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NEW ERBIUM DOPED ANTIMONY GLASSES FOR LASER AND GLASS AMPLIFICATION

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ABSTRACT

Because of the special spectroscopic properties of the rare earth ions, rare earth doped glasses are widely used in bulk and fiber lasers or amplifiers. The modelling of lasers and searching for new laser transitions require a precise knowledge of the spectroscopic properties of rare earth ions in different host glasses. In this poster will offer new doped erbium glasses synthesized in silicate crucibles were obtained in the combination Sb2O3-WO3-Na2O. Several properties are measured and correlated with glass compositions. The absorption spectral studies have been performed for erbium doped glasses. The intensities of various absorption bands of the doped glasses are measured and the Judd-Ofelt parameters have been computed. From the theory of Judd-Ofelt, various radiative properties, such as transition probability, branching ratio and radiative life time for various emission levels of these doped glasses have been determined and reported. These results confirm the ability of antimony glasses for glass amplification.

Keywords: antimony glasses, fiber lasers, amplifiers.

1. INTRODUCTION

Incorporation of rare earth (RE) elements into various oxide glasses has been a key to the development of many optical devices [1].

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Among the trivalent RE ions, Er3+ plays an important role in the development of broadband erbium doped fibre amplifiers (EDFA) at the third communication window (1.5µm) [2] and frequency up-conversion for their potential laser applications in many fields during the past few decades [3]. Therefore, the choice of the host material glass is very important in the development of more efficient optical devices based on Er3+ doped glasses.

Optical properties of erbium doped alkali-antimonite glasses have not been investigated to the best of our knowledge; however there are many reports on erbium doped glasses containing Sb_2O_3 as the second glass former in antimony-borate glasses [4], antimony-silicate glasses [5] or antimony-phosphate glasses [6].

In this paper we report radiative and spectroscopic properties of Er^{3+} ions in the novel vitreous system Sb_2O_3-Na_2O-WO_3 using Sb_2O_3 as a glass former, Na_2O and WO_3 as glass modifiers. The Judd–Ofelt (J–O) theory has been applied to the measured optical absorption intensities in order to determine the well known J–O intensity parameters Ω_2, Ω_4 and Ω_6, The effect of Er^{3+} doping level has been specified and the potential of these glasses as optical glasses for laser and optical amplifiers has been examined.

2. EXPERIMENTAL AND PHYSICAL PROPERTIES

The starting glass composition $(Sb_2O_3)_{80-x}(Na_2O)_{20}(WO_3)_x$ was chosen for doping with two different Er_2O_3 concentrations. The acronyms SN20W, SN30W are used to label the samples containing 20 and 30 mol % of WO_3, respectively. The synthesis was carried out through the conventional melt-quenching method from starting compounds Sb_2O_3 (Acros, 99%), WO_3 (Aldrich, 99%), Na_2CO_3 (Aldrich, 99.95%) and Er_2O_3 (Rhone Poulenc, 99.99%). The bulk glasses were prepared in open silica glass crucibles with 10 mm in diameter. The powder mixtures were flame heated until a clear liquid is obtained and then the melts were cast onto a brass plate. The samples were annealed near the glass transition temperature for 6 hours in order to minimize mechanical stress resulting from thermal gradients upon cooling. Finally, they were cut and polished for the optical measurements.

The amorphous nature of the samples was checked by X-ray diffraction (XRD), using a Philips PW3020 diffractometer with Cu Kα radiation.

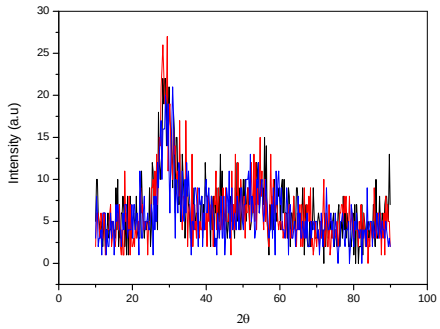

Fig.1. XRD spectrum of a glass in the system (80-X)Sb_2O_3-20Na_2O-(X) WO_3 with x=20

Thermal properties were measured by differential scanning calorimeter (DSC Q20 TA Instruments) with a heating rate of 10 $Kmin^{-1}$ and accuracy of ±2°C.

