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Tailoring rare-earth emission spectra through controlled energy transfer

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Abstract: Optical fiber preforms were solution doped with lanthanide-containing nanoparticles. The nanoparticles spatially localize the doping yielding multiply-doped glasses that did not show energy transfer. This approach opens doors to novel broadband amplifiers and lasers.
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1. Introduction

Rare-earth-doped materials are used in a very wide range of practical applications, including lasers, amplifiers, lighting, and displays. Typically, one particular lanthanide is used to provide a specific emission. However, there are several examples where multiple lanthanides are codoped in order to achieve some cooperative effect. The Yb^{3+}/Er^{3+} system is the most notable for amplifier and laser applications where the Yb^{3+} ion efficiently absorbs 980 nm pump light and then transfers this energy to an Er^{3+} ion, which subsequently emits at about 1550 nm [1].

Such energy transfer, however, is not always desirable and the presence of codopants can also reduce the performance of the principal dopant [2]. Generally, energy transfer limits the ability to controllably design a particular spectral profile. Such "designer spectra" have been realized recently in nanoparticles [3,4] and in optical fibers [5] by employing specific microstructures that spatially segregate the differing dopants within the overall material.

This talk will discuss the solution-doping of rare-earth-doped nanoparticles into a MCVD-derived silica preform.[7] The nanoparticles act to spatially-localize the lanthanides within the glass such that co-dopants can be made proximate, or not, to one another thereby controlling the possibility for energy transfer. Also discussed will be the role of the nanoparticle chemistry on the resultant spectral properties.

2. Experimental

More specifically, the focus of this work is the Tb^{3+}/Eu^{3+} system. When codoped an excited Tb^{3+} ion will transfer its energy to a neighboring Eu^{3+} ion thus quenching the green Tb^{3+} emission and yielding a strong Eu^{3+} red emission. Other reasons to study this canonical system are that their visible emissions are easily monitored and their spectroscopy and energy transfer dynamics are well studied.[3,7,8] LaF_3 was chosen as the nanoparticle host since the synthesis of small (~10 nm) nanoparticles is well established [4,8]. The nanoparticle spatially localizes the lanthanide in the glass matrix and provides the physical separation necessary to control energy transfer. Ideally, the codoped glass exhibits the discrete emissions of both Tb^{3+} and Eu^{3+} when each is excited.

Individually Eu^{3+}- and Tb^{3+}-doped LaF_3 nanoparticles as well as Eu^{3+}/Tb^{3+}-codoped LaF_3 nanoparticles, as a control, were synthesized as reported elsewhere.[9] The lanthanides were doped into a LaF_3 nanoparticle at a level of 5 weight percent. The nanoparticles were then suspended at a level of 2 weight percent in a water/ethanol solution. The nanoparticulate solution was then solution-doped [10] into silica soot using the MCVD process. The preform was dried and subsequently consolidated and collapsed. Photoluminescence spectra were collected on the resultant preforms using a Jobin–Yvon Fluorolog Tau 3 fluorometer.

3. Results

Figure 1 shows the energy-level diagram for Tb^{3+} and Eu^{3+} noting the pathways for radiative and nonradiative (NR) relaxations and energy transfer (ET). For wavelengths shorter than about 380 nm, both the Tb^{3+} $^5D_4$ and $^5D_3$ states and the Eu^{3+} ^5G_J (J=3,4,5,6) states are co-excited.[4] For Tb^{3+}, the large energy level separation between the $^5D_4$ level and the $^7F_0$ state favors an efficient radiative emission at about 540

nm. For Eu^{3+}, the large energy separation between the $^5D_0$ level and the $^7F_6$ state yields an efficient radiative emission at 610 nm and 590 nm, which corresponds to the $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_1$ transitions, respectively. When Tb^{3+} and Eu^{3+} are codoped into the same host, energy transfer can occur between the $Tb3+$ $^5D_4$ state and the Eu^{3+} $^5D_1$ level. As a result, investigating the Eu^{3+} emission at wavelengths that excite the Tb^{3+} are unique indications of energy transfer.
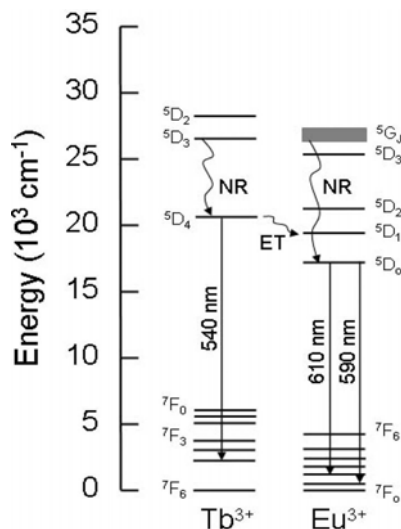

Fig. 1. Energy-level diagram for Tb^{3+} and Eu^{3+} [NR, nonradiative relaxation; ET, energy transfer].

Figure 2 shows the excitation spectrum of the Eu^{3+} emission at 611 nm from a silica preform that was doped either with Tb^{3+}:LaF_3 and Eu^{3+}:LaF_3 nanoparticles separately or codoped with Tb^{3+}/Eu^{3+}:LaF_3 nanoparticles. The preform prepared using the individually doped nanoparticles exhibits only a 462 nm peak. The codoped preform exhibits excitation peaks for the Eu^{3+} 610 nm emission at 462 nm and 485 nm. The peaks at 462 nm and 485 nm arise from the $^5D_2$ level of Eu^{3+} and the $^5D_4$ level of Tb^{3+}, respectively. Clearly, in the codoped sample, excitation of the Tb^{3+} $^5D_4$ level at 485 nm yields an emission from the Eu^{3+} $^5D_0$ state at 610 nm. This energy transfer is not present in the preform that was doped with Tb^{3+}:LaF_3 and Eu^{3+}:LaF_3.

