Spectroscopic Studies of Er³⁺-Yb³⁺ Codoped Multicomposition Tellurite Oxide Glass (Kajian Spektroskopi Kaca Telurit Teroksida Pelbagai Kandungan Terdop Er³⁺-Yb³⁺)

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ABSTRACT

Multicomposition of $Er^{3+}-Yb^{3+}$ codoped tellurite oxide, TeO_2 -ZnO-PbO-Ti O_2 -Na₂O glass has been investigated. A detailed spectroscopic study of the Judd-Ofelt analysis has been performed from the measured absorption spectrum in order to obtain the intensity parameters Ω_i (t=2, 4, 6). The calculated Ω_i values were then utilized in the determination of transition probabilities, radiative lifetimes and branching ratios of the Er^{3+} transitions between the J(upper)-J'(lower) manifolds. Both visible upconversion and near-infrared spectra were characterized under the 980 nm laser diode excitation at room temperature.

Keywords: Judd-Ofelt analysis; tellurite oxide glas; upconversion

ABSTRAK

Kaca telurit teroksida pelbagai kandungan TeO₂-ZnO-PbO-TiO₂-Na₂O terdop Er^{3+} -Yb³⁺ telah dikaji. Penyelidikan terperinci terhadap spektroskopi melalui analisis Judd-Ofelt telah dilakukan hasil daripada cerapan spektrum penyerapan untuk mendapatkan pemboleh ubah keamatan $\Omega_{_{1}}(t=2, 4, 6)$. Hasil pengiraan nilai $\Omega_{_{1}}$ telah digunakan dalam penentuan kebarangkalian peralihan, tempoh hayat sinaran dan nisbah cabangan peralihan Er^{3+} di antara jaluran J(atas)-J'(bawah). Spektra bagi anjakan-atas cahaya nampak dan infra-merah dekat telah dicirikan melalui pengujaan laser diod 980 nm pada suhu bilik.

Kata kunci: Analisis Judd-Ofelt; anjakan-atas; kaca telurit teroksida

INTRODUCTION

The role of rare-earth ions as optical activators in glasses and crystals have been continuously studied in recent years because of their interesting optical properties especially for photonic applications such as solid state lasers and optical fiber amplifiers. Among the lanthanides, primary attention has been focused on the trivalent erbium ion ion (Er^{3+}) which acts as luminescence center for the 1.5 µm emission due to the ${}^{4}I_{13/2} \rightarrow {}^{4}I_{15/2}$ transition of Er^{3+} . Moreover Er^{3+} is also an efficient ion for the upconversion process where several visible anti-stoke emission could be easily obtained with commercially infrared laser diodes (LD).

Selecting the suitable host material for Er^{3+} is an important criterion in the development of potential optical devices since the emission characteristic of Er^{3+} is strongly depends on the glass composition (Lakshminarayana et al. 2008a). The incorporation of Er^{3+} ions as luminescence centers in glasses have been attracted much attention especially in obtaining wide and flat gain spectrum of the 1.5 µm optical telecommunication window (Ding et al. 2000; Tanabe 1999; Tanabe et al. 2000; Yamada et al. 1998). In addition, Yb³⁺ ions has also been used as sensitizer by facilitating efficient energy transfer from the Yb³⁺ to Er^{3+} ions under the 980 nm laser diode (LD) excitation (Hu et al. 2001). Among glass host, tellurite oxide glasses have

shown interesting both physical and optical properties. They possess better chemical durability and thermal stability as compare to fluoride, chalcogenide and chloride glasses (Higuchi et al. 1998; Maciel et al. 1997; Oliveira et al. 1998). They have lower melting temperature and with high rare earth solubility as compare to silicate and borate glasses (Neindre et al. 1999; Pan et al. 1996; Wang et al. 1994; Weber et al. 1981). Moreover tellurite glasses also have lower phonon energy (700-800 cm⁻¹), high dielectric constant, wide transmission window (0.4-6 μ m) (Burger et al. 1985) and high refractive index (>2).

