

# Blue Up-Conversion Emission from a PbF<sub>2</sub>/GeO<sub>2</sub>/WO<sub>3</sub> Glass Doped with Tm<sup>3+</sup> or Tm<sup>3+</sup>/Tb<sup>3+</sup> Ions<sup>1</sup>

W. Xu,\* G. Chen,\*<sup>2</sup> and J. R. Peterson\*<sup>†,3</sup>

\*Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996-1600; and †Transuranium Research Laboratory (Chemical and Analytical Sciences Division), Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, Tennessee 37831-6375

Received May 12, 1994; in revised form July 7, 1994; accepted July 13, 1994

The blue up-conversion emission properties from Tm<sup>3+</sup> ions doped into a PbF<sub>2</sub>/GeO<sub>2</sub>/WO<sub>3</sub> heavy-metal fluoride glass upon 15,456 cm<sup>-1</sup> laser line excitation have been studied. In some cases both Tm<sup>3+</sup> and Tb<sup>3+</sup> ions were codoped into the same glass sample. Two blue emission bands, centered at 22,173 cm<sup>-1</sup> for the <sup>1</sup>D<sub>2</sub> → <sup>3</sup>H<sub>4</sub> Tm<sup>3+</sup> transition and at 20,833 cm<sup>-1</sup> for the <sup>1</sup>G<sub>4</sub> → <sup>3</sup>H<sub>6</sub> Tm<sup>3+</sup> transition, have been observed. The up-conversion emission follows a two-photon absorption process for both bands. Compared to Tm<sup>3+</sup> ion doping alone, codoping with Tb<sup>3+</sup> ions increases the 22,173 cm<sup>-1</sup> emission and decreases the 20,833 cm<sup>-1</sup> emission. These results are due to the energy transfer between Tm<sup>3+</sup> and Tb<sup>3+</sup> ions. A simple rate-equation model has been used to describe this energy transfer process. © 1995 Academic Press, Inc.

## INTRODUCTION

The study of luminescence and up-conversion processes in heavy-metal fluoride glasses doped with lanthanide ions has been attracting great interest (1-8). This interest arises from the need for higher densities in optical data storage and for infrared laser windows, fiber optic materials, and laser host materials. Furthermore, heavy-metal fluoride glasses have become available with up-conversion efficiencies comparable to those in fluoride crystals, which are the most efficient up-conversion materials known (9, 10). Such glasses allow high concentrations of trivalent lanthanide ions to be introduced into them.

Trivalent thulium ion is one of the possible candidates

<sup>1</sup> Research sponsored by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under Grant DE-FG05-88ER13865 to the University of Tennessee, Knoxville and Contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc. The U.S. Government's right to retain a nonexclusive royalty-free license in and to the copyright covering this paper, for governmental purposes, is acknowledged.

<sup>2</sup> Present address: Department of Materials Science, Jilin University, Changchun, People's Republic of China.

<sup>3</sup> To whom correspondence should be addressed.

for obtaining blue up-conversion emission when introduced into a Yb<sup>3+</sup>-doped glass and excited by infrared light (10,204 cm<sup>-1</sup>) (11, 12). This up-conversion process depends on a three-photon absorption for the blue Tm<sup>3+</sup> emission band (<sup>1</sup>G<sub>4</sub> → <sup>3</sup>H<sub>6</sub> transition, 20,833 cm<sup>-1</sup>), i.e., energy transfer from the <sup>2</sup>F<sub>5/2</sub> level of Yb<sup>3+</sup> to the <sup>3</sup>H<sub>4</sub> (via the <sup>3</sup>H<sub>5</sub> level), <sup>3</sup>F<sub>4</sub> (via the <sup>3</sup>F<sub>2</sub> level), and <sup>1</sup>G<sub>4</sub> levels of Tm<sup>3+</sup> in three steps. Up-conversion of red light into blue light in Tm<sup>3+</sup>-doped glass has also been reported (13-15). This work indicated that because the blue emission might result from a two-photon absorption process, the efficiency of the up-conversion would be higher. One of us has reported that the enhancement of blue emission from Tm<sup>3+</sup> ions (<sup>1</sup>G<sub>4</sub> → <sup>3</sup>H<sub>6</sub> transition) is due to the back energy transfer from Yb<sup>3+</sup> ions under 14,706 cm<sup>-1</sup> (680 nm) light excitation in fluorophosphate glass and glass ceramic (16, 17).

