Pressure dependent luminescence properties of Eu$^{3+}$:TeO$_2$-K$_2$O-Nb$_2$O$_5$ glass

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Abstract. Eu$^{3+}$-doped tellurite glass of molar composition: TeO$_2$ + K$_2$O + Nb$_2$O$_5$ + Eu$_2$O$_3$ (TKN1Eu) has been prepared by quenching the oxidic melts. The emission spectra and the decay curves for the $^5D_0$ level of Eu$^{3+}$ ions in TKN1Eu glass have been measured and analyzed as a function of pressure up to 14.8 GPa at room temperature. In this pressure range, the observed red shifts for the band positions of $^5D_0 \rightarrow ^7F_{0,1,2}$ could be attributed to an expansion of the 4f electron wave functions with increasing covalency. There is also a considerable pressure effect on the magnitude of crystal-field (CF) splitting in the $^5D_0 \rightarrow ^7F_1$ band, which increases with pressure. Stark components of the $^7F_1$ level have been used to evaluate the CF parameters, $B_{20}$ and $B_{22}$, which are in turn used to calculate the CF strength experienced by the Eu$^{3+}$ ions in the TKN1Eu glass. The CF strength increases from 1062 to 1358 cm$^{-1}$ from the ambient pressure to 14.8 GPa. Lifetime for the $^5D_0$ level of Eu$^{3+}$ is found to decrease from 0.76 ms (0 GPa) to 0.30 ms (14.8 GPa) with increase in pressure. The results of pressure induced energy shifts, CF strengths and lifetimes are well discussed both for increasing as well as decreasing pressures and are compared with those of Eu$^{3+}$:phosphate and lithium borate glasses.

1. Introduction
Research on glasses containing heavy network formers, such as TeO$_2$, have acquired considerable attention when doped with luminescent lanthanide (Ln) ions [1, 2], due to their low vibrational frequencies that leads to a reduction of the multiphonon deexcitation and improve cross-sections and quantum efficiency of these ions. In addition, tellurium oxide based glasses have been extensively investigated because of their interesting physical properties such as large infrared transparency, high linear and non-linear refractive indices, good thermal stability and corrosion resistance and suitability as a matrix for active element doping, represent the main justification for their continuous technological interest [3]. On the other hand, niobium containing glasses have several interesting non-linear refractive index $n_2$, which make them attractive materials for ultra-fast switching devices [4, 5].

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Moreover, second harmonic generation (SHG) was observed in borophosphate glasses containing Nb$_2$O$_5$ after a thermal poling treatment [6].

The development of optical and opto-electronic devices like optical sensors, phosphors, and optical data storage devices require a systematic knowledge of bonding environment of Ln$^{3+}$ ions and their luminescence properties. Inter-atomic distance can be reduced continuously by applying high pressure and therefore increases the overlap among the adjacent electronic orbitals and the crystal-field (CF) strength, without changing the other physical properties like the point group symmetry of the Ln$^{3+}$ ion site or the chemical composition. Different effects occur on different luminescent centers with the decrease in the effective volume of the Ln$^{3+}$ ion containing matrix with high pressure. Thus, a pressure dependent luminescence study provides sufficient information on the electronic states, the CF strength, the energy transfers and the interaction between luminescence centers and their hosts [7].