In this study, detailed spectroscopic studies of new multicomposition $Er^{3+}-Yb^{3+}$ codoped TeO_2 -ZnO-PbO-TiO₂-Na₂O (TZPTiN1) tellurite glass will be presented. Lead oxide, PbO was added into the glass as modifier in order to form more stable glass, larger linear and nonlinear refractive indexes due to its massive mass, low field strength and high polarizability. An addition of ZnO was reported could modify the basic TeO_4 *trigonal bypyramid* system of the TeO₂ parent host matrix and facilitate better glass formation (Burger et al. 1992). TiO₂ was also added to further enhance the glass stability and refractive index which could lead higher radiative transition probabilities (Kim & Yoko 1995; Lines 1991; Nasu et al. 1992). Furthermore the incorporation of Na₂O into the glass may

improve the rare-earth solubility for higher usage of dopant concentration which is important for the implementation of high efficiency short length fiber amplifiers (Byun et al. 1994; Hayden et al. 1990; Minami & Mackenzie 1997).

EXPERIMENTAL DETAILS

GLASS PREPARATION

In the present work the starting chemicals oxide powders of TeO₂ (99.9995%), ZnO (99.7%), PbO (99.97%), TiO₂ (99.99%), Na₂O (99.5%), Er₂O₃ (99.9%) and Yb₂O₃ (99.9%) were supplied by American Elements and Strem Chemicals. The Er3+-Yb3+ doped TeO2-ZnO-PbO-TiO₂-Na₂O (TZPTiN1) glass sample was prepared by substitutionally replaces PbO with 2.5 mol% Er³⁺ and 2 mol% Yb3+ into host glass with mol% composition of 60TeO₂-20ZnO-10PbO-5TiO₂-5Na₂O. All the chemicals were carefully weighed and mix thoroughly before melted in a closed-lid alumina crucible in an electrical furnace for an hour at 1000°C. Then the melt was quickly quenched onto a preheated stainless steel plate mold before immediately transferred into an annealing furnace at 200°C for 2 h in order to remove thermal strains before gradually cool down to room temperature. Circular glass discs with dimension of 2 cm diameter and 3 mm thickness were obtained and polished for optical measurement.

PROPERTIES CHARACTERIZATION

The density measurement was determined by the Archimedes principle with distilled water as an immersion liquid. The host glass structure was determined in bulk form through X-ray diffraction (XRD) analysis on a Siemens D5000 X-ray diffractometer at range of $2\theta =$ $(5 - 80^\circ)$ utilizing Cu-K α (1.5406 Å) radiation with an applied voltage of 40 KV and 40 mA anode current at rate of 2⁰ min⁻¹. Raman measurements of the host glass was performed with a Horiba Jobin Yvon micro Raman PL spectrometer (Model: DU420A-OE-325) using an Argon ion laser as an excitation source (514.5 nm) within the range of 100 - 1000 cm⁻¹. Refractive index of the host was measured by apparent depth technique utilizing high resolution ProScope HR2TM imaging tools. The optical absorption spectrum of the doped glass sample was recorded with Jasco V570 UV/VIS/NIR spectrophotometer in the range of 350-2000 nm. Both visible upconversion and NIR emissions under 980 nm laser diode excitation were obtained using fiber based measurements via the USB2000 Ocean Optics and Avantes AvaSpec-NIR512-2.2 spectrometers respectively. All measurements were performed at room temperature. results and discussion

