

Effect of Gamma Radiation on the Structure of Neodymium: Chromium Doped Silicate Glasses

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Abstract- The paper deals with the spectroscopic studies of sol-gel systems doped with rare-earth ions and co-doped with chromium. Doped samples of Nd³⁺: Cr³⁺ silica zero gels and silica glasses were prepared from hydrolysis and polycondensation of precursor solution Tetra Ethyl Ortho Silicate (TEOS), which allows incorporation of specifications by sol-gel method. The zero gels were characterized by XRD, TGA, FTIR & UV/VIS absorption spectra. The intensity and the behavior of the radiation-induced bands are seen to depend on the type of the 3d- transition metal in presence of Neodymium. The host silicate glass shows the stabilizing effect due to increase of more color centers on Gamma Radiation. Reduction in spectroscopic parameters (Racaah and naphelauxetic ratio) confirmed the increase in covalent character of the transition metal ion in the silica matrix due to irradiation.

Index Terms- Sol-Gel, XRD, TGA, FTIR, UV/VIS Absorption Spectra

I. INTRODUCTION

Sol gel method is one of the promising technologies for the production of amorphous materials. Amorphous materials doped with lanthanide ions and small metallic particles may be useful for the study of linear as well as non-linear processes. Glasses containing transition metal ions have been studied owing to their potential applications including radiation sensitive materials in addition to coloring agents in glasses [1-4]. Each 3d transition metal can exist in two or more oxidation or coordination states within the glass matrix depending on composition of the glass type. It is possible to dope the glass with a second ion that would absorb the pump radiation not absorbed by the primary activator, and then transfer the energy to the primary activator. Chromium absorbs spectral energy of 450 and 650 nm, which is not absorbed by Nd³⁺. The Cr³⁺ ions subsequently transfer their energy to the Nd³⁺ with an efficiency of 45%. Likewise, efficient transfer of energy from Nd³⁺ to Yb³⁺ and from Yb³⁺ to Er³⁺ has been observed [5]. The most widely known glass of all, silica has some ionic contribution to the predominant covalent bonding [6]. Fused silica is useful as an optical material because of its high transmission of visible and ultraviolet light. When silicates are irradiated with ultraviolet light, X-rays, or Gamma rays (ionizing radiation) or atomic particles, defects are formed that absorb light in the ultraviolet

light and visible parts of the electromagnetic spectrum. These irradiation effects in glasses, especially silica, are reviewed by several authors [7-9]. Each state normally gives rise to specific absorption spectra, which have been measured and explained by the application of ligand field and molecular orbital theories [10]. Silica Zero gels has a wide range of applications [11-14], which depend on their structural properties and on the variety of nano structures [15]. These materials have three dimensional SiO₂ network prepared by sol gel process [16-17]. Irradiation can further make the coloring components undergo reduction changes and some of these components can even act as stabilizers countering the effects of radiation. Hence we could explain only the aggregate effects of the complex. Irradiation by 0.258-to 2.58 Gy of radiation will give rise to colour centers, and glasses must be stabilized [18]. Neodymium – Chromium doped Phosphate glasses as luminescent solar concentrators have been designed by B. Jezowska and coworkers [19]. Energy transfer in Cr³⁺ : Nd³⁺ co doped borate glass was studied by several authors [20].

The first objective is to investigate the UV-Vis absorption of the host silicate glass co-doped with 3d transition element and the lanthanides and to find out response of Gamma Irradiation on such spectral measurements. The change in Band Gap energy is also calculated from the above spectra. The second objective is to characterize the induced colour centers either intrinsic or extrinsic due to co-dopants in the prepared glasses by analyzing the FTIR Spectrum, which will correspond to the characteristic functional groups and bonds present. In this paper we report the silicate glasses co-doped with Nd³⁺: Cr³⁺, and their optical as well as structural properties were analyzed.

