

Investigation on physical, structural and optical properties of Er³⁺ - doped bismuth borate glasses for optical fiber amplifier applications

¹B. Munisudhakar, ^{2*}C. Nageswara Raju, ³M. Reddi Babu, ⁴N. Manohar Reddy, ³A. Mohan Babu, ³L. Rama Moorthy

¹ Research Scholar, JNTUA, Ananthapuramu, India-515 002

²Department of Physics, Sri Venkateswara Degree College, Kadapa, India-516003

³Department of Physics, Chadalawada Ramanamma Engineering College, Tirupati, India-517506

⁴Department of Physics, Sri Venkateswara College of Engineering, Tirupati, India-517502

Abstract : A new series of Er³⁺ - doped bismuth borate glasses were prepared with the chemical composition of 5Bi₂O₃ - (65-x) B₂O₃ - 10ZnO - 10Pb₃O₄ - 10AlF₃ - xEr₂O₃ (where x = 0.0, 0.1, 0.5, 1.0, 2.0 and 3.0 mol %) using the melt quenching technique. The prepared glasses were characterized by XRD, absorption, luminescence and decay spectral analysis. From XRD spectra, the amorphous and homogeneous nature of the prepared bismuth borate glasses was confirmed. The physical and optical properties of the prepared glass samples were determined. From the intensities of absorption bands, the Judd-Ofelt analysis has been applied to determine the intensity parameters Ω_λ ($\lambda = 2, 4$ and 6) and the trend of these parameters has been observed as $\Omega_2 > \Omega_6 > \Omega_4$ and are used to calculate the various radiative parameters of the ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$ emission transition of Er³⁺ ions. The normalized NIR emission spectra for the ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er³⁺ - doped BBZPA glasses with various Er₂O₃ concentrations under 980 nm laser excitation were recorded in the wavelength region 1400 – 1700 nm. It has been observed that the spectra exhibited strong emission at 1530 nm corresponding to ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition. The other relative parameters such as stimulated emission cross-section (σ_e), optical gain (G), gain band width (ΔG) were calculated. The recorded fluorescence decay curves of the ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of the Er³⁺ - doped BBZPA glasses exhibited single exponential nature upto 1.0 mol% and then turned into non-exponential for 2.0 and 3.0 mol% of Er³⁺ ions concentrations. These results suggest that the present BBZPAEr1.0 glass system could be suitable for optical amplifier applications at 1.53 μm .

Index Terms - Bismuth borate glasses, XRD, Absorption, J-O parameters; emission spectra; decay time.

I. INTRODUCTION

In order to design and develop novel optical devices such as solid state lasers, optical fiber wave guides, sensors, color displays, optical data storages and optical amplifiers for optical communications, the rare earth (RE³⁺) ions plays a prominent role due to their high efficiency emissions corresponding to the 4f – 4f and 4f – 5d electronic transitions [1-4]. Among these, the 4f – 4f transitions exhibit more intense fluorescence patterns from the ultraviolet (UV) to the near infrared regions due to shielding effect. In the last few decades, tremendous amount of research work has been done on the luminescent properties of RE³⁺ ions doped different host matrices such as silicates, phosphates, tellurates and germanates. Among them, borate glasses have been extensively studied for the last few decades due to its novel properties like high transparency, high thermal stability, low refractive index and low dispersion and high solubility for RE³⁺ ions which make them more suitable optical materials for due to their versatile applications in the field of lasers and optical fiber communications [5, 6].

Though borate glasses possess high phonon energies due to stretching vibrations of the network forming oxides and it can be reduced by the addition of heavy metal oxides (HMO) to them. This leads to decrease of non-radiative relaxation rates and enhances quantum efficiencies of excited levels. Also, B₂O₃ is one of the best glass formers and can form a glass network at a low melting point with high chemical durability and ease of fabrication. When alkali or alkaline earth ions are introduced in the glass network, they can change the structural behavior and properties of the glass network. Addition of Bi₂O₃ into the borate glass network increases the glass chemical durability and thermal stability. Addition of ZnO into the borate glass network generates different dopant sites by creating a strong interaction that enhances optical and spectral properties. So, in this study, the authors concentrated on bismuth borate as glass host in order to meet the above device applications [7, 8].

Among different trivalent rare earth ions, the Er³⁺ ion is one of the most interesting ions for obtaining laser emission and frequency up-conversion. Generally, Er³⁺ ion exhibits mainly three emission transitions ${}^4I_{11/2} \rightarrow {}^4I_{15/2}$ at 3000 nm, ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$ at 1500 nm and ${}^4S_{3/2} \rightarrow {}^4I_{15/2}$ at 550 nm, [9]. Particularly, Er³⁺ ions doped glasses have been drawn much interest for the use in telecommunication applications such as waveguide lasers, frequency upconversion lasers, wavelength division multiplexing (WDM) network system, waveguide amplifier, erbium – doped fiber amplifier (EDFA), eye safe laser systems, full color solid state displays and lidar transmitters due to its characteristic infrared (NIR) emission at 1.5 μm through the ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition [10-12].

The aim of present work is (i) to prepare Er³⁺ doped bismuth borate glasses with different Er₂O₃ concentrations by traditional melt quenching method, (ii) to calculate physical and optical properties of the prepared glasses, (iii) to examine the structure of the glasses through XRD, (iv) to calculate oscillator strengths and Judd-Oflet (JO) intensity parameters (Ω_λ , $\lambda = 2,$

4 and 6) from the absorption spectra and finally (v) to determine various radiative properties for the ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition for laser and optical amplifier applications.

2. Experimental details

2.1. Glass preparation

The Er^{3+} -doped bismuth borate glasses were prepared using the chemical composition of $5 \text{ Bi}_2\text{O}_3 - (65-x) \text{ B}_2\text{O}_3 - 10 \text{ ZnO} - 10 \text{ Pb}_3\text{O}_4 - 10 \text{ AlF}_3 - x\text{Er}_2\text{O}_3$, where $x = 0.0, 0.1, 0.5, 1.0, 2.0$ and 3.0 mol% by conventional melt quench technique. Appropriate amounts of high purity raw materials, mentioned in the composition were thoroughly mixed and ground in an agate mortar in clean and dry environment until homogenous mixtures were obtained and taken into alumina crucibles. They were melted in a programmable electric furnace for 45 minutes, at 1100°C and the melts were then poured onto a preheated brass mould and then pressed with another brass plate. The glasses thus prepared were then annealed at 350°C for 15 h to eliminate thermal strains and stresses acquired by the glass matrix during sudden quenching. Finally, the prepared glasses were cut and polished to measure their, physical, structural optical properties and are labeled as BBZPAEr0.0, BBZPAEr0.1, BBZPAEr0.5, BBZPAEr1.0, BBZPAEr2.0 and BBZPAEr3.0 based on erbium ions concentrations used in the glass host matrix as presented in Table 1.