Table 1. Characteristic temperatures and CTE of the glasses in the system

Composition du verre (mol %)			**Temperatures (°C)**					**Coefficient de dilatation thermique 10^{-6} K [50-250°C]**
Sb_2O_3	Na_2O	WO_3	T_g (± 2)	T_x (± 2)	T_p (± 1)	T_f (± 2)	(T_x-T_g)	/
60	20	20	302	439	/	/	137	19
50	20	30	314	448	/	512	134	17,4

The density, accurate to ±0.05 %, was determined by Micromeritics Accupyc pycnometer under Helium pressure.

Table 2. Values of the density of glasses in the system (80-X)Sb_2O_3-20Na_2O-(X) WO_3

Composition du verre (mol %)			**(g.cm-3)**
Sb2O3	**Na2O**	**WO3**	**(± 0.01)**
60	**20**	**20**	**5,07**
50	**20**	**30**	**5,48**

The refractive index of the samples was measured using a Metricon M2010 with accuracy of ±1.10^{-4}.

Table 3. Refraction indices, molar volume in doped and undoped glasses.

Echantillons	Er (% mol)	Indice de refraction n	Volume Molaire Vm
60 Sb_2O_3 - 20 Na_2O – 20 WO_3	0	1,889	**46,078**
	0,2	2,029	**46,229**
	0,4	2,043	**46,379**
50 Sb_2O_3 - 20 Na_2O – 30 WO_3	0	1,956	**41,544**
	0,2	2,039	**41,683**
	0,4	**2,106**	**41,822**

The absorption spectra were measured by a Perkin Elmer Precisely UV-Vis-NIR spectrophotometer operating between 200 and 2500 nm, with around 2 nm resolution.

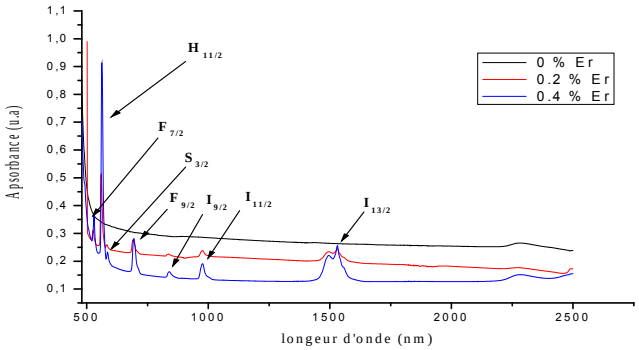

Fig.2. Absorption spectrum of Er+3 in the glass (60Sb2O3-20Na2O-20WO3)

Theory and estimation of different spectroscopic parameters of the Er+3 ions in the glass

To estimate the crystal field strength surrounding the Er+3 ions of the glass we have used Judd_Ofelt theory. In 1962, Judd [7] and Ofelt [8], working independently, developed the theory of electronic transition line intensities of LnC3 ions in crystals, which is very elegant and universal in estimating the optical and laser properties of LnC3 ions in crystals and glasses. According to the Judd_Ofelt theory [7-8], the electric and magnetic dipole line strength of an electronic transition from an initial $(S,L)J$ state to the final $(S',L')J'$ state is given respectively by the expressions

$$S_{ed}(J,J') = \sum_{i=2,4,6} \Omega_t \, |(S,L)J\|U^t\|(S',L')J'>|^2 \qquad (1)$$

