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Abstract

Fluorescence spectra and decay curves for the $^5D_4 \rightarrow {}^7F_5$ transition of Tb³⁺ ions in 59TeO$_2$–20ZnO–20LiF–1Tb$_4$O$_7$ (TZLFTb) glass have been measured and analysed as a function of pressure up to 14.9 GPa at room temperature. In this pressure range, the red shift for the band positions of $^5D_4 \rightarrow {}^7F_3$, $^7F_4$ and $^7F_5$ is found to be 3.2, 3.2 and 2.2 cm^{-1} GPa^{-1}, respectively, which could be attributed to an expansion of the 4f electron wavefunctions with increasing covalency. There is also a considerable pressure effect on the magnitude of the crystal-field splittings observed in the $^7F_4$ and $^7F_5$ transitions, which increases with pressure because of Coulomb interactions between the 4f electrons and their ligands. In addition, the decay curve is found to be perfectly single exponential at ambient pressure, and turns into a non-exponential with increasing pressure. The non-exponential decay curves at higher pressures are well fitted to the Inokuti–Hirayama model for $S = 6$, which indicates that the energy transfer between the donor and acceptor is of dipole–dipole nature. The decrease in the lifetime with increasing pressure is caused by an increase in the electronic transition probabilities, which is a result of the enhanced crystal-field strength around the Tb³⁺ ions. The results obtained after release of pressure show that local environment changes of the Tb³⁺ ions are reversible.

1. Introduction

Lanthanide (Ln) doped tellurite glasses have been the subject of recent investigations as novel materials for potential applications in photonics. These glasses have good optical quality and

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are stable against atmospheric moisture [1]. They have a wider transmission range (0.35–5 μm) compared to silicate glasses, good glass stability and corrosion resistance superior to fluoride glasses [2]. In addition, they exhibit the lowest average vibrational energy (about 780 cm^{-1}) among oxide glass formers and a low process temperature [1, 3]. Tellurite glasses possess a high refractive index ($\sim$2.0) which increases the local field correction at the doped Ln ion site leading to an enhancement of the radiative decay compared to silicate glasses and lowering thereby the non-radiative relaxation rates of the Ln ion excited states. Moreover, tellurite glasses have a high non-linear refractive index enabling applications for second harmonic generation [3, 4]. Lanthanide ions exhibit high solubility in these materials, allowing the incorporation of high concentrations; moreover, these glasses are non-hygroscopic as well as highly stable against crystallization [1]. Because of the above merits, tellurite based glasses have the potential as optical amplifiers for second and third telecommunication windows at 1.3 and 1.5 μm, respectively, frequency up-converters, colour displays, high density optical data reading and storage, biomedical diagnostics, infrared laser viewers and indicators [1–6].

Glasses doped with trivalent terbium (Tb^{3+}) ion have been used as optical devices in the blue and green regions and often used as phosphors in fluorescent lamps, projection television tubes and x-ray intensifying screens. They show prominent slow rise and afterglow components of luminescence after turning on and off the ultraviolet light excitation in the intrinsic absorption region of the glass host [7, 8].

Generally, the luminescence spectrum of Tb^{3+} is very complicated compared with that of Eu^{3+}. The electronic configuration of the Tb^{3+} ion is $4f^8$. Its emission mainly originates from $^5D_4$ and $^5D_3$ to ^7F_J ($J = 6, 5, 4, 3, 2, 1, 0$) levels [7–9]. Tb^{3+} ions offer a convenient means of understanding the nature of metal coordination in various systems. As a result of well isolated ^7F_J multiplet states and the large energy gap between these states and the emitting level, the luminescence property of Tb^{3+} has been proven to be useful in characterizing the energy level structure and optical transmission process.

Pressure changes the optical properties of lanthanide ions in two significant ways.

 (i) Decreases of the lanthanide free-ion atomic parameters shift emission bands to longer wavelength. This is correlated with an expansion of the 4f-electron wavefunctions with increasing covalency.