PHYSICAL PROPERTIES

The obtained host and doped glasses were homogenous, bubble-free and well transparent appearance. Figure 1 presents the photograph of the fabricated glasses in this study. The glassy nature of the host glass was confirmed from the XRD profile and is shown in Figure 2. The hollow with broad hump pattern indicates the amorphous nature of the surrounding glass host matrix at which the rare-earth site sites randomly situated. Table 1 lists out some of the obtained physical quantities value of the host and doped glasses. The increases in density in the doped glass was due to incorporation of higher molecular weight Er₂O₂ (382.52) g/mol) and Yb₂O₂ (394.11 g/mol) in replacement of lower molecular weight PbO (223.2 g/mol). As can be seen the molar volume also higher in the doped glass as compare to the host glass. The increase in molar volume is often relates to the formation of greater number of non-bridging oxygens (NBOs), which modified the tellurite host structure and creating more network spaces. These results are also explained in detail in the following section. Meanwhile the estimated optical energy gap, $E_{\rm opt}$ at the fundamental absorption edge is smaller in the doped glass as compare to the host glass. This condition has also proposed related to the creation of higher number of NBOs units after the incorporation of both Er3+ and Yb3+ ions into the host matrix (Nelson et al. 1983). In general this phenomenon is related to the oxygen bond strength in the glass network (Mcswain et al. 1963) and it is expected that electrons are less tightly bounded, hence caused the reduction of the E_{out} value. The obtained molar volume and optical energy gap values of the studied glasses are in agreement lie within the range of the values in various tellurite glasses reported by El-Mallawany (1998).



FIGURE 1. Fabricated host and $Er^{3+}\mbox{-}Yb^{3+}$ doped $TeO_2\mbox{-}ZnO\mbox{-}PbO\mbox{-}Ti_2O\mbox{-}Na_2O$ glasses

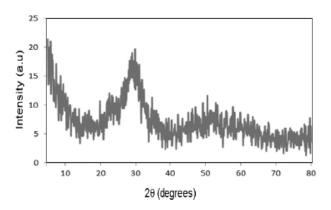


FIGURE 2. XRD profile of the 60TeO₂-20ZnO-5PbO-5TiO₂-10Na₂O host glass

TABLE 1. List of measured physical quantities value for TZPTiN1 glasses

Measured quantities	Host	Er3+-Yb3+doped
Molecular weight, M_{wt} (g/mol)	133.39	140.79
Molar volume, $V_m(g/cm^3)$	26.036	27.053
Density, ρ (g/cm ³)	5.1232	5.2042
Thickness, d (mm)	0.375	0.372
Optical energy gap (indirect), E_{opt} (eV)	2.81	2.67
Refractive index, n	2.042	2.375
${}^{1}\mathrm{Er}^{3+}$ concentration, N_{Fr}^{3+} (× 10 ²⁰ cm ⁻³)	-	11.131
$^{1}\text{Yb}^{3+}$ concentration, $N_{\text{Yb}}^{^{\text{E1}}3+}$ (× 10 ²⁰ cm ⁻³)	-	8.905

1. Concentration $N_{R3+} = 2 W \varrho/M$,

where W is weight fraction, M is mass of the rare-earth oxide molecule, R_2O_3 (R is the rare earth)

RAMAN SPECTRUM ANALYSIS

The Raman spectrum corresponding to the vibrational mode of certain TeO₂ polyhedral coordination of the TZPTiN1 host glass is shown in Figure 3. The obtained spectrum has been deconvoluted accordingly into four main symmetric Gaussian bands labeled as a, b, c, d around 770, 680, 460, 330 cm⁻¹, respectively (Takao et al. 1992). The band around 770 cm⁻¹ is attributed to stretching mode of the [TeO₃] tp (trigonal pyramids) units and (or) intermediate coordination of $[TeO_{3+1}]$ units, are found relatively more pronounce than its neighbor at 680 cm⁻¹. This lower frequency band is mostly often assigned to the stretching vibration of the [TeO₄] tbp (trigonal bipyramids) backbone units, which are dominantly exist in a pure TeO₂ based glass (inset spectrum of Figure 3). Thus it was suggested that the chain breaking of TeO₄ polyhedra involved by coordination transformation from $[TeO_4]$ tbp to $[TeO_{3+1}]$ and (or) $[TeO_3]$ tp via the $[TeO_{3+1}]$ units. The $[TeO_3]$ tp units are commonly contain terminal Te-O bonds (Te=O and Te-O) with non-bridging oxygens (NBOs) while $[TeO_4]$ tbp units with bridging oxygens (BOs). The formation of abundance NBOs which are with higher polarizability than the BOs have created relatively higher refractive index glass, beside the incorporation of TiO₂ with its high oxygen hyperpolarizability of Ti-O