$$S_{md}(J,J') = (h/4\pi mc)^2 |(S,L)J\|U^t\|(S',L')J'>|^2 \qquad (2)$$

where *e*= electronic charge, h = Planck's constant, c = speed of light, m= mass of electron, $<(S,L)J\|U^t\|(S',L')J'>$ is the reduced matrix element of the irreducible tensor operator of rank *t* calculated in the intermediate coupling approximation and depends only on the Er^{+3} ion concerned. The values of the square of the reduced matrix elements for various transitions of different Er^{+3} ions have already been calculated by Carnall et al. [9] and Kaminskii [10], and are available in literature. Ω_t (t = 2, 4, 6) are the three intensity parameters called the Judd_Ofelt parameters arising from the static crystal field. The value of magnetic dipole line strength (S_{md}) does not depend on the host material and it is an exclusive property of the rare earth ion itself. The probabilities of magnetic dipole transitions are generally lower than those of electric dipole transitions. In this case the only magnetic dipole transition for ions Er+3 is the $^4I_{15/2} \rightarrow {}^4I_{13/2}$ transition and all other transitions of absorption have a contribution hopeless magnetic dipole. The relation that permitted to calculate S_{md} is [9]

$$S_{DM} = 4547.68 \times \lambda . 10^{-20} cm^{-2} \quad (3)$$

The experimental integrated absorption of a transition of a Er^{+3} ion is related to the electric dipole oscillator strengths $f_{ed}(J \rightarrow J')$ of the transition by the expression:

$$f_{exp}^{de}(J \rightarrow J') = \frac{mc^2}{\pi e^2} \frac{1}{N\lambda_{max}^2} \int \alpha(\lambda) d\lambda \quad (4)$$

Table4. Measured and calculated oscillator strength of various transitions of Er^{+3} in the glass

Absorption	$^{a}\lambda_{max}\,(nm)$	$f^{mes}\left(\times 10^{-6}\,cm^2\right)$	$f_{ed}\left(\times 10^{-6}\,cm^2\right)$	$f_{md}\left(\times 10^{-6}\,cm^2\right)$	$f^{cal}\left(\times 10^{-6}\,cm^2\right)$	Δf
4I15/2 → 4I13/2	1531	1.4342	0.8321	0.6021	0.8889	0.0568
4I15/2 → 4I11/2	976	0.6374	0.6374	0	0.5009	-0.1365
4I15/2 → 4I9/2	799	0.1927	0.1927	0	0.2842	0.0915
4I15/2 → 4F9/2	653	1.6556	1.6556	0	1.6131	-0.0425
4I15/2 → 4S3/2	544	0.3117	0.3117	0	0.3293	0.0176
4I15/2 → 4H11/2	522	10.4696	10.4696	0	10.4785	0.0089
4I15/2 → 4F7/2	489	1.5392	1.5392	0	1.4394	-0.0998

$RMS_f = 0.1029 \times 10^{-6}\ cm^2$

Table 5. Measured and calculated values of electric dipole line strength, magnetic dipole line strength of various transitions and the three Judd_Ofelt parameters of Er^{+3} ions in $59.8Sb_2O_3$-$20Na_2O$-$20WO_3$ -0.2Er glass.

Absorption	$^{a}\lambda_{max}\,(nm)$	$S_{ed}^{mes}\left(\times 10^{-20}\,cm^2\right)$	$S_{md}\left(\times 10^{-20}\,cm^2\right)$	$S_{ed}^{cal}\left(\times 10^{-20}\,cm^2\right)$	ΔS_{ed}
$^4I_{15/2} \rightarrow 4I_{13/2}$	1531	0.9953	0.6962	1.0435	-0.0482
$^4I_{15/2} \rightarrow 4I_{11/2}$	976	0.4704	0	0.3696	0.1008
$^4I_{15/2} \rightarrow 4I_{9/2}$	799	0.1152	0	0.1698	-0.0547
$^4I_{15/2} \rightarrow 4F_{9/2}$	653	0.7974	0	0.7767	0.0206
$^4I_{15/2} \rightarrow 4S_{3/2}$	544	0.1224	0	0.1293	-0.0069
$^4I_{15/2} \rightarrow 4H_{11/2}$	522	3.9344	0	3.9370	-0.0027
$^4I_{15/2} \rightarrow 4F_{7/2}$	489	0.5405	0	0.5054	0.0351

$\Omega_2 = 4.9018 \times 10^{-20}\ cm^2$, $\Omega_4 = 0.9465 \times 10^{-20}\ cm^2$, $\Omega_6 = 0.5846 \times 10^{-20}\ cm^2$