Ln-doped glasses containing empty d shell transition metal ions could be interesting to develop new materials in which emission in the visible and infrared regions and optical amplification or self frequency sum mixing processes are simultaneously achieved [8]. Eu$^{3+}$ ions doped glasses are of special interest because of the following reasons: (1) persistent spectral hole burning can be performed in the $^7F_0 \rightarrow ^5D_0$ transition of the Eu$^{3+}$ ion at room temperature (RT) which has potential use in high-density optical storage [9], (2) the information on the local structure around Ln$^{3+}$ ions can be obtained with Eu$^{3+}$ ion as a probe using fluorescence line narrowing technique, (3) the nature of vibrations associated to Ln$^{3+}$ ion sites which affect the non-radiative decay can be obtained from the measurement of the phonon side band associated with $^7F_0 \rightarrow ^5D_0$ and $^7F_0 \rightarrow ^5D_2$ pure electronic excitation transitions in the excitation spectrum of the Eu$^{3+}$ ion, and (4) electron-phonon coupling strength in a host can also be evaluated as the ratio of the integrated intensities of the phonon side band to that of the pure electronic band [10]. When a Eu$^{3+}$ ion is incorporated into any host matrix, it experiences an inhomogeneous crystal-field produced by the surrounding charge distribution that results in two effects: (i) the centroid shifts of all the free-ion multiplets to the red/blue and (ii) the Stark splitting of the energy levels. The centroid shifts are ascribed as the Nephelauxetic effect that explains the change of Slater parameters ($F_K$) and the spin-orbit coupling parameter ($\xi_{4f}$) for the Eu$^{3+}$ ion in the host with respect to their free ion values of $F_K^0$ and $\xi_{4f}^0$. The Stark splitting of the multiplets is assigned to the change in the sum of various interactions such as covalence, overlap and Coulomb interactions between the 4f electrons of the Eu$^{3+}$ ions and their surrounding ligands. Depending on the number of Stark components into which the $^5D_0 \rightarrow ^7F_j$ emission transition split, the symmetry at the Eu$^{3+}$ ions site can be derived by CF parameterization. The CF parameters, $B_{20}$ and $B_{22}$, as well as their ratio have been used to describe the coordination of the Eu$^{3+}$ ions [11-13].

Besides the above crystal-field effects, also the pressure induced changes in the luminescence properties of Eu$^{3+}$ ions in the tellurite glass have been investigated in the present work. Luminescence spectra of $^5D_0 \rightarrow ^7F_{0,1,2}$ transitions and fluorescence lifetime measurements for the $^5D_0$ level of Eu$^{3+}$ ion in the tellurite glass under high pressure up to 14.8 GPa at RT are presented. The results obtained in this work have been compared with those of the Eu$^{3+}$:phosphate [14] and lithium borate glasses [15].

2. Glass preparation and spectroscopic measurements
The Eu$^{3+}$-doped tellurite glass with the composition (mol %) of 69 TeO$_2$ + 15 K$_2$O + 15 Nb$_2$O$_5$ + 1.0 Eu$_2$O$_3$ (TKN1Eu) was prepared by conventional melt quenching technique. The batch composition was melted in a platinum crucible placed in a furnace at temperature of 1000 °C for about 30 min. and then poured onto a preheated brass plate followed by 6 h annealing at 250 °C and then cooled down to RT. The TKN1Eu glass thus obtained was used for high pressure measurements.

The blue line of 465.8 nm from Ar$^+$ laser was selected to excite the Eu$^{3+}$ ion. The emission spectra were recorded with a double monochromator equipped with a photomultiplier tube [15]. A special miniature diamond anvil cell (DAC) was used to generate high pressures up to nearly 15 GPa at RT. A piece of the TKN1Eu glass along with ruby pressure sensor was placed in an 80 µm diameter hole of a
stainless steel (INCONEL X 750) 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, pressure sensor 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 R₁ lines [16]. Decay curves for ⁵D₀ → ⁷F₂ transition of Eu³⁺ ion were obtained using a mechanical chopper with a multi-channel scalar in the range from 2 µs to 2 s and interfaced to a personal computer that recorded and averaged the signal.

3. Theory

When a Ln³⁺ ion is doped into a solid matrix, there is an electrostatic interaction of the 4f electrons with the charge of host ligands, known as the CF interaction, whose magnitude is small compared with electrostatic and spin-orbit interaction. The CF interaction is responsible for the small shift of the 2S+1L⁹ equalitons as well as the appearance of Stark levels, arising from the removal of degeneracy of the 2S+1L⁹ levels. The Hamiltonian that represents the CF potential acting on the Ln³⁺ ion can be expressed in Wybourne’s notation [15, 17, 18] as

\[ H_{CF} = \sum_{k,q,i} B_{q}^{k} C_{q}^{(i)} \]  

where \( B_{q}^{k} \) are the coefficients of the CF expansion which represents the functions of the radial distances and \( C_{q}^{(k)} \) are tensor operators of rank k, related to the spherical harmonics, can be calculated exactly [18]. The number of parameters for \( H_{CF} \) in equation (1) is greatly reduced by the symmetry selection rules for the point symmetry at the Eu³⁺ ion site in the crystal. Any surrounding that breaks the spherical symmetry of the free ion can lead to a shift and splitting of the energy levels. Thus, the above considerations also apply to materials such as glasses where a long-range order does not exist.

