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Optical characterization, infrared emission and visible up-conversion in Er^{3+} doped tellurite glasses

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ABSTRACT

In this work, Er^{3+} doped tellurite glasses have been prepared with the composition (82.5-x) TeO_2 + 4.5Bi_2O_3 + 11.5ZnO + 1.5Nb_2O_5 + x Er_2O_3 (x = 0.1, 0.3, 0.5, 0.7, 1.0 mol%) by melt-quenching method and their physical, spectroscopic properties were investigated. The experimental oscillator strengths (f_{exp}) of individual absorption peaks are used to estimate the Judd–Ofelt intensity parameters ($\Omega_\lambda, \lambda = 2, 4, 6$). Judd–Ofelt intensity parameters are used to calculate the spontaneous transition probabilities, radiative lifetimes and branching ratios for certain excited states of Er^{3+} ions. NIR emission and visible up-conversion luminescence were observed at room temperature for all glasses by exciting with 980 nm laser radiation. The emission characteristics such as peak stimulated emission cross section, FWHM, figure of merit, optical gain cross sections and measured lifetimes have been obtained for the observed Er^{3+}: $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition in the above glass composition for all the concentrations and are compared with that of the reported. Finally, NIR to visible energy conversion has been analyzed for all glasses excited at 980 nm and suitable mechanism was proposed.

1. Introduction

In recent years there is an increasing demand in rare earth (RE) doped glasses for photonic applications such as up-conversion lasers, optical amplifiers, non-linear optical devices and production of optical fibers, etc [1–5]. In RE doped glasses, in-homogeneously broadened emission profiles are common due to the dopant ion location in a variety of chemical environments. In order to achieve broadband emission profile and efficient up-conversion emission, the choice of suitable host glass for rare earth ions is very important. Generally, the up-conversion is difficult to observe in oxide based glasses such as silicate or borate glasses because of the dominance of multi-phonon relaxation process that suppresses or even eradicate the transitions with small energy level difference due to their high phonon energies. However, oxide glasses are promising candidates for practical applications because of their high mechanical strength, thermal stability, chemical durability and ease of fabrication [6,7]. Among oxide glasses, tellurite glasses are of growing interest due to their special properties [8,9] even compared with fluoride glasses. The low phonon energy (750 cm^{-1}) of tellurite glasses may reduce non-radiative losses due to multi-phonon relaxation leading to strong up-conversion luminescence [10,11]. Tellurite glasses are capable of providing large and broad stimulated emission cross sections because of their high refractive indices at the communication band (C - band) and attractive host for broadband applications [12]. Tellurite glasses provide a broad bandwidth higher than 70 nm and a gain-flattened amplification of 20 dB receiving considerable attention for their use in erbium doped fiber amplifiers (EDFAs) [13].

On the other hand incorporation of RE ions into a variety of glasses has been considered as important factor in the development of optical devices based on suitable host materials, such as Infrared (IR) lasers, IR-Visible (Vis) converters, fiber and waveguide amplifiers for optical transmission network. Among RE ions, erbium ion (Er^{3+}) has been considered as one of the most efficient ion and the possibility to excite them with laser diode (LD) at 980 nm, promoting population from $^4I_{15/2}$ to $^4I_{11/2}$. The popular Er^{3+} ion energy level scheme allow many radiative transitions occur for a long excited state lifetime that can be conventionally populated by the absorption of photons in the near infrared (NIR) region. Moreover, Er^{3+} ion has the ability to convert IR light into Vis light and sufficiently emits photons in the blue, green and red region of the spectrum efficiently. Recently, NIR and Vis up-conversion luminescence in Er^{3+} doped different glass compositions and concentrations were reported by many authors [14–17].

Usually, Judd–Ofelt (J–O) theory [18,19] has been applied to estimate important spectroscopic properties of RE doped glasses by many researchers. In the present work, we report the spectroscopic properties of Er^{3+} doped TeO_2 + Bi_2O_3 + ZnO + Nb_2O_5 (TBZNb) glasses. J–O intensity parameters, radiative transition probabilities and branching

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ratios were estimated using UV–Vis–NIR absorption spectra. Broadband NIR emission at 1.5 μm and Vis up-conversion luminescence spectra were recorded under 980 nm excitation. The emission cross section (σ), FWHM, figure of merit, optical gain cross section and lifetime for the Er^{3+}: $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition has been analyzed. The energy conversion mechanism is explained with the help of energy level diagram through the energy transfer and cross-relaxation processes.

