Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Non-Crystalline Solids 347 (2004) 52–55
JOURNAL OF NON-CRYSTALLINE SOLIDS
www.elsevier.com/locate/jnoncrysol

Infrared-to-visible upconversion luminescence of Er^{3+} and Yb^{3+} co-doped germanate glass

Guanshi Qin, Weiping Qin *, Changfeng Wu, Dan Zhao, Jisen Zhang, Shaozhe Lu, Shihua Huang, Wu Xu

Key laboratory of excited states processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Ren-min road 140, Changchun 130022, People's Republic of China

Received 23 June 2004; received in revised form 16 August 2004

Abstract

Frequency upconversion into green and red luminescence in Er^{3+} and Yb^{3+} co-doped germanate glass pumped with a 978 nm diode laser was presented. With increasing the excitation density, the green upconversion emission intensity was enhanced relative to the red one. Based on the emission spectra and the excitation density dependence of the upconversion emission intensity, we attributed the change of the upconversion emission spectra to the enhancement of three-photon excitation process to produce green luminescence with increasing the excitation density. The effects of this three-photon process on the 1.54 μm emission were also discussed.

PACS: 78.55.Hx; 78.20.−e; 78.47.+p

1. Introduction

Recently, Er^{3+} doped materials received great interest. These materials are an efficient medium not only for an eye-safe 1.54 μm laser but also for the short wavelength solid-state laser, and they have been widely studied [1–10]. Hutchinson et al. [1] observed the upconversion phenomena when a 980 nm laser diode (LD) was used to pump Er/Yb phosphate glass for 1.54 μm laser. Polman et al. [2,3] studied cooperative upconversion phenomena in Er^{3+} doped Al_2O_3 optical waveguide amplifiers. We [4] reported intense violet upconversion luminescence from Er/Yb co-doped amorphous fluoride film. Therefore, all the investigations mean that the studies on the upconversion phenomena in Er/Yb co-doped materials are very necessary and valuable.

Rare earth doped oxide glasses possessing high chemical durability and thermal stability are excellent materials for optoelectronics applications [5,6]. Among the oxide glasses, germanate glass (the presence of ~50% GeO_2) is attractive because a direct ultraviolet (UV) writing technique can be used to make waveguide devices [7]. In this communication, we observed upconversion properties of Er/Yb co-doped germanate glass pumped by a 978 nm LD. With increasing the excitation density, the green upconversion emission intensity relative to the red was enhanced. Based on the emission spectra and dependence of the upconversion emission intensity on the pump power, we attributed the change of the upconversion emission spectra to enhancement of the three-photon excitation process to produce green luminescence with increasing the excitation density. The effects of this three-photon process on the 1.54 μm emission was also discussed.

* Corresponding author. Tel.: +86 431 617 6352.
E-mail address: gsqin@yahoo.com (W. Qin).

0022-3093/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnoncrysol.2004.08.268

2. Experiments

Glass ($59.5GeO_2$–$25NaF$–$10BaF_2$–$0.5Er_2O_3$–$5Yb_2O_3$ (mol%)) sample was melted from commercial (3N5 purity) raw materials at about 1200 °C (in a electric furnace) for 40 min in a corundum crucible. The liquid was poured on a copper plate preheated at 150 °C and quenched with another copper plate. The resulting glass sample was measured using a fluorescence spectrophotometer (Hitachi F-4500). The upconversion emission spectra of the sample were measured using the above Fluorescence Spectrophotometer with a 978 nm LD as excitation source. The excitation density of the 978 nm LD was changed by varying the excited surface area of the sample. All measurements were made at room temperature.

3. Results and discussions

Fig. 1 represents the upconversion emission spectra at different excitation density (all the spectra are normalized at 544 nm). With increasing the excitation density, the green upconversion emission intensity relative to the red one was enhanced. The 520 nm emission intensity was not changed relative to the 540 nm, which showed that the temperature of the sample was not changed when the excitation density increased [8]. The temperature effect on the change of the upconversion emission spectra would be excluded (ignored).

In Er/Yb co-doped systems, up-converted emission may be resulted from different processes, including multi-step excited state absorption (ESA), energy transfer (ET) between neighboring excited Er^{3+} ions, and APTE (Addition de photons par transfer d'Energie) between Yb^{3+} and Er^{3+}. Among these processes, APTE is the most efficient. Infrared to green ($^2H_{11/2}$, $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transitions) and red ($^4F_{9/2} \rightarrow {}^4I_{15/2}$ transition) upconversion emissions in Er/Yb co-doped systems have been widely investigated [4].