Table 1 Chemical composition of the Er^{3+} -doped bismuth borate (BBZPAEr x) glasses ($x = 0.0, 0.1, 0.5, 1.0, 2.0$ and 3.0 mol %)

Glass code	Glass composition (mol %)
BBZPAEr0.0	65-B ₂ O ₃ -10Pb ₃ O ₄ -5Bi ₂ O ₃ -10ZnO-10AlF ₃
BBZPAEr0.1	64.9-B ₂ O ₃ -10Pb ₃ O ₄ -5Bi ₂ O ₃ -10ZnO-10AlF ₃ -0.1Er ₂ O ₃
BBZPAEr0.5	64.9-B ₂ O ₃ -10Pb ₃ O ₄ -5Bi ₂ O ₃ -10ZnO-10AlF ₃ -0.5Er ₂ O ₃
BBZPAEr1.0	64.95-B ₂ O ₃ -10Pb ₃ O ₄ -5Bi ₂ O ₃ -10ZnO-10AlF ₃ -1.0Er ₂ O ₃
BBZPAEr2.0	64-B ₂ O ₃ -10Pb ₃ O ₄ -5Bi ₂ O ₃ -10ZnO-10AlF ₃ -2.0Er ₂ O ₃
BBZPAEr3.0	63-B ₂ O ₃ -10Pb ₃ O ₄ -5Bi ₂ O ₃ -10ZnO-10AlF ₃ -3.0Er ₂ O ₃

2.2.Characterization techniques

The refractive indices of the BBZPAEr x ($x = 0.0, 0.1, 0.5, 1.0, 2.0$ and 3.0 mol%) glasses were measured by using an Abbe refractometer (ATAGO) at sodium wavelength (589.3 nm) with mono-bromonaphthalene as contact liquid between sample and the prism of the refractometer and the densities of the prepared glasses were measured by Archimedes principle with distilled water as an immersion liquid. The X-ray diffraction (XRD) spectra were recorded using JEOL8530 x-ray diffractometer with CuK_α radiation source to confirm the amorphous nature of the prepared glasses. The optical absorption spectrum of BBZPAEr1.0 glass was recorded from wavelength 400-1000 nm range on a JASCO V-770 UV-Visible-NIR spectrophotometer. The photoluminescence spectra and decay profile measurements of the prepared glasses were carried out at room temperature using Edinburgh FLS-980 fluorescence spectrometer.

3. Results and discussion

3.1. Physical and optical properties

The physical properties of the prepared glass samples were calculated using the following expressions [13-16] and presented in Table 2.

Thicknesses, density and molar volume:

The thickness of the prepared glasses was measured by digital vernier callipers. The densities (ρ) of the prepared glasses were measured by the Archimedes' method with distilled water as an immersion liquid using the following expression

$$\rho = \frac{W_a \times \rho_b}{W_a - W_b} \quad (1)$$

where w_a is the weight of glass in air, w_b is the weight of glass when immersed in liquid and ρ_b is the density of liquid. The molar volume of the glass samples was calculated by

$$V_m = \frac{M_T}{\rho} \quad (2)$$

where M_T is the total molecular weight of the multi-component glass system.

Refractive Index

Refractive indices for the prepared glasses were measured by using Abbe refractometer at sodium wavelength (589.3 nm) with 1-bromonaphthalene ($\text{C}_{10}\text{H}_7\text{Br}$) as a contact liquid.

Reflection loss

The reflection loss from glass surface was calculated by using Fresnel's formula

$$R_L = \left[\frac{(n-1)}{(n+1)} \right]^2 \quad (3)$$

where n is the refractive index of the glass.

Molar refraction

The molar refraction (R_m) of the glass samples were calculated using the formula well known as Volf and Lorentz-Lorentz formula

$$R_m = \frac{(n^2-1)}{(n^2+2)} \times V_m \quad (4)$$

Molar electronic polarizability, dielectric constant and optical dielectric constant:

The molar refraction of the glass (R_m) is related to the structure of the glass and it is proportional to the molar electronic polarizability of the glass sample (α_m), according to the relation

$$\alpha_m = \frac{R_m}{2.52} \quad (5)$$

The dielectric constants (ϵ) were calculated using the refractive index of the glasses

$$\epsilon = n^2 \quad (6)$$

The optical dielectric constant ($P \frac{dt}{dp}$) of the glass is given as

$$P \frac{dt}{dp} = (\epsilon - 1) = n^2 - 1 \quad (7)$$

Electronic polarizability, ionic concentration and polaron radius

The electronic polarizability (α_e) was calculated using the formula

$$\alpha_e = \frac{3(n^2-1)}{4\pi A_v(n^2+2)} \quad (8)$$

where A_v is the Avogadro's number.

The rare earth ions concentration of the glasses were determined using the following relation

$$N(\text{ions/cm}^3) = \frac{N_A \rho}{M_{AV}} \times (\text{mol\% of rare earth ions}) \quad (9)$$

where M_{AV} is the average molecular weight.

The polaron (R_p) radii were calculated using the formula

$$R_p = \frac{1}{2} \times \left(\frac{\pi}{6N} \right)^{\frac{1}{3}} \quad (10)$$

Inter-ionic distance, field strength and oxygen packing density:

Inter-ionic distance (R) of the glass samples is given as

$$R_i = \left(\frac{1}{N} \right)^{\frac{1}{3}} \quad (11)$$

The field strengths were calculated using the formula

$$F (\text{cm}^3) = \left(\frac{t}{R_p^2} \right) \quad (12)$$

where t is the thickness of the samples.

