Indian Journal of Pure & Applied Physics
Vol. 42, February 2004, pp. 136-141

Excitation and emission spectra of anti-Stokes luminescence of Tm^{3+} in glass ceramics doped with various concentrations of sensitizer

R Kathuria[1], B P Chandra[2], M Ramrakhiani[3] & D P Bisen[3]

[1]Department of Physics, D. N. Jain College, Gole Bazar, Jabalpur 482 001
[2]Pt. Ravishankar Shukla University, Raipur 492 010
[3]Department of Postgraduate Studies & Research in Physics & Electronics
Rani Durgavati University, Jabalpur 482 001

Received 9 August 2003, accepted 17 November 2003

In certain rare-earth doped glass ceramics luminescence emission has been observed at wavelength shorter than the exciting wavelength. This is known as anti-Stokes luminescence or up-conversion, which is due to accumulation of excitation energy by rare-earth ions. In Tm^{3+} and Yb^{3+} doped glass ceramics, Tm^{3+} acts as an activator and Yb^{3+} acts as a sensitizer. The activator concentration was kept constant at 0.2 mol% and the sensitizer Yb^{3+} concentration was varied from 0.0 mol% to 20 mol%. In emission spectra of glass ceramics doped with Tm^{3+} and Yb^{3+}, under infrared excitation (966 nm) one peak of high intensity was found at different wavelengths between 400 to 500 nm for different concentrations of sensitizer. The peak is slightly shifted towards shorter wavelength with increasing concentrations of the sensitizer. This reveals that 3-photon up-conversion is prominent and presence of Yb^{3+} ions slightly shifts the energy levels of Tm^{3+}. In the excitation spectra of glass ceramics doped with Yb^{3+} and Tm^{3+}, initially the emission intensity increases with increasing wavelength, attains an optimum value for 920 nm, 930 nm, 950 nm and 960 nm and then it decreases with further increase in the wavelength. These photon energies may correspond to energy difference between levels of Tm^{3+} or Yb^{3+}. Both in the excitation spectra and emission spectra, initially the anti-Stokes luminescence intensity increases with sensitizer concentration, attains an optimum value and then it decreases with further increase in the sensitizer concentration.

[**Keywords:** Anti-Stokes luminescence, Rare-earth doped glass ceramic, Excitation and emission spectra, Luminescence of Tm^{3+}]
IPC Code : C09 11/07

I Introduction

Luminescence is the non-equilibrium phenomenon of excess light emission over and above the thermal emission of a body, in which emission has a duration considerably exceeding the period of oscillations. In other words, it is a process which involves at least two steps, the excitation of the electronic system of solid and the subsequent emission of photons. In certain rare-earth doped glass ceramics, the wavelength of emitted light is shorter than the wavelength of exciting light, and such type of luminescence is known as anti-Stokes luminescence or up-conversion. This unique process named either summation of photons, infrared to visible conversion or frequency up conversion, anti-Stokes luminescence, energy transfer up-conversion (ETU), quantum counting through energy transfer, or addition of photons by transfer of energy (APTE), has received a great deal of attention from solid state scientific community. The direct conversion of infrared radiation to visible light is possible in a number of rare-earth ion doped crystal phosphors and glass ceramic contrary to the empirical Stokes law. The study of anti-Stokes luminescence due to excitation energy accumulation by RE^{3+} ions, has been carried out initially by Bloembergen[1], Ovsyankin[2], Feofilov[3] and Auzel[4]. Several models have been proposed to explain the phenomenon of anti-Stokes luminescence. Number of researchers have reported anti-Stokes luminescence in rare-earth ions during recent past[5-8].

There is a good 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.

The present paper reports the excitation and emission spectra of the anti-Stokes luminescence of Tm^{3+} in glass ceramics doped with various concentrations of sensitizer.

