



Infrared-to-visible conversion luminescence of Tm^{3+} and Yb^{3+} ions in glass ceramics

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Abstract

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) has been investigated. The emission, excitation spectra, luminescence decay times and up-conversion efficiency were measured. The up-conversion of infrared into violet (363 nm), blue (451 and 478 nm) and red (680, 698 and 779 nm) was observed for Tm^{3+} ions in the sample. By a comparative method, an absolute fluorescence efficiencies of 10^{-6} and 5.86×10^{-3} have been obtained for dominant blue (478 nm) and red (779 nm) up-conversion when the sample is excited by 966 nm light with an absorbed intensity of 16.5 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 relatively large amount of trivalent rare-earth ions which can be introduced into the host. Auzel [1] 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 [2].

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In this work, we have studied the spectroscopic properties of the up-conversion emission of Tm^{3+} ions and mechanism of energy transfer between Yb^{3+} and Tm^{3+} in the glass ceramics by exciting at 966 nm corresponding to the ${}^2F_{5/2} \rightarrow {}^2F_{7/2}$ absorption of Yb^{3+} ion.

2. Experiments

The samples studied in this work were of the general composition $69.8\text{PbF}_2 + (20 - x/2)\text{GeO}_2 + (10 - x/2)\text{WO}_3 + x\text{YbF}_3 + 0.2\text{TmF}_3$, where $x = 0, 8, 10$ and 15. The preparation techniques and detailed composition of the sample have been described elsewhere [3]. 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 filtered or with a 150 W XBO xenon lamp (UV) filter by a Jobin-Yvon H10D double

monochromator. The emission signal was measured with a Jobin-Yvon HR 1000 spectrometer and a RTC 56 TVP photomultiplier tube.

3. Results

The emission spectra of Tm^{3+} for a sample containing 15 mol% YbF_3 and 0.2 mol% TmF_3 in the range of 420–820 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 have been recorded. 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 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 649 and 779 nm were observed upon 465 nm excitation. According to the energy level diagram of Tm^{3+} ion, 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.

Fig. 1 reports the up-conversion emission spectrum of Tm^{3+} ions for the same sample upon infrared excitation at 966 nm (excited in the $^2\text{F}_{5/2}$ level of Yb^{3+}) in the range 420–840 nm at room temperature. The up-conversion emission bands centered at 478, 649, 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. 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 $^1\text{D}_2 \rightarrow ^3\text{H}_5$ band at 451 nm. In addition, the spectra shape and position of the emission bands are consistent with those obtained under direct excitation.

The excitation spectra of all the emission bands of Tm^{3+} ions are the same and consist of two excitation bands centered at 940 and 980 nm. These excitation spectra have the similar features as the absorption spectrum of Yb^{3+} ions which corresponds to the $^2\text{F}_{7/2} \rightarrow ^2\text{F}_{5/2}$ absorbed. This shows that the $^2\text{F}_{5/2}$ level is the intermediate one in the up-conversion processes, i.e., when the Yb^{3+} ions are excited into the $^2\text{F}_{5/2}$ level, up-conversion emissions of Tm^{3+} ions are observed. It also implies that the emissions of Tm^{3+} ions are due to the energy transfer from the adjacent excited Yb^{3+} ions under infrared excitation.

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 measured. The experimental data have been fit to a straight line. The slopes are found to be about 4, 3 and 2 for the violet, blue and red emissions, respectively.

The decay times of the $^1\text{G}_4$ excited state of Tm^{3+} ions upon 465 or 966 nm pulse line excitation were measured at room temperature. Typical decay curves are presented in Fig. 2. Under direct excitation (excited into the $^1\text{G}_4$ level), a two-exponential decay curve of $^1\text{G}_4$ level (a) is obtained for all TmF_3 concentration. When the concentration of TmF_3 increases, the decay times for two processes are decreased. For example, the concentration of TmF_3 increases from 0.05 to 0.3 mol%, the decay times decrease from 90 and 290 μs to 70 and 218 μs , respectively. Obvious rising process has been observed in the up-conversion emission decay curve of $^1\text{G}_4$ level for the same sample upon 966 nm light excitation as shown on Fig. 2 (curve b). This rise process is due to the energy transfer from Yb^{3+} to Tm^{3+} ions.