In the present analysis, considering the J-mixing interaction as a perturbation over the CF interaction, the three Stark components of the ⁷F₁ are simply described by

\[ H_{CF} = B_{20} C_{0}^{(2)} + B_{22} (C_{-2}^{(2)} + C_{2}^{(2)}) \]  

where \( B_{20} \) and \( B_{22} \) are the real parts of the CF parameters in equation (1).

The CF strength parameter, \( N_{v} \), has been used to simplify the description of the CF parameters due to its independence from the specific crystal structure. The \( N_{v} \), corresponding only the second rank CF parameters, has been determined using the following relation [18, 19]

\[ N_{v} = \sqrt{\frac{4\pi}{5}} \left[ (B_{20})^2 + 2(B_{22})^2 \right] \]  

4. Results and Discussion

4.1. Fluorescence spectra

When Eu³⁺ ions are excited to the ⁵D₂ level using 465.8 nm radiation from Ar⁺ laser, the fluorescent ⁵D₀ level are populated by non-radiative mutiphonon relaxation. The resultant emission from ⁵D₀ level of the TKN1Eu glass as a function of pressure was measured at RT in the range of 15500-17500 cm⁻¹ (see figure 1). The spectra obtained are quite similar to those of other oxide glass hosts [20, 21]. The emission spectra of the TKN1Eu glass consists of three transitions from the lowest excited multiplet state ⁵D₀ to the ground state multiplets ⁷F₁ (J = 0, 1, 2). The following transitions corresponding to J = 3, 4, 5 and 6 are very weak and hence they are not considered for the analysis. The spectra are normalized to ⁵D₀ → ⁷F₂ transition. The observed emission bands of TKN1Eu glass at 597 nm (16868 cm⁻¹) ascribed to ⁵D₀ → ⁷F₁ and at 613 nm (16316 cm⁻¹) assigned to ⁵D₀ → ⁷F₂, which correspond to orange and red, respectively.
The $^5D_0 \rightarrow ^7F_2$ transition is electric dipole allowed and also hypersensitive (its intensity is very sensitive to the local environment of the Eu$^{3+}$ ion), whereas the transition $^5D_0 \rightarrow ^7F_1$ is magnetic dipole allowed and is independent of the local symmetry. The well resolved Stark splitting of the $^5D_0 \rightarrow ^7F_1$ transition into three components suggests that the Eu$^{3+}$ ions in this glass host occupy low symmetry sites such as orthorhombic, monoclinic or triclinic. If Eu$^{3+}$ ion occupies a spherically symmetric site, or, is at a centre of symmetry, the intensity of the $^5D_0 \rightarrow ^7F_2$ emission is zero (except for very weak vibronic contributions) but its intensity increases as the site symmetry decreases. Hence, quality of the host material for lasing action is often expressed through the fluorescence intensity ratio, $^5D_0 \rightarrow ^7F_2$ to $^5D_0 \rightarrow ^7F_1$ transitions denoted as $I_R (2/1)$, which is used to establish the degree of asymmetry in the vicinity of Eu$^{3+}$ ions [22-25]. Moreover, $I_R (2/1)$ value also depends on the Judd-Ofelt (JO) parameter $\Omega_2$ [26-28], which is used to explain the short range effects. Therefore, the variation of $I_R (2/1)$ and in turn $\Omega_2$ gives the information about the short range effect on local structure around Eu$^{3+}$ ions. The higher value of $I_R (2/1)$ suggests a lower symmetry around Eu$^{3+}$ ions [29-31]. For the present TKN1Eu glass system, the $I_R (2/1)$ values are found to decrease from 5.00 to 3.50 when the pressure is increased from 0 to 14.8 GPa. The variation of $I_R (2/1)$ with pressure is presented in figure 2. The decrease in the $I_R (2/1)$ value with increasing pressure reflects the increase of symmetry by narrowing the site distribution around Eu$^{3+}$ ion with pressure. From figure 2, it is evident that the $I_R (2/1)$ values are considerably higher while releasing the pressure which may be caused by the increase of pressure induced defect centers [7].

