Effect of Nd$_2$O$_3$ and Na$_2$O concentration on physical and spectroscopic properties of TeO$_2$–Bi$_2$O$_3$–ZnO–Na$_2$O–Nd$_2$O$_3$ glasses

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Abstract

Two series of tellurite glasses with molar compositions of (55TeO$_2$–2Bi$_2$O$_3$–(41–x)ZnO–2Na$_2$O–xNd$_2$O$_3$ (x = 0.5, 1.0, 1.5, 2.0 and 2.5) and 55TeO$_2$–2Bi$_2$O$_3$–(41–x)ZnO–xNa$_2$O–2Nd$_2$O$_3$ (x = 1.0, 2.0, 3.0, 4.0, 5.0) were fabricated using melt quenching technique. Based on the measured densities, refractive indices and absorption spectra, and spectroscopic properties of these two-glass series are evaluated and compared. Whereas substitution of ZnO by Nd$_2$O$_3$ causes the values of density and refractive index increase, the substitution of ZnO by Na$_2$O has been shown to impact the glass density and refractive index in the opposite manner. Molar volume of both series increases with an increase of either Nd$_2$O$_3$ or Na$_2$O concentrations. In this regard, a dynamical model explaining the density and molar volume was proposed. Additionally, Judd-Ofelt theory was applied in order to predict the physical and laser properties of the two glasses series as a function of glass compositions, i.e., Judd-Ofelt parameters $\Omega_i$ ($i = 2, 4, 6$), branching ratios ($\beta$), calculated lifetimes ($\tau$), the emission to excited state absorption intensity ratio ($A_{em}/A_{ESA}$) and spectroscopic quality $\chi = \Omega_4/\Omega_6$. Equations to relate $\chi$ with branching ratios for laser transitions $^4F_3/2$ to $^4I_1$ (with $J' = 9/2, 11/2, 13/2$ and 15/2) were also derived.

1. Introduction

The advancement of SiO$_2$ based optical communication requires the functionality of high gain optical amplifiers at the two main window telecommunications, i.e., second window telecommunication centred at 1310 nm and third window telecommunication centred at 1550 nm. Erbium doped fibre amplifier (EDFA) for the third window telecommunication has been found to be relatively established. The performance of optical amplifiers designed for the second telecommunication window, however, continues to be below EDFA.

Three rare earth ions, i.e., Nd$^{3+}$, Pr$^{3+}$ and Dy$^{3+}$, doped in various glass hosts are partly researched because of their emission at around 1300 nm [1–5]. Among them, the spectroscopic properties of Nd$^{3+}$ ion has been one of the most investigated subjects, not only due to its emission around 1310 nm [6, 7]; emission at around 1050 nm is also of interest [8–10]. Interestingly, pumping to generate these two emissions can be performed using the available diode laser that utilises its large absorption cross-section around 800 nm. Accordingly, electrons are pumped from ground energy state $^4I_{15/2}$ to $^4F_{5/2}$ before the non-radiatively decay to $^4F_{3/2}$. In high phonon energy glasses, this energy is converted into vibrational energy, thus decreasing radiative energy. Glass host with low phonon energy is required in order to minimize the multiphoton relaxation rates. TeO$_2$-based glasses are among those that meet this requirement. The maximum phonon energy of these glasses is about 800 cm$^{-1}$ [11], which is lower than that of silicate glasses (1050 cm$^{-1}$) [12], phosphate glasses (1300 cm$^{-1}$) [13] and borate glasses (1350 cm$^{-1}$) [14].

Due to competition of electronic de-excitation of $^4F_{3/2} \rightarrow ^4I_{9/2}$, $^4F_{3/2} \rightarrow ^4I_{11/2}$, and $^4F_{3/2} \rightarrow ^4I_{13/2}$, which results in emission at around 950 nm, 1300 and 1050 nm, respectively, it is necessary to better understand how the compositional dependence of the relative intensities (branching ratio) that lead to these emissions. In this
paper, two series of Nd$^{3+}$ ions doped tellurite glasses which have almost the same composition, are studied. They are glass series possessing varying Nd$^{3+}$ ions concentrations along with those with fixed ones. In this regard, discussion is focused not only on the effect of the compositional variation on the change in density, refractive index, Judd–Ofelt parameters ($\Omega_1, \Omega_2, \Omega_3$), spectroscopic quality factor ($\chi = \Omega_q/\Omega_k$), the emission/ESA intensity ratio ($\chi_{em}/\chi_{ESA}$), but also on calculated and radiative life-times ($\tau$).

