

phys. stat. sol. (a) **141**, 445 (1994)

Subject classification: 78.45 and 78.55; S10.15

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## **The Up-Conversion Luminescence of $\text{Tm}^{3+}$ in Glass Ceramics Doped with $\text{Yb}^{3+}$ under Infrared Excitation**

By

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A detailed study of the spectroscopic properties of the  $\text{PbF}_2 + \text{GeO}_2 + \text{WO}_3 : \text{YbF}_3, \text{TmF}_3$  glass ceramics under infrared excitation (966 nm) is performed. The absorption, emission, excitation spectra, luminescence decay times, and up-conversion efficiency are measured. The up-conversion of infrared into violet (363 nm), blue (451 and 478 nm), and red (680, 698, and 779 nm) is observed for  $\text{Tm}^{3+}$  ions in the sample. The up-conversion processes involve a two-photon and a three-photon absorption for the red and blue emissions (478 nm). A four-photon process happens for violet and another blue emissions (451 nm). In addition, the up-conversion emission spectra of violet, blue, and red bands of  $\text{Tm}^{3+}$  ions are obtained in the range of 12 to 320 K. It is found that the probability of energy transfer between  $\text{Yb}^{3+}$  and  $\text{Tm}^{3+}$  ions depends on temperature. By a comparative method, absolute fluorescence efficiencies of  $10^{-6}$  and  $5.86 \times 10^{-3}$  are obtained for the dominant blue (478 nm) and red (779 nm) up-conversions when the sample is excited by 966 nm light with an absorbed intensity of  $16.5 \text{ mW/cm}^2$  at room temperature.

### **1. Introduction**

Nowadays there is a great interest in glass ceramics for the conversion of infrared radiation into visible light. This phenomenon is useful for detection of infrared radiation by changing the light to a spectral region where detectors have higher efficiency. In addition, these compounds have some advantages because they present a high transparency from the UV to IR and relatively large amount of trivalent rare-earth ions can be introduced into the host. [1, 2] showed that  $\text{PbF}_2 + \text{GeO}_2 : \text{Yb}_2\text{O}_3, \text{Tm}_2\text{O}_3$  compound has higher blue up-conversion efficiency under infrared excitation. This high efficiency is due to the fact that rare-earths are located in the crystalline phase and are surrounded more by fluorine than oxygen ions [3].

To increase the blue up-conversion efficiency, we used  $\text{YbF}_3$  and  $\text{TmF}_3$  instead of  $\text{Yb}_2\text{O}_3$  and  $\text{Tm}_2\text{O}_3$ , respectively, to have a pure fluoride rare-earth environment, and substituted a small amount of  $\text{GeO}_2$  by heavy-metal  $\text{WO}_3$ .

In this work, we have studied the spectroscopic properties of the up-conversion emission of  $\text{Tm}^{3+}$  ions and the mechanism of energy transfer between  $\text{Yb}^{3+}$  and  $\text{Tm}^{3+}$  in the glass ceramics by exciting at 966 nm.

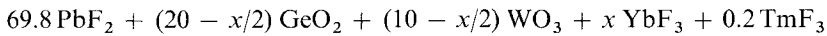
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## 2. Experiments

The sample was prepared by mixing together glass forming oxides  $\text{GeO}_2$  and  $\text{WO}_3$  with lead fluoride and high purity rare-earth fluoride (99.99%). The mixture was heated and melted inside a muffle furnace at  $950^\circ\text{C}$  for 20 min. The sample was then obtained by pouring the melt. The glass ceramics prepared for this investigation were:



with  $x = 8, 10, 12,$  and  $15,$



The optical absorption spectra were measured by using a double-beam Cary 17 spectrometer at room temperature. The luminescence spectra were observed by exciting the samples with a 250 W tungsten halogen lamp passed through an infrared (IR) monochromator and a RG 850 long-pass filter or with a 150 W XBO xenon lamp (UV) filtered by a Jobin-Yvon HP10 double monochromator. The emission signal was measured with a Jobin-Yvon HR 1000 spectrometer and a RTC 56 TVP photomultiplier tube.

Low-temperature measurements were made by mounting the sample in a CTC-70C cryostat. The temperature was varied from 12 to 320 K. For measurements of the luminescence decay curves, the excitation was provided by a dye laser (Coumarin 485) with a duration of 5 ns pumped by a  $\text{N}_2$  laser or by a GRT flash lamp with short duration (20  $\mu\text{s}$ ) fitting an RG 850 long-pass filter. The signal was detected by a photomultiplier tube (RTC 56 TVP) and then analyzed by a Tektronix 7912 AD digitizer interfaced with a PC-AT microcomputer.

For up-conversion efficiency measurement, the emission spectra were corrected based on the calibration of the optical system with a tungsten standard lamp traceable to the National Bureau of Standards. The intensity of exciting light at the sample position was detected with a Coherent 200 power-meter.

