Luminescence and decay characteristics of Tb$^{3+}$-doped fluorophosphate glasses

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ABSTRACT

Tb$^{3+}$-doped fluorophosphate glasses with the composition of P$_2$O$_5$–K$_2$O–SrF$_2$–Al$_2$O$_3$–x Tb$_2$O$_3$ (where x = 0.1, 0.5, 1.0, 2.0 and 4.0 mol%) were prepared by a conventional high temperature melt quenching technique and characterized through absorption, emission, excitation and decay measurements. From the emission studies, a strong green emission at around 546 nm was observed, which corresponds to the $^5D_4 \rightarrow ^7F_2$ transition of Tb$^{3+}$ ion. Green/blue intensity ratios (I$\text{green}/I\text{blue}$) were evaluated as a function of Tb$^{3+}$ concentration and vice versa. Higher I$\text{green}/I\text{blue}$ intensity ratio confirms the higher covalency between Tb–O bond and higher asymmetry around the Tb$^{3+}$ ions in the present fluorophosphate glasses. The decay curves for the $^5D_4$ level of Tb$^{3+}$ were measured and found that they exhibited single exponential nature irrespective to the dopant concentration. The experimental lifetime was determined using single exponential fitting and found that it increased from 2.65 to 2.95 ms when Tb$^{3+}$ concentration increased from 0.1 mol% to 4.0 mol%. The derived properties were compared to the other Tb$^{3+}$-doped glasses in order to see the potentiality of the material for visible laser gain media at 546 nm.

1. Introduction

Recently, visible fiber lasers especially in the green wavelength region have been attracted for the application in medical treatment, optical data storage and visible light communication technologies [1]. In the past decades, Er$^{3+}$-doped fluoride glass fibers have been studied for the development of green fiber laser upon either 800 or 980 nm laser diodes (LDs) through upconversion luminescence processes [2]. As is well known, upconversion processes make more energy loss due to the non-radiative relaxation processes; on the other hand, high pump power is required to get the laser output. In view of the above facts/importance, it has been essential to see the alternative process to get the visible laser output with high quantum efficiency. Oxide glasses activated by Tb$^{3+}$ have demonstrated to be attractive candidates for gain media in the green region around 546 nm, since the $^5D_4 \rightarrow ^7F_2$ transition of Tb$^{3+}$ ion provides a four-level laser system with a lower threshold pump power compared with that of Er$^{3+}$ ions [3–7]. Moreover, experimental branching ratios of the 546 nm band are usually more than 50%, which makes the Tb$^{3+}$ a promising ion for green laser applications. The green laser operation based on $^5D_4 \rightarrow ^7F_2$ transition of Tb$^{3+}$ was first reported in 1967 [8,9]. Furthermore, GaN-related LDs from ultraviolet to blue wavelength region have been available on the market in watt level, which promotes the rapid development of visible fiber lasers [10–13].

Yamashita et al. reported green laser emission from Tb$^{3+}$-doped ZBLAN glass fiber pumped by 488 nm laser diode [11]. However, the fibers used were all fluoride glass fibers, which are not stable as exposed in air. In addition, fluoride glasses are very difficult to be drawn into fibers because they easily crystallize during preform preparation and fiber drawing processes. Therefore, oxide-based glasses such as silicates, borates, tellurites and phosphates have been attracted due to their much higher mechanical, chemical and thermal stability than fluorides, and usually allow fairly high concentrations of rare earth (RE) dopants. However, still these glasses present high phonon energies and OH species at a level that can introduce high losses to the RE’s quantum efficiencies via non-radiative decay processes. On those bases, proper combinations of fluoride and oxide precursors can result in glasses that possess the merits of both types of glasses. Fluorophosphate glasses are promising materials as they possess the attributes of both fluoride and phosphate glasses such as large-scale manufacturability, melting techniques, low nonlinear refractive index, low OH contents, high solubility for rare-earth ions, wide transmission range, broad absorption and emission bands, long fluorescence lifetime and so on [14,15].

In this study, the optical and luminescence properties of Tb$^{3+}$-doped fluorophosphate glasses for different Tb$^{3+}$ concentrations were investigated through absorption, emission, excitation and decay
measurements to assess their potentiality as a gain media at 546 nm. The $I_{C}/I_{B}$ and $I_{y}/I_{C}$ intensity ratios and lifetime of $^5D_4 \rightarrow ^7F_6$ transition were evaluated and compared with the other Tb$^{3+}$-doped host matrices.

