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## Judd-Ofelt analysis and luminescence studies of Er<sup>3+</sup> doped halogeno-antimonate glasses

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### Abstract

This research paper emphasized on application of Judd-Ofelt's (JO) theory for low doped erbium (0.2 mol%) halogeno- antimonate based glasses with molar composition (90 -x) Sb<sub>2</sub>O<sub>3</sub> - x ZnBr<sub>2</sub> - 10 NaCl (where x = 10, 20, 30 and 40 mol%). 80 Sb<sub>2</sub>O<sub>3</sub> – 9.8 ZnBr<sub>2</sub> - 10 NaCl - 0.2 Er<sub>2</sub>O<sub>3</sub> glass sample has low phonon energy and high refractive index is a potential candidate for luminescence applications. Differential scanning calorimetry (DSC) measurements show good thermal stability of the prepared glass samples and on the other hand density, expansion coefficient and elastic moduli were reported. Judd-Ofelt's (JO) parameter intensities  $\Omega_2 = 3.27 \times 10^{-20} \text{ cm}^2$ ,  $\Omega_4 = 1.24 \times 10^{-20} \text{ cm}^2$  and  $\Omega_6 = 1.88 \times 10^{-20} \text{ cm}^2$  were found and these values were compared with the literature. Radiative parameters such as spontaneous emission rate, branching ratio and lifetime were calculated. We focused on a high branching ratio radiative transitions  $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$  ( $\beta = 0.94$ ) and  $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$  ( $\beta = 0.901$ ). The overlap between absorption and emission bands is partial and stokes type shifts were presented. The gain curves were determined after calculation of absorption and stimulated emission cross sections. The infrared transmission curve of the glass matrix was

marked extrinsic absorption bands SiO and hydroxyl OH possessed high vibration energy played quenching effect for photoluminescence.

**Keywords:** Er<sup>3+</sup> doped glass; Judd-Ofelt theory; antimonate glass; radiative properties; gain coefficient.

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## 1. Introduction

Glasses doped with trivalent lanthanides have potential photonics applications, namely optical amplifiers, sensors, colour displays and solid state lasers [1-3]. Erbium is an effective dopant due to regularly spaced 4f<sup>n</sup> energy levels [4] and it is used in telecommunications for signal amplification around 1530 nm [5]. Judd-Ofelt analysis is a powerful technique for determining radiative parameters such as spontaneous emission rate, lifetime and branching ratio [6-7]. Further, certain Judd-Ofelt's spectroscopic parameters are included in the calculation of gain and quantum efficiency [8-10]. The cross section of stimulating emission is an essential factor for the choice of vitreous matrix and in this aspect the chemical composition of different glasses has been optimized [11-12]. The low phonon energy glasses are the best candidates for photoluminescence; since low phonon energy significantly allows to increase radiative transition probabilities [13], glasses like fluoro-zirconate and heavy metal oxide based glasses (HMOGs) [11, 13–15].

Antimonate glasses are part of the HMOGs exhibit good optical, photonic and mechanical properties and these glasses have a good chemical durability and low characteristic temperatures [16,17]. Moreover, antimonate based glasses are free of conventional formers (P<sub>2</sub>O<sub>5</sub>; B<sub>2</sub>O<sub>3</sub>; SiO<sub>2</sub>) and exhibit low lanthanide solubility (Ln<sup>3+</sup>) and at the limit of 0.4 mol % it became completely crystallized. The addition of conventional formers increases the solubility but reduces the phonon energy, infrared transmission and the refractive index.

The present work focuses on the application of Judd-Ofelt formalism for stable antimonate based glasses doped with erbium 80 Sb<sub>2</sub>O<sub>3</sub> – 9.8 ZnBr<sub>2</sub> - 10 NaCl - 0.2 Er<sub>2</sub>O<sub>3</sub>. There are a few reports in literature relating to Judd-Ofelt calculations for doped antimonate glasses free of conventional formers. According to M. Legouera [18] the Sb<sub>2</sub>O<sub>3</sub> - ZnBr<sub>2</sub> system generates stable glasses in a wide range where the two components act as glass formers. In the present

work, the choice of the glass matrix is based on the insertion of an additional compound (NaCl) in order to obtain a ternary system with a large glass domain, in which we will look for stable glasses. The dopant  $\text{Er}_2\text{O}_3$  is intended for Photonics applications and this choice is supported by the low phonon energy of the antimonate and by the beneficial action of halogenated compounds ( $\text{ZnBr}_2$ ; NaCl) which decrease the phonon density[19]. By the present analysis, we want to determine the radiative parameters of this specific glass doped at low content of trivalent erbium (0.2 mol%) and especially focused on radiative transitions; where possess a high branching ratio for determining the variation of gain coefficient related to the stimulated emission.

## 2. Experimental

### 2.1. Glass synthesis

The glass samples were prepared by melt-quenching method; using high purity chemicals  $\text{Sb}_2\text{O}_3 \geq 99\%$  (Acros),  $\text{ZnBr}_2 > 99\%$  (MERCK-SCHUCHARDT),  $\text{NaCl} > 99\%$  (Acros),  $\text{Er}_2\text{O}_3 \approx 99.9\%$  (Sigma). We have synthesized the glass matrix according to the composition  $(90 - x) \text{Sb}_2\text{O}_3 - x \text{ZnBr}_2 - 10 \text{NaCl}$  (where  $x = 10, 20, 30$  and  $40$  mol%), and elaborated the doped glass sample at low (0.2 mol%) erbium trioxide concentration by a glass composition  $80 \text{Sb}_2\text{O}_3 - 10 \text{ZnBr}_2 - 9.8 \text{NaCl} - 0.2 \text{Er}_2\text{O}_3$  mentioned as SZNE02. The well mixed chemicals were taken in a silica crucible and brought first to around  $200^\circ \text{C}$  for 1 hour, and then to  $800^\circ \text{C}$  temperature for melting. The refining is maintained until a transparent liquid is obtained, then it is poured into brass moulds. The relaxation of the samples was carried out in an electric oven at a temperature of  $250^\circ \text{C}$  for 8 hours. After annealing, the samples are cut and polished in parallelepiped shapes with the dimensions of  $10 \text{ mm} \times 10 \text{ mm} \times 3 \text{ mm}$ .

### 2.2. Characterization

The density of the prepared samples was measured by the Archimedes principle with the distilled water as an immersion liquid. The DSC patterns were studied by a thermal analysis device model Q20 (TA instruments) with a heating rate  $10^\circ \text{C} / \text{min}$  and  $0.1^\circ \text{C}$  sensitivity. The sample was encapsulated in hermetic aluminium's crucible; and the oven's temperature does not exceed  $550^\circ \text{C}$ , in an argon atmosphere. Incertitude is  $\pm 2^\circ \text{C}$  for glass transition and onset crystallization temperatures, and  $\pm 1^\circ \text{C}$  for peak crystallization temperature. The expansion coefficient was measured using a TMA 2940 thermo-mechanical analyser (TA instruments) with heating rate of  $4^\circ \text{C} / \text{min}$  was done between room temperature and  $250^\circ \text{C}$  and the error in measuring of expansion coefficient is  $\pm 2 \times 10^{-7} \text{ K}^{-1}$ .