pairs (Dimitrov & Komatsu 2005). The role of Ti⁴⁺ ion most probably created greater occupying sites for dopant atoms (Lakshminarayana et al. 2008a) forming more complex and thermally stable (reported elsewhere, Baki et al. 2013) glass structure. Another important observation is the band around 460 cm⁻¹ which ascribed to the bending mode of Te-O-Te (or O-Te-O) linkages of TeO₂ (n=4, 3+1, 3+1)3) network backbone was also decreased as a result of the $[TeO_4]$ tbp to $[TeO_3]$ tp conversion. The emerging of another lower neighbor frequency band around 330 cm⁻¹ could be also assigned to the formation of another [TeO₂] tp structural units with NBOs which probably due to the progressive destruction of the TeO₂ network backbone of the studied glass (Komatsu et al. 1991). Similar results were obtained by Reza Dousti et al. (2013) especially at the lower vibrational Raman frequency, which is also in good agreement with our multicomposition glass behavior.

ABSORPTION SPECTRUM AND JUDD-OFELT ANALYSIS

Figure 4 shows the absorption spectrum of the Er^{3+} -Yb³⁺ codoped TZPTiN1 glass in the visible and NIR region. The absorption bands peaked at 452, 488, 524, 544, 654, 800, 1533 nm were associated with the transition from the ground state ${}^{4}I_{15/2}$ to the excited state ${}^{4}F_{5/2}$, ${}^{4}F_{7/2}$, ${}^{2}H_{11/2}$, ${}^{4}S_{3/2}$, ${}^{4}F_{9/2}$, ${}^{4}I_{9/2}$ and ${}^{4}I_{13/2}$ of Er^{3+} , respectively. The strong

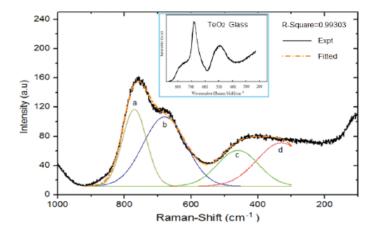


FIGURE 3. Raman spectrum of the 60TeO₂-20ZnO-5PbO-5TiO₂-10Na₂O host glass (The inset shows Raman spectrum for pure TeO₂ glass, (Takao et al. 1992) as comparison)

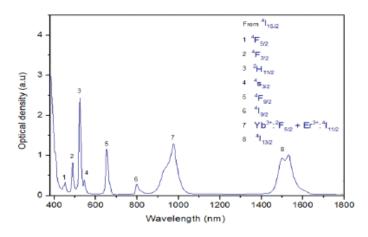


FIGURE 4. Absorption spectrum of Er³⁺-Yb³⁺ codoped TZPTiN1 glass

and broad absorption band at 977 nm is mostly attributed to the ${}^{2}F_{7/2} \rightarrow {}^{2}F_{5/2}$ transition of the Yb³⁺ ground state absorption and it coincides with ${}^{4}I_{11/2}$ level of Er³⁺ due to higher absorption cross section of Yb³⁺ as compared to Er³⁺ (Xiang et al. 2005). From the spectrum the studied glass exhibits good transparency within the visible range from 400 nm extended into near infrared region. It is to note that the high absorption at the ultraviolet edge below 400 nm is due to the fundamental absorption edge of the band gap of the glass matrix.

The Judd-Ofelt (JO) theory (Judd 1962; Ofelt 1962) stated that the electric dipole transition $S_{ed}(J \rightarrow J')$ for particular absorption of the rare-earth ions is given as:

$$S_{ed} (J \to J') = \sum_{t=2,4,6} \Omega_t \left| \left\langle (S,L) J \right\| U^{(t)} \| (S',L') J' \right\rangle \right|^2, \quad (1)$$

where Ω_2 , Ω_4 and Ω_6 are the JO intensity parameters. $||U^{(t)}||$ are the doubly reduced matrix elements of rank t (t=2, 4, 6) between the manifold states characterized by the quantum numbers (S, L, J) and (S', L', J') which are independent of the host matrix and can be found in published work by Carnall et al. (1965). From the above measured absorption profiles, the experimental line strengths S_{meas} between the ground state and the upper levels of the assigned bands could be obtained from the following relation:

