Chapter-6

Luminescence spectral studies of Tm^{3+} ions doped Lead Tungsten Tellurite glasses for visible Red and NIR Applications

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6.1. Introduction

The ongoing progress in the field of optical and photonic technology demands for new sources of radiation to fulfil the needs relating to not only just specified spectral properties, but also stability and compactness. These technologies present many advantages mainly suited for space applications, such as light weight, low volume (resulting in much reduced payload), immunity to electromagnetic interference, capability of operating in harsh environments and practically unlimited bandwidth [200]. Consequently, it is not amazing that, in the last decade the function of these photonic technologies increases especially in the field space systems. Among the photonic materials, glass plays an important role because of its unique structural and thermodynamic features. Glass also presents an excellent homogeneity, good thermo-mechanical properties and a viscosity-temperature relationship along with the stability that allows for fibre drawing and laser host applications. Moreover glass is highly potential for adopting the rare earth (RE) ions for high concentrations to get the desired emissions. The rare earth doped glassy materials are very attractive because of their well-defined energy levels which are marked by only small shifts, irrespective of the used host glass composition. For this reason, rare earth elements are frequently used to develop new laser systems. Rare earth ions can be doped in different materials as single/ double/ triple and these types of materials are also used for colour tuneable emissions which can be used to get white light emission [201,202].

Several key photonic devices are made of non-silica based oxide glasses belonging to the phosphate / borate / germinate / tellurite systems. Although these glass systems are not applied to mass production due to the higher cost of raw material (compared to silicate), lower chemical durability and mechanical strength. But they possess unique properties that cannot be obtained for silicate glasses. Among all the glasses, tellurite glasses possess some unique properties. They have a wide transmission bandwidth in the IR wavelength region (up to 5 μm) that makes them suitable for the mid-IR spectral range. Compared to other non-oxide glasses operating in this range, they demonstrate higher glass stability and corrosion resistance. Furthermore, they are non-hygroscopic, which allows storage in ambient air without any degradation to their transparency. In the field of colour tuneable emission, lot of efforts are being dedicated for the improvement of materials which can emit white light. Usually, white light is obtained by mixing Red-Green-Blue (RGB)

(monochromatic light sources) colours. The most frequent method of getting RGB light emissions is to include a variety of rare earth ions with colourful emissions. For example, white light emission is observed in the triply doped Yb^{3+}, Tm^{3+} and Er^{3+} system with 980 nm excitation, in which blue emission is from Tm^{3+} ions due to the transitions $^1D_2 \rightarrow {}^3F_4$, $^1G_4 \rightarrow {}^3H_6$, green and red emissions are from Er^{3+} ions due to the transitions $^2H_{11/2}$ ($^4S_{3/2}$) $\rightarrow$ $^4I_{15/2}$, $^4F_{9/2} \rightarrow {}^4I_{15/2}$ respectively [203]. Even though green and red emissions can also ($^1D_2 \rightarrow {}^3H_5$, $^1G_4 \rightarrow {}^3F_4$) be produced from$Tm^{3+}$ ion doped materials, but the main drawback is that these transitions are very weak due to low transition probabilities [203]. Subsequently, if the transition probabilities of these levels of Tm^{3+} ion ($^1D_2$ and $^1G_4$) could be sufficiently changed, the RGB light emissions from a single activator (Tm^{3+}) can be possible. The RGB light emissions of Tm^{3+} ions are usually originated from the excitation of high energy levels ($^1D_2$ and $^1G_4$). On the other hand, the sensitization for high energy level transition is rarely described in earlier studies [204-206]. Tm^{3+} ions doped materials are not only have the importance in the colour tunability but also have innumerable potential applications in the NIR and MID-IR regions, because of the $^3F_4 \rightarrow {}^3H_6$ transition (1.8-2.2 μm). Laser beam in this wavelength range has several applications such as laser microsurgery (high quality laser is required for tissue cutting and welding and this is possible due to high absorption of water in this spectral region), environment monitoring, Light Detection and Ranging (LIDAR), Optical Parametric Oscillation (OPO) pump sources, coherent Doppler velocimetry [207-211]. To get the laser emission in the MID-IR region, the Tm^{3+} ion doped materials became very popular because of the following three unique properties. The first one is Tm^{3+} doped materials possess a strong absorption spectrum that has good overlap with the luminescence band of commercially accessible AlGaAs laser diodes, which have been developed with an extraordinary speed. The second one is its special energy level structure which provides the special advantageous cross relaxation process ($^3H_4 + {}^3H_6 \rightarrow {}^3F_4 + {}^3F_4$) between Tm^{3+} ions. Due to this process the quantum efficiency of Tm^{3+} ions doped materials improved [212] (In this process, two excited-state ions can be obtained with diminution of one absorbed pump photon). The Third one is the Tm^{3+} doped fibre has a very broad emission band (> 400 nm). Due to this spectacular character, the Tm^{3+} doped fibre lasers are used in high degree wavelength tunability which is very helpful in spectroscopy, atmospheric sensing applications

[213]. In the present work, we have fabricated the lead tungsten tellurite (LTT) glasses by varying Tm^{3+} ion concentration to study their spectroscopic and luminescent properties such as optical absorption, photoluminescence and decay spectral profiles in order to explore the better glass for possibility of using these new materials for future photonic devices. With the help of J-O theory, we have analysed the absorption spectra as it is a standard tool in evaluating the radiative properties of the Tm^{3+} ions doped LTT glasses.