2 Experimental Procedure

The glass ceramics were prepared by heating the mixture of glass forming oxides – germanium oxides (GeO_2) and tungsten oxides (WO_3) with lead fluoride (PbF_2). For doping high purity (99.99%) rare-earth oxides – yttribium oxides (Yb_2O_3) and thulium oxides (Tm_2O_3) were also added to the initial mixture which was heated and melted inside a muffle furnace at 1100°C for 30 min[9]. The sample was then obtained by sudden cooling of the melt. In Tm^{3+} and Yb^{3+} doped glass ceramics, Tm^{3+} acts as an activator and Yb^{3+} acts as a sensitizer. The activator (Tm^{3+}) concentration was kept constant at 0.2 mol% and the sensitizer (Yb^{3+}) concentration was varied to 0.0 mol%, 8 mol%, 10 mol%, 12 mol%, 15 mol% and 20 mol%. The glass ceramics prepared for this investigation were :

$$69.8\,PbF_2 + 20\,GeO_2 + 10\,WO_3 + 0.2\,Tm_2O_3$$

$$69.8\,PbF_2 + (20\text{-}x/2)\,GeO_2 + (10\text{-}x/2)\,WO_3 + x\,Yb_2O_3 + 0.2\,Tm_2O_3$$

$x = 8, 10, 12, 15$

$$64.8\,PbF_2 + 10\,GeO_2 + 4\,WO_3 + 20\,Yb_2O_3 + 0.2\,Tm_2O_3$$

The experimental set-up used for recording the anti-Stokes luminescence intensity and spectra is shown in Fig. 1. The main units are light source (IR lamp of 250 W), grating monochromator, constant deviation spectrometer and detector unit consisting of RCA 931 photomultiplier tube, high voltage power supply and digital picoammeter.

For the measurement of anti-Stokes luminescence, a powder sample of glass ceramics was spread on a quartz plate using araldite as a binder. The quartz plate was then placed near the exit slit of the grating monochromator. This was placed at an angle of 45° to the incident rays coming from grating monochromator. For measuring the anti-Stokes emission spectra, the drum of grating monochromator was fixed at 966 nm, while the drum of constant deviation spectrometer was varied from 420 nm to 700 nm. For measuring the excitation spectra of glass ceramics doped with Yb^{3+} and Tm^{3+}, the sample was excited by light having wavelength ranging from 800 nm to 1000 nm and emission was measured at those wave lengths where the anti-Stokes luminescence emission was maximum.

3 Results

Fig. 2 (a,b) shows the up-conversion emission spectra of glass ceramics doped with Yb^{3+} and Tm^{3+} under infrared excitation (966 nm) in the wavelength range of 420 nm to 700 nm. In this case, the concentration of Tm^{3+} ions was kept constant at 0.2 mol%, while that of Yb^{3+} was varied from 0.0 mol%, 8.0 mol%, 10.0 mol%, 12 mol%, 15 mol% and 20 mol%. It is observed that main peaks are obtained between 400 and 500 nm at different wave lengths for different concentrations of sensitizer Yb^{3+}.

Fig. 3(a,b) shows the excitation spectra of the samples with different concentrations of Yb^{3+}. The sample was excited by light having wavelength ranging from 800 nm to 1000 nm and emission was measured at the main peak in the emission spectrum of the corresponding sample. It is seen that initially the emission intensity increases with

