Mid-infrared emissions of Dy^{3+} ions in CaF_2

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Abstract. We report on a comprehensive spectroscopic study of singly Dy^{3+} doped and Er^{3+},Dy^{3+} codoped calcium fluoride (CaF_2) crystals for mid-infrared laser applications. The *f-f* transition probabilities of Dy^{3+} were determined by the Judd-Ofelt theory. The stimulated-emission cross-section reaches 0.25×10^{-20} cm^2 at 2.93 μm corresponding to an emission bandwidth of 350 nm. The $Er^{3+} \rightarrow Dy^{3+}$ energy transfer efficiency in codoped crystals is quantified. The 4.4-μm Dy^{3+} emission is observed for the first time from fluoride crystals.

1 Introduction

Dysprosium ion (Dy^{3+}) is among the most promising candidates for the generation of mid-infrared (MIR) laser emission at 3 μm and 4.4 μm. Cubic calcium fluoride crystals (CaF_2) attract attention for rare-earth (RE) doping as they combine good thermal properties, low phonon energy behavior which is essential for reducing the rate of non-radiative transitions unlocking MIR emission, and a strong inhomogeneous spectral line broadening originating from rare-earth ion clustering [1]. The latter property is a prerequisite for broad wavelength tuning and ultrashort pulse generation. In the present work, we systematically study the spectroscopic properties of Dy^{3+} ions in CaF_2 crystals for MIR laser applications.

2 Results and discussion

Singly Dy^{3+}-doped and Dy^{3+},Er^{3+}-codoped CaF_2 crystals were grown by the Bridgman–Stockbarger method. The *f-f* transition probabilities of Er^{3+} were calculated in the framework of the modified Judd-Ofelt theory, see Fig. 1(b). The radiative lifetimes τ_{rad} for the $^6H_{13/2}$ and $^6H_{11/2}$ manifolds amount to 45.66 ms and 15.63 ms, respectively, and the luminescence branching ratio $\beta_{JJ'}$ for the $^6H_{11/2} \rightarrow {}^6H_{13/2}$ transition reaches 11.9%. The absorption, σ_{abs}, and stimulated-emission, σ_{SE}, cross-sections of Dy^{3+} ions in the spectral range around 3 μm (the $^6H_{15/2} \rightarrow {}^6H_{13/2}$ transition) are depicted in Fig. 1(c). The peak σ_{SE} value calculated using the Füchtbauer-Ladenburg equation reaches 0.25×10^{-20} cm^2 at 2933 nm. The emission spectrum is smooth and very broad (emission bandwidth (FWHM): ~350 nm). This behavior is due to the rare-earth ion clustering in fluorite-type CaF_2-REF_3 solid solutions. Notably, the emission extends far beyond 3 μm avoiding the structured water vapor absorption in air. The

luminescence lifetime of the $^6H_{13/2}$ Dy^{3+} state was measured as a function of Dy doping level, decreasing from 2.04 ms (0.1 at.% Dy) to 0.52 ms (0.5 at.% Dy), as shown in Figure 1(d). The main difficulty in exciting MIR Dy^{3+} emission consists of its weak absorption and non-conventional pump wavelengths. This problem can be resolved by Er^{3+} codoping: the donor Er^{3+} ions can be efficiently pumped at 0.96 µm by InGaAs diode lasers, and there exist two non-radiative energy-transfer (ET) processes, $^4I_{11/2}(Er^{3+}) \rightarrow {}^6H_{5/2}(Dy^{3+})$ and $^4I_{13/2}(Er^{3+}) \rightarrow {}^6H_{11/2}(Dy^{3+})$, enabling acceptor Dy^{3+} emission around 3 µm and 4.4 µm. Figure 1(e) depicts the broadband emission of codoped crystals around 3 µm, indicating enhanced Dy^{3+} emission on increasing the Dy/Er codoping ratio. The ET2 efficiency was estimated by monitoring the $^4I_{11/2}$ Er^{3+} luminescence lifetime with and without Dy^{3+}: $\eta_{ET} = \tau_{lum(D+A)}/\tau_{lumD}$, reaching 91.4% for the 3 at.% Er, 0.5 at.% Dy codoped crystal. Remarkably, Dy^{3+} luminescence at 4.4 µm ($^6H_{11/2} \rightarrow {}^6H_{13/2}$), Fig. 1(f), was detected for the first time from any fluorite-type crystal.

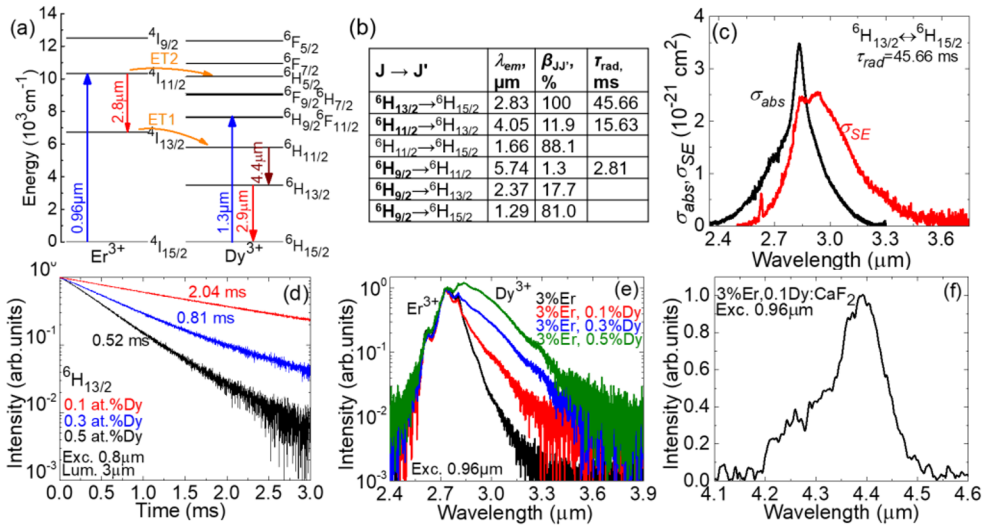

Fig. 1. Spectroscopy of Dy^{3+} ions in CaF_2 crystals: (a) energy-level scheme of Dy^{3+} and Er^{3+} ions showing pump and laser transitions, ET – energy-transfer; (b) probabilities of spontaneous radiative transitions for Dy^{3+} ions calculated using the Judd-Ofelt theory; (c) absorption, σ_{abs}, and stimulated-emission (SE), σ_{SE}, cross-sections for the $^6H_{13/2} \leftrightarrow {}^6H_{15/2}$ transition; (d) luminescence decay curves from the $^6H_{13/2}$ Dy^{3+} manifold; (e,f) mid-infrared emission spectra of Er^{3+},Dy^{3+}:CaF_2 crystals: (e) emission at ~3 µm; (f) emission at ~4.4 µm.

3 Conclusion

To conclude, Er^{3+},Dy^{3+} codoping represents a viable route for efficient excitation of MIR Dy^{3+} luminescence in CaF_2 crystals around 3 µm and 4.4 µm. Further work will focus on isostructural fluorite-type compounds, such as SrF_2 and BaF_2, possessing even low phonon energies, as well as alternative codoping schemes (Tm^{3+}-Dy^{3+}). *Funding*. French Agence Nationale de la Recherche (ANR-22-CE08-0031, FLAMIR); Région Normandie, France (Contrat de plan État-Région (CPER)).

References

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