6.2. Experimental Methods

6.2.1. Glass Synthesis

The Lead Tungsten Tellurite glasses were prepared by using melt quenching technique with a composition of (60-x) TeO_2+ $25WO_3$+$15PbF_2$+xTm_2O_3, (where x=0.1, 0.5, 1.0, 1.5, 2.0, 2.5 mol %). All chemicals used in the present work are of higher purity (99.99%) are used to prepare the glasses with required composition. These chemicals were thoroughly mixed and crushed in an agate mortar and melted in a silica crucible at 735°C for 30 min in an electrical furnace. The glass melts were removed from furnace and poured on a pre-heated brass plate and then pressed immediately with another brass plate. The obtained glasses are annealed at 350°C for 2 hrs to remove the thermal strains. Finally the prepared glasses were well polished with an emery paper before characterization.

6.2.2. Characterization

6.2.2.1. Physical Properties Measurement Details

For the polished glass samples density and refractive indices were measured using Archimedes principle (distilled water used as an immersion liquid) and Brewster's angle method (He-Ne laser - 632 nm) respectively.

6.2.2.2. Absorption Spectral Measurement Details

For all the samples Absorption spectra were recorded using JASCO V-670 (UV-vis-NIR) spectrophotometer in the wavelength range of 450-1900 nm with a resolution 1 nm.

6.2.2.3. Luminescence Spectral Measurement Details

All the photoluminescence excitation and emission spectra of LTT glasses were recorded at room temperature using Schimadzu RF-5301 PC Spectrofluorophotometer.

6.2.2.4. Decay Curves Measurement Details

Lifetime decay curves were recorded using an Edinburgh luminescence spectrometer (Model F 900) equipped with a microsecond Xe-flash lamp as the source of excitation (401 nm).

6.3. Results and discussion

6.3.1. Physical Properties

By using refractive index and density values, various other physical properties of glasses were evaluated using the equations eq.(2.1-2.10) given in chapter-2 and are shown in Table 6.1. From Table 6.1, it can be seen that the values of refractive index, densities of all LTT glasses increases with the increase of Tm^{3+} ions concentrations. , not only these two, all the other physical properties such as average molecular weight, Tm^{3+} ion concentration, mean atomic volume, dielectric constant, optical dielectric constant, refraction losses, molar refraction and field strength values are also increases and polaron radius, inter ionic distance and molecular electronic polarizability are decreases with the increase Tm^{3+} ion concentration.

Table 6.1.

Various physical properties of Tm^{3+} ions in LTT glasses

Physical Property	**LTT Tm01**	**LTT Tm05**	**LTT Tm10**	**LTT Tm15**	**LTT Tm20**	**LTT Tm25**
Refractive index(n_d)	2.481	2.510	2.543	2.548	2.554	2.572
Density (ρ) (g cm^{-3})	6.608	6.619	6.633	6.645	6.66	6.673
Average molecular weight, $\bar{M}$(g)	190.7	191.6	192.7	193.8	195.0	196.1
Tm^{3+} ion concentration,N (10^{22} ions/cm^3)	0.208	1.04	2.072	3.095	4.112	5.121
Mean atomic volume(g/cm^3/atom)	6.559	6.579	6.604	6.631	6.655	6.680
Dielectric constant(ε)	6.155	6.300	6.466	6.492	6.522	6.615
Optical dielectric constant (ε-1)	5.155	5.300	5.466	5.492	5.522	5.615
Reflection losses (R %)	0.181	0.185	0.189	0.190	0.191	0.193
Molar refraction (R_m)(cm^{-3})	18.24	18.48	18.76	18.87	18.97	19.15
Polaron radius (Å)	3.210	1.880	1.492	1.310	1.190	1.100
Inter ionic distance (Å)	7.960	4.660	3.703	3.240	2.950	2.74
Molecular electronic polarizability, α ($x10^{-24}cm^3$)	72.6	14.7	7.443	4.99	3.76	3.04
Field strength, F ($x10^{15}cm^{-2}$)	2.91	8.51	13.445	17.6	21.30	24.60

