

Compositional dependence of infrared to blue and red conversion luminescence in oxyfluoride glass-ceramics co-doped with Tm³⁺ and Yb³⁺ ions

J. P. Denis, G. Özen, Xu Wu,^{a)} A. Kermaoui,^{b)} F. Pellé, and B. Blanzat
Laboratoire de Physico-Chimie des Matériaux, C.N.R.S. (UPR-211) 92190 Meudon, France

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The upconversion of infrared radiation into visible light has been studied in heavy metal oxyfluoride glass-ceramics co-doped with Yb³⁺ and Tm³⁺ ions at 300 K. The general composition of the compounds is 69.9PbF₂ + 7.5WO₃ + 7.5MO₂ + 15YbF₃ + 0.1TmF₃ (M = Si, Ge, Zr, Te, and Th). Two main upconversion emissions were observed. They are centered at 477 and 775 nm, corresponding to the ¹G₄ → ³H₆ and ³F₄ → ³H₆ transitions, respectively. Slopes of the emission intensity versus excitation power measurements indicate that the blue emission is due to three-photon absorption, while two-photon absorption processes are responsible for the red emission. A comparative method was used to measure the upconversion efficiencies under 16.5 mW/cm² excitation power. Measurements were made after the compounds were annealed at 450 °C for 4 h. The best conversion efficiencies were obtained for the compound having silicon (Si). They are 28 × 10⁻⁶ for the blue and 18 × 10⁻² for the red emission.

I. INTRODUCTION

Among oxide glasses, the ones based on tellurite have the lowest nonradiative decay rates,^{1,2} resulting in higher quantum efficiency for direct and upconverted emissions.³⁻⁵ The effects of the host on the upconversion emissions have already been studied in different tellurite binary systems.^{6,7} It has been shown that heavy metal tellurite glasses can also be obtained in quaternary systems such as PbO + WO₃ + TeO₂ + Er₂O₃ with a high concentration of rare earths (Er₂O₃).⁸ Therefore we chose to study upconversion fluorescence in this system, substituting PbO, TeO₂, and Er₂O₃ with PbF₂, MO₂

(M = Si, Ge, Zr, Te, Th), and YbF₃ (TmF₃), respectively. The upconversion efficiencies have been shown to be much higher in the fluoride glasses than they are in the homologue oxides.⁹

The Li₂O + LiF + TeO₂ systems have been shown to contain two types of crystalline domains LiF and TeO₂ inside the amorphous matrix, and the extent of these domains increases, with fluorine to oxygen ratio.¹⁰ A similar effect has also been observed in oxyfluoride germanate glass-ceramics.¹¹ These glass-ceramics show two phases: (i) pure oxide and vitreous, and (ii) more fluoride and microcrystalline. This study has shown that the rare earths are mainly in the microcrystalline phase for which high quantum efficiencies have been obtained for the green (Er³⁺) and blue (Tm³⁺) upconverted emissions. We therefore chose to study the glass-ceramic compositions with a high F/O ratio, to have a large extent of crystalline domains.

^{a)}Permanent address: Changchun Institute of Physics, Academia Sinica, Changchun, People's Republic of China.

^{b)}Permanent address: Laboratoire Laser, CDTA 2bd Fanon, BP-1017 Alger Gare, Algeria.

TABLE I. Composition of the glass-ceramics (mol%).

