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Research Article

Optical and Structural Analysis of Ho^{3+} Ion Doped Sodium zirconium Silicate Gasses

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Abstract

Ho^{3+} ions doped sodium zirconium silicate glasses have been prepared by melt quenching technique and characterized by XRD, optical absorption, luminescence, FTIR and Raman spectral techniques. The XRD spectra of the glass samples reveal that these glasses have amorphous nature. In the Optical investigations, the Judd–Oflet theory could successfully applied, the value of Ω_2 is observed to be highest which suggests that highest covalent environment is present around Ho^{3+} ions. Various radiative properties such as transition probability, branching ratio β_r and radiative life time τ_R are estimated. The branching ratio for $^5F_5 \rightarrow {}^5I_8$ is found to be maximum (~50%) and it may be considered as a possible laser transitions. Structural properties reveals that the glass network becomes depolymerized with introduce of Ho^{3+} ions in the glass matrix.

Keywords: *Sodium zirconium silicate glasses, Ho^{3+} ions, optical investigations, radiative properties*

1. Introduction

Optical and structural properties of various RE^{3+} ions doped alkali silicate oxide glasses have been extensively investigated in the recent years because of their promising applications are spread in several fields such as optical amplifiers, up conversion emission, optical memories, and optoelectronics. Among various rare earth ions, Ho^{3+} ions doped materials are most important active materials for to luminescence lasers because of their favorable energy level structure because of their favorable energy level structure, moreover emission bands are distributed from UV to NIR regions. *I.V.Kityk et al 2001* have reported infrared and red luminescence of Ho^{3+} ions embedded in glass matrix at room temperature and helium liquid temperatures. In this study, they clearly suggested the influence of energy transfer processes between the host and Ho^{3+} ions. At the same time they also discussed on the quantitative aspects of photo induced anharmonicity in the phonon relaxation processes by measurements of luminescent kinetics in the polarized light.

High-silica glasses with high refractive indices, high thermal stability, chemical durability and good optical transparency over a wide range of wavelengths are particularly useful for optical fibers. The addition of Na_2O to silica glasses reduces its stability by forming NBO. Besides Na_2O, ZrO_2 strengthens the silicate network via forming the covalent Zr–O–Si bridges and it also influences various physical and chemical properties of the glass network *(H.A. Schaeer et al 1979), (C.A. Maynell et al 1973)*. Moreover it is interested to reveal that whether ZrO_2 is network- forming/modifying. *Ringwood et al 1955 and Linthout et al 1984* had given two contradictory statements. Nevertheless sodium zirconium silicate glasses are one of the choices for the fluorescence hosts, it is well established that the radiative parameters associated with luminescence transitions of Ho^{3+} ions in glass lattice are highly sensitive even for small changes in the chemical environment. The transition probabilities of emission transitions of Ho^{3+} ions are expected to increase with increase in covalency that depends upon the network forming ions. Network modifiers also change the local environment of Ho^{3+} ions to some extent. Here an attempt has been made to optimize the Ho^{3+} ion transitions for a deep understanding of their optical and structural properties by changing local environment around Ho^{3+} ion in sodium zirconium silicate glass network to facilitate future photonic device development.

2. Experimental technique

The Table 1 illustrates the details of composition of the glasses used for present investigation. The glasses samples are synthesized by melt quenching technique. In this technique, appropriate amounts (all in mol %) of Na_2CO_3, ZrO_2, SiO_2 and Ho_2O_3 (analytical grade reagents) are powdered and thoroughly mixed in agate mortar. Then it is taken in the silica crucible after calcination and placed in an automatic temperature controlled furnace at a temperature range 1430–1450 ^{0}C for 20 min. The molten form of the material is poured on the brass mould for the required shape and then annealed at 475 ^{0}C for removing thermal stress in the glasses. Then the samples are finely

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*Corresponding author: **M. Rami Reddy** polished to final dimensions 1cm×1cm×0.2 cm for the present measurements.