6.3.2. Absorption Spectral Analysis

6.3.2.1. Absorption spectral analysis

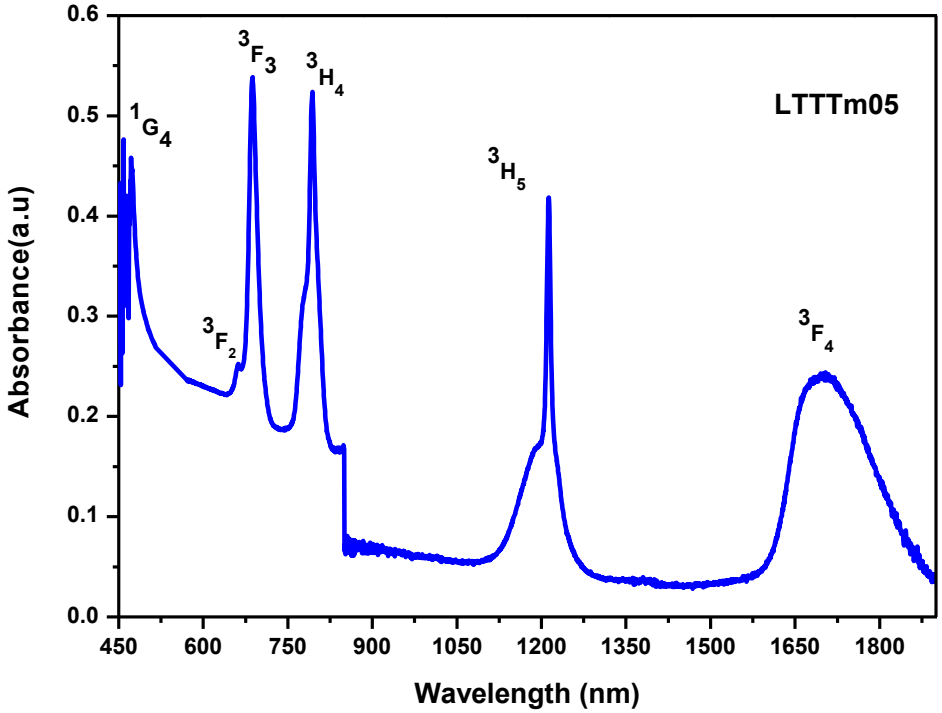

Fig. 6.1. Optical absorption spectrum of the LTTTm05 glass

Fig.6.1. shows the absorption spectrum of 0.5 mol% of Tm^{3+} ions doped LTT glass (LTTTm05). As the absorption spectra recorded for all the LTT glasses appear same with slight variation in intensity, we have shown only one absorption spectrum pertaining to LTTTm05 glass. The absorption spectra recorded for all the Tm^{3+} ions doped LTT glasses show 6 bands related to the transitions from the $^3H_6$ ground state to several higher energy states ($^1G_4$, $^3F_2$, $^3F_3$, $^3H_4$, $^3H_5$ and $^3F_4$). Identification of different bands observed in the present work has been done using the data given in carnal paper [105]. The bands are appeared at the wavelengths 474nm ($^3H_6 \rightarrow {}^1G_4$), 660 nm ($^3H_6 \rightarrow {}^3F_2$), 689 nm ($^3H_6 \rightarrow {}^3F_3$), 793 nm ($^3H_6 \rightarrow {}^3H_4$), 1212 nm ($^3H_6 \rightarrow {}^3H_5$) and 1703 nm ($^3H_6 \rightarrow {}^3F_4$). The position of the absorption peaks are similar to the reported spectra of other glasses doped with thulium [214-216].

6.3.2.2. Energy Band Gap

By using absorption spectral data, the energy band gaps for all the glasses were evaluated. The energy band gap is estimated by extrapolating the linear regions of the curves $(\alpha h\nu)^{1/2}$ vs. hν as shown in Fig. 6.2. From Fig. 6.2, it is observed that there is no evidence for the sharp absorption edges which is the main feature of most of the oxide glasses. The energy band gap values of all the glasses are LTTTm01 (2.59 eV), LTTTm05 (2.50 eV), LTTTm10 (2.44 eV), LTTTm15 (2.41 eV), LTTTm20 (2.38 eV) and LTTTm25 (2.34 eV). The optical band gap values decreases with the increase of Tm^{3+} ions concentration. The optical band gap of all the glasses is in the range of 2.34-2.59 eV which is very useful for the construction of optical devices.

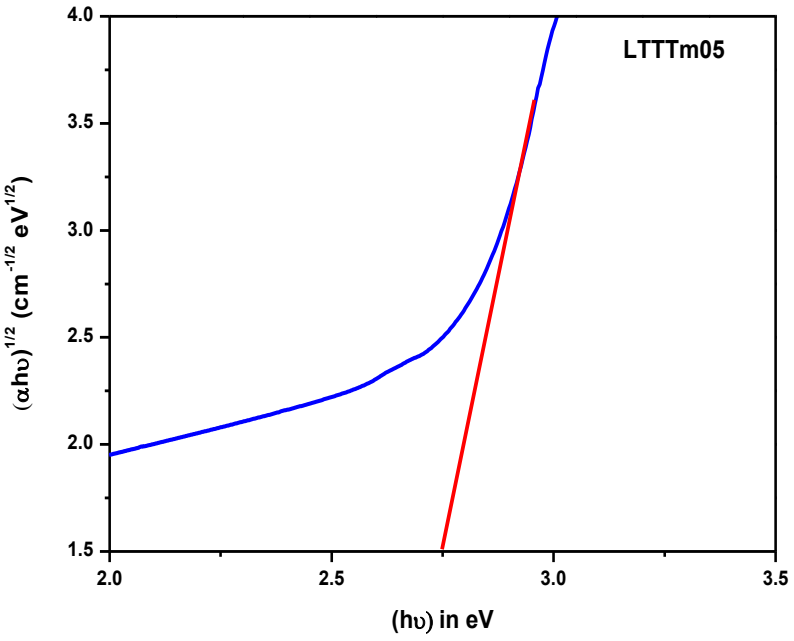

Fig. 6.2. Energy band gap of 0.5 mol % Tm^{3+} ions doped LTT glass

6.3.2.3. Oscillator Strengths

The intensities of absorption bands known as experimental oscillator strengths (f_{exp}) were evaluated using the eq.(1.8) is given in chapter-I [56] and are shown in Table 6.2. The calculated oscillator strengths of absorption bands are evaluated using J-O theory with the conventional equation (1.5) is given in chapter-I [47, 48].The quality of the fit is calculated by root mean square deviation (δ_{rms}) between the calculated and experimental oscillator strengths. The values of f_{exp} and f_{cal} together with the r.m.s deviation are represented in Table 6.2. The deviation parameter δ_{rms} is

calculated by using the expression given in literature [188-199]. From Table 6.2, it can be observed that, the variations in the magnitude of oscillator strengths are very small.