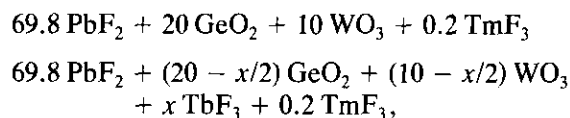
Blue laser action in Tm<sup>3+</sup> ions is, in principle, easy to obtain because the 22,173 cm<sup>-1</sup> emission (<sup>1</sup>D<sub>2</sub> → <sup>3</sup>H<sub>4</sub> transition) involves a transition to an excited state (<sup>3</sup>H<sub>4</sub> level) of the Tm<sup>3+</sup> ion which is not occupied at room temperature; therefore, population inversion between the <sup>1</sup>D<sub>2</sub> and <sup>3</sup>H<sub>4</sub> levels should be possible. However, the lifetime (9 msec) of the <sup>3</sup>H<sub>4</sub> level is much longer than that (40 μsec) of the <sup>1</sup>D<sub>2</sub> level, which makes operation of a 22,173 cm<sup>-1</sup> up-conversion laser only possible in a pulse mode unless the lifetime of the <sup>3</sup>H<sub>4</sub> level is considerably shortened (12). Recently a report appeared on the energy transfer between Tm<sup>3+</sup> and Eu<sup>3+</sup> ions in a fluorozirconate fiber codoped with these ions in order to shorten the lifetime of the <sup>3</sup>H<sub>4</sub> Tm<sup>3+</sup> level (18).

Because the <sup>3</sup>H<sub>4</sub> level of a Tm<sup>3+</sup> ion is nearly resonant with the <sup>7</sup>F<sub>0</sub> level of a Tb<sup>3+</sup> ion, it should be possible to quench the lifetime of the <sup>3</sup>H<sub>4</sub> Tm<sup>3+</sup> level by means of an energy transfer between these two ions. In this work we report our experimental results at room temperature upon red (15,456 cm<sup>-1</sup>) excitation into the <sup>3</sup>F<sub>2</sub> level of Tm<sup>3+</sup> ions doped into a PbF<sub>2</sub>/GeO<sub>2</sub>/WO<sub>3</sub> glass and into the same glass codoped with Tm<sup>3+</sup> and Tb<sup>3+</sup> ions. The properties of the blue up-conversion emission from the Tm<sup>3+</sup> ion

and the energy transfer between  $\text{Tb}^{3+}$  and  $\text{Tm}^{3+}$  ions have been studied as a function of the concentration of  $\text{Tb}^{3+}$  ions in the glass. The up-conversion processes and energy transfer mechanism are elucidated.

### EXPERIMENTAL DETAILS

The various glass samples were prepared by mixing together glass-forming oxides  $\text{GeO}_2$  and  $\text{WO}_3$  with lead(II) fluoride and lanthanide fluorides (99.995%). The mixture was heated and melted inside a muffle furnace at  $950^\circ\text{C}$  for 45 min in air. The sample was then obtained by quickly pouring the melt onto a metal sheet. The sample compositions (mole%) used in this work were



where  $x = 0.5, 0.8, 1.2,$  and  $1.5$ .

Optical absorption spectra were recorded by using a Cary 17 spectrophotometer that operates from 320 to 2100 nm. The  $15,456 \text{ cm}^{-1}$  ( $647.8 \text{ nm}$ ) line from a krypton laser (Spectra Physics Model 164) was used as the excitation source. The luminescence spectra were recorded with a Ramanor Model HG.2S spectrophotometer (Jobin-Yvon Instruments SA), having a resolution of  $0.5 \text{ cm}^{-1}$  at  $19,436 \text{ cm}^{-1}$ . The collected light was detected by a photon counting system, which employed a cooled photomultiplier tube (Hamamatsu 636) and a multichannel analyzer (Nicolet 1170) interfaced with an AT personal computer using "Spectra Calc" software (Galactic Industries Corp.).

The intensity of the exciting light was monitored with a Coherent Model 240 power meter.

