

## SPECTROSCOPIC PROPERTIES AND JUDD-OFELT INTENSITY PARAMETERS OF Er<sup>3+</sup> DOPED OXYCHLOROPHOSPHATE GLASSES FOR LASER APPLICATIONS

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### ABSTRACT

A new series of Er<sup>3+</sup> doped oxychlorophosphate glasses (NKAZCl) with the chemical composition based on (100-x) (NaPO<sub>3</sub>-KH<sub>2</sub>PO<sub>4</sub>-Al<sub>2</sub>O<sub>3</sub>-ZnCl<sub>2</sub>), with different xEr<sup>3+</sup> molar ratio (0.5≤x≤2), were prepared by conventional melting quenching method. The spectroscopic properties of proposed glasses are investigated by applied Judd-Ofelt theories to calculate the oscillator strengths S<sub>cal</sub>, the intensity parameters (Ω<sub>2</sub>, Ω<sub>4</sub>, Ω<sub>6</sub>). The absorption and emission cross section (σ<sub>abs</sub>(λ), σ<sub>em</sub>(λ)) respectively, and also the optical gain cross section parameter, at 1.53μm of <sup>4</sup>I<sub>13/2</sub>→<sup>4</sup>I<sub>15/2</sub> transition of Er<sup>3+</sup> ion are calculated by using Beer-Lambert law and the McCumber theory.

**Keywords:** Oxychlorophosphate glasses, Er<sup>3+</sup>, ZnCl<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, spectroscopic properties, Judd-Ofelt theory

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### 1. INTRODUCTION

Considerable research has been conducted on Er<sup>3+</sup> doped optical materials for improved quantum fluorescence performance in the visible and near infrared range [1-4]. The Er<sup>3+</sup> as doping element of host matrixes, is known for its emission around the wavelength of 1.5μm

which is used in telecommunication devices. The phosphate glasses are able to embed relatively a high concentration of rare earth ions before reaching the quenching effect.

In this work we report the optic and spectroscopic properties of  $\text{Er}^{3+}$  doped NKAZCl glasses for different  $\text{Er}_2\text{O}_3$  molar concentrations (0.5, 1 and 2% mol). An optimal composition has been obtained for this type of matrixes allowing a high fluorescence ratio at  $1.53 \mu\text{m}$ . All results are compared to those of other glasses.

## 2. EXPERIMENTAL

### Glass preparation:

The oxychlorophosphates glasses of molar compositions  $(100-x)$  ( $\text{NaPO}_3\text{-KH}_2\text{PO}_4\text{-Al}_2\text{O}_3\text{-ZnCl}_2$ ) with  $0.5 \leq x \leq 2$ , referred to as NKAZCl, were prepared by conventional melt quenching technique. The homogeneous mixture was transferred into a platinum crucible and kept in an electric furnace and then heated at  $1050^\circ\text{C}$  for 30min. In order to reduce the thermal and mechanical strains, the obtained glass samples were immediately introduced into the annealing furnace kept at  $300^\circ\text{C}$  for about 3h. The density for the prepared glasses was measured by using Archimedes principle, with distilled water as liquid-immersion.

### Optical measurements :

The room temperature transmission (absorption) spectra were obtained for all samples in 190-1100nm range by using the optizen 2120UV spectrophotometer and JASCO FT/IR-4100 spectrometer in the range of  $400$  to  $7000\text{cm}^{-1}$ .

