

Inhomogeneous spectral line broadening and site distribution in “mixed” Er:(Sc,Y)₂O₃ laser ceramics

Simone Normani^{1,*}, Pavel Loiko¹, Roman Maksimov^{2,3}, Vladislav Shitov³, Vladimir Osipov³, Alain Braud¹, and Patrice Camy¹

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

²Ural Federal University named after the first President of Russia B.N. Yeltsin, 19 Mira St., 620002 Ekaterinburg, Russia

³Institute of Electrophysics, Ural Branch of the Russian Academy of Sciences, 106 Amundsen St., 620016 Ekaterinburg, Russia

Abstract. Erbium-doped “mixed” yttria-scandia (Sc_xY_{1-x})₂O₃ transparent laser ceramics were fabricated by vacuum sintering at 1750 °C from laser-ablated nanoparticles. Their absorption and mid-infrared emission properties were studied. The addition of Sc³⁺ induces a strong inhomogeneous spectral line broadening, modifies the crystal field and affects the distribution of Er³⁺ ions over C₂ and C_{3i} symmetry sites. Due to their broadband emission properties, Er:(Sc_xY_{1-x})₂O₃ ceramics are appealing for 2.8-μm lasers.

1 Introduction

Trivalent erbium ions (Er³⁺) are known for their mid-infrared (MIR) emission at ~2.8 μm originating from the ⁴I_{15/2} → ⁴I_{13/2} electronic transition. MIR Er-lasers find applications in medicine due to the strong absorption of such radiation by water in bio-tissues. Polycrystalline cubic sesquioxide ceramics (A₂O₃, with A = Y, Lu, Sc, or their combination) are attractive for Er³⁺ doping for MIR laser development [1,2], as they possess low phonon energies, good thermal properties, and a favorable ratio of upper state (⁴I_{15/2}) to lower state (⁴I_{13/2}) lifetimes at moderate doping levels (7 – 10 at.%), leading to efficient and power-scalable continuous-wave laser emission [1,2]. Transparent sesquioxide ceramics offer relatively low synthesis temperatures compared to the corresponding crystals, easier doping and fabrication of “mixed” (solid-solution) compositions (A_xB_{1-x})₂O₃ [2]. They benefit from a strong inhomogeneous spectral line broadening [3], particularly interesting for the development of broadly tunable and mode-locked lasers [4].

In this paper, we report on the spectroscopy of compositionally “mixed” Er:(Sc,Y)₂O₃ sesquioxide laser ceramics, focusing on the inhomogeneous broadening and Er³⁺ site distribution as a function of scandium content.

2 Results and discussion

Transparent ceramics of Er³⁺-doped yttria-scandia (solid-solution) with a nominal composition of Er_{0.14}(Sc_xY_{1-x})_{1.86}O₃ (x = 0, 0.125, 0.25, and 0.5) were fabricated via solid-state vacuum sintering of nanopowders synthesized by the laser ablation method [5]. Vacuum sintering of powder compacts was conducted at 1750 °C for 5 h, followed by annealing in air at 1400 °C for 2 h. Figure 1

shows the absorption cross-section (σ_{abs}) spectra for the ⁴I_{15/2} → ⁴I_{11/2} pump transition of Er³⁺ in the (Sc_xY_{1-x})₂O₃ ceramics. The peak σ_{abs} value is 2.55 × 10⁻²¹ cm² at 981.1 nm for the (Er_{0.075}Y_{0.925})₂O₃ ceramic, corresponding to an absorption bandwidth (FWHM) of 1 nm. For the (Er_{0.073}Sc_{0.227}Y_{0.700})₂O₃ “mixed” ceramic, σ_{abs} slightly drops to 2.50 × 10⁻²¹ cm² at 981.1 nm, and the peak FWHM increases to 3.2 nm.