The X-ray diffraction spectra are measured on a diffractometer with copper target (XRDARLX'TRA) and nickel filter operated at 40 kV, 30 mA. The optical absorption (UV–Vis–NIR) spectra of these glasses are recorded from 300 to 2400 nm for using a recording spectrophotometer type JASCO, V-670 with spectral resolution of 0.1 nm. The luminescence spectra are recorded at room temperature on a Photon Technology International (PTI) spectrofluorometer with exited wavelength of 355 nm from 350 to 1200 nm, Fourier transform infrared spectra are recorded on a JASCO-FT/IR-5300 spectrophotometer with resolution of 0.1 cm^{-1} in the spectral range 400–1500 cm^{-1} using KBr pellets (300 mg) containing pulverized sample (1.5 mg). The Raman spectra (model Nexus 670 Nicolet–Madison–WI USA) have been recorded on Fourier Transform Raman spectrometer with resolution of 4 cm^{-1} in the range 200–2000 cm^{-1}

Tables 1: summary of glass composition

Glasses	Na_2O Mol %	ZrO Mol %	SiO_2 Mol %	Ho_2O_3 Mol %
Pure	40.0	5.0	55.0	-
Ho 2	39.8	5.0	55.0	0.2
Ho 4	39.6	5.0	55.0	0.4
Ho 6	39.4	5.0	55.0	0.6
Ho 8	39.2	5.0	55.0	0.8
Ho 10	39.0	5.0	55.0	1.0

3. Results

X-ray diffraction patterns of Ho^{3+} doped Na_2O-ZrO_2-SiO_2 glasses are shown in Fig 1. The spectra consist of a broad bump and no sharp lines are observed which reveals that all the prepared glass samples fully in amorphous nature.

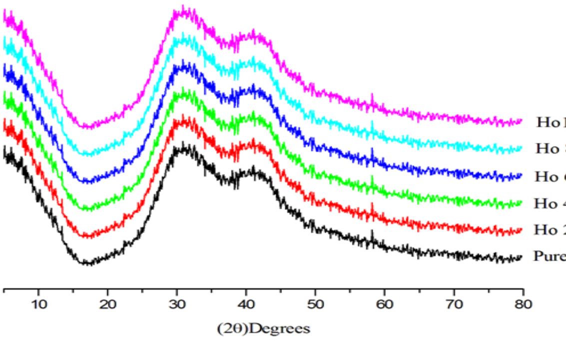

Fig 1 X-ray diffraction patterns of Ho^{3+} doped Na_2O-ZrO_2-SiO_2 glasses.

The Fig.2 illustrates absorption spectra specified glasses. No absorption bands are observed for host glass, on the other hand nine absorption bands are revealed with introduce of Ho^{3+} ions in the glass network at around ~360,~418, ~445, ~452, ~460, ~536, ~636, ~886, ~1095 and ~1158 nm. The bands are attributed to Ho^{3+} ions transitions from $^5I_8 \rightarrow {}^3H_6$, $^5G_5$, $^5F_1$, $^5G_6$, $^3K_8$, $^5F_4$, $^5F_5$, $^5I_5$, $^5I_6$ respectively *(Sk. Mahamuda et al, 2013)*. From the observed edge, we have evaluated the optical band gap (E_o) of these glasses by drawing Tauc's plots between $(\alpha h\nu)^{1/2}$, $(\alpha h\nu)^2$ (fig 3a & b) as a function of hν as per the given equation

$$\alpha(\nu)\, h\nu = C\,(h\nu - E_o)^n \qquad (1)$$

Here C is a constant and the exponent (n) can take values 1/2 and 2 for direct, indirect transitions in glasses respectively. Extrapolating the linear portion of these plots as $(\alpha h\nu)^{1/2} = 0$, $(\alpha h\nu)^2 = 0$ gives optical band gap, along with the theoretical optical band gap energy also calculated using equation $E = hc / \lambda$. Here h is the plank's constant, c is the velocity of light and λ is cutoff wavelength respectively. The optical band gap are found to decrease with an increasing the concentration of dopant Table 2 illustrated the optical data along with cutoff wavelength, optical band gap.