2. Experimentsal methods

Two series of new tellurite glasses of compositions: 55TeO$_2$–2Bi$_2$O$_3$–(41-x)ZnO–2Na$_2$O–xNd$_2$O$_3$ (where x = 0.5, 1.0, 1.5, 2.0, 2.5) and 55TeO$_2$–2Bi$_2$O$_3$–(41-x)ZnO–xNa$_2$O–2Nd$_2$O$_3$ (where x = 1.0, 2.0, 3.0, 4.0, 5.0) were prepared by applying standard procedure of melt quenching techniques. A total of 10 gram of starting materials was mixed and grounded thoroughly in an agate mortar. Subsequently, the mixture was melted in a platinum crucible in air atmosphere at temperature of 1000 °C for 30 min. A square flat shape of glass was obtained by pouring the melt into a preheated square parallel brass mold. In order to reduce inhomogeneity, the obtained glass was immediately annealed at temperature 265°C for about 60 min followed by cooling to room temperature at a cooling rate of 1 °C min$^{-1}$. For the purpose of optical characterization, the annealed glasses were then cut and polished down to optical quality.

Density measurement of all samples was carried out at room temperature with five repetitions using pycnometer with distilled water as the immersion fluid using equation:

$$\rho_g = \frac{m_g \rho_w}{(m_3 - m_0) - (m_2 - m_1)}$$

(1)

Here, $\rho_g$, $\rho_w$, $m_g$, $m_0$, $m_1$, $m_2$ and $m_3$ denote the density of glass, density of distilled water, mass of sample, mass of empty pycnometer, mass of pycnometer with a glass sample inside, mass of pycnometer filled with water and glass sample, and mass of pycnometer filled with water only, respectively. Refractive index of all glasses was measured at room temperature with three repetitions at wavelength of 650 nm using Brewster Angle method. A TM-polarized light was focused onto the glass sample as function of incident angle after which the reflected light was detected. A graph of the intensity of the reflected light against incident angle was then constructed. Refractive index of a glass sample can then be calculated using equation

$$\tan \theta_B = \frac{n_g}{n_a}$$

(2)

where $\theta_B$ is Brewster angle defined as the incident angle with minimum reflected light intensity, while $n_a$ and $n_a$ denote refractive index of glass and air, respectively. Absorption spectra of all glass samples were recorded at room temperature in the spectral range of 200–1100 nm using UV–Vis–NIR double beam spectrophotometer (Perkin-Elmer, model Lambda 900).

3. Results and discussion

3.1. Density

Density is one of the important properties of a glass from it is possible to determine a rough picture of several properties relating to structural variations, e.g., molar volume, structural compactness, the modification of geometrical configuration of the glassy network, the coordination change of the glass former ions as well as the variation in the dimension of the interstitial holes. Molar volume, which is the total volume housing 1 mole atoms, can be calculated by applying the following equation:

$$V_m = \frac{\sum C_i M_i}{\rho} = \frac{\bar{M}}{\rho}$$

(3)

where $\rho$ represents the measured density, $M_i$ and $\bar{M}$ are the molecular weight of the i-th component and the average molecular weight, respectively. $C_i$ is a fraction of the molecular concentration such that $\sum C_i = 1$. In order to ascertain the extent to which the volume is occupied, we calculated ionic packing ratio ($\eta$) defined as the ratio between total volume of 1 mole of atoms and molar volume expressed by equation:

$$\eta = \frac{\sum \frac{4}{3} \pi r_i^3 n_i N_A}{V_m}$$

(4)

Here $N_A$ denotes Avogadro number, whereas $r_i$ and $n_i$ are atomic radius and molar fraction of the constituent atoms of the i-th atom, respectively. From glass compositions, the densities can be calculated using equation:
Where $\rho_c$ is calculated glass density, $x_i$ represents molar fraction, $M_i$ is molecular weight and $\rho_i$ is density of the $i^{th}$ glass component.

Table 1 tabulates the measured and calculated density, average molecular weight, molar volume, ionic packing ratio as well as oxygen packing density, i.e., volume fraction occupied by oxygen atoms. It is shown that the magnitude of the measured densities of all glasses are about 1.5% less than that of the calculated densities. This difference may be understood by looking at equation (5) used to make calculation. Equation (5) must be understood as a glass density at a glassy state which is very close to its corresponding crystalline state.

From table 1 and figure 1, it can be seen that density increases with the increase of Nd$_2$O$_3$ incorporated into the glass to partially substitute ZnO (figure 1(a)) and decreases with the increase of Na$_2$O to partially substitute ZnO (figure 1(b)). Substituting lighter ions, i.e. Zn$^{2+}$ ($A_e = 65.38$), with heavier ions, i.e. Nd$^{3+}$ ($A_e = 144.24$), is shown to increase the average molecular weight, thus resulting in increased density [15]. In the same manner, partial substitution of ZnO with Na$_2$O ($A_e$ Na$_2$O = 22.99) reduces the average molecular weight of the glass, which causes a decline in its density. Increasing glass molar volume due to partial substitution of Zn$^{2+}$ ions ($r = 74$ pm) by ions with greater ionic radius, i.e. Nd$^{3+}$ ($r = 112$ pm) or Na$^+$ ($r = 102$ pm) does not contribute significantly to the density change.

