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Structural and Luminescence Studies of Sm^{3+} Doped Telluro-Fluoroborate Glasses for Photonic Applications

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Abstract

A new series of Sm^{3+} ions doped telluro-fluoroborate (xSTFB) glasses have been prepared following melt quenching technique and the structural and luminescence behaviors were studied by recording X-ray diffraction, FTIR, absorption and photoluminescence spectral measurements. The amorphous nature of the glasses was confirmed through XRD pattern and the different vibrational bonds of borate and tellurite networks were identified through FTIR spectra. The bonding parameters (β, δ) and Judd-Ofelt intensity parameters (Ω_λ) have been calculated from the absorption spectra in order to explore the bonding nature of the ligand environment around Sm^{3+} ions. The luminescence spectra exhibit four emission bands in the visible region due to the $^4G_{5/2} \rightarrow {}^6H_{5/2}$, $^6H_{7/2}$, $^6H_{9/2}$ and $^6H_{11/2}$ transitions and the same are characterized through CIE 1931 chromaticity diagram. The radiative parameters such as transition probability (A), stimulated emission cross-section (σ_e), branching ratios (β_R) and radiative lifetime (τ_R) have been determined to elucidate the suitability of the studied glasses for the fabrication of various photonic devices.

Keywords: Telluro-fluoroborate, Bonding parameter, JO intensity parameter, Luminescence, stimulated emission cross-section, Laser

1. Introduction

In the recent years, glasses doped with trivalent rare earth (RE^{3+}) ions receive lot of interest due to their potential applications in the design and development of photonic devices such as solid state lasers, display monitors, solar cells, sensors and light emitting diodes (LEDs) [1,2]. Among the variety of glass hosts, telluro-fluoroborate glasses are proven to be the better host due to their excellent physical and chemical properties such as high RE ion solubility, low melting point, high thermal stability, low phonon energy, super hardness and higher refractive index [3]. Among the RE ions, Sm^{3+} is one of the most attractive ion for investigating luminescent properties because of its applications in various fields such as visible solid state lasers, high density optical memory storage, under sea communications and color displays etc.,[4]. The motivation of the present investigation is to prepare a new series of Sm^{3+} doped telluro-fluoroborate glasses and to explore their structural and luminescence properties through XRD, FTIR, optical absorption and luminescence measurements for the possible photonic applications.

2. Experimental

Sm^{3+} ions doped telluro-fluoroborate glasses with the chemical composition $(40–x)B_2O_3 + 25TeO_2 + 20ZnF_2 + 15CaF_2 + xSm_2O_3$ (where x= 0.1, 0.25, 0.5, 1 and 1.5 in wt% hereafter named as 0.1STFB, 0.25STFB, 0.5STFB, 1STFB and 1.5STFB respectively) have been synthesized by conventional melt quenching technique following the procedure reported in literature [3]. The X-ray diffraction measurements were carried out using JEOL 8030 X-ray diffractometer employing CuKα radiation. The FTIR spectra have been recorded using Perkin-Elmer paragon-500 FTIR spectrophotometer following the KBr Pellet technique. The absorption spectra of the prepared glasses have been recorded using Perkin Elmer Lambda-950 UV-Vis-NIR spectrophotometer in the wavelength range 350–1700 nm. Jobin Yvon Fluorolog-3 Spectrofluorimeter was used to record the luminescence spectra with a spectral resolution of ±0.5 nm in the wavelength range 550–750 nm.

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3. X-ray diffraction and FTIR spectral analysis

The inset of figure 1 shows the XRD pattern of Sm^{3+} ions doped 1STFB glass recorded in the range of $5^{o} \leq \theta \geq 80^{o}$. The spectrum does not show any characteristic sharp diffraction crystalline peaks, but shows broad diffused scattering at lower angles which illustrate the amorphous nature of the prepared glasses. The FTIR spectroscopy is one of the efficient analytical tools to identify the functional groups and to characterize the bonding information in the glass samples. The FTIR spectra of the prepared glasses were recorded in the range between 400 to 4000 cm^{-1} and the FTIR spectrum of 1STFB glass is shown in figure 1 as a representative case. The broad IR transmission band at around 3422 cm^{-1} is due to the stretching vibrations of O–H groups. The observed bands at 2927 and 2857 cm^{-1} are the characteristic of the hydrogen bond present in the glasses. The asymmetric stretching vibrations of B–O bonds in BO_3 units have been identified through the band at 1275 cm^{-1}. The band positioned at 1018 cm^{-1} is attributed to the B–O stretch in BO_4 units from tri, tetra and penta-borate groups. The band observed around 684 cm^{-1} denotes the combined vibrations of B–O–B bending in BO_4 units and Te–O bond stretching in TeO_3 units. The band located around 490 cm^{-1} is due to the bending vibrations of Te–O–Te or O–Te–O linkages [3].