Composition	Glass-ceramics				
	PWSiYbTm	PWGeYbTm	PWZrYbTm	PWTeYbTm	PWThYbTm
PbF ₂	69.9	69.9	69.9	69.9	69.9
WO ₂	7.5	7.5	7.5	7.5	7.5
SiO ₂	7.5
GeO ₂	...	7.5
ZrO ₂	7.5
TeO ₂	7.5	...
ThO ₂	7.5
YbF ₃	15.0	15.0	15.0	15.0	15.0
TmF ₃	0.1	0.1	0.1	0.1	0.1

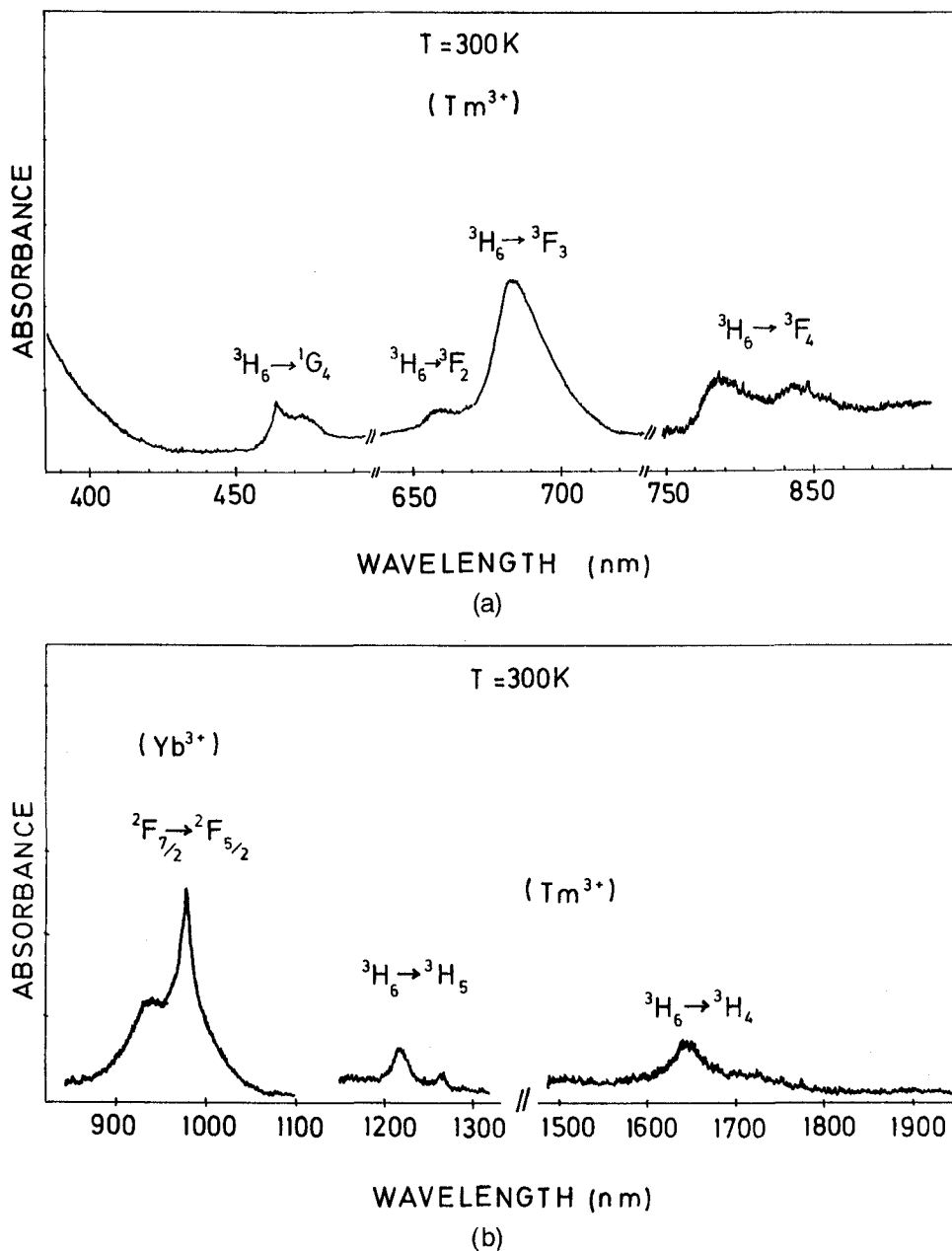


FIG. 1. Absorption spectrum of PWTeYbTm glass-ceramic obtained in the (a) visible and (b) infrared region at 300 K.