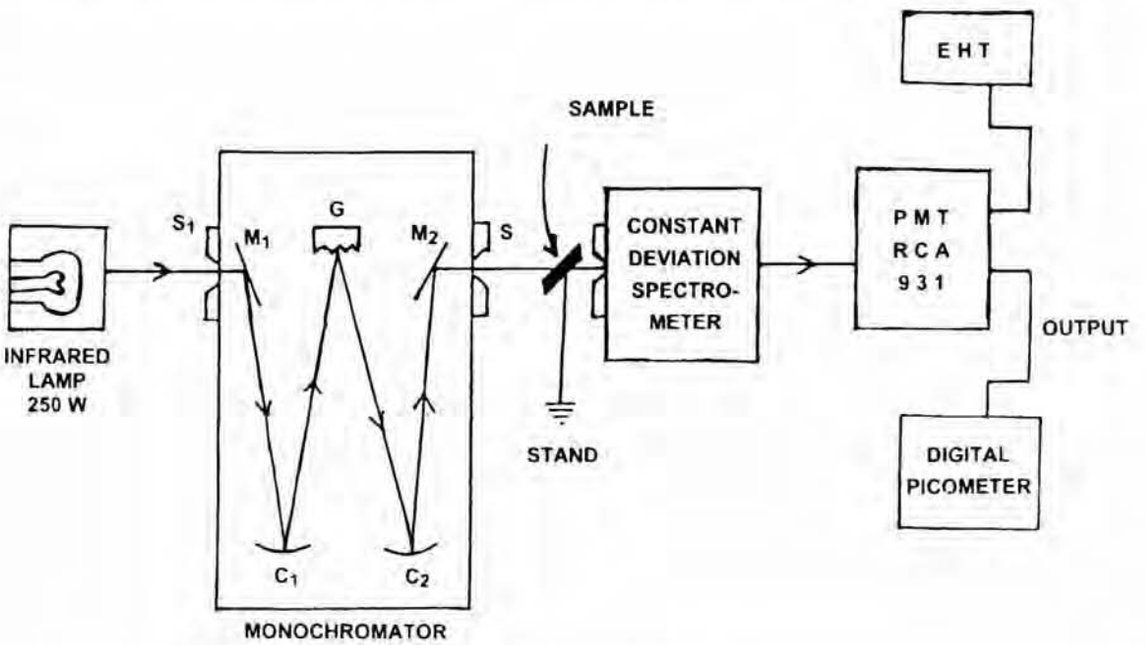

Fig. 1– Experimental set up of the measurement of anti-Stokes luminescence.