6.3.2.4. J-O Parameters Evaluation

The J-O intensity parameters Ω_2, Ω_4 and Ω_6 are evaluated through least square fitting analysis by using equation (1.5) and are given in Table 6.3 along with the other reported values [217-220]. Few transitions of rare earths are found to be dependent on the doped rare earth ion concentration and composition of host glass. These absorption levels show remarkable intensity deviations and are called as hypersensitive levels. For the Tm^{3+} ion, the transition $^5I_8 \rightarrow {}^5G_6$ is a hypersensitive transition and it satisfies the selection rules such as $|\Delta S|=0$, $|\Delta L| \leq 2$, $|\Delta J| \leq 2$. The spectral oscillator strengths of these transitions are strongly affected by the Judd-Ofelt intensity parameter Ω_2. The J-O intensity parameters follow the trend $\Omega_2 > \Omega_6 > \Omega_4$ for all the glasses and Ω_2 value is found to be more than the parameters Ω_4 & Ω_6. Hence present glass systems have more covalent nature. The J-O intensity parameters magnitude is mainly correlated with the physical and chemical properties such as viscosity and covalent character of the chemical bonds. The large values of Ω_2 parameter are the indicators of the covalent character of the chemical bonds between the glass matrix and rare earth ions [221]. This is due to O^{-2} ions possess higher polarizability than F^- leading to the increment of the covalency of the bond between Tm^{3+} and ligand [222]. In the present series of glasses, LTTTm05 glass possesses maximum value of Ω_2 parameter. Therefore LTT glass with 0.5 mol% of Tm^{3+} ions possesses higher asymmetry and greater degree of covalency of thulimium and oxygen bond than other reported values [217-220]. The large values of Ω_4 and Ω_6 are related to the bulk properties such as viscosity and rigidity of the glass structure [222].

Table 6.2.

Experimental (f_{exp} x 10^{-6}), calculated (f_{cal} x 10^{-6}) oscillator strengths and rms deviation of Tm^{3+} ions in LTT glasses

Transitions	LTTTm01		LTTTm05		LTTTm10		LTTTm15		LTTTm20		LTTTm25	
from $^3H_6$→	f_{exp}	f_{cal}	f_{exp}	f_{cal}	f_{exp}	f_{cal}	f_{exp}	f_{cal}	f_{exp}	f_{cal}	f_{exp}	f_{cal}
$^1G_4$	0.582	1.978	3.357	4.277	2.084	4.250	1.720	2.993	1.150	2.219	0.840	1.710
$^3F_2$	0.379	1.360	2.233	4.014	0.894	2.967	0.826	2.899	0.504	2.005	0.319	1.462
$^3F_3$	5.090	5.851	14.228	15.875	11.11	12.50	8.290	10.672	6.170	6.825	4.590	5.041
$^3H_4$	6.589	6.961	16.225	17.020	14.53	15.17	11.300	12.507	9.279	9.523	7.003	7.162
$^3H_5$	4.680	3.637	11.416	9.235	9.810	7.847	9.540	6.479	5.570	4.555	4.127	3.407
$^3F_4$	5.995	6.032	13.100	13.224	12.90	12.99	9.200	9.355	6.941	7.008	5.334	5.382
δ_{rms} (x10^{-6})	±0.887		±1.422		±1.593		±1.931		±0.906		±0.685	

Table 6.3.

Judd-Ofelt Parameters (Ω_λ x 10^{-20}cm^2) of the Tm^{3+} ions in LTT glasses

Glass System	Ω_2	Ω_4	Ω_6	Trend	References
LTTTm01	5.210	1.360	1.409	$\Omega_2>\Omega_6>\Omega_4$	present work
LTTTm05	10.936	2.734	4.062	$\Omega_2>\Omega_6>\Omega_4$	present work
LTTTm10	10.894	2.612	2.923	$\Omega_2>\Omega_6>\Omega_4$	present work
LTTTm15	8.255	1.305	2.827	$\Omega_2>\Omega_6>\Omega_4$	present work
LTTTm20	6.983	0.408	1.958	$\Omega_2>\Omega_6>\Omega_4$	present work
LTTTm25	5.267	0.347	1.407	$\Omega_2>\Omega_6>\Omega_4$	present work
PKMAT	9.32	1.82	3.21	$\Omega_2>\Omega_6>\Omega_4$	[217]
Oxyfluoroborate	8.37	3.20	4.34	$\Omega_2>\Omega_6>\Omega_4$	[218]
Tellurite	5.04	1.36	1.22	$\Omega_2>\Omega_4>\Omega_6$	[219]
GGLS	7.11	1.46	1.96	$\Omega_2>\Omega_6>\Omega_4$	[220]