### RESULTS

The absorption spectrum at room temperature of  $\text{Tm}^{3+}$  ions in a glass sample doped with 0.2 mole%  $\text{Tm}^{3+}$  was recorded in the wavelength range of 320–2100 nm. This portion of the spectrum exhibited seven absorption bands centered at 1700, 1210, 775, 680, 656, 465, and 356 nm corresponding to the absorption transitions from the  $^3\text{H}_6$  ground state to the  $^3\text{H}_4$ ,  $^3\text{H}_5$ ,  $^3\text{F}_4$ ,  $^3\text{F}_3$ ,  $^3\text{F}_2$ ,  $^1\text{G}_4$ , and  $^1\text{D}_2$  excited states of the  $\text{Tm}^{3+}$  ion (17), respectively. From this spectrum we determined the energies of the different states of the  $\text{Tm}^{3+}$  ion in the host glass.

Up-conversion emission spectra from the glass host doped with 0.2 mole%  $\text{TmF}_3$  and codoped with 0.2 mole%  $\text{TmF}_3$  and with 0.5 and 1.5 mole%  $\text{TbF}_3$  under  $15,456 \text{ cm}^{-1}$  light excitation in the range  $20,132$ – $23,000 \text{ cm}^{-1}$  are shown in Fig. 1. Two main emission bands centered at  $22,173 \text{ cm}^{-1}$  ( $450 \text{ nm}$ ) and  $20,833 \text{ cm}^{-1}$  ( $480 \text{ nm}$ ) are ob-

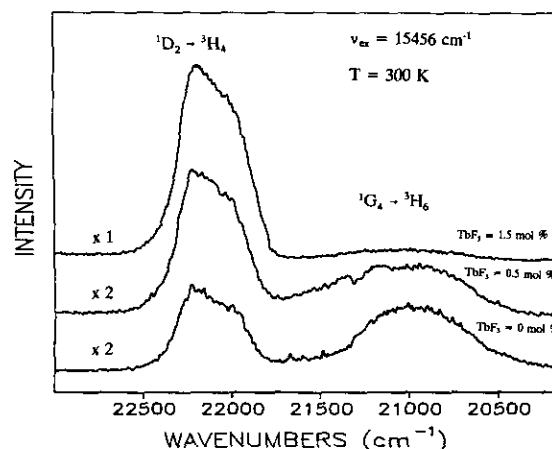


FIG. 1. Up-conversion emission spectrum at room temperature from  $\text{Tm}^{3+}$  ions in a glass doped with 0.2 mole%  $\text{TmF}_3$  only and codoped with 0.2 mole%  $\text{TmF}_3$  and 0.5 or 1.5 mole%  $\text{TbF}_3$ , under  $15,456 \text{ cm}^{-1}$  excitation.

served. According to the energy-level diagram of the  $\text{Tm}^{3+}$  ion, these emission bands are attributed to the  $^1\text{D}_2 \rightarrow ^3\text{H}_4$  and  $^1\text{G}_4 \rightarrow ^3\text{H}_6$  transitions, respectively. For the codoped samples, the spectral shape and position of the emission bands are consistent in all cases, but the intensity of the emission centered at  $20,833 \text{ cm}^{-1}$  decreases with increasing concentration of  $\text{TbF}_3$ , while that of the  $22,173 \text{ cm}^{-1}$  band increases with increasing concentration of  $\text{TbF}_3$ . It is clear that these significant changes in the intensity of the  $\text{Tm}^{3+}$  ion emission are caused by interaction between the  $\text{Tm}^{3+}$  and  $\text{Tb}^{3+}$  ions.

The intensities of the two blue up-conversion emission bands from the  $\text{Tm}^{3+}$  ion were measured as a function of the  $\text{TbF}_3$  concentration under red excitation. The results are plotted in Fig. 2. The intensity of the  $22,173 \text{ cm}^{-1}$

