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OPTICAL ABSORPTION SPECTRUM AND JUDD-OFELT ANALYSIS STUDY OF Eu^{3+} DOPED ZINC OXYCHLORIDE TELLURITE GLASSES.

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ABSTRACT

A series of glass samples in the TeO_2 - ZnO - $ZnCl_2$ - Li_2O - Eu_2O_3 glass system has been successfully made by the melt quenching technique. The density, the refractive index, the optical absorption, the Judd-Ofelt parameters and the spontaneous transition probabilities have been determined. Judd-Ofelt analysis was performed for the glass system to evaluate the spontaneous emission probability as well as the quality factor (Q), branching ratio (β) and radiative lifetime (τ_{rad}). The variation of Judd-Ofelt parameters (Ω_2, Ω_4 and Ω_6) were analyzed as a function of $ZnCl_2$ concentration. It was found that the Ω_2, Ω_4 , Ω_6, Q and τ_{rad} increase with $ZnCl_2$ concentration.

INTRODUCTION

Among many potential host materials for rare earth ions, zinc tellurite glasses show important advantages such as low-phonon energy environment to minimize nonradiative losses as well as possessing good chemical durability and optical properties [1]. The tellurite glasses are known to have a relatively high refractive index ($1.8 < n < 2.3$), a low melting temperature and represent something of a compromise between the requirement for both a low phonons energy as well as good mechanical characteristics [2]. Zinc tellurite glasses represent one of the best potential host materials for several rare earth dopants for laser applications [1]. The rare earth absorption and fluorescence spectra are quite sensitive to the local environment of the ion. Eu^{3+} is especially well suited as a probe ion as the $^7F_0 \rightarrow {}^5D_2$ absorption and $^5D_0 \rightarrow {}^7F_2$ emission in the Eu^{3+} are hypersensitive transitions and their intensities are very sensitive to the local environment [3]. The purpose of this paper is to investigate the spectroscopic properties as a function of $ZnCl_2$ concentration by using Judd-Ofelt parameter theory. Intensity parameters, radiative lifetime and branching ratio were determined from absorption spectra.

EXPERIMENT DETAILS

A series of glass samples, $(79 – z)TeO_2$ - 10ZnO - $zZnCl_2$ - $10Li_2O$ - $1Eu_2O_3$ where z = 0, 10, 20, 25, 30 mol% were prepared by melting mixtures of high-purity TeO_2, ZnO, $ZnCl_2$, Li_2CO_3 and Eu_2O_3 in a platinum crucible. The mixture was heated in an electrical furnace at a temperature 850° C for 30 minutes. To ensure proper mixing and homogeneity, the molten liquid was shaken frequently and vigorously. After being checked, the melt was cast by pouring into a preheat stainless steel split mould to

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quench to form a glass. The glass was immediately transferred to an annealing furnace at 260° C, 10°C above T_g. It was kept for 3 hours to relieve any residual stress, which could cause embrittlement. At the end of this annealing process, the glass left to slowly cool down to room temperature.

The amorphous nature of these samples has been confirmed by X-ray diffraction technique using Bruker axs D5005 X-ray Diffractometer. For optical measurement, the annealed glass plates were polished well on both side to dimension 20 mm x 20 mm x 2 mm. The optical absorption spectra of the glass were recorded using Jenway 6505 UV-vis Spectrophotometer.

RESULTS AND DISCUSSION

The absorption spectrum of Eu^{3+} for glass sample SZC3 with composition $59TeO_2$ - $10ZnO$ - $20ZnCl_2$ - $10Li_2O$ - $1Eu_2O_3$ recorded in the 350 – 600 nm at room temperature are shown in Figure 1. The ultraviolet (UV) cut-off is evident on the left in Figure 1 and several absorption lines are also observed. The absorption peak around 362, 375, 381, 393 and 464 cm^{-1} correspond to the transitions from ground state of $^7F_0$ to the excited state of $^5D_4$, $^5G_4$, $^5G_2$, $^5L_6$ and $^5D_2$ respectively. Using an absorption spectra, Judd-Ofelt (J-O) analysis was performed to determine the J-O parameters Ω_2, Ω_4 and Ω_6. The assignment of these absorption bands and the values of the measured (P_{mea}) and calculated (P_{cal}) oscillator strength obtained from J-O theory is tabulated in Table 1. The P_{mea} of the transitions was obtained by using an equation $P_{mea} = \frac{mc^2}{\pi e^2 N}\frac{2.303}{d}\int E(\lambda)d\lambda$. The P_{cal} of an electric-dipole absorption transition from initial state to final state, involving J-O parameters (Ω_2, Ω_4, Ω_6) which depend on the host matrix [4,5,6,7]. The P_{cal} can be calculated using the equation $P_{calc} = \frac{8\pi^2 mc}{3h\lambda(2J+1)}\frac{(n^2+2)^2}{9n}\sum_{t=2,4,6}\Omega_t \left\|U^t\right\|^2$. The Ω_2, Ω_4, Ω_6 were derived from P_{mea} using a least-squares fitting approach. Ω_t are important for investigating of local structure, bonding in the vicinity and transitions properties of rare-earth ions. Some important radiative properties can be calculated by use of the values of Ω_t .