 (ii) The Stark splittings of the multiplets increase, which is reflected by an increase in the splittings of the emission bands with pressure. This is related to an enhancement of the crystal-field interactions of the lanthanide 4f electrons and is ascribed to a change in the sum of various interactions such as covalency, overlap and Coulomb interactions between the 4f electrons and their ligands.

These factors can be tuned by changing the distances and bond angles between the Ln ion and ligands under pressure [10–12]. Also, a decrease in the matrix volume with pressure changes the distances among ions in the matrix and plays an important role in the energy transfer processes as well as in the quenching of lifetimes of fluorescent levels of Ln ions. Hence, it is interesting to investigate the luminescence properties of Tb^{3+} doped tellurite glass under pressure. This work presents the results of fluorescence spectra of $^5D_4 \rightarrow {}^7F_J$ ($J = 3, 4$ and 5) transitions and lifetime measurements of the $^5D_4$ level of Tb^{3+} in a tellurite glass under pressure up to 14.9 GPa. We also study the effects of the release of pressure on these properties by releasing the pressure down to 8.6 and 0.6 GPa. To the best of our knowledge this is the first high-pressure study of a Tb:glass system.

2. Experimental details

Tb^{3+} doped tellurite glass with the composition (in mol%) of 59TeO$_2$–20ZnO–20LiF–1Tb$_4$O$_7$ (TZLFTb) was prepared by a melt quenching technique. About 5 g of the batch composition was thoroughly crushed in an agate mortar and the homogeneous mixture was heated in a platinum crucible in an electronic furnace for 45 min at a temperature of 850 °C. The melt was poured onto a preheated brass mould at a temperature of 275 °C and annealed at this temperature for about 5 h to remove thermal strains. Then the sample was allowed to cool to room temperature and polished for the purpose of optical measurements.

The 488 nm line of an Ar$^+$ laser was used as an excitation source. The emission spectra were recorded with a double monochromator equipped with a photomultiplier. The resolution of the double monochromator depends on the wavelength and the slit width, and was typically set at 2.0 cm^{-1}. A special miniature diamond anvil cell (DAC) was used to generate pressures up to 15 GPa at room temperature. A piece of TZLFTb glass was placed together with a ruby pressure sensor into an 80 μm diameter hole of a stainless steel (INCONEL X750) gasket of 200 μm thickness. A mixture of methanol:ethanol:water (16:3:1) was used as the pressure transmitting medium. This gasket with the sample and pressure transmitting fluid was then compressed by the two opposed anvils of the DAC. The pressure and the hydrostatic conditions experienced by the sample were determined by the shift and broadening of the ruby R$_1$ lines [13]. A mechanical chopper in connection with a multi-channel scalar allowed for lifetime measurement in the range from 2 μs to 2 s.

3. Theory

At very low concentrations of dopants, where the interactions between the optically active ions are negligible, the decay curve of the fluorescence can be fitted to a single exponential, and the lifetime can be calculated directly. At higher concentrations, interactions between optically active ions and energy transfer processes between different lanthanide donor (excited state) and acceptor (ground state) ions have to be taken into account. In this case, the fluorescence decay, which is proportional to the probability that a donor is still excited after pulsed excitation $t = 0$, is given by

$$I(t) = I(0) \exp\left(-\frac{t}{\tau}\right) \prod_{K=1}^{N_A} \exp\{-t W_{DA}(R_K)\} \tag{1}$$

where τ is the intrinsic lifetime (radiative and non-radiative), N_A is the number of acceptors, and $W_{DA}(R_K)$ is the energy transfer probability between a donor and an acceptor separated by a distance R_K. Equation (1) describes donor decay modes which include intrinsic de-excitation (characterized by τ) and energy transfer processes to acceptors.

For a multipolar interaction between donors and acceptors, the energy transfer probability is given by [14]

$$W_{DA}(R_K) = \frac{C_{DA}^{(S)}}{R_K^S} \tag{2}$$

where $S = 6, 8$ or 10 depending on whether the dominant mechanism of the interaction is dipole–dipole, dipole–quadrupole or quadrupole–quadrupole, respectively, and the process is characterized by the microscopic parameter $C_{DA}^{(S)}$.