$$S_{meas} = \frac{3chn(2J+1)}{8N\pi^3 e^2 \lambda} \left(\frac{9}{\left(n^2 + 2\right)^2} \right)_{band} k(\lambda) d\lambda, \qquad (2)$$

where $\int_{band} k(\lambda) d(\lambda)$ is the integrated absorption coefficient for particular absorption band at wavelength λ (k =2.303(OD)/d, d is sample thickness), N is the concentration of the RE ion, λ is the mean wavelength of the absorption band, J is the total angular momentum of the lower state, from the ^{2S+1}L_j designation, J=15/2 for Er³⁺), n is the host refractive index, e is the elementary electric charge and his the Planck constant. A fitting procedure which performs a least-squares fit of S_{meas} to S_{ed} is commonly applied to obtain the JO intensity parameters. The radiative lifetime τ_{rad} , branching ratio β and the spontaneous emission probability A_{rad} are calculated by:

$$\tau_{\rm rad} = 1/A[\Sigma(J \to J')]. \tag{3}$$

$$\beta(J \rightarrow J') = A_{\rm rad}(J \rightarrow J') / \left[\sum A_{\rm rad}(J \rightarrow J') \right]. \tag{4}$$

$$A_{rad}(J \to J^{\prime}) = \frac{64\pi^4 e^2}{3ch(2J+1)\lambda^3} \left[n \left(\frac{(n^2+2)^2}{9} \right) S_{ed} + n^3 S_{md} \right], (5)$$

for each transition $(J \rightarrow J')$, where the sum runs over all final states J' (lower state). The magnetic dipole terms S_{md} is ignored in this study since the selected absorption bands are essentially electrical dipole in nature. The selected absorption bands and their calculated line strength S values were shown in Table 2. In this work both physical and chemistry properties of the Er³⁺ nature within glass matrix were justified from the obtained JO intensity parameters Ω_{i} . In general Ω_t values tends to show $\Omega_2 > \Omega_4 > \Omega_6$ trend. Ω_2 intensity parameter is known related to short-range effect and sensitive to glass asymmetry which represents the ligand field structural formation surrounding the Er³⁺ ions within the glass matrix (Shilong et al. 2005). Meanwhile the Ω_{c} intensity parameter was inversely proportional to the covalency of the Er-O bond as reported by El-Mallawany et al.(2004). The richly NBOs formation within the host glass matrix vicinity has resulted in the electron density increments of the ligand ions, specifically on oxygen ions and this has reflected the inorganic ligand fields character within the glass matrix. As a result higher local pH environment with weaker Er-O covalency behavior is created near the Er³⁺ sites. Detail JO analysis for the spontaneous probabilities, branching ratios and radiative lifetimes of some excited states of Er3+ in the studied glass are shown in Table 3.

NEAR-INFRARED AND UPCONVERSION EMISSION SPECTRA The near-infrared emission spectrum for Er³⁺-Yb³⁺ codoped TZPTiN1 glass under 980 nm excitation is shown in Figure

Transition (from ${}^{4}I_{15/2}$)	λ (nm)	Energy	$\int OD(\lambda) d\lambda$	Line strength, $S (\times 10^{-20} \text{ cm}^2)$		
		(cm ⁻¹)	(10 ⁻⁷)cm	Measured, S_{meas}	Calculated, S_{calc}	
${}^{4}I_{13/2}$	1532	6527	61.62	1.7989	2.0052	
⁴ <i>I</i> _{9/2}	800	12500	3.7	0.2069	0.1710	
${}^{4}F_{9/2}$	655	15267	13.3	0.9082	0.8982	
⁴ S _{3/2}	545	18349	2.6	0.2134	0.1894	
${}^{2}H_{11/2}$	524	19084	19.3	1.6473	1.6473	
${}^{4}F_{7/2}$	489	20433	6.987	0.6385	0.6747	

