Temperature dependent luminescence in erbium-doped zinc tellurite glass: A model investigation

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Temperature quenching characteristics of infrared-to-visible frequency up-conversion (UC) in erbium doped zinc tellurite glasses under infrared excitation 797 nm are presented. A comprehensive 4-level model has been developed and the derived rate equations have been exploited to examine the thermal quenching of efficiency and emission intensity for the UC. The green ($^4S_{3/2} \rightarrow ^4I_{15/2}$) and red ($^4F_{9/2} \rightarrow ^4I_{15/2}$) emissions over a temperature range 10-340 K and at concentration 2.0 mol% have been studied. The green emission shows a continuous increase with decrease of temperature while the red emission is not that sensitive to temperature. In addition, the temperature dependence on the multi-phonon relaxation rates is fitted with 4 phonons processes. These features are attributed to the non-radiative (NR) energy transfer processes, trapped impurity effects and thermal assisted hopping. It is further indicated that to achieve higher infrared to visible up-converted efficiency in zinc tellurite glasses the NR channels for energy and charge transfer by phonon and impurity mediated process has to be minimized. Our results on pump power dependent emission intensity, quantum efficiency, luminescence intensity and NR multi-phonon relaxation rates are in conformity with other findings. The present systematic study provides useful information for further development of UC lasers.

Keywords: Quenching, Up-conversion, Luminescence, Non-radiative, Quantum efficiency, Multi-phonon relaxation

1 Introduction

In the new millennium, there has been a renaissance to study the rare-earth (RE) doped glass materials for photonic applications, e.g. phosphors, display monitors, X-ray imaging, scintillators, lasers and amplifiers for fiber-optic communications1,2. The RE ions, especially erbium, have played an important role in the development of broadband erbium-doped fiber amplifiers in optical communication technology during the past few decades3. In recent years, tellurite glasses are of growing interest due to their unusual large infrared transparency, high linear and non-linear refractive indices, good thermal and mechanical stability and corrosion resistance, suitable as a matrix for active element doping, a wide transmission window, lowest cut-off phonon energy and the highest emission cross-section over the entire range of emission wavelength. These notable features make them promising candidates for photonic applications such as window materials, optical memory and UC laser4,5. Improving the UC efficiency is the key issue in tellurite glasses. The quantum efficiency, radiative transition rate and lifetimes of excited states are greatly influenced by the optical properties of the host material, ligand field, multi-phonon relaxation processes, impurities, temperature and concentration of erbium ions3,6.

Up-conversion luminescence is considered as a promising solution to obtain efficient visible lasers pumped with commercially available infrared laser diodes. Host materials for rare earth ions play an important role in obtaining high-efficient UC signals5. Their low maximum phonon energy and high refractive index also yield low NR decay rates and high radiative emission rates for the energy levels of RE ions7,8. Therefore, strong UC emission can be easily observed in erbium-doped tellurite glasses at room temperature and the mechanisms of UC have been analyzed in detail. Most of the research using RE doped binary and ternary tellurite systems focus on preparation, synthesis and characterization techniques viz. XRD, DTA, DSC, TEM, Raman, UV-VIS-NIR spectroscopy, XPS, Ellipsometry, Ultrasonic Attenuation, and Photo-acoustic method etc. to cite a few7-16. Despite of several experimental and few theoretical efforts the effect of concentration and temperature on frequency UC processes are far from being understood17,18. In the present paper,
The temperature quenching behaviour of infrared-to-visible frequency UC in erbium-doped tellurite glasses are reported, and results are analyzed systematically by appropriate rate equations.

**2 Four Level Model for the Rate Equation**

Although a full theoretical calculation of the emission processes and enhanced luminescence in erbium-doped zinc tellurite glasses is still lacking due to the formidable difficulties, a rather simplified phenomenological approach is possible. On the basis of the experimental findings, a rate equation model is proposed to explain the major features of the infrared to visible UC experiments: (i) the strong temperature dependent green emission; (ii) the enhancement of the UC efficiency for the red emission as a function of concentration; (iii) the quenching of the UC efficiency for the green emission as a function of temperature; and (iv) the role of NR multi-phonon relaxation process. These four items can be explained within an effective four-level model.