Figure 1. Luminescence spectra of TKN1Eu glass at different pressures. The spectra are normalized to maximum of the $^5D_0 \rightarrow ^7F_2$ transition.
Figure 2. Luminescence intensity ratio $I_R(2/1)$ as a function of pressure. The solid (open) symbols correspond to data taken at increasing (decreasing) pressure. The curve serves as a guide to the eye.

Figure 3 presents the pressure induced red shift of the $^5D_0 \rightarrow ^7F_{0,1,2}$ emission band positions of the Eu$^{3+}$ ions along with a linear fit to the data obtained with increasing pressure. The barycentres of $^5D_0 \rightarrow ^7F_J$ ($J = 0$, 1 and 2) emission bands are presented in table 1. As can be seen from figure 3, the pressure dependent energy levels shift can be expressed quite well as a linear function [32, 33].

$$E_i(p) = E_i(0) + \alpha_i p$$

(with $p$ in GPa)

where $i$ labels the three different transitions. The $E_i(0)$ values correspond to the values at 0 GPa and the coefficients $\alpha_i$ are determined from the fits as

$$\alpha(^5D_0 \rightarrow ^7F_0) = -4.1(1) \text{ cm}^{-1}/\text{GPa}$$

$$\alpha(^5D_0 \rightarrow ^7F_1) = -2.6(1) \text{ cm}^{-1}/\text{GPa}$$

$$\alpha(^5D_0 \rightarrow ^7F_2) = -2.8(1) \text{ cm}^{-1}/\text{GPa}$$

Figure 3. Peak positions of the $^5D_0 \rightarrow ^7F_0$, $^7F_1$ and $^7F_2$ transitions of the Eu$^{3+}$ ions in TKN1Eu glass as a function of pressure. For the $^5D_0 \rightarrow ^7F_1$ transitions, the data points correspond to the barycentre of this transition (see figure 6) and the data points for the $^5D_0 \rightarrow ^7F_0$ and $^7F_2$ transitions correspond to the peak maximum. The solid (open) symbols correspond to data taken at increasing (decreasing) pressure. The solid line is the fit to a linear equation for the data at increasing pressure.
Shift of peak positions of $^7F_0$ level with increasing pressure in the TKN1Eu glass is observed to be more than that of phosphate [14] and lithium borate [15] glasses due to higher covalent nature of Eu-O in tellurite glass. Pressure-induced peak position shifts result from different mechanisms. For example, the relative shift of the LS manifolds with respect to each other is due to variations in the Coulomb interactions. For a given LS value, the shift of each crystal-field split J manifold results from the variation of the spin-orbit coupling constant, $\xi_{4f}$. For a given SLJ value, the shift and splittings of the Stark levels with respect to each other arises from the variations in strength and symmetry of the crystal-field around the Eu$^{3+}$ ions. Thus, the measured shifts and splittings of each luminescence peak with pressure can provide the data necessary for probing the Coulomb interactions, 4f wave functions and/or the crystal-field.

As a first approximation, the peak (the maximum intensity) of each $^7F_J$ manifold should be independent of the crystal-field. On the other hand, the ligand orbital affects the 4f wave functions to produce small variations in the spin-orbit coupling constant, $\xi_{4f}$. The variation of $\xi_{4f}$ with pressure can be determined by use of the Landè rule [34]

$$E (^7F_J) - E (^7F_{J-1}) = J \xi_{4f}$$

(4)

The values of $\xi_{4f}(p)$, normalized to ambient pressure has been calculated from our experimental data relating to the $^7F_0$ and $^7F_1$ levels. The results are collected in table 1 and figure 4 which show that $\xi_{4f}$ decreases with pressure, in accordance with the findings in similar studies [35, 36].

Figure 4. The variation of spin-orbit coupling ($\xi_{4f}$) with pressure relating to the $^7F_0$ and $^7F_1$ levels of Eu$^{3+}$ ions in TKN1Eu glass. The solid (open) symbols correspond to data taken at increasing (decreasing) pressure. Solid line is guide to the eye for increasing pressure.