II. EXPERIMENTAL DETAILS

The silica gels were synthesized from Tetra ethoxy – silane (CH₃CH₂O)₄ Si [TEOS], of density 93 Kg/l, water, ethanol and the nitrates of the dopants [21]. The molar ratio of ethanol to TEOS and water to TEOS were made 2:1 and 14:1 respectively. The dopants were added in the form of their nitrates. The preparation method is found elsewhere [22]. Samples co-doped with Nd³⁺: Cr³⁺ were prepared in the different weight %. Sample list is shown in Table.1. The glass structure was characterized by XRD spectra and Fourier transforms infra red (FTIR) spectroscopy. XRD was recorded by D8 Advance X-ray Diffractometer with X- ray source Cu, wavelength 1.5406 Å.

The Thermo gravimetric analysis (TGA) of the dried samples were carried out at a heating rate of 20.000C/min from room temperature (28⁰C) to 1010⁰C, using Shimadzu thermal analyzer DT40 under N₂ atmosphere at 100.0ml/min. The FTIR spectra were recorded over the frequency range 4000 – 500 cm⁻¹ using Thermo Nicolet, avatar 370 FTIR Spectrometer with a resolution of 0.9 cm⁻¹. The absorption spectra were recorded in a Shimadzu

spectrophotometer (UVPC 2450) in the wavelength range 200-900 nm. All measurements were done at room temperature and for the same instrument parameters. An Indian 60Co gamma cell (5000 cc) was used as a gamma ray source with a dose rate of 2.5 Gy /sec.

Table 1. Sample List

Serial Number	Sample	Conc: Nd. ion	Conc: Cr.ion
1	A	1%	1%
2	B	2%	1%
3	C	3%	1%
4	D	4%	1%
5	E	1%	0%
6	F	0%	1%

III. RESULTS AND DISCUSSIONS

1.1. X-ray Diffraction Analysis.

Figure.1: represents X ray Diffraction Pattern (XRD) of the sample D at room temperature. It shows irregular peaks, which is indicative of an amorphous structure free from any

sharp peaks. The typical harrow-like pattern obtained at 20~30⁰ is attributed to amorphous silica gel [23].

1 Figure 1. XRD Spectra of Sample D

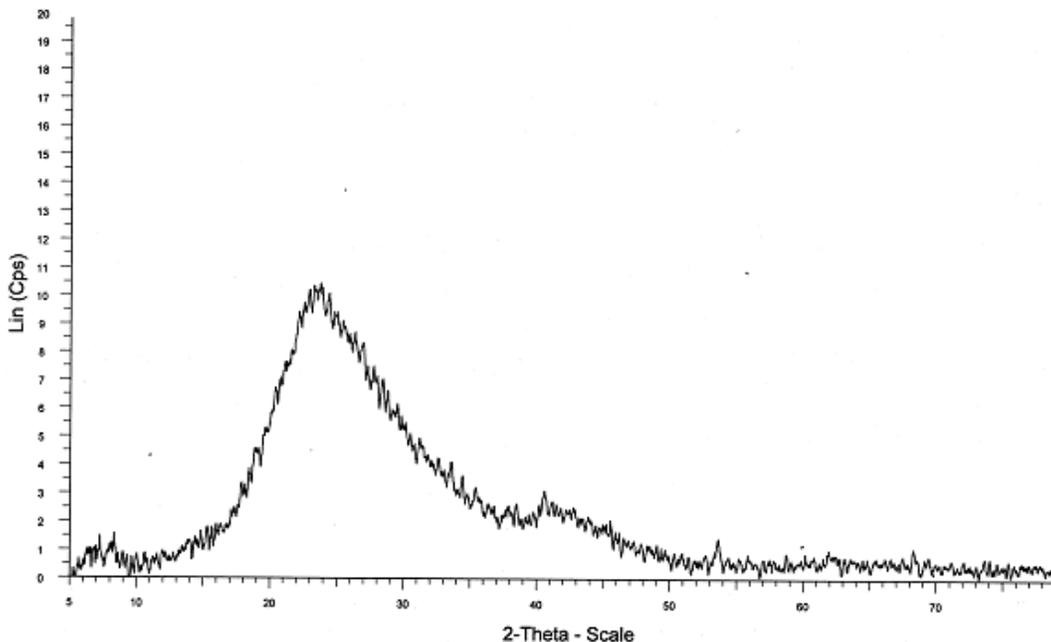


Fig.1. XRD of Sample D

1.2. Thermo Gravimetric Analysis (TGA)

Figure. 2: shows the TGA curve of gel sample D from room temperature to 1010°C. Major part of the weight loss occurs between room temperature and 200°C owing to the vaporization of the absorbed water and residual organic molecules. A substantial amount of water and other organics

present in the dried gel are removed below 600°C. Beyond 600°C the weight loss is small with further heat treatment. The small weight loss at high temperature can be attributed to the removal of trapped residual hydroxyls.