## 3. Results

The absorption spectra of  $\text{Tm}^{3+}$  and  $\text{Yb}^{3+}$  ions for glass ceramic at room temperature are shown Fig. 1 a, b, respectively. The absorption spectrum of  $\text{Tm}^{3+}$  ions (Fig. 1 a) consists of seven absorption bands centered at 1724, 1210, 780, 698, 680, 465, and 356 nm corresponding to the absorptions from the ground state  $^3\text{H}_6$  to the excited states  $^3\text{H}_4$ ,  $^3\text{H}_5$ ,  $^3\text{F}_4$ ,  $^3\text{F}_3$ ,  $^3\text{F}_2$ ,  $^1\text{G}_4$ , and  $^1\text{D}_2$ , respectively. The absorption band of  $\text{Yb}^{3+}$  ions due to the transition  $^2\text{F}_{7/2} \rightarrow ^2\text{F}_{5/2}$  shows two peaks centered at 940 and 976 nm in the sample. This allowed us to determine the energy level diagram of the different states of  $\text{Tm}^{3+}$  and  $\text{Yb}^{3+}$  ions in the hosts.

Fig. 2 represents the energy level diagram of  $\text{Yb}^{3+}$  and  $\text{Tm}^{3+}$  ions obtained from the absorption spectra of the samples.

The emission spectra of  $\text{Tm}^{3+}$  for a sample containing 15 mol%  $\text{YbF}_3$  and 0.2 mol%  $\text{TmF}_3$  in the range of 400 to 820 nm under the direct excitation at 360 nm (excited in the  $^1\text{D}_2$  level) or 465 nm (excited in the  $^1\text{G}_4$  level) at room temperature are shown in Fig. 3. Under 360 nm excitation, these spectra reveal only emission from the  $^1\text{D}_2$  level, i.e. a strong blue emission peaking at 451 nm ( $^1\text{D}_2 \rightarrow ^3\text{H}_4$ ) and three weaker emissions peaking at

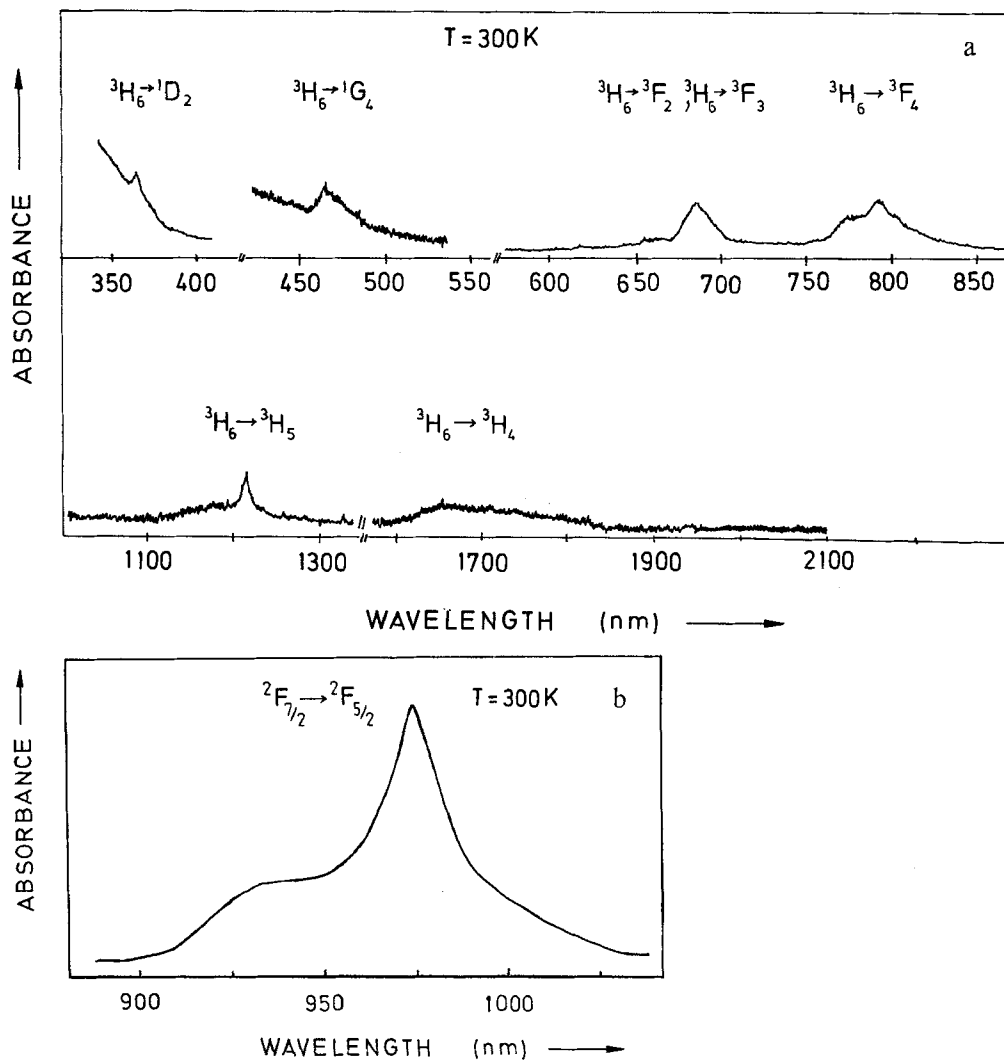


Fig. 1. Absorption spectrum of a)  $\text{Tm}^{3+}$  ions in the range of 320 to 2100 nm for a sample containing 0.2 mol%  $\text{TmF}_3$  and b)  $\text{Yb}^{3+}$  ions in the range of 880 to 1100 nm for the sample containing 15 mol%  $\text{YbF}_3$  and 0.2 mol%  $\text{TmF}_3$  at room temperature