Theoretically computed radiative properties of Eu^{3+} in the glass system including radiative transition probabilities (A), branching ratio (β) and radiative lifetime (τ_{rad}) are listed in Table 2. Judd-Ofelt analysis was performed to determine the τ_{rad} for these samples,. The spontaneous transition probability is given by $A = \frac{64\pi^4}{3h\lambda^3(2J+1)}\left[\frac{n(n^2+2)^2}{9}S_{ed} + n^3 S_{md}\right]$ where the electric-dipole line strengths, $S_{ed} = e^2\sum_{t=2,4,6}\Omega_t\left\|U^t\right\|^2$ and the magnetic-dipole line strengths, $S_{md} = \frac{e^2\eta^2}{4m^2c^2}\left\|L+2S\right\|^2$.

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The fluorescence branching ratio of transitions is given by $\beta = \frac{A}{\sum A}$. The total radiative transition probabilities A_{total} for seven emission transitions ($^7F_0$, $^7F_1$, $^7F_2$, $^7F_3$, $^7F_4$, $^7F_5$, $^7F_6$) are summed up to obtain the τ_{rad} from the $^5D_0$ state using equation $\tau_{rad} = 1/A_{total}$ According to the equation, the τ_{rad} lifetimes of these levels are determined to be 0.759 ms as given in Table 2. The predicted spontaneous-radiative transition rate for $^5D_0 \rightarrow {}^7F_2$ transition is 991 s^{-1} and fluorescence branching ratio is 75%, showing this transition can be expected to be the most intense emission in the glasses.