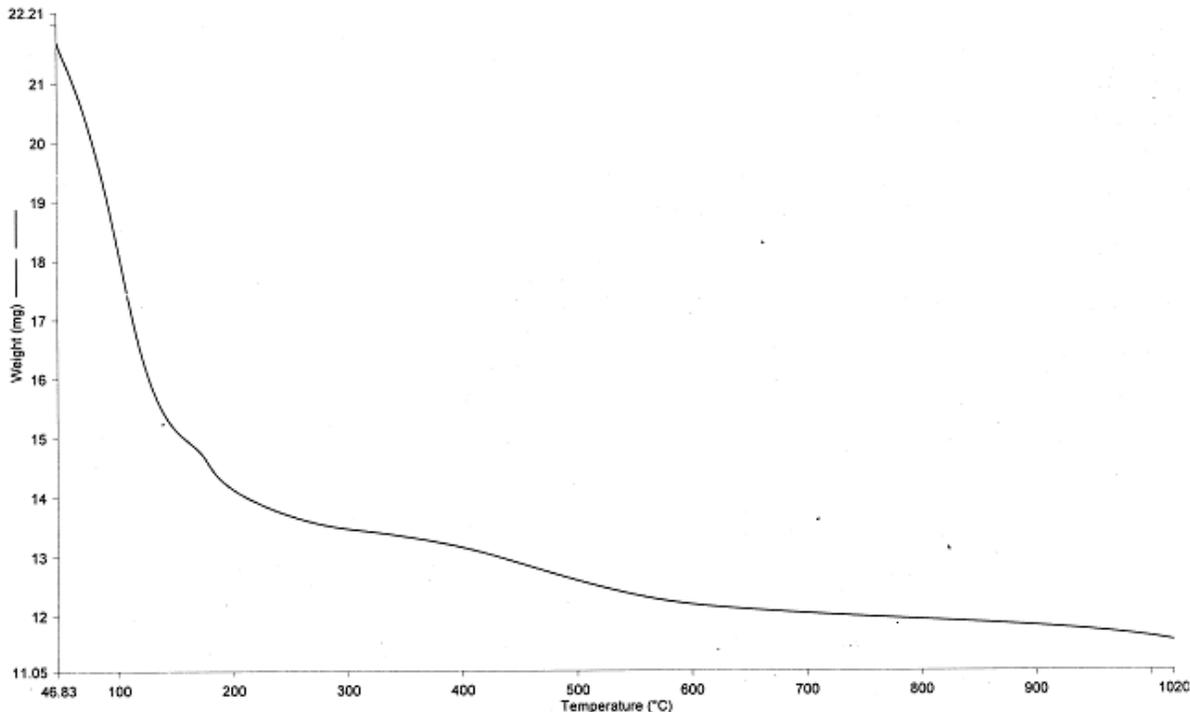


Fig:2. TGA of Sample D

The gels are micro porous in nature and contain a large number of internal silanol groups. On heating the gel, the pores collapse gradually with increasing temperature and the gels are converted to pore-free materials similar to silica glass.