Figure 2 is illustrated to better understand these results. Atoms are closely packed together in crystal structure. In crystalline materials (figure 2(a)), replacing ions with smaller ionic radius (A) with the greater ions (X) can significantly alter the molar volume. With ionic packing ratio within the range 17.0% - 17.6%, table 1, it can be deciphered that the empty space in the glass matrix, not necessarily interstice, occupies more than 80%. However, substitution might not automatically expand the glass volume. Although there may be an increase in volume, it is not as significant as in crystalline state. Glass volume is mainly determined by the nature of glass formation. In glassy materials, contribution of the volume change caused by the above substitution is therefore less significant than that which occurs in crystalline materials of the same composition. As long as glass stability upon addition of ions is relatively unchanged, glass density is predominantly attributed to the average change in molecular weight and less by molar volume.

Table 1. Measured and calculated densities ($\rho$$_{meas,\,calc}$), average molar weights ($M_{avg}$), molar volumes ($V_m$), ionic packing ratios ($\eta$), measured refractive index ($n_{meas}$) and calculated refractive index ($n_{calc}$) of all the investigated glasses.

| Sample ID | $\rho_{meas}$ (g cm$^{-3}$) | $\rho_{calc}$ (g cm$^{-3}$) | $M_{avg}$ (g mol$^{-1}$) | $V_m$ (cm$^3$ mol$^{-1}$) | $\eta$ (%) | $n_{meas}$ | $n_{calc}$ |
|-----------|-----------------------------|-----------------------------|---------------------------|-----------------------------|-------------|-------------|-------------|
| ND-1      | 5.6291                      | 5.7363                      | 132.9792                  | 23.624                      | 17.49       | 1.8766      | 2.2182      |
| ND-2      | 5.6663                      | 5.7517                      | 134.2547                  | 23.694                      | 17.39       | 1.9256      | 2.2256      |
| ND-3      | 5.6987                      | 5.7699                      | 135.5302                  | 23.793                      | 17.29       | 1.9816      | 2.2329      |
| ND-4      | 5.7063                      | 5.7818                      | 136.8057                  | 23.975                      | 17.20       | 1.9864      | 2.2401      |
| ND-5      | 5.7211                      | 5.7966                      | 138.0812                  | 24.135                      | 17.11       | 2.0316      | 2.2473      |
| NA-1      | 5.7362                      | 5.8215                      | 136.9997                  | 23.883                      | 17.26       | 1.9912      | 2.2484      |
| NA-2      | 5.7063                      | 5.7818                      | 136.8057                  | 23.974                      | 17.20       | 1.9864      | 2.2401      |
| NA-3      | 5.6206                      | 5.7425                      | 136.6117                  | 24.306                      | 17.15       | 1.9257      | 2.2320      |
| NA-4      | 5.6219                      | 5.7473                      | 136.4177                  | 24.265                      | 17.09       | 1.9166      | 2.2240      |
| NA-5      | 5.5536                      | 5.6633                      | 136.2237                  | 24.329                      | 17.04       | 1.9074      | 2.2162      |

\[
\rho_c = \frac{\sum x_i M_i}{\sum (x_i M_i)/\rho_i}
\]  

(5)
3.2. Refractive index

If a dielectric material is subjected to an external electric field \( E \) such as electromagnetic wave exposition, polarization will occur. The bound charged elements of its molecules are displaced in such a manner that positive charged elements are displaced toward the electric field direction and negative charged elements are displaced in opposite direction. The polarization density \( P \) is related to the electric field \( E \) by the equation:

\[
P = \varepsilon_0 \chi E
\]

Where \( \chi \) is electric susceptibility, \( \varepsilon_0 \) refers to the permeability of free space and \( E \) is electric field composing electromagnetic wave. In this equation, \( \chi \) is related to the refractive index \( n \) as

\[
n^2 = 1 + \chi
\]

Where \( n \) is related to the mass an electron \( m_e \), charge of an electron, damping coefficient \( \gamma \), frequency of incident light and the density of the polarizable electrons \( N_p \) as expressed by:

\[
\chi = \frac{N_p e^2}{m_e \varepsilon_0 (\omega_0^2 - \omega^2) + 2i\gamma \omega}
\]

With the regard to this work, \( n \) can be related to the mass density (can be interpreted as electronic density) \( \rho \) and molecular polarizability \( \alpha \) by applying Lorentz-Lorenz equation in the following manner:

\[
n = \sqrt{\frac{2N_0 \alpha m \rho + \sum_\alpha x_i M_i}{3 \sum_\alpha x_i M_i - N_0 \alpha m \rho}}
\]