6.3.3. Emission Spectral Analysis

Fig. 6.3 shows the excitation spectrum of LTTTm05 glass in the region 450-500 nm at an emission wavelength 650 nm. The excitation spectrum has one prominent peak at wavelength 472 nm corresponding to the transition $^3H_6 \rightarrow {}^1G_4$. The luminescence spectra of the all LTT glasses were recorded at an excitation wavelength 472 nm in the visible and NIR regions. Fig.6.4 shows the luminescence spectrum recorded for LTTTm05 at 472 nm excitation wavelengths. The inset in Fig. 6.4 shows the luminescence spectra of all the LTT glasses under 472 nm excitation. The luminescence spectra consists of two prominent emission bands at 650 nm (red region) and 800 nm (NIR region) corresponding to the transitions $^1G_4 \rightarrow {}^3F_4$ and $^3H_4 \rightarrow {}^3H_6$ respectively. Among the two emission bands, the intensity of the peak at 650 nm is higher than the peak at 800 nm. The peak corresponding to the transition $^1G_4 \rightarrow {}^3F_4$ at 650 nm is very sharp and intense while the other one appears as broad.

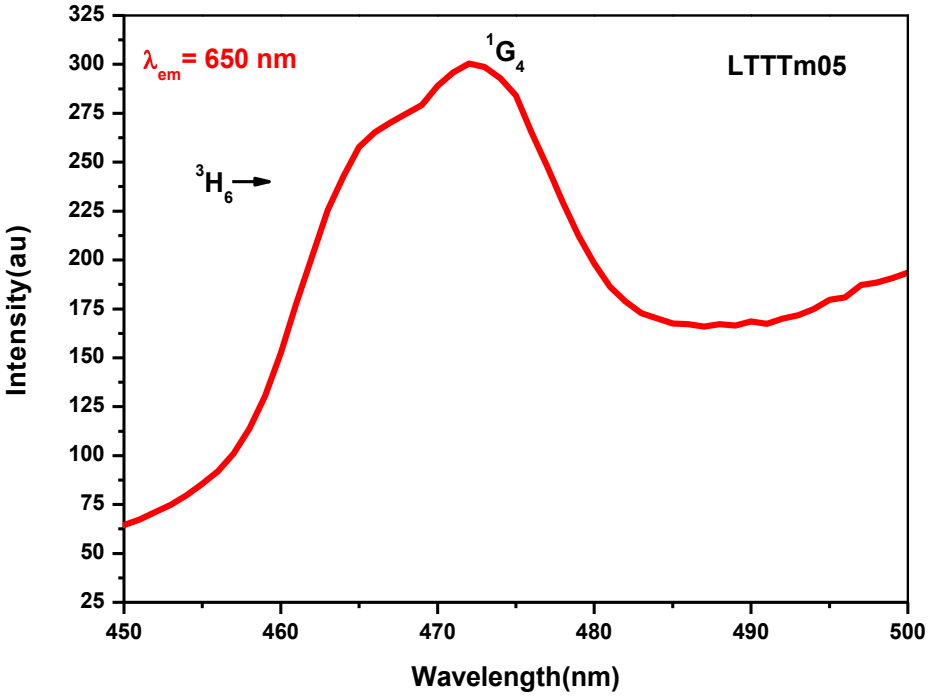

Fig. 6.3. Excitation spectrum of the LTTTm05 glass

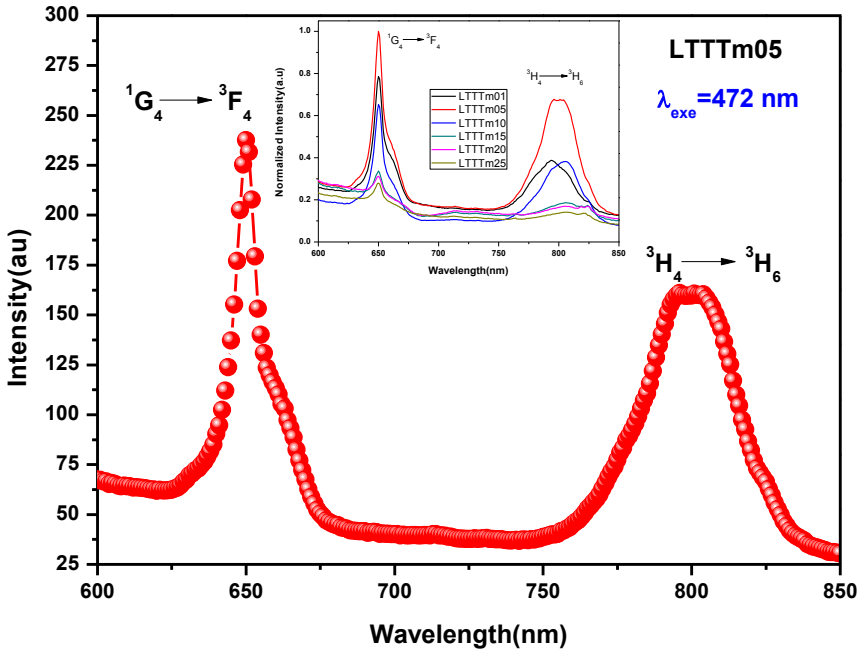

Fig. 6.4. Emission spectrum of LTTTm05 glass and the inset figure shows the emission spectra of all the LTT glasses doped with different concentrations of Tm^{3+} ions

From Fig. 6.4, it is observed that the intensity of the two transitions at 650 nm, 800 nm increases with increasing concentration of Tm^{3+} ions up to 0.5 mol % and then decreases. Hence in the present series of glasses, the concentration quenching is observed at 0.5 mol % of Tm^{3+} ions concentration.

