BRIGHT VISIBLE UPCONVERSION EMISSION AND THERMALLY ENHANCED COOPERATIVE ENERGY-TRANSFER IN Tb³⁺/Yb³⁺- CODOPED TELLURITE GLASS

A. S. Gouveia-Neto

Departamento de Física e Matemática – Universidade Federal Rural de Pernambuco Recife – 52171/900 – PE – Brasil

*P. V. dos Santos, M. V. D. Vermelho, and M. T. de Araújo*Departamento de Física – Universidade Federal de Alagoas – Maceió – 57072/970 – AL – Brasil

F. C. Cassanjes, S. J. L. Ribeiro, and Y. Messaddeq
Instituto de Química – UNESP – Araraquara – 14800/900 - SP – Brasil

Abstract

Bright multiwavelength visible upconversion luminescence through cooperative energy-transfer in Tb^{3+}/Yb^{3+} -codoped tellurite glasses excited at 1.064 μ m is reported. A fourfold thermally induced enhancement in the cooperative energy-transfer process is demonstrated.

Introduction

Multi-ion interaction in novel rare-earth doped materials has recently attracted much attention owing to the fact that the effect can be beneficial in the construction of photonic devices. The multi-ion interaction warrants conditions for the so called sensitization process where the species excited by a pump photon transfer its excitation to the other species present in the material [1]. The ion-pair interaction referred to as energy-transfer has been extensively investigated in trivalent Er-, Pr-, and Tm-doped samples sensitized with trivalent-ytterbium. In this work, bright visible upconversion emission excited through cooperative energy-transfer and thermal effects in Tb^{3+}/Yb^{3+} -codoped $60TeO_2$ - $10GeO_2$ - $10K_2O$ - $10Li_2O$ - $10Nb_2O_5$ glasses excited at $1.064~\mu m$ is investigated.

Experimental Setup

The tellurium-oxide glass samples used in our measurements had a composition of $60\text{TeO}_2\text{-}10\text{GeO}_2\text{-}10\text{K}_2\text{O}\text{-}10\text{Nb}_2\text{O}_5$ doped with 10000 ppm/wt of Tb³+ ions and 20000 ppm/wt of ytterbium. Glasses were prepared with high purity (99.9999%) rare-earth oxides and all special care was taken in the lab during the glass preparation in order to avoid contamination due to other rare-earth ions. The host material presents very good optical quality, is stable against atmospheric moisture, it exhibits low optical attenuation from 400 nm to 5.0 μ m, and due to the >2.0 refractive index, one expects to obtain significantly high radiative decay rates of rare-earth energy levels. The material also exhibits high solubility allowing the incorporation of high lanthanide concentrations apart from being nonhygroscopic and possess high thermal stability against crystallization. The samples thickness were ~ 2.5 mm and the excitation source was a cw Nd:YAG laser operated at 1.064 μ m. The pump beam was focused down into the samples by a 5 cm focal length lens and the pump beam waist at the samples location was ~60 μ m. The fluorescence signal was collected by a fiber-bundle, and was dispersed by a 0.34 m scanning spectrograph with operating resolution of 0.5 nm and detected by a S-20 uncooled photomultiplier tube. A lock-in amplifier in conjunction with a storage-scope coupled to a microcomputer was used for data acquisition and storage.

Results and Discussions

Bright upconversion luminescence around 485, 550, 590, 625 and 655 nm, identified as due to the ${}^5D_4 \rightarrow {}^7F_J$ (J= 6, 5, 4, 3, and 2) transitions of the terbium-ions, respectively, was generated as presented in the spectrum portrayed in figure 1. Bright upconversion luminescence around 485, 550, 590, 625 and 655 nm, identified as due to the ${}^5D_4 \rightarrow {}^7F_J$ (J= 6, 5, 4, 3, and 2) transitions of the terbium-ions, respectively, was generated as presented in the spectrum portrayed in figure 1. The population of the ${}^5D_4 \rightarrow {}^5D_4$ excited-state level is assigned to cooperative energy-transfer from pairs of ytterbium-ions excited via a phonon-assisted anti-Stokes process. The dependence of the visible upconversion luminescence as a function of the sample temperature was

examined in the interval between 300K and 500K and the results showed an enhancement in the emission intensities as depicted by the green emission in the plot of figure 2. A fourfold upconversion emission enhancement was observed with a peak intensity occurring around 410K as indicated in the plot depicted in fig. 2. The enhancement of the upconversion process is due to the temperature dependence of the Yb³⁺-sensitizer absorption cross-section under anti-Stokes excitation. A model based upon conventional rate-equations using multiphonon-assisted absorption for the ytterbium excitation combined to the energy migration effect between Yb³⁺-Yb³⁺ pairs and Tb³⁺ ground-state depopulation via multiphonon excitation of the ⁷F's excited-states, described quite well the experimental results[2].

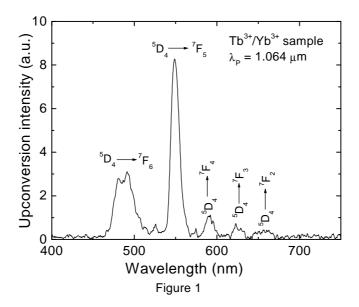


Figure 1- Room-temperature upconversion emission spectrum for the Tb^{3+}/Yb^{3+} -codoped sample under 1.0 W excitation power at 1.064 μm .

