text{dop}}$, where N_2 is the population of the first excited state. The results are shown in Fig. 5(d) for β ranging from 0.2 to 0.45. For higher inversion levels, the maximum in the gain profiles experiences a blue shift due to the ground state bleaching and reduced reabsorption. It is expected that in the free-running regime, without any spectrally selective elements in the cavity, Dy^{3+} :fluoroindate glass lasers will operate between 3 and 3.2 μm , in agreement with the previous reports [7,23]. For $\beta = 0.3$, the gain bandwidth (FWHM) is about 500 nm indicating an excellent potential for wavelength tuning.

The broad gain profile of Dysprosium in the InF_3 -based glass originates from both intrinsic and host-related factors. Dy^{3+} is characterized by a relatively large crystal-field splitting of its ground multiplet $^6\text{H}_{15/2}$, yielding eight Kramers doublets (or a distribution of sublevels in amorphous hosts). Furthermore, relatively strong electron–phonon coupling (among other rare-earth ions) contributes to vibronic broadening. In fluoride glasses, structural disorder induces additional inhomogeneous broadening.

We further examined the long-wavelength, phonon-assisted (Stokes) emission of Dy^{3+} ions associated with the $^6\text{H}_{13/2} \rightarrow ^6\text{H}_{15/2}$ electronic transition. For this, we used a sensitive detection setup including a monochromator (Oriel 74086), a lock-in amplifier (SR810 DSP, Stanford Research Systems), and a liquid N_2 cooled InSb detector with a preamplifier, and a 915 nm laser diode (Lumics) as excitation source. This emission extends to wavelengths of at least 4 μm and originates from multiphonon-assisted radiative relaxation processes. These transitions terminate in a manifold of vibronic levels formed through the interaction of both Raman- and infrared-active phonons from the host lattice phonon bath with the higher-lying Stark sublevels of the $^6\text{H}_{15/2}$ ground-state manifold. The measured luminescence spectrum was subsequently transformed into the SE cross-section profile using the F–L equation, as shown in Fig. 6. The latter shows a nearly exponential profile which was then fitted using the expression [37,38]:

$$\sigma_{\text{SE},ph}(\lambda) = \sigma_{\text{SE},0} e^{-\alpha_S \Delta E}, \quad (10)$$

where ΔE represents the energy mismatch between the vibronic and the purely electronic transitions, and $\sigma_{\text{SE},0}$ denotes the cross-section at the photon energy of the electronic transition. The Stokes factor, α_S , is host dependent. The exponential dependence reflects a weak ion–lattice (electron–phonon) coupling, which is characteristic of $4f^n$ transitions in rare-earth ions. The

Stokes factor α_S is given by [39]:

$$\alpha_S = \frac{1}{h\nu_{ph}} \ln \left[\frac{\langle N \rangle}{S_0 (\langle n \rangle + 1)} - 1 \right], \quad (11)$$

where $h\nu_{ph}$ is the maximum phonon energy of the host lattice, $\langle N \rangle$ is the average number of phonons participating in the phonon-assisted transition, S_0 is the Pekar–Huang–Rhys coupling constant, and $\langle n \rangle$ is the occupation number of the effective phonon mode with energy $h\nu_{ph}$.

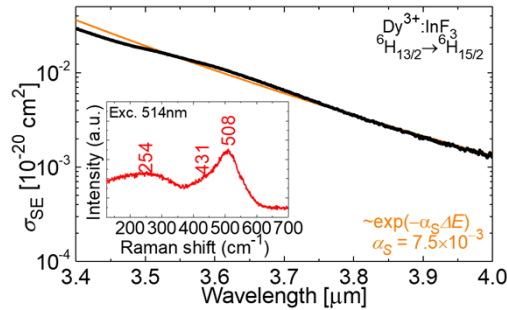


Fig. 6. Stokes multiphonon emission sideband of Dy^{3+} ions associated with the ${}^6\text{H}_{13/2} \rightarrow {}^6\text{H}_{15/2}$ transition, inset – Raman spectrum of the glass, $\lambda_{exc} = 514$ nm.

Our analysis yields $\alpha_S = 7.5 \pm 0.5 \times 10^{-3}$ cm, being close to the value reported recently for the BaF_2 crystal, $\alpha_S = 7.9 \times 10^{-3}$ cm [40].