510 ( ${}^1\text{D}_2 \rightarrow {}^3\text{H}_5$ ), 650 ( ${}^1\text{D}_2 \rightarrow {}^3\text{F}_4$ ), and 753 nm ( ${}^1\text{D}_2 \rightarrow {}^3\text{F}_3$ ), respectively. Two emission bands centered at 648 and 779 nm were observed upon 465 nm excitation. According to the energy level diagram of  $\text{Tm}^{3+}$  ion (Fig. 2), these emission bands correspond to the internal transitions from the  ${}^1\text{G}_4$  to the  ${}^3\text{H}_4$  and the  ${}^3\text{F}_4$  to the  ${}^3\text{H}_6$  levels. On the other hand, the  ${}^1\text{G}_4$  level is not populated by relaxation or any other process from the  ${}^1\text{D}_2$  level in the sample.

Fig. 4a, b report the up-conversion emission spectra of  $\text{Tm}^{3+}$  ions for the same sample upon infrared excitation at 966 nm (excited in the  ${}^2\text{F}_{5/2}$  level of  $\text{Yb}^{3+}$ ) in the range of 320 to 840 nm at room temperature. The up-conversion emission bands centered at 478, 648,

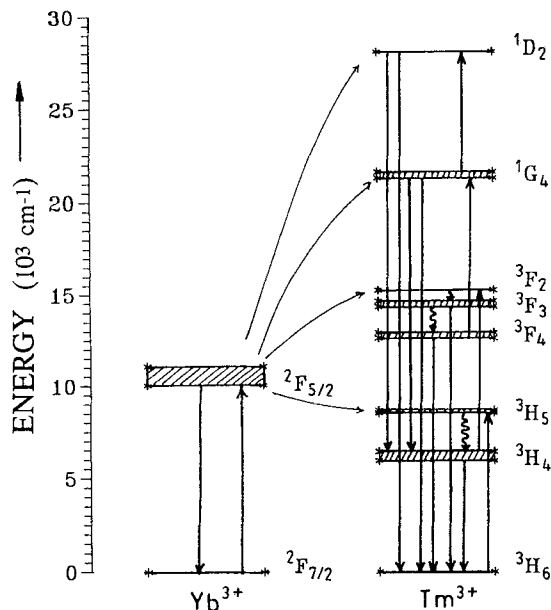


Fig. 2. Energy level diagram of  $\text{Yb}^{3+}$  and  $\text{Tm}^{3+}$  ions and schematic processes for four-, three-, and two-photon processes

680, 698 and 779 nm are attributed to the transitions  $^1\text{G}_4 \rightarrow ^3\text{H}_6$ ,  $^1\text{G}_4 \rightarrow ^3\text{H}_4$ ,  $^3\text{F}_2 \rightarrow ^3\text{H}_6$ ,  $^3\text{F}_3 \rightarrow ^3\text{H}_6$ , and  $^3\text{F}_4 \rightarrow ^3\text{H}_6$ , respectively (Fig. 4a). Furthermore, two other weak emissions can be discerned, viz. the  $^1\text{D}_2 \rightarrow ^3\text{H}_6$  band at 363 nm and the  $^1\text{D}_2 \rightarrow ^3\text{H}_4$  band at 451 nm (Fig. 4b). In addition, the spectral shape and position of the emission bands (for example,  $^1\text{D}_2 \rightarrow ^3\text{H}_5$ ,  $^1\text{G}_4 \rightarrow ^3\text{H}_4$ , and  $^3\text{F}_4 \rightarrow ^3\text{H}_6$  transitions) are consistent with those obtained under direct excitation.

In order to select the proper concentration of  $\text{YbF}_3$  or  $\text{TmF}_3$  in the sample for up-conversion processes, the dominant blue emission intensity (478 nm) was measured as a function of concentration under infrared excitation. Fig. 5a, b show the dependence of the intensity of blue emission centered at 478 nm on the concentration of  $\text{YbF}_3$  (Fig. 5a) or  $\text{TmF}_3$  (Fig. 5b) by exciting 966 nm. It follows from Fig. 5 that the strongest blue emission occurs when the concentration of  $\text{YbF}_3$  and  $\text{TmF}_3$  are around 15 and 0.1 mol%, respectively.