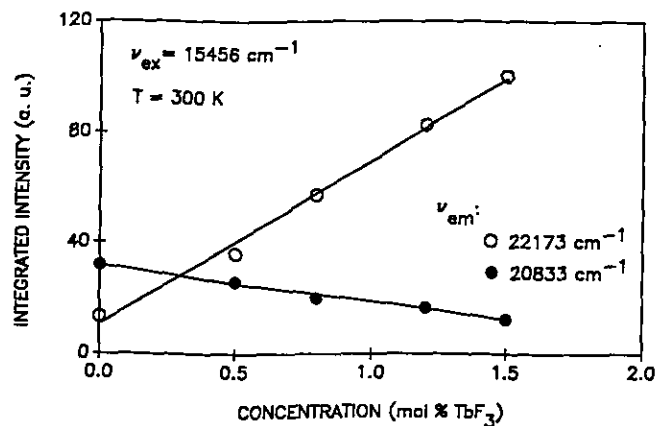


FIG. 2. Dependence of the two blue up-conversion emission intensities from  $\text{Tm}^{3+}$  ions in a glass on the dopant  $\text{TbF}_3$  concentration under identical red light excitation.

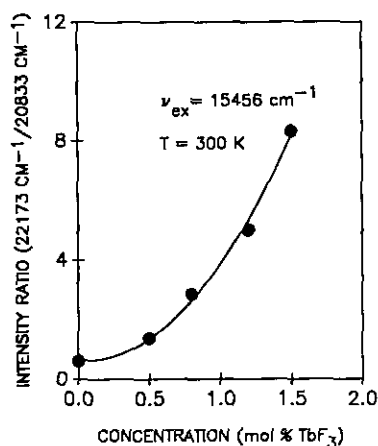


FIG. 3. Ratio of the intensities of the  $Tm^{3+}$  ion  ${}^1D_2 \rightarrow {}^3H_4$  emission ( $22,173\text{ cm}^{-1}$ ) to the  ${}^1G_4 \rightarrow {}^3H_6$  emission ( $20,833\text{ cm}^{-1}$ ) as a function of the  $TbF_3$  concentration under constant  $15,456\text{ cm}^{-1}$  excitation.

emission increases linearly with increasing  $TbF_3$  concentration, while the  $20,833\text{ cm}^{-1}$  emission intensity decreases at a slower linear rate over the same  $TbF_3$  range. When the concentration of  $TbF_3$  changes from 0 to 1.5 mole%, the  $22,173\text{ cm}^{-1}$  emission increases about 5 times while the  $20,833\text{ cm}^{-1}$  emission decreases about 2.5 times. The ratio of the intensity of the  $22,173\text{ cm}^{-1}$  emission to that of the  $20,833\text{ cm}^{-1}$  emission versus  $TbF_3$  concentration is shown in Fig. 3, with a 12-fold increase over the 0–1.5 mole%  $TbF_3$  concentration range.

The dependence of the intensities of the two blue up-conversion emission bands from the  $Tm^{3+}$  ion on the  $15,456\text{ cm}^{-1}$  excitation light intensity for the singly doped sample is reported in Fig. 4. The experimental data have been fit to straight lines, whose slopes are about 2. Similar results were obtained for the same two blue emission bands exhibited by the codoped samples.

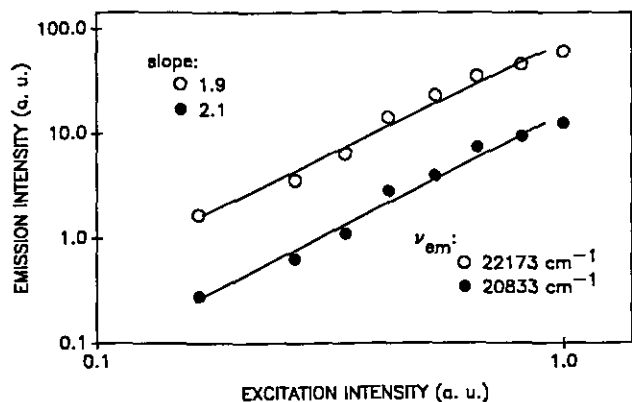


FIG. 4. Two blue up-conversion emission intensities from  $Tm^{3+}$  ions in a glass doped with 0.2 mole%  $TmF_3$ , as a function of red light excitation intensity.