## 3. RESULTS AND DISCUSSION

### Physical properties:

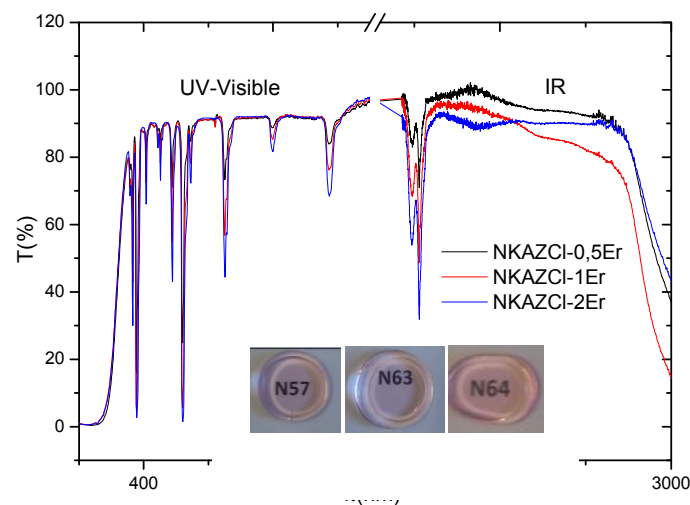
Table 1 illustrates the codes of glasses, and some physical properties of the glasses studies in the present work.

**Table1** Glass codes, and physical properties of Er<sup>3+</sup> doped oxychlorophosphate glasses

Codes	Density (g/cm <sup>3</sup> )	n <sub>d</sub> (580)	concentration N (10 <sup>20</sup> ions/cm <sup>3</sup> )
NKAZCl-0.5Er <sup>3+</sup>	2.731	1.513	1.366
NKAZCl-1Er <sup>3+</sup>	2.750	1.518	2.733
NKAZCl-2Er <sup>3+</sup>	2.820	1.519	5.465

### Optical properties:

The optical properties are defined as the maximum transmission window and the transparency of the different structures. The addition of ZnCl<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> to the glasses, overcomes the hygroscopic nature of phosphates structures and increase the transparency of such as glasses (show Fig.1.).



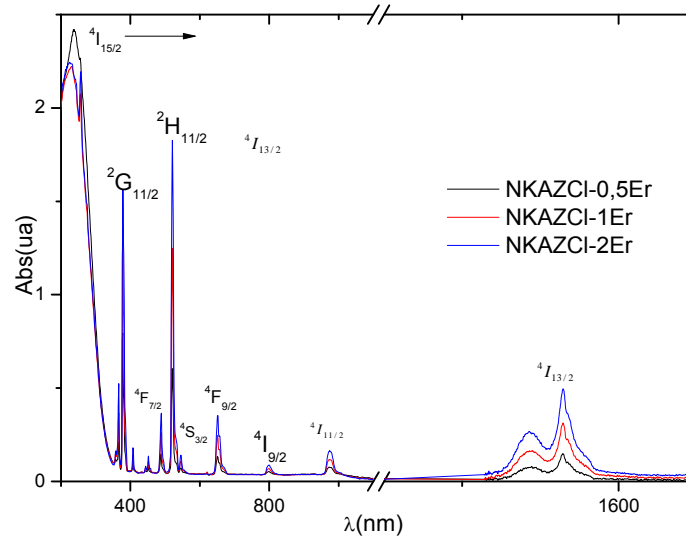
**Fig.1.** Transmission spectrum of NKAZCl doped Er<sup>3+</sup> glasses in the region 190-3000nm

### 4. Spectroscopic properties of Er<sup>3+</sup>:

#### Absorption Spectrum

The absorption spectra of oxychlorophosphate glasses, doped with 0.5, 1 and 2% mol of Er<sup>3+</sup> at room temperature, in the 190-1700nm wavelength range, are illustrated in Fig-2-. These spectra are composed of several absorption bands centered essentially at 6524, 10235, 12500,

15313, 18348, 19157, 20491 and 24570  $\text{cm}^{-1}$ , corresponding to transitions from the ground state  $^4I_{15/2}$  of  $\text{Er}^{3+}$  ions to  $^4I_{13/2}$ ,  $^4I_{11/2}$ ,  $^4I_{9/2}$ ,  $^4F_{9/2}$ ,  $^4S_{3/2}$ ,  $^2H_{11/2}$ ,  $^4F_{7/2}$  and  $^2G_{9/2}$  excited states, respectively. The assignments of these transitions have been made on the basis of Carnall [7]. The absorption spectrum of present work is very similar to those of other reported  $\text{Er}^{3+}$  doped glass systems except for small changes in the peak position and relative intensities. This can be attributed to the nature of various ligand field of different glass matrices.