Where \( N_A \) is Avogadro’s number and \( \alpha_m \) is molecular polarizability expressed by equation:

\[
\alpha_m = \frac{\alpha_O}{N_O} + \sum \alpha_i
\]

Where \( \alpha_O \) is oxide ion polarizability, \( N_O \) is the number of oxide ions in glass composition, and \( \alpha_i \) denotes molar cation polarizability. For a given glass composition, e.g., \( x_1A_{p_1}O_{y_1} - x_2B_{p_2}O_{y_2} \), \( N_O \) and \( \sum \alpha_i \) are given by

\[
N_O = x_1p_1 + x_2p_2
\]

\[
\sum \alpha_i = x_1\alpha_A + x_2\alpha_B
\]

Referring to equation (6), it can be seen that refractive index increases with increasing either electronic cloud density (structural dependence) or electronic polarizability. A similar trend in density change (figure 1) and refractive index change (figure 3) is caused due to the concentration change of either Nd\(^{3+}\) or Na\(^+\) ions in the glasses that can be easily understood from the frame of equation (8). The increase in density due to increasing Nd\(^{3+}\) ions content leads to increase glass refractive index and so is the effect of increasing Na\(^+\) ions content in the
Figure 3. Refractive index change as function of mole fraction of (a) Nd2O3 and (b) Na2O.

Figure 4. Refractive index dependence on glass density for two glass series, i.e., glass at which ZnO is partially substituted by either Na2O or Nd2O3.

glass. Figure 4 illustrates the dependence of the glass refractive index on its density. It can be seen that glass with variation in Nd3+ ions content has a steeper slope than that which has variation in Na+ ions content. This result confirms that density is not the only factor affecting glass refractive index. For a given temperature, average molecular weight and molecular polarizability are also important factors that control glass refractive index. Molar cation polarizability for all the glasses investigated in this work, i.e., Te4+, Bi3+, Zn2+, Na+, and Nd3+ ions; are (in Å3) 1.595, 1.508, 0.286, 0.181 and 2.546, respectively. Following equation (9), since molar cation polarizability of Nd3+ ion is greater than that of Zn2+ ions, addition of Nd3+ ions to partially substitute Zn2+ can contribute to the increase of glass refractive index. Applying a similar reason, glass refractive index decreases when Na+ content increases in the glass.

3.3. Absorption spectra

The absorption spectra of all the investigated glasses recorded within UV–vis-NIR range at room temperature are illustrated in figure 5. Nine distinct absorption bands are observed at 431, 473, 527, 586, 628, 684, 749, 805 and 878 nm corresponding to electronic transition configuration within multiples of the 4f0 from energy ground state (4I9/2) to the exited states: (2F1/2 + 4D3/2), (2G5/2 + 4G7/2 + 4G9/2), (4G7/2 + 4H5/2), (2F5/2 + 4S3/2), (2H9/2), (2G11/2), (2G9/2), (2D5/2 + 2D3/2), (2F3/2), respectively. As shown in the figure, the peak position of all absorption bands varies only slightly (±1 nm) and is within the range of those reported by many authors [9, 16–20] thus confirming a strong shielding of 4f orbital from the outside ligands. Due to UV absorption edge around 400 nm, absorption bands at wavelength less than 400 nm that appears in many glasses [19, 21–23] are blocked.
Furthermore, it is event from figure 5 that the relative intensity of all the absorption bands depends strongly on Nd\(^{3+}\) ions concentration and glass host. It increases with an increase in Nd\(^{3+}\) ions concentration (figure 5(a)) and varies only slightly as Nd\(^{3+}\) ions concentration is constant (figure 5(b)). This can be explained in terms of Maxwell-Boltzmann distribution. Suppose we have \(N\) photons incident onto a glass sample with a thickness \(dx\). If population density of Nd\(^{3+}\) ions is \(n_{Nd}\), the number of photons absorbed can be expressed as follows:

\[
\frac{dN}{dx} = -N n_{Nd} \sigma
\]

where \(\sigma\) is absorption cross section. Accordingly, raising Nd\(^{3+}\) ions concentration may result in heightened absorption intensity \(\frac{dN}{dx}\). For TBZNNdx glass series, the intensity of all absorption bands increases by increasing the concentration of Nd\(^{3+}\) ions. A significant change is observed for the absorption band intensity corresponding to electronic dipole transition from \(4I_{9/2}\) to \((2G_{7/2} + 4H_{5/2})\). However, a similar trend is not found for TBZNNxNd glass series. The absorption intensity of the four main absorption bands peaking at 586 nm, 749 nm, 805 nm and 878 nm does not change significantly, thus indicating that incorporating Na\(^+\) ions up to 5 mol\% into the glass matrix does not significantly change the ligand field.