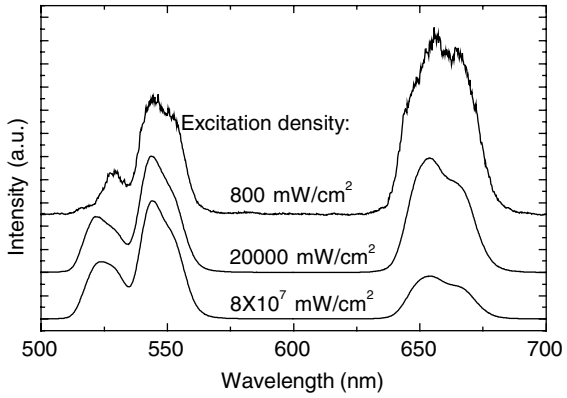

Fig. 1. The upconversion emission spectra at different excitation density (all the spectra are normalized at 544 nm).

For our germanate glass, the phonon side-band spectrum (data not shown) show that the phonon energy coupled with rare earth ions is about 800 cm^{-1}. With the excitation of a 978 nm LD, the below processes would produce green upconversion luminescence. They are:

$^2F_{5/2} \rightarrow {}^2F_{7/2}$ (Yb^{3+}): $^4I_{15/2} \rightarrow {}^4I_{11/2}$ (Er^{3+}), $^2F_{5/2} \rightarrow {}^2F_{7/2}$ (Yb^{3+}): $^4I_{11/2} \rightarrow {}^4F_{7/2}$ (Er^{3+}), $^4F_{7/2} \rightarrow {}^2H_{11/2}$, $^4S_{3/2}$ (Er^{3+}) (non-radiative relaxation) (two photon upconversion, TWU1); $^2F_{5/2} \rightarrow {}^2F_{7/2}$ (Yb^{3+}): $^4S_{3/2} \rightarrow {}^2G_{7/2}$ (Er^{3+}) (three photon upconversion, THU1); $^2F_{5/2} \rightarrow {}^2F_{7/2}$ (Yb^{3+}): $^4F_{9/2} \rightarrow {}^2H_{9/2}$ (Er^{3+}), followed by fast cascading relaxation to the $^2H_{11/2}$ and $^4S_{3/2}$ levels (three photon upconversion, THU2).

The population of the $^4F_{9/2}$ level producing red upconversion luminescence may come from the following processes:

$^2F_{5/2} \rightarrow {}^2F_{7/2}$($Yb^{3+}$):$^4I_{15/2} \rightarrow {}^4I_{11/2}$($Er^{3+}$),$^4I_{11/2} \rightarrow {}^4I_{13/2}$ (non-radiative relaxation),$^2F_{5/2} \rightarrow {}^2F_{7/2}$ (Yb^{3+}): $^4I_{13/2} \rightarrow {}^4F_{9/2}$ (Er^{3+}) (two photon upconversion, TWU2) and the cross-relaxation between nearby $Er^{3+} \ldots Er^{3+}$ ($^4S_{3/2} \rightarrow {}^4F_{9/2}$: $^4I_{9/2} \rightarrow {}^4F_{9/2}$) (high Er^{3+} concentration) (CR1).

Fig. 2 shows the emission spectra of the sample (a) excitation $\lambda_{exc} = 379$ nm and (b) excitation $\lambda_{exc} = 487$ nm. The results show that the excitation of the $^4F_{7/2}$ or $^4G_{11/2}$ level would produce intense green emission, which is attributed to fast cascading relaxation from

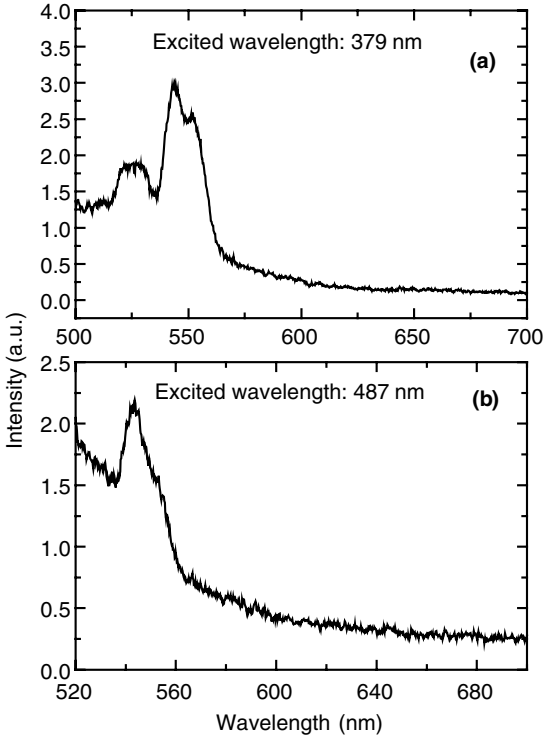

Fig. 2. The emission spectra of the sample (a) $\lambda_{exc} = 379$ nm and (b) $\lambda_{exc} = 487$ nm.