2. Experimental

Er^{3+} doped tellurite glass samples were prepared with high purity raw materials, TeO_2 (99.995%), Bi_2O_3 (99.995); ZnO (99.995); Nb_2O_5 (99.995%) and Er_2O_3 (99.995%) using melt quenching method. The samples were weighed according to the molar composition: (82.5-x) TeO_2 + 4.5Bi_2O_3 + 11.5ZnO + 1.5Nb_2O_5 + x Er_2O_3 and are referred as TBZNbEr01, TBZNbEr03, TBZNbEr05, TBZNbEr07 and TBZNbEr10 glasses for x = 0.1, 0.3, 0.5, 0.7 and 1.0 mol%, respectively. The powder mixture was taken in platinum crucible and melted at 800–850 °C using induction furnace located inside a hermetic box (glove-box) with a controlled dry N_2 atmosphere (<2 ppm of water). The melt was cast into stainless steel plate and the samples obtained were polished for optical measurements.

The Vis–NIR absorption spectra were recorded in the spectral range of 300–1700 nm using a UV–Vis–NIR Perkin-Elmer Lambda 9 spectrophotometer. The NIR emission at 1.5 μm and NIR to Vis up conversion emission spectra was measured using Jobin-Yvon Fluorolog-3 spectrofluorimeter (Horiba FL3-22iHR320) with a 980 nm crystal laser (DL series). The emission lifetimes were measured using the above mentioned instrument with a pulsed 150 W Xenon lamp using multi channel system (Fluoro Hub-B) and 1024 channels. All these measurements were carried at room temperature.

Densities of glass samples were determined by Archimedes principle using distilled water as an immersion liquid. The refractive indices of the samples were measured by the prism coupling method (Metricon Model 2010) at 633 nm, 1305 and 1536 nm. Table 1 shows certain physical properties of Er^{3+} doped TBZNb glasses.

3. Results and discussion

3.1. Absorption spectra and Judd–Ofelt analysis

Optical absorption spectrum of TBZNbEr10 glass recorded in the spectral region 390–1700 nm is shown in Fig. 1. The absorption spectrum consists of nine absorption bands at 407, 443, 452, 489, 522, 545, 653, 977 and 1531 nm associated to the absorption from the $^4I_{15/2}$ ground state to the $^2G_{9/2}$, $^4F_{3/2}$, $^4F_{5/2}$, $^4F_{7/2}$, $^2H_{11/2}$, $^4S_{3/2}$, $^4F_{9/2}$, $^4I_{11/2}$ and $^4I_{13/2}$ excited states of Er^{3+} ions, respectively. The absorption spectra of all other samples are qualitatively similar in shape except variation in intensities. From the optical transmittance spectra (see inset of Fig. 1(a)), it is observed that optical absorption edge is not sharply defined in the present glass which clearly indicates its amorphous nature. The absorption edge in amorphous materials at absorption coefficients > 10^4 cm^{-1} is interpreted in terms of indirect transitions across an optical band gap [20]. For absorption by indirect transitions the absorption coefficient, α(ω), is given by [21]

$$\alpha(\omega) = A\left(\hbar\omega - E_{opt}\right)^2/\hbar\omega \quad (1)$$

where α(ω) is the absorption coefficient, A is a constant, E_{opt} is the optical band gap and ħω the photon energy of the incident radiation. Fig. 2 represents ħ $(\alpha\omega)^{1/2}$ as a function of phonon energy, ħω, for the measurement of energy gap in TBZNbEr10 glass. The optical energy gap (E_{opt}) is obtained by extrapolating from the linear region of the plot of ħ $(\alpha\omega)^{1/2}$ against ħω. For TBZNbEr10 glass, the value of E_{opt} is found to be 2.98 ± 0.21 eV which is higher than the reported PTBEr10 glass (2.57 eV) [22] and lower than SALSFEr10 glass (3.62 eV) [23].