The oxygen packing density (O.P.D) of the glass samples were calculated using the following relation

$$\text{O.P.D} = x \left(\frac{\rho}{M} \right) \times 1000 \quad (13)$$

where ρ the density of desired glass samples, M is the molecular weight of the sample and x is the number of oxygen atoms in the composition.

Table 2 Physical properties of Er^{3+} -doped bismuth borate (BBZPAEr x) glasses ($x = 0.0, 1.0, 0.5, 1.0, 2.0$ and 3.0 mol %)

Physical properties	BBZPAEr0.0	BBZPAEr0.1	BBZPAEr0.5	BBZPAEr1.0	BBZPAEr2.0	BBZPAEr3.0
Sample thickness(cm)	0.15	0.24	0.14	0.18	0.21	0.22
Refractive index(n)	1.631	1.653	1.653	1.652	1.653	1.653
Density(g/ cm ³)	5.30	5.28	5.20	5.18	5.10	5.08
Molecular weight(M)g/mol	153.64	153.95	155.20	156.77	156.90	156.90
Er ³⁺ ion concentration (mol/lit)	0	0.034	0.168	0.331	0.647	0.937
Er ³⁺ ion concentration (10 ²⁰ ions/ cm ³)	0	2.050	1.014	1.997	3.902	5.643
Oxygen packing density(O) m ³ /mol	8.98	8.94	8.75	8.59	8.45	8.41
Polaron radius(r _p)A ⁰	0	3.250	2.580	1.310	0.610	0.463
Field strength(F) in 10 ¹⁵ /cm ²	0	22.722	21.032	10.488	5.643	9.799
Inter ionic distance(r _i)A ⁰	0	7.867	9.953	7.940	6.351	5.616
Molar volume (V _m)cm ³ /mol	28.988	29.157	29.674	30.148	30.868	31.966

Molar refractivity(R_m) cm^3	13.172	10.671	10.861	11.034	11.298	11.700
Electronic polarizability (α_e) in 10^{-25} cm^3	1.412	1.450	1.450	1.450	1.450	1.450
Molar electronic polarizability (α_m) in $10^{-24} \text{ cm}^3/\text{mol}$	5.226	4.234	4.309	4.378	4.483	4.642
Reflection losses(R) in%	5.70	6.05	6.05	6.04	6.05	6.05
Dielectric constant(ϵ)	2.660	2.732	2.729	2.732	2.732	2.732
Optical dielectric constant ($\epsilon - 1$)	1.660	1.732	1.729	1.732	1.732	1.732
Metallization factor(M)	0.545	0.634	0.633	0.634	0.634	0.634
Numerical aperture (NA)	0.230	0.230	0.233	0.233	0.233	0.233

3.2. Structural analysis

3.2.1. XRD analysis

The x-ray diffraction (XRD) spectra of Er^{3+} - doped bismuth borate glasses been recorded in the range $20^\circ \leq \theta \leq 90^\circ$ and are shown in Fig. 1. It is clear that, the XRD spectra show no sharp Bragg's peak, but only a broad diffuse hump around lower angle region which indicates a long range structural disorder and hence confirms the amorphous nature of the prepared glasses.

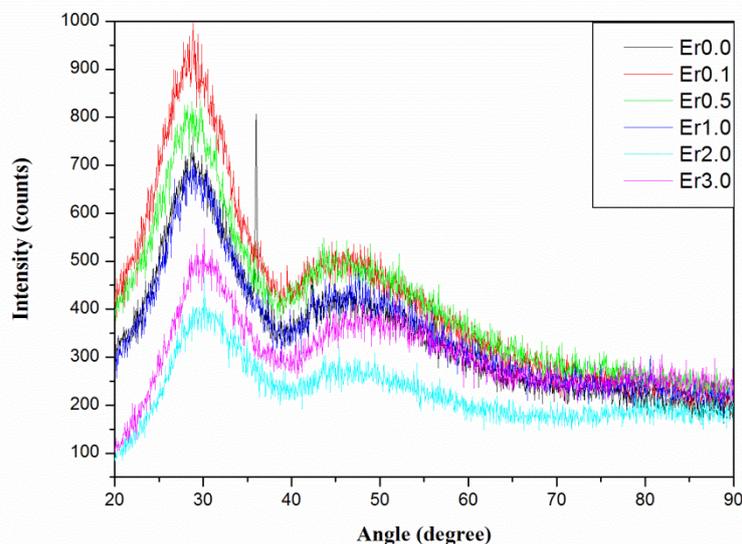


Fig. 1 XRD spectra of BBZPAEr_x (x = 0.0, 1.0, 0.5, 1.0, 2.0 and 3.0 mol %) glasses

3.3. Optical Studies

3.3.1. Optical absorption spectrum and J-O analysis

Fig. 2 shows the optical absorption spectrum of BBZPAEr1.0 (1.0 mol % Er^{3+}) glass recorded in the UV-Vis-NIR region at room temperature. The absorption spectrum exhibits nine transitions from ground state $^4I_{15/2}$ to the various excited states $^4I_{13/2}$, $^4I_{11/2}$, $^4F_{9/2}$, $^4S_{3/2}$, $^2H_{11/2}$, $^4F_{7/2}$, $4F_{5/2}$, $^2G_{9/2}$ and $4G_{11/2}$ corresponding to the peak positions at 1526, 973, 652, 543, 521, 488, 451, 407 and 378 nm respectively. The assignment of absorption bands are done according to the reported data [17-19].

Among all the transitions of Er^{3+} ions, the transitions $^4I_{15/2} \rightarrow ^4G_{11/2}$ and $^4I_{15/2} \rightarrow ^2H_{11/2}$ located at 378 and 521 nm bands are hypersensitive in nature because they strongly depends upon the Er-ligand environment and obey the selection rules $|\Delta L| \leq 2, |\Delta J| \leq 2, |\Delta S|=0$. In general, the hypersensitive transitions possess higher reduced matrix elements $\|U^2\|^2$ and also higher oscillator strengths compared to other transitions.