For the case of a small number of excited ions compared to the total number of active ions, equation (1) has been modified by Inokuti and Hirayama [14] who obtained the following
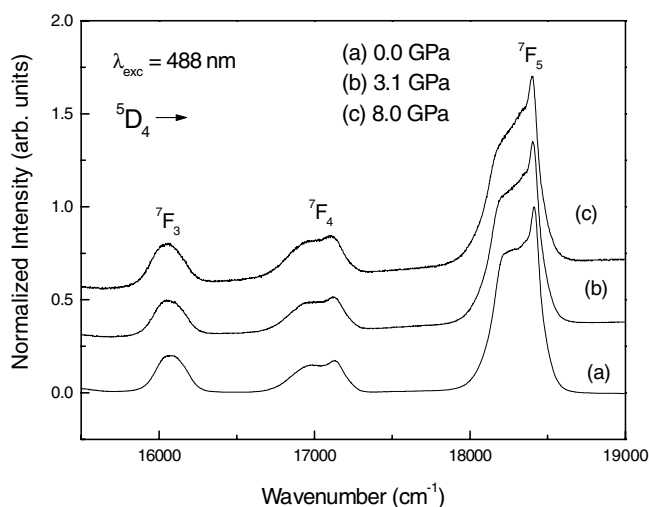
Figure 1. Emission spectra of TZLFTb glass under pressure ($\lambda_{\text{exc}} = 488$ nm) at room temperature. The spectra are normalized to the $^5D_4 \rightarrow {}^7F_5$ transition.

equation (3) which is widely referred to as the IH model:

$$I(t) = I(0) \exp\left\{-\frac{t}{\tau} - Qt^{3/S}\right\} \tag{3}$$

where Q is the energy transfer parameter and is given by

$$Q = \frac{4\pi}{3}C_A\Gamma\left(1 - \frac{3}{S}\right)(C_{\text{DA}}^{(S)})^{3/S}. \tag{4}$$

Here, C_A is the concentration of acceptors, and $\Gamma(x)$ is the gamma function, which is equal to 1.77 in the case of dipole–dipole interactions ($S = 6$), 1.43 for dipole–quadrupole interactions ($S = 8$) and 1.3 for quadrupole–quadrupole interactions ($S = 10$).

In this IH model, equation (3), a decrease in the distance between donor and acceptor ions (due to either an increase in the pressure or in the doping concentration) causes an increase in the Q parameter, leading to faster fluorescence decays. Moreover, equation (3) is valid for the special case of pulsed excitation and a random distribution of optically active ions (donors and acceptors) in the sample. This is due to the fact that during the pulsed excitation (in the order of a nanosecond) there is not enough time for the donors to transfer the excitation energy to other ions (donors and acceptors).

4. Results and discussion

Figure 1 shows the emission spectra of TZLFTb glass, obtained at an excitation of 488 nm, into the $^5D_4$ level of Tb^{3+} at three different pressures of 0, 3.1 and 8.0 GPa at room temperature in the energy range of 15 500–19 000 cm^{-1}. The spectra consist of three dominant bands, which correspond to $^5D_4 \rightarrow {}^7F_J$ ($J = 3, 4$ and 5) transitions (the labelling is shown in the figure). Stark effects of crystal-fields (CFs) from the surroundings of the Tb^{3+} ions split the $^5D_4 \rightarrow {}^7F_4$ and $^7F_5$ transitions into two components. With increasing pressure, the emission band positions shift towards lower energies (red shift). Emission band positions of the $^5D_4 \rightarrow {}^7F_J$ ($J = 3, 4$ and 5) levels are given in table 1 for various pressures. The energy positions of the emission