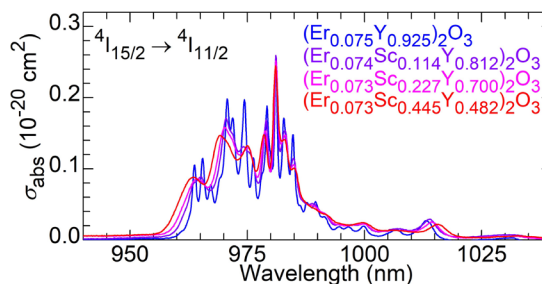


Fig. 1. Absorption cross-sections, σ_{abs}, for the ⁴I_{15/2} → ⁴I_{11/2} transition of Er³⁺ in (Sc,Y)₂O₃ ceramics.

Figure 2 presents the stimulated-emission cross-sections, σ_{SE}, for the ⁴I_{11/2} → ⁴I_{13/2} transition of Er³⁺ in the studied ceramics, falling in the mid-infrared (MIR) spectral range, calculated via the Füchtbauer-Ladenburg equation. For the parent (Er_{0.075}Y_{0.925})₂O₃ ceramic, in the spectral range where laser emission occurs (determined by both excited-state absorption from the terminal laser level and water vapor absorption lines), the peak σ_{SE} is 0.62 × 10⁻²⁰ cm² at 2842 nm and the emission bandwidth is 22 nm. For the (Er_{0.073}Sc_{0.227}Y_{0.700})₂O₃ ceramic, the peak SE cross-section is lower, 0.38 × 10⁻²⁰ cm² at 2845 nm, and the emission peak is broadened to 34 nm.

The individual peaks in both the absorption and emission spectra show significant inhomogeneous spectral line broadening with the gradual increase in Sc³⁺ content x.

* Corresponding author: simone.normani@ensicaen.fr

This broadening is induced by the increasing compositional disorder, stemming from the difference in the ionic radii between Er^{3+} (0.89 Å), Y^{3+} (0.9 Å), and Sc^{3+} (0.75 Å) for VI-fold oxygen coordination.

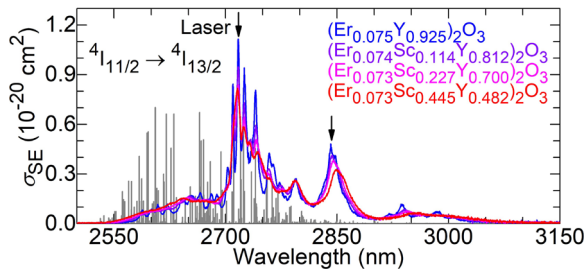


Fig. 2. Stimulated emission (SE) cross-sections, σ_{SE} , for the $4I_{11/2} \rightarrow 4I_{13/2}$ transition of Er^{3+} in $(\text{Sc},\text{Y})_2\text{O}_3$ ceramics. *Arrows* – observed laser wavelengths; *grey lines* – structured water absorption spectrum (HITRAN database).

Er^{3+} ions occupy two non-equivalent sites of symmetries C_2 and C_{3i} (Wyckoff: $24d$ and $8b$) in cubic A_2O_3 sesquioxides. In the undistorted lattice, the A^{3+} cations are distributed over these sites in the proportions of $3/4$ and $1/4$, respectively. The electric dipole (ED) transitions are strictly forbidden for ions in C_{3i} symmetry sites, due to the presence of a center of inversion, and only magnetic dipole (MD) ones are allowed, in accordance with the selection rule $\Delta J = 0, \pm 1$. Thus, ions occupying C_{3i} sites are silent for purely ED transitions.

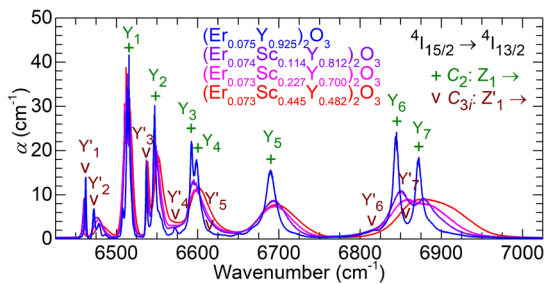


Fig. 3. LT (12 K) absorption spectra for the $4I_{15/2} \rightarrow 4I_{13/2}$ Er^{3+} transition in $(\text{Sc},\text{Y})_2\text{O}_3$ ceramics. The + and v signs mark the individual electronic transitions to Stark sub-levels of the $4I_{13/2}$ manifold for the C_2 and C_{3i} sites, respectively.

