

Spectroscopic Investigations on Er³⁺ doped Lead Borotellurite Glasses for Amplifier Applications

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Abstract

Er³⁺ ions doped lead borotellurite glasses were prepared by melt quenching technique and their structural and spectroscopic behaviors were studied through recording FTIR, UV–Vis–NIR absorption and photoluminescence measurements. Through the absorption spectra the bonding parameters (δ) and Judd–Ofelt intensity parameters Ω_λ ($\lambda = 2, 4$ and 6) has been evaluated. From the JO intensity parameters the radiative properties such as transition probability (A), stimulated emission cross section (σ_e), radiative life time (τ_{cal}) and branching ratios (β_R) of the prepared glasses were determined and their results were discussed and reported. The obtained higher values of A , σ_e , FWHM and ΔG for the LTB0.5E glass suggest its feasibility for the development of laser and optical amplifier devices.

Keywords: Amplifier, Bonding Parameter, JO intensity parameter, Gain Bandwidth, Stimulated emission cross section

1. Introduction

Rare earth (RE) ions are visible to near-infrared ultra narrow band emitters with long luminescence lifetimes and thus have wide applications in many fields such as solid laser, display and optical amplification [1]. Er³⁺ doped glasses are especially attractive for numerous applications mainly due to the 1550 nm emission and in fact, Er³⁺-doped fiber amplifiers (EDFA) are well known and used in telecommunication systems, temperature sensors, solar cells, light

wave circuits [1,2]. Owing to the low phonon energy, excellent material exhibiting low melting points, higher chemical stability, high refractive index and suitable lattice size for doping rare earth ions borotellurite based glass system has been selected as the host matrix [1–3]. In this present work, the concentration effect on spectroscopic behaviors of Er³⁺ ions doped lead borotellurite glasses have been investigated and reported.

2. Experimental

Er³⁺ ions doped lead borotellurite glasses were prepared by melt quenching technique with the chemical composition of $(45-x)\text{B}_2\text{O}_3+30\text{TeO}_2+15\text{PbO}+10\text{Na}_2\text{O}+x\text{Er}_2\text{O}_3$ (where $x = 0.1, 0.25, 0.5, 1$ and 2 wt%) following the procedure reported in literature [3]. The prepared Er³⁺ ions doped lead borotellurite glasses are labeled as LTB0.1E, LTB0.25E, LTB0.5E, LTB1E and LTB2E with respect to the erbium ion concentration in the host matrix. The FTIR spectrum has been recorded using Perkin–Elmer Paragon–500 spectrophotometer in the wave number region 400–4000 cm^{-1} following KBr pellet method. The optical absorption spectra were recorded in the wavelength range 350–2000 nm using CARY 500 UV–Vis–NIR spectrophotometer. The NIR emission spectra were carried out using JOBIN YVON fluorolog–3 spectrofluorometer with a PMT by exciting at 980 nm laser diode with a resolution of ± 1.0 nm. All these measurements were carried out at room temperature (RT) only.

3. FTIR analysis

The FTIR spectra of LTB0.5E glass displayed in figure 1 as a representative case which is used to identify the existing functional groups present in the borotellurite glasses. The presence of principle IR vibration bond around 703 cm^{-1} is attributed B–O–B bond bending vibrations in $[\text{BO}_3]$ units and Te–O bond stretching vibrations in TeO_3 and TeO_6 units [4]. The absence of O–B–O boroxol ring formation in the prepared glass around the region 806 cm^{-1} confirms that the glass system consists of randomly connected BO_3 and BO_4 groups. The broad band around 1004 cm^{-1} is due to B–O stretching vibrations of BO_4 units in tri-, tetra- and penta borate groups. The peaks observed around 1370 cm^{-1} indicates the presence of B–O stretching in $[\text{BO}_3]$ units [3,4]. The small hump observed around 1632 cm^{-1} is due to the asymmetric stretching relaxation of the B–O bond of trigonal BO_3 units [3,4]. The presence of small peak around 3422 cm^{-1} indicates the OH bond vibrations in the titled glass [4].

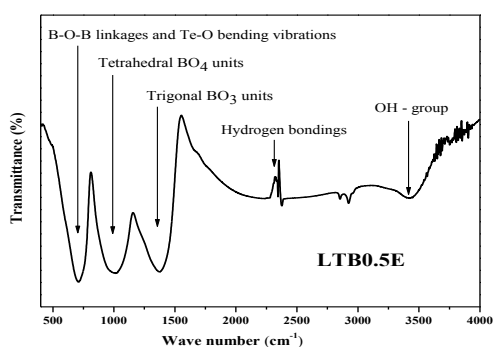


Figure 1. FTIR spectrum of the Er^{3+} doped LTB0.5E glass

Thus the presence of bending and stretching vibrations of borate and tellurite are confirmed in the prepared glasses.