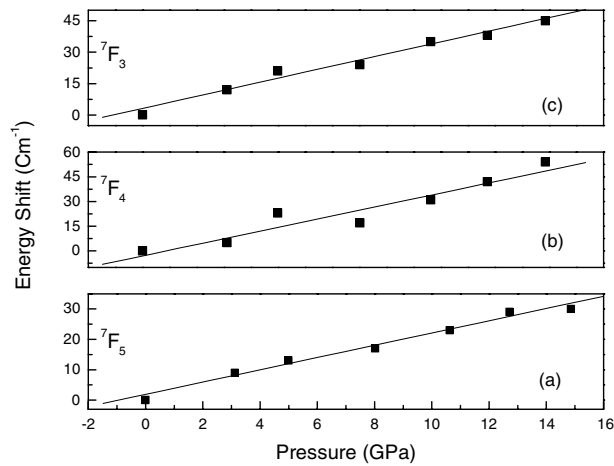**Figure 2.** Energy shifts of the $^5D_4 \to {}^7F_3$, $^7F_4$ and $^7F_5$ bands of Tb³⁺ in TZLFTb glass at different pressures. The points are experimental data (decreasing pressures were not included) and the solid line indicates the fit to a linear equation.

Table 1. Lifetimes of the $^5D_4$ level, energy transfer parameter (Q), emission band positions for the transitions of $^5D_4 \to {}^7F_5$, $^7F_4$ and $^7F_3$ and CF splittings for the transitions of $^5D_4 \to {}^7F_5$ and $^7F_4$ for the TZLFTb glass at various pressures.

Pressure (GPa)	Lifetime (μs)	Transfer parameter (Q)	Energy positions (cm⁻¹)			CF splittings (cm⁻¹)	
			$^7F_5$	$^7F_4$	$^7F_3$	$^7F_5$	$^7F_4$
0.0	1053	0.02	18 417	17 147	16 077	188	158
0.6[a]	959	0.33	18 419	17 139	16 077	196	174
3.1	872	0.54	18 408	17 142	16 065	206	190
5.0	706	1.22	18 404	17 124	16 056	216	198
8.0	551	1.70	18 399	17 130	16 053	228	214
8.6[a]	412	2.61	18 397	17 117	16 047	236	210
10.6	395	2.62	18 394	17 116	16 042	244	220
12.7	384	3.37	18 388	17 105	16 039	248	226
14.9	326	4.02	18 387	17 093	16 032	252	230

[a] Releasing pressure.

bands are taken as peak position (peak maximum) of the bands. Figure 2 shows the pressure dependence of the shifts of the Tb³⁺ emission lines of the $^5D_4 \to {}^7F_3$, $^7F_4$ and $^7F_5$, where the points are experimental data and solid line is the best fit to a linear relation:

$$E_i(p) = E_i(0) + \alpha_i p \qquad \text{(with } p \text{ in GPa)},$$

where 'i' labels one of the three observed transitions. The $E_i(0)$ values correspond to the values at 0.0 GPa and the coefficients α_i are determined from the fits as follows:

$$\alpha(^7F_3) = -3.2 \text{ cm}^{-1} \text{ GPa}^{-1}$$
$$\alpha(^7F_4) = -3.2 \text{ cm}^{-1} \text{ GPa}^{-1}$$
$$\alpha(^7F_5) = -2.2 \text{ cm}^{-1} \text{ GPa}^{-1}.$$