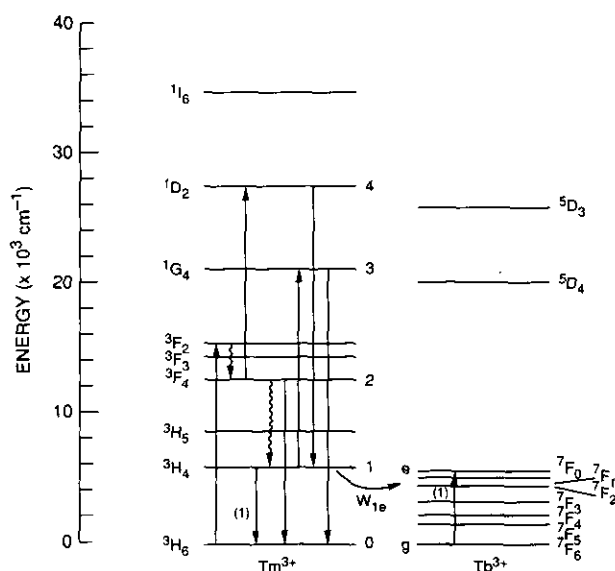


FIG. 5. Schematic energy-level diagrams of  $Tm^{3+}$  and  $Tb^{3+}$  ions with electronic transitions indicated for excitation and up-conversion processes.

## DISCUSSION

Two blue emission bands peaking at  $22,173$  and  $20,833\text{ cm}^{-1}$  are observed under  $15,456\text{ cm}^{-1}$  light excitation and their intensities depend quadratically on the excitation light intensity for both the singly and the codoped glasses. This means that both up-conversion processes involve two-photon absorptions (4, 19). In the first photon absorption step,  $Tm^{3+}$  ions are excited directly into the  ${}^3F_2$  level. Then they may relax to the  ${}^3F_4$  and  ${}^3H_4$  levels. A second  $15,456\text{ cm}^{-1}$  photon absorption by these excited  $Tm^{3+}$  ions raises them to the  ${}^1D_2$  and  ${}^1G_4$  levels, respectively (see Fig. 5). The observed blue emissions result from the  ${}^1D_2 \rightarrow {}^3H_4$  and  ${}^1G_4 \rightarrow {}^3H_6$  transitions. This up-conversion mechanism is referred to as an excited state absorption (ESA) process (12, 14).

For the codoped sample under the same excitation conditions, the  $20,833\text{ cm}^{-1}$  emission band decreases and the  $22,173\text{ cm}^{-1}$  emission band increases with an increasing concentration of  $TbF_3$ . We suggest that this result is due to energy transfer between the  $Tm^{3+}$  and  $Tb^{3+}$  ions. For instance, excited  $Tm^{3+}$  ions in the  ${}^3H_4$  level may transfer their energy to nearby ground-state  $Tb^{3+}$  ions, exciting them to the  ${}^7F_0$  level ((1) in Fig. 5):  $Tm^{3+}({}^3H_4) + Tb^{3+}({}^7F_6) \rightarrow Tm^{3+}({}^3H_6) + Tb^{3+}({}^7F_0)$ . This process decreases the population of  $Tm^{3+}({}^3H_4)$ , thereby reducing the probability of ESA from this level to the  $Tm^{3+}({}^1G_4)$  level, and therefore the  $20,833\text{ cm}^{-1}$  emission from  $Tm^{3+}$  ions decreases with increasing  $Tb^{3+}$  ion concentration. Energy transfer from  $Tm^{3+}$  to  $Tb^{3+}$  ions as described above results in depopulation of the  ${}^3H_4$  level in the  $Tm^{3+}$  ions,

which further reduces the probability of  $\text{Tm}^{3+}$  ion excitation to the  ${}^1G_4$  level relative to that to the  ${}^1D_2$  level. Thus, energy transfer plays a vital role in increasing the 22,173  $\text{cm}^{-1}$  and decreasing the 20,833  $\text{cm}^{-1}$  up-conversion emissions from  $\text{Tm}^{3+}$  ions in the codoped glasses.