4. Absorption spectral analysis

Figure 2 shows the UV–Vis absorption spectrum of the 0.5 wt% Er^{3+} doped lead borotellurite glass recorded in the wavelength region 400–850 nm. The sharp and narrow peaks of the titled glasses which arise due to the electrostatic and spin orbit interactions of the $4f-4f$ energy level. The spectrum consist of 6 absorption bands, which attributed to the transition from ground level $^4\text{I}_{15/2}$ to the various excited states $^4\text{I}_{9/2}$, $^4\text{F}_{9/2}$, $^4\text{S}_{3/2}$, $^2\text{H}_{11/2}$, $^4\text{F}_{7/2}$, and $^4\text{F}_{3/2}$ at around 797, 651, 544, 521, 487 and 450 nm respectively.

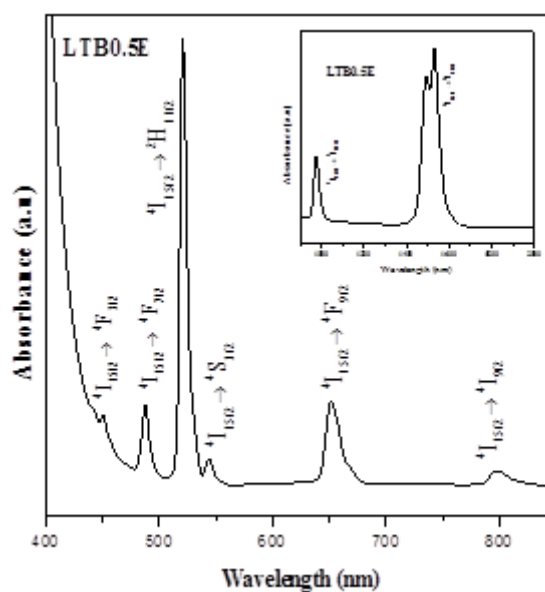


Figure 2. Absorption spectrum of the Er^{3+} doped LTB0.5E glass. [Inset shows the NIR Absorption spectrum of the LTB0.5E glass]

The inset of figure 2 shows the NIR absorption spectra of the same glass recorded in the wavelength region 900–2000 nm which exhibits two intense bands due to the transition from $^4\text{I}_{15/2} \rightarrow ^4\text{I}_{11/2}$ and $^4\text{F}_{13/2}$ at around 977 and 1527 nm. The hypersensitive nature of the rare earth ion to the host matrix, which holds it, must satisfies the

forbidden selection rule $|\Delta L| \leq 2$, $|\Delta J| \leq 2$ and $\Delta S = 0$. According to it, ${}^4I_{15/2} \rightarrow {}^2H_{11/2}$ is hypersensitive in nature. The predominant covalent/ionic nature can be determined by Nephelauxetic ratios (β) and bonding parameter (δ) values which are calculated using the reported expressions [4,5]. The obtained bonding parameter values are tabulated in table 1 and the negative δ values indicate the ionic nature of the Er^{3+} metal-ligand bond. It founds to be ionic and on higher concentration a gradual increase is observed owing to the ionic nature in the glass, which means interaction between electron is reduced in lower concentration and increased in higher concentration due to increase in erbium content.

5. Judd-Ofelt Intensity Parameters

From the spectral intensities of the absorption spectra, the JO intensity parameters were determined by least squares fitting method [4,5] and are presented in Table 1 along with the spectroscopic quality factor. Judd-Ofelt theory is the most useful theory in estimating the probability of forced electric dipole transitions of rare earth ions in various environments. Generally, Ω_2 intensity parameter describes asymmetric of coordinate structure, bonding nature and polarizability of ligand ion or molecule, Ω_4 and Ω_6 refers to the viscosity of the glass matrix and dielectric of the media.

Table 1. Judd-Ofelt ($\times 10^{-20} \text{cm}^2$) parameters and bonding parameters (δ) of Er^{3+} doped $LTBxE$ glasses

Glass codes	Ω_2	Ω_4	Ω_6	Ω_4/Ω_6	δ
LTB0.1E	4.61	1.36	1.11	1.23	-0.113
LTB0.25E	4.69	1.43	1.19	1.20	-0.125
LTB0.5E	4.77	1.60	1.25	1.28	-0.138

LTB1E	4.86	1.74	1.37	1.27	-0.162
LTB2E	5.27	1.81	1.44	1.26	-0.227

In the present study, the trends of the JO parameters are found to be in the order $\Omega_2 > \Omega_4 > \Omega_6$ for all the prepared glasses. The higher Ω_2 values suggest the higher rigidity and higher covalency around the Er^{3+} ion site. The ratio between Ω_4 and Ω_6 is known as spectroscopic quality factor and the magnitude of the same is important predictor to claim a good laser material. The higher Ω_4/Ω_6 value of the prepared LTB0.5E glass can be suggesting the suitability for the development of lasers and photonic devices.