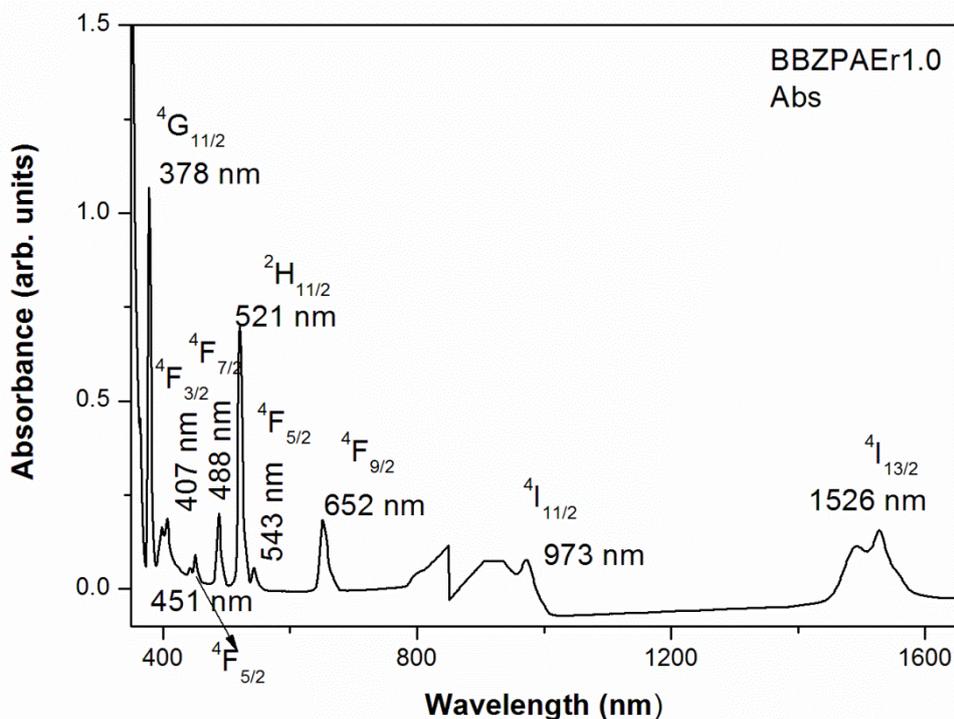


Fig.2 Optical absorption spectrum of BBZPAEr1.0 glass in UV-visible and NIR regions.

3.3.2. Oscillator strengths and JO intensity parameters

Oscillator strength (f) is a dimensionless quantity, which gives the intensity of the absorption band corresponding to a particular transition. From the absorption spectrum, the experimental oscillator strength of a particular transition is determined by calculating the area under the absorption band and is expressed as [20-21].

$$f_{exp} = 4.32 \times 10^{-9} \int \epsilon(\nu) d\nu \tag{14}$$

where $\epsilon(\nu) = OD/Ct$ is the molar extinction coefficient at mean energy ν (cm^{-1}) and it represents the area under an absorption peak, 'OD' is the optical density, 'C' is the concentration of rare earth ions in moles/lit and 't' is the optical length (thickness) of the glass in cm.

The theoretical oscillator strength (f_{cal}) for the absorption peak corresponding to the electric dipole f-f transition from the initial state ΨJ to final state $\Psi' J'$ is evaluated from the J-O theory using the following equation [22];

$$f_{cal}(\Psi J, \Psi' J') = \frac{8\pi^2 mc \nu}{3h(2J+1)} \left[\frac{(n^2 + 2)^2}{9n} S_{ed}(\Psi J, \Psi' J') + n S_{md}(\Psi J, \Psi' J') \right] \tag{15}$$

where $(2J+1)$ is the degeneracy of the ground state of Er^{3+} ions, 'm' is mass of the electron, 'c' is the velocity of light, ν is the mean energy of the transition in cm^{-1} , 'h' is the Planck's constant, S_{ed} and S_{md} are the line strengths for induced electric and magnetic dipole transitions and are given by,

$$S_{ed}(\Psi J, \Psi' J') = e^2 \sum_{\lambda=2,4,6} \Omega_{\lambda} \left| \langle \Psi J || U^{\lambda} || \Psi' J' \rangle \right|^2 \tag{16}$$

$$S_{md}(\Psi J, \Psi' J') = \frac{e^2 h^2}{16\pi^2 m^2 c^2} \left| \langle \Psi J || (L + 2S) || \Psi' J' \rangle \right|^2 \tag{17}$$

where Ω_{λ} ($\lambda = 2, 4$ and 6) are the J - O intensity parameters, which depends on the host material and $||U^{\lambda}||$ are the doubly reduced matrix element of the unit tensor operator.

The J-O intensity parameters, Ω_{λ} ($\lambda = 2, 4$ and 6) are determined by a standard least square fitting between the experimental (f_{exp}) and calculated (f_{cal}) oscillator strengths. The quality of fit between the experimental (f_{exp}) and calculated (f_{cal}) oscillator strengths is determined by rms deviation using the following expression

$$\delta_{rms} = \left[\frac{\sum (f_{exp} - f_{cal})^2}{P} \right]^{\frac{1}{2}} \tag{18}$$

where 'P' is the total number of energy levels used in the fitting procedure.

The experimental (f_{exp}) and calculated (f_{cal}) oscillator strengths along with their r.m.s deviation (δ_{rms}) are tabulated in Table 3. It is clear that, the obtained δ_{rms} is $\pm 0.505 \times 10^{-6}$, indicates an amazing match between the experimental and calculated oscillator strengths.

Table 3 Observed band positions λ_p (cm), energies (cm^{-1}), experimental ($f_{exp} \times 10^{-6}$), calculated ($f_{cal} \times 10^{-6}$) oscillator strengths and root mean square deviation ($\delta_{rms} \times 10^{-6}$) of BBZPAEr1.0 glass.

