Zincborophosphate glasses doped with Tb$^{3+}$ ions for green emission– Spectroscopic studies

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Abstract
The present study reports the preparation of various concentrations of Tb$^{3+}$ ions doped zincborophosphate glasses and analysis by XRD, FTIR, optical, emission and decay curve spectras. The effect of borate groups on the phosphate was evidenced by FTIR spectroscopy. The JO intensity parameters was calculated using Judd-Offlet theory. The fluorescence spectra of Tb$^{3+}$ doped zincborophosphate glasses revealed the efficient blue and green emissions due to $^5D_3$ and $^5D_4$ excited levels to $^7F_4$ ground state respectively. The decay curves exhibits single exponential curves for all the Tb$^{3+}$ ion concentrations. Various radiative and fluorescence parameters are calculated using JO intensity parameters. Based on the results obtained in the present study, the Tb$^{3+}$ ions doped zincborophosphate glasses behaves as a efficient laser active materials for high intensity emissions in the green region.

Keywords:
Zincborophosphate glasses, physical properties, optical absorption, photoluminescence, Green emissions, life times.

Introduction
Lanthanide ions (Ln$^{3+}$) like europium (Eu$^{3+}$) and terbium (Tb$^{3+}$) ions have a number of efficient and narrow emission lines in the visible wavelength region whose positions are insensitive to their matrices due to the shielding effect of outer 5S and 5P electrons. Ln$^{3+}$ ions doped glasses, therefore plays an important role in optical applications such as glass lasers and optical fiber amplifiers and also hold the promise for photo chemical hole-burning memory, flat panel display etc., [1]. Among the oxides, ZnO was widely used to improve the chemical stability of phosphate glasses [2]. Participation of Zinc oxide in the glass forming creates low rates of crystallization, decreases the melting point and increases the glass forming ability. The addition of zinc oxide decreases the optical energy gap and increases the refractive index [3]. Zinc oxide can occupy both network forming and modifying positions in the borate network and as a result, the physical properties of such glass exhibit discontinuous changes, when the structural role of the cation changes [4,5]. Borate is the one of the most important glass forming oxide and the pure borate glasses posses low refractive index, high melting point and high phonon energies nearly 1300-1500 cm$^{-1}$. They are highly suitable in designing new optical devices due to their good RE ion solubility, easy preparation on large scale shaping and cost effectiveness [6]. The rare earth doped borate glasses are among those materials which have number of optic and photonic applications [7]. Phosphate glasses are good to be used to fabricate optical fibers due to high transmission in the range of UV-VIS-NIR, low refractive index, dispersion, thermal stability, mechanical resistance and good solubility of high concentration of RE ions. The high solubility of rare earth ions in phosphate glasses enables the construction of short fiber amplifiers and fiber lasers [8].

From the literature, it is quite clear to understand that these glasses when doped with relevant rare earth ions, these optical materials could display encouraging and important optical results. This could lead to them for identification as an optical system of potential functional applications [9]. Borophosphate glasses are promising host materials for optical applications because of their optical properties, low refractive indices, low dispersion and good transparency from the ultraviolet to the near infrared regions [10]. However, RE doped Zincborophospgate glasses are promising materials due to
their mechanical, chemical and thermo optical performance compared to other glasses and lead to more luminescent applications [11].

Terbium is used in many optoelectronic devices such as mass storage with higher capacity, 3D displays, photovoltaic applications and sources of radiation in the visible range [12]. It has been found that Tb$^{3+}$ doped samples show very poor absorption spectrum. Among the rare earths, Tb$^{3+}$ ion is an important ion because the PL spectrum of Tb$^{3+}$ ion gives very intense bands in the ultraviolet and visible regions with an intense green light emission in different hosts which has found applications for phosphors [13] and hence this ion is used for the development of efficient green emitting phosphors and scintillator materials.

The aim of the present study was to investigate the effect of Tb$^{3+}$ concentration on optical properties and the glass forming characteristics of zincborophosphate (ZBP) glasses. The terbium doped zincborophosphate (ZBP) glasses have been prepared by conventional melt quenching technique and investigated by X-ray diffraction analysis (XRD), FTIR spectroscopy, UV-VIS spectroscopy and photoluminescence spectroscopy. The Judd-Ofelt (JO) parameters ($\Omega_{\lambda}$, $\lambda=2$, 4 and 6) have been determined and are used to predict the radiative properties of the excited levels of Tb$^{3+}$ ions. The decay characteristic of $^5D_4$ level of Tb$^{3+}$ ion has also been recorded and analyzed. In addition to these, the density, molar volume and refractive index measurements are determined for these glasses.

**Experimental**

A series of Tb$^{3+}$ glasses were synthesized having the general formula, $40\text{ZnO}+(30-x)\text{B}_2\text{O}_3+30\text{P}_2\text{O}_5+x\text{Tb}_2\text{O}_7$ (0.1 ≤ $x$ ≤ 0.9 mol%). All the chemicals were weighed separately in 15g of each batch, thoroughly mixed and finely powdered using agate mortar and pestle. Each batch of chemical mix was taken into silica crucible and placed in an electric furnace for 45 min at 1150 °C. The melts were then poured onto a pre-heated brass plate and pressed quickly with another plate. The prepared glass samples were transferred to an annealing furnace at 350 °C for 4h in order to eliminate internal mechanical stress. The glasses, thus obtained were transparent and white in colour. The prepared glasses were finely polished in order to study their spectroscopic properties. The ratio of the chemical compositions used to prepare the glass samples are given in Table 1.