$RMS = 0.0656 \times 10^{-20}\ cm^2$; Nc= $3.6 * 10^{19}$

Table 6. Judd-Ofelt parameters of Er^{+3} ions in the various composition glass

	% Er	$\Omega_2 \times 10^{-20}\, cm^2$	$\Omega_4 \times 10^{-20}\, cm^2$	$\Omega_6 \times 10^{-20}\, cm^2$	RMS $\times 10^{-20}\, cm^2$
20WO3	**0.2**	**4.9018**	**0.9465**	**0.5846**	**0 .0656**
	0.4	**4.300**	**0.905**	**0.817**	**0.145**
30WO3	**0.2**	**6.767**	**1.138**	**0.543**	**0.134**
	0.4	**3.691**	**1.137**	**0.929**	**0.143**

We have first determined the measured f_{exp}^{de} of all the strong absorption bands of Er^{+3} with the help of expression (4) by using their base glass corrected integrated coefficient of absorption of the glass at the related band's wavelength.

The Although most of the transitions are electric dipole in nature, in the case of a transition like $^4I_{15/2} \rightarrow {}^4I_{13/2}$ the contribution of magnetic dipole transitions to the total transition probability is rather high. So we have included the magnetic dipole contribution in the expression while calculating the line strength of the $^4I_{15/2} \rightarrow {}^4I_{13/2}$ transition.

The f_{exp}^{de} values of different transitions are given in Table 4 of a particular transition of frequency λ can also be used to obtain the measured line strength, S_{exp}^{de} of the transition using the relation

$$S_{exp}^{de} = \frac{9n}{(n^2+2)^2}\left[\frac{3hc(2j+1)}{8\pi^3 e^2 \lambda^2 N}\int \alpha(\lambda)d\lambda - n(\lambda)S_{md}\right] \qquad (5)$$

The value of nS_{md} in the expression may be $\geq$0 depending on the magnetic dipole contribution to the particular transition.The measured line strength (S_{exp}^{de}) values determined for different transitions of Er^{+3} ions in the glass are given in Table 6.

The three intensity parameters $\Omega_2, \Omega_4, \Omega_6$ respectively, for t = 2, 4 and 6, of the Er^{+3} ions in various composition glass for are given in Table (6) were calculated from the measured electric dipole line strengths $S_{exp}^{de}(J \rightarrow J')$ of different transitions, utilizing relation (1) and solving the equations by a least square fitting method. The values of the squares of the reduced matrix elements for the transitions were taken from Kaminskii

[10]. The best-fitted values obtained for $20WO_3 0.2Er$ are $\Omega_2 = 4.9018 \times 10^{-20}\ cm^2$, $\Omega_4 = 0.9465 \times 10^{-20}\ cm^2$,$\Omega_6 = 0.5846 \times 10^{-20}\ cm^2$ respectively.

Using the best fit values of the three Judd_Ofelt parameters of Er^{+3} ions in the glass, it is also possible to calculate the theoretical values of the electric dipole line strengths (S_{cal}) of different transitions (Table 5) with the help of relation (1). In these calculations also, we used the values of squares of the reduced matrix elements $|(S,L)J\|U^t\|(S',L')J'>|^2$ of the different transitions of Er^{+3} ion from Kaminskii [10]. Theoretical total oscillator strengths (f_{cal}) for different transitions can be obtained by using the calculated values of the electric dipole line strengths (S_{cal}). These are also shown in Table 4.

To check the reliability of the data, the root mean square value (RMS) of the deviations between the measured and the calculated values of electric dipole line strengths, and the same (RMS_f) of the deviations between the measured and the calculated values of total oscillator strengths were determined with the help of Eqs. (6) and (7):

$$RMS = \left[\sum (S^{ed}_{exp} - S^{ed}_{cal})^2/(p-q)\right]^{1/2} \quad (6)$$

$$RMS_f = \left[\sum (f^{ed}_{exp} - f_{cal})^2/(p-q)\right]^{1/2} \quad (7)$$

Here p denotes the number of absorption transitions considered and q the total number of parameters used. The values of RMS and of RMS_f obtained are $RMS = 0.0656 \times 10^{-20}\ cm^2$

$RMS_f = 0.1029 \times 10^{-6}\ cm^2$, respectively; the results demonstrate good reliability of the data.