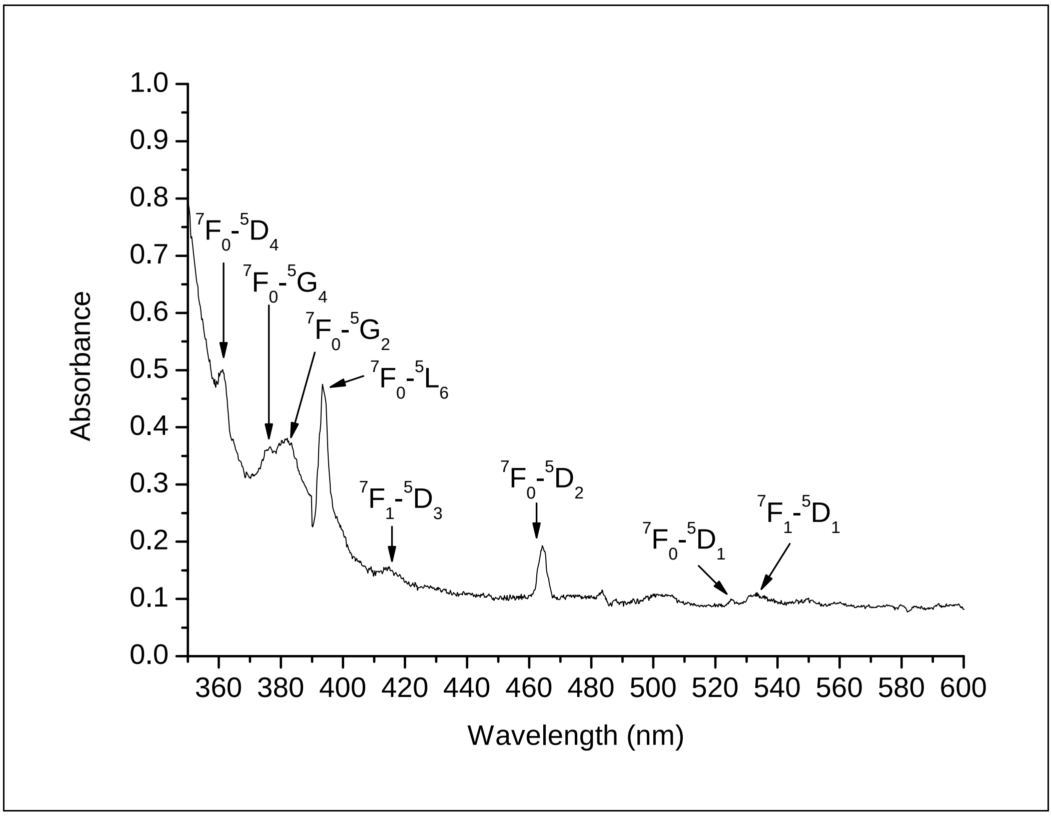

Figure 1: Absorption spectrum of Eu^{3+} ion for glass sample $59TeO_2$ - 10ZnO - $20ZnCl_2$ - $10Li_2O$ - $1Eu_2O_3$ at room temperature.

The absorption spectra of the (79 – z)TeO_2 - 10ZnO - (z)$ZnCl_2$ - $10Li_2O$ - $1Eu_2O_3$ glass system with various $ZnCl_2$ content (z = 0, 10, 20, 25, 30 mol %) is shown in Figure 2. It can be seen that the transitions $^7F_0 \rightarrow {}^5L_6$ and $^7F_0 \rightarrow {}^5D_2$ occur in all sample, but for transition $^7F_0 \rightarrow {}^5D_4$ and $^7F_0 \rightarrow {}^5G_2$ can only be observed clearly for $ZnCl_2$ concentration more than 20 mol %. The increase in $ZnCl_2$ leads to a shift of the UV cut off to shorter wavelengths. In Figure 2, the absorption edge of rare-earth Eu_2O_3 doped glass occurs in the near-UV region. The optical absorption edge becomes more prominent as Eu_2O_3 is incorporated in the glass. The J-O parameters (Ω_2, Ω_4, Ω_6) for various $ZnCl_2$ content is

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shown in Table 3. These Ω_2, Ω_4 , Ω_6 parameters were derived using least-squares fitting approach between the P_{mea} and the P_{cal}. The values for the optical spectroscopic ratio or spectroscopic quality factor $Q = \Omega_4/\ \Omega_6$ introduced by Jacobs and Weber [8] is also inserted. It can be clearly seen that all J-O parameters (Ω_2, Ω_4 , Ω_6) show increase with $ZnCl_2$ concentration as shown in Figure 3. It increases from 1.270 x 10^{-19} to 1.517 x 10^{-19} cm^2, 0.244 x 10^{-19} to 0.644 x 10^{-19} cm^2 and 0.118 x 10^{-19} to 0.193 x 10^{-19} cm^2, respectively with $ZnCl_2$ concentration from 0 mol % to 30 mol %.

Table 1: Values of the P_{mea} and P_{cal} for the chosen absorption of Eu^{3+} for $59TeO_2$ - $10ZnO$ - $20ZnCl_2$ - $10Li_2O$ - $1Eu_2O_3$ glass.

Wave length λ(nm)	Energy (cm^{-1})	Assignments	Area $\int E(\gamma)d\gamma$	Reduced matrix elements			Oscillator strengths, P	
				$[U_2]^2$	$[U_4]^2$	$[U_6]^2$	P_{mea} ($x10^{-7}$)	P_{calc} ($x10^{-7}$)
362	27624	$^7F_0\rightarrow{}^5D_4$	9.6077	0.0000	0.0011	0.0000	2.1514	3.2019
375	26635	$^7F_0\rightarrow{}^5G_4$	15.7938	0.0000	0.0007	0.0000	3.5367	1.9539
381	26211	$^7F_0\rightarrow{}^5G_2$	36.8522	0.0006	0.0000	0.0000	8.2523	4.5207
393	25445	$^7F_0\rightarrow{}^5L_6$	40.8609	0.0000	0.0000	0.0155	9.1500	9.1493
464	21551	$^7F_0\rightarrow{}^5D_2$	11.5157	0.0008	0.0000	0.0000	2.5787	4.8136
Deviation parameter, δ_{rms} = 3.3562 x 10^{-7}								
Judd-Ofelt parameters (cm^2): Ω_2 = 1.248x 10^{-19} , Ω_4 = 0.454x 10^{-19} , Ω_6 = 0.101x 10^{-19}								

Table 2: Predicted spontaneous-radiative transition rate (A), fluorescence branching ratio (β) and lifetime (τ_{rad}) of Eu^{3+} in $59TeO_2$ - $10ZnO$ - $20ZnCl_2$ - $10Li_2O$ - $1Eu_2O_3$ glass.