The young's modulus, shear modulus and Poisson's ratio were determined by ultrasonic velocimetry with an electrical pulse generator, provides the starting signal which is connected to a piezoelectric probe (transmitter/receiver) of the Panametrics 5800 model. An acoustic coupling resin must connect to the probe and the sample in order to ensure good transmission of the ultrasonic waves. The longitudinal and transverse echoes are displayed by a Hewlett-Packard digital oscilloscope and are used to determine the time to transit of ultrasonic waves through the sample. The relative error in the values of the elastic moduli and the Poisson's ratio depends directly from the error made in reading the time  $\tau$  which is estimated at  $\Delta\tau = 0.04 \mu\text{s}$  and the error made in measuring the thickness of the sample estimated at  $\Delta e = 0.02 \text{ mm}$ . The calculation formulas are reported in our previous work [16].

The absorbance of doped sample was measured with a Perkin Elmer model spectrophotometer fitted with a TDS WB InGaAs detector at an interval between 200 nm and 2000 nm with a resolution of  $\pm 1 \text{ nm}$ . The emission of trivalent erbium was measured, under 378 nm excitation wavelength at room temperature by a "Fluorolog FL3 - 22 SPEX - Jobin – Yvon" fluorometer model and it is equipped with a 450 watt xenon arc lamp and emits radiation between 200 nm and 900 nm.

The double monochromator has two gratings of 1200 lines per mm for excitation at 250 nm but the emission one has the same number of lines at 500 nm. This configuration allows the first dual monochromator to have high stray white light rejection, and the second have optimum sensitivity in the range (300 nm – 850 nm). The samples are placed in cuvettes tilted  $22.5^\circ$  from the incident light to avoid interference between the excitation and emission light with the estimated resolution of  $\pm 0.5 \text{ nm}$ . Infrared transmission spectra were measured between  $400 \text{ cm}^{-1}$  and  $4000 \text{ cm}^{-1}$  using Fourier transform spectrophotometer TENSOR 37 FTIR with the  $0.01 \text{ cm}^{-1}$  accuracy and  $1 \text{ cm}^{-1}$  resolution.

### 3. Results and discussion

This section focused on glass matrix properties,  $\text{Er}^{3+}$  absorption spectra, refractive index determination, and finally Judd-Ofelt and luminescence analysis.

#### 3.1. Glass matrix properties

**Figure 1** represents the DSC patterns of the glass system  $(90 - x) \text{ Sb}_2\text{O}_3 - x \text{ ZnBr}_2 - 10 \text{ NaCl}$ , with  $10 \leq x \leq 40$  (mol.%) is used to identify the stable glass sample as a function of molar percentage of  $\text{ZnBr}_2$ , according to the criterion:

$$\Delta T = T_x - T_g \quad (1)$$

$T_x$  and  $T_g$  are the crystallization onset and glass transition temperatures [38], respectively.

**Figure 2** shows clearly the monotonic decrease in stability as a function of chemical composition and 80 Sb<sub>2</sub>O<sub>3</sub> - 10 ZnBr<sub>2</sub> - 10 NaCl is the most stable glass. The other physical parameters density, expansion coefficient and elastic moduli have been summarized in Table 1; which are within the limits of antimonate glasses and the corresponding formulas are given by [16], [18], [20]:

$$\text{Density: } \rho = \frac{w_a}{w_a - w_b} \rho_x \quad (2)$$

Where  $w_a$  and  $w_b$  are the weights of glass sample in air and in immersion liquid respectively; and  $\rho_x$  is the density of immersion liquid, distilled water.

$$\text{Expansion coefficient: } \alpha_L = \frac{1}{L} \frac{\Delta L}{\Delta T} \quad (3)$$

Where  $L$  is sample's length and  $\Delta L/\Delta T$  is the rate of change in length per change in temperature.

The Young's and Shear modulus are given by equations (4) and (5) respectively and the Poisson's ratio is expressed by equation (6):

$$E = \frac{\rho V_T^2 (3V_L^2 - 4V_T^2)}{V_L^2 - V_T^2} \quad (4)$$

$$G = \rho V_T^2 \quad (5)$$

$$\eta = \frac{E}{2G} - 1 \quad (6)$$

Where  $\rho$  is the density of glass sample; and  $V_L$  and  $V_T$  are the longitudinal and transverse ultrasonic velocities respectively.

### 3.2. Absorption spectra and refractive index of doped glass sample

The base glass was doped with the trivalent erbium, in order to determine its radiative properties, the dopant substitutes zinc bromide: 80 Sb<sub>2</sub>O<sub>3</sub> - 9.8 ZnBr<sub>2</sub> - 10 NaCl - 0.2 Er<sub>2</sub>O<sub>3</sub>.

**Figure 3a** and **3b** show the absorption spectrum of Er<sup>3+</sup> in the antimonate matrix where the different absorption bands are marked with red arrows. **Figure 4** represents the Er<sup>3+</sup> bands as a function of wavenumber (expressed in cm<sup>-1</sup>) and were made from <sup>4</sup>I<sub>15/2</sub> ground state, with

corrected baseline. We established the Urbach [21] plot to determine the optical gap of the doped glass sample. The optical absorption data were shown in **Figure 5**, which was used for the calculation of optical gap energy ( $E_p = 2.95$  eV). The  $E_p$  value allowed to calculate the refractive index of doped glass according to Dimitov and Sakka formula [22]:

$$\frac{n^2 - 1}{n^2 + 2} = \sqrt{\frac{E_p}{20}} \quad (7)$$

Where the refractive index  $n = 2.25$  is high when compared to the conventional glasses; and it is due to the high polarizability of antimonate [16], [18] and the addition of dopant erbium oxide.

### 3.3. Judd-Ofelt and luminescence analysis

The experimental oscillator force is calculated from the absorbance data [23]:

$$F_{expt} = \frac{2330 mc^2}{\pi e^2 N_0} \int \varepsilon(\nu) d\nu \quad (8)$$

Where  $m$  and  $e$  are the mass and charge of the electron respectively,  $c$  is the speed of light,  $N_0$  is the Avogadro's number and  $\varepsilon(\nu)$  is the extinction coefficient which is determined with the Beer-Lambert law [24]:

$$\varepsilon(\nu) = \frac{\log\left(\frac{I_0}{I}\right)}{Cd} \quad (9)$$

Where  $\log(I_0 / I)$  absorbance measured as a function of wavenumber  $\nu$  ( $\text{cm}^{-1}$ );  $C$  is the concentration of lanthanide in the sample (mol /L) and  $d$  is the thickness (cm).