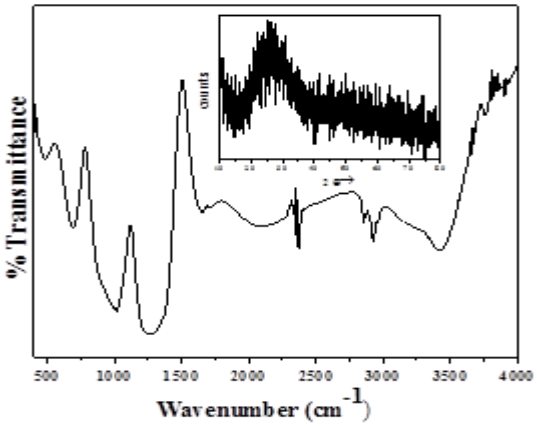

Figure 1. FTIR spectrum of the Sm^{3+} doped 1STFB glass. [Inset shows the XRD spectrum of the 1STFB glass]

4. Absorption spectral analysis and Judd–Ofelt parameters

The absorption spectrum of one of the Sm^{3+} ions doped 1STFB glass recorded in the UV-Vis-NIR region of wavelength range between 350–1700 nm is show in figure 2 as a representative case. The spectrum exhibit several absorption bands corresponds to the f-f transitions from the $^6H_{5/2}$ ground state to the different excited states of Sm^{3+} ions such as $^6F_{1/2}$, $^6H_{15/2}$, $^6F_{3/2}$, $^6F_{5/2}$, $^6F_{7/2}$, $^6F_{9/2}$, $^6F_{11/2}$, $^4I_{11/2}+^4M_{13/2}+^4I_{9/2}$, $^4I_{13/2}$, $^4G_{9/2}+^4M_{17/2}$, $^6P_{5/2}$, $^4M_{19/2}$, $^4L_{13/2}+^4F_{7/2}+^6P_{3/2}$, $^4L_{15/2}$, $^6P_{7/2}$ and $^4D_{3/2}$ positioned at around 6549, 6792, 7301, 8147, 9285, 10593, 17794, 21277, 21645, 22831, 23635, 23992, 24814, 25641, 26738 and 27777 cm^{-1} respectively [1,4]. Among all the absorption transitions, intensity of the $^6H_{5/2} \rightarrow {}^6F_{7/2}$ and $^6H_{5/2} \rightarrow {}^6P_{3/2}$ transitions are found to be sensitive to the nature of the ligand field environment around the RE ion site thus called as hypersensitive transitions. Further these transitions obey the selection rules, $|\Delta S| = 0$, $|\Delta S| \leq 2$ and $|\Delta J| \leq 2$. The bonding nature of the Sm^{3+}-ligand can be determined from the nephelauxetic ratios (β) and bonding parameter (δ) values since the RE^{3+} ions produce nephelauxetic effect when doped into the glass host matrix. From the average values of β (taken as $\bar{\beta}$) the bonding parameter can be evaluated from the formula $\delta = [(1-\bar{\beta})/\bar{\beta}] \times 100$, where β is the nephelauxetic ratio which calculated using the relation $\beta = \nu_c/\nu_a$, where ν_c is the wave number (in cm^{-1}) of a particular transition for an ion in the glass matrix and ν_a is the wave number (in cm^{-1}) of the same transition for the aqua-ion. The bonding nature (Sm^{3+}-ligand) will be covalent or ionic depending upon the positive or negative sign of δ [3,4]. The δ values of the studied glasses are presented in table 1 and the negative sign of δ values observed for all the glasses indicates the ionic nature of the Sm^{3+} ions with the surrounding ligands O^{2-}/F^- and the ionicity decreases gradually with the increase in Sm^{3+} concentration in the prepared glasses.

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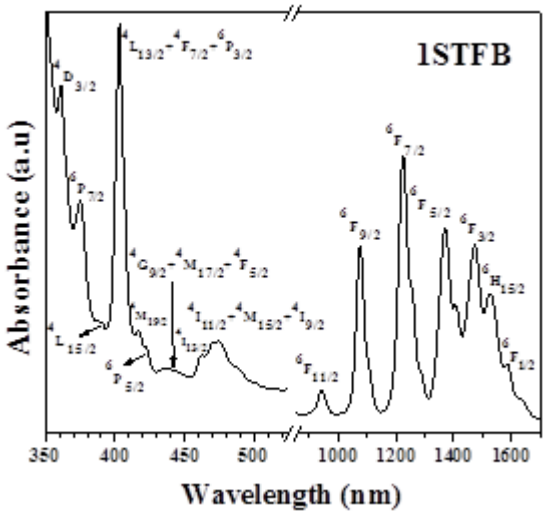