The ratio of intensities of this blue emission (478 nm) to the red emission (779 nm) versus concentration of  $\text{YbF}_3$  in the sample upon infrared excitation is shown in Fig. 6. As can

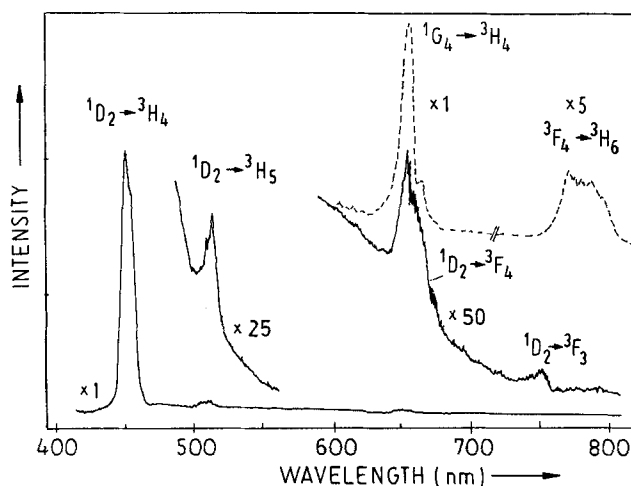


Fig. 3. Emission spectra of  $\text{Tm}^{3+}$  ions for a sample containing 15 mol%  $\text{YbF}_3$  and 0.2 mol%  $\text{TmF}_3$  under 360 (—) or 465 nm (---) excitation at  $T = 300$  K

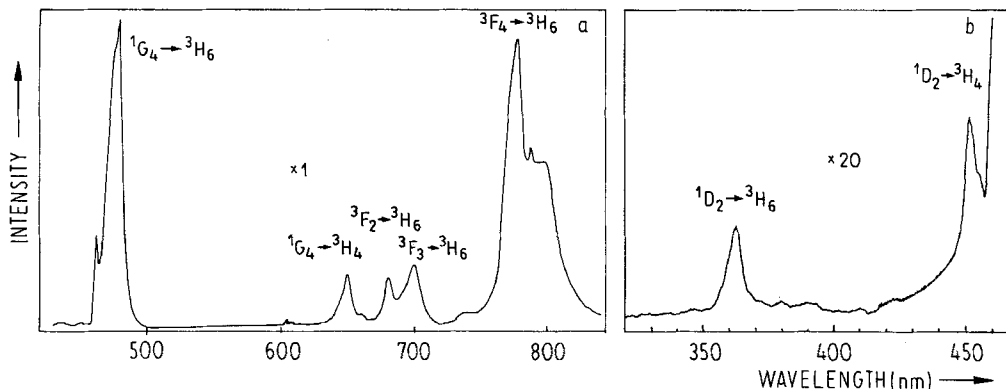


Fig. 4. Up-conversion emission spectra of  $\text{Tm}^{3+}$  ions for the same sample under infrared excitation (966 nm) in the range of a) 430 to 840 nm and b) 320 to 470 nm at  $T = 300$  K

be seen from the figure the ratio increases with the concentration of  $\text{YbF}_3$  up to 20 mol%. In addition, we also have found that the ratio remains almost constant with concentration of  $\text{TmF}_3$  up to 0.3 mol %.

The measurement of excitation spectra in the infrared region for anti-Stokes emissions is important to determine the excitation route in the up-conversion process. Fig. 7 reports the excitation spectra of emission bands of  $\text{Tm}^{3+}$  ions centered at 451, 478, 648, 698, and 779 nm. The excitation spectra of all the emission bands are the same. There are two excitation bands centered at 940 and 976 nm, and these excitation spectra have similar features as the absorption spectrum of  $\text{Yb}^{3+}$  ions corresponding to the  $^2F_{7/2} \rightarrow ^2F_{5/2}$  transition (Fig. 7, dashed curve). This shows that the  $^2F_{5/2}$  level is the intermediate one in the up-conversion processes, i.e., when the  $\text{Yb}^{3+}$  ions are excited into the  $^2F_{5/2}$  level, up-conversion emissions of  $\text{Tm}^{3+}$  ions are observed. It also implies that the emissions of  $\text{Tm}^{3+}$  ions are due to the energy transfer from the adjacent excited  $\text{Yb}^{3+}$  ions under infrared excitation.

