Emission Spectra and Temperature Effect on the Intensity of Anti-Stokes Luminescence of Tm^{3+} and Yb^{3+} Doped Glass Ceramics with Various concentration of Sensitizer

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Abstract - For certain luminescent materials , the wavelength of exciting light is longer than the wavelength of emitted light, and such type of luminescence is known as anti-Stokes luminescence or up-conversion. 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 (966nm) one peak of high intensity was found at different wavelengths between 400 to 500 nm for different concentrations of sensitizer. The effect of temperature on the intensity of anti-Stokes luminescence of glass ceramics has been investigated in the temperature range of 30^oC to 110^oC, where the sample was excited by 966 nm light.

Keywords: Anti-Stokes luminescence, Rare-earth doped glass ceramic, Emission Spectra, Temperature effect

I INTRODUCTION

All types of emission except incandescent emission, ,are known as luminescence. 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, which is due to accumulation of excitation energy by rare-earth ions . The direct conversion of infrared radiation to visible light is possible in a number of rare-earth ion doped crystal phosphors and glass ceramic 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. Ovsyankin2, Feofiloy3, and Auzel4, Several models have been proposed to explain the phenomenon of anti-Stokes luminescence [1-5].

The temperature dependence study of luminescence is interesting not only because it modifies the emission but it yields information to understand the nature of the phosphor or glass ceramics and the effective trap depths may be determined [6-8]. An approach for the quantitative interpretation of the effect of a temperature change on the efficiency of the transformation of infrared (IR) radiation into visible radiation by anti-Stokes luminophors based on rare-earth elements was developed by Brenier and Jurdy on the basis of qualitative ideas presented by Sergeev and Kuzenetsova [12-18].

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

II 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-yttriblium oxides (Yb_2O_3) were also added to the initial mixture which was heated and melted inside a muffle furnace at 1100° C for 30min. The sample was then obtained by sudden cooling of the melt. In $Tm^{3+}$and Yb^{3+} doped glass ceramics, $Tm^{3+;}$ acts as activator and Yb3+ act as a sensitizer. The activator (Tm^{3+}) concentration was kept constant at 0.2 mol % and the sensitizer (Yb^{3+}) concentration varied to 0.0 mol%, 10 mol%, 12 mol%, 15 mol% .and 20 mol%. The glass ceramics prepared for this investigation were:

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

$69.8\ PbF_2 + (20-x/2)\ GeO_2 + (10-x/2)\ WO_3 + xYb_2O_3 + 0.2Tm_2O_3$

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 Fig1. The main units are light source (IR lamp of 250W), grating monochromator, constant deviation spectrometer and detector unit consisting of RCA 931 photomultiplier tube, high voltage power supply and digital pioammeter. For measuring the anti-Stokes emission spectra, the drum of grating Monochromator

was fixed at 966 nm, while the drum of constan deviation spectrometer was varied from 420 nm to 700 nm.

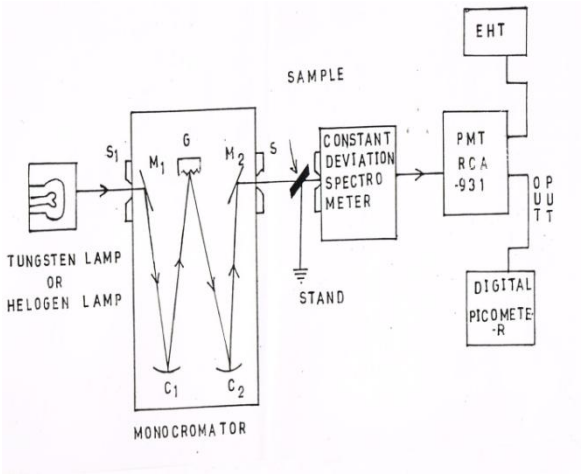


Fig.1 Experimental setup of the measurement of anti-Stokes luminescence

Fig.2 shows the experimental setup for the measurement of effect of temperature on the intensity of anti-Stokes luminescence in Tm^{3+} and Yb^{3+} doped glass ceramics. For measuring the effect of temperature on anti-Stokes emission spectra, the glass ceramics was spread on a quartz plate using araldite as a binder and it was heated by using heating filament fixed close to it. The emission spectrum of Tm^{3+} and Yb^{3+} doped glass ceramics gives peaks at 440 nm, 530 nm, 630 nm, and 660 nm. The intensity of light emission at all the wavelength has been measured at various temperatures ranging from 30°C to 110°C.The temperature of the glass ceramics was directly measured by a K-type thermocouple. The samples were excited by 966 nm. The intensity of anti-Stokes luminescence was measured by PMT at 440 nm , 530 nm , 630 nm and 660 nm which are the main peaks in the emission spectrum

