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Efficient blue and red upconversion of infrared light in oxyfluoride tellurite ceramics

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ABSTRACT- The upconversion of 966nm infrared radiation into visible light has been studied in 69.9 PbF₂ + 7.5WO₃ + 7.5TeO₂ : 15YbF₃ ; 0.1TmF₃ ceramic. Several upconversion emission bands were observed in the spectral range of 460 and 830nm. The blue and red emission bands are centered at 478 and 775nm, respectively. Intensity versus excitation power measurements confirm that the red emission was due to the two photon absorption while the blue emission was a result of three photon absorption processes.

Absolute fluorescence efficiencies were determined at room temperature for 16.5mW/cm² excitation intensity, using a comparative method. Values obtained for the red and blue emissions are 5.8 · 10⁻² and 7.5 · 10⁻⁶, respectively in the compound prepared at 900°C.

Annealing the compound at 460°C for four hours increases the upconversion efficiencies of the 478 and 775 nm emissions about two times. Temperature dependence of these upconverted emissions was investigated for the annealed and not annealed samples

INTRODUCTION

Among oxide glasses, tellurite ones have the lowest nonradiative decay rates [1,2] which result in higher quantum efficiency for direct and upconverted emissions [3-5].

Upconversion emissions have been studied in different tellurite binary systems [6,7]. It has been shown that heavy metal tellurite glasses can be obtained in the quaternary system : Er₂O₃ - TeO₂ - WO₃-PbO with a high concentration of rare earths (Er₂O₃) [8]. Therefore we chose to study upconversion fluorescence in this system substituting PbO and Er₂O₃ by PbF₂ and YbF₃ (TmF₃), respectively. Fluoride glasses have much higher upconversion efficiencies than their homologue oxides [9].

By studying oxyfluoride tellurite glasses Kojo et al [10] showed that the $Li_2O - LiF - TeO_2$ system contains two types of crystalline domains LiF and TeO_2 inside the amorphous matrix and that the extend of these domains increase with fluorine ratio. A similar effect has been observed by Auzel et al [11] in oxyfluoride germanate glass ceramics. For these glass ceramics two phases have been observed : one, purely oxide and vitreous and the other is more fluoride and microcrystalline. In the last article it has been shown that the rare earths are mainly in the microcrystalline phase for which high quantum efficiencies have been obtained for the green (Er^{3+}) and blue (Tm^{3+}) upconverted emissions.

We chose to study a composition with a high F/O ratio, to have a large extend of crystalline domains. Optical properties of the upconverted emissions of Tm^{3+} in this ceramic have been studied as a function of temperature. Quantum efficiencies of these upconverted emissions were measured in the samples prepared at three different elaboration temperatures : 850, 900 and 950°C, using a comparative method with the upconverted red emission of Tm^{3+} in a heavy metal fluoride glass [12]. The efficiencies are found to be 100 times higher than those obtained for the last glass [13].

EXPERIMENTAL

The ceramics have been prepared by using reagent grade PbF_2 , TeO_2 , W_2O_3 and 4N purity YbF_3 and TmF_3 , as starting materials. The nomenclature of these ceramics is $PWTeYbTm$, Lead - Tungsten - Tellurium - Ytterbium - Thulium. The mixtures were melted in a silica crucible with a cover inside an electric furnace at different temperatures of 850, 900 and 950°C. The melt was kept at the elaboration temperature for about 30 minutes for homogenisation and bubbling and then poured on a stainless steel plate and pressed with another plate. Initially, the ceramics were not annealed but to study heat-treatment effect some samples were annealed at 460°C for 4 hours, after this time the furnace was turned off and allowed to cool. Powder with grains of approximately the same size, ~ 5µm were made from these samples and fixed homogeneously on a bronze plate with a cavity of 30mm² surface area and 1mm depth for fluorescence measurements. Excited area of the sample was 4 mm².

Sample density was determined from the weight loss on immersion in water and an average value of 6.8 g/cm³ was obtained. Absorption spectra were recorded with a Cary 17 spectrophotometer. Fluorescence and excitation spectra and upconversion efficiencies measurements were investigated using a 250W tungsten halogen lamp with a Jobin-Yvon HD20 IR grating monochromator. For the time dependance a Moletron dye laser pumped by a Sopra pulsed N₂ laser was used for direct excitation and GR tungsten flash lamp for IR excitation.