The shift of each J-manifold with pressure results from the variation of the spin–orbit coupling constant, ξ_{4f}, due to changes in the overlap of the ligand orbitals with the 4f wavefunctions of the Tb³⁺ ion [15].
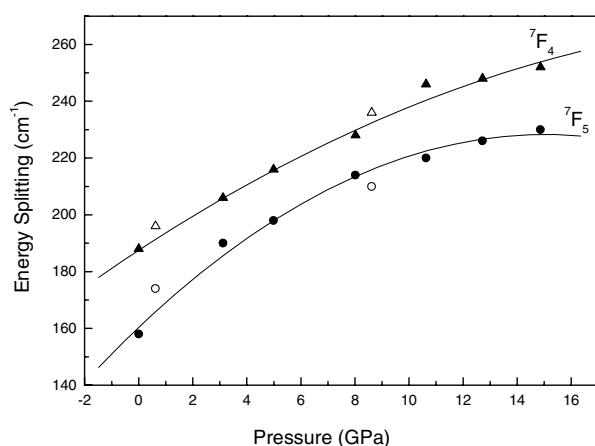
Figure 3. Energy splitting of the $^5D_4 \rightarrow {}^7F_4$ and $^7F_5$ transitions of Tb^{3+} in TZLFTb glass versus pressure. The solid points indicate increase of pressure while the open points correspond to release of pressure. The solid curves are drawn as a guide to the eye.
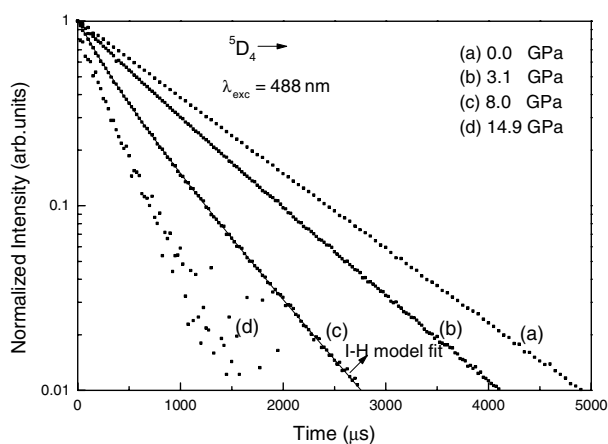

Figure 4. Decay profiles of the $^5D_4$ level in TZLFTb glass at various pressures. A fit with the IH model ($S = 6$) is included for the decay curve at 8.0 GPa (solid line).

The CF splittings of the transitions are well resolved even at high pressure. The magnitude of the splitting increases with pressure for the $^7F_4$ and $^7F_5$ transitions, by an initial slope of $\sim$4.8 and 4.3 cm^{-1} GPa^{-1}, respectively. The values of the CF splittings for the $^7F_4$ and $^7F_5$ levels at different pressures are presented in table 1 and in figure 3, demonstrating the variation of CF splittings with pressure arising from the variation in strength and symmetry of the CF around the Tb^{3+} ion.

The fluorescence decay of the $^5D_4 \rightarrow {}^7F_5$ transition in TZLFTb glass has been also measured up to 14.9 GPa. Figure 4 shows the decay profiles at different pressures. The decay profiles up to 5.0 GPa are nearly single exponential and the curves for pressures greater than 5.0 GPa are found to be non-exponential. Table 1 presents the lifetimes of the $^5D_4$ level in TZLFTb glass at different pressures. The lifetimes for both exponential and non-exponential decay curves are obtained by taking the first e-folding time of the decay curve; for details see [16, 17]. The decay curve at ambient condition is found to be perfectly single exponential,

with a lifetime (τ) of 1053 μs. The decay of the $^5D_4$ level is purely radiative, as there is a large energy gap of around 15 000 cm^{-1} between $^5D_4$ and the next lower level $^7F_0$, indicating that the quantum efficiency for the $^5D_4$ level is almost unity. From figure 4 it is clear that the lifetime decreases and the decay curves become non-exponential as the pressure increases. The quenching of lifetime and the onset of a non-exponential behaviour for the decay curves at higher pressures is attributed to the gradual increase in energy transfer processes, probably caused by pressure induced defect centres. Such processes are reviewed in detail by one of the present authors [12].