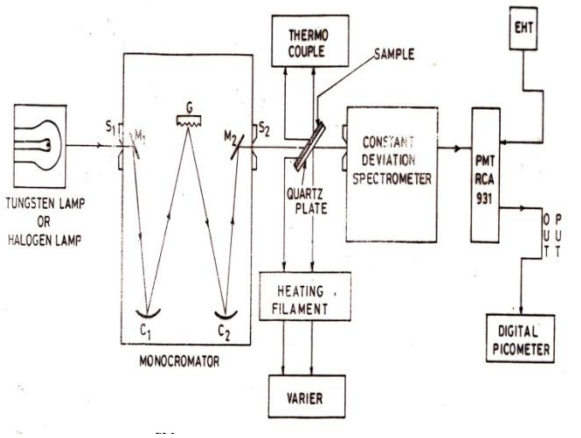
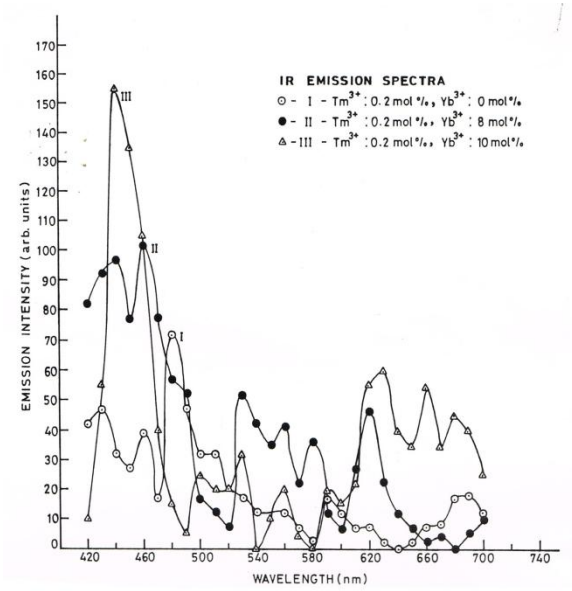


Fig 2. Experimental setup for the measurement of effect of temperature on the intensity of anti-Stokes luminescence in Tm^{3+} and Yb^{3+} doped glass ceramics.

III RESULT

Fig3 (a.b) shows the up-conversion emission spectra of glass ceramics doped with Tm^{3+} and different concentration of Yb^{3+} under infrared Excitation (966 nm) in the wavelength range of 420 nm 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%, 10.0mol%, 12mol%, 15mol% and 20mol%. It is observed that main peaks are obtained between 400 and 500nm at different wave lengths for different concentrations of sensitizer Yb^{3+}.



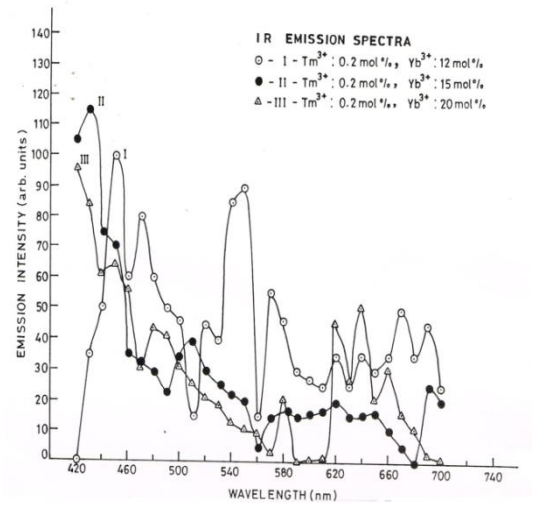


Fig3 (a.b) shows the up-conversion emission spectra of glass ceramics doped with Yb^{3+} and Tm^{3}

Fig. 4 shows the variation in emission intensity at all the four wavelengths due to change in temperature. The emission spectra were measured in the temperature range from 30°C to 100°C. The emission intensity initially decreases with increasing temperature of the glass ceramics and then increases attains a maximum value at 50°C temperature and then it decreases with

further increase in the temperature , and remains practically constant from 60°C to 100°C.