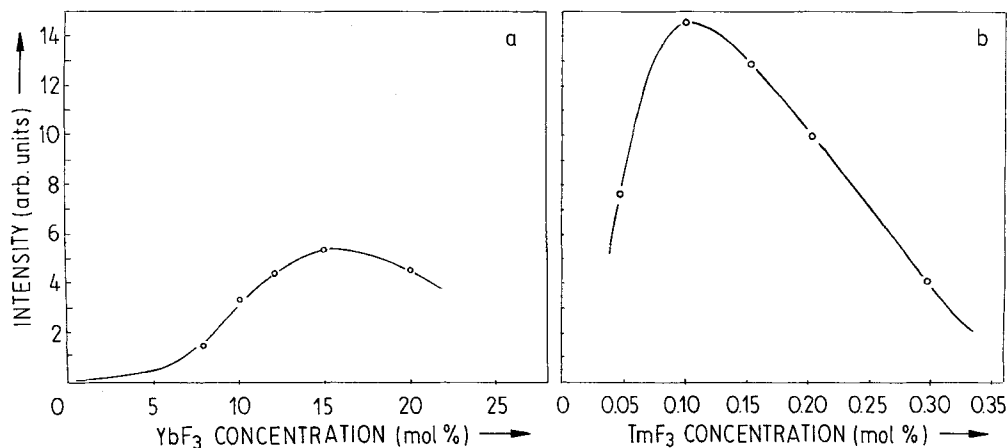


Fig. 5. Dependence of blue emission (478 nm) intensity of a)  $\text{Tm}^{3+}$  ions on the  $\text{YbF}_3$  concentration for 0.2 mol% of  $\text{TmF}_3$  under infrared excitation and b)  $\text{Tm}^{3+}$  ions on the  $\text{TmF}_3$  concentration for 15 mol%  $\text{YbF}_3$  under infrared excitation (966 nm) at  $T = 300$  K

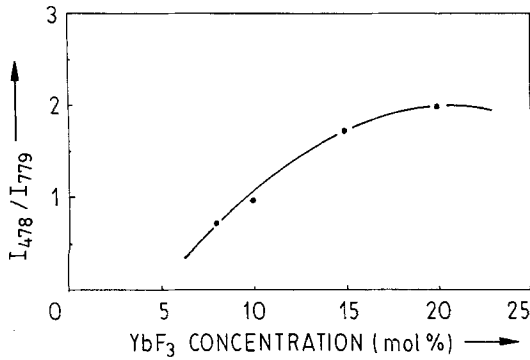
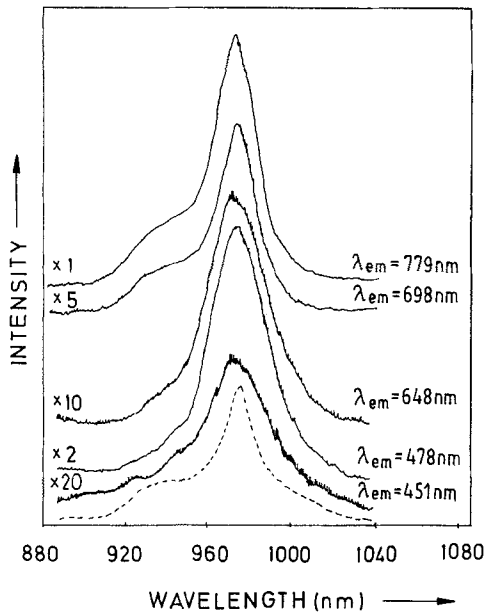


Fig. 6. The ratio of intensities of blue emission (478 nm) to red emission (779 nm) vs. concentration of YbF<sub>3</sub> under infrared excitation (966 nm) at  $T = 300\text{K}$

The dependence of the intensities of the violet (363 nm), blue (478 nm) and red (698 and 779 nm) up-conversion emission bands on the 966 nm light intensity is reported in Fig. 8. The experimental data have been fitted to a straight line. The slopes are found to be about 4, 3, and 2 for the violet, blue, and red emission, respectively.

Luminescence decay curves can show directly the process of energy transfer between Yb<sup>3+</sup> and Tm<sup>3+</sup> ions. The decay times of the <sup>1</sup>G<sub>4</sub> excited state of Tm<sup>3+</sup> ions upon 465 or 966 nm pulse line excitation are measured at room temperature. Typical decay curves are presented in Fig. 9. Under direct excitation (excited <sup>1</sup>G<sub>4</sub> level), a two-exponential decay curve of <sup>1</sup>G<sub>4</sub> level (curve a) is obtained for all TmF<sub>3</sub> concentrations. When the concentration of TmF<sub>3</sub> increases, the decay times for two processes decrease. For example, when the concentration of TmF<sub>3</sub> increases from 0.05 to 0.3 mol%, the decay times of the <sup>1</sup>G<sub>4</sub> level decrease from 90 and 290 μs to 70 and 218 μs, respectively. An obvious rising process has been observed in the up-conversion emission decay curve of <sup>1</sup>G<sub>4</sub> level for the same sample upon 966 nm light excitation (curve b). This phenomenon is absent upon direct excitation.



In addition, the decay curve of <sup>1</sup>D<sub>2</sub> level has similar features as that of the <sup>1</sup>G<sub>4</sub> level in the sample under infrared excitation. The decays of the <sup>1</sup>G<sub>4</sub> level are not exponential which may be another reflection of different site host [4]. The rise and decay times obtained are presented in Table 1.