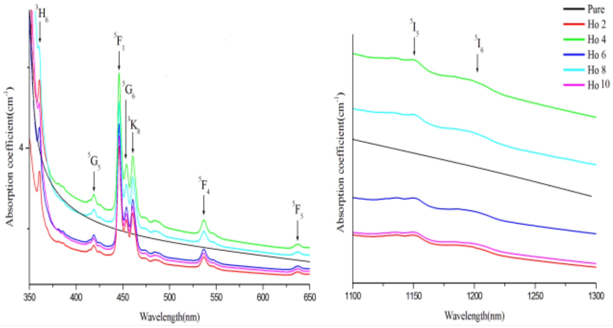

Fig. 2 Optical absorption spectra of Ho^{3+} doped Na_2O-ZrO_2-SiO_2 glasses

Table 2: Optical band gaps of the specified glasses

Glasses	Cutoff wavelength nm	Optical band gap (eV)		
		Direct band gap	Indirect band gap	Theoretical band gap
Pure	359	3.555	3.508	3.460
Ho 2	377	3.516	3.470	3.294
Ho 4	390	3.424	3.388	3.185
Ho 6	398	3.476	3.432	3.121
Ho 8	386	3.495	3.458	3.218
Ho 10	392	3.464	3.418	3.168

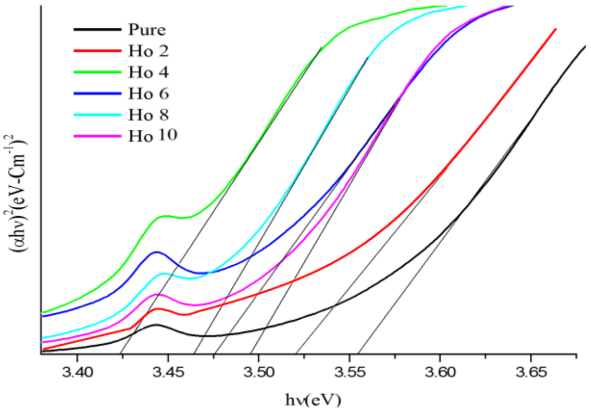

Fig 3a Tauc's plots for direct band gap

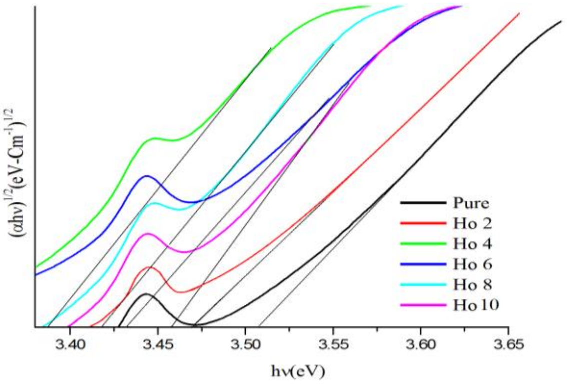

Fig 3b Tauc's plots for indirect band gap

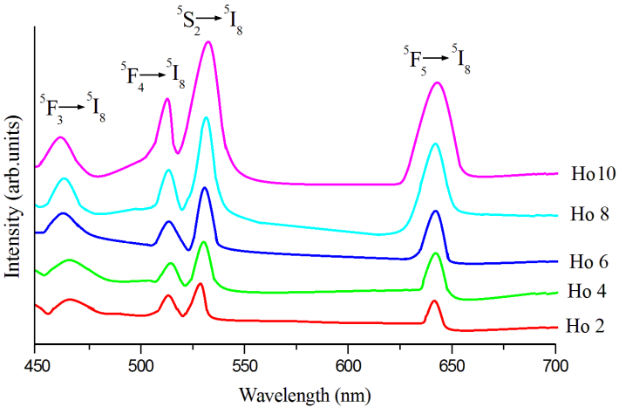

Fig 4 The Photoluminescence spectra of Ho^{3+}doped Na_2O-ZrO_2-SiO_2 glasses

Fig 4 represents the photoluminescence spectra of Ho^{3+} doped Na_2O-ZrO_2-SiO_2 glasses are recorded at room temperature with excited wavelength 400 nm in region 400-850 nm. Here four emission bands are observed at around ~466, ~525, ~561 and ~665 nm. They are assigned as $^5F_3 \rightarrow ^5I_8$, $^5S_2 \rightarrow ^5I_8$, $^5F_4 \rightarrow ^5I_8$ and $^5F_5 \rightarrow ^5I_8$ transitions of Ho^{3+} ions *(Manabu Ichikawa et al, 2012)*. The intensities of the bands are gradually increased with increasing the content of Ho_2O_3 in the glass matrix. Various radiative properties are evaluated and presented in the Table 3. Regarding luminescence data, the chromaticity coordinates (x, y) are deliberate by means of MATLAB CIE