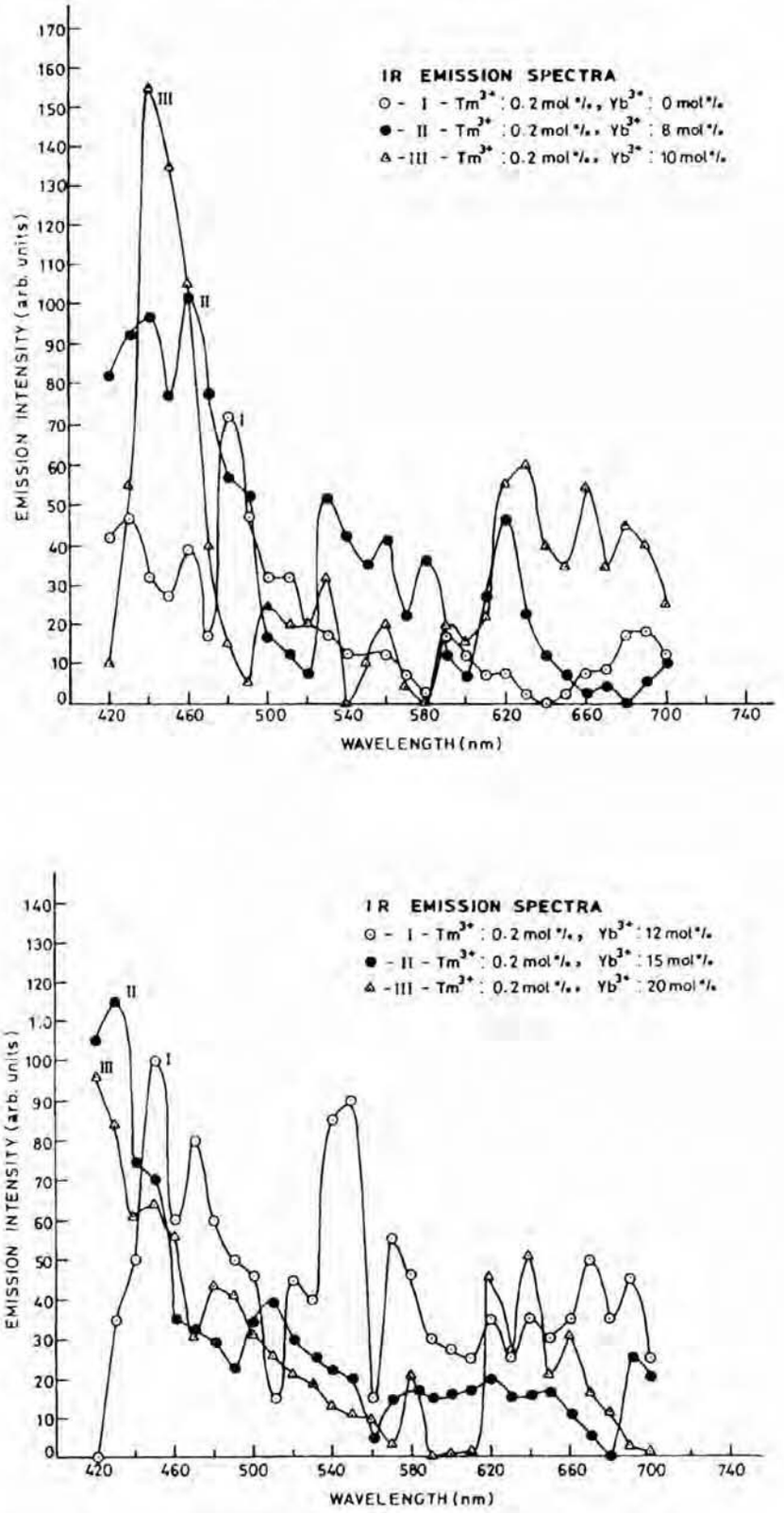

Fig. 2– (a,b) – Up-conversion emission spectra of glass ceramics doped with Yb^{3+} and Tm^{3+} under infrared excitation (966 nm) in the range of 420 to 700 nm at T=300 K for constant (0.2 mol%) Tm^{3+} concentration (a) Curves I, II and III correspond to Yb^{3+}:0 mol%, Yb^{3+}:8 mol%, Yb^{3+}:10 mol%, respectively, (b) Curve I, II and III correspond to Yb^{3+}:12 mol%, Yb^{3+}:15 mol%, Yb^{3+}:20 mol%, respectively.