The four levels in our model are the ground state \(^4I_{15/2}\), and three excited states \(^4I_{9/2}\), \(^4F_{9/2}\) and \(^4S_{3/2}\) for red emission and \(^4I_{13/2}\), \(^4I_{9/2}\) and \(^4S_{3/2}\) for the green emission, respectively as shown in Fig. 1. The corresponding set of rate equations for photons and carriers includes amplified stimulated emission, recombination, NR energy transfer mediated by multi-phonon process and/or a charge transfer through trapping impurities. The ground state is considered as level 1 and other three excited states as level 2, 3 and 4 along increasing direction of energy axis. In particular, we assume that the two intermediate levels 2-4 are empty before the excitation occurs. This allows us to reduce the four level schemes to an effectively two level scheme. The four level schemes are shown in Fig. 2(left and right panel) for green and red emission processes, respectively.

Once the pumping starts, levels begin to be populated and two different NR recombination processes can in principle take place. The first consists in an electron relaxation from energy level 3 to level 2 with the energy given to a second electron which is also present in the same level 3 which is promoted to higher lying levels in the conduction band from which a very fast relaxation to level 4 occurs. This process involves two electrons in the same level, and therefore, the rate of the process depends quadratically through a coefficient \(Q_{A1}\) on the level population \(N_3\). Another NR mechanism involving an electron in the level 3 and a free hole in the valence band edge (level 1) can in principle occur, where the hole is sent deep in the valence band and then very rapidly relaxes again to the band edge. This process has to be proportional through a coefficient \(Q_{A2}\) to the product of the population of the emitting level 3 (\(N_3\)) and the hole concentration in the valence band edge (\(N_h\)). The hole concentration \(N_h\) equals to the total concentration of electrons in the various
excited levels, that is \( N_h = N_2 + N_3 + N_4 \). Within the four level schemes proposed, the relaxation times of electrons from levels 4 and level 2 are so fast that \( N_4 \) and \( N_2 \) are always almost empty, therefore \( N_h \approx N_3 \).

Hence, we end up with a set of four coupled rate equation that has to be integrated. Denoting \( N_i \) as the level population densities (i=1,..,4), \( \sigma_P \) is the absorption cross-section at the wavelength of the pump, \( \phi_P \) is the time dependent pumping photon flux, \( \Gamma_{ij} \) are the relaxation rates from the i to the j energy levels, \( \tau \) is the total lifetime of the emitting level \( N_3 \), \( B \) is the stimulated transition rate which implicitly contains the gain cross-section \( \sigma \), \( n_{ph} \) is the emitted photons number, \( V_a \) the optical mode volume, \( \tau_{ph} \) the photon lifetime, \( \beta \) the spontaneous emission factor and \( \tau_r \) is the radiative lifetime of \( N_3 \) and \( Q_{nr} \) is an effective NR decay coefficient equal to \( 2Q_{A1} + Q_{A2} \). It is possible to observe optical gain whenever the stimulated emission rate is greater than the NR recombination rate.

Considering the fast subsystem to be in a stationary state one can write the exciton concentration in terms of the absorption coefficient (\( \alpha \)) of photons for band-to-band transition as:

\[
n_{ex} = \alpha \phi_p \tau \quad \ldots(8)
\]

Introducing an effective cross-section of erbium excitation \( \sigma_{eff} \) allows us to write Eq. (7) in the stationary approximation as:

\[
\frac{dN_{eff}^*}{dt} = \sigma_{eff} \phi_p (N_{Er} - N_{Er}^*) - \frac{N_{Er}^*}{\tau} \quad \ldots(9)
\]

with

\[
\sigma_{eff} = \alpha Q_{ex} \tau_{ex} \quad \ldots(10)
\]

\[
\sigma_{eff} = \frac{\alpha}{N_{Er}} \quad \ldots(11)
\]

\[
\tau_{ex} = \frac{1}{Q_{ex} N_{Er}} \quad \ldots(12)
\]

Solving Eq. (9), we arrive at the expression for the time dependent population of excited carriers as:

\[
N_{Er}^*(t) = N_{Er}^* \frac{\sigma_{eff} \phi_p}{(1 + \sigma_{eff} \phi_p \tau)} \times \left[ 1 + \frac{1}{\sigma_{eff} \phi_p \tau} \exp \left\{ -\frac{t}{\tau} (1 + \sigma_{eff} \phi_p \tau) \right\} \right] \ldots(13)
\]
The luminescence intensity for UC in terms of the total radiative recombination rate ($R$) is written as:

$$I(t) = N_{Er}^* (t) R$$ \hspace{1cm} (14)

It is clear from Eq. (14) when, $\sigma_{eff} \Phi_p \rightarrow 0$ then $N_{Er}^*(t) \rightarrow 0$ as a result $I(t) \rightarrow 0$. This expression can be exploited for calculating the pump power dependence of the luminescence intensity.