**Material Characterization**

The density of the glass samples was measured at room temperature by using the Archimedes principle and xylene is used as an immersion liquid. The optical properties such as refractive index (n) of the prepared glasses were measured using an Abbe’s refractometer at sodium wavelength (589.3 nm) with mono-bromonaphthalene (C$_{10}$H$_7$Br) as the contact liquid.

The parameters Oxygen packing density, Molar volume and Terbium ion concentration are calculated from the density value using the expressions given below.

**Oxygen packing density**

The oxygen packing density is an important parameter in explaining the structure of the glass sample. The oxygen packing density was calculated using the following expression [14],

$$\text{Oxygen packing density (g.atm/L)} = \left(\frac{1000 \times d \times [O]}{M}\right)$$

where $M$ is the molecular weight of the glass composition, $[O]$ is the number of oxygen atoms in the composition and $d$ is the density of the glass sample.

**Molar volume ($V_m$)**

The Molar volume of zinc borophosphate glasses has been estimated by the relation,

$$\text{Molar volume } V_m (cm^3) = \frac{M}{d}$$

where $M$ is the molecular weight of the glass composition and $d$ is the density of the measured glass sample.

**Terbium ion concentration ($N$)**

The concentration of rare earth ion is an important parameter, which affects the laser gain of the host material. The terbium ion concentration ($N$) of zincborophosphate glasses was determined by using the relation,

$$N (ions/cm^3) = \left(\frac{x d N_A}{M_T}\right)$$
where $d$ is the density of the measured glass sample, $N_A$ is the Avagadro’s number, $x$ is the mole fraction of rare-earth oxide and $M_F$ is the average molecular weight of the glass composition.

The obtained values of $N$ are used to calculate the Polaron radius ($r_p$) and inter nuclear distance ($r_i$) using the following relations,

\[
\text{Polaron radius, } r_p (\text{Å}) = (1/2) (\pi/6N)^{1/3} \\
\text{Inter nuclear distance, } r_i (\text{Å}) = (1/N)^{1/3}
\]

The field strength ($F$) around Tb$^{3+}$ ion is calculated using the equation,

\[
F (\text{cm}^2) = (Z/r_p^2)
\]

where $Z$ is the oxidation number of Tb ion.

The molar refraction ($R_M$) was calculated by using the relation,

\[
(n^2 - 1 / n^2 + 2) (M/d) = R_M
\]

where $M$ is the molecular weight, $d$ is the density of glass samples and $n$ is the refractive index. The polarizabilities of these glasses have been estimated by using the Lorentz–Lorentz relation

\[
(n^2 - 1 / n^2 + 2) (V_m) = 4/3 \pi N_A \alpha_e
\]

where $V_m$ is the molar volume, $N_A$ is the Avagadro’s number and $\alpha_e$ is the polarizability. The optical absorption coefficient $\alpha(\nu)$ was calculated using the relation,

\[
\alpha(\nu) = 2.303 (A/d)
\]

where $A$ denotes the absorbance and $d$ is the thickness of the glass sample. Optical energy gap ($E_g$) is calculated for direct and indirect transitions can be calculated by plotting $(\alpha h \nu)^2$ and $(\alpha h \nu)^{1/2}$ as a function of photon energy ($h \nu$).

The amorphous nature of the glasses was confirmed using X-ray diffractometer by employing CuKα radiation. Optical absorption spectra of all the prepared glasses were recorded at room temperature on a UV-VIS-JASCO-V670 spectrophotometer in the wavelength region 250-2400 nm. Fourier Transform infrared spectra were recorded for each concentration of Tb$^{3+}$ ions over the range 400-4000 cm$^{-1}$ on an IR affinity-1S, Shimadzu spectrometer. Photoluminescence measurements were made using a fluorescence spectrophotometer (Hitachi 650-10s). For the lifetime measurements, decay curves were measured by using a mechanical chopper with a multi channel scalar within the range of 2μs-2s was employed and the data were collected to a personal computer which records and averages the signals at room temperature.

**Results and discussion**

**Density and Molar volume**

Density is an effective tool to explore the degree of structural compactness, modification of the geometrical configurations of the glass network, change in coordination and the variation of the dimension of the interstitial holes [15]. The density, refractive index and some other physical properties such as oxygen packing density, molar volume ($V_m$), Tb$^{3+}$ ion concentration ($N$), optical energy band gap ($E_g$), inter nuclear distance ($r_i$), Polaron radius ($r_p$), field strength ($F$), polarizability ($\alpha_e$), reflection loss ($R$) as well as optical dielectric constant ($\varepsilon$) for the present glasses are calculated using the above relations. The calculated values of Tb$^{3+}$ (0.9 mol%): ZB glass is presented in Table 2.

The variation of density ($d$) and average molecular weight ($M$) as a function of Tb$_4$O$_7$ (mol%) content are shown in Fig.1. It can be observed that, the density ($d$) and average molecular weight ($M$) of the present glass system increases with increasing Tb$^{3+}$ ion concentration. Eraiah et al.,[16] proposed that the addition of a small amount of Tb$_4$O$_7$ into the glass network may resist the creation of non-bridging oxygen. This will result the increase in density of the glass system.