Judd-Ofelt [6], [7] analysis allows the determination of the radiative parameters of a trivalent lanthanide doping a vitreous matrix. This concerns the determination of the  $\Omega_k$  parameters ( $k=2,4$  and  $6$ ) by fitting the experimental and theoretical oscillator forces of the different absorbing transitions of a given  $\text{Ln}^{3+}$  lanthanide (except  $\text{Yb}^{3+}$ ). If the fitting is validated, the parameters of Judd-Ofelt,  $\Omega_k$  are used to calculate the radiative parameters.

According to Judd-Ofelt theory the oscillator force for a transformation  $aJ \rightarrow bJ'$  is expressed [6], [7]:

$$F_{cal} = F_{ed} + F_{md} = \frac{8\pi^2 m c \nu}{3h(2J + 1)e^2 n^2} (\chi_{ed} S_{ed} + \chi_{md} S_{md}) \quad (10)$$

Note that  $\chi_{ed}$  and  $\chi_{md}$  are given by:

$$\chi_{ed} = \frac{n(n^2 + 2)^2}{9} \quad (11)$$

$$\chi_{md} = n^3 \quad (12)$$

The electric and magnetic dipole line forces are given by:

$$S_{ed}(aJ \rightarrow bJ') = e^2 \sum_{t=2,4,6} \Omega_t |\langle aJ | U^t | bJ' \rangle|^2 \quad (13)$$

$$S_{md}(aJ \rightarrow bJ') = \frac{e^2}{4m^2c^2} |\langle aJ | L + 2S | bJ' \rangle|^2 \quad (14)$$

The probable magnetic dipole transitions are only which obey the selection rule

$\Delta S = \Delta L = 0, \Delta J = 0, \pm 1$  and contributing to the oscillator force. The Judd-Ofelt parameters are obtained by least-squared fitting of the experimental values of the oscillator force using equation 8. According to Carnall et al. [25] the elements of the reduced matrix

$$|\langle aJ | U^t | bJ' \rangle|^2$$

are invariable with respect to the change of vitreous matrix. The fitting precision is given by root mean square error:

$$RMSE = \sqrt{\frac{\sum (F_{cal} - F_{exp})^2}{\xi - 3}} \quad (15)$$

Such that  $\xi$  is the number of considered transitions; and note that:  $\xi > 3$ .

The spontaneous emission rate probability is calculated using the equation:

$$A(aJ, bJ') = A_{ed} + A_{md} = \frac{64\pi^4\nu^3}{3h(2J + 1)} (\chi_{ed}S_{ed} + \chi_{md}S_{md}) \quad (16)$$

Where  $A_{ed}$  and  $A_{md}$  are the electric and magnetic parts of spontaneous emission rate probabilities respectively. In this work,  $A_{md}$  values have been calculated from the values of  $\text{LaF}_3$  ( $A'_{md}$ ) and corrected for the refractive index difference using [26]:

$$A_{md} = \left(\frac{n}{n'}\right)^3 A'_{md} \quad (17)$$

Where  $n$  and  $n'$  are the refractive indices of  $\text{Er}^{3+}$  doped antimonate glass and  $\text{LaF}_3$ , respectively. The branching ratio is expressed as follows:

$$\beta = A(aJ, bJ') / \sum_{bJ'} A(aJ, bJ') \quad (18)$$

The lifetime is the inverse of the total spontaneous emission rate probability:

$$\tau = 1 / \sum_{bJ'} A(aJ, bJ') \quad (19)$$

The cross section of stimulated emission is given by [9]:

$$\sigma(J \rightarrow J') = \frac{\lambda^4}{8\pi c n^2 \Delta\lambda_{eff}} A(J \rightarrow J') \quad (20)$$

Where  $\Delta\lambda_{eff}$  is full width at half maximum of emission peak (FWHM); and it is given by [4]:

$$\Delta\lambda_{eff} = \frac{1}{I_p} \int I(\lambda) d\lambda \quad (21)$$

The first results of the application of the Judd-Ofelt formalism to the glass sample 80  $\text{Sb}_2\text{O}_3$  - 9.8  $\text{ZnBr}_2$  - 10  $\text{NaCl}$  - 0.2  $\text{Er}_2\text{O}_3$  are reported in **Table 2**, in terms of barycentre wavelengths and oscillator forces; related to the absorption bands of  $\text{Er}^{3+}$  from  $^4\text{I}_{15/2}$  ground state. Judd-Ofelt's method is validated with  $RMSE = 119.26 \times 10^{-8}$ , and the percentage of relative error [27] is 8.12.

The relative error is obtained by the normalized RMSE [28]:

$$NRMS = Error \% = \frac{RMSE}{F_{exp\ max} - F_{exp\ min}} \quad (22)$$

$F_{exp\ max}$  and  $F_{exp\ min}$  are the maximum (hypersensitive transition) and minimum experimental oscillator forces, respectively.

**Table 3** presents the Judd-Ofelt's parameters  $\Omega_2 = 3.27 \times 10^{-20} \text{ cm}^2$ ;  $\Omega_4 = 1.24 \times 10^{-20} \text{ cm}^2$  and  $\Omega_6 = 1.88 \times 10^{-20} \text{ cm}^2$ , and the consecutive spectroscopic quality parameter  $\Omega_4/\Omega_6 = 0.66$  this value is very close to the mean ( $\Omega_4/\Omega_6 = 0.7$ ); knowing that the series of parameters is in

the order  $\Omega_2 > \Omega_6 > \Omega_4$ . In other words, the value of  $\Omega_2$  is lower than the average ( $\Omega_{2\text{ ev}} = 5.17 \times 10^{-20} \text{ cm}^2$ ) compared to the values reported in table 3; indicating that the erbium - ligand bond inserted into the antimonate matrix has the lowest degree of covalency [29] compared to other glasses.

**Table 4** gives the radiative parameters of the glass sample 80  $\text{Sb}_2\text{O}_3$  - 9.8  $\text{ZnBr}_2$  - 10  $\text{NaCl}$  - 0.2  $\text{Er}_2\text{O}_3$  such as the spontaneous emission rate  $A$ , the lifetime  $\tau$  and the branching ratio  $\beta$ . The infrared emission  $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$  has the maximum branching ratio  $\beta = 1$ ; and the highest lifetime  $\tau = 1.07 \text{ ms}$  (for the present work); this transition is essential in optical amplification for telecommunications [5]. Similarly, there are two other transitions with high branching ratios; and are within the detection limits of the fluorometer used in this study. The emissions are due to  $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$  ( $\beta = 0.94$ ) and  $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$  ( $\beta = 0.901$ ) and the emission spectrum (**Figure 6**) was measured at ambient temperature. We have established a Gaussian deconvolution between 500 nm and 600 nm in order to separate the  $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$  and  $^3\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$  emissions. **Figure 7 and 8**; demonstrates the intervals of the overlap between emission and absorption cross section for the considered transitions. There is a partial overlap in the two considered cases, with the stocks type shift of emission peaks compared to the absorbances.