Albin and Horrocks [37] have reported a phenomenological equation which relates the energy ($\nu$ (cm$^{-1}$)) of the $^5D_0 \rightarrow ^7F_0$ transition to the sum of the formal negative charge $q$ on the ligands directly bonded to the Eu$^{3+}$ ion given by:

$$\nu (\text{cm}^{-1}) = 17273 + 2029 q - 0.76 q^2 \quad \text{(at T = 296 K)}$$

(5)

This relationship is based on the energy of the $^5D_0 \rightarrow ^7F_0$ transition being a function of the interelectronic repulsion parameter and that any changes in energy can be regarded as a nephelauxetic effect, i.e., expansion of the f-orbitals of Eu$^{3+}$ ion. Using equation (5) and measured transition energies and by taking the negative root of the solution of equation (5) as the possible value, one can calculate the formal negative charge on the neighboring oxygen at various applied pressures (see table 1 and figure 5).
Table 1: Energies (cm$^{-1}$) for $^5$D$_0 \rightarrow ^7$F$_0$ and $^7$F$_1$ transitions, luminescence intensity ratio of $^5$D$_0 \rightarrow ^7$F$_2$ to $^5$D$_0 \rightarrow ^7$F$_1$ (I$_{R}(2/1)$), lifetime of $^5$D$_0$ ($\tau$, $\mu$s), spin-orbit coupling constant ($\xi_{4f}$), formal negative charge (Q), crystal field parameters (B$_{20}$, B$_{22}$, cm$^{-1}$) and their ratios (B$_{22}$/B$_{20}$) and crystal-field strength parameter (N$_v$, cm$^{-1}$) for the TKNEu glass under (a) increasing and (b) decreasing pressure (GPa).

| P (GPa) | $^5$D$_0 \rightarrow$ F$_0$ | F$_1$ | F$_2$ | F$_3$ | I$_{R}(2/1)$ | $\tau$ (µs) | $\xi_{4f}$ | Q | B$_{20}$ | B$_{22}$ | B$_{22}$/B$_{20}$ | N$_v$ |
|---------|-----------------|------|------|------|-------------|--------|--------|---|-------|-------|----------------|------|
| (a) Increasing pressure |
| 0       | 17267           | 16975| 16873| 16757| 5.00        | 741    | 1      | -1.68| 607   | 200   | 0.33           | 1062 |
| 3.0     | 17243           | 16965| 16852| 16728| 4.35        | 685    | 0.990  | -4.95| 636   | 220   | 0.35           | 1123 |
| 5.9     | 17223           | 16955| 16832| 16708| 4.04        | 599    | 0.982  | -6.47| 662   | 229   | 0.35           | 1169 |
| 7.9     | 17219           | 16955| 16842| 16708| 3.92        | 545    | 0.962  | -7.06| 676   | 225   | 0.33           | 1185 |
| 8.8     | 17215           | 16955| 16842| 16698| 3.70        | 528    | 0.960  | -7.36| 680   | 213   | 0.31           | 1179 |
| 11.2    | 17212           | 16975| 16844| 16687| 3.71        | 422    | 0.945  | -7.58| 730   | 250   | 0.34           | 1286 |
| 14.8    | 17200           | 16979| 16828| 16676| 3.50        | 299    | 0.932  | -8.41| 761   | 278   | 0.37           | 1358 |
| (b) Decreasing pressure |
| 11.6    | 17212           | 16986| 16842| 16687| 3.92        | 387    | 0.937  | -7.58| 761   | 272   | 0.36           | 1352 |
| 9.8     | 17216           | 16972| 16851| 16699| 4.08        | 432    | 0.941  | -7.28| 712   | 233   | 0.33           | 1249 |
| 6.7     | 17220           | 16955| 16845| 16708| 4.50        | 494    | 0.962  | -6.98| 647   | 234   | 0.36           | 1152 |
| 4.1     | 17245           | 16979| 16860| 16721| 4.80        | 586    | 0.965  | -4.75| 674   | 236   | 0.35           | 1153 |
| 0.5     | 17264           | 17007| 16873| 16749| 5.55        | 643    | 0.980  | -2.25| 643   | 276   | 0.43           | 1193 |