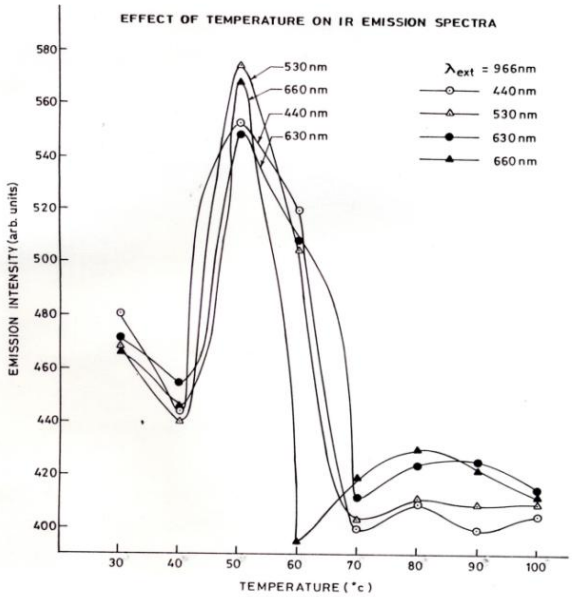


Fig. 4 Effect of temperature on infrared emission spectra of glass ceramics doped with Yb^{3+} and Tm^{3+} (Yb^{3+} : 10 mol% , Tm^{3+} : 0.2 mol%)

Fig.5 shows the sensitizer concentration dependent of the anti-Stokes emissionK 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.

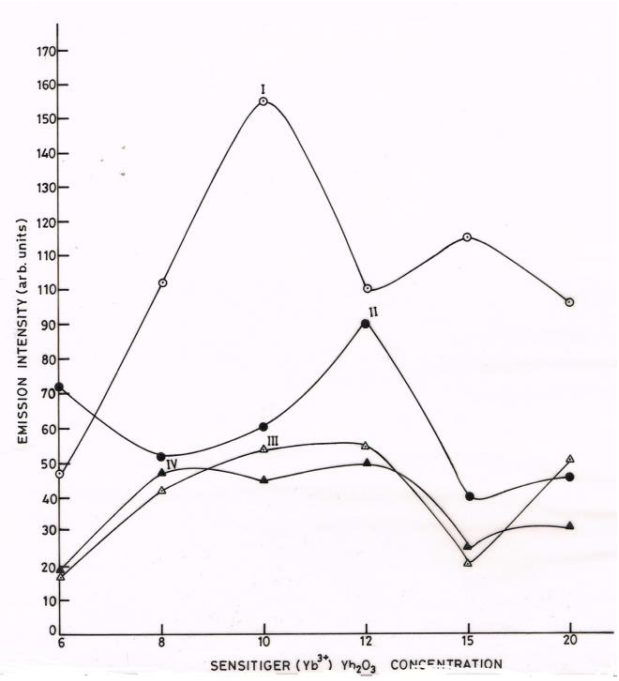


Fig. 5 Concentration dependence of emission spectra of Yb_2O_3.

IV DISCUSSION

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 metsastable state from which up on 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 6. The IR photons Transfer the activator Tm^{3+} from 3 H_6 to $^3H_5$ and if Sensitizer Yb^{3+} is present it is also excited from $^3F_{7/2}$ to $^3F_{5/2}$. The lifetime of Yb^{3+} $^3F_{5/2}$ 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 are 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 $^3F_4$ 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. Radiactive relax-ion of Tm^{3+} from $^1G_4$ to $^3H_6$ gives blue emission, 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-conversions. Sensitizer Yb^{3+}increases population of $^3H_4$, $^3F_4$ 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.