The temperature dependence of the integrated intensity for the violet (363 nm), blue (451 and 478 nm), and red (698 and

Fig. 7. Excitation spectra for violet, blue, and red up-conversion emissions of Tm<sup>3+</sup> ions in the sample at room temperature. The dashed curve: absorption spectrum of the <sup>2</sup>F<sub>5/2</sub> level of Yb<sup>3+</sup> ions

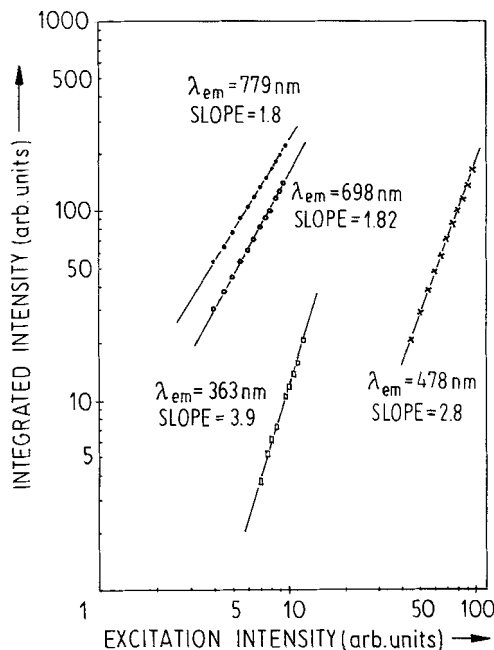


Fig. 8. Up-conversion emission intensities of  $Tm^{3+}$  ions at  $T = 300 \text{ K}$  vs. infrared excitation power

779 nm) emissions of  $Tm^{3+}$  ions under direct and infrared excitations are represented in Fig. 10 and 11, respectively. The experimental results are as follows:

(i) Under the direct excitation, the emission intensities corresponding to the transitions  $^1G_4 \rightarrow ^3H_4$  and  $^3F_4 \rightarrow ^3H_6$  decrease slowly with temperature from 12 to 320 K. For the blue emission centered at 451 nm ( $^1D_2 \rightarrow ^3H_4$ ), the intensity decreases slowly up to 100 K and then the decrease becomes rapid above 100 K due to thermal quenching.

(ii) For the infrared excitation, the intensities of all the up-conversion emissions first show an increase and then a decrease

with temperature. The decreasing processes have the similar behavior as that upon direct excitation.

By Raman spectrum measurements the phonon energy in this glass ceramic is found to be  $780 \text{ cm}^{-1}$ .

Table 1

Decay times of the  $^1G_4$  level of  $Tm^{3+}$  ions in glass ceramics under 465 or 966 nm excitation at room temperature.  $C_{Yb}$  and  $C_{Tm}$  denote the  $YbF_3$  and  $TmF_3$  concentrations,  $\tau_R$ ,  $\tau_1$ , and  $\tau_2$  denote the rise and fast and slow decay times

$C_{Yb}$ (mol%)	$C_{Tm}$ (mol%)	$\lambda_{ex} = 465 \text{ nm}$		$\lambda_{ex} = 966 \text{ nm}$	
		$\tau_1$ ( $\mu\text{s}$ )	$\tau_2$ ( $\mu\text{s}$ )	$\tau_R$ ( $\mu\text{s}$ )	$\tau_2$ ( $\mu\text{s}$ )
15	0.05	90	290	185	307
15	0.1	87	287	178	304
15	0.15	80	263	177	280
15	0.2	73	230	174	245
15	0.3	70	218	170	228

#### 4. Discussion

The number of IR photons absorbed per photon emitted for an up-conversion mechanism can be identified from the dependence of the emission intensity on infrared input intensity. The visible output intensity ( $I_V$ ) of the sample will be proportional to a power  $n$  on the

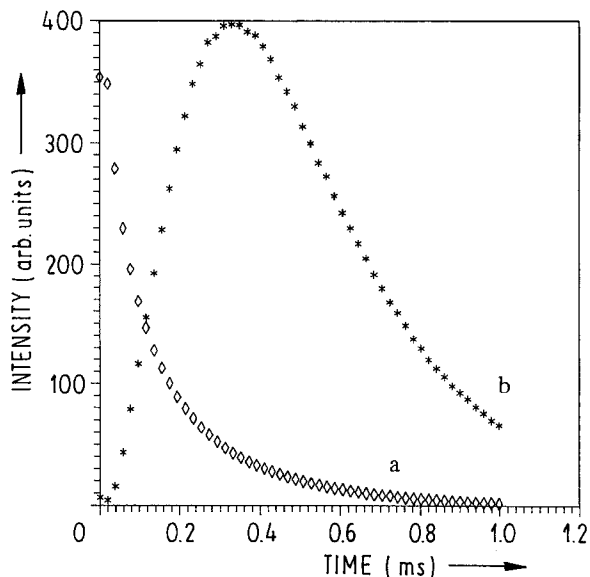


Fig. 9. Blue emission decay curves ( $^1G_4$ ) of  $Tm^{3+}$  ions under (a) 465 nm and (b) 966 nm excitation for a sample containing 0.2 mol%  $TmF_3$  and 15 mol%  $YbF_3$  at room temperature

infrared excitation intensity ( $I_{IR}$ ), i.e.,

$$I_V \propto I_{IR}^n, \quad (1)$$

where  $n$  is the number of infrared absorbed per visible photon emitted. Fig. 8 is a plot of the logarithm of  $I_V$  versus the logarithm of  $I_{IR}$  for the violet, blue, and red emission bands of  $Tm^{3+}$  ions. The data have been fitted to straight lines, the slopes of which are equal to  $n$ .