RESULTS AND DISCUSSION

Absorption spectrum of $PWTeYbTm$ ceramic recorded at 300 K is presented in fig. 1. Because of the opacity of this ceramic, the usual spectroscopic measurements (oscillator strengths) can not be carried out.

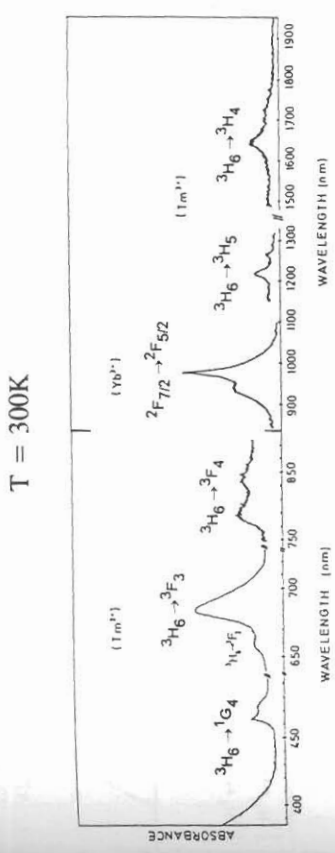


Fig. 1 - Absorption spectrum of $PWTeYbTm$ ceramic.

However, the positions of the bands observed are in agreement with those reported for Tm^{3+} in fluoride glasses [14]. This enables us to draw the energy levels diagram of Tm^{3+} and Yb^{3+} in $PWTeYb$ ceramic (fig. 2).

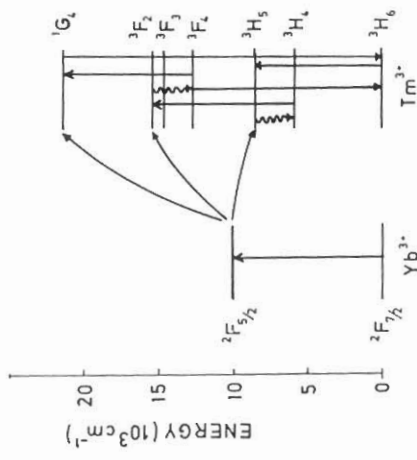


Fig. 2 - Energy levels of Tm^{3+} and Yb^{3+} in $PWTeYbTm$ ceramic and the excitation roots for the upconversion emissions.

The upconversion of the low intensity ($I = 16.5 \text{ mW/cm}^2$) 966 nm radiation into two main emissions of Tm^{3+} in PWTeYb ceramic is shown in fig. 3. These emission bands (fig. 3a) correspond in order of increasing wavelengths to ${}^1\text{G}_4 \rightarrow {}^3\text{H}_6$ and ${}^3\text{F}_4 \rightarrow {}^3\text{H}_6$ transitions. For these low excitation intensities, no emission has been observed from the ${}^1\text{D}_2$ level, which requires four photon absorption process.