**Fig.2.** Absorption spectrum of NKAZCl doped  $\text{Er}^{3+}$  glasses in the region 190-1700nm

### Judd Ofelt Analysis :

Judd–Ofelt analysis is applied to calculate the line strengths for electric dipole transitions between  $|4f\alpha[SL]J\rangle$  and  $|4f\alpha'[S'L]J'\rangle$  states through the determination of phenomenological intensity parameters ( $\Omega_t, t=2,4,6$ ). The procedure is based on comparison between expressions for the theoretical line strength ( $S_{cal}$ ) (Eq 01), which contain the  $\Omega_\lambda$  parameters and the experimental line strength ( $S_{exp}$ ) (Eq 02) determined from the absorption spectra.

$$S_{cal} = \sum_{k=2,4,6} \Omega_k | \langle J' | U^{(k)} | J \rangle |^2 \quad [\text{Eq 01}]$$

(Where  $(\Omega, t=2,4,6)$  are the host dependent JO intensity parameters and  $\|U^{(k)}\|$  are the doubly reduced matrix elements of the unit tensor operator which are considered to be the independent of the host [7].)

$$S_{mes} = \frac{9n}{(n^2 + 2)^2} \left[ \frac{3hc(2J + 1)}{8\pi^3 e^2 N} \int_{J \rightarrow J'} \alpha(\sigma) d\sigma - S_{md} \right] \quad [\text{Eq 02}]$$

$(9n/(n^2+2)^2)$  is the Lorentz local field correction for the absorption band,  $N$  the concentration of ions / $\text{cm}^3$ ,  $\alpha(\sigma)$  the absorption coefficient in  $\text{cm}^{-1}$ ,  $\sigma$  the wave number,  $n$  the refractive index,  $c$  the celerity of light,  $m$  and  $e$  the mass and electric charge of an electron,  $S_{md}$  the magnetic line strength.)

The experimental and theoretical line strengths obtained from the J-O analysis for the considered glasses are presented in **Table 2**. J-O intensity parameters are estimated by a least-squar fit between ( $S_{\text{exp}}$ ) and ( $S_{\text{cal}}$ ). The small variations in the values of root-mean-square deviation (RMS), indicate the good quality of the fit between experimental and calculated line strengths.

**Table 2:** Measured and calculated line strengths  $S$  ( $\times 10^{-20} \text{cm}^2$ ) of different transitions.

Transition	$\sigma(\text{cm}^{-1})$	NKAZCl-0.5Er		NKAZCl-1Er		NKAZCl-2Er	
		$S_{\text{exp}}$	$S_{\text{cal}}$	$S_{\text{exp}}$	$S_{\text{cal}}$	$S_{\text{exp}}$	$S_{\text{cal}}$
${}^4I_{15/2} \rightarrow$							
${}^4I_{13/2}$	6540	1.941	1.320	2.698	1.960	2.167	1.480
${}^4I_{11/2}$	10266	0.5255	0.4510	0.5983	0.6560	0.5253	0.490
${}^4I_{9/2}$	12531	0.1754	0.2330	0.2123	0.2700	0.1788	0.23
${}^4F_{9/2}$	15360	0.9916	0.9800	1.289	1.260	1.067	1.04
${}^4S_{3/2}$	18348	0.2371	0.1690	0.2695	0.2620	0.2258	0.194
${}^2H_{11/2}$	19193	4.339	4.340	5.458	5.450	4.372	4.373
${}^4F_{7/2}$	20533	0.7875	0.6540	0.9266	0.9400	0.7505	0.725
${}^2G_{9/2}$	24570	0.2413	0.1920	0.3133	0.2890	0.2255	0.217

It observed from **Table2** that the line strength values of the hypersensitive transition  $^4I_{15/2} \rightarrow ^2H_{11/2}$  is larger than other transition. The Judd-Ofelt intensity parameters listed in **Table 3** have important values to investigate the local structure and bonding nature in vicinity of the Er<sup>3+</sup> ions.