TABLE 2. Integrated areas, dipole line strengths *S* and calculated JO intensity parameters $\Omega_{r}=(t=2,4,6)$ value for Er³⁺-Yb³⁺ codoped TZPTiN1 glass

 $\Omega_2 = 1.66 \times 10^{-20} \text{ cm}^2, \ \Omega_4 = 0.94 \times 10^{-20} \text{ cm}^2, \ \Omega_6 = 0.86 \times 10^{-20} \text{ cm}^2,$

 $\Delta(S) = 0.051 \times 10^{-20} \text{ cm}^2$, where $\Delta(S) = [\Sigma(\Delta S)^2/2]^{1/2}$

Transition		Energy $A_{rad}(s^{-1})$		β	t _{rad}		
			(cm ⁻¹)	A _{ed}	$A_{_{ m md}}$		(ms)
⁴ <i>I</i> _{13/2}	\rightarrow	⁴ <i>I</i> _{15/2}	6527	169.96	77.87	1.000	4.035
${}^{4}I_{11/2}$	\rightarrow	⁴ <i>I</i> _{13/2}	3729	30.95	17.49	0.183	
		${}^{4}I_{15/2}$	10256	216.73		0.817	3.771
${}^{4}I_{9/2}$	\rightarrow	${}^{4}I_{11/2}$	2244	1.25	2.60	0.013	
		⁴ <i>I</i> _{13/2}	5973	83.12		0.281	
		⁴ <i>I</i> _{15/2}	12500	208.77		0.706	3.381
${}^{4}F_{9/2}$	\rightarrow	⁴ <i>I</i> _{9/2}	2767	3.20	5.84	0.004	
		${}^{4}I_{11/2}$	5011	96.49	13.85	0.050	
		⁴ <i>I</i> _{13/2}	8740	92.53		0.042	
		⁴ <i>I</i> _{15/2}	15267	1997.64		0.904	0.453
${}^{4}S_{3/2}$	\rightarrow	⁴ <i>I</i> _{9/2}	5849	91.19		0.033	
		${}^{4}I_{11/2}$	8092	55.69		0.020	
		⁴ <i>I</i> _{13/2}	11821	765.56		0.279	
		⁴ <i>I</i> _{15/2}	18349	1828.38		0.667	0.365
${}^{2}H_{11/2}$	\rightarrow	${}^{4}F_{_{9/2}}$	3817	18.08		0.003	
		${}^{4}I_{9/2}$	6584	96.81		0.015	
		${}^{4}I_{11/2}$	8828	79.06		0.013	
		⁴ <i>I</i> _{13/2}	12557	144.99		0.023	
		⁴ <i>I</i> _{15/2}	19084	5962.74		0.946	0.159

TABLE 3. Calculated spontaneous emission probabilities A_{rad} , branching ratios β and radiative lifetime τ_{rad} in $Er^{3+}-Yb^{3+}$ codoped TZPTiN1 glass

5. Broad full width at half maximum (FWHM) emission centered at 1564 nm with 70 nm bandwidth corresponding to the ${}^{4}I_{13/2} \rightarrow {}^{4}I_{15/2}$ transition of Er^{3+} was observed from the spectrum. Such inhomogenous broadening has been suggested due to the complexness of the glass network structure which offered greater variety of dopant sites and as consequences modified the local crystal field surrounding the Er^{3+} ions (Lakshminarayana et al. 2008b). In general FWHM represents the bandwidth measure for an emission band. Wider and flat gain at 1.5 µm communication window are the two known important parameters required

for the development of high performance broadband erbium doped fiber amplifier. For this purpose both S and A_{rad} optical parameters should be higher. As given in (5), the larger refractive index (n~2) of the host glass may contribute to the high spontaneous emission probability. In addition the calculated electric dipole line strength S_{ed} which correspond to the ${}^{4}I_{13/2} \rightarrow {}^{4}I_{15/2}$ transition of Er³⁺ from the Judd Ofelt theory is given as; S_{ed} [${}^{4}I_{13/2} \rightarrow {}^{4}I_{15/2}$] = 0.0195 Ω_{2} + 0.1173 Ω_{4} + 1.4316 Ω_{6} , which is significantly dominated by larger Ω_{6} value. The weak Er-O covalency or inorganic ligand characteristic behavior shown by the doped glass is expected responsible for the broadness of the emission spectrum. The calculated radiative lifetime τ_{rad} of the ${}^{4}I_{13/2} \rightarrow {}^{4}I_{15/2}$ transition for this emission is 4.04 ms. Although the studied glass was with heavily Er^{3+} doped, the Yb³⁺ codoping may probably responsible for such longer lifetime by promoting an efficient energy transfer by eliminating the possibility of ion interactions among the Er^{3+} ions.