The aim of this work was to investigate the optical properties and to measure the efficiencies of infrared (IR) to red and blue upconversion emissions of Tm^{3+} ions in different glass-ceramic compositions at room temperature.

The quantum efficiencies of these upconverted emissions were calculated using a comparative method with the upconverted emissions of Tm^{3+} in a heavy metal fluoride glass.¹²

II. EXPERIMENTAL

The glass-ceramics have been prepared using reagent grade PbF_2 , MO_2 ($M = \text{Si, Ge, Zr, Te, Th}$),

WO_3 , and 4N purity YbF_3 and TmF_3 as starting materials. They are called PWMYbTm in this article, and their compositions are listed in Table I.

The mixtures were melted in silica crucibles with covers, inside an electric furnace at 950 °C. The melt was kept at this temperature for about 30 min, then was poured on a stainless steel plate and pressed with another stainless steel plate. Initially, the glass-ceramics were not annealed, but, to measure the upconversion efficiencies, all the samples were annealed at 460 °C for 4 h. After this time the furnace was turned off and allowed to cool.

Powder with grains of approximately the same size (about 5 μm) were made from these samples and fixed

TABLE II. Energy positions of the absorption bands of Tm^{3+} and Yb^{3+} measured in the PWTeYbTm compound at 300 K.

Transition	Wavelength (nm)	Energy (cm^{-1})
(Tm) $^3H_6 \rightarrow ^3H_4$	1650	6060
$\rightarrow ^3H_5$	1220	8196
$\rightarrow ^3F_4$	780	12820
$\rightarrow ^3F_3$	690	14493
$\rightarrow ^3F_2$	660	15151
$\rightarrow ^1G_4$	465	21505
(Yb) $^2F_{7/2} \rightarrow ^2F_{5/2}$	966	10352

homogeneously on a bronze plate with a cavity of 30 mm² surface area and 1 mm depth for fluorescence measurements. The excited area of the sample was 4 mm².

Absorption spectra were recorded by using a double beam Cary 17 spectrophotometer. Emission and excitation spectra were measured by exciting the samples with light from a 250 W tungsten halogen lamp passed through a Jobin-Yvon IR-H20 monochromator and an RG 850 nm long pass filter.

The fluorescence signals were analyzed with an HR 1000 Jobin-Yvon monochromator equipped with an RTC 56 TVP photomultiplier in the visible region and a silicon photodiode type PIN-10DP in the IR region.

For the time dependences of upconverted emissions, a General Radio flash lamp with an RG 850 nm long pass filter was used as the excitation source. The signal detected with an RTC 56 TVP photomultiplier was recorded with a digitizer, then was processed with a computer. The decay time of the 1G_4 level was measured under a direct excitation in this level. The excitation was provided by a dye laser (Molelectron, Model DL-100) pumped by a nitrogen laser (Sopra, Model N.2100). The signal was analyzed by a photomultiplier connected to a Boxcar Integrator (PAR model 162).

The emission spectra used to calculate the absolute quantum efficiencies were corrected for the wavelength variations in the system response by calibrating the monochromator-photomultiplier unit with a standard tungsten halogen lamp.

III. RESULTS AND DISCUSSION

The absorption spectrum of the PWTeYbTm glass-ceramic recorded at 300 K is presented in Fig. 1. The bands observed are due to the transitions of Tm^{3+} and Yb^{3+} from their ground state to the excited states, and they are in agreement with those previously reported for Tm^{3+} in fluoride glasses.¹³ The energy of the bary-center of the absorption bands is presented in Table II and Fig. 2.