Using the Ω_t values, various important radiative properties of a radiative transition, such as spontaneous emission rate (A_r), branching ratios (β_c), lifetime of the radiative transition (τ_r), and the total emission cross-section [$\sum \sigma_r(J \rightarrow J')$], were also calculated on the basis of Judd_Ofelt theory by using the following equations[11]:

$$A_r(J \rightarrow J') = \frac{64\pi^4 e^2}{3h(2J+1)\lambda^3}\left[\frac{n(n^2+2)^2}{9} S_{ed} + n^3 S_{md}\right] \quad (8)$$

Table 7. The parameters of different radiative transitions of Er^{+3} in the glass.

Transition	λ_{max}	A_r (s^{-1})	$A_r ed$ (s^{-1})	$A_r md$ (s^{-1})	β_c	τ_f (ms)	$\Sigma\sigma$ (10^{-18} cm)
$^4I_{13/2} \rightarrow {}^4I_{15/2}$	1533	193	110	83.5398	1	5.18	**1.5811**
$^4I_{11/2} \rightarrow {}^4I_{13/2}$	2686.1	24	24		0.117	4.87	**0.5714**
$^4I_{11/2} \rightarrow {}^4I_{15/2}$	976	181	181		0.882		**0.5902**
$^4I_{9/2} \rightarrow {}^4I_{11/2}$	4629.6	8	8		0.034	4.36	**0.1958**
$^4I_{9/2} \rightarrow {}^4I_{13/2}$	1739.1	43	43		0.187		**0.4555**
$^4I_{9/2} \rightarrow {}^4I_{15/2}$	811.49	178	178		0.777		**0.3960**
$^4F_{9/2} \rightarrow {}^4I_{9/2}$	3553.7	15	15		0.0066	0.44	**0.4585**
$^4F_{9/2} \rightarrow {}^4I_{11/2}$	1973.2	75	75		0.0330		**1.0286**
$^4F_{9/2} \rightarrow {}^4I_{13/2}$	1137.6	565	565		0.2489		**2.5231**
$^4F_{9/2} \rightarrow {}^4I_{15/2}$	653	1615	1615		0.7115		**2.2847**
$^4S_{3/2} \rightarrow {}^4I_{9/2}$	1719.7	58	58		0.0334	0.58	**0.5968**
$^4S_{3/2} \rightarrow {}^4I_{11/2}$	1239.3	33	33		0.0190		**0.1768**
$^4S_{3/2} \rightarrow {}^4I_{13/2}$	848	461	461		0.2657		**1.1251**
$^4S_{3/2} \rightarrow {}^4I_{15/2}$	548	1183	1183		0.6818		**1.1535**
$^4H_{11/2} \rightarrow {}^4F_{9/2}$	2545.2	50	50		0.0034	0.087	**1.1103**
$^4H_{11/2} \rightarrow {}^4I_{9/2}$	1467.1	175	175		0.0120		**1.3112**
$^4H_{11/2} \rightarrow {}^4I_{11/2}$	1114.1	107	107		0.0073		**0.4562**
$^4H_{11/2} \rightarrow {}^4I_{13/2}$	795.7	181	181		0.0124		**0.3938**
$^4H_{11/2} \rightarrow {}^4I_{15/2}$	**522**	**14077**	**14077**		**0.9648**		**12.3661**

$$\beta_c = A_r(J \rightarrow J')/\Sigma_{J'} A_r(J \rightarrow J') \quad (9)$$

$$\tau_r = [\Sigma_{J'} A_r(J \rightarrow J')]^{-1} \quad (10)$$

$$\Sigma\sigma_r(J \rightarrow J') = [\lambda_{max}^2/8\pi cn^2] A_r(J \rightarrow J') \quad (11)$$

The terms used in the equations have the usual meanings. The parameters calculated are listed in Table 7.

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