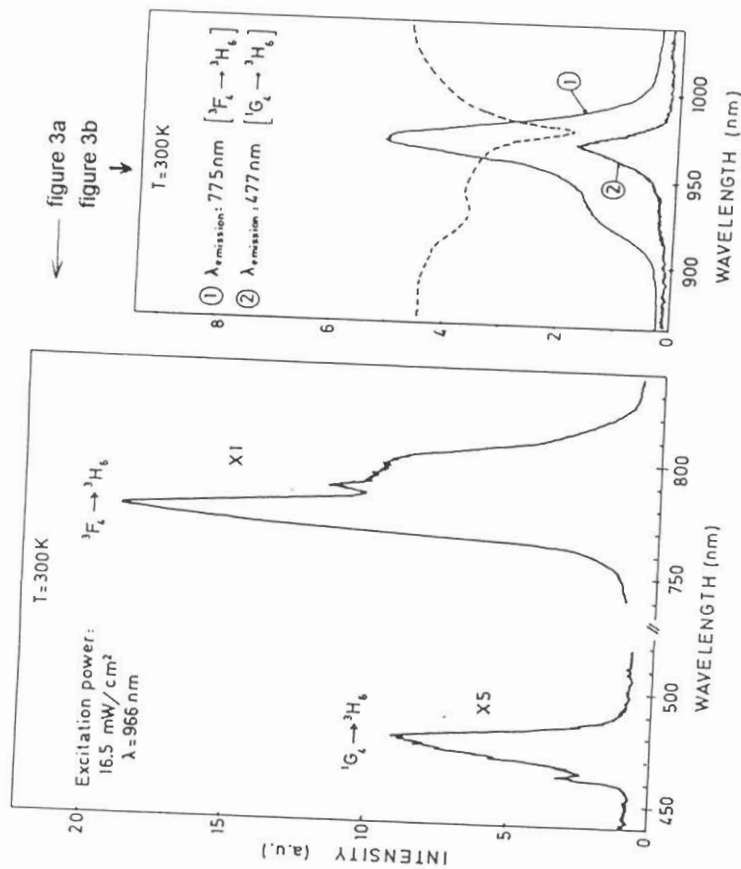


Fig. 3 - (a) Upconversion emission spectrum of PWTeYbTm ceramic. (b) Excitation spectra of upconversion emission (solid curves) and absorption spectrum of Yb^{3+} (dashed curve) in PWTeYbTm ceramic.

The excitation spectra of the two main emission bands observed on infrared excitation are illustrated in fig. 3b. These spectra have the same spectral structure as the ${}^2\text{F}_{7/2} \rightarrow {}^2\text{F}_{5/2}$ absorption band of Yb^{3+} in this ceramic, showing that the different emitting levels are excited by energy transfers (APTE effect) from Yb^{3+} ions.

The variation of the upconverted red and blue emissions intensities, as a function of excitation power is shown in fig. 4.

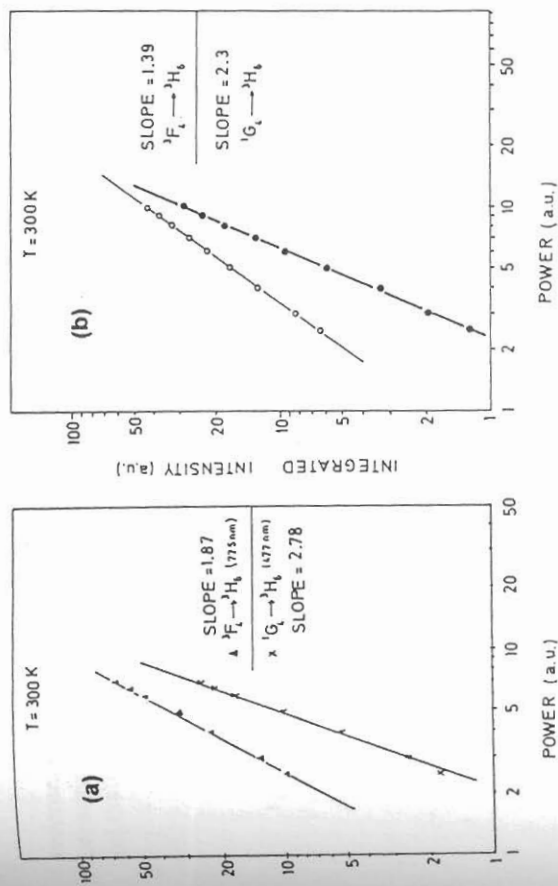


Fig. 4 - Blue and red upconversion emission intensities versus excitation power for the PWTeYbTm ceramic

For low excitation powers, the slopes of the two curves are practically equal to 2 and 3 (fig. 4a), indicating that the red (${}^3\text{F}_4$) and blue (${}^1\text{G}_4$) emitting levels are predominantly populated by two and three photon absorption processes, respectively.

For higher excitation powers, the two slopes decrease as shown in fig. 4b. This decrease is attributed to the saturation of the ${}^3\text{H}_4$ level [15].

Time development of the fluorescence from ${}^1\text{G}_4$ level presented in fig. 5 was measured at 300K under infrared and visible excitation. In the later case, we obtained two decay times of 87 and 244 μs , whereas in the former case we obtained a rise time of 190 μs and only one decay time of 277 μs .

The last decay time is related to the lifetimes of intermediate states such as ${}^3\text{F}_4$, ${}^3\text{H}_4$ and ${}^2\text{F}_{5/2}$, so we can not deduce to which ${}^1\text{G}_4$ lifetime it corresponds. The rise time confirms energy transfer processes from Yb^{3+} to Tm^{3+} ions.