The inset of Fig. 6 shows the Raman spectrum of the fluoroindate glass, which exhibits three broad bands centered at 254, 431, and 508 cm^{-1} , characteristic of the vibrational modes of the indium–fluoride network [41]. The band at 254 cm^{-1} is attributed to F–In–F bending vibrations and In–F–In bridging modes, reflecting network connectivity, while the sideband at 431 cm^{-1} corresponds to the symmetric stretching vibrations of In–F bonds within distorted $[\text{InF}_6]^{3-}$ octahedra. The higher-frequency intense band at 508 cm^{-1} is associated with asymmetric In–F stretching modes and the presence of non-bridging fluorine atoms, indicating partial depolymerization of the glass network. ZrF_4 based fluoride glasses (ZBLAN) exhibit a higher maximum phonon energy (570 cm^{-1}) because its network is primarily built from $[\text{ZrF}_6]^{3-}$ octahedra containing lighter Zr^{4+} cations and relatively stronger Zr–F bonds. According to lattice vibrational theory ($\nu \propto (k/\mu)^{1/2}$) [42], the lower reduced mass (μ) of the Zr–F bond and its comparatively higher bond force constant (k) shift the vibrational frequencies toward higher wavenumbers. In contrast, the heavier In^{3+} cation in fluoroindate glass increases the reduced mass of the In–F bond, resulting in lower vibrational frequencies, which is favorable for reducing the non-radiative path, especially for mid-infrared transitions.

2.5. Luminescence lifetimes, energy transfer and non-radiative relaxation

The luminescence decay from the ${}^4\text{I}_{13/2}$ and ${}^4\text{I}_{11/2}$ Er^{3+} manifolds was investigated using a nanosecond optical parametric oscillator (*Horizon*, Continuum) as excitation source. The emission was recorded with an experimental setup comprising a monochromator (*Oriel 77200*), InGaAs detectors (*Hamamatsu*), a preamplifier (*DHPCA-100*, *FEMTO*), and an 8 GHz digital oscilloscope (*DSA70804B*, *Tektronix*). For the decay from the ${}^6\text{H}_{13/2}$ Dy^{3+} manifold, we used the setup comprising a liquid N_2 cooled InSb detector described above, coupled with the same oscilloscope.

To quantify the ET efficiency for the codoped glasses, the luminescence lifetimes τ_{lum} of the donor (D, Er^{3+}) manifolds, ${}^4\text{I}_{11/2}$ and ${}^4\text{I}_{13/2}$, were measured without and with acceptor (A,

Dy³⁺) ions, Fig. 7(a,b). For the singly Er³⁺ doped glass, they amount to 8.09 ms and 10.18 ms, respectively, being reasonably close to the corresponding radiative lifetimes (7.63 ms and 7.98 ms, respectively) thus indicating an almost unity quantum efficiency which is expected for these manifolds according to the energy-gap law. The residual difference is mainly assigned to the reabsorption (radiation trapping) effects in bulk glass, as well as precision of the J-O theory. Upon codoping with Dy³⁺ ions, both Er³⁺ luminescence lifetimes progressively shorten, see Fig. 7(a,b).

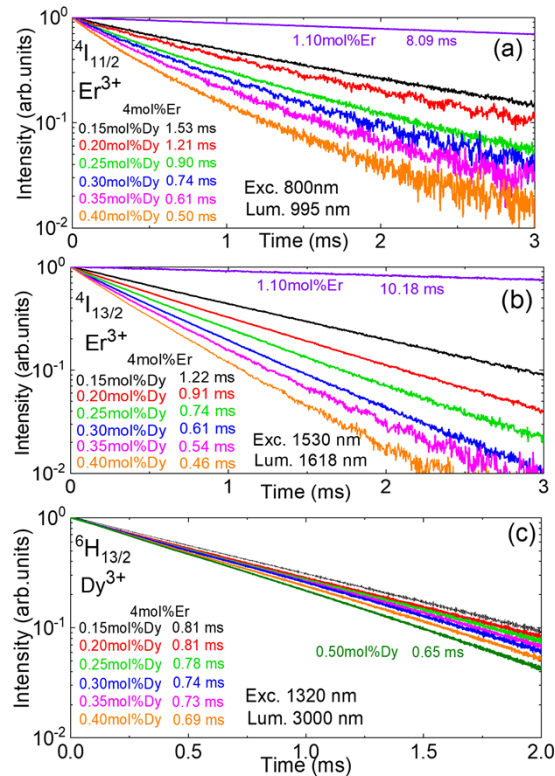


Fig. 7. Luminescence dynamics of Er^{3+} and Dy^{3+} ions in InF_3 -based glasses: (a) $4I_{11/2}$ Er^{3+} ; (b) $4I_{13/2}$ Er^{3+} and (c) $6H_{13/2}$ Dy^{3+} manifolds.