Figure 2. Absorption spectrum of the Sm^{3+} doped 1STFB glass

The Judd-Ofelt intensity parameters Ω_λ (λ= 2, 4 and 6) were calculated from the spectral intensities of the absorption spectra by using least square fitting method and the values of the same are presented in table 1. The Ω_2 parameter is sensitive to the chemical bonding between RE^{3+} ions and the ligand anions as well as asymmetry of local host environment around the RE^{3+} ions, whereas the Ω_4 and Ω_6 parameters are related to the rigidity and bulk properties of the host matrix [4,5]. In the present investigation, the trends of JO parameters are found to be in the order $\Omega_4>\Omega_6>\Omega_2$ for all the glasses and the lower Ω_2 values implies less covalent characteristic (more ionic) and higher symmetry around the Sm^{3+} ions with their surrounding ligands. The ratio between Ω_4 and Ω_6 is known as spectroscopic quality factor and the magnitude of the same is significant predictor to claim a good laser material. The higher Ω_4/Ω_6 value obtained for the prepared 1STFB glass can be suggesting the suitability for the development of lasers and various optical devices.

Table 1. Bonding parameters (δ) and Judd-Ofelt ($\times10^{-20}cm^2$) parameters of the Sm^{3+} doped xSTFB glasses

Glass codes		0.1S TFB	0.25S TFB	0.5S TFB	1S TFB	1.5S TFB
Parameters	δ	–0.253	–0.265	–0.269	–0.284	–0.313
	Ω_2	2.238	2.213	1.469	1.272	1.192
	Ω_4	5.724	5.427	3.309	5.072	5.931
	Ω_6	5.145	3.921	2.761	2.459	2.886
	Ω_4/Ω_6	1.113	1.384	1.198	2.063	2.055

5. Luminescence spectra and radiative parameters

The luminescence spectra of the xSTFB glasses recorded in the wavelength range of 550–750 nm with an excitation wavelength of 404 nm is depicted in figure 3. Each emission spectrum contains four emission bands centered at 563, 599, 646 and 708 nm corresponding to the transitions $^4G_{5/2}\rightarrow{}^6H_J$ (J = 5/2, 7/2, 9/2 and 11/2) respectively with considerable variation in their intensities. Among these, the transition $^4G_{5/2}\rightarrow{}^6H_{7/2}$ (at 599 nm) demonstrates maximum intensity in the unique reddish-orange region for all the glasses which appears to be suitable candidate for visible lasers emission [1,4,6].

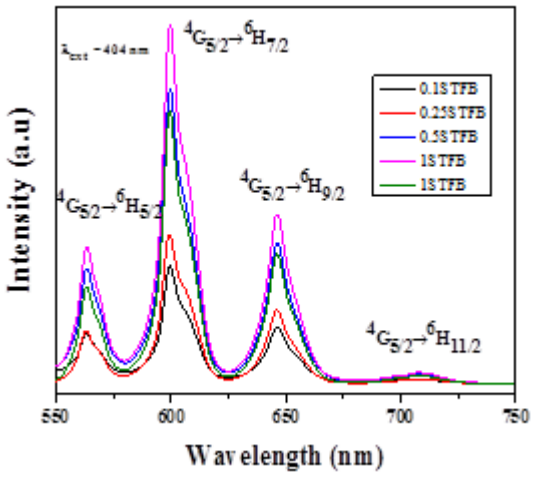

Figure 3. Luminescence spectra of the Sm^{3+} doped telluro-fluoroborate glasses

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It is evident from figure 3 that, the luminescence quenching takes place at 0.5wt% of sm^{3+} ions in the studies glasses for all the emission bands. The same may occur either due to efficient energy transfer between nearby Sm^{3+} ions or cross-relaxation process which produced at higher Sm^{3+} ion concentrations.

From the luminescence spectral data along with JO parameters, the important laser properties such as effective bandwidth ($\Delta\lambda_{eff}$), stimulated emission cross-section (σ_e), radiative and experimental branching ratios (β_R) and radiative lifetime (τ_R) for the $^4G_{5/2}\rightarrow{}^6H_{5/2}$, $^6H_{7/2}$ and $^6H_{9/2}$ emission transitions of the title glasses were calculated and the results are presented in table 2. The β_R and σ_e are the significant lasing parameters which used to characterize the potential laser transition of the RE ions in the glass host matrices [4-7]. It is observed from the tabulated results that, of all the prepared glasses 1STFB glass exhibit higher β_R and σ_e values for the $^4G_{5/2}\rightarrow{}^6H_{7/2}$ (599 nm) transition and the same may be suggested for the fabrication of lasers and photonic devices operating in the visible region.