Variation of the integrated intensities of the upconverted blue and red emissions, as a function of temperature is portrayed in fig. 6. These intensities increase with temperature until $T = 100\text{K}$ and 125K for the blue and red emissions, respectively. These maximum intensities stay practically constant until 200 K and after they decrease slowly.

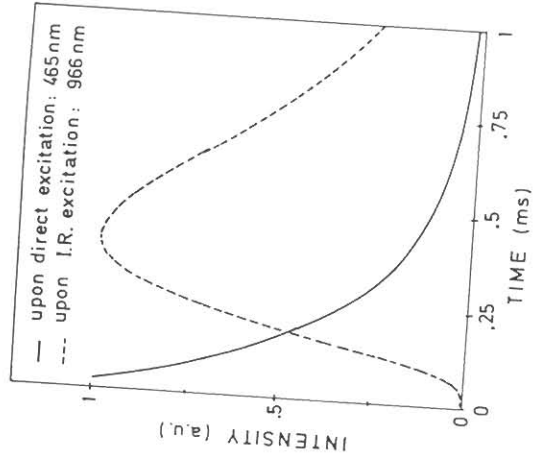


Fig. 5 - Time development of the ${}^1G_4 \rightarrow {}^3H_6$ emission upon direct and infrared excitation. $T = 300$ K.

These variations (increase and decrease in the intensities) are due to change in stark levels populations of the emitting levels and in non-radiative processes [16].

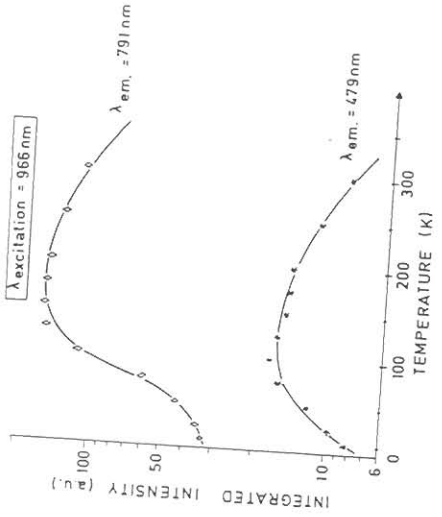


Fig. 6 - Temperature dependences of upconverted blue and red emission intensities of Tm^{3+} in PWTeYbTm ceramic.

Slow decrease of the blue emission compared to that found in reference 13, must be due to higher phonon energy of PWTeYbTm ceramic (fig. 7) which lower the order process P of multiphonon relaxation as a function of temperature :

$$W(T) = W_0 [1 - \exp(-\hbar\omega/KT)]^{-P}$$

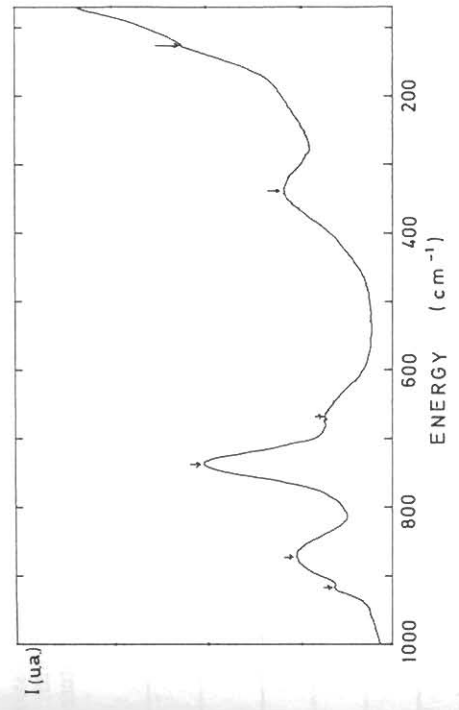


Fig. 7 - Raman spectrum of PWTe ceramic.

The absolute quantum efficiencies of the red and blue emissions were calculated by the comparison method [17], using the quantum yield of the red (${}^3F_4 \rightarrow {}^3H_6$) emission obtained by Yeh *et al* [12] as reference without considering the order of the process.

The following equation was used :

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

where η_u and η_s are quantum yields of unknown (u) and standard (s) respectively, η_u and η_s are refraction 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.