2. Experimental details

The fluorophosphate glasses with the chemical composition of 44 P$_2$O$_5$-17 K$_2$O-(29-x) SrF$_2$-9 Al$_2$O$_3$-x Tb$_2$O$_3$, where $x$ = 0.1, 0.5, 1.0, 2.0 and 4.0 mol%, were prepared by a melt quenching method. Each 20 g of homogeneously mixed batches were taken in platinum crucible and melted in an electric furnace at 1150°C for 1 h and later poured onto a brass mold that was preheated at 380°C. Further, the obtained glasses were annealed at 380°C for 12 h in order to relieve thermal stress and strain inside the glass samples and then slowly cooled down to the room temperature. The prepared glass samples were cut and polished for optical and luminescence measurements.

The physical parameters were calculated for 1.0 mol% Tb$^{3+}$-doped fluorophosphate glass. The density was measured by Archimedes’ method using water as an immersion liquid and found to be 2.890 g/cm$^3$. The refractive index was determined to be 1.576 at sodium wavelength (589.3 nm) using Abbe refractometer with 1-bromonaphthalene as contact liquid. The concentration was calculated to be $2.778 \times 10^{20}$ ions/cm$^3$. Luminescence, excitation and decay curves of Tb$^{3+}$-doped glasses were recorded using Jobin-Yvon Fluorolog-3 spectrofluorimeter with Xe arc lamp as an excitation source (450 W). All these measurements were carried out at room temperature.

3. Results and discussion

3.1. Absorption, emission and decay properties

It is well known that the optical properties of RE ions depend on their local structure (bonding between RE and ligand, field strength, and symmetry in the vicinity of RE ions) in which the ions are incorporated. In other words, the surrounding ligand field can have a considerable influence on the optical absorption and emission as well as fluorescence decay properties. The knowledge of such relationships between host glass structure and RE properties is vital to design and develop glasses for laser as well as optical amplifier applications. Judd–Ofelt intensity parameters are important spectroscopic parameters of radiative processes of RE ions. They are phenomenological characteristics for the influence of host matrix on the absorption and emission properties and are sensitive to changes in the local environment [16–18]. Previous studies have shown that Tb$^{3+}$ and Eu$^{3+}$ are appropriate indicator ions for local structure investigations around the RE ions due to their electronic structure [18,19]. Tb$^{3+}$ ions are used for examination of radiative decay rates and energy transfer processes [3–5,18–23]. Therefore, in the present study, absorption, emission and decay properties (intensity ratios and lifetime) were derived for the Tb$^{3+}$-doped fluorophosphate glasses in order to know the local structure properties around the RE ions for definite applications.

Figure 1 shows the absorption spectrum of 1.0 mol % Tb$_2$O$_3$-doped fluorophosphate glass. As can be seen, the absorption spectrum consists of bands at 368, 377, and 486 nm corresponding to $^7F_6 \rightarrow ^5L_{10}$, $^5D_3$, $^5D_4$, transitions of Tb$^{3+}$ ions, respectively. The absorption band at around 1900 nm was deconvoluted into three absorption bands using Gaussian distributions, which are due to the transitions from the ground state $^7F_6$ to the excited states $^7F_2$, $^7F_1$, $^7F_0$.
The band at 2248 nm is due to the $^7F_6 \rightarrow ^7F_3$ transition of Tb$^{3+}$ ion. It was also found that the spectrum is similar to the other Tb$^{3+}$-doped host matrices [23].