Approximating the decay curves as single exponential, the effective lifetime $\tau$ can be obtained from time integrated luminescence intensity as:

$$\tau = \frac{\int I(t) dt}{\int I(t) dt}$$ \hspace{1cm} (15)

The temperature dependent relationship of emission intensity can be analyzed by considering three level system comprised of $^4I_{15/2}$ (ground state), $^4S_{3/2}$ or $^4F_{9/2}$ (excited level b) and $^4I_{13/2}$ (excited level a). The thermalization can be expressed by the following equations:

$$\frac{I_b}{I_a} = \frac{N_b}{N_a} = C_{ab} \exp \left( -\frac{E_{ab}}{k_B T} \right)$$ \hspace{1cm} (16)

with

$$C_{ab} = \frac{\Sigma_A \Psi_b h\nu_b}{\Sigma_A \Psi_a h\nu_a} \text{Constant}$$ \hspace{1cm} (17)

where $\Sigma_A$ and $\Sigma_a$ are the total spontaneous emission rates, $h\nu_b$ and $h\nu_a$ are the photon energies, $I_b$ and $I_a$ are temperature dependent integrated intensities for a given transition (red or green), and $\psi_b$ and $\psi_a$ are the degeneracies (2J+1) of the $^4S_{3/2}$ and $^4I_{13/2}$ levels, respectively. The $E_{ab}$ term is the energy gap between $^4S_{3/2}$ and $^4I_{13/2}$ levels, and $k_B$ is the Boltzmann’s constant. The temperature variation of $I_b/I_a$ is calculated over a temperature range 10-340 K. A value of the energy gap $E_{ab} = 658 \text{ cm}^{-1}$ is obtained in fitting Eq. (16) with the experimental data. This value is reasonable because in our calculation we neglect the Stoke’s shifts caused by the temperature.

The fact that the population at the excited level is proportional to the emission intensity implies:

$$N_a + N_b = N_{Er}^*$$ \hspace{1cm} (18)

$$N_a = \frac{N_{Er}^*}{[1 + C_{ab} \exp(-E_{ab}/k_B T)]}$$ \hspace{1cm} (19)

It is the exponential factor that plays the dominant role in deciding the temperature dependence of the luminescence intensity.

3 Results and Discussion

Solving the rate equations of four levels model one gets the emitted photon numbers. Using Eqs (13) and (14), the pump power dependence of luminescence intensity is calculated as shown in Fig. 3 that demonstrates a strong correlation between erbium and exciton photoluminescence. We take NR lifetime of 20 ns, gain cross-section of $1.2 \times 10^{-17} \text{ cm}^2$, density of Er$^{3+}$6×10$^{19}$ cm$^{-3}$, pumping photon flux of 10$^{18}$ photons/(s cm$^2$), $\tau = 3.86 \text{ ms}$, stimulated emission cross-sections $\sim 9.0 \times 10^{-21} \text{ cm}^2$ phonon energy of the host glass$^{19,20,23}$ as 760 cm$^{-1}$ and 2.0 mol% Er$^{3+}$ at 300 K. Fortran program is used to solve the equations numerically.

At low pumping intensity the lifetime of exciton is determined mainly by the NR process assisted by Er excitation (Fig. 3). It should also be noted that with an increasing pump power, i.e. the amount of excited erbium, effective cross-section will increase. This result is determined by the fact that the band-to-band absorption coefficient is an intrinsic property of the host matrix and does not depend on the concentration of erbium dopant (as is the case for excitation of erbium in dielectric matrices). Quite naturally, under these conditions the probability to excite a single ion increases when the total number of excitable ions decreases at a given photon flux. There are many NR processes that control the lifetime as a result the effective cross-section is less as compared to pure radiative case.