The molar volume is an important parameter which describes the structure of glass network and arrangements of building units, since it deals directly with the special structure of the oxygen network. The molar volume also indicates the spatial distribution of the oxygen atoms in the glass network [17]. Fig.2 shows the variation of molar volume as well as oxygen packing density (OPD) with Tb$_3$O$_7$ (mol%) content. From the Fig.2, It can be observed that, with increasing terbium ion concentration, the oxygen packing density decreases and this causes the increase in molar volume. From this we can conclude that, the molar volume follows the opposite trend to that of OPD [18].
XRD analysis

Fig. 3 shows the typical XRD patterns for the undoped (ZBP) and Tb$^{3+}$ (0.9 mol%) ZBP glass systems. The XRD spectra exhibit broad scattering at lower angles, which is a characteristic of long range structural disorder indicating the amorphous nature of the present glass.

FTIR spectra analysis

The study of the structure is very important for the investigation of the glass properties. IR transmitting glasses can be highly functional material in terms of field structures and also IR spectra of materials may help to get the idea of the nature of vibrations in a disordered system [19]. FTIR spectra of 40ZnO+(30-x)B$_2$O$_3$+30P$_2$O$_5$+xTb$_2$O$_7$ (0≤x≤0.9 mol%) glasses were obtained using a KBr pellet technique in the range 400-4000 cm$^{-1}$ and are presented in Fig. 4. The obtained bands and their corresponding assignments are listed in Table 3.

From the Fig. 4, it can be observed that, the main absorption bands of the pure zincborophosphate glass occurs around the wave number 428, 514, 848, 1055, 1170, 1321, 1456, and 1602 cm$^{-1}$. The absorption bands centered at ~428 cm$^{-1}$ and 648 cm$^{-1}$ are attributed to the ZnO stretching modes [20]. The band observed at 514 cm$^{-1}$ can be assigned to the bending vibration of P-O bond [21] and this can overlap with B-O-B bending vibrations [22]. The small peak at 750 cm$^{-1}$ is attributed to the symmetric stretching vibrations of P-O-P rings. The addition of B$_2$O$_3$ changes the structure of phosphate in the present glass and due to this the band at 750 cm$^{-1}$ shifts to 848 cm$^{-1}$. The absorption band around at 847-880 cm$^{-1}$ could be attributed to symmetric stretching vibrations of B-O bonds in BO$_3$ units [23] and this can be superimposed with the different metaphosphate groups [24].

The band at 1055 cm$^{-1}$ can be attributed to asymmetric stretching of P-O-P groups [24] and overlaps with B-O stretching vibrations in BO$_4$ units from tri-(B$_2$O$_3$), tetra-(B$_8$ O$_{13}$)$^2$) and penta-borate(B$_2$O$_6$) groups. The band at 1170-1200 cm$^{-1}$ could be attributed to symmetric stretching vibration of P=O and overlaps with stretching B-O bonds in BO$_3$ units from meta and ortho-borate groups [26]. The band at 1321 cm$^{-1}$ could be attributed to zirconate vibrations. The band at 1456-1481 cm$^{-1}$ could be attributed to B-O bond vibrations in BO$_3$ units [27]. The bands around 1600 cm$^{-1}$ could be attributed to OH, BOH and POH vibrations.

On adding different concentrations of Tb$_4$O$_7$ to the zincborophosphate glasses, it can be observed that a new band appears at 418 cm$^{-1}$ which can be attributed to Tb-O absorption band [28].

Optical absorption studies

The optical absorption spectrum of Terbium doped zincborophosphate glasses was recorded at room temperature in the wavelength region 225-2400 nm. The spectrum of 0.9 mol% Tb$_2$O$_7$ doped ZBP glass is shown in Fig. 5(a) & (b) and the transitions corresponds to the ground state $^7F_0$ of Tb$^{3+}$ ions. All the spectra of different mole % of Tb$^{3+}$ ions doped ZBP glasses are similar in shape with a small difference only in absorption and hence the highest concentration of Tb$^{3+}$ ions doped ZBP glass is shown in Fig. 5 as a remarkable spectrum. From the absorption spectrum shown in Fig. 5(a), it is clear that the bands in the UV-Vis region corresponds to $^7F_0$→$^5D_2$, $^5D_3$ and $^5D_4$ transitions. The bands in the NIR region corresponds to $^7F_0$→$^7F_2$, $^7F_4$ and $^7F_6$ transitions respectively. The assignment of these absorption transitions has done based on the earlier literature [29]. All these transitions are originating from the induced electric dipole interactions obeying the selection rules $\Delta S = 0$, $\Delta L \leq 6$, $|\Delta J| \leq 6$ [30].