Two main upconversion emissions of Tm^{3+} (red and blue) in the PWTeYbTm sample observed in the visible region upon 966 nm excitation are shown in Fig. 3 as

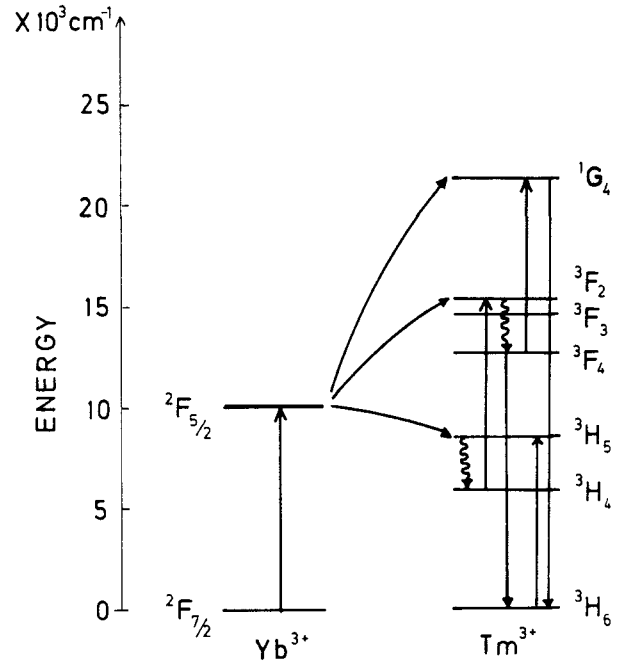


FIG. 2. Energy level diagram of Tm^{3+} and Yb^{3+} ions in PWTeYbTm glass-ceramic and the upconversion routes upon infrared excitation.

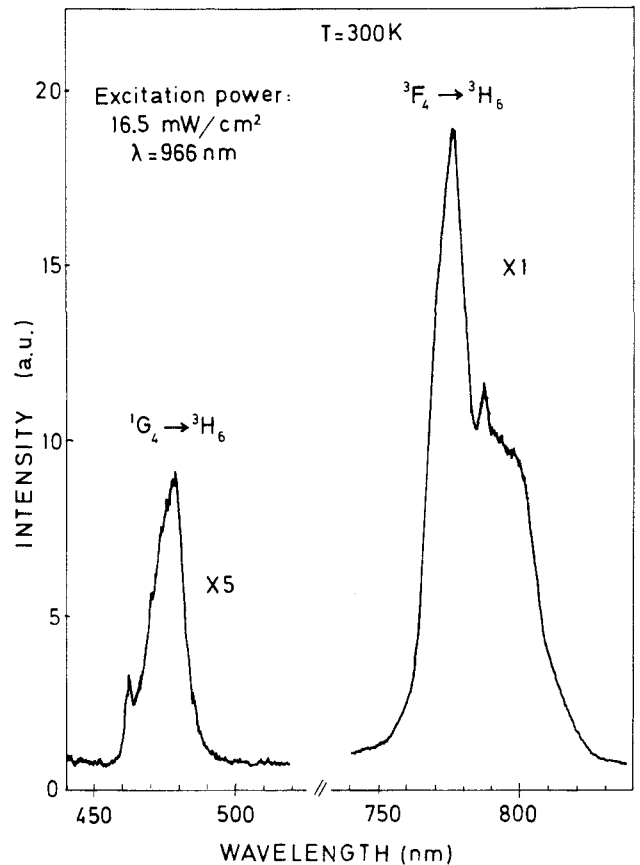


FIG. 3. Upconversion emission spectrum of PWTeYbTm glass-ceramic measured upon 966 nm excitation at 300 K.

examples. All the samples gave the same emissions originating from the 1G_4 and 3F_4 metastable levels of the Tm^{3+} ion. The strongest blue and red emissions are centered at 478 and 791 nm, and they correspond to the $^1G_4 \rightarrow ^3H_6$ and $^3F_4 \rightarrow ^3H_6$ transitions, respectively.