This increase in the formal negative charge on oxygen between ambient and 14.8 GPa is induced by the expansion of the f-orbitals (nephelauxetic effect) of Eu$^{3+}$ ion. The increase of the formal negative charge on coordinating ligands is a result of the partial transfer of valence (sd) electrons, which correlates with a decrease in the electronegativity of Eu$^{3+}$ ion. It is well known that electronegativity should be considered as an orbital property rather than as an atomic property [38]. It is also recognized that the electronegativity of an orbital is a function of the electron occupancy of that orbital [38]. Therefore, the expansion of the 4f orbitals of Eu$^{3+}$ ion with the application of pressure decrease concomitantly the electronegativity of Eu$^{3+}$ ion.
4.2. Crystal-field analysis

For a free Eu$^{3+}$ ion, all the 4$^\text{th}$ intraconfigurational transitions are forbidden by the Laporte rule [22, 39]. However, the ligand field (due to ions constituting the glass host) around the ion, distorts the free ion levels, causing higher energy states to admix and allow transitions between the different levels of the f$^\text{th}$ configuration [23]. Slight differences in the bonding parameters (e.g. ligand distance, ligand angle, coordination number and covalency) cause variations in the strength of the ligand field which modify the free ion levels. Figure 6 shows the three Stark splittings obtained for the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition of Eu$^{3+}$ ions in the TKN1Eu glass under pressure. The complete removal of degeneracy for the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition at all pressures suggests that the local symmetry of the Eu$^{3+}$ ions in TKN1Eu glass is low corresponding to orthorhombic, monoclinic or triclinic symmetry in a crystal [17, 18]. From figure 6, the observed increase in the energy separation between the two extreme Stark components with increasing pressure quantitatively reflects an increase in the CF strength at the Eu$^{3+}$ ion sites under pressure.

![Figure 6. Peak positions of the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ Stark transitions of Eu$^{3+}$ ions in TKN1Eu glass as a function of pressure. The solid (open) symbols correspond to data taken at increasing (decreasing) pressure.](image)

From the Stark splittings of the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition, the CF analysis has been carried out by assuming $\text{C}_{2v}$ point symmetry for the local structure around the Eu$^{3+}$ ions [18, 40-43]. Therefore, the second rank even CF parameters, $B_{20}$ and $B_{22}$, have been calculated by diagonalizing the complete Hamiltonian (free ion and crystal-field) using $\text{C}_{2v}$ symmetry by taking into account J-mixing [18]. From the 11 SLJ multiplets, a total of 69 JM$^J_J$ states are used in the basis set for the CF calculations. During the fitting of these energy levels, all 19 free ion parameters ($F_2^2$, $F_4^4$, $F_6^6$, $\xi$, $\alpha$, $\beta$, $\gamma$, $T_0^4$, $T_1^4$, $T_4^4$, $T_7^4$, $T_8^4$, $M_0^0$, $M_2^2$, $M_4^4$, $P_2^2$, $P_4^4$, $P_6^4$) are fixed to the values of Eu$^{3+}$:LaCl$_3$ [44] and only the second rank CF parameters have been optimized. The fitting process minimizes the root mean square deviation between the
experimental and calculated $^7F_1$ Stark levels [45]. The $B_{20}$, $B_{22}$ (with J-mixing), $B_{22}/B_{20}$ and $N_v$ using equation (3) thus calculated are collected in table 1 and plotted in figure 7. It is interesting to note that the values of CF and strength parameters ($B_{20}$, $B_{22}$ and $N_v$) in the present glass are almost same as those of Eu$^{3+}$:lithium borate glass up to 6 GPa (figure 8) [15]. It implies that Eu$^{3+}$ ions in TKN1Eu glass experiences almost the same environmental strength, as delivered predominantly from the oxygen neighbors in the lithium borate glass. At above 6 GPa, the $N_v$ values are in between those obtained for lithium borate and phosphate glasses that reflects the different environment around the Eu$^{3+}$ ion. As can be seen from figure 7, the variation of $B_{20}$, $B_{22}$, $B_{22}/B_{20}$ and $N_v$ with pressure exhibits a linear dependence on pressure.

![Figure 7](image1.png)

**Figure 7.** Variations of $B_{20}$, $B_{22}$, $B_{22}/B_{20}$ and $N_v$ with pressure. The solid (open) points correspond to data taken at increasing (decreasing) pressure. Lines indicate linear fits to the data at increasing pressure.