### 3.3.1. Judd-Ofelt analysis

In this section, the lasing properties of all samples will be predicted by analysing absorption spectra data using Judd-Ofelt theory [24, 25]. Firstly, the experimental oscillator line strength \(f_{\text{exp}}\) for an electric dipole absorption transitions from initial angular momentum \(J\) to the final angular momentum \(J'\) was calculated using the following equation:

\[
f_{\text{meas}} = \frac{3c(2J + 1)}{8\pi^{-1}e^2N} \left(\frac{9n}{(n^2 + 2)^2}\right) \frac{1}{\lambda} \int_{\lambda_{\text{f}} - \lambda_{\text{i}}} \alpha(\lambda) d\lambda
\]

where \(c\) refers to the speed of light in free space, \(h\) is the Planck’s constant, \(e\) is the charge of an electron, \(\lambda\) signifies the mean wavelength of an absorption band, and \(\alpha(\lambda)\) is the absorption coefficient at wavelength \(\lambda\). According to Judd-Ofelt theory, the theoretical line strength \(f_{\text{theo}}\) can be expressed as:

\[
f_{\text{calc}} (J \rightarrow J') = \sum_{i=2,4,6} \Omega_i \mathcal{P}(S, L)\mathcal{P}(S', L') |U(i)|^2\]

where \(\Omega_i\) are the Judd-Ofelt intensity parameters and elements \(\mathcal{P}(S, L)\) and \(\mathcal{P}(S', L')\) are doubly reduced unit tensor operators. Their values are taken from literature since these elements are considered almost invariant with respect to the Nd\(^{3+}\) environment [26]. The best set of J-O intensity parameters \(\Omega_i\) was then calculated using the least square fitting by taking:

\[
\Delta = \sum_{i=1}^n \left( f_{\text{exp}} - (\Omega_2 U_2 + \Omega_4 U_4 + \Omega_6 U_6) \right)^2
\]

This is followed by minimizing \(\Delta\) with respect to \(\Omega_i\):

\[
\frac{\delta \Delta}{\delta \Omega_2} = 0, \quad \frac{\delta \Delta}{\delta \Omega_4} = 0, \quad \frac{\delta \Delta}{\delta \Omega_6} = 0
\]

The J-O intensity parameters \(\Omega_i\) were then obtained by solving equation (16) simultaneously, in the results of which are summarised in table 3. These results can then be used to calculate other radiative parameters such as radiative transition rate, branching ratio, and radiative lifetime using the following equations:

![Figure 5. Absorption spectra of (a) TBZNNdx glass series, (b) TBZNNxNd glass series.](image)
In this paper, all Judd-Olfet calculations were made based on room temperature refractive index recorded at 650 nm, a wavelength located between absorption bands corresponding to electronic transition $^4I_{9/2} \rightarrow ^4I_{15/2} + ^4I_{11/2}$ and $^4I_{9/2} \rightarrow ^4I_{13/2}$. Regardless of the limited laser source in our lab, the choice of this refractive index can compensate the refractive index difference arising from material dispersion, i.e., higher refractive index located at wavelength shorter than 650 nm and lower refractive index at longer wavelength. Perhaps for this reason, most works on Judd-Olfet analysis published nowadays is based on such a single refractive index.

### 3.3.2. Judd-Olfet parameters

Table 2 depicts that the values of all J-O intensity parameters $\Omega_i$ obtained in this work are comparable to those reported in literatures [32, 33] and that they share the same trend as $\Omega_2 < \Omega_6 < \Omega_4$, similar to the findings in tellurite glasses [34, 35]. Figure 6 shows compositional dependence of J-O parameters for the two glasses series that have been studied in this work. Many papers report that $\Omega_2$ is related to the degree of covalency and asymmetry of local structure at which higher value of $\Omega_2$ means a higher degree of covalent bond between Nd$^{3+}$ ions and the vicinity ligand as well as lower degree of symmetry around Nd$^{3+}$ ions [36, 37]. Accordingly, a trend of increasing $\Omega_2$ with the increase of Na$_2$O concentration (figure 6(a)) and especially Nd$_2$O$_3$ concentration (figure 6(b)) can be interpreted as an increase in covalence bond strength and the degree of asymmetry relating Nd$^{3+}$ to the vicinity ligands. According to many previous studies, $\Omega_6^{-1}$ is related to the ionicity of Nd$^{3+}$ ions in ligand field at which higher value of $\Omega_6^{-1}$ corresponds to stronger ionic bonds or weaker covalent bonds [36–38].