Transition from ground state $4I_{15/2} \rightarrow$	Wavelength(nm)	Energy(cm^{-1})	Oscillator strengths	
			f_{exp}	f_{cal}
$^4I_{13/2}$	1526	6553	4.0000	3.7929
$^4I_{11/2}$	973	10277	0.9200	1.7091
$^4F_{9/2}$	652	15337	3.8700	3.8715
$^4S_{3/2}$	543	18416	1.7900	1.5736
$^2H_{11/2}$	521	19194	7.8900	8.3222
$^4F_{7/2}$	488	20492	4.8400	5.3782
$^4F_{5/2}$	451	22173	2.4700	1.9126
$^2G_{9/2}$	407	24570	1.4700	2.2063
$^4G_{11/2}$	378	26455	15.2500	14.7431
			$\delta_{rms} = \pm 0.505$	

The relative magnitudes of JO intensity parameters Ω_λ ($\lambda = 2, 4$ and 6) depend on the symmetry and rigidity of the host glass matrix, and bonding nature between rare earth ions. The magnitude of Ω_2 indicates the sensitivity of the local structure of the Er^{3+} ions site symmetry, ligand anions and is affected by covalence between the Er^{3+} ions and ligands, whereas, the Ω_4 and Ω_6 parameters indicate the viscosity and rigidity of the host glass matrix [23]. The evaluated Judd-Oflet intensity parameters Ω_2 , Ω_4 and Ω_6 of BBZPAEr1.0 are presented in Table 4. It is noticed that Ω_2 , Ω_4 and Ω_6 values for the BBZPAEr1.0 glass follow the trend $\Omega_2 > \Omega_6 > \Omega_4$ and similar trend has been observed for the other reported Er^{3+} - doped glasses [24-28].

Table 4 Comparison of Judd-Oflet (JO) intensity parameters ($\Omega_\lambda, \times 10^{-20} cm^2$) and spectroscopic quality factor (χ) of BBZPAEr1.0 glass with other reported glasses.

Glass code	JO Parameters			Trends of Ω_λ	$\chi = \Omega_4/\Omega_6$
	Ω_2	Ω_4	Ω_6		
BBZPAEr1.0 [Present work]	4.69	1.35	3.78	$\Omega_2 > \Omega_6 > \Omega_4$	0.35
TBZNbEr10[27]	4.41	1.07	1.57	$\Omega_2 > \Omega_6 > \Omega_4$	0.24
Oxyfluoroxirconate[24]	3.01	1.03	1.64	$\Omega_2 > \Omega_6 > \Omega_4$	0.34
SLBiB15E[25]	3.91	1.17	2.35	$\Omega_2 > \Omega_6 > \Omega_4$	0.29
BTFBEr10[6]	3.53	1.02	1.651	$\Omega_2 > \Omega_6 > \Omega_4$	0.62
BaLiBO[26]	1.80	0.28	0.90	$\Omega_2 > \Omega_6 > \Omega_4$	0.31
CaLiBO[26]	3.68	0.76	1.52	$\Omega_2 > \Omega_6 > \Omega_4$	0.50
SrLiBO[26]	2.53	0.39	1.10	$\Omega_2 > \Omega_6 > \Omega_4$	0.35
MgLiBO[26]	1.33	0.39	0.62	$\Omega_2 > \Omega_6 > \Omega_4$	1.12
SALSFer10[28]	8.57	2.05	2.60	$\Omega_2 > \Omega_6 > \Omega_4$	0.23

3.4. NIR photoluminescence and decay life time analysis

Fig.3 shows the normalized NIR emission spectra of the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition of Er^{3+} - doped BBZPA glasses for various Er_2O_3 concentrations under 980 nm laser excitation. The intensity of the emission peak at 1530 nm increases with an increase in Er^{3+} ions concentration from 0.1 to 1.0 mol% and thereafter decreases for 2.0, 3.0 mol% concentrations due to the phenomenon of quenching effect.

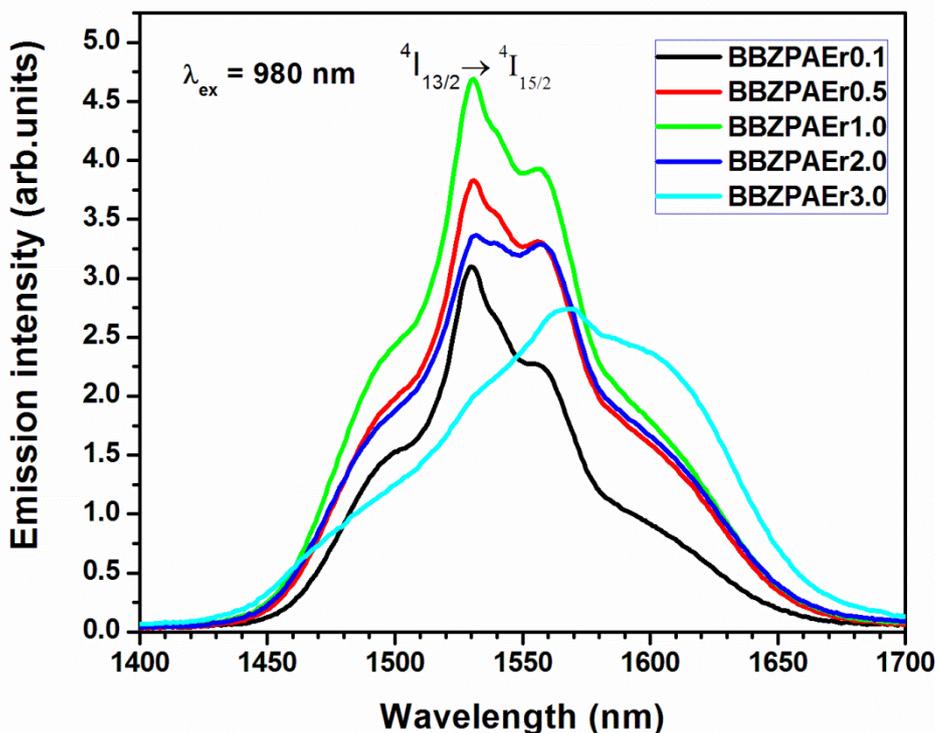


Fig. 3 Normalized NIR emission spectra of BBZPAEr_x (x = 0.0, 1.0, 0.5, 1.0, 2.0 and 3.0 mol %) glasses.

The intensity parameters (Ω_λ , $\lambda = 2, 4$ and 6) have been used to calculate the radiative properties such as branching ratios (β_R), radiative decay time (τ_R), radiative transition probabilities (A_R), effective band width ($\Delta\lambda_{exp}$), stimulated emission cross-sections (σ_e), gain band width ($\sigma_e \times \Delta\lambda_{exp}$), optical gain ($\sigma_e \times \tau_{rad}$), and figure of merit ($\sigma_e \times \tau_{exp}$) values for the $^4I_{13/2} \rightarrow ^4I_{15/2}$ emission transition of the BBZPAEr1.0 glass and compared in Table 5.