coordinates program. They are indicated in the perimeter of CIE (Commission International edeI Eclairage) 1931 chromaticity diagram as shown in the Fig 5. All the specified samples are lay nearer to the white color region in chromaticity diagram, further they are shifted towards within the region by the gradually increasing the content of Ho^{3+} ions in the glass network.

The FT-IR spectra of the Ho^{3+} doped Na_2O-ZrO_2-SiO_2 glasses are shown as Fig. 6. The data related to FT-IR spectra is given in Table 4. The characteristics of FT-IR spectra consist five bands at about ~482, ~736, ~820, ~972 and ~1014 cm^{-1}.These bands are assigned to Characteristic vibrations of Zr-O/ deformed vibrations of Si-O, Zr-O-Zr vibrations/ ZrO_4 units, Symmetrical bending vibrations of $[SiO_4]^{4-}$ units, Rocking vibrations of Zr-O-Si, Asymmetric stretching vibrations of Si-O in the glass matrix respectively (*T. Suhasini et al, 2012), (S. Buddhudu et al, 1988), (Rukmini et al, 1995), (Y.N. Ch. Ravi Babu et al, 2013)*. Here considerable changes are observed in the band intensities with increasing Ho^{3+} ion content in the glass matrix, especially symmetric stretching vibrations of Si-O are observed to be increased.

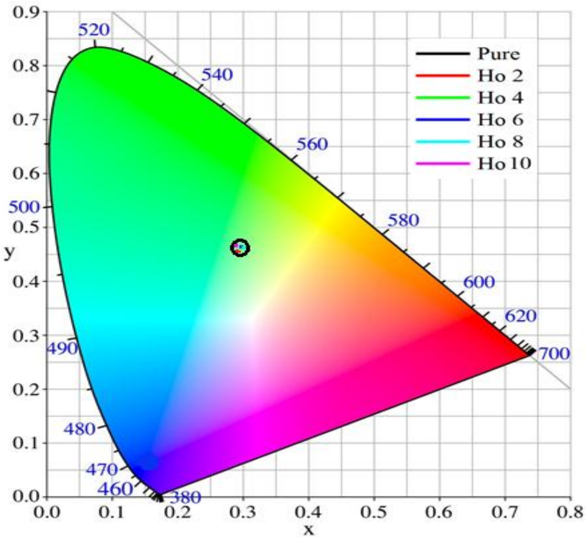

Fig 5 the color chromatic diagram of Ho^{3+} ions doped sodium zirconium silicate glasses

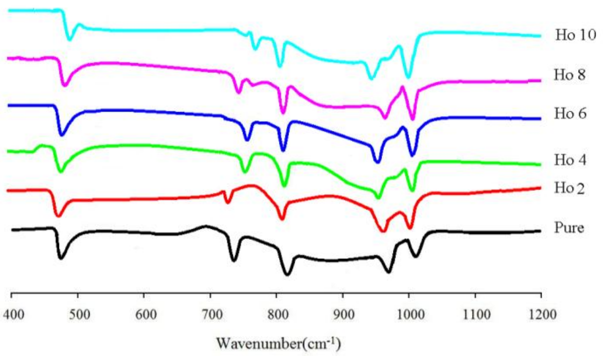

Fig. 6. The FT-IR spectra of the Ho^{3+} doped Na_2O-ZrO_2-SiO_2 glasses.