1.3. FTIR Studies

1.3.1. Before Gamma Irradiation

The purpose of the present work is to use FTIR spectroscopy to investigate the effects of doping with Chromium ions on the structure of the silica gels and the gel derived glasses. The FTIR transmittance curves of sample D extending from 500-4000 cm⁻¹ region has been studied and shown in figure.3. Transition metal ions have been used in glasses for their luminescence properties or as probes to follow the structural evolution of the host matrix

[24, 25]. Table 2 shows positions and assignments of the observed FTIR spectrum. The band at 3472.48cm⁻¹ corresponds to the fundamental vibrations of different hydroxyl groups. The presence of adsorbed water is indicated by the absorption band at 1642.73cm⁻¹, which is assigned as bending mode of water molecules. The characteristic bands at 1085.95 cm⁻¹ are due to asymmetric stretching vibrations peaks of Si-O-Si. The bending mode is at 465.74 cm⁻¹. The 796.76 cm⁻¹ vibration peak is associated with symmetric stretching or vibrational modes of ring structures [26, 27]. Thus the results of IR spectral Studies point out that there is an increasing degree of disorder in the glass network when Cr₂O₃ is present in higher concentration.

Table :2. FTIR Peaks of Sample D (Fig 3 &4) Before and After Irradiation

No	Before Irradiation cm^{-1}	Assignment	After Irradiation cm^{-1}	Assignment
1	3472.48	-OH group vibrations	3452.47	-OH group vibrations
2	1642.73	Bending mode of H_2O	2934.72	CH stretching vibrations.
3	1085.95	Asymmetric stretching of vibration of Si-O-Si	1655.21	Bending mode of H_2O
4	796.76	Symmetric stretching of ring structure	1384.31	vibrations of [TEOS and Ethoxy groups]
5	465.74	Bending mode of SiO_2	1074.4	Asymmetric stretching of vibration of Si-O-Si
6	-----	---	964.66	C=C-H bands of substituted ethylene system
7	-----	----	791.49	Symmetric stretching of ring structure
8	-----	----	462.59	Bending of Si-O-Si bond

