

Optical spectroscopy of erbium-doped fluorohafnate glasses for 2.8 μm lasers

Simone Normani¹, Pavel Loiko^{1*}, Liudmila Moiseeva², Valeria Vinokurova³, Leonid Vaimugin³, Elena Dunina⁴, Alexey Kornienko⁴, Alain Braud¹, and Maria Brekhovskikh³

¹Centre de Recherche sur les Ions, les Matériaux et la Photonique (CIMAP), UMR 6252 CEA-CNRS-ENSICAEN, Université de Caen Normandie, 6 Boulevard Maréchal Juin, 14050 Caen, France

²Prokhorov General Physics Institute RAS, Laboratory of Crystal and Glass Spectroscopy, 38 Vavilov St., 119991 Moscow, Russian Federation

³Kurnakov Institute of General and Inorganic Chemistry RAS, Laboratory of High Purity Substances, 31 Leninsky Ave., 119991 Moscow, Russian Federation

⁴Vitebsk State Technological University, 210035 Vitebsk, Belarus

Abstract. Fluorohafnate glasses ($\text{HfF}_4\text{--BaF}_2\text{--LaF}_3\text{--AlF}_3\text{--NaF}$) doped with erbium ions were fabricated by the melt-quenching technique at 870 °C in argon atmosphere, and their spectroscopic properties were studied. The glasses exhibit a low phonon energy (575 cm^{-1}), a broadband mid-infrared emission (stimulated-emission cross-section: $0.51 \times 10^{-20} \text{ cm}^2$ at 2.76 μm), and long luminescence lifetimes of the $^4\text{I}_{11/2}$ and $^4\text{I}_{13/2}$ manifolds making them attractive for 2.8- μm laser sources.

1 Introduction

Mid-infrared (MIR) lasers emitting around 3 μm represent a hot research topic due to their applications in the biomedical field, determined by the strong water absorption of biological tissues. Such emission can be readily achieved using Er^{3+} -doped materials relying on the $^4\text{I}_{11/2} \rightarrow ^4\text{I}_{13/2}$ electronic transition. Fluoride materials (crystals and glasses) are appealing as host matrices for Er^{3+} doping targeting MIR emission [1], owing to their low-phonon energy behavior reducing the non-radiative path. Among heavy metal fluoride glasses, those based on ZrF_4 (abbreviated: ZBLAN) attract the most attention, although other glass systems based on InF_3 or HfF_4 have recently raised significant interest due to their lower phonon energies and broader infrared transparency. We report on the synthesis and spectroscopy of Er^{3+} ions in fluorohafnate glasses with the goal of developing novel MIR laser media.

2 Glass synthesis and spectroscopy

Er^{3+} -doped fluorohafnate glasses were obtained by the melt-quenching technique. The glasses were synthesized from a starting fluoride mixture with a composition of $58\text{HfF}_4 - 20\text{BaF}_2 - 2\text{LaF}_3 - 3\text{AlF}_3 - 17\text{NaF}$ (HBLAN). Erbium was incorporated in the form of ErF_3 in a concentration of 0.5 to 2 mol%. Starting fluorides were ground in an agate mortar and

*Corresponding author: pavel.loiko@ensicaen.fr

mixed in a glove box filled with nitrogen to prevent hydration. Glasses were prepared in glassy carbon crucibles enclosed in an argon-filled quartz reactor. To reduce the HfF_4 losses due to vaporization, the crucibles were sealed with glassy carbon stoppers. After melting at 870°C , the samples were cooled in flowing argon down to room temperature.