This proposed energy transfer process can be described using the following rate-equation model. The  $\text{Tm}^{3+}$  and  $\text{Tb}^{3+}$  ion energy levels involved are denoted in Fig. 5 by Arabic numerals to the right of the  $\text{Tm}^{3+}$  ion energy level diagram and by e (excited state) and g (ground state) to the left of the  $\text{Tb}^{3+}$  ion energy level diagram. To excite the  ${}^3F_2$  level of  $\text{Tm}^{3+}$  ion from its ground state ( ${}^3H_6$ ) by 15,456  $\text{cm}^{-1}$  light, the appropriate steady-state rate equations are

$$dN_1/dt = \alpha A_{21} N_2 - N_1/\tau_1 - W_{1e} N_g N_1 - \sigma_{13} P N_1 = 0 \quad [1]$$

$$dN_2/dt = \sigma_{02} P N_0 - N_2/\tau_2 - \sigma_{24} P N_2 = 0 \quad [2]$$

$$dN_3/dt = \sigma_{13} P N_1 - N_3/\tau_3 = 0 \quad [3]$$

$$dN_4/dt = \sigma_{24} P N_2 - N_4/\tau_4 = 0 \quad [4]$$

$$dN_e/dt = W_{1e} N_g N_1 - N_e/\tau_e = 0 \quad [5]$$

where  $N_i$  is the electron population in the  $\text{Tm}^{3+}$  ion energy level  $i$ ;  $N_e$  and  $N_g$  are the respective electron populations in the  ${}^7F_0$  and  ${}^7F_6$  levels of the  $\text{Tb}^{3+}$  ion;  $W_{1e}$  represents the energy transfer rate from  $\text{Tm}^{3+}$  to  $\text{Tb}^{3+}$  ions;  $\tau_i$  is the radiative lifetime of  $\text{Tm}^{3+}$  ions in level  $i$ ;  $\tau_e$  is the radiative lifetime of the  ${}^7F_0$  level of  $\text{Tb}^{3+}$  ions;  $P$  is the excitation intensity;  $\sigma_{ij}$  is the ESA coefficient between  $\text{Tm}^{3+}$  ion energy levels  $i$  and  $j$ ;  $N_0$  is the electron population of the ground state in  $\text{Tm}^{3+}$  ions;  $\alpha$  is the fraction of radiative decays from the  ${}^3F_4$  level in  $\text{Tm}^{3+}$  ions; and  $A_{21}$  is the probability of radiative decay from the  ${}^3F_4$  to  ${}^3H_4$  levels in the  $\text{Tm}^{3+}$  ions. These rate equations neglect stimulated emission. The steady-state populations of the  ${}^1D_2$  and  ${}^1G_4$  levels in excited  $\text{Tm}^{3+}$  ions are obtained by solving Eqs. [1]–[5] simultaneously and are given by

$$N_4 \approx \tau_4 N_e [A/(\tau_1)^* + A\sigma_{13}P] \quad [6]$$

and

$$N_3 = \sigma_{13} P \tau_3 N_1, \quad [7]$$

where

$$A = \sigma_{24} P / \alpha A_{21} W_{1e} N_g \tau_e \quad [8]$$

and

$$1/(\tau_1)^* = 1/\tau_1 + W_{1e} N_g. \quad [9]$$

From Eq. [6] the population of (and therefore the emission

intensity from) the  ${}^1D_2$  level in  $\text{Tm}^{3+}$  ions is proportional to  $1/(\tau_1)^*$ . Because of the possible energy transfer from the  $\text{Tm}^{3+}({}^3H_4)$  to the  $\text{Tb}^{3+}({}^7F_0)$  levels, the lifetime ( $(\tau_1)^*$ ) of the  $\text{Tm}^{3+}({}^3H_4)$  level is shortened (7, 17). As the  $\text{Tb}^{3+}$  ion concentration is increased,  $(\tau_1)^*$  decreases, and the emission intensity from the  ${}^1D_2$  level of  $\text{Tm}^{3+}$  ions is increased (according to Eqs. [9] and [6]).

From Eq. [7] the population of the  ${}^1G_4$  level in  $\text{Tm}^{3+}$  ions is proportional to that of the  ${}^3H_4$  level ( $N_1$ ), which is reduced by efficient energy transfer to  $\text{Tb}^{3+}$  ions. Therefore the excited state absorption (ESA) process from the  ${}^3H_4$  level to the  ${}^1G_4$  level becomes less probable, thus decreasing the emission intensity from the  ${}^1G_4$  level. Our experimental observations are in agreement with this result from the rate-equation model.

In summary, two blue up-conversion emission bands centered at 22,173 and 20,833  $\text{cm}^{-1}$  have been observed under red light excitation of  $\text{PbF}_2/\text{GeO}_2/\text{WO}_3$  heavy-metal fluoride glass doped with  $\text{Tm}^{3+}$  ions. This up-conversion involves a two-photon absorption process for both blue emission bands.