**Figure 9 and 10** exhibits the variation of stimulated emission coefficient (gain) as a function of wavelength for different states of population inversion. The best gains correspond to the  $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$  transition; from the point of view for gain level, its flattening and minimum value of the population inversion index is  $\gamma$ . However, this transition presents a positive gain starting from  $\gamma = 20 \%$  and takes an average value of  $5.5 \times 10^{-20} \text{ cm}^2$ , for total population inversion ( $\gamma = 100\%$ ). While the gains of the  $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$  transition are positive starting from  $\gamma = 40 \%$  and admit an average value of  $4 \times 10^{-20} \text{ cm}^2$  for a complete population inversion. The curvature is less pronounced as the population inversion index increases and tends towards a flattening for  $\gamma = 100 \%$ .

The typical stokes shift between luminescence and absorption bands testifies a notable presence of non-radiative processes, which make the overlap between the two curves relatively reduced. Non-radiative processes are of two types, intrinsic and extrinsic. The first one involves energy transfer, cross relaxation between lanthanides and the second one related to the multiphonon relaxation in the host matrix [30]. Likewise, the excessive concentration of lanthanide and the appearance of clusters influence negatively on the luminescence. In the

present case these processes are limited because the studied glass has low phonon energy and a relatively low doping level.

**Figure 11** represents the infrared transmission of the matrix shows the existence of an OH group, and the SiO absorption band, mainly due to the silica crucible. The latter are real extrinsic luminescence extinguishers since the OH vibration takes place at the higher order vibration energy  $3200\text{ cm}^{-1}$  and similarly SiO has high energy and it scales towards  $1800\text{ cm}^{-1}$ . The OH content is estimated at around 190 ppm and is calculated according to:  $Q = 30 \alpha_{\text{OH}}$  the absorption coefficient  $\alpha_{\text{OH}}$  extracted from the infrared curve [30].

A multiphonon relaxation comprising many phonons (6 phonons) is prohibited in the antimonate matrix, on the other hand it is allowed by the vibrations of OH or SiO bonds since it requires a limited number of phonons compared to the latter. Some studies show that the presence of hydroxyl groups reduces the lifetime and efficiency of luminescence [31]. The prepared glass sample has attractive qualities, a low phonon energy  $602\text{ cm}^{-1}$  [32] and endowed with halogenated compounds (ZnBr<sub>2</sub> and NaCl) reducing the phonon density. Further the high value of the refractive index ( $n = 2.25$ ) increases the probability of radiative processes.

#### 4. Conclusion

The Judd-Ofelt analysis applied to the trivalent doped erbium antimonate based oxy-halogenated HMOGs  $80\text{ Sb}_2\text{O}_3 - 9.8\text{ ZnBr}_2 - 10\text{ NaCl} - 0.2\text{ Er}_2\text{O}_3$ . DSC analysis showed that the glass matrix  $(90 - x)\text{ Sb}_2\text{O}_3 - x\text{ ZnBr}_2 - 10\text{ NaCl}$  is the most stable in the system at  $10 \leq x \leq 40$  (mol.%). In addition to thermal analysis; other physical parameters density; expansion coefficient; elastic moduli and Poisson's ratio were calculated. The validity of Judd-Ofelt's method for the prepared glass sample is confirmed by positive  $\Omega_2$  value and 8.12 % for normalized root mean square error. Judd –Ofelt's ( $\Omega_K$ ,  $K= 2,4, 6$ ) parameters take the values  $\Omega_2 = 3.27 \times 10^{-20}\text{ cm}^2$ ;  $\Omega_4 = 1.24 \times 10^{-20}\text{ cm}^2$  and  $\Omega_6 = 1.88 \times 10^{-20}\text{ cm}^2$  ( $\Omega_2 > \Omega_6 > \Omega_4$ ) are comparable to those reported in the literature.

The transitions admitting high branching ratio is  $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$  ( $\beta = 0.94$ ) and  $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$  ( $\beta = 0.901$ ) and are detected during luminescence measurements at room temperature around 378 nm excitation. Since the branching ratio values are greater than 50 %, the prepared glass sample will be suitable for the photonics applications. The calculated lifetimes are 39.4  $\mu\text{s}$  and

117  $\mu\text{s}$  and the overlap between the emission and absorbance peaks of these transitions are partial, with the stokes type shift between them. The stimulated emission gains as a function of wavelength for different states of population inversion have been calculated. The best gain is obtained for the second transition in terms of gain levels, as well as the minimum value of the population inversion coefficient which leading to a positive gain and its flattening. The infrared transmission of the glass matrix marks the presence of SiO and hydroxyl OH bonds, which are extrinsic extinguishers of luminescence.

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## FIGURE CAPTIONS

**Fig.1.** DSC patterns of glass system  $(90 - x) \text{ Sb}_2\text{O}_3 - x \text{ ZnBr}_2 - 10 \text{ NaCl}$  ( $10 \leq x \leq 40 \text{ mol.}\%$ ).

**Fig.2.** Stability of glass matrix  $(90 - x) \text{ Sb}_2\text{O}_3 - x \text{ ZnBr}_2 - 10 \text{ NaCl}$  as a function of molar percentage of  $\text{ZnBr}_2$ .

**Fig.3a.**  $\text{Er}^{3+}$  absorption bands recorded between 360 nm and 460 nm for a glass sample  $80 \text{ Sb}_2\text{O}_3 - 9.8 \text{ ZnBr}_2 - 10 \text{ NaCl} - 0.2 \text{ Er}_2\text{O}_3$ .

**Fig.3b.**  $\text{Er}^{3+}$  absorption bands recorded between 460 nm and 1600 nm for a glass sample  $80 \text{ Sb}_2\text{O}_3 - 9.8 \text{ ZnBr}_2 - 10 \text{ NaCl} - 0.2 \text{ Er}_2\text{O}_3$ .

**Fig.4.**  $\text{Er}^{3+}$  absorption bands as a function of wavenumber and correction of the absorbance's baseline for the sample  $80 \text{ Sb}_2\text{O}_3 - 9.8 \text{ ZnBr}_2 - 10 \text{ NaCl} - 0.2 \text{ Er}_2\text{O}_3$ .

**Fig.5.** Urbach plot of glass sample  $80 \text{ Sb}_2\text{O}_3 - 9.8 \text{ ZnBr}_2 - 10 \text{ NaCl} - 0.2 \text{ Er}_2\text{O}_3$ .