In order to verify the luminescence performance of present series of LTT glasses, various radiative parameters were calculated using J-O intensity parameters and are given in Table 6.4 and Table 6.5. The radiative parameters are evaluated using the equations (1.10-1.13) are given in chapter-I. From the Table 6.4, it is observed that, the transition probability (A_R) and branching ratio (β_R) values of LTTTm05 glass are relatively large for the two transitions $^1G_4 \rightarrow {}^3F_4$ (650 nm) and $^3H_4 \rightarrow {}^3H_6$ (800 nm). From the Table 6.5 it is also observed that the radiative and experimental branching ratios (β_R & β_{exp}) are in good agreement with each other.

Table 6.4.

Transition probabilities (A_R) (s^{-1}), luminescence branching ratios (β_R), total transition probability (A_T) (s^{-1}) and radiative lifetimes (τ_R) (μs) for the observed emission transitions of Tm^{3+} ions in LTT glasses

Transition	A_R	β_R	A_T	τ_R
LTTTm01				
$^1G_4 \rightarrow {}^3F_4$	7085.07	0.424	16703.26	59.86
$^3H_4 \rightarrow {}^3H_6$	24179.87	0.951	25404.76	39.36
LTTTm05				
$^1G_4 \rightarrow {}^3F_4$	19456.54	0.472	41184.79	24.28
$^3H_4 \rightarrow {}^3H_6$	58509.18	0.957	61097.41	16.36
LTTTm10				
$^1G_4 \rightarrow {}^3F_4$	16309.50	0.428	38067.86	26.26
$^3H_4 \rightarrow {}^3H_6$	52708.64	0.949	55508.97	18.01
LTTTm15				
$^1G_4 \rightarrow {}^3F_4$	12752.83	0.412	30945.60	32.31
$^3H_4 \rightarrow {}^3H_6$	40295.84	0.945	42614.89	23.46
LTTTm20				
$^1G_4 \rightarrow {}^3F_4$	10873.87	0.382	28473.45	35.12
$^3H_4 \rightarrow {}^3H_6$	39359.01	0.943	41729.04	23.96
LTTTm25				
$^1G_4 \rightarrow {}^3F_4$	6225.45	0.346	17978.43	55.62
$^3H_4 \rightarrow {}^3H_6$	24699.21	0.941	26232.78	38.41

It is well known that if the branching ratio (β_R) of an emission level is greater than or equal to 50%, then that transition is known to be a potential transition for lasing action [223]. The lasing potentiality of an emission transition can also be decided by the

value of stimulated emission cross-section (σ_{se}). The peak wavelength, half width maxima ($\Delta\lambda_P$) and stimulated emission cross-section (σ_{se}) values along with the optical gain parameters are given in Table 6.5 for all the Tm^{3+} ions doped LTT glasses. From this table it can be seen that, the LTTTm05 glass possesses maximum values of stimulated emission cross-section (σ_{se}) and optical gain parameters for the two transitions at 650 nm and 800 nm. From these results, we can suggest that the LTTTm05 glass is suitable to emit laser at 650 nm and 800 nm in visible Red and NIR regions respectively. The energy level diagram which shows the absorption, excitation and emission phenomenon of Tm^{3+} ions doped LTT glasses is shown in Fig. 6.5.

Table 6.5.

Emission peak wavelength (λ_P)(nm), effective band widths ($\Delta\lambda_P$)(nm), radiative and experimental branching ratios (β_R & β_{exp}), stimulated emission cross-sections (σ_{se}) (x 10^{-18}) (cm^2), gain band width (σ_{se} x $\Delta\lambda_p$) (x 10^{-26}) (cm^3) and optical gain (σ_{se} x τ_R) (x 10^{-22}) (cm^2 s) parameters for the emission transitions of Tm^{3+} ions in LTT glasses.

Spectral parameters	LTTTm01	LTTTm05	LTTTm10	LTTTm15	LTTTm20	LTTTm25
			$^1G_4 \rightarrow {}^3F_4$ (Red)			
λ_P	650	650	650	650	650	650
$\Delta\lambda_p$	8.108	8.108	9.459	10.811	13.514	13.514
β_R	0.951	0.957	0.949	0.945	0.943	0.941
β_{exp}	0.507	0.589	0.559	0.489	0.462	0.446
σ_{se}	3.36	9.02	6.32	4.30	2.92	2.18
σ_{se} x $\Delta\lambda_p$	2.73	7.32	5.97	4.65	3.95	2.95
σ_{se} x τ_R	2.01	2.19	1.66	1.39	1.03	1.21
			$^3H_4 \rightarrow {}^3H_6$ (Infrared)			
λ_P	806	800	806	793	806	806
$\Delta\lambda_p$	37.84	35.14	37.84	37.84	39.19	40.54
β_R	0.424	0.472	0.428	0.412	0.382	0.346
β_{exp}	0.412	0.482	0.440	0.437	0.410	0.393
σ_{se}	5.81	14.40	12.10	8.61	8.51	5.16
σ_{se} x $\Delta\lambda_p$	22.0	50.50	45.60	32.60	33.80	20.90
σ_{se} x τ_R	2.29	2.36	2.17	2.02	2.04	1.98