Table 2. The values of λ_p (nm), $\Delta\lambda_{eff}$ (nm), A (s^{-1}), β_R, σ_e (10^{-22} cm^2) and τ_R (ms) for the $^4G_{5/2}\rightarrow{}^6H_{5/2}$, $^6H_{7/2}$ and $^6H_{9/2}$ transitions of the prepared xSTFB glasses

Parameters		0.1STFB	0.25STFB	0.5STFB	1STFB	1.5STFB
$^4G_{5/2}\rightarrow{}^6H_{5/2}$	λ_p	563	563	563	563	563
	$\Delta\lambda_{eff}$	7.141	8.289	8.365	9.753	8.308
	σ_e	1.082	1.105	1.125	1.388	1.132
	β_R(cal)	0.048	0.051	0.057	0.059	0.053
	β_R(ex)	0.167	0.173	0.182	0.191	0.172
$^4G_{5/2}\rightarrow{}^6H_{7/2}$	λ_p	599	599	599	599	599
	$\Delta\lambda_{eff}$	8.471	8.562	8.893	9.329	8.775
	σ_e	7.351	7.819	8.214	9.652	8.712
	β_R(cal)	0.573	0.584	0.579	0.591	0.532
	β_R(ex)	0.652	0.667	0.672	0.694	0.661
$^4G_{5/2}\rightarrow{}^6H_{9/2}$	λ_p	646	646	646	646	646
	$\Delta\lambda_{eff}$	7.556	7.953	8.345	9.231	8.841
	σ_e	3.716	3.882	4.014	4.865	3.916
	β_R(cal)	0.303	0.316	0.332	0.341	0.317
	β_R(ex)	0.421	0.446	0.463	0.485	0.449
τ(cal)		2.831	3.016	3.281	2.912	2.721

6. CIE chromaticity co-ordinates

The chromaticity co-ordinates (x,y) of the Sm^{3+} telluro-fluoroborate glasses have been evaluated from the luminescence spectra using CIE 1931 system as per the procedure reported in the literature [3] in order to explore the prominent emission exhibited by the title glasses. The obtained values of chromaticity coordinates (x, y) are found to be (0.523, 0.465), (0.558, 0.441), (0.541, 0.452), (0.586, 0.403) and (0.511, 0.471) for the 0.1STFB, 0.25STFB, 0.5STFB, 1STFB and 1.5STFB glasses respectively.

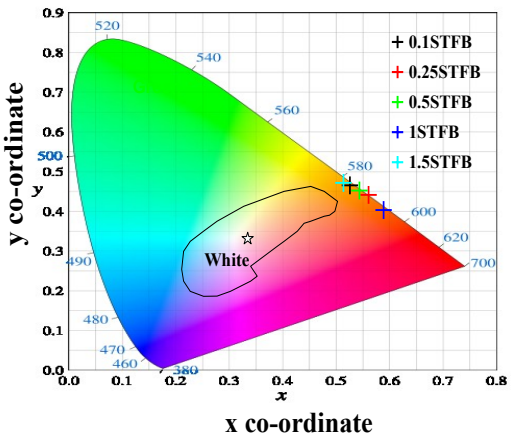

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Figure 4. CIE coordinate diagram of the Sm^{3+} doped telluro-fluoroborate glasses

Figure 4 displays the CIE chromaticity diagram of the present glasses and it is observed from the figure that the x,y values of all the samples fall in the reddish-orange region. Hence, it is suggested that the prepared glasses are potential candidate for reddish-orange laser, light emitting diode and display device applications.

7. Conclusion

Concentration dependent Sm^{3+} ions doped telluro-fluoroborate glasses have been prepared and their structural, luminescence behaviors were explored through XRD, FTIR, absorption and luminescence measurements. The presence of fundamental functional groups such as OH stretching vibrations, B–O bond stretching vibrations in BO_3 and BO_4 units, O_3B–O–BO_3 bending vibrations and Te–O stretching vibrations in TeO_3 and TeO_4 units in the present glass network were analysed through FTIR spectral analysis. JO intensity parameters of the titled glasses follow the trend as $\Omega_4>\Omega_6>\Omega_2$ for all the glasses and the lower Ω_2 values implies less covalent characteristic and higher symmetry around the Sm^{3+} ions with their surrounding ligands. Emission spectra of the prepared glasses exhibit, unique strong reddish-orange emission for the transition $^4G_{5/2}\rightarrow{}^6H_{7/2}$ (at 599 nm) and the CIE coordinates of all the samples fall in the reddish-orange region suggest their potential for the reddish-orange laser, light emitting diode and display device applications. Among the prepared glasses 1STFB glass exhibit higher β_R and σ_e values for the $^4G_{5/2}\rightarrow{}^6H_{7/2}$ transition and the same may be suggested for the fabrication of lasers and photonic devices operating in the visible region.

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