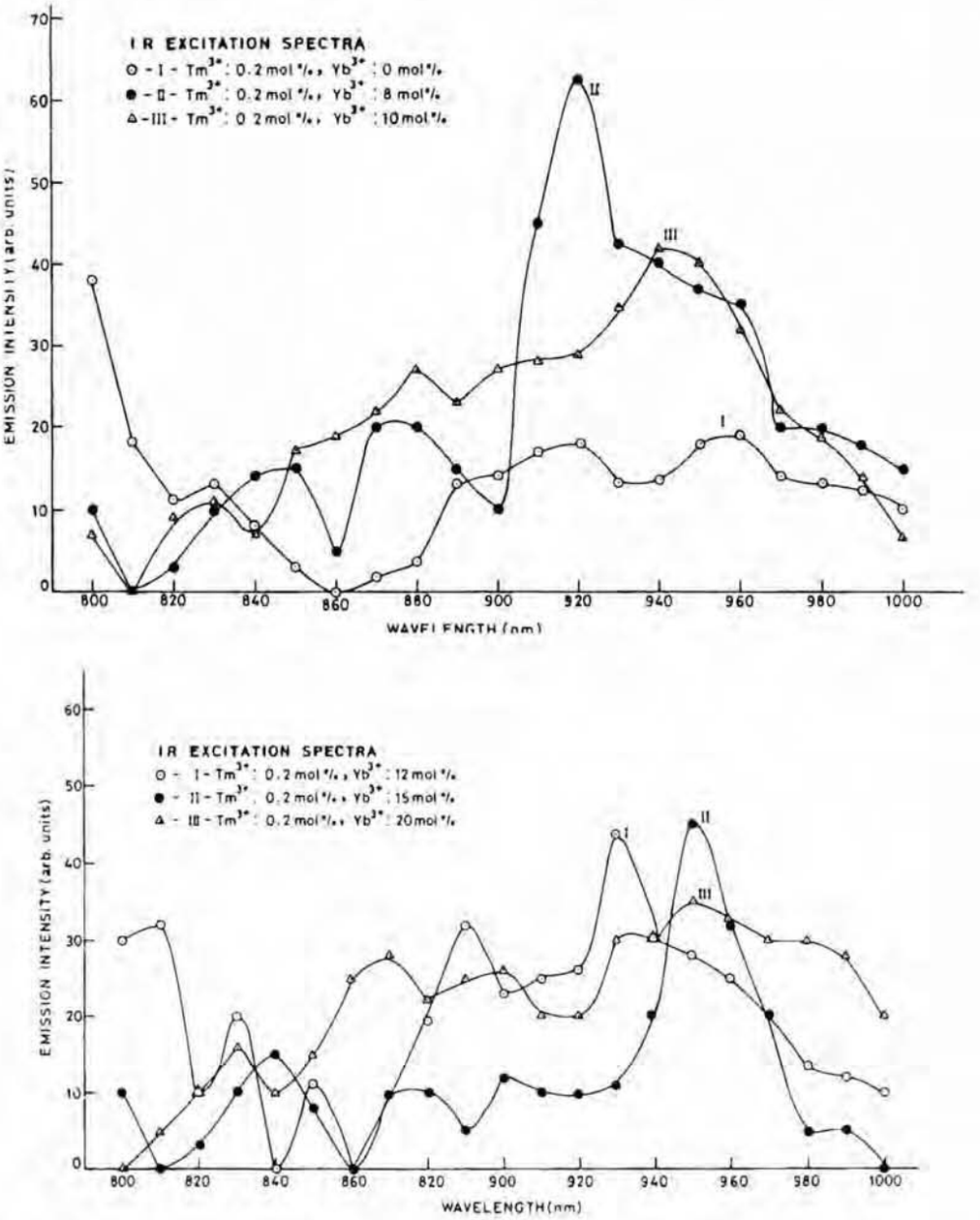

Fig. 3– (a,b) – Excitation spectra of glass ceramics doped with Yb^{3+} and Tm^{3+} under infrared (IR) excitation for constant (0.2 mol%) Tm^{3+} concentration at room temperature (a) Curves I, II and III correspond to Yb^{3+}:0 mol%, Yb^{3+}:8 mol%, Yb^{3+}:10 mol%, respectively, (b) Curves I, II and III correspond to Yb^{3+}:12 mol%, Yb^{3+}:15 mol%, Yb^{3+}:20 mol%, respectively.

increasing wavelength, attains an optimum value for a particular exciting wavelength ranging from 920 nm and 940 nm, different for different samples and then it decreases with further increase in the wavelength.

Fig. 4 shows the sensitizer concentration dependence of the anti-Stokes emission and excitation spectra of glass ceramics doped with Yb^{3+} and Tm^{3+}. It is seen that initially luminescence emission intensity increases with increasing concentration of sensitizer Yb^{3+} in both cases of emission as well as excitation spectra. Luminescence intensity is maximum for 10 mol% in case of emission spectra and for 8 mol% in case of excitation spectra. It decreases with further increase in the sensitizer concentration.

4 Discussion

At the present time, several mechanisms are known for summing the energy of simple pumping of RE^{3+} ions that leads to direct conversion of infrared radiation to visible