This leads to the postulation that the LaF_3 nanoparticles, although most certainly oxidized during the MCVD process, spatially localizes the lanthanide in the glass host. In other words, although some diffusion is expected at the elevated processing temperatures, the rare-earth ions largely remain near the volume of the original nanoparticle. For the individually-doped nanoparticles, there is a spatial localization of the Eu^{3+} in one place and a similar localization of Tb^{3+} in another. For the codoped nanoparticles, the volume would include both Tb^{3+} and Eu^{3+} ions such that energy transfer can, and indeed does, occur.
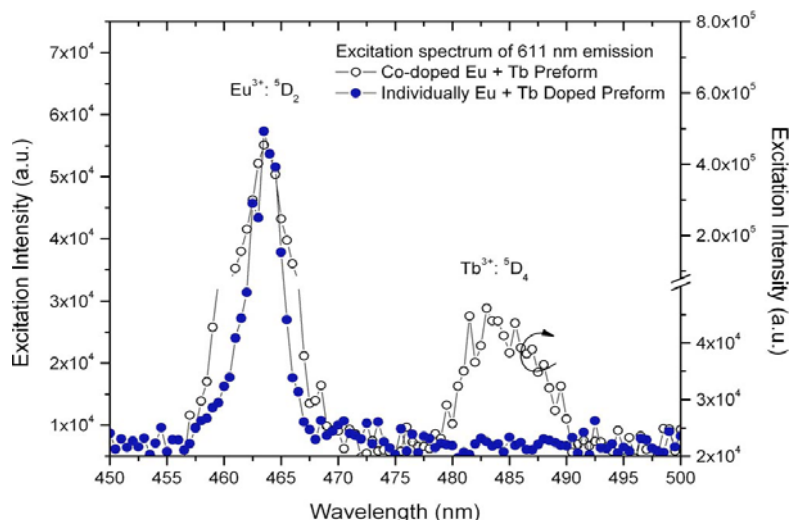
Fig. 2. Excitation spectrum of the Eu^{3+} 611 nm emission from a solution containing individually Eu^{3+}- and Tb^{3+}-doped nanoparticles (●) and from a solution containing Eu^{3+}- and Tb^{3+}-codoped nanoparticles (○).

4. Conclusion

A silica glass preform was solution doped with individually Eu^{3+}- and Tb^{3+}-doped LaF_3 nanoparticles and Eu^{3+}/Tb^{3+}-codoped nanoparticles. This approach provides a spatial localization of the lanthanide within the glass host which was shown to control the energy transfer between the Tb^{3+} and Eu^{3+}. This spatial localization of rare earths in the glass provides a method to control energy transfer and could yield broadband amplifiers and lasers as well as spectrally engineered emissive structures.

5. References

[1] E. Snitzer and R. Woodcock, "Yb^{3+} - Er^{3+} glass laser," Appl. Phys. Lett. **6**, 45 – 46 (1966).

[2] M. Furtado, R. Shori, O. Stafsudd, J. Stone-Sundberg, and M. Kokta, "Multiphonon relaxation studies of $^4I_{11/2}$ and $^4I_{13/2}$ energy levels in Er,RE:YAG laser crystals," in Advanced Solid-State Photonics, Technical Digest (Optical Society of America, 2005), paper MB10.

[3] J. DiMaio, B. Kokuoz and J. Ballato, "White light emissions through down-conversion of rare-earth doped LaF_3 nanoparticles," Opt. Express **14**, 11412 – 11417 (2006).

[4] J. DiMaio, C. Sabieter, B. Kokuoz and J. Ballato, "Controlling energy transfer in multiply doped LaF_3 nanoparticle via core-shell architectures," Proc. Nat. Acad. Sci. **105**, 1809 - 1813 (2008).

[5] L. DiLabio, W. Lüthy, V. Romano, F. Sandoz, and T. Feurer, "Broadband emission from a multicore fiber fabricated with granulated oxides," Appl. Opt. **47**, 1581 – 1584 (2008).

[6] C. Kucera, B. Kokuoz, D. Edmondson, D. Griese, M. Miller, A. James, W. Baker, and J. Ballato, "Designer Emission Spectra through Tailored Energy Transfer in Nanoparticle Doped Silica Preforms," *Optics Letters* **34**, 2339 – 2341 (2009).

[7] K. Oh, T. Morse, L. Reinhart, A. Kilian, and W. Risen, "Spectroscopic analysis of a Eu-doped aluminosilicate optical fiber preform," J. Non-Crystal Solids **149**, 229 – 242 (1992).

[8] J. DiMaio, B. Kokuoz, T. James, and J. Ballato, "Structure/property effects in light emissive inorganic nanoparticles with complex core-shell architectures," Adv. Mater. **19**, 3266 – 3270 (2007).

[9] V. Sudarsan, F. van Veggel, R. Herring, and M. Raudsepp, " Surface Eu^{3+} ions are different than 'Bulk' Eu^{3+} ions in crystalline doped LaF_3 nanoparticles," J. Mater. Chem **15**, 1332-1342 (2005).

[10] J. Townsend, S. Poole, and D. Payne, "Solution-doping technique for fabrication of rare-earth-doped optical fibers," Electron. Lett. **23**, 329 – 331 (1987).