| Sample  | $\Omega_2$ | $\Omega_4$ | $\Omega_6$ | $1/\Omega_6$ | $\chi$ |
|---------|-----------|-----------|-----------|-------------|-------|
| ND-1    | 0.68      | 0.95      | 0.75      | 1.333       | 1.267 |
| ND-2    | 1.14      | 1.64      | 1.18      | 0.848       | 1.390 |
| ND-3    | 1.65      | 2.4       | 1.74      | 0.575       | 1.379 |
| ND-4    | 2.15      | 3.04      | 2.32      | 0.431       | 1.310 |
| ND-5    | 2.25      | 3.81      | 2.85      | 0.351       | 1.337 |
| NA-1    | 2.07      | 3.1       | 2.28      | 0.439       | 1.360 |
| NA-2    | 2.15      | 3.09      | 2.25      | 0.444       | 1.373 |
| NA-3    | 2.22      | 3.33      | 2.41      | 0.415       | 1.382 |
| NA-4    | 2.18      | 3.41      | 2.44      | 0.410       | 1.398 |
| NA-5    | 2.28      | 3.37      | 2.42      | 0.413       | 1.393 |

(i) Radiative transition rate ($A$)

\[
A[(S, L)J; (S', L')J'] = \frac{64\pi^4 n^4}{3h(2J+1) \lambda^5} \left( \frac{n^2 + 2}{9} \right)^2 \sum \Omega_i |(S, L)J||U||(S', L')J'|^2 \]  

(ii) Branching ratio

\[
\beta[(S, L)J; (S', L')J'] = \frac{A[(S, L)J; (S', L')J']}{\sum_{S', L', J'} A[(S, L)J; (S', L')J']} \]  

(iii) Radiative lifetime ($\tau_R$)

\[
\tau_R = \left[ \sum_{S', L', J'} A[(S, L)J; (S', L')J'] \right]^{-1} \]  

In this paper, all Judd-Olfet calculations were made based on room temperature refractive index recorded at 650 nm, a wavelength located between absorption bands corresponding to electronic transition $^4I_{9/2} \rightarrow ^4I_{15/2} + ^4I_{11/2}$ and $^4I_{9/2} \rightarrow ^4I_{13/2}$. Regardless of the limited laser source in our lab, the choice of this refractive index can compensate the refractive index difference arising from material dispersion, i.e., higher refractive index located at wavelength shorter than 650 nm and lower refractive index at longer wavelength. Perhaps for this reason, most works on Judd-Olfet analysis published nowadays is based on such a single refractive index [27–30]. There are only few papers reporting Judd-Olfet calculation by taking into account material dispersion [31].
concentration increase provides the same information, namely, the glass becomes less ionic (stronger covalent bond).

3.3.3. Branching ratio
With regard to laser transition in Nd$^{3+}$-doped glass, we have used J-O parameters to calculate branching ratios for electronic transition from $^4F_{3/2}$ to $^4I_{J'}$ with $J' = 9/2, 11/2, 13/2$ and $15/2$ abbreviated as $\beta(^4F_{3/2} \rightarrow ^4I_{J'} = 9/2, 11/2, 13/2$ and $15/2)$. No distinct relation between $\beta$ and Nd$_2$O concentration is observed for the first glass series (figure 7). For the second series (figure 8), however, $\beta(^4F_{3/2} \rightarrow ^4I_{9/2})$ increases with an increase in Nd$_2$O concentration of up to 4.0 mol%; for other transitions the opposite trend occurs. It is believed that the ratio of $\Omega_4$ to $\Omega_6$, known as spectroscopic quality factor and usually expressed as $\chi = \Omega_4/\Omega_6$, can be linked to electronic transition $^4F_{3/2}$ to $^4I_{9/2}$ [39-41]. They demonstrated that the smaller the value of this ratio, the more intense the electronic transition $^4F_{3/2}$ to $^4I_{9/2}$ will be. In addition to transitioning $^4F_{3/2}$ to $^4I_{9/2}$, Choi et al [35] added $\chi$ to analyse the change in electronic transition $^4F_{3/2}$ to $^4I_{11/2}$ and observed that the intensity of this laser transition decreases with an increase of $\chi$. Figures 7 and 8 depict the dependence of both $\chi$ and

![Figure 6](image-url) Behaviour of J-O parameters ($\Omega_{2,4,6}$) as function of (a) Na$_2$O concentration and (b) Nd$_2$O$_3$ concentration.