the $^4F_{7/2}$ or $^4G_{11/2}$ level to $^2H_{11/2}$ and $^4S_{3/2}$ levels, and no red emission, which indicates that the CR1 process to populate the red emission state $^4F_{9/2}$ is ineffective in our sample. Based on above discussions, the upconversion mechanism is given in Fig. 3.

Considering Fig. 3, a possible explanation responsible for the change of the upconversion emission spectra with the excitation density is the intensification of THU2: $^2F_{5/2} \rightarrow {}^2F_{7/2}$ (Yb^{3+}): $^4F_{9/2} \rightarrow {}^2H_{9/2}$ (Er^{3+}), followed by fast cascading relaxation to the $^2H_{11/2}$ and $^4S_{3/2}$ levels (three photon upconversion process). The intensification of this process may depopulate the $^4F_{9/2}$ level, populate the $^2H_{11/2}$, $^4S_{3/2}$ levels and enhance the green upconversion emission intensity relative to the red with increasing the excitation density. To clarify the efficiency of this process, we carried out (did) the following experiments.

For unsaturated upconversion, emission intensity, I_s, is proportional to I^n, where I is the excitation light intensity and n, the number of photons absorbed per up-converted photon emitted [4]. The intensity dependence of the upconversion emissions was obtained, as shown in Fig. 4(a) at low excitation density (the excitation area is $\sim 9\,mm^2$) and (b) at high excitation density (the excitation area is $\sim 0.04\,mm^2$). From Fig. 4, at low excitation density, $n_{green} = 1.93$ and $n_{red} = 2.02$; at high excitation density $n_{green} = 2.56$ and $n_{red} = 1.73$. That is to say, with increasing the excitation density, n_{green} increases from 1.93 to 2.56, and n_{red} decreases from 2.02 to 1.73. These results confirm that the THU2 (three-photon upconversion process) is the most possible process to cause the change of the upconversion emission spectra, and it populates the $^2H_{11/2}$, $^4S_{3/2}$ levels, makes n_{green} increased; and depopulate the $^4F_{9/2}$ level, n_{red} decreased.

In Er/Yb co-doped oxide glasses, we believe that three-photon upconversion (THU2) is a general phenomenon due to their high phonon energy. When the excitation density is high enough, the population in

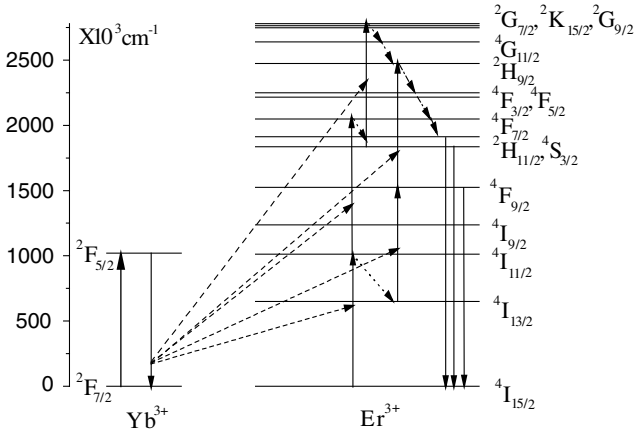

Fig. 3. The upconversion mechanism in our sample.

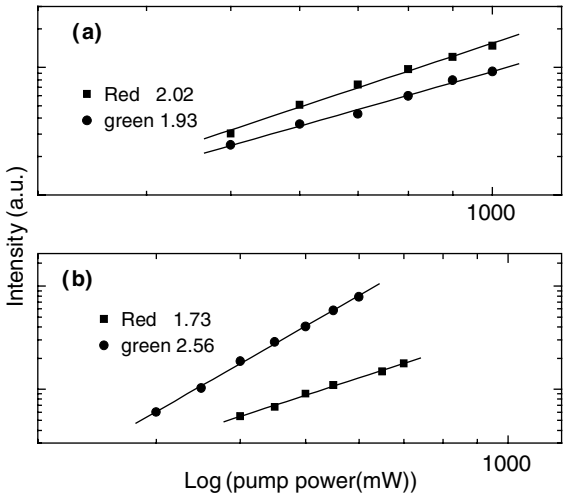

Fig. 4. Intensity dependence of the upconversion emissions (a) at low excitation density (the excited surface area of the sample is $9\,mm^2$) and (b) at high excitation density (the excited surface area of the sample is $0.04\,mm^2$).