6. NIR Luminescence spectral analysis

NIR emission spectra of the Er^{3+} ions in the title glasses monitoring at an excitation wavelength at 980 nm displayed in the figure 3. The emission band at around 1554 nm corresponding to ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition which is most important one has received much attention as it is useful for optical communication, IR laser applications and eye-safe laser for range finding applications. It is observed from the figure that, the luminescence intensity of the ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition is found to increase with the increase in Er^{3+} ion concentration upto 0.5wt% of Er^{3+} ion content and after that quenching occurs. Decreases of luminescence intensity at higher concentration of Er^{3+} ions is mainly due to the higher prospect of $Er^{3+}-Er^{3+}$ interactions where the inter ionic distance decreases thus in turn causes the close packing of large number of Er^{3+} ions energy levels and it shortens the lifetime of the ${}^4I_{13/2}$ excited level.

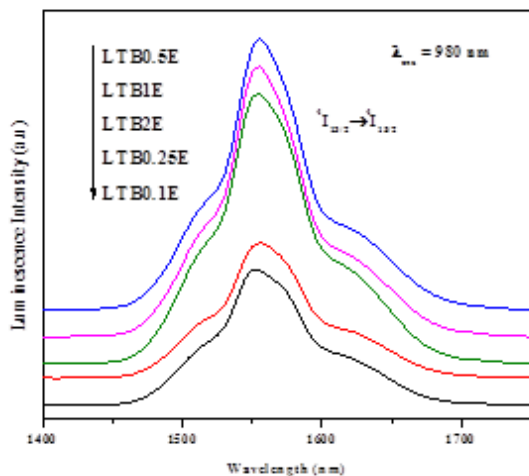


Figure 3. NIR Emission spectra of the Er³⁺ doped lead borotellurite glasses

The Decreases of luminescence intensity at higher concentration of Er³⁺ ions is mainly due to the higher prospect of Er³⁺-Er³⁺ interactions where the inter ionic distance decreases thus in turn causes the close packing of large number of Er³⁺ ions energy levels and it shortens the lifetime of the ⁴I_{13/2} excited level.

7. Radiative properties

The radiative properties helpful in determining the best optical device such as transition probability (A), gain band width, emission cross-section(σ_e) and branching ratio (β_R) for this NIR transition were calculated using formulae available in the literature [4]. The most predominant parameter the full width at half maximum (FWHM) of the ⁴I_{13/2} → ⁴I_{15/2} transition is very important in telecommunication since it allows to cover two of the optical communication bands, the C and L bands and another important parameter is the Gain band width (ΔG) which is the product of effective band width ($\Delta\lambda_{eff}$) and stimulated emission cross-section (σ_e). The FWHM values for

the prepared glasses are found to 61, 63, 77, 73 and 70 nm corresponding to the as LTB0.1E, LTB0.25E, LTB0.5E, LTB1E and LTB2E glasses respectively. Among all the prepared glasses, the A, σ_e , FWHM and ΔG for the LTB0.5E glass is found to be higher and same is compared with the reported glasses [4,5,7] and displayed in the table 2.

Table 2. Radiative properties (λ_p (nm), $\Delta\lambda_{eff}$ (nm), A (s⁻¹), τ_R (ms), σ_e (×10⁻²² cm²), β_R and ΔG (×10⁻²⁸)) for the ⁴I_{13/2} level under 980 nm excitation of the LTB0.5E glass with the other reported Er³⁺ doped glasses

Transition ⁴ I _{13/2} → ⁴ I _{15/2}	Paramete	LTB	LZB	A05	PKAZF
	rs	0.5E	0.5E[4]	[5]	Er10[7]
	λ_p	155	1532	153	1529
	$\Delta\lambda_{eff}$	4	66	73	-
	A	62	184	137	230
	τ_R	4.27	4.40	7.31	4.36
	σ_e	86	93	54	32
	β_R (cal)	1	1	1	1
	β_R (exp)	1	1	1	1
ΔG	527.7	613.8	466.3	260.8	

It is observed from the table that, the radiative properties A, σ_e , FWHM and ΔG of LTB0.5E glass comparable to the reported glasses, it can be suggested as the potential candidate for the development of laser and optical amplifier devices.

8. Conclusion

In the present work, the presence of B-O stretching vibrations of [BO₃]⁻ units and in BO₄ units and the stretching vibrations of Te-O-Te linkages in TeO₄ units were confirmed through FTIR spectra. The bonding parameter of all the

glasses was calculated and the increasing negative values indicate the increasing ionic nature in the LTbxE glasses. The trend follows the usual manner of erbium as $\Omega_2 > \Omega_4 > \Omega_6$. The spectroscopic factor (Ω_4/Ω_6) was found to be 1.28 for LTb0.5E glass which suggest for photonic applications. The broad luminescence with high intensity was observed in LTb0.5E glass and the other optical device determining properties such as A , σ_e , FWHM and ΔG for the same glass is found to be higher thus, suggest its feasibility for the development of laser and optical amplifier devices.

9. References

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