From table 1, one observes that the lifetimes decrease with increasing pressure by a factor of 3.25 in the pressure range 0–14.9 GPa. In particular, the lifetimes decrease rapidly from 0 to 8.6 GPa and thereafter the decrease is smaller. Variations of τ with pressure may be well expressed by the equation

$$\tau \ (\mu s) = 1069.3 - 83.2p + 2.2p^2 \qquad \text{(with } p \text{ in GPa).}$$

In general, either increase of the multiphonon de-excitation probability or increase of the electronic transition probability can explain the observed decrease of lifetimes under pressure. The latter effect could be explained by the gradual increase in CF strengths around the Tb^{3+} ions with pressure. This results in an enhanced mixing of opposite parity configurations with the 4f^8 configuration, due to the odd-parity CF Hamiltonians, leading to an increase in the transition probabilities. This type of behaviour has been noticed in the case of Sm^{3+} and other Ln^{3+} ions in crystalline solids [18]. The second one involves the enhancement of electron–phonon coupling with pressure leading to an increased non-radiative relaxation as observed for the $^5D_0$ level of Eu^{3+} in Na silicate glasses by Lochhead and Bray [19]. However, Lavin *et al* [18] have clearly shown that drastic change in the multiphonon relaxation cannot be responsible for the observed lifetime decrease in glasses under pressure.

Hence, the only mechanism which could successfully explain the observed decrease in lifetime with pressure in the present TZLFTb glass is an increase in electronic transition probabilities. This is caused by the enhanced configuration interactions due to the stronger CFs at higher pressures. The increase in pressure, which can modify the bond angles and lengths, causes a gradual increase in the CF strengths around the Tb^{3+} ion. This is clearly evident from the curves of the $^5D_4 \to {}^7F_5$ and $^5D_4 \to {}^7F_4$ level splittings versus pressure shown in figure 3. Therefore, the increase in configuration interactions under pressure, which in turn increases electronic transition probabilities, can explain the decreasing lifetimes in the TZLFTb glass. Lavin *et al* [18] used similar arguments to account for the decrease in lifetime with pressure in Sm^{3+}:lithium fluoroborate glass.

The non-exponential nature of the decay curves at higher pressures is fitted to the IH model, equation (3), to unravel the nature of the interactions responsible for the energy transfer. The fit with $S = 6$ shown as example for the 8.0 GPa in figure 4 is better than for $S = 8$ and 10, indicating that the interaction for energy transfer is of dipole–dipole type. Using the above equation, the energy transfer parameter (Q) has been evaluated at various pressures and the values are presented in table 1. The ambient pressure lifetime ($\tau = 1053 \ \mu$s), which represents the lifetime of the isolated donors in the absence of energy transfer (with negligible value of $Q = 0.02 \ S^{-1/2}$, table 1), has been used while fitting the Q values in equation (3), for all pressures of the present study. The value of Q increases with pressure, as shown in figure 5, along with the pressure dependence of the lifetime.

The increase of Q value with pressure observed in figure 5 is an indication for the increase of energy transfer between the Tb^{3+} ions and hence results in a non-exponential nature for the decay curves. But the detailed mechanism of energy transfer in the present case of TZLFTb glass with 488 nm excitation (into the $^5D_4$ level) is not clear. This is because there is neither

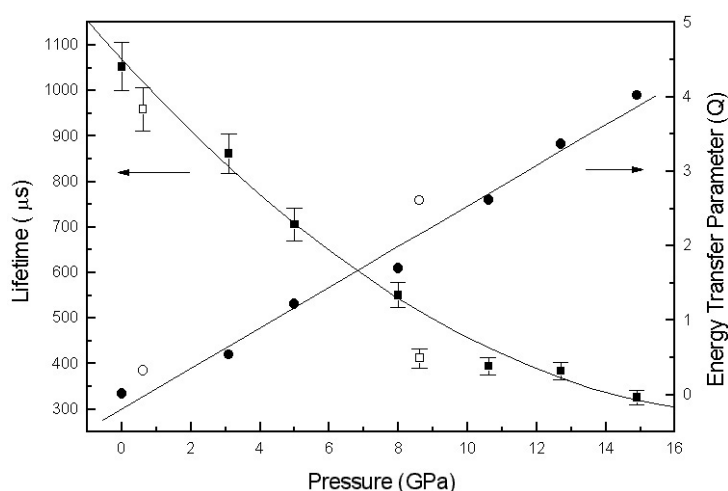**Figure 5.** Variation of lifetimes and energy transfer parameter (Q) with pressure. The solid points correspond to increase of pressure while the open points indicate release of pressure. The solid lines are drawn as a guide to the eye.