The luminescence decay from the $6H_{13/2}$ Dy^{3+} manifold is illustrated in Fig. 7(c). For all the studied glass compositions, the decay is close to single exponential. The luminescence lifetime decreases with Dy^{3+} content, from 0.81 ms to 0.69 ms (0.15–0.40 mol% Dy^{3+} in the codoped glass) and further to 0.65 ms (0.50 mol% Dy^{3+} , singly doped glass), see Fig. 8. These values are well below the radiative lifetime (43.35 ms) due to a significant multiphonon non-radiative relaxation for this transition. The luminescence quantum efficiency $\eta_q = \tau_{lum}/\tau_{rad}$ is $\sim 2\%$ for the lowest studied Dy^{3+} content. Fleischman *et al.* reported on the $6H_{13/2}$ luminescence lifetime for the 1 at.% Dy^{3+} :BaF₂ crystal of 1.56 ms at room temperature ($\eta_q = 3.4\%$) [34]. The observed concentration quenching of the 3- μ m luminescence of Dy^{3+} is predominantly governed by energy migration to non-radiative quenching centers, such as defects and impurities, whereas ion clustering is likely negligible within the investigated concentration range.

The ET efficiency is then calculated as $\eta_{ET} = 1 - \tau_{DA}/\tau_D$, as depicted by curves in Fig. 8(a). For the 4 mol% Er^{3+} , 0.4 mol% Dy^{3+} codoped glass, this formula yields $>94\%$ for both ET processes, indicating an efficient $Er^{3+} \rightarrow Dy^{3+}$ energy transfer.

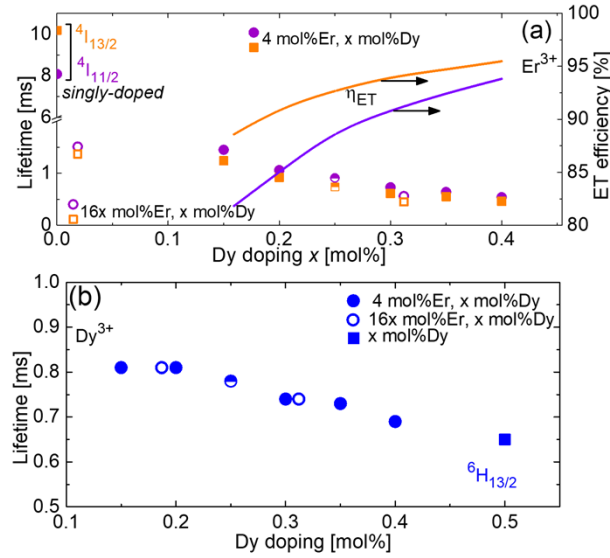


Fig. 8. Luminescence lifetimes and energy transfer (ET) efficiency in Er^{3+} , Dy^{3+} codoped InF_3 -based glasses: (a) $^4\text{I}_{11/2}$ and $^4\text{I}_{13/2}$ Er^{3+} manifolds; (b) $^6\text{H}_{13/2}$ Dy^{3+} manifold.

The low doping level of Dy^{3+} in codoped glasses reduces the energy transfer efficiency, whereas its high content introduces strong concentration quenching of luminescence. Therefore, a compromise between these processes must be achieved to realize an efficient Er^{3+} , Dy^{3+} codoped fluorindate fiber laser.

The rate of non-radiative relaxation from the $^6\text{H}_{13/2}$ state is $W_{NR} = (1/\tau_{lum}) - (1/\tau_{rad}) = 1.21 \times 10^3 \text{ s}^{-1}$ corresponding to an energy gap to the lower lying manifold of $\Delta E = 3466 \text{ cm}^{-1}$ (calculated based on the free-ion manifold energies). This value is notably higher than those for the $^4\text{I}_{11/2}$ Er^{3+} state ($25\text{--}38 \text{ s}^{-1}$, after Catunda *et al.* [43], and this work) and $^5\text{I}_6$ Ho^{3+} state (47 s^{-1} , after Gomes *et al.* [44]) even despite the energy gaps for the latter two manifolds are only slightly higher. It means that the exponential dependence of W_{NR} rate on ΔE ,

$$W_{NR} = Ce^{-\alpha\Delta E}, \quad (12)$$

where C is a constant corresponding to the nonradiative relaxation rate in the limit of a vanishing energy gap ($\Delta E \rightarrow 0$), and α is a material-dependent constant, which is usually well working for manifolds of various rare-earth ions in the same host matrix may not be sufficient for Dy^{3+} ions. To illustrate this, we systematically traced the W_{NR} rates for Er^{3+} , Tm^{3+} , Ho^{3+} , and Dy^{3+} ions (combining data from [44,45] and this work) in InF_3 -based glasses versus ΔE , as shown in Fig. 9. The best fit to the experimental data using Eq. (12) is shown by the grey line, yielding parameters of $C = 7.5 \times 10^9 \text{ s}^{-1}$ and $\alpha = 5.1 \times 10^{-3} \text{ cm}$. For comparison, our analysis of a BaF_2 single crystal gives $C = 2.1 \times 10^8 \text{ s}^{-1}$ and $\alpha = 4.0 \times 10^{-3} \text{ cm}$ [46]. The deviation of the experimental data points in Fig. 9 from the fitted curve may arise from several sources of uncertainty. These include: i) a reduction of the effective ΔE due to crystal-field splitting of rare-earth manifolds, which is difficult to accurately account for in glasses; ii) limitations in the accuracy of the Judd–Ofelt theory when estimating radiative lifetimes; and iii) the possible influence of additional quenching mechanisms affecting the measured luminescence lifetimes.