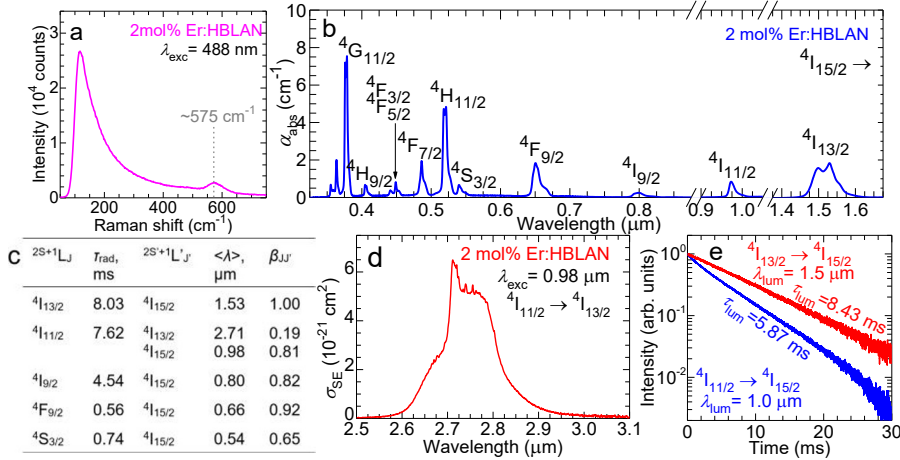


Fig. 1. Spectroscopy of Er^{3+} ions in HBLAN glass: (a) Raman spectrum; (b) an overview absorption spectrum (2 mol% Er doping); (c) selected probabilities of radiative transitions calculated via the Judd-Ofelt theory; (d) stimulated-emission cross-section, σ_{SE} , spectrum around $2.8\ \mu\text{m}$; (e) luminescence decay curves from the $4I_{11/2}$ and $4I_{13/2}$ manifolds (0.5 mol% Er doping).

Figure 1(a) shows the Raman spectrum of the 2 mol.% Er:HBLAN glass, presenting a dominant Raman peak at $575\ \text{cm}^{-1}$. The absorption spectrum of Er^{3+} ions in the same glass is presented in Fig. 1(b). For the $4I_{15/2} \rightarrow 4I_{11/2}$ pump transition, the absorption cross-section $\sigma_{\text{abs}} = 0.21 \times 10^{-20}\ \text{cm}^2$ at $973\ \text{nm}$ (absorption bandwidth: $17\ \text{nm}$). The radiative lifetimes, τ_{rad} , and luminescence branching ratios, $\beta_{JJ'}$, of radiative transitions of Er^{3+} ions were calculated using the standard Judd-Ofelt theory, Fig. 1(c). The $4I_{11/2} \rightarrow 4I_{13/2}$ MIR transition corresponds to a relatively large $\beta_{JJ'}$ of 19%. The radiative lifetimes of the upper and lower manifolds are $7.62\ \text{ms}$ and $8.03\ \text{ms}$, respectively. The stimulated-emission (SE) cross-section, σ_{SE} , for this transition was calculated, Fig. 1(d), yielding $0.51 \times 10^{-20}\ \text{cm}^2$ at $2.76\ \mu\text{m}$ (the expected laser wavelength). The luminescence decay from both levels was studied using a 0.5 mol% Er doped glass, see Fig. 1(e). The luminescence lifetimes, τ_{lum} , amount to $5.87\ \text{ms}$ ($4I_{11/2}$) and $8.43\ \text{ms}$ ($4I_{13/2}$).

3 Conclusion

Erbium-doped fluorohafnate glasses possesses attractive vibronic (phonon energy: $575\ \text{cm}^{-1}$) and spectroscopic properties (broadband emission around $2.8\ \mu\text{m}$, a favorable ratio of the $4I_{11/2}$ to $4I_{13/2}$ luminescence lifetimes) and consequently are of interest for the development of MIR lasers, including fiber sources (given the resistance to crystallization of these materials). *Funding.* Contrat de plan État-Région (CPER) de Normandie.

References

1. S. Normani, S. Idlahcen, P. Loiko, S. Hatim, P.-H. Hanzard, A. R. De Paula, L. Guillemot, T. Godin, T. Berthelot, S. Cozic, S. Poulain, E. Koivusalo, M. Guina, P. Camy, and A. Hideur, *Opt. Express* **32**, 15106-15114 (2024).