The band positions were calculated following the procedure outlined by Lakshman and Jayasankar [24]. The rms deviation between experimental and calculated band position were reasonable which indicates the full matrix diagonalisation. According to the method of Wong [25] and Taylor's series expansion and using the observed band energies as E_J, zero order energies E_{0J} and partial derivatives of the RE ion [26], the correction factors ΔE^k, $\Delta\xi_{4f}$ and Δα are evaluated by least squares fit method. From the known free ion parameters ΔE^0, ΔE^0_{4f} and α^0, the parameters E^k, ξ_{4f} and α in the complex are determined. Racah (E^1, E^2 and E^3), spin orbit (ξ_{4f}), configuration interaction (α) parameters and hydrogenic ratios (E^1/E^3 and E^2/E^3) for TBZNBEr10 glass were evaluated and are reported in Table 2 along with some other reported glasses. From Table 2, the hydrogenic ratios, E^1/E^3 (10.23) and E^2/E^3 (0.048) are comparable with the other host glasses which suggest that even though the matrix changes from glass to glass, the radial properties of the Er^{3+} remains unchanged.

In general, the absorption spectrum of RE ions serves as a basis for understanding the radiative properties of the excited luminescent levels which arises due to the sharp absorption lines from 4f–4f electronic transitions. Using the absorption spectrum of Er^{3+} ion in TBZNb glass, the radiative transitions associated to the $4f^n$ configuration of RE ions can be analyzed by the Judd–Ofelt (J–O) theory. According to J–O theory, the theoretical oscillator strength (f_{cal}) of an electric dipole absorption transition from the initial state, (SLJ) to the final state, (S′L′J′), depends on the three J–O intensity parameters, Ω_λ (λ = 2, 4 and 6) as

$$f_{cal} = \frac{8\pi^2 mc\cdot\left(n^2+2\right)^2}{3h(2J+1)\,\lambda\cdot 9n}\times\sum_{\lambda=2,4,6}\Omega_\lambda\left|\left\langle (SL)J\left\|U^{(\lambda)}\right\|(S'L')J'\right\rangle\right|^2 \quad (2)$$

where λ is the mean wavelength of the transition, m is the mass of the electron, c is the speed of light and n is the refractive index, h is the Plank constant and $\|U^{(\lambda)}\|$ are the doubly reduced matrix elements of the tensor operators that are considered to be independent of the host matrix, we have used the doubly reduced matrix elements given in Ref. [27].

Table 1
Certain physical properties of Er^{3+} doped TBZNb glasses.

Parameter	TBZNbEr01	TBZNbEr03	TBZNbEr05	TBZNbEr07	TBZNbEr10
Average molecular weight, M (g)	162.2	166.6	167.1	167.5	168.2
Density, d (g/cm^3)	4.002 ± 0.088	4.173 ± 0.098	4.214 ± 0.094	4.273 ± 0.085	5.091 ± 0.096
Refractive index, n_d (633 nm)	2.1547 ± 0.001	2.1521 ± 0.001	2.1515 ± 0.001	2.1495 ± 0.001	2.1476 ± 0.001
Molar refractivity, R_M (cm^{-3})	11.543 ± 0.122	11.080 ± 0.054	10.997 ± 0.042	10.862 ± 0.031	9.142 ± 0.025
Dielectric constant, ε	4.642 ± 0.002	4.631 ± 0.002	4.628 ± 0.002	4.620 ± 0.002	4.612 ± 0.002
Polarisability, $\alpha_e \times 10^{24}$ (cm^3)	9.03 ± 0.02	8.67 ± 0.02	8.60 ± 0.02	8.50 ± 0.02	7.16 ± 0.02
Ion concentration, $N \times 10^{20}$ (ions/cm^3)	0.290 ± 0.003	0.905 ± 0.101	1.519 ± 0.093	2.151 ± 0.081	3.646 ± 0.064
Ionic radius, r_i (A^0)	13.10 ± 0.06	8.97 ± 0.04	7.55 ± 0.03	6.73 ± 0.02	5.64 ± 0.02
Inter ionic distance, r_p (A^0)	32.55 ± 0.12	22.37 ± 0.04	18.74 ± 0.07	16.69 ± 0.056	14.00 ± 0.043
Field strength, $F \times 10^{-14}$ (cm^2)	1.74 ± 0.01	3.72 ± 0.027	5.26 ± 0.039	6.63 ± 0.043	9.43 ± 0.059
Reflection loss, R%	13.39 ± 0.04	13.36 ± 0.08	13.35 ± 0.07	13.32 ± 0.06	13.29 ± 0.06