According to these experimental results, four-photon and three-photon absorptions are happening for  $^1D_2$  (363 nm, 451 nm) and  $^1G_4$  (478 nm) levels. The red emission bands (698 and 779 nm) are the result of a two-photon up-conversion process (Fig. 2). In the first transfer step, the excited  $Yb^{3+}$  ions transfer their energy to  $Tm^{3+}$  ions exciting them to the  $^3H_5$  level, and these excited  $Tm^{3+}$  ions reach the  $^3F_2$  level by a second transfer and then they may relax to different lower levels  $^3F_3$  and  $^3F_4$ , respectively. The red up-conversion emissions are observed. Moreover  $Yb^{3+}$  ions absorb third

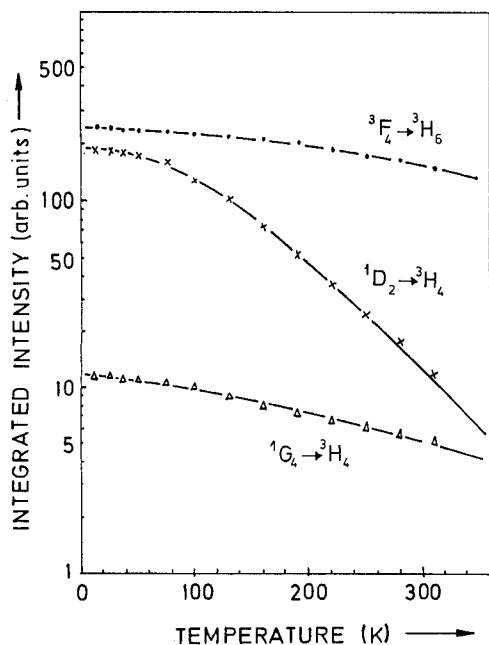


Fig. 10. Blue ( $^1D_2 \rightarrow ^3H_4$ ) and red ( $^1G_4 \rightarrow ^3H_4$ ,  $^3F_4 \rightarrow ^3H_6$ ) emission intensities vs. temperature under direct excitation for the same sample



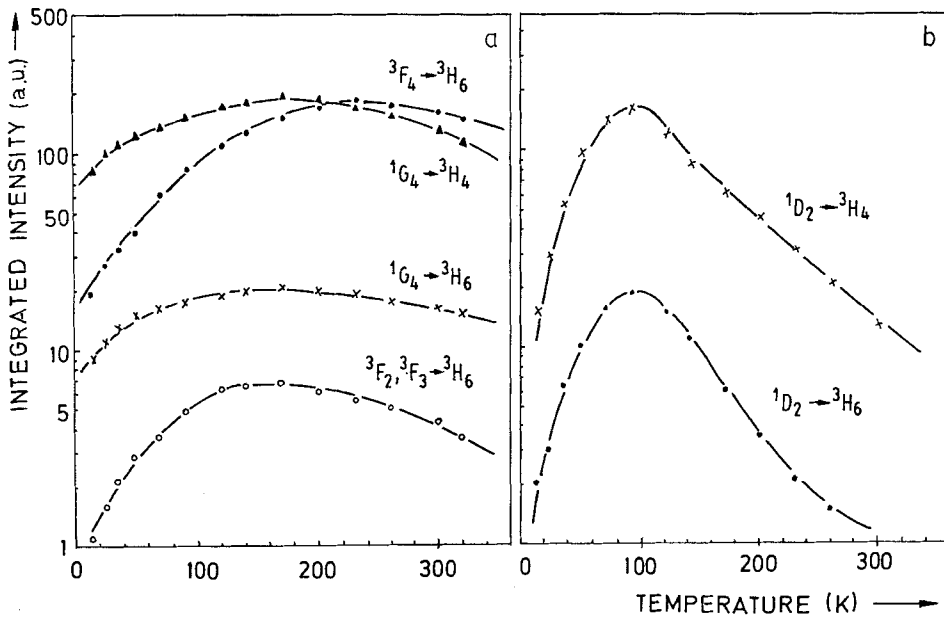
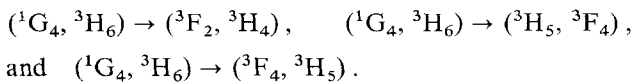


Fig. 11. Violet (363 nm, (●) in b)), blue (451, (×) in b) and 478 nm, (×) in a)) and red (648 (▲), 680, 698 (○), and 779 nm (●) in a)) up-conversion intensities vs. temperature under infrared excitation (966 nm) for the same sample

infrared photons and transfer the energy to these  $Tm^{3+}$  ions, exciting them from  $^3F_4$  to  $^1G_4$  level, the blue up-conversion emission is obtained. The violet (363 nm) and another blue (451 nm) up-conversion emissions are measured when a part of the population of  $^1G_4$  level is excited into  $^1D_2$  level by means of energy transfer from excited  $Yb^{3+}$  ions.