![Figure 7](image-url) Compositional dependence of $\Omega_4/\Omega_6$ and branching ratio for laser transition in TZBNNdx glass series from $^4F_{3/2}$ to: (a) $^4I_{9/2}$, (b) $^4I_{11/2}$, (c) $^4I_{13/2}$, (d) $^4I_{15/2}$.
\[ \beta(\frac{4}{3}F_{3/2} \rightarrow \frac{4}{1}I_{9/2}, \frac{4}{1}I_{11/2}, \frac{4}{1}I_{13/2}, \frac{4}{1}I_{15/2}) = \frac{C_{4-9/2} \Omega_4 + C_{6-9/2} \Omega_6}{C_4 \Omega_4 + C_6 \Omega_6} \]  

Whereas compositional dependence of \( \beta(\frac{4}{3}F_{3/2} \rightarrow \frac{4}{1}I_{9/2}) \) and \( \Omega_4/\Omega_6 \) behave in exactly the same manner (figures 7(a) and 8(a)), compositional dependence of \( \beta(\frac{4}{3}F_{3/2} \rightarrow \frac{4}{1}I_{9/2}, \frac{4}{1}I_{11/2}, \frac{4}{1}I_{13/2}, \frac{4}{1}I_{15/2}) \) and \( \Omega_4/\Omega_6 \) behave in the opposite way (figures 7(b)–(d) and 8(b)–(d)). The use of \( \chi \) to characterise all branching ratios of emission originated from \( \frac{4}{3}F_{3/2} \) to all possible \( \frac{4}{1}I_{9/2}, \frac{4}{1}I_{11/2}, \frac{4}{1}I_{13/2}, \frac{4}{1}I_{15/2} \) as tabulated in Table 3 into equations (15) and (16). This gives us the following equations:

\[ \beta(\frac{4}{3}F_{3/2} \rightarrow \frac{4}{1}I_{9/2}) = \frac{C_{4-9/2} \Omega_4 + C_{6-9/2} \Omega_6}{C_4 \Omega_4 + C_6 \Omega_6} \]  

\[ \beta(\frac{4}{3}F_{3/2} \rightarrow \frac{4}{1}I_{11/2}) = \frac{C_{4-11/2} \Omega_4 + C_{6-11/2} \Omega_6}{C_4 \Omega_4 + C_6 \Omega_6} \]  

\[ \beta(\frac{4}{3}F_{3/2} \rightarrow \frac{4}{1}I_{13/2}) = \frac{C_{6-13/2} \Omega_6}{C_4 \Omega_4 + C_6 \Omega_6} \]  

\[ \beta(\frac{4}{3}F_{3/2} \rightarrow \frac{4}{1}I_{15/2}) = \frac{C_{6-15/2} \Omega_6}{C_4 \Omega_4 + C_6 \Omega_6} \]
signal resulting from the transition 4F3/2 to 4I, where J′ = 9/2, 11/2, 13/2 and 15/2 (β in %), spectroscopic factor (χ) radiative lifetime (τ) and the emission/ESA intensity ratio (Aem/ĀESA) of all investigated glasses.

| Sample | [Nd³⁺] | 4F3/2 | 4I11/2 | 4I13/2 | 4I15/2 | τ (μs) | Aem/ĀESA |
|--------|--------|-------|--------|--------|--------|--------|-----------|
| ND-1   | 1.24   | 44.64 | 46.68  | 8.33   | 0.35   | 960    | 1.170     |
| ND-2   | 2.51   | 45.96 | 45.78  | 7.93   | 0.33   | 529    | 1.083     |
| ND-3   | 3.75   | 45.73 | 45.93  | 8.00   | 0.33   | 324    | 1.098     |
| ND-4   | 4.99   | 45.07 | 46.39  | 8.20   | 0.34   | 248    | 1.138     |
| ND-5   | 6.20   | 43.53 | 46.21  | 8.12   | 0.34   | 184    | 1.228     |
| NA-1   | 5.04   | 45.57 | 45.05  | 8.05   | 0.34   | 245    | 1.132     |
| NA-2   | 5.02   | 45.76 | 45.91  | 7.99   | 0.33   | 249    | 1.096     |
| NA-3   | 4.96   | 45.84 | 45.86  | 7.97   | 0.33   | 259    | 1.115     |
| NA-4   | 4.96   | 45.95 | 45.79  | 7.94   | 0.33   | 259    | 1.127     |
| NA-5   | 4.91   | 45.89 | 45.83  | 7.95   | 0.33   | 266    | 1.097     |

Where C₄,₆ and C₆,₆ refer to the constants obtained from multiplication between $\frac{6\hbar^2\omega_0^2}{3h(2J'^2 + 1)} \left( \frac{\chi + 2}{\chi} \right)^2$ and $\langle 4F_3/2|U'|4I_n \rangle$ obtained from table 4. C₄,₆ = ΣC₄,₆ and C₆,₆ = ΣC₆,₆ with J′ = 9/2, 11/2, 13/2 and 15/2. Dividing both numerator and denominator for equations (22) to (25) by Ω₆, we obtain:

$$\beta(4F_3/2 \rightarrow 4I_9/2) = \frac{C_4 - 9/2 \chi + C_6 - 9/2}{C_4 \chi + C_6}$$ \hspace{1cm} (24)

$$\beta(4F_3/2 \rightarrow 4I_{11/2}) = \frac{C_4 - 11/2 \chi + C_6 - 11/2}{C_4 \chi + C_6}$$ \hspace{1cm} (25)

$$\beta(4F_3/2 \rightarrow 4I_{13/2}) = \frac{C_6 - 13/2}{C_4 \chi + C_6}$$ \hspace{1cm} (26)

$$\beta(4F_3/2 \rightarrow 4I_{15/2}) = \frac{C_6 - 15/2}{C_4 \chi + C_6}$$ \hspace{1cm} (27)