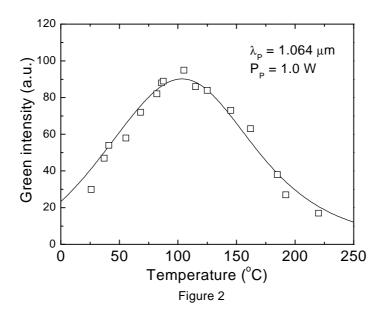


Figure 2 - Green upconversion emission intensity as a function of the sample temperature at a fixed excitation power of 1.0 W. Symbols stand for experimental data and solid line is the theoretical fit.

Conclusions

In conclusion, thermally induced enhancement of infrared-to-visible frequency upconversion through cooperative energy-transfer in Tb^{3+}/Yb^{3+} -codoped tellurite glass was demonstrated. Bright upconversion emission extending from blue to red corresponding to transitions commencing at the 5D_4 excited-state of the terbium-ions was observed. The population of the Tb^{3+} -ions 5D_4 excited-state level is assigned to cooperative energy-transfer from pairs of ytterbium-ions. A fourfold upconversion luminescence enhancement in the 300K-500K interval was also observed. The enhancement of the upconversion process is due to the temperature dependence of the Yb^{3+} -sensitizer absorption cross-section under anti-Stokes excitation. A model based upon conventional rate-equations using multiphonon-assisted absorption for the ytterbium excitation combined to the energy migration effect between Yb-Yb pair and Tb^{3+} ground-state depopulation via multiphonon excitation of the 7F 's excited-states, described quite well the experimental results.

Acknowledgements

The financial support for this research by **FINEP**, **CNPq**, **PADCT**, and **PRONEX-NEON**, Brazilian agencies, is gratefully acknowledged. The work of F. C. Cassanjes, S. J. L. Ribeiro and Y. Messaddeq has the financial support from **FAPESP** - SP - Brasil.

References

- [1] J. C. Wright, Top. Appl. Phys. 15 (1975) 239
- [2] D. C. Hanna, R. M. Percival, I. R. Perry, R. G. Smart, J. E. Townsend, A. C. Tropper, Opt. Comm. 78, 187 (1990)
- [3] Y-M. Hua, Q. Li, Y-L Chen, Y-X Chen, Opt. Comm. 88, 441 (1992)
- [4] A. S. Oliveira, M. T. de Araujo, A. S. Gouveia-Neto, A. S. B. Sombra, J. A. Medeiros Neto, N. Aranha, J. Appl. Phys. 83, 604 (1998)
- [5] A. S. Oliveira, M. T. de Araujo, A. S. Gouveia-Neto, A. S. B. Sombra, J. A. Medeiros Neto, Y. Messaddeq, Appl. Phys. Lett. 72, 753 (1998)
- [6] D. M. Baney, G. Rankin, K. W. Chang, Appl. Phys. Lett. 69, 1662 (1996)
- [7] T. R. Gosnell, Elect. Lett. 33, 411 (1997)
- [8] V. V. Ovsyankin, P. P. Feofilov, ZhETF Pis'ma 4 (1966) 471 {Sov. Phys. JETP Lett. 4 (1966) 317
- [9] G. S. Maciel, A. Biswas, P. N. Prasad, Opt. Commun. 178, 65 (2000)
- [10] L. D. Livanova, I. G. Saitkulov, A. L. Stolov, Sov. Phys. Solid State 11 (1969) 750
- [11] F. W. Ostermayer, L. G. VanUitert, Phys. Rev. B 1 (1970) 4208
- [12] R. S. Brown, W. S. Brocklesby, W. L. Barnes, J. E. Townsend, J. Lum. 63 (1995) 1
- [13] E. Martins, C. B. de Araujo, J. R. Delben, A. S. L. Gomes, B. J. da Costa, Y. Messaddeq, Opt. Commun. **158** (1998) 61
- [14] I. R. Martin, A. C. Yanes, J. Mendez-Ramos, M. E. Torres, V. D. Rodriguez, J. Appl. Phys. 89 (2001) 2520
- [15] G. M. Salley, R. Valiente, H. U. Guedel, J. Lum. 94-95 (2001) 305
- [16] F. Auzel, Phys. Rev. B 13 (1976) 2809
- [17] A. S. Oliveira, E. A. Gouveia, M. T. de Araujo, A. S. Gouveia-Neto, C. B. de Araújo, Y. Messaddeq, J. Appl. Phys. 87 (2000) 4274
- [18] P. V. dos Santos, E. A. Gouveia, M. T. de Araujo, A. S. Gouveia-Neto, A. S. B. Sombra, J. A. Medeiros Neto, Appl. Phys. Lett. **74** (1999) 3607; C. J. da Silva, M. T. de Araujo, E. A. Gouveia, A. S. Gouveia-Neto, Appl. Phys. B **70** (2000) 185
- [19] P. V. dos Santos, E. A. Gouveia, M. T. de Araujo, A. S. Gouveia-Neto, S. J. L. Ribeiro, S. H. S. Benedicto, J. Phys. : Condens. Matter **12** (2000) 10003
- [20] P. V. dos Santos, M. V. D. Vermelho, E. A. Gouveia, M. T. de Araujo, A. S. Gouveia-Neto, F. C. Cassanjes, S. J. L. Ribeiro, Y. Messaddeq, J. Appl. Phys. **90** (2001) 6550
- [21] L. de S. Menezes, G. S. Maciel, C. B. de Araújo, J. Appl. Phys. 90 (2001) 4498
- [22] P. V. dos Santos, M. V. D. Vermelho, E. A. Gouveia, M. T. de Araujo, A. S. Gouveia-Neto, F. C. Cassanjes, S. J. L. Ribeiro, Y. Messaddeq, J. Chem. Phys. **116** (2002) 6772