It is noteworthy that the multiphonon non-radiative relaxation rate for Dy^{3+} ions is higher than that predicted by the best-fit energy gap law. This was pointed out by Quimby and Saad for fluoride materials (crystals and glasses) [47]. The authors indicated that this observation is rather

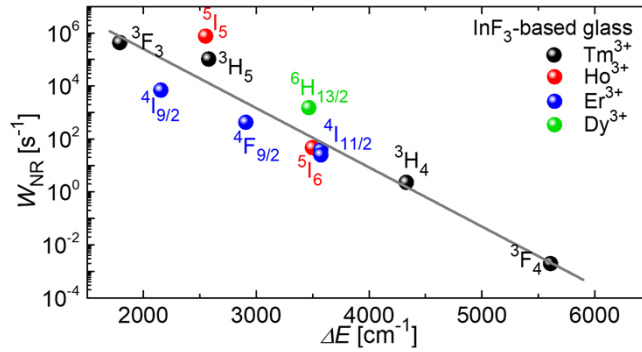


Fig. 9. Multiphonon non-radiative relaxation rates W_{NR} from excited manifolds of various rare-earth ions in fluorindate glasses plotted versus the energy gap to the next lower-lying level ΔE . Circles – data derived from the luminescence and radiative lifetimes, line – their fit using the energy-gap law, Eq. (12).

intrinsic to Dy^{3+} than host specific and propose that Dy^{3+} possesses stronger electron–phonon coupling, represented by larger interaction terms in the electron–phonon Hamiltonian. This enhanced coupling may be linked to relatively low-lying $5d$ energy levels in Dy^{3+} , which increase $4f$ – $5d$ mixing and strengthen vibrational interactions [48].

Orlovskii *et al.* reported that nonradiative relaxation rates of rare-earth ions scale with the squared reduced matrix elements $U^{(2)}$ of the corresponding electronic transitions [49], in agreement with the nonlinear theory of multiphonon relaxation [50]. This suggests that the dependence of W_{NR} on $U^{(2)}$ can be stronger than the conventional energy gap law. In Table 4, we list the calculated $U^{(k)}$ values for transition of Er^{3+} , Ho^{3+} , and Dy^{3+} ions originating from their first two excited states. It is remarkable that the $U^{(2)}$ values for transitions of Dy^{3+} ions from the ${}^6\text{H}_{13/2}$ and ${}^6\text{H}_{11/2}$ states are by an order of magnitude higher than the corresponding values for the Er^{3+} and Ho^{3+} ions, aligning with the observed enhanced non-radiative decay for the former ion.

Table 4. Squared Reduced Matrix Elements for Selected Transitions of Er^{3+} , Ho^{3+} and Dy^{3+} Ions

Ion	Emitting state	Terminal state	$U^{(2)}$	$U^{(4)}$	$U^{(6)}$
Er^{3+}	${}^4\text{I}_{13/2} \rightarrow$	${}^4\text{I}_{15/2}$	0.0195	0.1173	1.4316
	${}^4\text{I}_{11/2} \rightarrow$	${}^4\text{I}_{13/2}$	0.0331	0.1708	1.0864
		${}^4\text{I}_{15/2}$	0.0282	0.0003	0.3953
Ho^{3+}	${}^5\text{I}_7 \rightarrow$	${}^5\text{I}_8$	0.0248	0.1341	1.5199
	${}^5\text{I}_6 \rightarrow$	${}^5\text{I}_7$	0.0317	0.1331	0.9307
		${}^5\text{I}_8$	0.0083	0.0385	0.6912
Dy^{3+}	${}^6\text{H}_{13/2} \rightarrow$	${}^6\text{H}_{15/2}$	0.2459	0.4143	0.6838
	${}^6\text{H}_{11/2} \rightarrow$	${}^6\text{H}_{13/2}$	0.2597	0.4878	0.0328
		${}^6\text{H}_{15/2}$	0.0864	0.0396	0.6333

2.6. Overview of Dy^{3+} emission in low-phonon energy hosts

It is instructive to directly compare the probabilities of radiative and non-radiative transitions from the ${}^6\text{H}_{13/2}$ manifold of Dy^{3+} , which is responsible for emission at $3\ \mu\text{m}$ and beyond, in various low-phonon-energy host materials (both crystals and glasses), as shown in Table 5. A

clear trend emerges: moving from fluorides to chlorides and chalcogenides leads to a substantial increase in luminescence quantum efficiency, >95% in Ge–Al–Ga–Se glasses. However, the fabrication of high-optical-quality, low-loss materials of this type remains challenging due to the stringent purification requirements needed to suppress extrinsic absorption and scattering losses [51]. InF₃-based glasses represent a practical compromise, extending the performance limits of fluoride hosts while approaching the spectroscopic characteristics of Ba-containing fluoride crystals.