Figure 4 presents the excitation spectra of the different upconversion emissions observed upon IR excitation. These spectra have the same spectral structure as the $^2F_{7/2} \rightarrow ^2F_{5/2}$ absorption band of the Yb^{3+} ions, confirming that the different emitting levels of the Tm^{3+} ions were excited by energy transfer processes (APTE effect) from the Yb^{3+} ions.

The variations of the upconverted red and blue emission intensities with the excitation power are given in Fig. 5. The former emission shows a quadratic dependence on the excitation power, while the latter shows a cubic dependence. This means that the red and blue upconverted emissions in all the studied compounds are due to two- and three-photon absorption processes, respectively.

The mechanism for the conversion of IR to visible light was also identified by measuring the decay profiles of the emissions from the 1G_4 level upon direct and IR

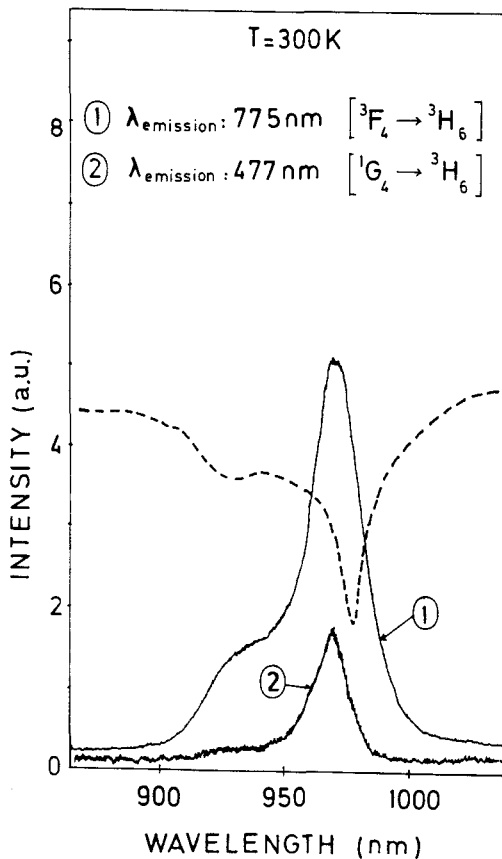


FIG. 4. Excitation spectra of the upconverted emissions in PWTe-YbTm glass-ceramics. Dotted line corresponds to the absorption band of Yb^{3+} ions ($^2F_{7/2} \rightarrow ^2F_{5/2}$ transition).

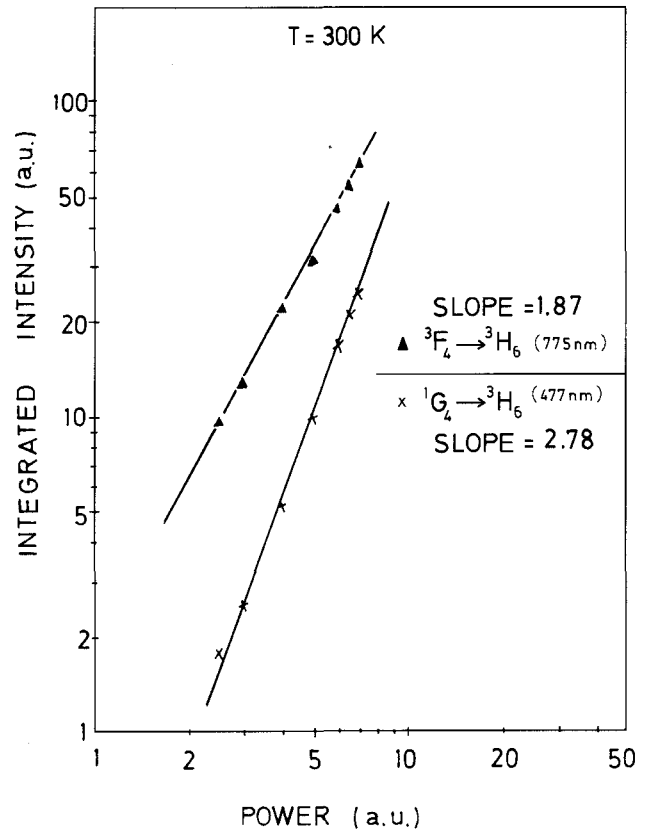


FIG. 5. Excitation power dependence of the upconverted emissions centered at 477 and 775 nm.