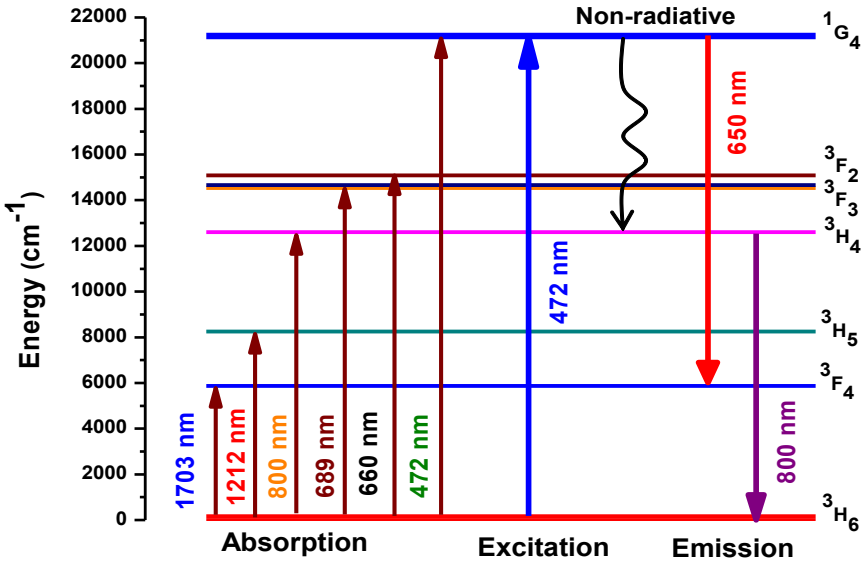

Fig. 6.5. Energy level diagram of Tm^{3+} ions doped LTT glasses

6.3.4. Luminescence Decay Analysis

The luminescence spectral decay curves of the $^1G_4$ fluorescent level of Tm^{3+} doped LTT glasses have been measured at room temperature and are shown in Fig. 6.6. All the experimental spectral decay curves are single exponential in nature. The experimental life time (τ_{exp}) of the $^1G_4$ excited level has been found by taking the first e- fold times of the decay curves [224]. The experimental lifetimes (τ_{exp}) and the radiative lifetimes (τ_R) obtained for the present glasses are given in Table 6.6 for all Tm^{3+} doped LTT glasses. The experimental lifetimes are considerably smaller than the radiative lifetimes evaluated by using the J-O theory may be due to the energy transfer through cross-relaxation [225].

For rare-earth ions, the quantum efficiency (η) is another important parameter; which is used to predict the efficiency/quality of the laser host material. This can be evaluated by using eq.(1.16) given in chapter-I. The quantum efficiency (η) depends on emission cross-section (σ_{se}), radiative transition probabilities (A_R), lifetimes (τ_R & τ_{exp}) of the excited states, concentration of rare-earth ions and ligand field produced by network modifiers. The quantum efficiency for all glasses are given in Table 6.6 along with the radiative and experimental lifetimes (τ_R & τ_{exp}) for the transition $^1G_4 \rightarrow {}^3F_4$. From the Table 6.6 it can be seen that, among the all glasses, the

LTTTm05 glass possess maximum values of quantum efficiency. Hence it can be concluded that the LTTTm05 glass is quite able to emit bright red colour laser at 650 nm.

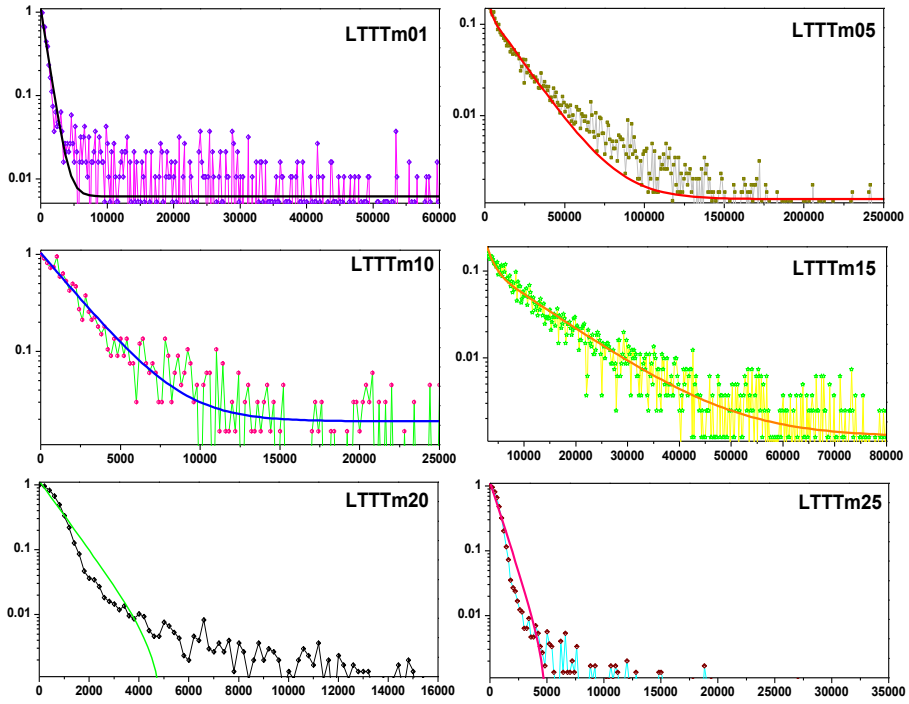

Fig. 6.6. Decay curves for the luminescent transition $^1G_4 \rightarrow {}^3F_4$ of Tm^{3+} ions doped LTT glasses at 472 nm excitation