Table 5. Evaluation of Multiphonon Non-Radiative Relaxation Rates^a for the ⁶H_{13/2} Dy³⁺ Manifold in Different Low-Phonon-Energy Materials

Material	$h\nu_{ph,max}$, cm ⁻¹	τ_{rad} , ms	τ_{lum} , ms	η_q , %	W_{NR} , s ⁻¹	σ_{SE} , 10 ⁻²¹ cm ²	λ_{em} , μm	Ref.
Dy:ZrF ₄ -based glass	570	46.8	0.64	1.37	1.54×10^3	2.98	2.88	[52]
Dy:InF ₃ -based glass	508	43.4	0.81	1.87	1.21×10^3	3.10	2.92	This work
Dy:BaF ₂	319 ^{IR}	45.7	1.13	2.47	863.1	3.71	2.85	^b
Dy:Ga ₂ Ge ₅ S ₁₃ glass	435	9.89	1.42	14.4	603.1	–	2.97	[53]
Dy:CsGdCl ₃	~250	31.5	14.5	46.0	37.26	–	2.90	[53]
Dy:KPb ₂ Cl ₅	203	16.2	14.6	90.2	6.67	6.10	2.80	[54]
Dy:GeAsGaSe glass	257	6.20	6.00	96.8	5.38	9.30	3.00	[55]

^a τ_{rad} – radiative lifetime, τ_{lum} – luminescence lifetime, η_q – luminescence quantum efficiency, W_{NR} – multiphonon non-radiative relaxation rate, σ_{SE} – SE cross-section, λ_{em} – peak emission wavelength. ^bOur results, unpublished.

Figure 10 shows the dependence of the multiphonon nonradiative relaxation rate W_{NR} from the ⁶H_{13/2} manifold of Dy³⁺ ion on the maximum phonon energy of the host. The exponential energy-gap law can be extended to include the host maximum phonon energy $h\nu_{ph}$ [56,57]:

$$W_{NR} = Ce^{-\ln(\varepsilon)\frac{\Delta E}{h\nu_{ph}}}, \quad (13)$$

where ε denotes the ratio between the probabilities of m -phonon and $(m-1)$ -phonon relaxation processes. Assuming a near constant energy gap ΔE and neglecting the host dependence of the material parameters C and ε , the available experimental data for W_{NR} were fitted using Eq. (12). The model provides a reasonably good description of the observed evolution of the nonradiative relaxation rate with increasing maximum phonon energy of the host matrix.

2.7. Laser action in Er³⁺, Dy³⁺-codoped glass

A preliminary laser experiment was conducted using a bulk 4 mol% Er³⁺, 0.4 mol% Dy³⁺ co-doped fluoroindate glass slab to demonstrate its functionality for broadband mid-infrared emission. The sample was mounted on a water-cooled (12 °C) copper holder. A nearly hemispherical cavity was formed by a plane dichroic pump mirror (HT at 0.98 μm, HR at 2.7–3.35 μm) and a concave output coupler (radius of curvature: –100 mm) with ~0.5% transmission over 2.8–3.4 μm. The gain medium was positioned close to the input mirror. Pumping was provided by an Yb-fiber laser (Azur Light Systems, ALS-IR-122) operating at 975.8 nm (laser linewidth: 0.3 nm, M² = 1.02), exciting the ⁴I_{15/2} → ⁴I_{11/2} Er³⁺ transition. The pump beam was focused with an antireflection-coated achromatic lens (f = 75 mm). Residual pump light was suppressed using a long-pass filter (LP1300, Spectrogon). Emission spectra were recorded with an optical spectrum analyzer (Yokogawa AQ6376) via an InF₃-based fiber (Thorlabs).

Continuous-wave laser action was achieved in the codoped glass. The laser thresholds for Er³⁺ and Dy³⁺ oscillations amounted to $P_{th,Er}$ = 118 mW and $P_{th,Dy}$ = 171 mW. They only slightly increased with respect to the value for the singly 4 mol% Er³⁺ doped glass ($P_{th,Er}$ = 42 mW). At high pump levels, colasing of both ions was observed. Representative laser emission