an energy level matching for cross-relaxation nor a suitable energy gap to the lower level that can influence multiphonon relaxation. On the other hand, in the case of Tb^{3+}:fluorophosphate glass, Duhamel-Henry *et al* [20] fitted the non-exponential decay curves of the $^5D_3$ level to the IH model and obtained good fits for $S = 6$, indicating that the cross-relaxation process between the levels $^5D_3 \rightarrow {}^5D_4$ and $^7F_6 \rightarrow {}^7F_0$, which provide a good energy matching, is responsible for the energy transfer and is mainly governed by dipole–dipole interaction.

As can be seen from figure 5, the change of the transfer parameter Q with pressure is opposite to that of the lifetime. Since the non-exponential nature for the decay curves is well seen for pressures at and above 5.0 GPa, the values obtained for Q from the fits are reliable for this pressure range. This observation could be explained by the increase of the effective density of donors and acceptors with the reduction of matrix volume under pressure and the change in the transition probabilities [18]. But Duhamel-Henry *et al* [20] observed that in a Tb^{3+}:fluorophosphate glass the $^5D_4$ decays are perfectly single exponential and independent of the concentration of Tb^{3+} ions. Further, they noted that the $^5D_4$ lifetime quenching starts beyond the Tb^{3+} concentration of 20 mol%. Since the above authors worked on glasses of different compositions, their conclusions are not fully transferable to the present material, as the nature of the energy acceptors could be different. Hence, in the case of TZLFTb glass, we believe that the pressure induced increase in effective density of donors and acceptors is only partly responsible for the onset of non-exponential nature for the decay curves above 5.0 GPa. However, this will not affect the lifetimes of the $^5D_4$ level, as they are extracted, both for exponential and non-exponential decay curves, by taking the first e-folding time of the decay curves. The other possibility, which could easily explain both the observed pressure dependence of the lifetime and the transfer parameter, is the increase in transition probability arising from the increased CF strength around the Tb^{3+} ions. These explanations are in agreement with the results obtained in the present work.

The luminescence properties of TZLFTb glass have also been measured while releasing the pressure to two different pressures of 8.6 and 0.6 GPa. It is interesting to note that the properties measured in this case follow the same trend as an increase of pressure, as can be seen from figures 3 and 5. This implies that the pressure induced structural changes around the

Tb^{3+} ions are reversible; i.e., no hysteresis is observed, similar to the situation for crystalline SrFCl:Sm^{2+} [21].

5. Conclusions

Luminescence studies of Tb^{3+}-doped tellurite glass have been performed under pressures up to 14.9 GPa at room temperature. The red shift observed for the emission band positions with increasing pressure is attributed to the variations of the spin–orbit coupling constant. The continuous increase in the magnitude of splittings observed for the $^7F_4$ and $^7F_5$ levels with pressure arises from the variations in the strength and symmetry of the CF around the Tb^{3+} ion. The decay curve of the $^5D_4$ level at ambient pressure is perfectly single exponential. With increase in pressure, the decay curves tend to exhibit a non-exponential behaviour and to become prominently non-exponential at pressures above 5 GPa. The non-exponential decay curves are best fitted to the IH model with $S = 6$, indicating that the interaction for energy transfer is most probably dipole–dipole type. The linear increase of the energy transfer parameter Q suggests an enhancement of the energy transfer processes at higher pressures. The quenching of the lifetime of the $^5D_4$ level with increase in pressure can be explained by an increase in the electronic transition probabilities arising from the gradual increase in the CF strengths around the Tb^{3+} ions with pressure. The luminescence properties measured at decreasing pressures show that no significant structural hysteresis is observable in the glass matrix.

Acknowledgments

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