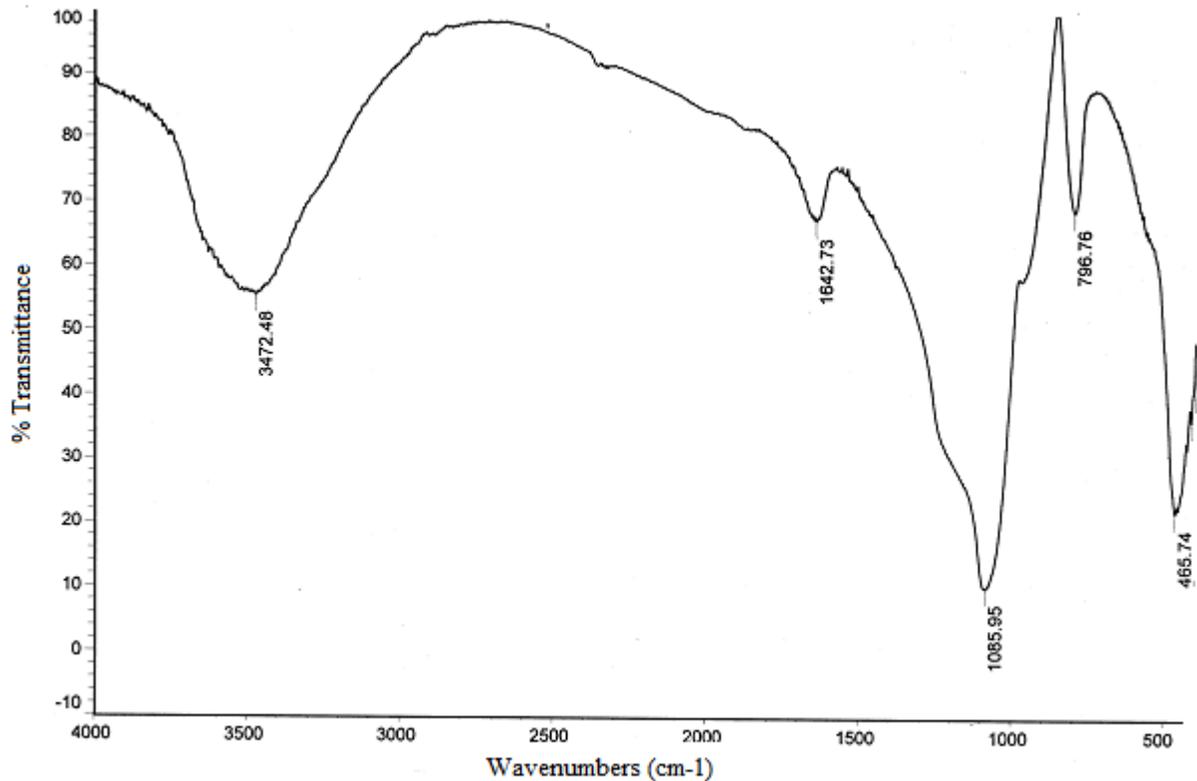


Fig.3.FTIR Sp.of Sample D before Irradiation

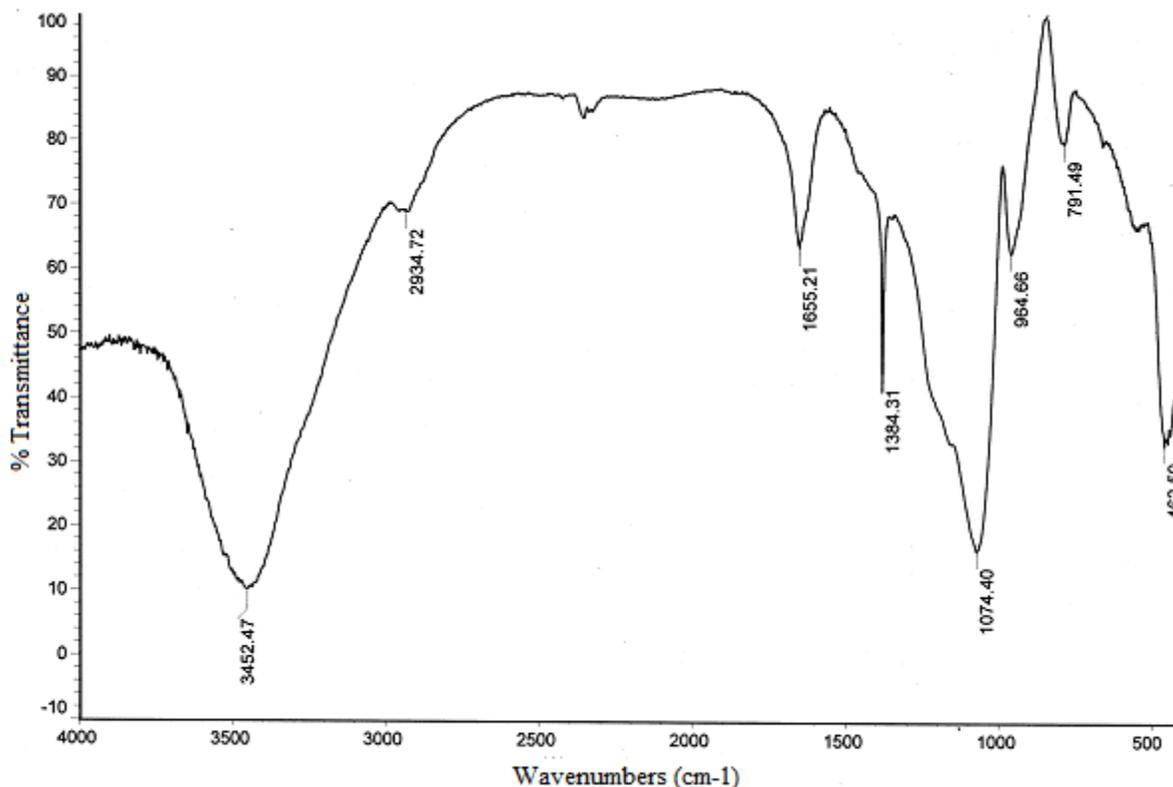


Fig.4.FTIR Sp.of Sample D after Irradiation

1.3.2. Effect of Gamma Irradiation.

High energy radiations like gamma rays change the spectral as well as structural defects called colour centers of the materials. Figure. 4: shows the FTIR spectra of sample D after Gama ray irradiation. A number of structural changes could be observed in the network as a result of irradiation. It is due to the bonding mechanisms of the formation of non bridging oxygens. Moreover silicon – oxygen bond is strongly affected by irradiation. As a result of gamma ray irradiation the vibrational modes H2O and H OH bending mode are extended. It is observed that on irradiation more stability is obtained due to the increase in number of oxygen ions available in the glass network. Hence more stable glasses with compact tetrahedral structure are formed. The positions and assignments of the observed FTIR spectrum after Gama radiation are also included in Table 2.