The dependence of the blue up-conversion emission intensity of  $^1G_4$  level upon the  $TmF_3$  and  $YbF_3$  concentrations has been measured. The blue emission intensity starts decreasing above 0.1 mol%  $TmF_3$  (Fig. 5b). We suggest that quenching of  $^1G_4$  level emission is due to the cross-relaxation processes between two  $Tm^{3+}$  ions [4 to 6]. Cross-relaxation is an energy transfer process between two  $Tm^{3+}$  ions resulting in depopulation of higher excited states. Therefore, cross-relaxation processes decrease the up-conversion emission of  $^1G_4$  level.

The  $^1G_4$  emission can be quenched by three most efficient cross-relaxation processes in  $Tm^{3+}$ -doped glass ceramics:



On the other hand, the intensity of  $^1G_4$  emission increases with  $YbF_3$  concentration up to 15 mol% and then becomes decreasing. The quenching of this emission by  $YbF_3$  concentration may be due to the back energy transfer from  $Tm^{3+}$  to  $Yb^{3+}$  ions [7] and energy diffusion between  $Yb^{3+}$  ions.

For time-dependent measurements, as can be seen from Table 1 [1], the emission decay time of  $^1G_4$  level is almost constant with concentration of  $TmF_3$  up to 0.1 mol% and then decreases rapidly. The results are in agreement with the dependence of the emission

intensity of this level on the  $\text{TmF}_3$  concentration. Therefore, it is also due to the cross-relaxation processes between two  $\text{Tm}^{3+}$  ions. Because of the energy transfer from  $\text{Yb}^{3+}$  to  $\text{Tm}^{3+}$  ions upon infrared excitation, the obvious rise process of  ${}^1\text{G}_4$  level in the codoped sample has been observed (Fig. 9).

In order to calculate the fluorescence efficiencies for the dominant blue (478 nm) and red (779 nm) emissions of  $\text{Tm}^{3+}$  ions upon 966 nm light excitation, a comparative method with the standard sample has been used. On the basis of [8, 9], the fluorescence efficiency is defined as

$$\eta_u = \eta_s \frac{n_u^2 F_u I(\lambda_s) A_s}{n_s^2 F_s I(\lambda_u) A_u}, \quad (2)$$

where  $\eta_u$ ,  $\eta_s$  are efficiencies of unknown and standard, respectively,  $n$  is the index of refraction,  $A$  the absorbance,  $F$  the integrated area under the corrected emission spectrum, and  $I(\lambda)$  the relative irradiance of the exciting light at wavelength  $\lambda$ . For determining  $A$ ,  $F$ , and  $I(\lambda)$ , the detection system must be calibrated. In this work, the BZYL $\text{Tm}$  glass [10, 11] has been taken as standard sample. According to (2), the absolute fluorescence efficiencies of 478 and 779 nm up-conversion emission of  $\text{Tm}^{3+}$  ions in the sample containing 0.1 mol%  $\text{TmF}_3$  and 15 mol%  $\text{YbF}_3$  are  $10^{-6}$  and  $5.86 \times 10^{-3}$ , respectively, at room temperature when the sample is excited by 966 nm light with an absolute intensity of  $16.5 \text{ mW/cm}^2$ .

By comparing the temperature dependences of the emission intensities of  $\text{Tm}^{3+}$  ions under direct and infrared excitations, the intensities of all up-conversion emissions first increase with temperature, while the opposite happens for these emissions upon direct excitation. It means that the energy transfer probability between  $\text{Yb}^{3+}$  and  $\text{Tm}^{3+}$  ions depends on temperature. On the other hand, according to the energy level diagram of  $\text{Yb}^{3+}$  and  $\text{Tm}^{3+}$  ions, the energy mismatches between two ions are about 1800, 1200, and  $1680 \text{ cm}^{-1}$ , respectively, for the first, second, and third transfer processes. By considering these two facts, the energy transfer from  $\text{Yb}^{3+}$  to  $\text{Tm}^{3+}$  ions under infrared excitation is due to phonon-assisted energy transfer.

In conclusion, we have observed violet, blue, and red up-conversion emissions of  $\text{Tm}^{3+}$  ions in the glass ceramics under infrared excitation. The up-conversions involve four-photon and three-photon absorption processes for violet (363 nm) and blue (478 nm) emission bands. The two-photon absorption process is required for red (680 nm, 698 nm, 775 nm) emissions.

The energy transfer probability between  $\text{Yb}^{3+}$  and  $\text{Tm}^{3+}$  ions depends on temperature under infrared excitation, it implies that the energy transfer from  $\text{Yb}^{3+}$  to  $\text{Tm}^{3+}$  ions is assisted by phonons.

By a comparative method, the absolute fluorescence efficiencies of  $10^{-6}$  and  $5.86 \times 10^{-3}$  have been obtained for blue (478 nm) and red (779 nm) up-conversion emissions for a  $16.5 \text{ mW/cm}^{-2}$  infrared excitation at room temperature.

### Acknowledgements

The authors are grateful to M. Genotelle for glass ceramics preparation and to Dr. Ph. Goldner for interesting discussions.

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*(Received August 16, 1993; in revised form September 13, 1993)*