The Raman spectra of the Ho^{3+} doped Na_2O-ZrO_2-SiO_2 glasses are given in Fig. 7. Here four Raman bands are revealed at about ~324, ~628, ~974 and ~1100 cm^{-1}. These bands are assigned to Characteristic vibrations of Zr-O/ deformed vibrations of Si-O, Zr-O-Zr vibrations/ ZrO_4 units, Symmetrical bending vibrations of $[SiO_4]^{4-}$ units, Rocking vibrations of Zr-O-Si, Asymmetric stretching vibrations of Si-O in the glass matrix respectively*)*. All these bands assignments are given as per the literature survey *(S. Buddhudu et al, 1988), (Y.N. Ch. Ravi Babu et al, 2013)* and it is clearly given in Table 5.

4. Discussions

Normally the present investigating glasses are the combination of glass former (SiO_2), modifier (Na_2O, ZrO_2) and spectra materials (Ho_2O_3). The SiO_2 are the most common glass formers because of their commercial and technological applications. In these glasses, silicon occurs in 4-fold coordination.

Table 3: Radiative properties of Ho^{3+} ions doped sodium zirconium silicate glasses

Transitions	Ho 2		Ho 4		Ho 6		Ho 8		Ho 10	
	$A(s^{-1})$	β%	$A(s^{-1})$	β%	$A(s^{-1})$	β%	$A(s^{-1})$	β%	$A(s^{-1})$	β%
$^5F_3$	924.6	7.47	952.8	7.52	984.8	7.64	976.5	7.67	964.8	7.65
$^5F_4$	231.7	1.87	233.8	1.84	234.2	1.81	237.1	1.86	235.7	1.87
$^5S_2$	4654.2	37.6	4626.4	36.55	4686.6	36.40	4645.8	36.51	4624.5	36.69
$^5F_5$	6564.8	53.04	6842.6	54.07	6968.5	54.13	6867.4	53.96	6776.8	53.78
$A_T(s^{-1})$ =	12375.3		12655.6		12874.8		12726.8		12601.8	
τ_R(ms)=	0.0808		0.0790		0.0777		0.0786		0.0794	

Table 4: FT-IR spectral data of Ho^{3+} ions doped sodium zirconium silicate glasses

Glasses						Band assignments
Pure	Ho 2	Ho 4	Ho 6	Ho 8	Ho 10	
482	478	483	482	482	483	Characteristic vibrations of Zr-O/ deformed vibrations of Si-O
740	736	740	740	736	736	Zr-O-Zr/ZrO4 structural units
810	806	806	806	806	804	Symmetrical bending vibrations of $[SiO_4]^{4-}$units
969	969	956	956	969	956	Rocking vibrations of Zr-O-Si
1012	1012	1014	1012	1014	1014	Asymmetric stretching vibrations of Si-O

Table 5: Raman spectral data of Ho^{3+} ions doped sodium zirconium silicate glasses

Glasses						Band assignments
Pure	Ho2	Ho4	Ho6	Ho8	Ho10	
324	325	324	324	325	324	Rocking vibrations of Si-O-Si
628	628	629	628	630	630	Symmetrical bending vibrations of $[SiO_4]^{4-}$units
970	973	972	974	973	974	Rocking vibrations of Zr-O-Si
1106	1104	1104	1106	1104	1106	Asymmetric stretching vibrations of Si-O

Table 6: the experimental and theoretical strengths of Ho^{3+} ions in sodium zirconium silicate glasses

