Spectroscopy of Ho:Y_2O_3 transparent ceramics: Effect of YF_3 addition

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Abstract. Transparent ceramics of Holmium-doped yttria (Ho:Y_2O_3) were fabricated by Hot Isostatic Pressing at 1720 °C / 190 MPa in argon, and the effect of YF_3 addition on their microstructure, optical, vibronic and infrared emission properties was studied. The fluorine addition improves the ceramic transparency, accelerates the grain growth and enhances the luminescence lifetimes of Ho^{3+} states responsible for emissions at 2 μm and 3 μm.

1 Introduction

Holmium ions (Ho^{3+}) gain interest owing to their short-wave infrared emission according to cascade laser at 2.1 μm ($^5I_7 \rightarrow {}^5I_8$) and 2.9 μm ($^5I_6 \rightarrow {}^5I_7$). Cubic rare-earth sesquioxides, *e.g.*, yttria (Y_2O_3) attract attention for Ho^{3+} doping due to their i) high thermal conductivity, ii) low phonon energies, iii) strong crystal-fields, and iv) high doping levels. The interest in the transparent ceramic technology for cubic sesquioxides is driven by their high melting point (2410 °C for Y_2O_3), as the sintering temperatures are reduced to 1600 – 1800 °C [1]. Sintering aids are used to eliminate porosity, reduce the sintering temperature, and control the grain growth leading to improved transparency. Various sintering aids have been employed for yttria ceramics, *e.g.*, ZrF_4, La_2O_3, or LiF. In the present work, we report on the effect of YF_3 addition on the microstructure, Raman spectra and spectroscopic properties of Ho^{3+}-doped Y_2O_3 transparent ceramics with the goal of developing gain media for 2 – 3 μm lasers.

2 Results and discussion

The starting materials were nanopowders with a mean particle size of <400 nm, Y_2O_3, Ho_2O_3 (0.5 mol%) and YF_3 (0 or 4500 ppm mol). The powder mixtures were uniaxially pressed at 50 MPa and then cold isostatic pressing was performed at 100 MPa. A pre-sintering step was conducted in air at 1600°C for 1 h. The pre-sintered samples were post-sintered using Hot Isostatic Pressing (HIP) at 1720°C / 190 MPa in argon for 30 min. The samples were annealed in air at 975°C for 48 h. A photograph of a polished and annealed ceramic with YF_3 is shown in Fig. 1(a). The addition of YF_3 improves the transparency of ceramics, reaching >70% around 2 μm. It also accelerates the grain growth (grain size with and without YF_3: 2.9±0.2

µm and 56±13 µm, respectively). X-ray powder diffraction indicates a partial dissolution of F in Y_2O_3. The vibronic properties of ceramics were analyzed by Raman spectroscopy, Fig. 1(b). The dominant peak at 376 cm^{-1} is attributed to stretching vibrations ($A_g + F_g$) of cubic C-type bixbyite structure. µ-Raman mapping was performed on the polished samples to reveal their microstructure by monitoring the intensity of the 376 cm^{-1} peak, Fig. 1(c).

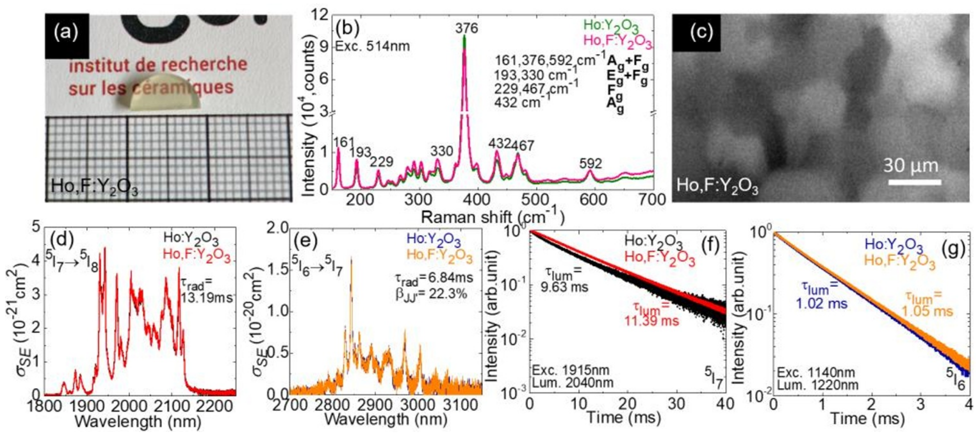

Fig. 1. $Ho:Y_2O_3$ transparent ceramics fabricated by HIP with or without YF_3: (a) a photograph of a polished and annealed sample (with YF_3); (b,c) µ-Raman spectroscopy: (b) Raman spectra; (c) mapping of the Raman peak intensity at 376 cm^{-1}, λ_{exc} = 514 nm; (d-g) short-wave infrared emissions of Ho^{3+} ions: (d,e) stimulated-emission cross-sections: (d) at 2.1 µm and (e) at 2.9 µm; (f,g) luminescence decay curves from (f) $^5I_7$ and (g) $^5I_6$ Ho^{3+} manifolds.

The absorption and infrared emission properties (spectra and lifetimes) of Ho^{3+} ions were studied. The stimulated-emission cross-sections, σ_{SE}, for the emissions at 2.1 µm (the $^5I_7 \rightarrow$ $^5I_8$ transition) and 2.9 µm (the $^5I_6 \rightarrow$ $^5I_7$ one) were calculated using the Füchtbauer-Ladenburg equation, Fig. 1(d,e). The fluorine addition does not alter the spectral emission profiles. In the spectral range where laser operation is expected, σ_{SE} is 0.38×10^{-20} cm^2 at 2116.6 nm and 0.82×10^{-20} cm^2 at 2968.8 nm. The luminescence decay curves from the $^5I_7$ and $^5I_6$ Ho^{3+} levels are shown in Fig. 1(f,g). The fluorine addition leads to an increase of luminescence lifetimes τ_{lum}, from 9.63 to 11.39 ms for the $^5I_7$ state and from 1.02 to 1.05 ms for the $^5I_6$ one. This is in line with the higher crystallinity and better structural perfection of the ceramic with YF_3. The relatively long τ_{lum} value for the $^5I_6$ state highlights the potential of ceramics for 3-µm lasers, considering less important scattering losses in the mid-infrared.

3 Conclusion

The addition of YF_3 into Ho^{3+}-doped Y_2O_3 transparent ceramics fabricated by HIP results in an improved transparency, enhanced grain growth, and longer luminescence lifetimes of Ho^{3+} multiplets giving rise to emissions at 2 - 3 µm being of interest for laser development, while it does not change the spectral absorption and emission profiles. *Funding*. Region Nouvelle-Aquitaine (HICEMIR program No. 2020-RNA20435), National Research Agency (ANR-10-LABX-0074-01 Sigma-LIM); HEMERALD (ANR-20-CE08-0016).

References

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