The energy transfer probability between Yb^{3+} and Tm^{3+} ions depends on temperature. On the other hand, according to the energy level diagram of Yb^{3+} and Tm^{3+} ions (Fig 6), the energy mismatches between two ions are about 1800, 1200 and 1680 cm^{-1} , respectively, for the first, second and third transfer processes. It seems from these two facts, that the energy transfer probability between Yb^{3+} and Tm^{3+} ions depends on temperature under infrared excitation, and therefore, it implies that the energy transfer is assisted by phonons.

At low temperature, only spontaneous emission of phonons can occur. As temperature is raised, phonon assisted energy transfer rate grows and stimulated emission of phonons becomes operative. The increase in the intensity of the red and green luminescence with increasing temperature is due to an increase in the

probabilities of the non-resonance multi phonon processes involved in the transfer of electron excitation energy from the sensitizer to the activator, which results in the populating of the highly excited levels of the activator.

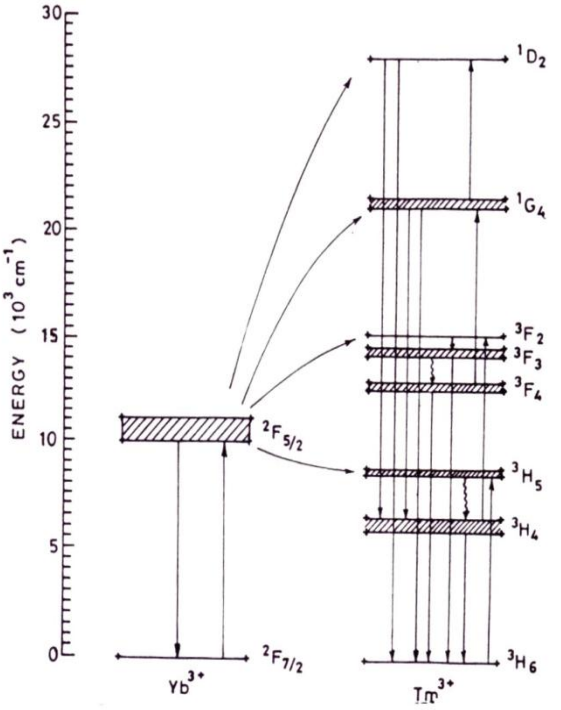


Fig.6 Energy level diagram of Yb^{3+} and Tm^{3+} ions and schematic processes for four-, three-, and two- photon processes.

However, an increase in the temperature also causes an increase in the probabilities of the multi phonon relaxation transitions processes involved in the reverse transfer to electron- excitation energy from the activator to the sensitizer, which deplete the radiative levels of the activator. In the case of anti-Stokes luminescence, the probability of non-radiative transitions may increase with increasing temperature of the glass ceramics. Therefore, the anti-Stokes luminescence intensity may decrease with increasing temperature.

As a result of the combined competitive action of such processes, an extreme value of the intensity of the anti-Stokes luminescence is attained at a certain temperature, and the intensity drops with further increase in the temperature [9-11].

V CONCLUTIONS

The main conclusions drawn from the studies of emission spectra of the anti stokes luminescence of Tm^{3+} in glass ceramics doped with various concentrations of Yb^{3+} sensitizer are the emission spectra of glass ceramics 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 concentration 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+}. 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. The up-conversion of Tm^{3+}glass ceramics doped with Yb^{3+}, involves four-photon and three photon absorption processes for Violet (363nm) and blue (478 nm) emission bands, respectively. The two photon absorption process is required for red (680nm, 698nm, 779nm) emissions.

The intensity of anti-Stokes luminescence in Tm^{3+} and Yb^{3+} doped glass ceramics first slightly decreases with increasing temperature from 30°C, and then increases to a high value at about 50°C , then later on it decreases with further increase in the temperature. As the energy transfer probability between Tm^{3+} and Yb^{3+} ions depends on temperature under infrared excitation, it implies that the energy transfer from Tm^{3+} to Yb^{3+} ions is assisted by phonons. The increase in the intensity of anti-Stokes luminescence with increasing temperature is due to an increase in the probabilities of the non-resonance multi phonon process involved in the transfer of electron-excitation energy from the sensitizer to the activator, which results in the population of the highly excited levels of the activator. As temperature is further increased, probability of non-radioactive transition may increase reducing the luminescence intensity.

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