Transition $^5I_8\rightarrow$	Ho 2		Ho 4		Ho 6		Ho 8		Ho 10	
	f_{cal}	f_{exp}	f_{cal}	f_{exp}	f_{cal}	f_{exp}	f_{cal}	f_{exp}	f_{cal}	f_{exp}
$^3H_6$	0.468	0.462	0.448	0.441	0.489	0.486	0.475	0.471	0.499	0.497
$^5G_5$	0.343	0.334	0.323	0.329	0.324	0.327	0.351	0.352	0.345	0.348
$^5F_1+{}^5G_6+{}^3K_8$	3.123	3.114	3.156	3.162	3.213	3.217	3.214	3.219	3.228	3.247
$^5F_4$	2.755	2.723	2.672	2.613	2.678	2.681	2.612	2.621	2.724	2.729
$^5F_5$	1.831	1.819	1.742	1.741	1.765	1.762	1.789	1.768	1.847	1.843
$^5I_5$	1.253	1.251	1.235	1.238	1.205	1.201	1.231	1.234	1.246	1.247
$^5I_6$	0.577	0.574	0.578	0.571	0.601	0.598	0.544	0.548	0.591	0.598
Rms deviation	±0.0186		±0.0303		±0.0142		±0.0121		±0.0108	

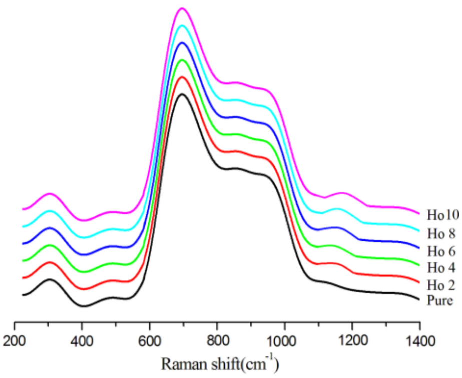

Fig 7 The Raman spectra of the Ho^{3+} doped Na_2O-ZrO_2-SiO_2 glasses

The network connectivity of these structural units is represented by Q_n, where n (0–4) signifies the number of bridging oxygen atoms per tetrahedron. Here the modifiers are added to the glass matrix; the glass forming tendency is increased, especially Na_2O is participated in important structural modification of glass network which results to the formation of meta silicates, pyro silicates and ortho silicates. Finally the spectra materials are responsible for optical studies and how they act in the structural modification is enlightened in latter.

The optical absorption spectra Ho^{3+} ions doped sodium zirconium silicate glasses, the transition are takes place from $^5I_8$ to various excited states. Here the optical spectra arise due to the intra-configurational transitions within incompletely filled 4*f* shell. The 4*f* orbital lies inside the ion and is shielded from the surroundings by the filled $5s^2$ and $5p^6$ orbitals. Therefore the influence of the host lattice on the optical transitions within $4f^n$ configuration is small but essential. As a result the $4f^{\,n}$ configuration is slightly affected by their surroundings and the RE ions reside in sites of low symmetry (C_1) with each site having a slightly different crystal field interaction. Generally, the Judd-Ofelt parameters provide information regarding the nature of bond between RE ion - ligands as well as the symmetry of the environment around the RE ions. The spectral intensities for the observed bands in the optical absorption spectra are often expressed in terms of oscillator strength of forced electronic dipole transitions, have been analyzed as follows and presented in Table 6.

$$f(\varphi_J,\varphi_{J'}) = \frac{8\pi^2 m\nu}{3h(2J+1)e^2 nd^2}\left[X_{ed}S_{ed} + X_{md}S_{md}\right] \tag{2}$$

Here (2J+1) is the multiplicity of the lower states, m is the mass of the electron and n is the absorption peak positions in cm^{-1}, $X_{ed}=n_d(n_d^2+2)2/9$ and $X_{md}=n_d^3$. Experimental values of oscillator strengths were evaluated from the expression

$$f_{\exp} = 2.302\left(\frac{mc^2}{N_A \pi e^2}\right)\int \varepsilon(\nu)d\nu \tag{3}$$