1.54 μm laser upper state $^4I_{13/2}$ will increase due to the increasing excitation density. However, meanwhile, because of three-photon process dominating at high excitation density, some of the ions at $^4I_{13/2}$ level will be excited to $^4F_{9/2}$ by energy transfer: $^2F_{5/2} \rightarrow {}^2F_{7/2}$ (Yb^{3+}): $^4I_{13/2} \rightarrow {}^4F_{9/2}$ (Er^{3+}) and then to high state $^2H_{9/2}$ by THU2: $^2F_{5/2} \rightarrow {}^2F_{7/2}$ (Yb^{3+}): $^4F_{9/2} \rightarrow {}^2H_{9/2}$ (Er^{3+}), followed by fast cascading relaxation to the $^2H_{11/2}$ and $^4S_{3/2}$ levels (three photon upconversion). This three-photon process will decrease the population inversion in laser upper level and hence the 1.54 μm laser output will not increase significantly while the excitation density increases. We believe that the saturation of 1.54 μm laser power in Er/Yb co-doped oxide glasses is not only due to the well-known thermal effect [9–12], but also the three-photon upconversion process.

4. Conclusion

In conclusion, we studied upconversion properties of Er/Yb co-doped germanate glass pumped by a 978 nm LD. With increasing the excitation density, the green upconversion emission intensity relative to the red one was enhanced. Based on the emission spectra and the dependence of the upconversion emission intensity on the pump power, we attributed the change of the upconversion emission spectra to the enhancement of the three-photon excitation process (THU2) to produce green luminescence with increasing the excitation density. The THU2 process at high excitation density provided a good basis for explaining the effect of the three-photon process on the saturation of 1.54 μm laser power of Er/Yb co-doped oxide glass laser.

Acknowledgments

This work was supported by State Key Project of Basic Research of China (973), NSF of China (10274082) and NSF of Jilin province (19990514).

References

[1] J.A. Huchinson, T.H. Allik, Appl. Phys. Lett. 60 (1992) 1424.
[2] G.N. van den Hoven, E. Snoeks, A. Polman, C. van Dam, J.W.M. van Uffelen, M.K. Smit, Upconversion in Er-implanted Al_2O_3 wave-guides, J. Appl. Phys. 79 (1996) 1528.
[3] P.G. Kik, A. Polman, Cooperative upconversion as the gain-limiting factor in Er doped miniature Al_2O_3 optical wave-guide amplifiers, J. Appl. Phys. 93 (2003) 1.
[4] G. Qin, W. Qin, S. Huang, C. Wu, D. Zhao, B. Chen, S. Lv, E. Shulin, Infrared to violet upconversion from Yb^{3+} and Er^{3+} co-doped amorphous fluoride film prepared by pulsed laser deposition, J. Appl. Phys. 92 (2002) 6936.
[5] H. Lin, S. Jiang, J. Wu, F. Song, N. Peyghambarian, E.Y.B. Pun, Er^{3+} doped Na_2O–Nb_2O_5–TeO_2 glasses for optical waveguide laser and amplifier, J. Phys. D: Appl. Phys. 36 (2003) 812.
[6] A. Jha, S. Shen, M. Naftaly, Structure origin of spectral broadening of 1.54 μm emission in Er^{3+}-doped tellurite glasses, Phys. Rev. B 62 (2000) 6215.
[7] H. Lin, E.Y.B. Pun, S.Q. Man, X.R. Liu, Optical transitions and frequency upconversion of Er^{3+} ions in $Na_2O \cdot Ca_3Al_2Ge_3O_{12}$ glasses, J. Opt. Soc Am. B 18 (2001) 602.
[8] J.F. Philipps, T. Topfer, H. Ebendorff-Heidepriem, D. Ehrt, R. Sauerbrey, Spectroscopic and lasing properties of Er/Yb co-doped fluoride phosphate glasses, Appl. Phys. B 72 (2001) 399.
[9] S. Jiang, J. Myers, D. Rhonehouse, M. Myers, R. Belford, S. Hamlin, Proc. SPIE 2138 (1994) 166.
[10] M. Lukac, M. Maricek, IEEE J. Quantum Electron 26 (1990) 1779.
[11] M. Tilleman, S. Jackel, I. Moshe, Proc. SPIE 3264 (1998) 126.
[12] M. Tilleman, S. Jackel, I. Moshe, Opt. Eng. 37 (1998) 2512.