Transition	Energy (cm^{-1})	Reduced matrix elements			A_{ed} (s^{-1})	A_{md} (s^{-1})	β (%)
		$[U_2]^2$	$[U_4]^2$	$[U_6]^2$			
$^5D_0\rightarrow{}^7F_6$	12437	0	0.0006	0.0002	30.20	0	2.29
$^5D_0\rightarrow{}^7F_5$	13495	0	0	0	0	0	0
$^5D_0\rightarrow{}^7F_4$	14534	0	0.0023	0	177.46	0	13.47
$^5D_0\rightarrow{}^7F_3$	15479	0	0	0	0	0	0
$^5D_0\rightarrow{}^7F_2$	16339	0.0032	0	0	991.52	0	75.27
$^5D_0\rightarrow{}^7F_1$	16977	0	0	0	0	118.07	8.96
$^5D_0\rightarrow{}^7F_0$	17361	0	0	0	0	0	0
A_{total} (s^{-1}) = 1317.2 , τ_{rad} (ms)= 0.759							

The trend for the Ω parameters in the glass system is such that $\Omega_2 > \Omega_4 > \Omega_6$. It is well known that the parameter Ω_2, exhibits the dependence on the covalency between rare earth ions and ligands anions, since Ω_2 reflect the asymmetry of the local environment at the Eu^{3+} ion site. The higher the value of Ω_2 the less centrosymmetrical the ion site is

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and the less ionic its chemical bond with the ligands [9]. The slight increase of Ω_2 with an increasing of $ZnCl_2$ concentration in the glass system could indicate the increase of covalent character because of the different site occupancy of the ions on average [10].

Figure 4 shows the dependence of the *Q* as a function of $ZnCl_2$ concentration. The Q increase from 2.062 to 4.491 for 20 mol % $ZnCl_2$ then decrease to 3.341 for 30 mol % $ZnCl_2$. It indicates that the higher the value of Q, the better is the optical glass and the stronger the laser $^5D_0 \rightarrow {}^7F_2$ transitions. On the other hand, the efficiency of $^5D_0 \rightarrow {}^7F_1$ transition becomes reduced [11,12].