From equations (26) and (27), it is clear that $\chi = \Omega_4/\Omega_6$ exists only in the denominator, which means that alteration in the value of $\chi$ can be directly interpreted as the change in $\beta(4F_3/2 \rightarrow 4I_{13/2} \text{ or } 15/2)$. The greater the value of $\chi$, the smaller these two branching ratios will be. From equations (24) and (25), on the other hand, $\chi$ exists in both numerator and denominator to cause $\beta(4F_3/2 \rightarrow 4I_9/2 \text{ or } 11/2)$ which cannot be directly concluded. Conclusion can only be drawn after considering the value of $\lambda$ and its corresponding value of refractive index (n) at $\lambda$ to create C₄,₆ and C₆,₆.

3.3.4. Emission to ESA intensity ratio

Relating to emission at 1.3 μm used for second telecommunication window, the Excited State Absorption (ESA) signal resulting from the transition 4F3/2 → 4G7/2 red-shifts the gain curve at around 1.3 μm even further and consequently prevents gains in this region. In the majority of glass hosts, the emission and ESA signal are comparable and vary greatly, depending on the glass hosts. Using Judd-Ofelt parameters, the emission/ESA intensity ratio (Aem/ĀESA) can be estimated as expressed by the following equation [43]:

$$\frac{A_{em}}{A_{ESA}} = \frac{0.21\Omega_6}{0.11\Omega_2 + 0.063\Omega_4}$$ \hspace{1cm} (28)

The Aem/ĀESA values for the present glasses are shown in table 4. The ratios higher than 1 imply that it is possible for amplification to occur. In this respect, Nd³⁺ doped glasses possessing higher value of Ω₆ and lower value of Ω₂ are deemed desirable.

3.3.5. Lifetime

Further from equations (17) and (19), the radiative lifetime of 4F3/2 state can be calculated (table 4). It decreases with an increase in Nd³⁺ ions concentrations (increasing Nd₂O₃ or decreasing Na₂O). Similar results were also reported in previous works [16, 20, 44, 45]. This lifetime reduction of electrons remaining in this state as the Nd³⁺ concentration decreases may be attributed to multiphotons’ transition to lower levels energy state or energy transfer processes to either other Nd³⁺ ions or other ions in glass matrix.
4. Conclusions

Two series of new tellurite glasses, namely, varying and fixed Nd$_2$O$_3$ concentration, have been fabricated and characterized for their density, refractive index, absorption index and dispersion spectra. It is seen that density and refractive index for both series are in opposite manner. For this finding, an atomic arrangement model during glass formation is proposed. Further discussion from Judd-Ofelt analysis revealed that the intensity parameters $\Omega_2$, $\Omega_4$ and $\Omega_6$ increase almost linearly when the Nd$_2$O$_3$ concentration increases. No distinct trend is observed for glass series with fixed Nd$_2$O concentration. From J-O parameters comparison, all glasses are seen to share the same trend as $\Omega_2 < \Omega_4 < \Omega_6$ thus suggesting that they have strong ionicity. This ionicity, however, decreases as the Nd$_2$O$_3$ concentration increases. We have used these parameters to calculate branching ratios ($\beta$). For the first glass series, no distinct relation between $\beta$ and Nd$_2$O$_3$ concentration is observed. For the second series, however, $\beta(F_{3/2} \rightarrow 4I_{9/2})$ increases when the Nd$_2$O$_3$ concentration increases up to 4.0 molar%; for other transitions, the opposite trend occurs. Interestingly, $\beta(F_{3/2} \rightarrow 4I_{9/2})$ and $\chi$ respond to the change in Na$_2$O concentration in the same manner. They increase with an increase in Na$_2$O concentration. On the contrary, branching ratios $\beta(F_{3/2} \rightarrow 4I_{11/2, 13/2, 15/2})$ behave in opposite manner. In this regard, equations explaining these results are derived. Further, we have also calculated the emission to ESA intensity ratio ($A_{em}/A_{ESA}$). The $A_{em}/A_{ESA}$ ratios for all investigated glasses are shown to higher than 1, thus implying that amplification can occur.

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