Figure 6 shows the upconversion spectra of the Er³⁺-Yb³⁺ codoped TZPTiN1 glass under 980 nm LD excitation. A significant increase of the visible intensity bands can be observed as the excitation power increases. Two green emission bands centered at 530 and 544 nm are assigned to the transitions from the Er³⁺ excited state levels ²H_{11/2} and ⁴S_{3/2} to the ground state level ⁴I_{15/2}, respectively. Meanwhile the red emission band centered at 660 nm corresponding to ⁴F_{9/2} \rightarrow ⁴I_{15/2} transition consists of shoulder around 670 nm which possibly due to intense Stark splitting of the level ⁴F_{9/2}. In addition as the excitation power increases the intensity of the red emission band are relatively stronger

than the green emission bands. The above upconversion processes could be analyzed by power dependence study (not shown here) which relates the integrated upconverted (I_{uc}) emission intensities and excitation pumping power (I_{exc}) as; $I_{uc} \alpha (I_{exc})^n$, where *n* denotes the number of photons absorbed per upconversion photon emitted. An approximate quadratic dependence $(n \sim 2)$ was exhibited in all emission intensities indicate that two photons were involved in the upconversion processes.

CONCLUSION

The multicomposition $Er^{3+}-Yb^{3+}$ codoped TeO_2 -ZnO-PbO-TiO₂-Na₂O (TZPTiN1) glass was successfully prepared and analyzed for both structural and optical properties. The glass matrix consisted of richly of NBOs within the surrounding TeO₂ glassy network of [TeO₃], [TeO₃₊₁] and [TeO₄] units. Important spectroscopic parameters such as the JO intensity parameters $\Omega_{1}(t = 2, 4, 6)$, electric dipole line strength, transition probability,

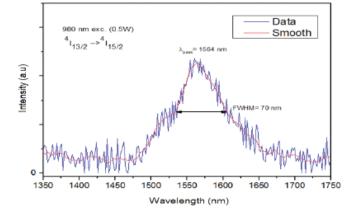


FIGURE 5. NIR emission spectrum of Er³⁺-Yb³⁺ codoped TZPTiN1 glass under 980 nm LD excitation

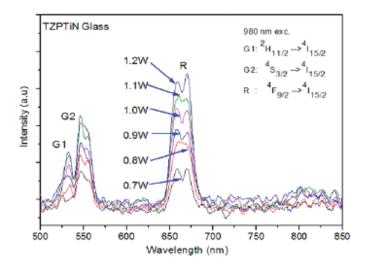


FIGURE 6. Upconversion spectrum of Er³⁺-Yb³⁺ codoped TZPTiN1 glass under different excitation power of 980 nm LD

branching ratio and radiative lifetime were determined by the JO theory. The Ω_{t} values showed the inorganic ligand characteristic behavior with much weaker Er-O covalency nature in the doped glass. Broad near-infrared emission centered at 1564 nm with FWHM around 70 nm was observed upon excitation with 980 nm LD. The role of Yb³⁺ ions as sensitizer in this complex glass has also promoted an efficient energy transfer among the Er³⁺ ions and lengthened the radiative lifetime of the ${}^{4}I_{13/2} \rightarrow {}^{4}I_{15/2}$ transition. Strong green and red upconversion emissions corresponding to the sequential of two-photon absorption process were also obtained from this glass. The upconverted emission intensities were found increased as the excitation power at 980 nm LD increased. From the results presented the proposed multicomposition glass in this work is a potential optical material for the future optical technology applications.

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