### 4.3. Fluorescence decay

The fluorescence decay from the $^5D_0$ level has been measured by exciting the Eu$^{3+}$ ions to the excited state, $^5D_2$, using as in the previous studies the 465.8 nm line of Ar$^+$ laser. A fast non-radiative decay populates the emitting level, $^5D_0$. Figure 9 shows the decay profiles at different pressures. The decay curves at all the pressures are found to be single exponential in good approximation up to 14.8 GPa, as indicated in figure 9 for the 11.2 GPa data. From the decay curves lifetimes have been evaluated by finding first e-folding times. The lifetimes at different pressures are presented in table 1 as well as plotted in figure 10. As can be seen from figure 10, lifetime of the $^5D_0$ level decreases with increasing pressure.
The observed decrease of lifetime with increasing the pressure can be explained by either enhanced multi-phonon deexcitation probability or an increase of electronic transition probabilities. Because of the large energy gap (12,000 cm$^{-1}$) between emitting level $^5D_0$ and next lower $^7F_6$ level, the role of multi-phonon relaxation in depleting the $^5D_0$ level in any Eu$^{3+}$:glass system is regarded as negligible. On the other hand, the increase of electronic transition probability results from an increase in CF strengths around the Eu$^{3+}$ ions with pressure. The increase in CF strengths results in an enhanced configuration interaction leading to a mixing of opposite parity configurations with the $4f^6$ configuration, due to the odd-parity CF Hamiltonians, causing the observed increase in the transition probabilities. Similar trends have been noticed in our earlier studies [14, 15, 18]. In the Eu$^{3+}$-doped phosphate [14], lithium borate [15] and tellurite glasses, lifetimes for the $^5D_0$ level at 0 GPa are found to decrease in the order of phosphate > lithium borate > tellurite as shown in figure 10. According to Allred-Rochow, Li, K and Nb have electronegativities 0.97, 0.91 and 1.23, respectively, which allows one to propose that the cation with higher electronegativity lowers the lifetime of the fluorescent level of the RE ion in the glass matrix when present as a modifier. This may be due to the increase of covalency between the cation and oxygen ion in the order KO < LiO < NbO which in turn decreases the covalency of Eu-O bond in the glass matrix causing the observed reduction of lifetime. Further, it is interesting to note that lifetime values increase with increase in the atomic radii of the modifier.

The $I_{R}$ (2/1) values are considerably higher while releasing pressure indicating that application of pressure caused local deformation around the Eu$^{3+}$ ions resulting in higher asymmetry for the Eu$^{3+}$ ion sites. From figures 2-8, one can see that release of pressure (data shown as open points) has no significant hysteresis effect. Over all, pressure induced changes in inter-atomic bond lengths and bond angles are almost continuous as reflected from the pressure induced variations in lifetimes and crystal field parameters and strengths.
Figure 9. Decay profiles for the $^5D_0$ level of Eu$^{3+}$ in TKN1Eu glass at various increasing pressures. The single exponential fit is also shown for 11.2 GPa.

Figure 10. Variation of lifetime for the level $^5D_0$ of Eu$^{3+}$ ions phosphate, lithium borate and tellurite glasses with increasing pressure. The solid (open) symbols correspond to data taken at increasing (decreasing) pressure and the solid line gives a guide to the eye.
5. Conclusions

Eu$^{3+}$-doped potassium niobium tellurite glass has been prepared and characterised for luminescence properties under pressure up to 14.8 GPa at RT. Red shifts of the emission band positions with pressure are attributed to an expansion of the 4f electron wavefunctions with increasing covalency. The decrease of emission intensity ratio $I_{R}(2/1)$ with increasing pressure attributed to lowering of asymmetry around the Eu$^{3+}$ ions. The CF splitting of the emission $^{5}D_{0} \rightarrow ^{7}F_{1}$ band increases with pressure due to increase in the CF strength at the Eu$^{3+}$ ion sites as reflected from the increase in CF strength parameter from 1062 to 1358 cm$^{-1}$ in the pressure range studied. The fluorescence decay curves for the $^{5}D_{0}$ level remain single exponential for the entire pressure range but the lifetimes decreases drastically from 0.76 ms to 0.30 ms with increase of pressure from 0 to 14.8 GPa. The quenching of lifetime for the $^{5}D_{0}$ level with pressure is attributed due to increase in electronic transition probabilities arising from increase in CF strengths around Eu$^{3+}$ ions.

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