1.4. Absorption Spectra

1.4.1. Before Gamma Irradiation

Optical absorption due to transitions within the d shell of Cr as an impurity in silicate glasses has been observed and interpreted. The intense bands centered on 409 and 578 corresponds to $4A_2 \rightarrow 4T_1$ and the latter to the $4A_2 \rightarrow 4T_2$ due to Cr^{3+} in octahedral co-ordination [28]. Absorption in Neodymium arises due to transition from the ground $^4I_{9/2}$ state to other excited states and are predominantly due to $4f-4f$ electric dipole induced in nature. The Absorption spectra of Nd-Cr-SiO₂ are shown in figure.5: before Gamma radiation. The observed spectrum corresponds to collective absorption bands due to $^4I_{9/2} \rightarrow ^2D_{3/2}$ (300nm), $^4D_{3/2}$ (353 nm), $^2D_{5/2}$ (409 nm), $^4G_{7/2}$ (525 nm), $^4G_{5/2}$ (578 nm), $^4S_{3/2}$ (742 nm), $^2H_{9/2}$ (797 nm), $^4F_{3/2}$

(868 nm), and $^4I_{15/2}$ (887 nm) in accordance to several authors [29-33].

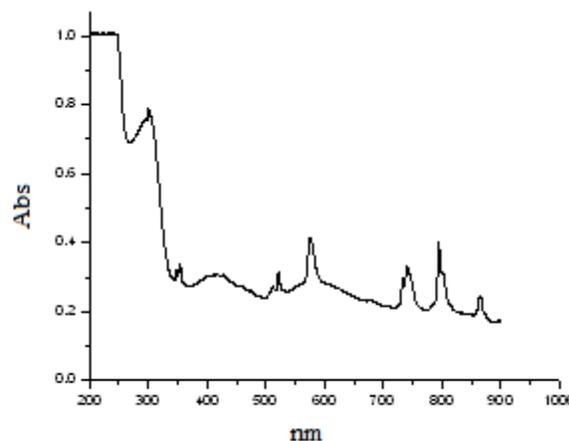


Fig.5. Ab. Sp.of Sample D before Irradiation

1.4.2. Effect of Gamma Irradiation

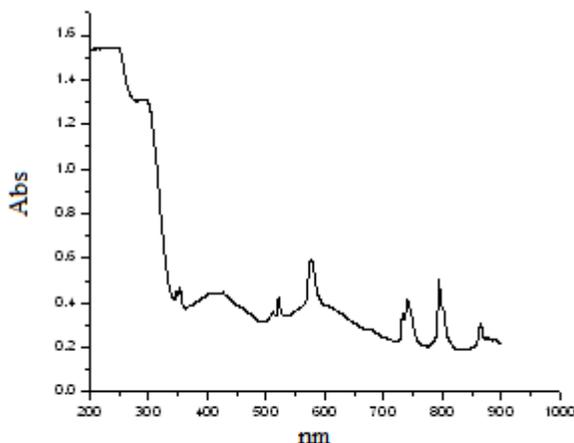


Fig : 6. Ab. Sp. of Sample D After Irradiation

Figure. 6: represents the absorption spectrum of same sample after Gamma ray irradiation. It is observed that the visible bands become more identified with Gamma radiation, and absorption bands increases in intensity. The band at 409 shifts to 420 nm. The hexavalent Chromium has a 3d0 configuration and therefore exhibits only sharp charge transfer band giving rise to strong absorption band around 380 nm because of its large intensity [34]. It can be assumed that some of the Cr⁶⁺ ions capture liberated electrons during Gamma radiation and are converted to induced Cr³⁺ ions producing absorption in the same position of the trivalent Chromium having the photochemical reaction as Cr⁶⁺+3e⁻ → Cr³⁺.