From the Fig. 5(b), it is observed that, the transitions in the NIR region are found to be more intense than the transitions in the UV region because of the forbidden nature of 4f-4f transitions [31]. The spectral intensities for the observed absorption transitions are expressed in terms of oscillator strengths ($f_{exp}$) and is calculated using the expression [32],

$$f_{exp} = 2.303(mc^2/N_A\pi e^2) \int \epsilon(v)dv$$

where $m$ and $e$ are the mass and charge of an electron, $c$ is the velocity of light, $\int \epsilon(v)dv$ is the integral absorption coefficient corresponding to the mean energy $\nu$ (cm$^{-1}$) of the absorption band which can be computed from the measured absorbance, concentration of the Tb$^{3+}$ ions (mol/lit) and the thickness of the sample. The JO intensity parameter values are calculated using the experimental oscillator strength.
values ($f_{exp}$) and the reduced matrix elements by the least square fit method. The calculated oscillator strength ($f_{cal}$) of electric dipole transition from the initial state $\Psi I$ to the final state $\Psi J$ within 4f$^8$ configuration can be determined by the least square fit procedure using $f_{exp}$ values and JO intensity parameters $\Omega_h (\lambda = 2,4,6)$ from the following equation [33].

$$f_{cal} = [8\pi^2 mcv / 3h(2J+1)] [(n^2+2)^2 / 9n] \sum \Omega_h (\Psi I||U^2||\Psi J)^2 \quad \lambda = 2,4,6$$

where $||U^2||$ are the squared reduced matrix elements of the unit tensor operator, $(n^2+2)^2 / 9n$ is the local field correction factor for the electric dipole transition and $n$ is the refractive index. The small mean square deviation of 0.036×10$^{-6}$ indicates the good fit between $f_{exp}$ and $f_{cal}$ values. Table 4, represents the absorption band positions and their transitions, oscillator strengths of Tb$^{3+}$ (0.9 mol%):ZBP glass.

The JO parameters thus obtained for the Tb$^{3+}$ (0.9 mol%):ZBP glass are presented in Table 5. The JO parameters for the present investigation follow the trend $\Omega_2 > \Omega_6 > \Omega_4$. The order of $\Omega_h$ parameters of Tb$^{3+}$ (0.9 mol%) ion in the studied glass is well with the trends available in various other glass matrices [34,35]. Different coordination sites are occupied by the rare earth ions with non-centro symmetric potential which contribute mainly to $\Omega_2$. The reason for this variation sites are due to the influence of dielectric media, the rare earth ion environment and nephelauxetic effect. These vibrations in the sites with non-centro symmetric potential cause changes in $\Omega_2$ value. Generally, $\Omega_2$ parameter is related to the covalence and structural changes in the vicinity of the Tb$^{3+}$ ion. $\Omega_4$ and $\Omega_6$ are related to the long-range effects and are strongly influenced by the vibrational levels associated with the central rare earth ions bound to the ligand atoms. The higher magnitude of $\Omega_2$ for the present glass indicates stronger field and lower the symmetry around the rare-earth ions. And also the high value of $\Omega_2$ parameter indicates the higher degree of covalence of rare earth oxygen bond when compared to the other hosts [34,35]. The sites occupied by Tb$^{3+}$ (0.9 mol%):ZBP glass posses lower symmetry and greater degree of covalence for Tb-O bond. Based on these intensity parameters, the ZBP:Tb glasses exhibit better luminescence properties.

From the optical absorption analysis the optical energy bandgap ($E_g$) is obtained by extrapolating of the linear region to meet $hv$ axis at $(ahv)^2 = 0$ for direct transition and $(ahv)^{1/2} = 0$ for indirect transition. Fig. 6 represents tauc’s plot of the $(ahv)^2$ and $(ahv)^{1/2}$ as a function of $hv$ for (0.9 mol%)Tb$^{3+}$:ZBP glass and obtained values are presented in Table 2.

**Photoluminescence analysis of Tb$^{3+}$: ZBP glasses**

**Excitation spectra**

The excitation spectra of Tb$^{3+}$: ZBP glasses were obtained by monitoring with bright green emission and strongest band $^3D_{4} \rightarrow ^5F_3$ at an emission wavelength of 545 nm and is shown in Fig.7. From the Fig.7, it is observed that, the excitation spectra is combination of two parts: the intense broad band in the range 200-300 nm are attributed to the spin allowed transitions from 4f$^8$– 4f$^7$5d (f-d transition) of Tb$^{3+}$, and the intensity of small bands which are in the long wavelength region from 300-400 nm represents the 4f-4f transition (f-f transition) of Tb$^{3+}$. The excitation peaks were observed at 285, 304, 319, 341, 370, 378 and 485 nm corresponding to $^7F_0 \rightarrow ^5F_5$, $^7F_0 \rightarrow ^5H_6$, $^7F_0 \rightarrow ^5H_7$, $^7F_0 \rightarrow ^5D_2$, $^7F_0 \rightarrow ^5L_6$, $^7F_0 \rightarrow ^5L_{10}$, $^7F_0 \rightarrow ^5G_6$ and $^7F_0 \rightarrow ^5D_4$ transitions respectively [36,37]. Among all the transitions observed in the excitation spectra, the transition $^7F_0 \rightarrow ^5G_6$ (378 nm) shows highest intensity for all the Tb$^{3+}$: ZBP glasses.