![Fig. 3 — Pump power excitation dependent intensity of the up-converted red and green emission from Er$^{3+}$ for a 2.0 mol % Er$^{3+}$ at $T = 300 \text{ K}$](image-url)
For rare earth doped glass, a relationship exists between the NR decay rate and the total relaxation rate. Taking all possible NR mechanism into account, we can write the total decay rate as:

\[
\frac{1}{\tau} = \frac{1}{\tau_{\text{r}}} + \frac{1}{\tau_{\text{nr}}} = R_{\text{r}} + R_{\text{nr}}
\]

\[= R_{\text{r}} + (R_{\text{p}} + R_{\text{r}} + R_{\text{Er}} + R_{\text{OH}} + R_{\text{met}}) \quad \ldots(21)
\]

In Eq. (21) \(R_{\text{nr}}\) is the total rate of NR decay including multi-phonon relaxation rate \(R_{\text{p}}\), thermal quenching rate \(R_{\text{r}}\), self-quenching rate \(R_{\text{Er}}\) of Er\(^{3+}\), relaxation rate \(R_{\text{OH}}\) induced by hydroxyl groups and relaxation rate \(R_{\text{met}}\) induced by certain transition metal ions and other rare earth ions.\(^{22}\) For simplicity, last two terms are ignored here as they do not play dominant role as far as the temperature quenching of UC is concerned. Self-quenching rate \(R_{\text{Er}}\) results from the resonant energy exchange between a pair of Er\(^{3+}\) ions. This energy exchange can occur by two mechanisms. One is UC process in which two neighbouring ions pull energy to one, as a result one comes back to the ground state by NR decay and the other ion excited to a higher energy level, returns to the ground state by UC emission. The other is the hopping mechanism, which involves the migration of the excitation energy from one ion to the next. In short, self-quenching rate depends greatly on the concentration of Er\(^{3+}\). The resonant energy transfer model provides the energy transfer rate by dipole-dipole mechanism that can be incorporated in our model.\(^{23}\)

The temperature dependence of the UC intensity for both \(^{4}\text{S}_{3/2} \rightarrow ^{4}\text{I}_{15/2}\) and \(^{4}\text{F}_{9/2} \rightarrow ^{4}\text{I}_{15/2}\) emissions is calculated and shown in Fig. 4. The intensity of the \(^{4}\text{S}_{3/2} \rightarrow ^{4}\text{I}_{15/2}\) transition decreases as the temperature increases from 100 to 340 K. The red emission \(^{4}\text{F}_{9/2} \rightarrow ^{4}\text{I}_{15/2}\), however, does not show a significant thermal quenching in the temperature range 10-340 K studied. This behaviour can be understood possibly due to large activation energy for the \(^{4}\text{F}_{9/2}\) level. Theoretically, this quenching has usually been analyzed by taking into account the multi-phonon relaxation process\(^{20}\). Accordingly, the fact that the red up-converted line quenches smoothly compared with the green emission \(^{4}\text{S}_{3/2} \rightarrow ^{4}\text{I}_{15/2}\) which means that the multi-phonon relaxation channel mainly affects the emitting level \(^{4}\text{S}_{3/2}\). On the other hand, the reason for saturation phenomena at low temperature may be attributed due to the \(\exp(-E_g/k_B T)\) factor when the temperature is low enough this factor goes to zero.

Assuming that the thermal quenching of UC is induced only by the multi-phonon relaxation process, the decay rate can be expressed as the sum of the radiative and multi-phonon relaxation rates \(R_{\text{r}}\) and \(R_{\text{p}}\), respectively and is given by, \(R = R_{\text{r}} + R_{\text{p}}\). The multi-phonon relaxation rate can be found out by using Bose-Einstein statistics as:

\[
R_{\text{p}}(T) = C_p \exp(-\gamma \Delta E) \left[1 - \exp\left(-\frac{\hbar \omega}{k_B T}\right)\right]^p \quad \ldots(22)
\]

\[
R_{\text{p}}(T) = C_p \exp(-\gamma \Delta E) \left[1 - \exp\left(-\frac{\hbar \omega}{k_B T}\right)\right]^{-\Delta E/\hbar \omega_{\text{max}}} \quad \ldots(23)
\]