The stronger blue emission, centered at 22,173  $\text{cm}^{-1}$ , is obtained in the glass codoped with  $\text{Tm}^{3+}$  and  $\text{Tb}^{3+}$  ions. This emission intensity increases with concentration of  $\text{Tb}^{3+}$  ions, while the other blue emission (20,833  $\text{cm}^{-1}$ ) decreases. We suggest that this result is due to energy transfer from  $\text{Tm}^{3+}$  to  $\text{Tb}^{3+}$  ions, which increases the deactivation rate of the  ${}^3H_4$  level in  $\text{Tm}^{3+}$  ions. This decrease in the effective  ${}^3H_4$  level lifetime has potential implications toward increasing the efficiency of a 22,173  $\text{cm}^{-1}$  laser (12). Laser action at 22,173  $\text{cm}^{-1}$  seems promising because the  ${}^3H_4$  level in  $\text{Tm}^{3+}$  ions is not occupied at room temperature, and the energy gap between this level and the ground state ( ${}^3H_6$ ) is over 6000  $\text{cm}^{-1}$ . Therefore, population inversion between the  ${}^1D_2$  and the  ${}^3H_4$  levels should be possible. On the other hand, an energy transfer process from  $\text{Tb}^{3+}$  to  $\text{Tm}^{3+}$  ions has also been observed in the present work.

## REFERENCES

1. M. Poulain, *J. Non-Cryst. Solids* **56**, 1 (1983).
2. D. C. Tran, G. H. Sigel, Jr., and B. Bendow, *J. Lightwave Technol.* **LT-2**, 566 (1984).
3. J. P. Van der Ziel, L. G. Van Uitert, W. H. Grokiewicz, and R. M. Mikuljak, *J. Appl. Phys.* **60**, 4262 (1986).
4. D. C. Yeh, W. A. Sibley, M. J. Suscavage, and M. G. Drexhage, *J. Appl. Phys.* **62**, 266 (1987).
5. M. G. Drexhage, B. Bendow, and C. T. Moynihan, *Laser Focus* **10**, 61 (1980).
6. B. Bendow and M. G. Drexhage, *Proc. Photo-Opt. Instrum. Eng.* **266**, 16 (1981).
7. Xu Wu, J. P. Denis, G. Ozen, Ph. Goldner, M. Genotelle, and F. Pelle, *Chem. Phys. Lett.* **203**, 211 (1993).

8. Xu Wu, J. P. Denis, G. Ozen, A. Kermaoui, and F. Pelle, *Phys. Status Solidi A* **141**, 445 (1993).
9. R. S. Quimby, M. G. Drexhage, and M. J. Suscavage, *Electron. Lett.* **23**, 32 (1987).
10. D. C. Yeh, W. A. Sibley, and M. J. Suscavage, *J. Appl. Phys.* **63**, 4644 (1988).
11. W. Ryba-Romannowski, S. Golab, and G. Dominiak-Dzik, *J. Phys. Chem. Solids* **54**, 153 (1993).
12. E. W. Oomen, *J. Lumin.* **50**, 317 (1992).
13. W. Lenth and R. M. Macfarlane, *J. Lumin.* **45**, 346 (1990).
14. J. Y. Allain, M. Monerie, and H. Poignant, *Electron. Lett.* **26**, 166 (1990).
15. M. Monerie, T. Georges, P. L. Francois, J. Y. Allain, and D. Neveux, *Electron. Lett.* **26**, 320 (1990).
16. G. Ozen, J. P. Denis, Ph. Goldner, Xu Wu, M. Genotelle, and F. Pelle, *Appl. Phys. Lett.* **62**, 928 (1993).
17. Xu Wu, J. P. Denis, G. Ozen, A. Kermaoui, F. Pelle, and B. Blanzat, *J. Appl. Phys.* **75**(8), 4180 (1994).
18. G. Tohmon, H. Sato, J. Ohya, and T. Fujita, *J. Appl. Phys.* **73**, 1528 (1993).
19. M. A. Chamarro and R. Cases, *J. Lumin.* **46**, 59 (1990).