For the same excitation intensity (16.5 mW/cm²) used in the above article and $T = 300$ K, the efficiencies obtained for the red and blue emissions in the ceramics prepared at different temperatures, are given in table 1. Highest efficiencies were obtained in the compound prepared at 900°C, temperature which seems to give the most homogeneous ceramic.

These efficiencies are 100 times higher than those obtained for Tm^{3+} in heavy metal fluoride glass which is considered until now as the best glass for upconversion emissions [2].

These high upconversion efficiencies are due to the low rare earth site symmetry and high covalence activator ligand bond in tellurite hosts [18] which are important criteria in the choice of matrices for direct and upconverted emissions [19, 20].

TABLE I. Room temperature upconversion efficiencies of the red and blue emissions in the ceramic prepared at different temperatures (ceramics were not annealed; excitation power was 16.5 mW/cm²). $T_p(^{\circ}C)$ denotes the preparation temperature of the ceramic.

$T_p(^{\circ}C)$	η (Upconversion Efficiency)	
	$^1G_4 \rightarrow ^3H_6$ (478 nm) ($\times 10^{-6}$)	$^3F_4 \rightarrow ^3H_6$ (791 nm) ($\times 10^{-2}$)
850	5.5	4.0
900	7.5	5.8
950	6.3	4.8

By annealing the PWTeYbTm ceramic at 460°C for 4 hours, the blue and red emissions intensities increase by a factor of about 2 (fig. 8).

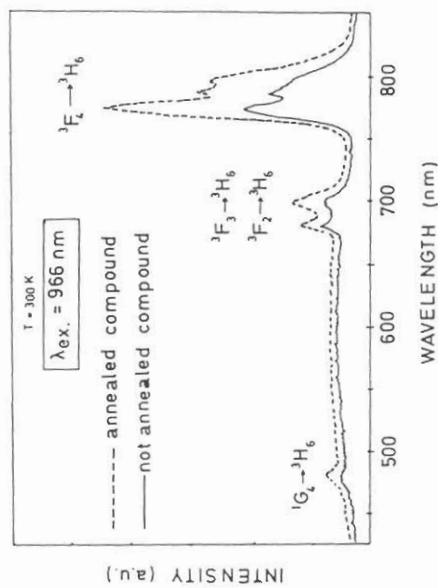


Fig. 8 - Upconversion emission spectra of annealed and not annealed PWTeYbTm ceramic ($P = 16.5$ mW/cm²)

Under infrared excitation, the rise and decay times of the $^1G_4 \rightarrow ^3H_6$ emission changed also with heat-treatment. The first one decreased from 190 to 180 μ sec, whereas the last one increased from 277 to 337 μ s.

Temperature dependence of the red emission does not significantly change with heat-treatment although for the blue emission we observe some change for low temperatures (fig. 9) This emission does not increase with temperature.

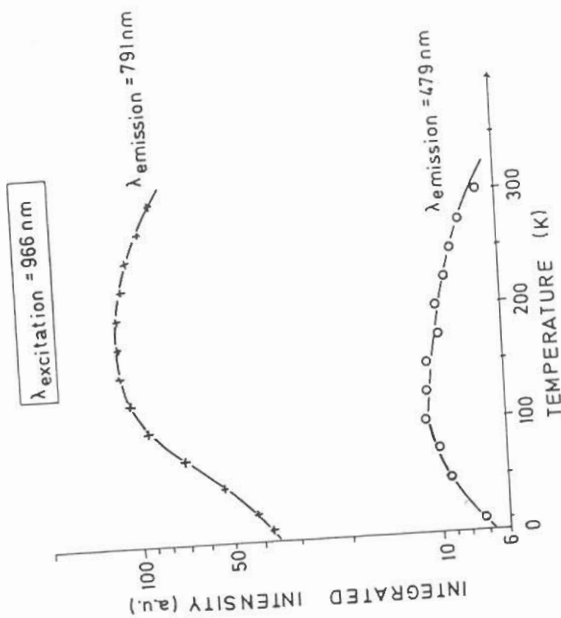


fig. 9 - Temperature dependences of upconverted blue and red emission intensities of Tm^{3+} in annealed and not annealed PWTeYbTm ceramics.

In conclusion, the high upconversion efficiencies obtained at room temperature make this ceramic a promising candidate for new display devices.

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