**Emission spectra**

Fig.8. shows the emission spectra recorded for all the concentrations of Tb$^{3+}$: ZBP glasses by exciting them with ($^7F_0 \rightarrow ^5G_6$) 378 nm wavelength. The emission spectra consists of two parts: Tb$^{3+}$: ZBP glasses show weak blue emission in the wavelength range 400-460 nm and strong green emission in the wavelength range 475-650 nm. From the Fig.8, it is observed that, the $^3D_{3} \rightarrow ^1F_2$ transitions are responsible for blue emission below 460 nm and $^3D_{4} \rightarrow ^1F_2$ transitions are responsible for green emission above 480 nm. The peaks arising from blue region are at 414, 437 and 459 nm corresponding
to transitions $^5\text{D}_3\rightarrow^7\text{F}_5$, $^5\text{D}_3\rightarrow^7\text{F}_4$ and $^5\text{D}_3\rightarrow^7\text{F}_3$ respectively. The peaks originating from green emission region from $^5\text{D}_4$ metastable state are 490, 545, 586 and 622 nm corresponding to the transitions $^5\text{D}_4\rightarrow^7\text{F}_6$, $^5\text{D}_4\rightarrow^7\text{F}_5$, $^5\text{D}_4\rightarrow^7\text{F}_4$ and $^5\text{D}_4\rightarrow^7\text{F}_3$ respectively. Among all the green emission transitions observed from the spectrum, the transition $^5\text{D}_4\rightarrow^7\text{F}_4$ (545 nm) is prominent one which indicates that the spectrum is dominated by the hypersensitive transition from $^5\text{D}_4$ to the $^7\text{F}_4$ manifolds and obeying the selection rule $\Delta J = \pm 1$. This hypersensitive transition is the true finger print of the characteristic emission lines corresponding to the $4f^6 – 4f^4$ transition of terbium ion, which is induced by the change in chemical environment between host and the terbium metal ion [38]. Hence it can provide information about the chemical environment of Tb$^{3+}$ ion [39]. From the spectrum, it is observed that, with increasing Tb$_4$O$_7$ concentration the intensity of transition from $^5\text{D}_3\rightarrow^7\text{F}_3$ decreases where as the intensity of transition from $^5\text{D}_3\rightarrow^7\text{F}_1$ increases due to cross-relaxation between $^5\text{D}_3$ and $^5\text{D}_4$ [40].

The energy level diagram for terbium doped ZBP glasses is shown in Fig.9. When Tb$^{3+}$ ion is excited to $^5\text{D}_3$ or a higher level causes the radiative transition from $^5\text{D}_3$ to $^7\text{F}_1$ ($J$=0-6) which results in series of $^5\text{D}_4$ emission in the blue region, while that from $^5\text{D}_3\rightarrow^7\text{F}_1$ yields another series of $^5\text{D}_4$ emission in the green region. Since the energy gap between $^5\text{D}_3$ and $^5\text{D}_4$ is small and matches with that between $^7\text{F}_0$ and $^7\text{F}_1$ levels. If an excited Tb$^{3+}$ ion in $^5\text{D}_3$ metastable state relaxes non-radiatively to $^5\text{D}_4$ state by releasing the energy to resonantly excite the nearest unexcited Tb$^{3+}$ ion (energy acceptor) from $^7\text{F}_6$ (ground state) to $^7\text{F}_0$ state. This process is called resonant energy transfer, whose probability is proportional to $(R/R_0)^6$. Where R stands for inter-ionic distance and $R_0$ stands for the critical distance. The value of $R_0$ for typical multipolar interaction is in the range of 10-20 Å and s=8 for dipole-dipole and s=6 for dipole-quadrupole interactions.

Radiative properties

The radiative properties such as spontaneous transition probability ($A_R$), radiative lifetime ($\tau_R$) and radiative branching ratio ($\beta_R$) for the $(^5\text{D}_3, ^5\text{D}_4)\rightarrow^7\text{F}_1$ transitions are determined using JO intensity parameters and are presented in Table 6. The necessary equations used to calculate above said properties are taken from C.Madhukar Reddy et al.,[29].

From the Table 6, it is observed that, $^5\text{D}_4\rightarrow^7\text{F}_5$ transition show highest radiative transition rate compared to other emission transitions. The radiative branching ratio ($\beta_R$) defines luminescence efficiency of transition and also characterizes the probability of attaining stimulated emission cross-section. Usually an emission transition having branching ratio $\geq 0.50$ can emit laser radiation more efficiently. For the present Tb$^{3+}$ (0.9 mol%):ZBP glass, the radiative and measured branching ratio ($\beta_R$ and $\beta_m$) for $^5\text{D}_4\rightarrow^7\text{F}_5$ transition are $\geq 0.50$ tells about the lasing potentiality of this transition. The measured branching ratios ($\beta_m$) have been calculated from the relative areas under the emission peaks of emission spectra. The other lasing parameters such as peak stimulated emission cross-section ($\sigma_e$), optical gain parameter ($\sigma_e \times \tau_m$), effective band width ($\Delta \lambda_g$) and gain band width ($\sigma_e \times \Delta \lambda_p$) are calculated and are presented in Table 7. The stimulated emission cross-section ($\sigma_e$) value is found to be higher for the $^5\text{D}_4\rightarrow^7\text{F}_5$ transition compared to other excited transitions for the present glass. Among the prepared Tb$^{3+}$: ZBP glasses, Tb$^{3+}$ (0.9 mol%) :ZBP glass is found to be exhibiting intense green emission at 545 nm which is used for phosphor of fluorescent light.