Low-temperature (LT, 12 K) spectroscopy was involved to i) observe the experimental crystal-field splitting of upper and lower laser levels of Er^{3+} for MIR emission ($4I_{11/2}$ and $4I_{13/2}$), ii) reveal the effect of Sc^{3+} addition on inhomogeneous spectral broadening in “mixed” ceramics, and iii) quantify the relative fraction of Er^{3+} ions in C_{3i} sites. Figure 3 illustrates the LT absorption spectra at $\sim 1.5 \mu\text{m}$ for all studied ceramic samples, allowing the assignment of the C_2 and C_{3i} site Stark-split sub-levels (Y_n and Y'_n , $n = 1, \dots, 7$) of the $4I_{13/2}$ manifold for the parent $(\text{Er}_{0.075}\text{Y}_{0.925})_2\text{O}_3$ ceramic. Upon increasing the Sc^{3+} content, the LT spectra of “mixed” ceramics progressively broaden, individual electronic transitions become non-resolved and a shift to higher wavenumbers occurs. The first effect is clear even for a relatively low Sc^{3+} fraction (11.4 at.%) and is ascribed to the compositional disorder. The spectral shifts are due to the increased crystal-field strength for Sc_2O_3 as compared to Y_2O_3 [3]. The energy diagram of crystal-field split $4I_{11/2}$ and $4I_{13/2}$ manifolds of

Er^{3+} ions residing in C_2 sites in $(\text{Sc}_x\text{Y}_{1-x})_2\text{O}_3$ ceramics was traced by assessing the spectral widths of LT absorption peaks. Figure 4(a) reveals the effect of Sc^{3+} addition: the electronic transitions to individual sub-levels broaden enough to overlap, while the barycenter of the whole multiplet gradually shifts to higher energies (as does the total Stark splitting).

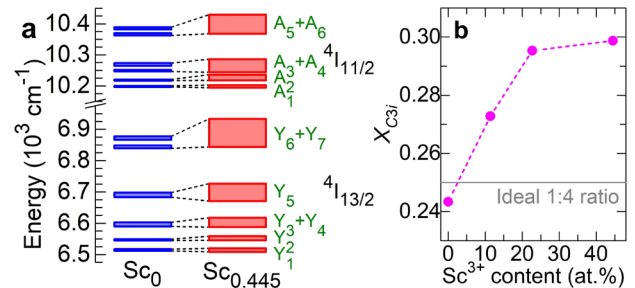


Fig. 4. (a) Crystal-field splitting of the $4I_{13/2}$ and $4I_{11/2}$ multiplets of Er^{3+} ions in C_2 sites, showing the energy-level position shift and inhomogeneous spectral line broadening. (b) Erbium C_{3i} site occupancy, $X_{C_{3i}}$, vs. Sc^{3+} content in $\text{Er}:(\text{Sc},\text{Y})_2\text{O}_3$ ceramics.

The site occupancies X_{C_2} and $X_{C_{3i}}$ ($X_{C_2} + X_{C_{3i}} = 1$) for Er^{3+} ions were estimated based on the separated absorption coefficient integrals of both sites, as well as Judd-Ofelt calculation of ED and MD transition intensities, see the result in Fig. 4(b) showing the C_{3i} site occupancy, wherein $X_{C_{3i}}$ rises as a function of Sc^{3+} concentration, moving further away from the aforementioned “ideal” case of the parent Y_2O_3 ceramics, where $X_{C_{3i}} = 1/4$.

3 Conclusion

To conclude, “mixed” sesquioxide ceramics in the yttria-scandia binary system feature broadband MIR emission properties. Considering the effect of Sc^{3+} addition on the inhomogeneous spectral line broadening, redistribution of Er^{3+} ions over C_2 / C_{3i} sites, and deterioration of thermal properties, it is preferable to use ceramics low in Sc^{3+} , < 25 at.%. The developed ceramics are of interest for tunable and ultrashort pulse MIR lasers. *Funding.* CNRS (France), project IEA No. 00432.

References

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