The Judd-Ofelt intensity parameters for all samples as follow the trend  $\Omega_2 > \Omega_4 > \Omega_6$  which is similar to Er<sup>3+</sup> doped phosphate and Tellurites glasses [8, 10]. The parameter  $\Omega_2$  is attributed to the symmetry of the surrounding media containing rare earth ion and a decrease in the symmetry is assigned to the increase in the  $\Omega_2$  value. Comparing our values of  $\Omega_2$  reported in **Table 3**, it is clear that the degree of covalency remains quite high as compared to chlorophosphate and oxyphosphate glasses [8-9] and very close to tellurite glasses [10]. On the other hand, the  $\Omega_4$  and  $\Omega_6$  parameters are related to the rigidity of the matrix.

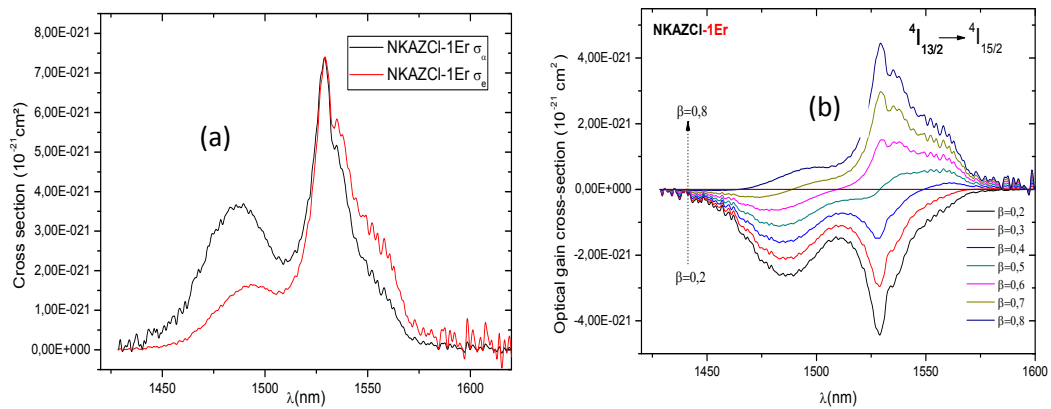
The parameter  $\chi = \Omega_4/\Omega_6$  known as spectroscopic quality factor define the fluorescence intensity. These values are very high than NNPO and NNP30 glasses, and quite less compared with other glasses (**see table 3**).

**Table3:** Judd-Ofelt intensity parameters,  $\Omega_{2,4,6}$  ( $10^{-20}$  cm<sup>2</sup>), spectroscopic quality factor ( $\chi = \Omega_4/\Omega_6$ ) of the different glasses samples and the root-mean-square deviation (RMS).

Samples	$\Omega_2$	$\Omega_4$	$\Omega_6$	$\chi$	RMS	
KNAZCl-0.5Er	5.13	1.20	0.75	1.59	0.093	Present work
	2	8	9			
KNAZCl-1Er	6.50	1.38	1.17	1.17	0.040	Present work
KNAZCl-2Er	5.15	1.22	0.87	1.40	0.038	Present work
	4		0			
55P <sub>2</sub> O <sub>5</sub> -40BaO-5Al <sub>2</sub> O <sub>3</sub>	4.67	1.37	0.77	1.78	-	[8]
NNP0 (chlorophosphate)	3.36	0.51	1.51	0.33	-	[9]
NNP30	3.79	0.13	1.21	0.10	-	[9]
TeO <sub>2</sub> -ZnO-Nb <sub>2</sub> O <sub>5</sub> -BaF <sub>2</sub> -Er <sub>2</sub> O <sub>3</sub> - Yb <sub>2</sub> O <sub>3</sub>	5.97	1.97	0.88	2.24	0.073	[10]