Figure 2 shows the emission spectra of Tb$^{3+}$-doped fluorophosphate glasses for different Tb$^{3+}$ concentrations. The spectra were obtained by exciting the samples at 376 nm. As can be seen, the spectra exhibited the bands at 417, 439 and 459 corresponding to the $^5D_3 \rightarrow ^7F_{5,4,3}$ transitions, respectively, and those peaked at 491, 546, 585, and 622 nm attributed to the $^5D_4 \rightarrow ^7F_{6,5,4,3}$ transitions, respectively. All these emissions were due to the 4F$^7$-4F$^8$ transitions from the $^5D_3$ (blue emissions) and $^5D_4$ (green-red emissions) levels to the $^7F_i$ multiplets of Tb$^{3+}$ (see the Tb$^{3+}$ partial energy level diagram shown in Figure 3). This energy-level diagram was drawn from the excitation and emission spectra recorded for the Tb$^{3+}$-doped fluorophosphate glasses. The observation of the emissions from the $^5D_3$ level is due to a slow non-radiative relaxation from the $^5D_3$ to $^5D_4$ level by cross-relaxation to a neighbor Tb$^{3+}$. As can be seen from Figure 2, the green emission peaked at 546 nm ($^5D_4 \rightarrow ^7F_5$ transition) intensity increased with increase in Tb$^{3+}$ concentration, without luminescence quenching even the Tb$^{3+}$ concentration was increased up to 4.0 mol%, while the intensity of the blue band peaked at 439 nm ($^5D_3 \rightarrow ^7F_4$ transition) decreased with Tb$^{3+}$ concentration. It is suggested that the two different mechanisms, namely multiphonon relaxation and cross-relaxation (Tb$^{3+}$ ($^5D_3$) + Tb$^{3+}$ ($^7F_6$) → Tb$^{3+}$ ($^5D_4$) + Tb$^{3+}$ ($^7F_0$)) by resonant energy transfer are responsible for the blue emission quenching and the green emission enhancement as described elsewhere [3,5]. In other Tb$^{3+}$-doped glasses [7,23–25], the concentration quenching was observed when Tb$^{3+}$ concentration was more than 15 mol%. The experimental branching ratios describe the spectral distribution of the emission intensity. The branching ratios were calculated for each transition from the $^5D_4$ level considering the integrated intensity ratio of each transition $^5D_4 \rightarrow ^7F_j$ ($j = 6, 5, 4$ and $3$) to the whole spectrum in the region of $^5D_4$ level emissions (480–640 nm). The experimental branching ratios were found to be 33.2 ~ 35.0%, 55.5 ~ 57.39%, 5.94 ~ 6.30% and 2.6 ~ 2.84%, for the $^5D_4 \rightarrow ^7F_{6,5,4,3}$ transitions, respectively. It can be noticed that the $^5D_4 \rightarrow ^7F_5$ transition (green emission) exhibits a branching ratio higher than 50%, and therefore it could be promising for green laser emission.

Figure 4(a) shows the variation of the blue emission ($^5D_3 \rightarrow ^7F_5$ transition) intensity ($I_{B}$) and green emission ($^5D_4 \rightarrow ^7F_5$ transition) intensity ($I_{G}$) as a function of Tb$^{3+}$ concentration. It was found that the blue emission intensity decreased whereas green emission intensity increased with increase in Tb$^{3+}$ concentration. The ratio of integrated emission intensity of the $^5D_4 \rightarrow ^7F_5$ transition (green emission) to the $^5D_3 \rightarrow ^7F_5$ transition (blue emission) allows to determine the green/blue intensity ratio ($I_{G}/I_{B}$). The ratio of integrated emission intensity of the $^5D_3 \rightarrow ^7F_5$ transition (blue emission) and $^5D_4 \rightarrow ^7F_5$ transition (green emission) allows to determine the blue/green intensity ratio ($I_{B}/I_{G}$). The $I_{C}/I_{B}$ ratio could play the same role as red/orange intensity ratio (R/O) of Eu$^{3+}$ or yellow/blue intensity ratio (Y/B) of Dy$^{3+}$, and also describe the symmetry of the local environment around the optically active dopant and covalent/ionic bonding between Tb$^{3+}$ and O$^{2-}$. Therefore, Tb$^{3+}$ ions could be used as a spectroscopic probe similarly to Eu$^{3+}$ or Dy$^{3+}$ ions [26]. The $I_{C}/I_{B}$ and $I_{B}/I_{C}$ intensity ratios as a function of Tb$^{3+}$ concentration were evaluated and are shown in Figure 4(b). As can be seen from the figure, the $I_{C}/I_{B}$ intensity ratio increased with increase in Tb$^{3+}$ concentration. This indicates that the present fluorophosphate glasses exhibited a higher covalency between Tb–O bond and higher asymmetry in the vicinity of Tb$^{3+}$ ions. It can be noticed that the $I_{B}/I_{C}$ ratio decreased with increasing Tb$^{3+}$ concentration due to quenching of the...
Variation of blue and green emissions (a) and blue/green/blue intensity ratios (b) as a function of Tb
emission. The similar behavior has been reported in other Tb\(^{3+}\)-doped glasses [3,4,22]. Therefore, the \(I_B/I_G\) parameter is useful to detect the quenching degree of the Tb\(^{3+}\) blue emission.