6.3.5. Evaluation of CIE Colour Co-Ordinates:

The visible emission shown by the glasses doped with rare earth ions can be further confirmed by colour chromaticity diagram drawn from the emission spectral data. For different concentrations of Tm^{3+} ions doped LTT glasses, the colour chromaticity coordinates were evaluated from the luminescence spectra using the CIE (Commission International de l'Eclairage France) system. Fig. 6.7 presents the CIE plot with colour coordinates of the LTTTm glasses. The chromaticity coordinates of the Tm^{3+} ions doped LTT glasses were calculated using eq. (1.21-1.25) given in chapter-I [**64-67**] and are given in Table 6.6. All the evaluated colour co-ordinates of LTT glasses exactly fall in the red region. From the measured branching ratios,

stimulated emitted cross-sections, quantum efficiency and colour chromaticity co-ordinates evaluated for Tm^{3+} ions doped LTT glasses, it is concluded that the LTTTm05 glass is the best optical material to generate bright red colour laser at 650 nm. The same glass is also suitable to emit NIR laser emission at 800 nm.

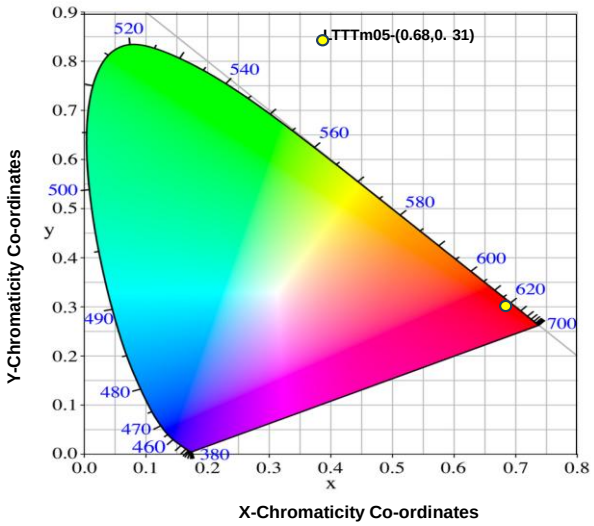

Fig. 6.7. CIE 1931colour chromaticity diagram for LTTTm05 glass

Table 6.6.

Colour co-ordinates of Tm^{3+} ions in LTT glasses life times (τ_R (μs), τ_{exp}(μs)) and Quantum Efficiency (η)

Name of the Sample	Colour Co-ordinates λ_{exc} =472 nm	τ_R (μs)	τ_{exp} (μs)	Quantum Efficiency (η)%
LTTTm01	(0.670, 0.300)	59.86	36.16	60.4
LTTTm05	(0.680, 0.310)	24.28	19.5	80.3
LTTTm10	(0.670, 0.310)	26.26	17.65	67.2
LTTTm15	(0.670, 0.310)	32.37	15.32	47.3
LTTTm20	(0.685, 0.305)	35.12	13.65	38.8
LTTTm25	(0.690, 0.310)	55.62	11.38	20.4

6.4. Conclusions

Different concentrations of Tm^{3+} ions doped LTT glasses have been synthesized by using melt quenching method and characterized with the help of the spectroscopic techniques such as optical absorption, excitation, emission and decay spectral measurements to optimise the concentration of the doped rare earth ion for better luminescence efficiency. The J-O intensity parameters (Ω_2, Ω_4 and Ω_6) evaluated for LTT glasses are found to be high for LTTTm05 glass indicating that this glass is more asymmetric, and more covalent in nature than the other glasses. The emission spectra recorded for different concentrations of Tm^{3+} ions in LTT glasses show two emission bands at 650 and 800 nm corresponding transitions to $^1G_4 \rightarrow {}^3F_4$ and $^3H_4 \rightarrow {}^3H_6$ respectively. Among these two emission transitions observed, $^1G_4 \rightarrow {}^3F_4$ is more intense and is falling in red region the other one is broad and falling in the Near-Infrared region. Relatively higher values of stimulated emission cross-section and branching ratios values observed for for all these LTT glasses suggest the possibility of using these materials as lasers in red ($^1G_4 \rightarrow {}^3F_4$) and NIR ($^3H_4 \rightarrow {}^3H_6$) regions. From the decay curves, experimental lifetimes were measured which are in turn used to evaluate the quantum efficiencies. The CIE chromaticity co-ordinates evaluated from the emission spectra recorded at 472 nm excitation for all LTT glasses confirms the suitability of these glassy materials for red emission. From the measured emission cross-sections, quantum efficiency and CIE chromaticity co-ordinates, it was found that 0.5 mol% of Tm^{3+} ions doped LTT glass (LTTTm05) is suitable for the improvement of bright visible red lasers to operate at 650 nm from these LTT glasses. The LTTTm05 glass is also equally useful to generate NIR lasers at 800 nm.