The temperature dependence of the integrated intensity for the violet (363 nm), blue (451 and 478 nm) and red (698 and 779 nm) emissions of Tm^{3+} ions under direct and infrared excitations

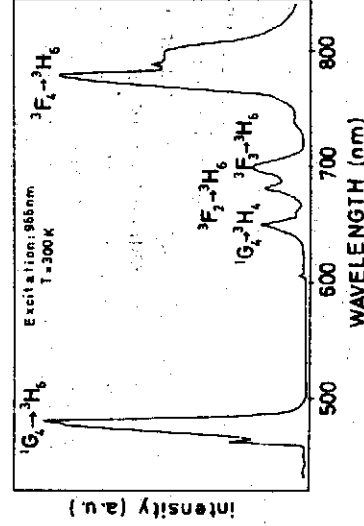


Fig. 1. Up-conversion emission spectra of Tm^{3+} ions for a sample containing 15 mol% YbF_3 and 0.2 mol% TmF_3 under infrared excitation (966 nm) in the range 420–840 nm.

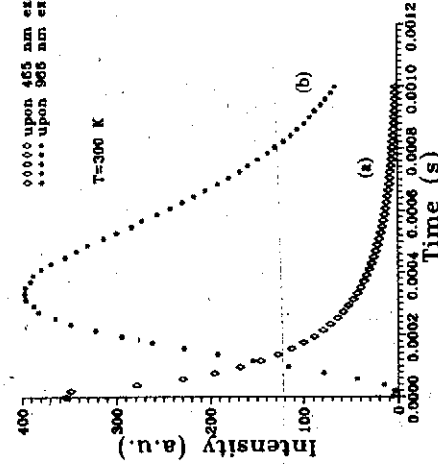


Fig. 2. Blue emission decay curves (1G_4) of Tm^{3+} ions under 465 nm (a) and 966 nm (b) excitation for the sample containing 15 mol% YbF_3 and 0.2 mol% TmF_3 at room temperature.

are obtained. 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 (${}^1D_2 \rightarrow {}^3H_5$), 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 intensity of all the up-conversion emissions first shows an increase and then a decrease with temperature. The decreasing processes have the similar behaviour as that upon direct excitation.

4. Discussion

The number of IR photon 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 of the infrared excitation intensity (I_{IR}), i.e., $I_v \propto I_{IR}^n$, where n is the number of infrared absorbed per visible photon emitted. According to our experimental results, the four-photon and three-photon absorptions happened to populate 1D_2 (363, 451 nm) and 1G_4 (478 nm)

levels. The red emission bands (698 and 779 nm) result from a two-photon up-conversion process.

In order to calculate the fluorescence efficiencies for dominant blue (478 nm) and red (779 nm) of Tm^{3+} ions upon 966 nm light excitation, a comparative method with the standard sample has been used. On the basis of Ref. [4], the fluorescence efficiency is defined as

$$\eta_u = \eta_s n_s^2 F_u I(\lambda_s) A_s / n_u^2 F_s I(\lambda_u) A_u, \quad (1)$$

where η_u, η_s are efficiencies of unknown and standard, respectively, n is the index of refraction, A is the absorbance, F is the integrated area under the corrected emission spectrum and $I(\lambda)$ is the relative irradiance of the exciting light at wavelength λ . To determine A, F and $I(\lambda)$, the detecting system must be calibrated. In this work, the BZYL:Tm glass [5] has been taken for standard sample. According to (1), the absolute fluorescence efficiencies of 478 and 779 nm up-conversion emissions of Tm^{3+} ions in the sample containing 0.1 mol% TmF_3 and 15 mol% YbF_3 are 10^{-6} and 5.86×10^{-3} , respectively, at room temperature when the sample is excited by 966 nm light with an absolute intensity of 16.5 mW/cm².

By comparing the temperature dependence of the emission intensities of Tm^{3+} ions under the direct and infrared excitation, 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 Yb^{3+} and Tm^{3+} ions depends on the temperature. On the other hand, according to the energy level diagram of Yb^{3+} and Tm^{3+} ions, the energy mismatches between these ions are about 1800, 1200 and 1680 cm^{-1} , respectively for first, second and third transfer. By considering these two facts, the energy transfer from Yb^{3+} to 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 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. A two-photon absorption process is required for red (680, 698, 779 nm) emissions.

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

Acknowledgements

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

References

- [1] F. Auzel, Proc. IEEE 61 (1973) 758.
- [2] F. Auzel, P. Pecile and D. Morin, J. Electrochem. Soc. 122 (1975) 101.
- [3] Xu Wu, J.P. Denis, G. Özen, Ph. Goldner, M. Genotelle and F. Pellé, Chem. Phys. Lett. 203 (1993) 211.
- [4] A. Kisilev and R. Reisfeld, Solar Energy 2 (1984) 163.
- [5] D.C. Yeh and W.A. Sibley, J. Appl. Phys. 63 (1988) 4644.