excitations. A rise process was observed in addition to the decay process when the Yb^{3+} ions were excited with a 966 nm light as seen in Fig. 6. Here the rise process confirms that the upconversion emissions of Tm^{3+} are due to the energy transfer from the Yb^{3+} ions.

The absolute upconversion efficiencies of the red and blue emissions were calculated using the comparison method.¹⁴ The efficiency of the red emission ($^3F_4 \rightarrow ^3H_6$ transition) obtained by Yeh *et al.*¹² was taken as the standard value in our calculations.

The following equation was used:

$$\eta_u = \eta_s F_u A_s \lambda_s n_u / F_s A_u \lambda_u n_s,$$

where η_u and η_s are quantum yields of unknown and standard samples, respectively; n_u and n_s are the refractive indexes; A is the absorbance at the wavelength of excitation; F is the integrated area under the emission spectrum; and λ is the excitation wavelength.

Table III shows the upconversion efficiencies for the blue (478 nm) and the red (791 nm) emissions measured under 16.5 mW/cm² excitation power at 300 K. The dependences of these emission intensities on the kind of MO_2 species by taking the intensity of Si-based glass-ceramics as unity are presented in Fig. 7. As shown in

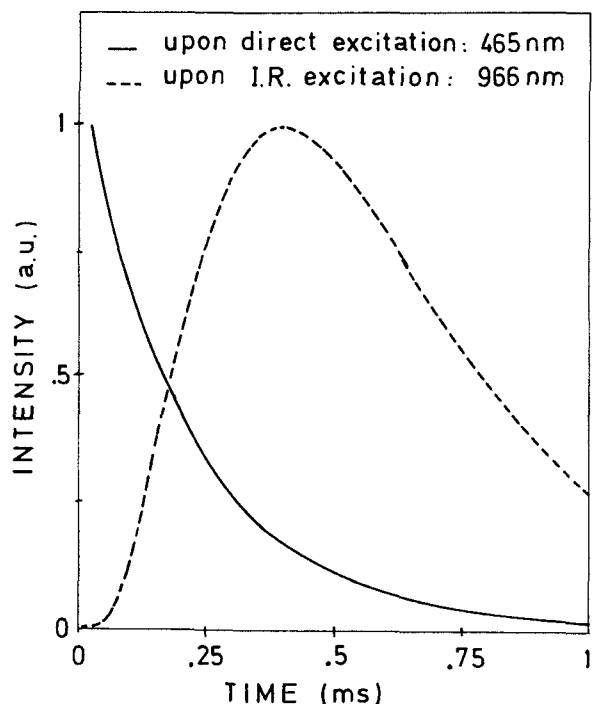


FIG. 6. Decay profiles of (Tm) 1G_4 excited level obtained upon direct and infrared excitation in PWTeYbTm glass-ceramics.

this table, the blue and red emissions have the largest value for the Si-substituted compound.

The ratio of the blue to red upconversion emission efficiency gives information about the energy transfer process from the Yb^{3+} ions in the $^2F_{5/2}$ level to the Tm^{3+} ions in the 3F_4 excited level. Table IV presents this ratio for different compounds. The largest value was obtained for the sample containing silicon. This indicates that the efficiency of the $^2F_{5/2} (Yb^{3+}) \rightarrow ^3F_4 (Tm^{3+})$ transfer in this glass-ceramic is the highest among these compounds. The role of phonon cutoff frequency in this enhanced transfer is currently investigated by studying the lifetimes of the different levels involved.