**Fig.6.**  $\text{Er}^{3+}$  emission spectrum (at room temperature) of sample  $80 \text{ Sb}_2\text{O}_3 - 9.8 \text{ ZnBr}_2 - 10 \text{ NaCl} - 0.2 \text{ Er}_2\text{O}_3$ ; at excitation wavelength  $\lambda_{\text{ex}} = 378 \text{ nm}$ .

**Fig.7.** Graphs of overlap limits between absorption and emission of  $^4\text{F}_{9/2}$  and  $^4\text{I}_{15/2}$  levels.

**Fig.8.** Graphs of overlap limits between absorption and emission of  $^2\text{H}_{11/2}$  and  $^4\text{I}_{15/2}$  levels.

**Fig.9.** Variation of the stimulated emission gain coefficient versus wavelength corresponding to the transition  $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$  for different states of population inversion.

**Fig.10.** Variation of the stimulated emission gain coefficient versus wavelength corresponding to the transition  $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$  for different states of population inversion.

**Fig.11.** Infrared transmission curve of 80 Sb<sub>2</sub>O<sub>3</sub> - 10 ZnBr<sub>2</sub> - 10 NaCl glass.

## FIGURES

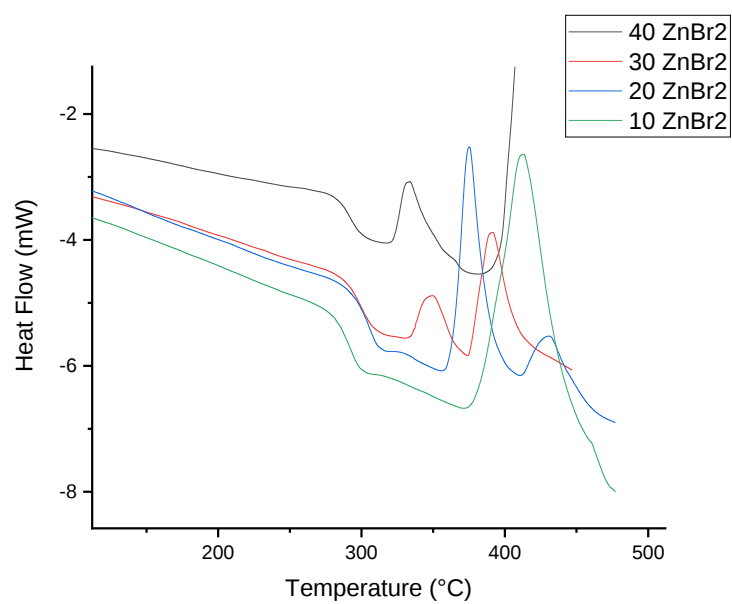


Figure 1

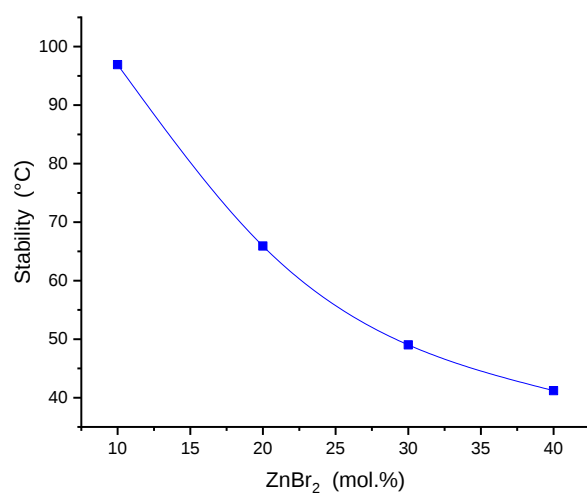


Figure 2

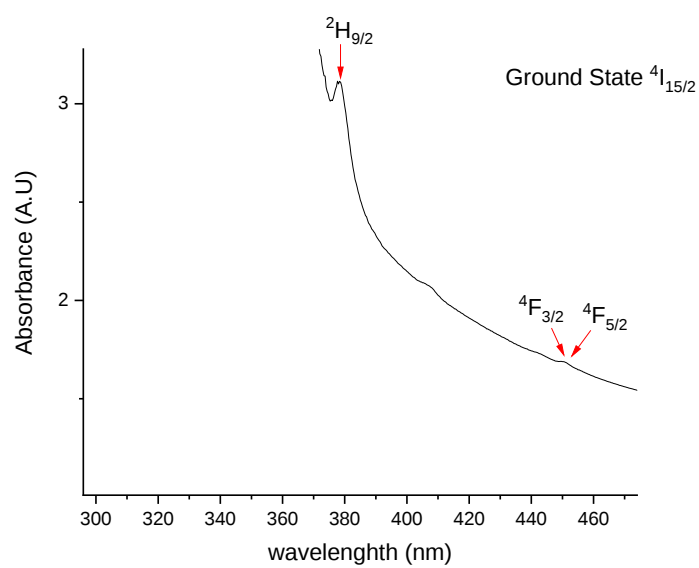


Figure 3a

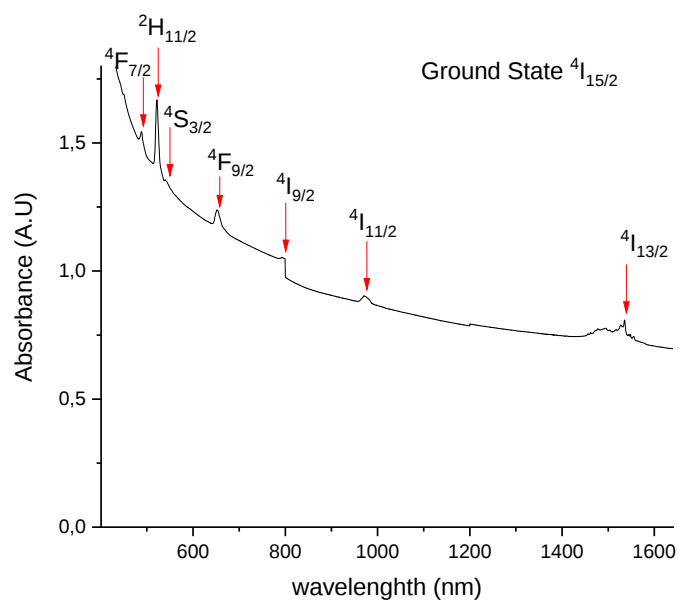


Figure 3b

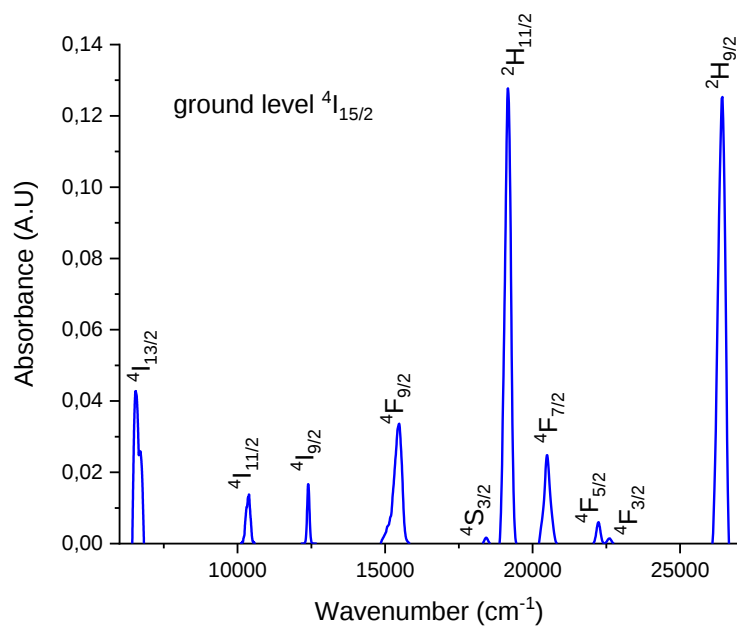


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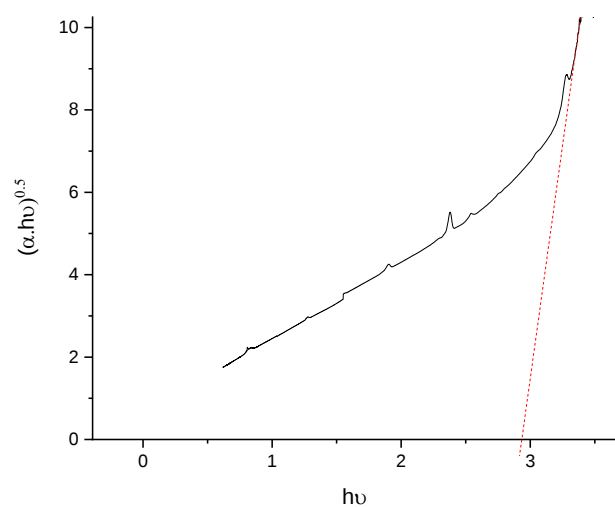


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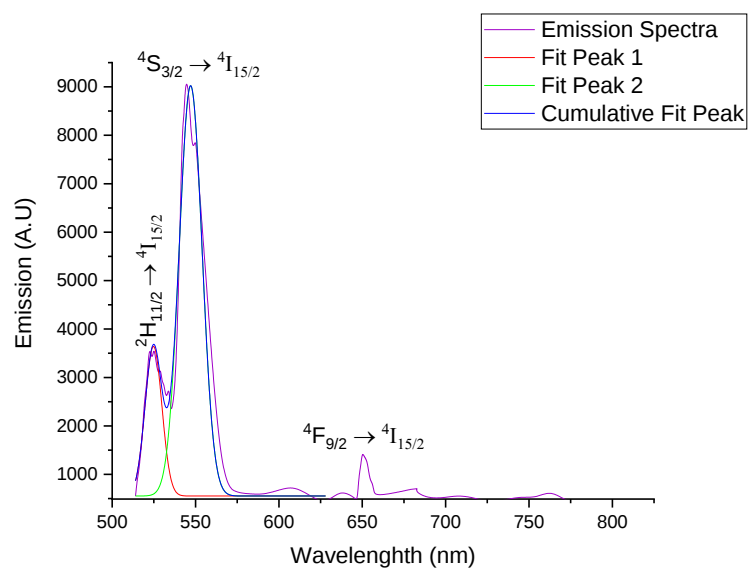


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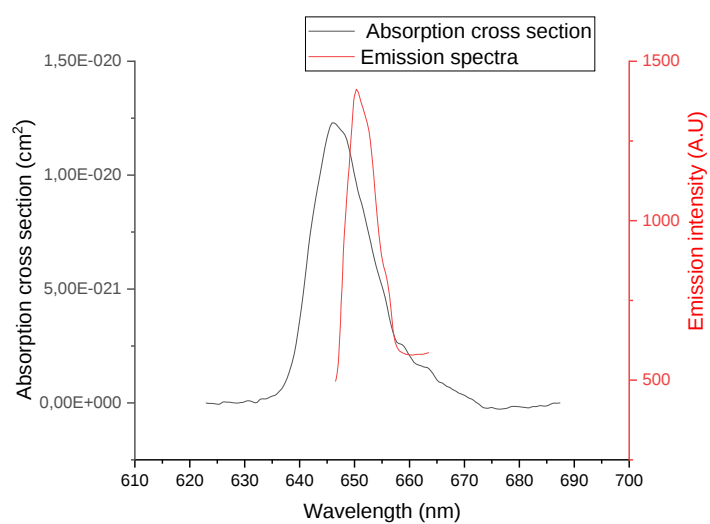