Figure 5 shows the excitation spectra of Tb\(^{3+}\)-doped fluorophosphate glasses for different concentrations of Tb\(^{3+}\) ion. They were recorded by monitoring emission at 546 nm attributed to \(^5D_4 \rightarrow ^7F_3\) transition. The spectra display the bands centered at 303, 318, 340, 357 and 483 nm, which are associated with transitions from the \(^7F_6\) ground state to the \((^7H_{5/2}, ^7H_{7/2}), (^7F_{5/2}, ^7D_1), (^7L_{7/2}, ^5G_3), (^7L_{9/2}, ^7D_2, ^5G_5), (^7L_{11/2}, ^7D_3, ^5G_6)\) and \(^5D_4\) excited levels, respectively [27]. As can be seen from the figure, the intensity of the bands increased with increase in Tb\(^{3+}\) concentration. The intensity of the excitation band at 377 nm \((^7F_6 \rightarrow ^5D_3\) transition\) of Tb\(^{3+}\) ion was found to be higher than the other transitions, which shows that the allowed \(^7F_6 \rightarrow ^5D_3\) transition can increase the intensity of Tb\(^{3+}\) emissions. In addition, the excitation bands become lower and broader with the increment of Tb\(^{3+}\) concentration. But the position of peaks has not been changed for the 4f electrons of Tb\(^{3+}\) ions since they are shielded by 5s\(^2\)5p\(^6\) shells.

Decay analysis is very useful to understand the energy transfer mechanism and luminescence quenching of Tb\(^{3+}\) ions. Figure 6 shows the decay curves for the \(^5D_4\) level of Tb\(^{3+}\) ion for different Tb\(^{3+}\) concentrations. They were obtained by monitoring the green emission at 546 nm \((^7D_4 \rightarrow ^7F_3\) transition\) under 376 nm excitation. As can be seen from the figure, the decay curves for the \(^5D_4\) level of Tb\(^{3+}\) ion exhibit single exponential nature for all the concentrations. The experimental lifetime \((\tau_{\exp})\) was determined using single exponential equation given by

\[
I(t) = I_0 \exp(-t/\tau)
\]

where \(I(t)\) and \(I_0\) are the luminescence intensities at time \(t = t\) and \(t = 0\), respectively, and \(\tau\) is the decay time. The \(\tau_{\exp}\) was found to be 2.65, 2.91, 2.93, 2.94 and 2.94 ms for 0.1, 0.5, 1.0, 2.0 and 4.0 mol\% of Tb\(_4\)O\(_7\)-doped fluorophosphate glasses, respectively. In the present study, it was found that the lifetime increased with increase in Tb\(^{3+}\) concentration varied from 0.1 to 4.0 mol\%. Previous studies [7,23–25] reported that the decay time decreased when Tb\(^{3+}\) concentration was...
more than 15 mol%. The lifetime of the present glasses were compared with other Tb$^{3+}$-doped glasses. It can be noticed that the lifetime of 1.0 mol% Tb$^{3+}$-doped fluorophosphate glass was more or less to the zinc phosphate [3] and zinc fluorophosphate [4] glasses but higher than borgermanate [28] and lead germanate [29] glasses (see Table 1). It is well known that the longer lifetime of the $^5D_4$ level could reduce the pump threshold to get visible laser output. So the present studied glasses are promising candidates for the green laser emission at 546 nm.

4. Conclusions

Tb$^{3+}$-doped fluorophosphate glasses for different dopant concentrations were successfully prepared by the conventional melt quenching technique. Concentration-dependent photoluminescence and lifetime were studied for the Tb$^{3+}$-doped fluorophosphate glasses. The $^3D_3$ level (blue emission) intensity ($I_B$) decreased with increase in Tb$^{3+}$ concentration, while the $^5D_4$ level (green emission) intensity ($I_C$) increased with increase in Tb$^{3+}$ concentration. The increased $I_C/I_B$ ratio up to a factor of 140 in the strontium fluorophosphate glasses, indicating the present fluorophosphate glasses exhibit higher covalency between Tb–O bond and higher asymmetry around the Tb$^{3+}$ ions. The experimental branching ratios were evaluated for the $^5D_4$ to $^7F_J$ multiplets ($J = 6, 5, 4, \text{and } 3$) and found that $^5D_4 \rightarrow ^7F_5$ transition had branching ratio larger than 50%, indicating the potentiality of the present strontium fluorophosphate glasses for the green laser emission at 546 nm. The decay curves for the $^3D_3$ level of Tb$^{3+}$ ion follow a single-exponential decay for all the concentrations with a small lifetime variation from 2.65 to 2.91 ms. The longer lifetime of the $^3D_3$ level could reduce the pump threshold to get visible laser emission. The results suggest that the present strontium fluorophosphate glasses could be useful as a visible green laser media at 546 nm.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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