Decay rate analysis

To understand the energy transfer mechanism and luminescence quenching, decay analysis is used. Fig.9 shows the decay rates for the $^5\text{D}_4$ level of Tb$^{3+}$ ion for different concentrations in the zincborophosphate glasses under 378 nm excitation. Due to weak luminescence intensity of $^5\text{D}_3\rightarrow^7\text{F}_{5,4,3}$ transitions, the decay rates for $^5\text{D}_3$ level are not reported. From the Fig.10, it is noticed that, the decay rates exhibit single exponential nature for all the concentrations of Tb$^{3+}$: ZBP glasses. The measured lifetime ($\tau_m$) values for the $^5\text{D}_4$ level are 2.15, 1.95, 1.89, 1.64 and 1.45 ms for 0.1, 0.3, 0.5, 0.7 and 0.9 mol% of Tb$^{3+}$ and are presented in Table 8. On increasing Tb$^{3+}$ ion concentration the measured lifetime ($\tau_m$) values decreases due to resonant energy transfer. The quantum efficiency ($\eta$)
which is used to measure the efficiency of the laser materials and also used to control the performance of the material is calculated using \( \eta = \left( \frac{\tau_m}{\tau_R} \right) \times 100\% \) for the \( ^5D_4 \) level and are given in Table 8. From Table 8, it can be observed that 0.1 concentration shows the highest quantum efficiency (87%) for Tb\(^{3+}\):ZBP glass.

Conclusions

A series of Tb\(^{3+}\) doped zincborophosphate glasses have been successfully prepared by a melt-quenching method. The prepared glasses were recorded and analyzed by using XRD, FTIR, optical, photoluminescence and decay curves. The FTIR studies reveal the presence of BO\(_3\) and BO\(_4\) units due to tri, tetra and penta borate groups in the present glass system. From the analysis of optical and photoluminescence studies, the JO intensity parameters, radiative transition parameters and other parameters are calculated and is found to be comparable with other reported values. The photoluminescence studies reveal the effect of Tb\(^{3+}\) ion concentration on ZBP glass system showing the increase in intensity of peaks originating from \( ^3D_4 \) state. The transition \( ^3D_4 \to ^7F_5 \) (545 nm) of Tb\(^{3+}\) ions in ZBP glass gives the intense green emission. For all the concentrations of Tb\(^{3+}\) ions, the decay curves shows the single exponential curves. The decrease in lifetimes with the increase in concentration of Tb\(^{3+}\) ions may be due to the resonant energy transfer. Based on the studied properties and the reasonable high quantum efficiency of 87% for \( ^3D_4 \to ^7F_5 \) transition, the ZBP:Tb\(^{3+}\) glass system can be used as green emission laser at 545 nm.

References


Table 1.
Nominal chemical compositions of Tb$^{3+}$ (mol%) doped ZBP glasses.

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<tr>
<th>Glass Code</th>
<th>ZnO</th>
<th>B$_2$O$_3$</th>
<th>P$_2$O$_5$</th>
<th>Tb$_4$O$_7$</th>
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<td>ZBP</td>
<td>40</td>
<td>30</td>
<td>30</td>
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<tr>
<td>ZBP:Tb(0.1)</td>
<td>40</td>
<td>29.9</td>
<td>30</td>
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<tr>
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<td>29.5</td>
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<tr>
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<td>40</td>
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<tr>
<td>ZBP:Tb(0.9)</td>
<td>40</td>
<td>29.1</td>
<td>30</td>
<td>0.9</td>
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Table 2.
Measured and calculated physical properties of 0.9 mol% Tb$^{3+}$ doped ZBP glass system.

<table>
<thead>
<tr>
<th>Physical parameters</th>
<th>calculated value</th>
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<td>Density (gm/cc)</td>
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<tr>
<td>Molar volume $V_m$ (cm$^3$)</td>
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<tr>
<td>Refractive index (n)</td>
<td>1.547</td>
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<tr>
<td>Concentration of Tb$^{3+}$ ions (10$^{20}$ ions/cc)</td>
<td>1.681</td>
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<tr>
<td>Concentration of Tb$^{3+}$ ions (mol/l)</td>
<td>0.279</td>
</tr>
<tr>
<td>Polar radius $\gamma_p$ (Å)</td>
<td>7.301</td>
</tr>
<tr>
<td>Inter nuclear distance $\gamma_i$ (Å)</td>
<td>8.410</td>
</tr>
<tr>
<td>Field strength $F$ (10$^{14}$) cm$^{-2}$</td>
<td>7.504</td>
</tr>
<tr>
<td>Polarizability $\alpha_e$ (10$^{-24}$ cm$^3$)</td>
<td>4.054</td>
</tr>
<tr>
<td>Molar Refraction $R_m$ (cm$^3$)</td>
<td>10.221</td>
</tr>
<tr>
<td>Dielectric constant ($\varepsilon$)</td>
<td>2.393</td>
</tr>
<tr>
<td>Reflection loss R (%)</td>
<td>4.611</td>
</tr>
<tr>
<td>Average molecular weight (g)</td>
<td>102.12</td>
</tr>
<tr>
<td>Oxygen packing density (g-atm/Lt)</td>
<td>87.97</td>
</tr>
<tr>
<td>Direct band gap (eV)</td>
<td>4.385</td>
</tr>
<tr>
<td>Indirect band gap (eV)</td>
<td>3.305</td>
</tr>
</tbody>
</table>

Table 3.
Vibrational frequencies and their assignment for FTIR spectra of pure ZBP and Tb$^{3+}$ (0.1, 0.3, 0.5, 0.7 & 0.9 mol%) : ZBP glasses.