Figure 7

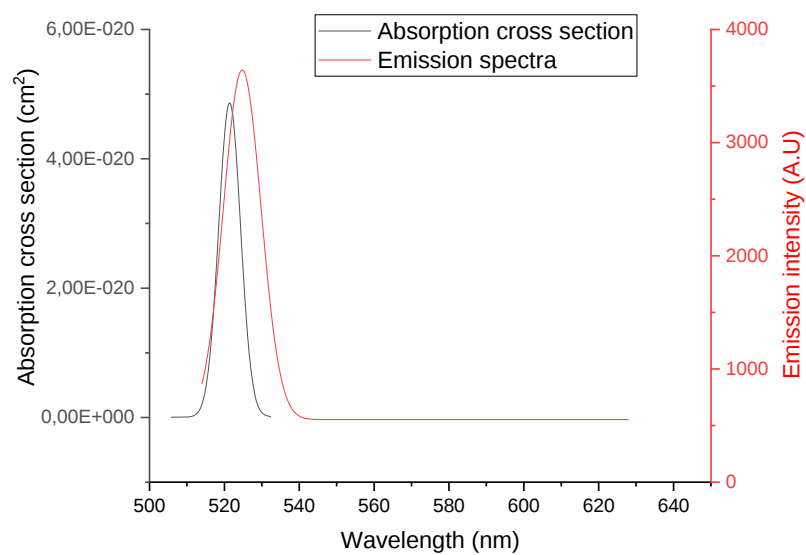


Figure 8

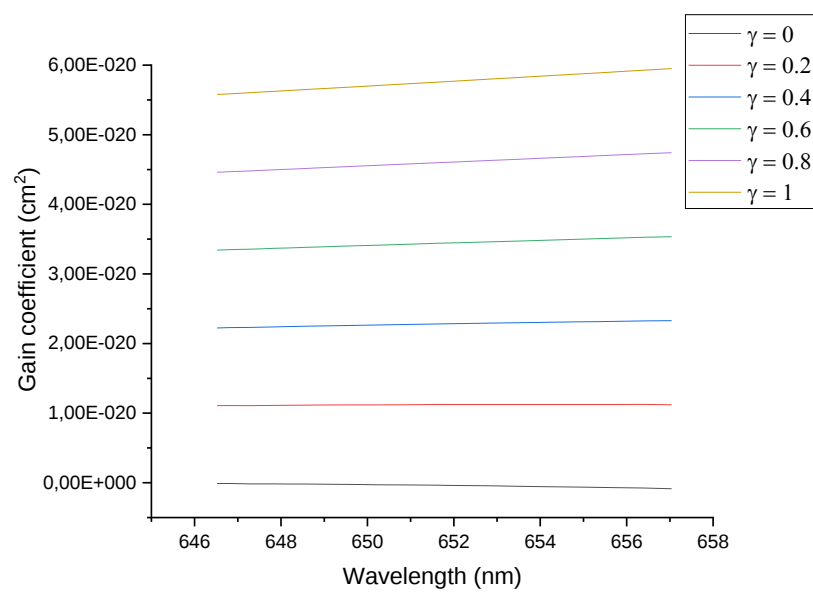


Figure 9

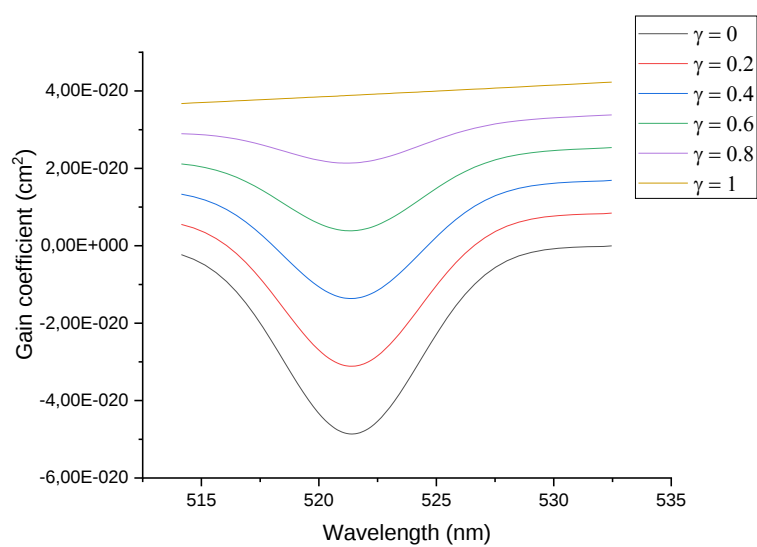


Figure 10

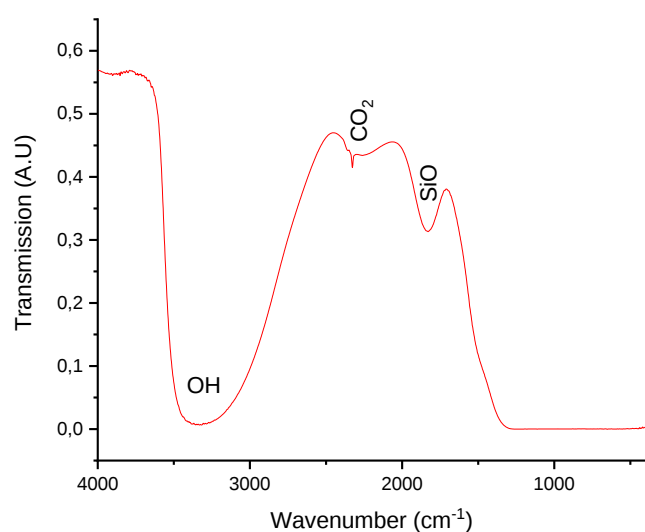


Figure 11

## Tables

**Table 1.** Physical parameters of the glass sample 80 Sb<sub>2</sub>O<sub>3</sub> - 10 ZnBr<sub>2</sub> - 10 NaCl

| Density<br>(g/cm <sup>3</sup> ) | Characteristic temperatures (°C) |                |                | Thermal<br>expansion<br>coefficient<br>(10 <sup>-6</sup> K <sup>-1</sup> ) | Elastic modulus and Poisson<br>coefficient |         |        |
|---------------------------------|----------------------------------|----------------|----------------|----------------------------------------------------------------------------|--------------------------------------------|---------|--------|
|                                 | T <sub>g</sub>                   | T <sub>x</sub> | T <sub>p</sub> |                                                                            | E (GPa)                                    | G (GPa) | η      |
| 4.515                           | 279                              | 376            | 413            | 19.92                                                                      | 26.24                                      | 10.64   | 0.2323 |

**Table 2:** Barycentre wavelengths and oscillator forces of Er<sup>3+</sup> absorption bands in a glass sample 80 Sb<sub>2</sub>O<sub>3</sub> - 9.8 ZnBr<sub>2</sub> - 10 NaCl - 0.2 Er<sub>2</sub>O<sub>3</sub>

| Transition                                                      | Peak's barycenter (cm <sup>-1</sup> ) | Oscillator line strength x 10 <sup>-8</sup> |                  |
|-----------------------------------------------------------------|---------------------------------------|---------------------------------------------|------------------|
|                                                                 |                                       | F <sub>EXP</sub>                            | F <sub>CAL</sub> |
| <sup>4</sup> I <sub>15/2</sub> → <sup>4</sup> I <sub>13/2</sub> | 6624.74                               | 446.94                                      | 389.52           |
| <sup>4</sup> I <sub>15/2</sub> → <sup>4</sup> I <sub>11/2</sub> | 10379.53                              | 79.4                                        | 143.75           |
| <sup>4</sup> I <sub>15/2</sub> → <sup>4</sup> I <sub>9/2</sub>  | 12629.98                              | 25.53                                       | 49.27            |
| <sup>4</sup> I <sub>15/2</sub> → <sup>4</sup> F <sub>9/2</sub>  | 15441.06                              | 420.87                                      | 395.35           |
| <sup>4</sup> I <sub>15/2</sub> → <sup>4</sup> S <sub>3/2</sub>  | 18424.44                              | 12.94                                       | 128.96           |
| <sup>4</sup> I <sub>15/2</sub> → <sup>2</sup> H <sub>11/2</sub> | 19158.37                              | 1479.7                                      | 942.69           |
| <sup>4</sup> I <sub>15/2</sub> → <sup>4</sup> F <sub>7/2</sub>  | 20486.33                              | 256.85                                      | 465.69           |
| <sup>4</sup> I <sub>15/2</sub> → <sup>4</sup> F <sub>5/2</sub>  | 22230.69                              | 42.31                                       | 154.34           |
| <sup>4</sup> I <sub>15/2</sub> → <sup>4</sup> F <sub>3/2</sub>  | 22602.65                              | 11.89                                       | 183.83           |
| <sup>4</sup> I <sub>15/2</sub> → <sup>2</sup> H <sub>9/2</sub>  | 26422.27                              | 1163.2                                      | 1711.44          |
| RMSE X 10 <sup>-8</sup>                                         |                                       | 119.26                                      |                  |
| Error %                                                         |                                       | 8.12                                        |                  |