### IR Emission properties : ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition

We have calculated, absorption cross section,  $\sigma_{abs}(\lambda)$ , emission cross section  $\sigma_{em}(\lambda)$ , and optical gain cross section of the  ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$  ( $\text{Er}^{3+}$ ) laser transition using the Beer-Lambert Law and McCumber theory. Using the Judd Ofelt parameters, we have also calculated the spectroscopic parameters as : the transition probabilities  $A$  ( $\text{S}^{-1}$ ), radiative life time  $\tau$  (ms), and branching ratio  $\beta$  (%), for the transition  ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$   $\text{Er}^{3+}$  ion. It observed from **table 4** that the sample  $\text{KNAZCl-1Er}^{3+}$  has the highest value of  $\sigma_a$  and  $\sigma_e$ .



**Fig.3.** (a) Cross section ( $\sigma_a, \sigma_e$ ), (b) Optical gain cross section of the sample  $\text{NKAZCl-1Er}$ .

**Table.4.** Absorption  $\sigma_a$  and emission  $\sigma_e$  cross section and transition probabilities  $A$ , radiative lifetime  $\tau$  and branching ratio  $\beta$  (%) of  $\text{Er}^{3+}$  transition  ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$  in tellurite glasses

Samples	$\sigma_a$ ( $10^{-21}$ )	$\sigma_e$ ( $10^{-21}$ )	$\tau$ (ms)	$A$ ( $\text{S}^{-1}$ )	$\beta$ (%)	
KNAZCl-0.5Er	5.88	5.86	16.01	62.46	100	Present work
KNAZCl-1Er	7.37	7.401	10.83	92.3	100	Present work

KNAZCl-2Er	6.114	6.158	14.33	69.78	100	Present work
74TeO <sub>2</sub> -10CdO- 15WO <sub>3</sub> -Er <sub>2</sub> O <sub>3</sub>	6.40	6.9	-	-	-	[11]
50P <sub>2</sub> O <sub>5</sub> -30CaO- 12Na <sub>2</sub> O-Al <sub>2</sub> O <sub>3</sub> - 2AgO-Er <sub>2</sub> O <sub>3</sub> - 4Yb <sub>2</sub> O <sub>3</sub>	6.0	6.9	-	-	-	[12]

**Fig3** (b) shows the optical gain cross section of the  ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$  ( $\text{Er}^{3+}$ ) laser transition, when the inversion rate of population  $\beta$  (%), assumes values greater than 0.4, the emission cross section at 1530 nm becomes positive, which predicts the amplification ease of emission around this wavelength.

## 5. CONCLUSION

The spectroscopic properties of  $\text{Er}^{3+}$  doped oxychlorophosphate glasses were investigated by calculating the J-O intensity parameters. The magnitude of the J-O parameters follow the trend as  $\Omega_2 > \Omega_4 > \Omega_6$  for all the glasses. It's found that the rigidity and the degree of covalency of our glasses samples remain quite high as compared to other phosphates glasses. The good spectroscopic parameters such as high quality spectroscopy factor  $\chi$ , radiative transition probabilities  $A$ , branching ratio  $\beta$  (%), for transition  ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$  and a large absorption and stimulated emission cross-sections ( $\sigma_a, \sigma_e$ ), of  $\text{Er}^{3+}$  around 1530 nm in  $\text{Er}^{3+}$  doped oxychlorophosphates glasses found that this matrix are a suitable laser material for 1.53  $\mu\text{m}$ . Finally, the samples KNAZCl-1Er, present a high emission parameters at 1.53  $\mu\text{m}$ .

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