where \(C_p\) and \(\gamma\) are NR parameters which depend on the host material, \(\Delta E\) represents the energy gap between two successive levels (e.g., \(^{4}\text{I}_{13/2}\) and \(^{4}\text{I}_{15/2}\)) and \(p = \Delta E/\hbar \omega\) is the number of phonons emitted in the relaxation process. The parameter \(\gamma\) represents a constant related to the electron-phonon coupling constant. In the case of the \(^{4}\text{S}_{3/2} \rightarrow ^{4}\text{I}_{15/2}\) transition we have chosen \(\Delta E = 3000 \text{ cm}^{-1}\), \(C_p = 7.48 \times 10^9 \text{ s}^{-1}\), \(\gamma = 4.7 \times 10^{-3} \text{ cm}\), and \(\hbar \omega = 750 \text{ cm}^{-1}\). The best fit with the experimental data is obtained when the multi-phonon relaxation rates are considered as 4-phonon relaxation process of the 750 cm\(^{-1}\) frequency vibration.\(^{12}\) This vibration is associated with the stretching vibrations of TeO\(_4\) and TeO\(_3\) groups. The temperature dependence of multi-phonon relaxation rates is investigated by using Eq. (23) and is shown in Fig. 5. It is observed that the multi-phonon relaxation rate increases rather slowly in the temperature region 20-150 K due to the spontaneous emission of phonons. At temperatures higher than 150 K, it increases because of the stimulated emission of the thermally activated phonons.
Considering $R_t$ and $R_{Er}$ as the decay rate describing processes, other than the radiative and the multi-phonon relaxation mechanisms, which could be at the origin of the thermal quenching of UC and quenching of Er$^{3+}$ ion. To express the rate $R_t$ and $R_{Er}$ we have adopted the experimental law obtained from the variation of the PL intensity versus temperature$^{21-24}$:

$$R_t = C_T \exp \left( -\frac{E_t}{k_BT} \right) \quad \ldots(24)$$

$$R_{Er} = C_{Er} \exp \left( -\frac{E_{Er}}{k_BT} \right) \quad \ldots(25)$$

where $E_t$ and $E_{Er}$ represent the activation energies and $C_T$ and $C_{Er}$ are constants, treated as a fitting parameters. Here, we assumed the weak Arrhenius dependence in describing the rate processes$^2$. Using the latter expressions for $R_t$ and $R_{Er}$ the quantum efficiency of UC is given by:

$$\eta = \frac{R_t}{R_t + R_F + R_t + R_{Er}}$$

$$= \frac{1}{1 + (R_F / R_t) + \exp(-E_t / k_BT)C_T / R_t + \exp(-E_{Er} / k_BT)C_{Er} / R_t} \quad \ldots(26)$$

The computed temperature dependent quantum efficiency $\eta$ from Eq. (26) for both red and green emission are shown in Fig. 6. The numerical results are obtained by taking, $R_t = 3528 \text{ s}^{-1}$, $C_T = 1.3 \times 10^3 \text{ s}^{-1}$ and $E_t \sim 59 \text{ meV}$. It is found that the efficiency for the red emission is higher than the green emission$^{6,11,9}$. This is due to more NR processes are involved in the green UC than the red one.

The results for temperature dependent efficiency are in good agreement with earlier observations$^{23}$. 

Theoretical analysis is well consistent with experimental data. Temperature dependence of the multi-phonon relaxation rates is well fitted with 4-phonons processes. It is hoped that our rate equations may provide useful information for exploiting RE doped tellurite glasses in fabricating UC lasers. In addition, this model can be extended to examine the temporal behaviour of UC emission and Stokes emission for red and green transition. A complete microscopic model, however, requires the incorporation of the local bonding environment and

4 Conclusions

The present work aims in answering in a systematic way the temperature quenching characteristics of infrared-to-visible frequency UC in erbium-doped zinc tellurite glasses excited by laser radiation at 797 nm by developing a model. The rate equations are derived using both 4 level and equivalent 2 level schemes and the results on pump power dependent emission intensity, temperature dependent quantum efficiency, multi-phonon relaxation rate and PL intensity are presented over a temperature range of 10-340 K at fixed concentration 2.0 mol%. It is observed that the thermal quenching of the green emission is large compared with those of the red transition. The thermal quenching is analyzed in terms of multi-phonon relaxation by adding other NR transition rate to the total relaxation rate. It is, further, attributed that the origin of these NR rates could be presumably due to an energy transfer from Er$^{3+}$ ions to energy sinks or a charge transfer through trapping impurities. Our model is quite general and can be applied to investigate the temperature and concentration dependent quenching effects in other families of Er$^{3+}$ doped tellurite glasses. It is, further, demonstrated that the NR channels for energy and charge transfer by phonon and impurity mediated process play crucial role in controlling UC efficiency. The theoretical analysis is well consistent with experimental data.
the local vibrational density of states of the rare earth ion within the matrix because some of these vibrational modes may or may not be coupled to electronic excited states.

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