**Table 3:** Comparison of the Judd-Ofelt parameters  $\Omega_K$  ( $K = 2; 4; 6$ ) and the spectroscopic quality parameter  $\Omega_4 / \Omega_6$  of glass sample 80 Sb<sub>2</sub>O<sub>3</sub> - 9.8 ZnBr<sub>2</sub> - 10 NaCl - 0.2 Er<sub>2</sub>O<sub>3</sub> (SZNE02).

| Glass system | $\Omega_2$ (x10 <sup>-20</sup> cm <sup>2</sup> ) | $\Omega_4$ (x10 <sup>-20</sup> cm <sup>2</sup> ) | $\Omega_6$ (x10 <sup>-20</sup> cm <sup>2</sup> ) | $\Omega_4 / \Omega_6$ | Trends                           |
|--------------|--------------------------------------------------|--------------------------------------------------|--------------------------------------------------|-----------------------|----------------------------------|
| SZNE02       | 3.27                                             | 1.24                                             | 1.88                                             | 0.66                  | $\Omega_2 > \Omega_6 > \Omega_4$ |
| Present work |                                                  |                                                  |                                                  |                       |                                  |

|                    |      |      |      |      |                                  |
|--------------------|------|------|------|------|----------------------------------|
| BTNME2<br>[4]      | 8.13 | 1.71 | 2.45 | 0.70 | $\Omega_2 > \Omega_6 > \Omega_4$ |
| BTNME5<br>[4]      | 3.53 | 1.18 | 2.06 | 0.57 | $\Omega_2 > \Omega_6 > \Omega_4$ |
| TZNEr<br>[33]      | 5.98 | 1.32 | 1.47 | 0.89 | $\Omega_2 > \Omega_6 > \Omega_4$ |
| TZNBG2<br>[34]     | 5.02 | 0.95 | 1.21 | 0.78 | $\Omega_2 > \Omega_6 > \Omega_4$ |
| 1.5ErBT<br>[35]    | 3.18 | 1.49 | 1.81 | 0.82 | $\Omega_2 > \Omega_6 > \Omega_4$ |
| TPBKZFEr05<br>[36] | 7.23 | 1.02 | 1.46 | 0.70 | $\Omega_2 > \Omega_6 > \Omega_4$ |
| KTFP<br>[37]       | 5.09 | 0.69 | 1.45 | 0.48 | $\Omega_2 > \Omega_6 > \Omega_4$ |

**Table 4:** Radiative properties of glass sample 80 Sb<sub>2</sub>O<sub>3</sub> - 9.8 ZnBr<sub>2</sub> - 10 NaCl - 0.2 Er<sub>2</sub>O<sub>3</sub>

| Transition                              | $A_{ed} (s^{-1})$ | $A_{md} (s^{-1})$ | $A (s^{-1})$ | $\sum A (s^{-1})$ | $\tau (ms)$ | $\beta$ |
|-----------------------------------------|-------------------|-------------------|--------------|-------------------|-------------|---------|
| ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$ | 816               | 120.44            | 937          | 937               | 1.07        | 1       |
| ${}^4I_{11/2} \rightarrow {}^4I_{13/2}$ | 141               | 28.65             | 170          |                   |             | 0.139   |

|                                                       |       |       |       |       |        |            |
|-------------------------------------------------------|-------|-------|-------|-------|--------|------------|
| ${}^4\text{I}_{11/2} \rightarrow {}^4\text{I}_{15/2}$ | 1050  |       | 1050  | 1220  | 0.82   | 0.861      |
| ${}^4\text{I}_{9/2} \rightarrow {}^4\text{I}_{11/2}$  | 5.44  | 3.05  | 8.49  |       |        | 0.00834    |
| ${}^4\text{I}_{9/2} \rightarrow {}^4\text{I}_{13/2}$  | 399   |       | 399   |       |        | 0.392      |
| ${}^4\text{I}_{9/2} \rightarrow {}^4\text{I}_{15/2}$  | 611   |       | 611   | 1020  | 0.98   | 0.6        |
| ${}^4\text{F}_{9/2} \rightarrow {}^4\text{I}_{9/2}$   | 14    | 6.29  | 20.3  |       |        | 0.00237    |
| ${}^4\text{F}_{9/2} \rightarrow {}^4\text{I}_{11/2}$  | 464   | 20.12 | 484   |       |        | 0.0566     |
| ${}^4\text{F}_{9/2} \rightarrow {}^4\text{I}_{13/2}$  | 344   |       | 344   |       |        | 0.0402     |
| ${}^4\text{F}_{9/2} \rightarrow {}^4\text{I}_{15/2}$  | 7710  |       | 7710  | 8850  | 0.117  | 0.901      |
| ${}^4\text{S}_{3/2} \rightarrow {}^4\text{F}_{9/2}$   | 4.31  |       | 4.31  |       |        | 0.000329   |
| ${}^4\text{S}_{3/2} \rightarrow {}^4\text{I}_{9/2}$   | 376   |       | 376   |       |        | 0.0287     |
| ${}^4\text{S}_{3/2} \rightarrow {}^4\text{I}_{11/2}$  | 270   |       | 270   |       |        | 0.0206     |
| ${}^4\text{S}_{3/2} \rightarrow {}^4\text{I}_{13/2}$  | 3560  |       | 3560  |       |        | 0.272      |
| ${}^4\text{S}_{3/2} \rightarrow {}^4\text{I}_{15/2}$  | 8890  |       | 8890  | 13100 | 0.0763 | 0.679      |
| ${}^2\text{H}_{11/2} \rightarrow {}^4\text{S}_{3/2}$  | 0.119 |       | 0.119 |       |        | 0.00000468 |
| ${}^2\text{H}_{11/2} \rightarrow {}^4\text{F}_{9/2}$  | 71.6  |       | 71.6  |       |        | 0.00282    |
| ${}^2\text{H}_{11/2} \rightarrow {}^4\text{I}_{9/2}$  | 401   | 3.11  | 404   |       |        | 0.0159     |
| ${}^2\text{H}_{11/2} \rightarrow {}^4\text{I}_{11/2}$ | 275   | 22.48 | 298   |       |        | 0.0117     |
| ${}^2\text{H}_{11/2} \rightarrow {}^4\text{I}_{13/2}$ | 553   | 195.8 | 749   |       |        | 0.0295     |
| ${}^2\text{H}_{11/2} \rightarrow {}^4\text{I}_{15/2}$ | 23800 |       | 23800 | 25400 | 0.0394 | 0.94       |