TABLE III. Upconversion efficiencies of the blue (478 nm) and the red (791 nm) emissions under 16.5 mW/cm² IR excitation power.

Sample	Transition		Reference
	$^1G_4 \rightarrow ^3H_6$ (478 nm)	$^3F_4 \rightarrow ^3H_6$ (791 nm)	
BZYTLTm	...	0.2×10^{-2}	12
APbF	0.1×10^{-6}	0.1×10^{-2}	15
PWSiYbTm	28×10^{-6}	18×10^{-2}	This work
PWGeYbTm	15×10^{-6}	11×10^{-2}	This work
PWZrYbTm	13×10^{-6}	13×10^{-2}	This work
PWTeYbTm	14×10^{-6}	11×10^{-2}	This work
PWThYbTm	16×10^{-6}	10×10^{-2}	This work

The estimated accuracy of the values obtained in this work is 10%.

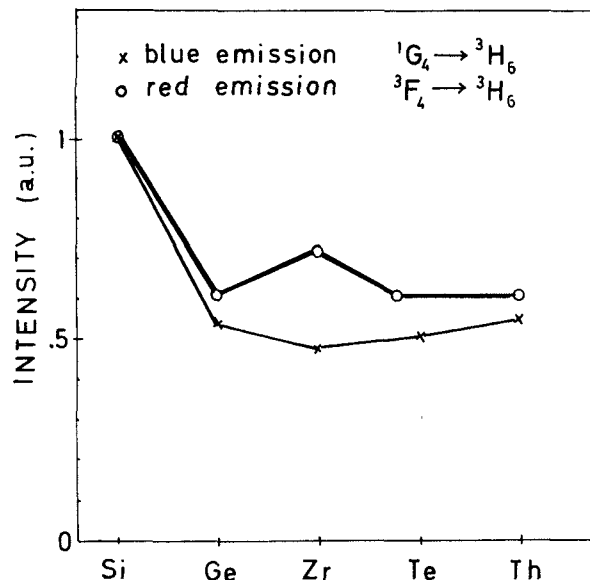


FIG. 7. Dependence of the upconverted emission intensities on the MO_2 (M = Si, Ge, Zr, Te, and Th) species.

IV. CONCLUSION

The upconversion processes for the blue ($^1G_4 \rightarrow ^3H_6$ transition) and the red ($^3F_4 \rightarrow ^3H_6$ transition) emissions of Tm^{3+} in $69.9PbF_2 + 7.5WO_3 + 7.5MO_2 + 15YbF_3 + 0.1TmF_3$ (M = Si, Ge, Zr, Te, and Th) glass-ceramics have been studied under 966 nm light with 16.5 mW/cm² incident power at 300 K. The mechanism for these emissions was explained by energy transfer processes from the Yb^{3+} ions to different excited levels of the Tm^{3+} ions. The blue emission was found to be due to three-photon absorption and the red emission was due to two-photon absorption processes in all the compounds studied.

The Si-substituted glass-ceramics were found to give the highest conversion efficiency for both red and blue upconverted emissions for the 16.5 mW/cm² IR excitation power. The values obtained are 28×10^{-6} and 18×10^{-2} for the blue and red emissions, respectively. This work shows that the Si-substituted glass-ceramic is the best compound of the compounds investigated in

TABLE IV. Ratio of the blue (478 nm) to red (791 nm) upconverted emission efficiencies η versus the matrix of glass-ceramics upon 16.5 mW/cm² IR excitation power at 300 K.

Sample	η_{blue}/η_{red}
BZYTLTm	...
APbF	1.00×10^{-4}
PWSiYbTm	1.56×10^{-4}
PWGeYbTm	1.36×10^{-4}
PWZrYbTm	1.00×10^{-4}
PWTeYbTm	1.27×10^{-4}
PWThYbTm	1.52×10^{-4}

this article for practical applications such as optical data storage, projection television, and so on.

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