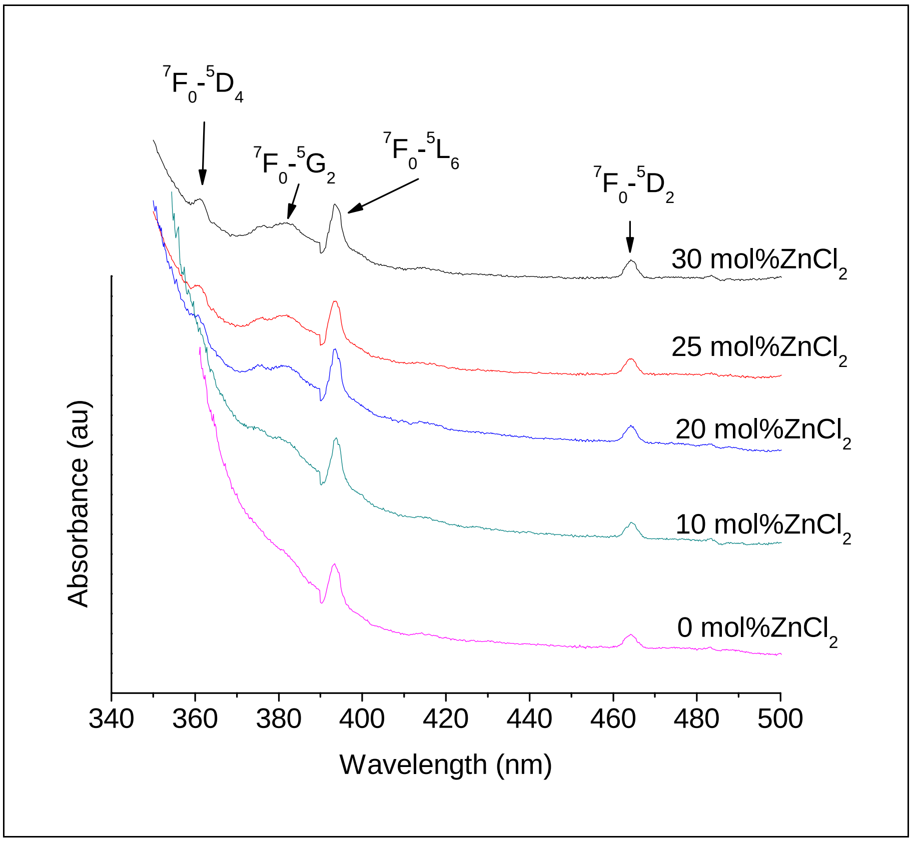

Figure 2: Absorption spectrum of Eu^{3+} in the (79 – z)TeO_2 - 10ZnO - z$ZnCl_2$ -10Li_2O - 1Eu_2O_3 glass system, where z = 0, 10, 20, 25 and 30.

The τ_{rad} increases substantially with the introduction of zinc chloride into the tellurite matrix as shown in Figure 4. The τ_{rad} increased from about 0.617 ms in sample SZC1 to 0.759 ms in sample SZC3 where 20 mol% $ZnCl_2$ was introduced into the tellurite matrix. The τ_{rad} is also desired to be as long as possible in order to permit a greater pulsed power. For higher $ZnCl_2$ content, the τ_{rad} decreases from 0.759 to 0.665 ms for 30 mol % $ZnCl_2$. This change clearly shows a maximum at about 20 mol % $ZnCl_2$, at a maximum τ_{rad}. This is evident that halide $ZnCl_2$ does modify the local electrostatic field

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symmetry of the rare earth ion Eu^{3+} and can produce a substantial increase of the intrinsic radiative lifetime. The chloride ion Cl^- may be replaced an oxygen ion somewhere in coordination sphere and disturbing the local electron density so the electrostatic environment of rare earth ion was altered.

Table 3: Calculated Judd-Ofelt parameters and spectroscopic ratio Q for Eu^{3+} in the $(79 – z)TeO_2$ - $10ZnO$ - $(z)ZnCl_2$ - $10Li_2O$ - $1Eu_2O_3$ glass system.

Sample No.	Mol% $ZnCl_2$	δ_{rms} (10^{-7})	Judd-Ofelt Parameters (10^{-19}) cm^2			$Q = \Omega_4/\Omega_6$
			Ω_2	Ω_4	Ω_6	
SZC1	0	4.427	1.270	0.244	0.118	2.062
SZC2	10	4.572	1.317	0.367	0.121	3.025
SZC3	20	3.356	1.248	0.454	0.101	4.491
SZC4	25	3.692	1.413	0.527	0.124	4.231
SZC5	30	3.451	1.517	0.644	0.193	3.341