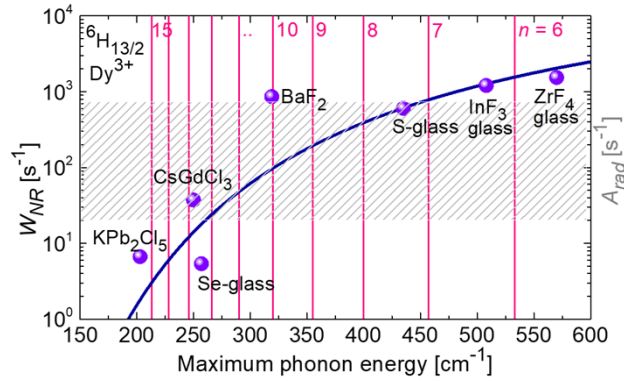


Fig. 10. The relationship between the multiphonon non-radiative relaxation rate W_{NR} from the ${}^6H_{13/2}$ Dy^{3+} manifold and the maximum host phonon energy for different laser materials. Circles – experimental data derived from the luminescence and radiative lifetimes, curve – their fit using Eq. (13), vertical lines mark n -phonon transitions, dashed area – the range of radiative emission probabilities A_{rad} .

spectra, recorded well above threshold, are shown in Fig. 11. The Er^{3+} laser lines span 2.715–2.792 μm clearly located between structured atmospheric water vapor absorption lines and closely matching the spectral gain profile. The Dy^{3+} laser lines appear at 2.911–2.924, 3.065–3.136 and 3.234–3.399 μm (the latter range limited by the OSA's sensitivity). The periodic modulation visible in the spectrum is due to the etalon (Fabry-Pérot) effect at the glass/input mirror interface. These preliminary laser results provide strong evidence for the significant potential of InF_3 -based glass fibers codoped with Er^{3+} and Dy^{3+} ions, employing optimized compositions, as broadly tunable laser sources spanning the ultrabroad 2.7–3.4 μm spectral range and potentially extending beyond. Efficient pumping can be achieved using conventional $InGaAs$ diode lasers operating near 960–980 nm.

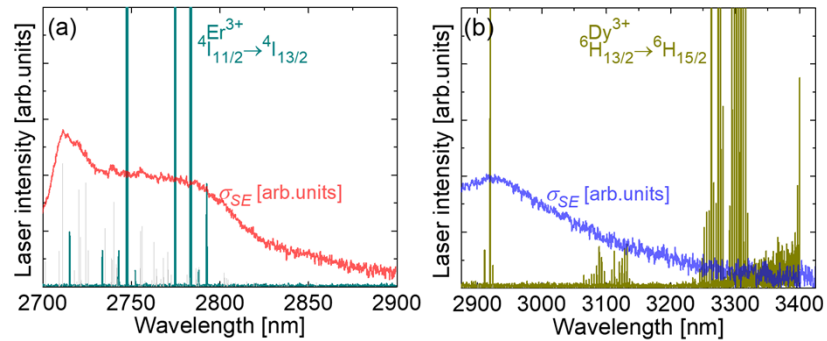


Fig. 11. Free-running, continuous-wave laser spectra of 4 mol% Er^{3+} , 0.4 mol% Dy^{3+} codoped bulk InF_3 -based glasses: (a) Er^{3+} and (b) Dy^{3+} contributions. The σ_{SE} spectral profiles of both ions are shown for comparison. Grey lines – water vapor absorption. The periodic modulation of the Dy^{3+} laser spectrum is due to the etalon effect at the glass / mirror interface.

2.8. Laser action in $\text{Er}^{3+}, \text{Dy}^{3+}$ -codoped fiber

A double-clad fluoroindate glass fiber co-doped with Er^{3+} and Dy^{3+} ions was developed by *Le Verre Fluoré* following the spectroscopic study described above. The fiber featured a 10 μm core with a numerical aperture (NA) exceeding 0.20, enabling single-mode operation beyond 3.4 μm . The active core was doped with 4 mol% Er^{3+} and 0.4 mol% Dy^{3+} to optimize mid-infrared gain performance. The inner cladding had a circular diameter of 125 μm and was surrounded by a low-index fluoroacrylate coating, resulting in an outer cladding diameter of 240 μm . A schematic of the laser configuration is presented in Fig. 12(a). A fiber length of 10 m was chosen to ensure sufficient gain at longer wavelengths. Both fiber end facets were angle-cleaved at 10° to suppress parasitic lasing and minimize unwanted feedback.

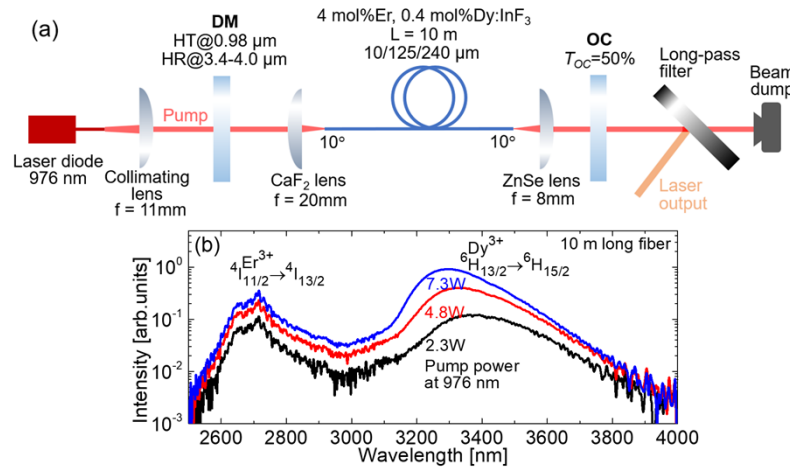


Fig. 12. Diode-pumped mid-infrared $\text{Er}^{3+}, \text{Dy}^{3+}:\text{InF}_3$ -based fiber laser: (a) scheme of the laser setup, DM: dichroic pump mirror, OC: output coupler; (b) spectra of amplified spontaneous emission from the fiber measured at different pump levels.