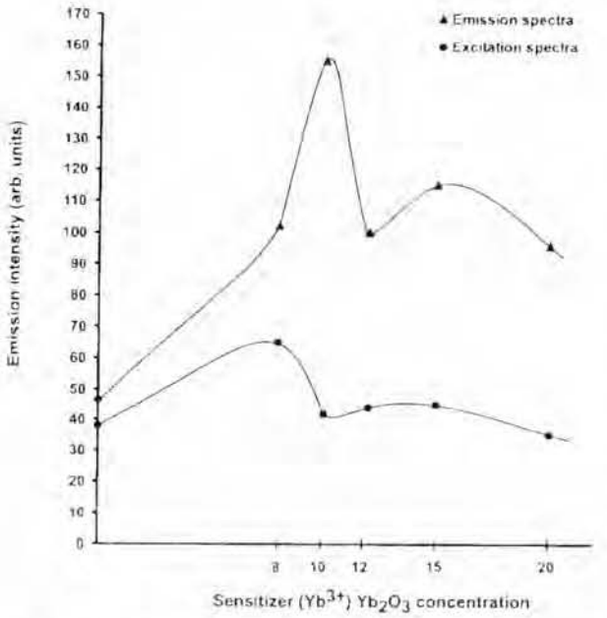

Fig. 4—Concentration dependence of emission and excitation spectra of Yb_2O_3:Yb^{3+},Tm^{3+} under infrared excitation for constant 0.2 mol% Tm_2O_3 doped concentration at room temperature.

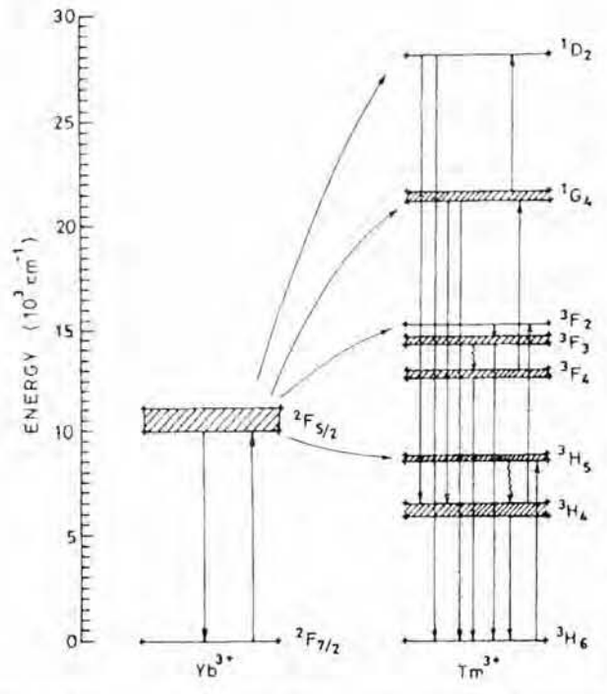

Fig. 5—Energy level diagram of Yb^{3+} and Tm^{3+} ions and schematic processes for four-, three-, and two-photon processes.

light. Historically, the first to be examined was the mechanism of sequential (stepwise) absorption of several IR photons in the same rare-earth ion which thereupon made the transition to a higher energy state. Such a scheme was proposed by Bloembergan[1] for an IR photon counter. The different models used to explain the phenomenon of anti-Stokes luminescence are (i) sequential absorption, (ii) cooperative sensitization, (iii) sequential sensitization (stepwise) model, and (iv) multiphonon-assisted anti-Stokes excitation model[10,11]. The present observation can be explained by sequential absorption, sequential sensitization and phonon assisted energy transfers. The first infrared photon brings a system into some intermediate metastable state from which upon absorption of a second photon, it goes to the upper level. The transition scheme for Yb^{3+} sensitizer and Tm^{3+} activator in a glass ceramic host is shown in Fig. 5. The IR photons transfer the activator Tm^{3+} from $^3H_6$ to $^3H_5$ and if sensitizer Yb^{3+} is present it is also excited from $^2F_{7/2}$ to $^2F_{5/2}$. The lifetime of Yb^{3+} $^2F_{5/2}$ is large, hence it transfers the energy to Tm^{3+} $^3H_5$ assisted with phonon emissions. These excited Tm^{3+} ions relax to $^3H_4$ level by non-radiative transitions which is again a metastable state. The Tm^{3+} ion is then excited to $^3F_2$ or $^3F_3$ levels either by absorption by another IR photon or by another phonon assisted energy transfer from excited Yb^{3+} ion, then they may relax to different lower levels $^3F_3$ and $^3F_2$ respectively. Transition from $^3F_4$ to $^3H_6$ gives red emission, but at the same time Tm^{3+} ions in $^3F_4$ level may absorb third IR photon, or acquire energy from excited Yb^{3+} ions and go to $^1G_4$ level. Radiative relaxation of Tm^{3+} from $^1G_4$ to $^3H_6$ gives blue emission and to $^3H_4$ gives red emission. A part of population of $^1G_4$ level may be excited to a $^1D_2$ level by means of photon absorption or energy transfer from excited Yb^{3+} ions. Radiative relaxation from $^1D_2$ to $^3H_6$ gives violet emission and to $^3H_4$ gives blue emission.