Here N_A is Avogadro's number and ε (ν) is the molar absorption coefficient to determine from Beer's law. The comparison of experimental and theoretical strengths shows a reasonable agreement for Ho^{3+} ions in all the four glasses. The R. M. S. deviations of oscillator strengths of experimental and calculated values are presented in Table 6; the relatively small values of these deviations confirm the validity and applicability of Judd–Ofelt theory for these glasses.The Judd–Ofelt parameters Ω_2, Ω_4 and Ω_6 were computed by the least square fitting analysis of the experimental oscillator strengths using matrix elements (*S.B Rai et al, 2002*) and are presented in Table 7 along with the other pertinent data. The values of Ω_λ are found to be in the following order for all the glasses: $\Omega_2>\Omega_6>\Omega_4$ .The relatively higher value of Ω_2 (among the three c values) obtained for all the glasses is mainly due to the high intensity of the $^5I_8 \rightarrow {}^5G_6$ hypersensitive transition, whose intensity is strongly connected to the value of this parameter. Using J–O parameters Ω_λ, the radiative properties of various fluorescent transitions are determined. The spontaneous emission probability A is calculated using the expression

Table 7: The Judd–Ofelt parameters of Ho^{3+} ions doped sodium zirconium silicate glasses

Glasses	Ω_2x10^{-20} (cm^{-2})	Ω_4 x10^{-20} (cm^{-2})	Ω_6 x10^{-20} (cm^{-2})
Ho 2	6.92	2.68	3.48
Ho 4	6.48	2.56	3.36
Ho 6	6.36	2.84	3.32
Ho 8	6.25	2.67	3.28
Ho 10	6.43	2.59	3.47

$$A(\varphi_J,\varphi_{J'}) = \frac{64\pi^2 e^2\nu^3}{3h(2J'+1)}\left[\frac{n_d(n_d^{\,2}+2)^2}{9}S_{ed} + n^3 S_{md}\right] \tag{4}$$

$$S_{ed} = \sum_{\lambda=2,4,6}\Omega_\lambda \left\|U^\lambda\right\|^2 \tag{5}$$

$$S_{md} = \frac{e^2h^2}{16\pi^2 m^2 c^2}\left(\varphi J\left\|L+2S\right\|^2\varphi' J'\right) \tag{6}$$

Here (2J'+1) is the multiplicity of the upper state and n is the wave number of the fluorescence peak. Then the total emission probability A_T involving all the intermediate terms, the radiative lifetime (τ_r) of the excited states and the fluorescent branching ratio for various transitions have also been evaluated using the standard equations reported in the earlier papers *N.V.V. Prasad et al 2003, T Schweizer et al 1999* and are presented in Table 3. The parameter branching ratio describes the lasing action of the potential laser transitions and the relative areas under the luminescence transitions peaks, gives experimental branching ratios. It was well known that the branching ratio value nearly equal to ~50% is a potential laser emission. Among various transitions, $^5F_5 \rightarrow {}^5I_8$ transitions found to have the higher values; these transitions may be considered as a possible laser transitions and the color intensity chromaticity diagram also supports earlier discussion.

FTIR and Raman spectra are non-destructive technique for investigating nature of the bonds in the glass matrix. The introduce of Ho_2O_3 by replacing Na_2O in the glass network, here asymmetric stretching vibrations of Si-O signal strength is gradually reduced up to Ho 4 then reversal tend is observed; this may be due to modifier action of Ho_2O_3, Na_2O in the glass matrix which disturb Si-O-Si, Zr-O-Zr network strongly to forms NBO by causing depolymerization and Ho^{3+} ions cannot enter into the matrix due to large radius. As a result, the electron distribution around Si^{4+}, Zr^{4+} get modification which leads to the formation of Si–O–Zr by replacing Si-O-Si, Zr-O-Zr. Therefore the network connectivity is gradually increased. These trends also supported by the optical band gaps of the specified samples. All the results reveal that the network becomes polymerized at higher concentration.

5. Conclusion

Optical and structural analysis of the Ho^{3+} ions doped sodium zirconium silicate glasses has been studied. Quantitative analysis of these results suggested that the prepared glasses are fully amorphous in nature. Optical investigations, the Judd–Ofelt theory could successfully be applied to characterize the optical absorption spectra; out of the three J–O parameters, the value of Ω_2 is observed to be highest which suggests that highest covalent environment is present around Ho^{3+} ions. The branching ratio value is ~50% for $^5F_5 \rightarrow {}^5I_8$ and it may be considered as a possible laser transitions. Structural properties reveals that the glass network becomes polymerize of Ho^{3+} ions in the glass matrix.

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