The linear laser cavity was formed by two external mirrors: a plane pump dichroic mirror (DM) coated for high transmission (HT) at 976 nm and high reflectivity (HR) spanning 3.4–4.0 μm , and a plane output coupler (OC) which exhibited a transmission (T_{OC}) of $50 \pm 2\%$ over 3.2–3.4 μm . The pump source was a spatially multimode, fiber-coupled (core diameter: 105 μm , NA = 0.22) InGaAs laser diode (*BWT Beijing Ltd.*) delivering a maximum output power of 30 W at 976 nm. The pump beam was collimated using an antireflection-coated aspherical lens ($f = 11$ mm) and subsequently coupled into the inner cladding through a plano-convex CaF_2 lens ($f = 20$ mm). To filter out the residual pump, we employed an identical DM acting as a long-pass filter, placed at 22° . Laser emission spectra were recorded with a laser spectrum analyzer (*Bristol Instruments*, 771B-IR) having a spectral resolution of 0.3 nm around 3300 nm. The laser cavity initially employed a pair of identical short focal length lenses, which resulted in premature damage to the pump fiber facet. Using a focusing lens with a longer focal length lens led to a noticeable improvement, with the onset of damage occurring at higher pump levels and a reduction in the lasing threshold.

Prior to the laser experiments, the amplified spontaneous emission (ASE) spectra of the fiber were measured. Fluorescence was collected in the forward-propagation direction without cavity mirrors to avoid any spectral filtering. Spectra were recorded over 2.5–4.0 μm using a Fourier-transform infrared spectrometer equipped with a liquid-nitrogen-cooled HgCdTe detector (*ARCoptix*, FTIR Rocket 2–16 μm). A long-pass filter (*Spectrogon*, LP2440) was employed to remove residual pump light. The ASE spectra at various launched pump powers P_l are

shown on a semi-log scale in Fig. 12(b). The emission is remarkably broad, spanning the entire monitored range, demonstrating the potential of the designed fiber for broadly tunable mid-infrared lasers. At P_l up to 2 W, the $^4I_{11/2} \rightarrow ^4I_{13/2}$ Er^{3+} emission dominates. At higher pump levels, the longer-wavelength $^6H_{13/2} \rightarrow ^6H_{15/2}$ Dy^{3+} emission which spectral shape is affected by reabsorption from the ground state gradually increases, providing direct evidence of efficient non-radiative $\text{Er}^{3+} \rightarrow \text{Dy}^{3+}$ energy transfer. Furthermore, the peak wavelength of the Dy^{3+} band shifts from 3.36 μm at $P_l = 2.3$ W to 3.29 μm at a higher pump level of $P_l = 7.8$ W, consistent with increased ground-state bleaching and weaker reabsorption effect.

The performance characteristics of the Er,Dy:InF_3 -based fiber laser are presented in Fig. 13. The laser achieved a maximum continuous-wave output power of 93 mW at 3.309–3.335 μm , with a slope efficiency η of 3.7% relative to the launched pump power and a threshold of 4.79 W, Fig. 13(a). In a repeated experiment, a higher output power of 143 mW at 3.275–3.292 μm was achieved with a comparable slope efficiency, although this was accompanied by an increased lasing threshold. The blue shift of the laser spectrum, together with the increased threshold power, indicates higher roundtrip losses, most likely resulting from reduced fiber cleaving quality. No Er^{3+} colasing at 2.8 μm was observed in both cases. Both laser emission spectra, acquired well above threshold, together with the transmission spectra of the cavity mirrors, are shown in Fig. 13(b). It should be noted that leakage of mid-infrared emission through the DM cannot be excluded, owing to its non-negligible transmission at the laser wavelengths.