Table 5 Comparison of emission peak positions (λ_p , nm), radiative decay time (τ_R), radiative transition probabilities (A_R, s^{-1}), effective band width ($\Delta\lambda_{exp}$, nm), stimulated emission cross-sections ($\sigma_e, \times 10^{-21} \text{ cm}^2$) and optical gain ($(\sigma_e \times \tau_{rad}), \times 10^{-24} \text{ cm}^2$), figure of merit ($(\sigma_e \times \tau_{exp}), \times 10^{-24} \text{ cm}^2$) and gain bandwidth ($(\sigma_e \times \Delta\lambda_{exp}), \times 10^{-25} \text{ cm}^3$) values for $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition of the BBZPAEr1.0 glass.

Glass System	λ_p (nm)	τ_R	A_R	$\Delta\lambda_{exp}$	σ_{emi}	$\sigma_e \times \Delta\lambda_{exp}$	$\sigma_e \times \tau_{rad}$	$\sigma_e \times \tau_{exp}$
BBZPA Er1.0 [Present work]	1531	2.60	383	101	10.2	1.03	2.65	3.55
SANSCEr10[13]	1535	5.18	193	53	9.8	0.52	-	3.57
SALSFEr10[28]	1533	3.99	250	63	11.6	0.73	4.62	-
LZBEr0.5[17]	1532	4.40	184	66	9.3	0.61	4.09	4.03
PKAPbNEr10[18]	1550	6.91	144	46	6.7	0.31	4.62	1.38
PKSAEr10[19]	1533	7.43	134	34	6.0	0.20	4.45	-
LBSEr10[22]	1529	2.19	338	38	17.0	0.64	5.02	-
PTBEr10[21]	1531	7.31	137	87	9.3	0.61	6.79	4.09
LBTAFEr10[20]	1532	6.51	153	103	4.4	0.45	2.89	2.89

The spontaneous transition probabilities (A_R) of each transition from the initial state ΨJ to final state $\Psi' J'$ can be calculated using the expression [29,30]

$$A_R(\Psi J \rightarrow \Psi' J') = \frac{64 \pi^4 \nu^3}{3h (2J + 1)} \left[\frac{n(n^2 + 2)^2}{9} S_{ed}(\Psi J \rightarrow \Psi' J') + n^3 S_{md}(\Psi J \rightarrow \Psi' J') \right] \quad (19)$$

where S_{ed} and S_{md} electric and magnetic dipole strength respectively.

The total radiative transition probability (A_T) for an excited level is expressed as the sum of radiative transition probability $A_R(\psi J \rightarrow \psi' J')$ from a particular energy level to all possible terminal levels and is given by

$$A_T(\Psi J) = \sum_{\Psi' J'} A_R(\Psi J \rightarrow \Psi' J') \quad (20)$$

The radiative lifetime (τ_R) of an excited level $\Psi' J'$ is given by

$$\tau_R(\Psi J) = \frac{1}{\sum_{\Psi' J'} A_R(\Psi J \rightarrow \Psi' J')} \quad (21)$$

The fluorescence branching ratio (β_R) corresponding to each transition from the initial state ΨJ to final state $\Psi' J'$ can be calculated using the expression

$$\beta_R(\Psi J \rightarrow \Psi' J') = \frac{A_R(\Psi J, \Psi' J')}{A_T(\Psi J)} \quad (22)$$

The stimulated emission cross-sections (σ_e) between ΨJ and $\Psi' J'$ levels is determined by Fauchbauer-Ladenburg [F-L] formula [31].

$$\sigma_e(\Psi J \rightarrow \Psi' J') = \frac{\lambda_p^4}{8 \pi c n^2 \Delta \lambda_{eff}} A_R(\Psi J \rightarrow \Psi' J') \quad (23)$$

where λ_p is the emission peak wavelength and $\Delta \lambda_{eff}$ is the effective line width of the transition observed and is given by

$$\Delta \lambda_{eff} = \frac{1}{I_{max}} \int I(\lambda) d\lambda \quad (24)$$

where I is the fluorescence intensity and I_{max} is the intensity at band maximum. The stimulated emission cross-section (σ_e) of the ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+} ion by Fauchbauer-Ladenburg formula is $102.96 \times 10^{-22} \text{ cm}^2$.

The fluorescence lifetime of ${}^4I_{13/2}$ excited level is a very important parameter for investigation of laser gain medium and optical amplifier. The higher magnitude of the ${}^4I_{13/2}$ level lifetime is the key factor in the possibility of Er^{3+} -doped laser gain medium and optical amplifiers in optical communication. The fluorescence decay curves of the ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of the Er^{3+} -doped BBZPA glasses are recorded with an excitation wavelength of 980 nm and monitored at 1535 nm emission and are shown in Fig.4. It is observed that the decay curves exhibit single exponential nature upto 1.0 mol% of Er^{3+} concentration and then it turned into non-exponential for 2.0 and 3.0 mol% of Er^{3+} concentrations.