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Pure</th>
<th>0.1</th>
<th>0.3</th>
<th>0.5</th>
<th>0.7</th>
<th>0.9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tb-O absorption band</td>
<td>------</td>
<td>418</td>
<td>418</td>
<td>418</td>
<td>418</td>
<td>418</td>
</tr>
<tr>
<td>ZnO$_4$ structural units</td>
<td>428</td>
<td>428</td>
<td>430</td>
<td>430</td>
<td>432</td>
<td>435</td>
</tr>
<tr>
<td>Bending vibration of P-O&amp;BiO-B</td>
<td>514</td>
<td>514</td>
<td>516</td>
<td>514</td>
<td>511</td>
<td>516</td>
</tr>
<tr>
<td>B-O symmetric stretching of vibrations of BO$_4$ units, metaphosphate groups</td>
<td>848</td>
<td>856</td>
<td>835</td>
<td>850</td>
<td>846</td>
<td>842</td>
</tr>
<tr>
<td>Asymmetric stretching of P-O-P groups, stretching vibration of B-O bonds in BO$_4$ units from tri-, tetra-, and penta-borate glasses</td>
<td>1055</td>
<td>1066</td>
<td>1047</td>
<td>1060</td>
<td>1076</td>
<td>1049</td>
</tr>
<tr>
<td>Symmetric stretching vibration of P=O, B-O bonds in BO$_3$ units from meta- and ortho-borate groups</td>
<td>1170</td>
<td>1197</td>
<td>1199</td>
<td>1201</td>
<td>1207</td>
<td>1209</td>
</tr>
<tr>
<td>Zinc borate vibrations</td>
<td>1321</td>
<td>1323</td>
<td>1327</td>
<td>1328</td>
<td>1327</td>
<td>1340</td>
</tr>
<tr>
<td>B-O stretching vibration of BO$_3$ units (OH), POH and BOH vibrations</td>
<td>1456</td>
<td>1481</td>
<td>1485</td>
<td>1481</td>
<td>1489</td>
<td>1481</td>
</tr>
<tr>
<td></td>
<td>1602</td>
<td>1614</td>
<td>1622</td>
<td>1624</td>
<td>1628</td>
<td>1639</td>
</tr>
</tbody>
</table>
Table 4.
Absorption transitions, their energies, experimental and calculated oscillator strengths ($\times 10^{-6}$) for Tb$^{3+}$ (0.9 mol%): ZBP glass system.

<table>
<thead>
<tr>
<th>Transition $^7F_6 \rightarrow$</th>
<th>Energy (eV cm$^{-1}$)</th>
<th>$f_{exp}$</th>
<th>$f_{cal}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^5D_2$</td>
<td>31545</td>
<td>0.014</td>
<td>0.008</td>
</tr>
<tr>
<td>$^5D_3$</td>
<td>26525</td>
<td>0.036</td>
<td>0.013</td>
</tr>
<tr>
<td>$^5D_4$</td>
<td>20746</td>
<td>0.038</td>
<td>0.038</td>
</tr>
<tr>
<td>$^7F_1$</td>
<td>5437</td>
<td>0.639</td>
<td>0.707</td>
</tr>
<tr>
<td>$^7F_2$</td>
<td>5249</td>
<td>0.946</td>
<td>0.882</td>
</tr>
<tr>
<td>$^7F_3$</td>
<td>2191</td>
<td>0.765</td>
<td>0.011</td>
</tr>
</tbody>
</table>

$\delta_{ms} = \pm 0.036 \times 10^{-6}$

Table 5.
Comparison of JO intensity parameters ($\times 10^{-20}$ cm$^2$), their trends for Tb$^{3+}$ (0.9 mol%) ions in ZBP glass.

<table>
<thead>
<tr>
<th>Glass system</th>
<th>$\Omega_2$</th>
<th>$\Omega_4$</th>
<th>$\Omega_6$</th>
<th>Trend</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZBPTb [present glass]</td>
<td>11.266</td>
<td>1.027</td>
<td>3.008</td>
<td>$\Omega_2 &gt; \Omega_6 &gt; \Omega_4$</td>
</tr>
<tr>
<td>PTBTb [34]</td>
<td>11.98</td>
<td>2.87</td>
<td>10.51</td>
<td>$\Omega_2 &gt; \Omega_6 &gt; \Omega_4$</td>
</tr>
<tr>
<td>LBTA [35]</td>
<td>13.23</td>
<td>1.23</td>
<td>2.96</td>
<td>$\Omega_2 &gt; \Omega_6 &gt; \Omega_4$</td>
</tr>
</tbody>
</table>

Table 6.
Peak emission wavelength ($\lambda_p$), radiative transition probability ($A_R$, s$^{-1}$), total radiative transition probability ($A_T$, s$^{-1}$), radiative lifetime ($\tau_R$, ms), radiative branching ratios ($\beta_R$) of $^5D_3 \rightarrow ^7F_J$ and $^5D_4 \rightarrow ^7F_J$ transitions for 0.9 mol% of Tb$^{3+}$ doped ZBP glass.