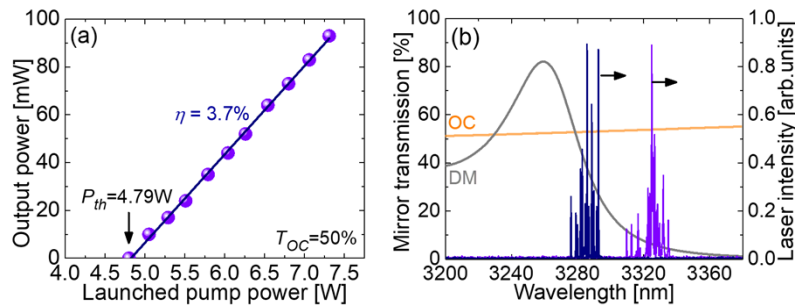


Fig. 13. Mid-infrared laser performance of the $\text{Er}^{3+}, \text{Dy}^{3+}:\text{InF}_3$ -based fiber: (a) power transfer curve, η – slope efficiency, P_{th} – laser threshold; (b) laser emission spectra for two successive experiments, the transmission spectra of both cavity mirrors (DM, dichroic mirror; OC, output coupler), are shown for comparison.

Further power scaling was limited by damage to the pumped fiber end facet. Microscopic examination indicated that the damage was confined to the core, while the inner cladding remained intact and continued to support light guidance. Hydroxyl (OH) absorption is a well-known limiting factor in mid-infrared fiber performance, particularly around 2.8 μm , where the fundamental O–H vibrational overtone strongly overlaps with Er^{3+} laser emission [58]. In fluoride fibers, such as ZrF_4 or InF_3 based, trace amounts of OH groups can arise from residual moisture during fabrication process. At the fiber end facet, humid air reacts with metal–fluoride bonds via hydrolysis, forming a thin OH-rich surface layer [59]. This process occurs rapidly at freshly cleaved surfaces. The generated hydroxyl groups introduce strong absorption near 2.8 μm , causing localized heating under laser irradiation. Indium fluoride glasses tend to have a more open structure and higher chemical reactivity, which facilitates surface hydration (as compared to ZrF_4 glasses). We suspect that the observed damage is initiated by the onset of Er^{3+} colasing at 2.8 μm . This overlap leads to intense localized absorption at the fiber end facet, causing rapid heating and potentially triggering micro-explosive damage at the fiber tip. Note that we always operated below the thermal damage threshold of the fiber.

Further improvements in output power and extension toward longer wavelengths are anticipated by: i) employing optimized broadband cavity mirrors, ii) protecting the fiber facets with endcaps, and iii) increasing the inner cladding diameter to enhance pump-coupling efficiency and reduce the thermal load at the input facet.

3. Conclusions

In conclusion, dysprosium ions in fluorindate glasses constitute a highly promising material platform for ultrabroadband mid-infrared emission. In case of single doping, they combine a broad ${}^6\text{H}_{13/2} \rightarrow {}^6\text{H}_{15/2}$ emission extending to at least $4\text{ }\mu\text{m}$, supported by a Stokes multiphonon sideband, with a reasonably high stimulated-emission cross-section of $0.31 \times 10^{-20}\text{ cm}^2$ at 2924 nm , and relatively weak concentration quenching of luminescence. The luminescence lifetime of the ${}^6\text{H}_{13/2}$ manifold decreases from 0.81 to 0.50 ms when the DyF_3 concentration is increased up to $0.5\text{ mol}\%$. The anomalously strong multiphonon non-radiative decay from this level, however, requires further investigation.

Codoping with Er^{3+} and Dy^{3+} ions enables pumping at conventional wavelengths around $0.98\text{ }\mu\text{m}$ while providing a combined gain bandwidth from both ions. A $\text{Dy}^{3+}/\text{Er}^{3+}$ codoping ratio of about $1:10$ appears close to optimal for achieving high energy-transfer efficiencies ($>95\%$), whereas the Dy^{3+} concentration must remain sufficiently low to prevent excessive luminescence quenching. In a preliminary laser experiment with a bulk $\text{Er}^{3+}, \text{Dy}^{3+}:\text{InF}_3$ -based glass, we demonstrated free-running emission comprising multiple lines spanning across $2.7\text{--}3.4\text{ }\mu\text{m}$. Furthermore, in the fiber geometry, continuous-wave laser operation at $3.3\text{ }\mu\text{m}$ was successfully achieved under 976 nm diode pumping corresponding to 100-mW level output powers. These results highlight the potential of optimized compositions for ultrabroadband wavelength tuning and for femtosecond pulse generation in a mode-locked fiber-laser architecture.

Owing to the low phonon energy of fluorindate glasses, emission near $4\text{ }\mu\text{m}$ (${}^6\text{H}_{11/2} \rightarrow {}^6\text{H}_{13/2}$) should also be feasible in fiber form. The main limitations are the much stronger non-radiative decay from the upper laser level, leading to luminescence lifetimes of only a few μs , and the self-terminating nature of the transition. These challenges could potentially be mitigated by cascade lasing on two successive electronic transitions [60]. Alternatively, phonon-terminated (vibronic) lasing at $4\text{ }\mu\text{m}$ may provide an effective route toward accessing this highly demanded spectral region.

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Data availability. Data underlying the results presented in this paper are not publicly available at this time but may be obtained from the authors upon reasonable request.

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