In our samples the blue emission is prominent due to $^1G_4$ to $^3H_6$ transition which is three photon up-conversion. Sensitizer Yb^{3+} increases the population of $^3H_5$, $^3F_4$ and $^1G_4$ levels of Tm^{3+} and hence increasing the intensity of blue emission. This effect initially increases with Yb^{3+} concentration. For higher value of concentration of sensitizer Yb^{3+}, the quenching of this emission may be due to back energy transfer from Tm^{3+} to Yb^{3+} ions and energy diffusion between Yb^{3+} ions.

Thus, the anti-Stokes luminescence intensity is optimum for a particular concentration of the sensitizer.

5 Conclusions

The main conclusions drawn from the studies of excitation and emission spectra of the anti-stokes luminescence of Tm^{3+} in glass ceramics doped with various concentrations of Yb^{3+} sensitizer are :

(i) In the emission spectra of glass ceramics doped with Tm^{3+} and Yb^{3+}, one peak of high intensity was found at different wavelengths between 400 and 500 nm for different concentrations of sensitizer. The peak is slightly shifted towards shorter

wavelength with increasing concentrations of the sensitizer. This reveals that 3-photon up-conversion is prominent and presence of Yb^{3+} ions slightly shifts the energy levels of Tm^{3+}.

(ii) In the excitation spectra of glass ceramics doped with Yb^{3+} and Tm^{3+}, initially the emission intensity increases with increasing wavelength, attains an optimum value for 920 nm, 930 nm, 950 nm and 960 nm and then it decreases with further increase in the wavelength. These photon energies may correspond to energy difference between the levels of Tm^{3+} or Yb^{3+}.

(iii) Both in the excitation spectra and emission spectra, initially the anti-Stokes luminescence intensity increases with sensitizer concentration, attains an optimum value and then it decreases with further increase in the sensitizer concentration.

(iv) The up-conversion of Tm^{3+} glass ceramics doped with Yb^{3+}, involves four-photon and three-photon absorption processes for violet (363 nm) and blue (478 nm) emission bands, respectively. The two-photon absorption process is required for red (680 nm, 698 nm, 779 nm) emissions.

References

1 Bloembergen N, *Phys Rev Lett*, 2 (1959) 84.

2 Ovsyankin V V & Feofilov P P, *Soviet Phys JETP Lett*, 3 (1986a) 332.

3 Feofilov P P, Proc. internet seminar on selected problems in the theory of crystal impurity center, (1972), p. 539.

4 Auzel F, *Compt Rend (France)*, 262B (1966a) 1016.

5 Malinowski M, Joubert M F & Jacquier B, *Phy Rev*, B 50 (1994) 12367.

6 Remillieux A & Jacquier B, *J Lumin*, 68 (1996) 279, 289.

7 Oomen E W J L, *J Lumin*, 50 (1992) 317.

8 Kisilev A & Reisfeld R, *Solar Energy*, 2 (1984) 163.

9 Xu X, Denis J P, Ozen G, Kermoni A & Pelle F, *Phys Status Solidi(a)*, 141 (1994) 445.

10 Ovsyankin V V & Feofilov P P, *Soviet Phys JETP Lett*, 4 (1966b) 317.

11 Ovsyankin V V & Feofilov P P, *Izvestiya An SSSR Ser Fiz*, 37 (1973) 262.