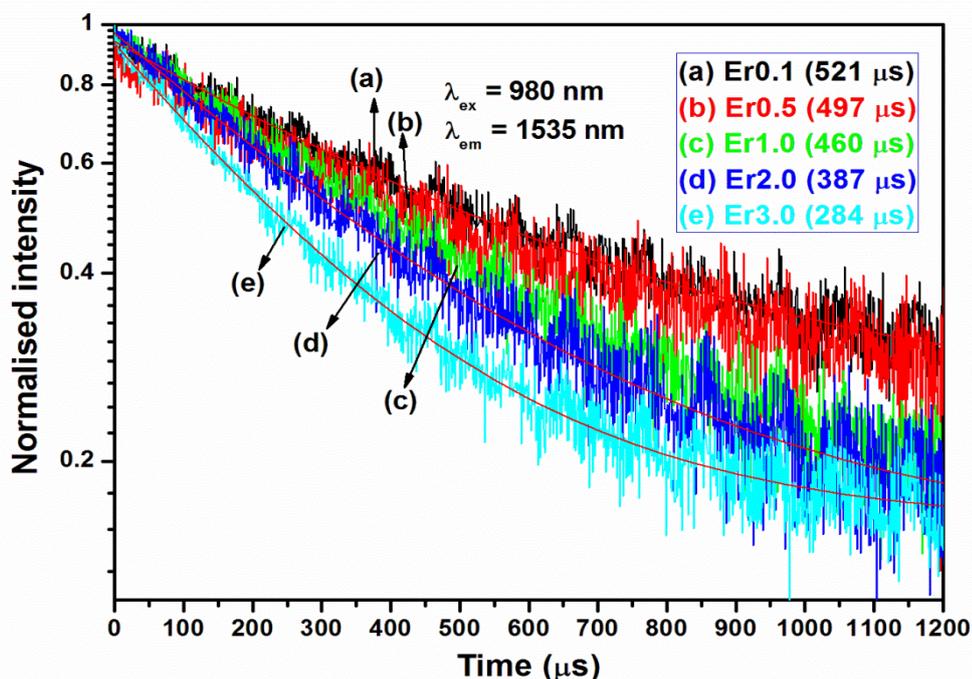


Fig.4 Fluorescence decay curves for ${}^4I_{13/2}$ excited state of BBZPAEr ($x = 0.0, 1.0, 0.5, 1.0, 2.0$ and 3.0 mol %) glasses.

From Table 5 and based on the radiative parameters, it is suggested that BBZPA1.0 glass is more suitable for lasing action and also active media for optical fiber amplifier applications.

4. Conclusions

In the present work, bismuth borate (BBZPA) glasses doped with different Er^{3+} ions concentrations were prepared by conventional melt quenching technique. The amorphous nature of Er^{3+} -doped BBZPA glasses were confirmed from results of XRD investigation. The physical and optical properties were calculated to optimize these glasses for 1.53 μm laser applications. From absorption spectra, the three intensity parameters (Ω_λ , $\lambda = 2, 4$ and 6) were calculated and their trend has been observed as $\Omega_2 > \Omega_6 > \Omega_4$. The higher value of the Ω_2 parameter indicates the higher covalence and /or higher asymmetric around Er^{3+} ions in the present host glass matrix. The radiative properties such as radiative transition probabilities (A_R), total radiative transition probability (A_T), radiative lifetime (τ_R), branching ratios (β_R) and stimulated emission cross-section (σ_e) of the emission transition ${}^4\text{I}_{13/2} \rightarrow {}^4\text{I}_{15/2}$ of the Er^{3+} -doped BBZPA glasses were calculated. From emission spectra, it is observed that ${}^4\text{I}_{13/2} \rightarrow {}^4\text{I}_{15/2}$ transition intensity increases upto 1.0 mol% of Er^{3+} ions concentrations and decreases at higher Er^{3+} ions concentrations due to concentration quenching effect. The stimulated emission cross-section (σ_e) has been calculated for the ${}^4\text{I}_{13/2} \rightarrow {}^4\text{I}_{15/2}$ transition from Fauchbauer-Ladenburg formula. From the fluorescence decay profile, it is observed that the decay curves exhibited single exponential nature upto 1.0 mol% of Er^{3+} concentration and then it turned into non-exponential for 2.0 and 3.0 mol% of Er^{3+} ions concentrations. All the results suggest that the prepared BBZPAEr glass could be attractive for NIR laser and optical amplifier applications.

REFERENCES

- [1] S. Hraiech, M. Ferid, Y. Guyot, G. Boulon, Structural and optical studies of Yb^{3+} , Er^{3+} and $\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped phosphate glasses, *J. of Rare Earths*, 31 (2013)685 – 693.
- [2] D. Ramachari, L. Rama Moorthy, C.K. Jayasankar, Optical absorption and emission properties of Nd^{3+} -doped oxyfluorosilicate glasses for solid state lasers, *Infrared Physics & Technology*, 67 (2014) 555–559.
- [3] G. Gupta, A.D. Sontakke, P. Karmakar, K. Biswas, S. Balaji, R. Saha, R. Sen, K. Annapurna, Influence of bismuth on structural, elastic and spectroscopic properties of Nd^{3+} doped zinc-boro-bismuthate glasses, *J. Lumin.* 149 (2014) 163 – 169.
- [4] W.T. Carnall, F.R. Fields and K. Rajnak, Electron energy levels in trivalent lanthanide aquo ions: I. Pr^{3+} , Nd^{3+} , Sm^{3+} , Dy^{3+} , Ho^{3+} , Er^{3+} , and Tm^{3+} , *J. Chem. Phys.*, 49 (1968) 4424 – 4442.
- [5] S. Damodaraiah, V. Reddy Prasad, Y. C. Rathnakaram, Investigations of Green and 1.53 μm emission characteristics of Er^{3+} doped bismuth phosphate glasses for laser applications, *J. of Alloys and comp.* 741(2018) 269-280.
- [6] K. Annapoorani, K. Maheshvaran, S. Arunkumar, N. Surya, Murthy, K. Marimuthu, Structural and luminescence behaviour of Er^{3+} ions doped Barium tellurofluoro borate glasses, *Spectrochimica Acta, Part A: Mol. and Biomol. Spectroscopy* 135 C (2014) 1090-1098.
- [7] Priyanka Goyal, Yogesh Kumar Sharma, Sudha Pal, Umesh Chandra Bind, Shu-Chi Huang, Shyan-Lung Chung, The effect of SiO_2 content on structural, physical and spectroscopic properties of Er^{3+} doped $\text{B}_2\text{O}_3\text{-SiO}_2\text{-Na}_2\text{O-PbO-ZnO}$, *J. of Non-cry. solids* 463(2017)118-127.
- [8] Kaky, Kawa M and Lakshminarayana, G. and Baki, S. O. and Lira, A. and Caldino, U. and Meza-Rocha, A. N. and Falcony, C. and Kityk, I. V. and Taufiq-Yap, Y. H. and Halimah, M. K. and Mahdi, M. A., Structural and optical studies of Er^{3+} -doped alkali/alkaline oxide containing zinc boro-aluminosilicate glasses for 1.5 μm optical amplifier applications. *Opt. Mat.* 69 (2017) 401-419.
- [9] S. Gaafar, S.Y. Marzouk, Judd-Ofelt analysis of spectroscopic properties of Er^{3+} doped $\text{TeO}_2\text{-BaO-ZnO}$ glasses, 723(2017)1070-1078.
- [10] P. Suthanthira Kumar, P. Karthikeyan, P. K. Manimozhi, K. Marimuthu, Structural and spectroscopic behavior of $\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped boro-tellurite glasses, *J. Non-Cryst. Solids*, 410 (2015) 26-34.
- [11] ZHAO Yingang, SHI Dongmei, Effect of alkali metal oxides R_2O ($\text{R} = \text{Na}, \text{K}$) on 1.53 μm luminescence of Er^{3+} -doped $\text{Ga}_2\text{O}_3\text{-GeO}_2$ glasses for optical amplification, *J. of Rare Earths*, 31 (2013) 857 –863.
- [12] S E. J. Friebele, Eds D. R. Uhlmann, N. J. Kreidl, In: Optical properties of glasses, American Ceramic Society, Westerville, OH, U. S. A. (1991) p.205 – 262.
- [13] G. Devarajulu, O. Ravi, C. Madhukar Reddy, Sd. Zulfiqar Ali Ahamad, B. Deva Prasad, Raju, Spectroscopic properties and up conversion studies of Er^{3+} -doped $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-Na}_2\text{CO}_3\text{-SrF-CaF}_2$ oxyfluoride glasses for optical amplifier, *J. of Lumin.* 194(2018) 499-506.
- [14] Beena Bhatia, S. L. Meena, Vishal Parihar, Monika Poonia, Optical basicity and polarizability of Nd^{3+} doped bismuth borate glasses, *New Journal of Glass and Ceramics*, 5(2015) 44-52.
- [15] Ohishi, Y., Mitachi, S., Kanamori, T. and Manabe, T, Optical Absorption of 3d Transition metal and rare earth elements in zirconium fluoride glasses. *Physics and Chemistry of Glasses*, 24(1983) 135-140.
- [16] Shelby, J.E. and Ruller, J, Properties of Barium Gallium Germanate Glasses. *Physics and Chemistry of Glasses*, 28(1987) 262.
- [17] K. Annapoorani, Ch. Basavapoonima, N. Surya, Murthy, K. Marimuthu, Investigations on structural and behavior of Er^{3+} doped Lithium Zinc borate glasses for lasers and optical amplifier applications, *J. Non-cryst. Solid.* 447(2016)273-282.
- [18] Ch. Basavapoonima, K. Linganna, C.R. Kesavulu, S. Ju, B.H. Kim, W-T. Han, C.K. Jayasankar, Spectroscopic and pump power dependent up conversion studies of Er^{3+} -doped lead phosphate glasses for photonic applications, *Journal of Alloys and*