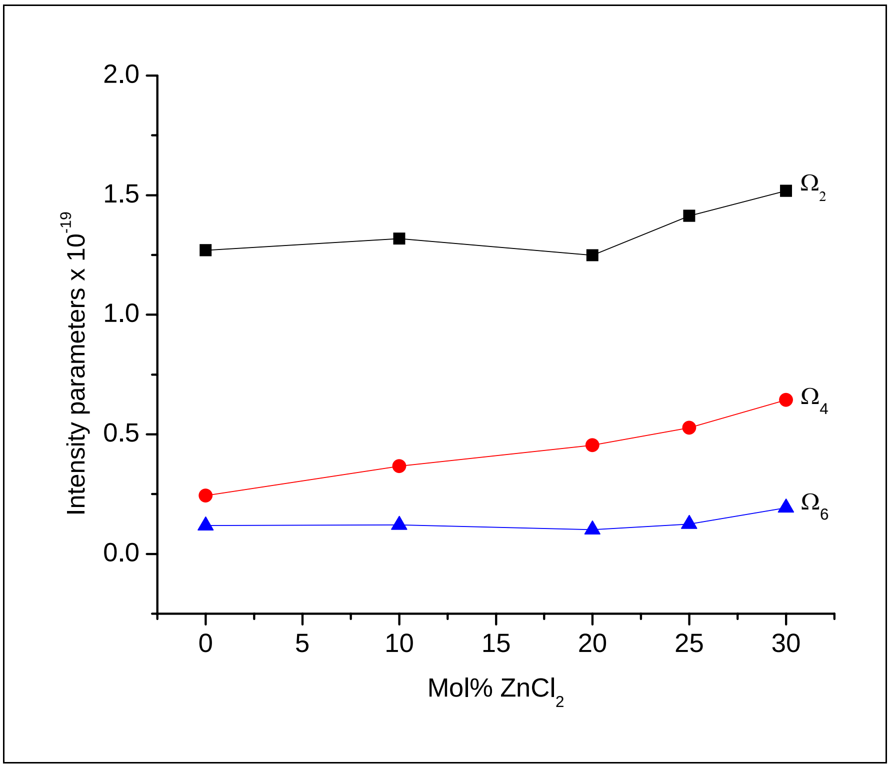

Figure. 3: Variations of intensity parameters (Ω_2, Ω_4, Ω_6) with $ZnCl_2$ concentration of $(79 – z)TeO_2$ - $10ZnO$ - $(z)ZnCl_2$ - $10Li_2O$ - $1Eu_2O_3$ glass system.

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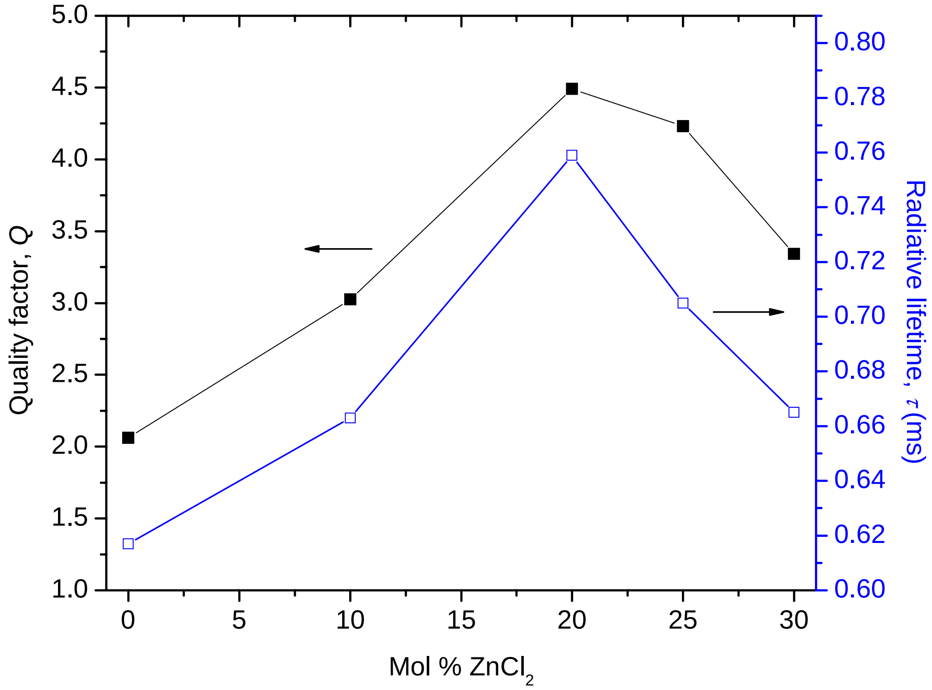

Figure 4: Spectroscopic quality factor, Q and radiative lifetime, τ_{rad} of the $^5D_0$ level as a function of $ZnCl_2$ concentration.

The OH content of these glass also decreased with zinc chloride as shown from the FTIR spectra, suggesting that this compound may react with the OH group, probably giving zinc oxide and HCl [13]. This dehydration effect may explain the fact that the fluorescence intensities and lifetimes appear to reach a maximum for 20 mol% $ZnCl_2$ after which it may lead to an increase in ion-ion interactions, clustering and nonradiative decay from $^7F_6$ to ground $^7F_0$ along with multiphonon relaxation, which is responsible for the subsequent decrease of the lifetimes.

CONCLUSIONS

The Ω intensity parameters, the radiative transition rates, the branching ratio and the fluorescence lifetimes were successfully calculated based upon the experimental absorption spectrum and the Judd-Ofelt theory. It was found that Ω, Q, A, β and τ_{rad} increased with increasing of $ZnCl_2$ content. The progressive replacement of TeO_2 by $ZnCl_2$ improved the optical quality of the glasses and the halide $ZnCl_2$ does modify the local electrostatic field symmetry of the rare earth ion, Eu^{3+}. The optical properties of Eu^{3+} ions doped in halide tellurite glass suggest that it is a good laser material at 612 nm ($^5D_0 \rightarrow {}^7F_2$ transition).

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