<table>
<thead>
<tr>
<th>Transition $^5D_3 \rightarrow ^7F_J$</th>
<th>$\lambda_p$ (nm)</th>
<th>$A_R$</th>
<th>$\beta_R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^5D_3 \rightarrow ^7F_3$</td>
<td>414</td>
<td>48.86</td>
<td>0.22</td>
</tr>
<tr>
<td>$^5D_3 \rightarrow ^7F_4$</td>
<td>437</td>
<td>259.29</td>
<td>0.68</td>
</tr>
<tr>
<td>$^5D_3 \rightarrow ^7F_5$</td>
<td>459</td>
<td>29.93</td>
<td>0.08</td>
</tr>
</tbody>
</table>

$A_T = 338.08$ s$^{-1}$; $\tau_R = 2.95$ ms

<table>
<thead>
<tr>
<th>Transition $^5D_4 \rightarrow ^7F_J$</th>
<th>$\lambda_p$ (nm)</th>
<th>$A_R$</th>
<th>$\beta_R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^5D_4 \rightarrow ^7F_6$</td>
<td>489</td>
<td>38</td>
<td>0.09</td>
</tr>
<tr>
<td>$^5D_4 \rightarrow ^7F_5$</td>
<td>545</td>
<td>315</td>
<td>0.72</td>
</tr>
<tr>
<td>$^5D_4 \rightarrow ^7F_4$</td>
<td>586</td>
<td>12</td>
<td>0.04</td>
</tr>
<tr>
<td>$^5D_4 \rightarrow ^7F_3$</td>
<td>622</td>
<td>40</td>
<td>0.07</td>
</tr>
</tbody>
</table>

$A_T = 405$ s$^{-1}$; $\tau_R = 2.46$ ms

Table 7.
Peak emission wavelength ($\lambda_p$), effective line width ($\Delta \lambda_p$, nm), stimulated emission cross-section ($\sigma_e \times 10^{22}$), gain band width ($\sigma_e (\lambda_p) \times 10^{-27}$ cm$^3$), optical gain ($\sigma_e \times \tau_m \times 10^{22}$) and measured branching ratios ($\beta_m$) for $^5D_4 \rightarrow ^7F_J$ transitions in 0.9 mol% of Tb$^{3+}$ doped ZBP glass.
Table 8.
Variation of lifetime ($\tau_m$, ms) and quantum efficiency ($\eta$ %) for $^5D_4 \rightarrow ^7F_J$ transition in different mol% of Tb$^{3+}$ doped ZBP glasses.

<table>
<thead>
<tr>
<th>Concentration (mol%)</th>
<th>$\tau_m$ (ms)</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>2.15</td>
<td>87</td>
</tr>
<tr>
<td>0.3</td>
<td>1.95</td>
<td>79</td>
</tr>
<tr>
<td>0.5</td>
<td>1.89</td>
<td>76</td>
</tr>
<tr>
<td>0.7</td>
<td>1.64</td>
<td>66</td>
</tr>
<tr>
<td>0.9</td>
<td>1.45</td>
<td>58</td>
</tr>
</tbody>
</table>

Fig.1:

Fig.2:
Fig. 3:

![Graph showing intensity vs. 2θ for ZBP:Tb and Undoped samples.](image)

Fig. 4:

![Graph showing transmittance % vs. wavenumber for pure and doped samples.](image)

Fig. 5:

![Graph showing absorbance vs. wavelength for different D bands.](image)
Fig 6:

![Graph with absorbance (a.u) vs. wavelength (nm)](image)

Fig.7:

![Graph with intensity (a.u) vs. wavelength (nm)](image)
Fig. 8: 

![Graph showing intensity vs wavelength for different transitions. 

Fig. 9: 

![Diagram of energy levels and transitions for Tb^{3+}. 

Fig. 10: 

![Plot showing intensity decay over time with different concentrations.
Captions for figures:

**Fig. 1:** The variation of density and average molecular weight as a function of Tb$_4$O$_7$ content in the ZBP glasses.

**Fig. 2:** The variation of molar volume and oxygen packing density as a function of Tb$_4$O$_7$ content in the ZBP glasses.

**Fig. 3:** XRD pattern of pure and Tb$^{3+}$ (0.9 mol%) doped ZBP glasses.

**Fig. 4:** The FTIR spectra of pure and Tb$^{3+}$ doped ZBP glasses.

**Fig. 5:** Optical absorption spectrum of ZBP: Tb$^{3+}$ (0.9 mol%) glass in the (a) UV-VIS and (b) NIR region.

**Fig. 6:** The variation of direct and indirect band gaps as a function of $h\nu$ for ZBP:Tb$^{3+}$ (0.9 mol%) glass.

**Fig. 7:** Excitation spectra of Tb$^{3+}$: ZBP glasses.

**Fig. 8:** The emission spectra of the ZBP: Tb$^{3+}$ glasses recorded in the spectral region 500-750 nm by exciting the samples with 378 nm.

**Fig. 9:** Partial energy level diagram for Tb$^{3+}$ ions in ZBP glasses.

**Fig. 10:** The decay plots of ZBP: Tb$^{3+}$ glasses.