Compounds 699(2017) 959-968.

- [19] K.Linganna, M.Rathaih, N.Vijaya, Ch. Basavapoonima, C.K.Jayasankar, S.Ju, W-T.Han, V.Venkaramu, 1.53 μ m luminescence properties of Er³⁺-doped K-Sr-Al phosphate glasses, *Ceramics International*, 41(4) (2014) 5765-5771.
- [20] B.C.Jamalah, Suhasini, L. Rama Moorthy, K. Janardhan Reddy, I.-G. Kim, D.-S. Yoo, K. Jang, Visible and nearinfrare luminescence properties of Er³⁺-doped LBTAf glasses for optical amplifiers *Opt. Mater.* 34 (2012) 861.
- [21] M.V. Vijaya Kumar, K. Rama Gopal, R.R. Reddy, G.V. Lokeswara Reddy, B.C.Jamalah, Luminescence and gain characteristics of 1.53 μ m broadband of Er³⁺ in lead telluroborate glasses, *J. Lumin.* 142 (2013) 128.
- [22] Midde Reddi Babu, N. Madhusudhana Rao, A. Mohan Babu, Effect of erbium ion concentration on structural and luminescence properties of lead borosilicate glasses for fiber amplifiers, *The J. Biological and Chemical Luminescence*, 33(1)(2017) 71-78.
- [23] L.Vijaya Lakshmi, K.Naveenkumar, K.Srinivasa Rao, Pyung Hwang, Bright up-conversion white light emission from Er³⁺ doped lithium fluoro zinc borate glasses for photonic applications, *J. Molecular Structure*, 1155(2018) 394-402.
- [24] Feifei Huang, Xueqiang Liu, Lili Hu, Danping Chen, Spectroscopic properties and energy transfer parameters of Er³⁺-doped fluorozirconate and oxyfluoroaluminate glasses, *Scientific Reports* 4 (5053)(2014)1.
- [25] D. Rajesh, Y.C. Ratnakaram, A. Balakrishna, The electronic and optical properties of quaternary B_xGa_{1-x}As_{1-y}Sb_y alloys with low boron concentration, *J. Alloys Compd.* 563 (2013) 22.
- [26] A.Renuka Devi, C.K.Jayasankar Optical properties of Er³⁺ ions in lithium borate glasses and comparative energy level analyses of Er³⁺ ions in various glasses, *J. Non-Cryst. Solids* 197 (1996) 111.
- [27] M.Seshadri, E.F.Chillce, J.D.Marconi, F.A.Sigoli, Y.C.Ratnakaram, L.C.Barbosa, Optical characterization, infrared emission and visible up-conversion in Er³⁺ doped tellurite glasses, *J. Non-Cryst. Solids*, 402 (2014) 141-148.
- [28] C.R.Kesavulu, V.B.Sreedhar, C.K.Jayasankar, Kiwan Jang, Dong-Soo Shin, Soung Soo Yi, Structural, thermal and spectroscopic properties of highly Er³⁺-doped novel oxyfluoride glasses for photonic application, *Materials Research Bulletin* 51(2014)336- 344.
- [29] P. Manasa, D. Ramachari, J. Kaewkhao, P. Meejitpaisan, E. Kaewnuam, A.S. Joshi, C.K. Jayasankar, Studies of radiative and mechanical properties of Nd³⁺-doped lead fluorosilicate glasses for broadband amplification in a chirped pulse amplification based high power laser system, *J. of. Lumi.* 188 (2017) 558 – 566.
- [30] Jiang, J. Yang, S. Dai, Optical spectroscopy and gain properties of Nd³⁺-doped oxide glasses, *J. Opt. Soc. Am. B* 21 (2004) 739 –744.
- [31] A. Madhu, B. Eraiah, P. Manasa, N. Srinatha, Nd³⁺-doped lead boro-tellurite glass for lasing and amplification applications, *Opt.Mater.* 75 (2018) 357 – 366.