It is reported that the colour of the Cr-SiO₂ made by the Sol-gel method [35] and by the fused method are due to Cr⁶⁺ ions present in the matrix [36]. Building metallic ions into the structure of the glass will extend the structure owing to the formation of non bridging oxygen's. The electron transitions from the non bridging oxygen's into the conductance band then require far less energy than the bridging oxygens so that the absorption is shifted towards the longer wavelength [18]. Since the concentration of dopants is small, the respective absorption bands show an increase in intensity with increase of doped ions

1.5. Crystal field parameters

1.5.1. Before Gamma Irradiation

The Racah parameter B and nephelauxetic ratio (β) can be used to find the degree of covalence of the transition metal ion in the present matrix. From the absorption measurements, using the Tanabe-Sugano model a complete level scheme of chromium in the gel host was obtained. A direct indication of the value of the local field Dq can be derived from the average peak energy of the 4A₂→4T₂ transition [37].

$$Dq = \frac{E_a(4T_2) - E_b(4A_2)}{10} = 214.1 \text{ meV}$$

More over from the average peak energies of the 4A₂→4T₂ and 4A₂→4T₁ transitions the Racah parameter B can be evaluated. Indeed B and Dq are related through the equation

$$\frac{Dq}{B} = \frac{15(x-8)}{x^2-10x}$$

Where the parameter x is defined by the following equation

$$x = \frac{E_a(4T_1) - E_a(4T_2)}{Dq}$$

from the experimental results one obtains

$$x = 4.12$$

$$B = 89.2 \text{ meV (720.8cm}^{-1}\text{)}$$

The nephelauxetic parameter is readily obtained by using the relation

$$\beta = B_{(\text{matrix})} / B_{(\text{free ion})} \text{ In sol-gel silica } \beta = 0.782.$$

The Cr³⁺ ion have a low value of Racah parameter i.e. 720.8cm⁻¹, which is 22% less from that of the free ion value(918 cm⁻¹) [38] and indicates a greater degree of covalence. The Tanabe-Sugano diagram of Cr³⁺ in the octahedral symmetry is shown in figure 7. Furthermore the nephelauxetic parameter indicates that the chromium ion have appreciable covalent character in metal ligand bond.

1.5.2. Effect of Gamma Irradiation

Irradiation with gamma rays lead to significant modification of the glassy system. The effect of gamma radiation was manifested in change in the Racah parameter and nephelauxetic ratio. After irradiation the Racah parameter and nephelauxetic ratio became B = 85.002 meV(618cm⁻¹) and 0.673 respectively. A significant reduction in Racah parameter and nephelauxetic ratio are associated with a reduction in nuclear charge on the cation and the smaller effective charge experienced by the d electrons [39].

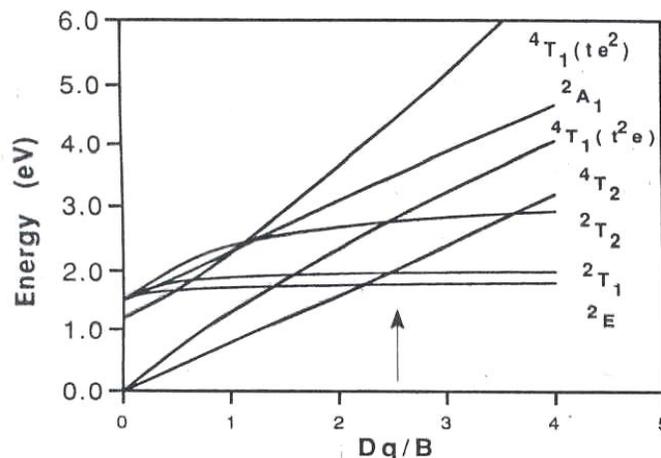


Figure. 7 Cr³⁺ levels in octahedral symmetry

1.6. Optical Band-gap

1.6.1. Before Gamma Irradiation

Tauc [40] showed that the shape and position of the absorption edge for high absorption region could be represented by an equation of the form,

$$\alpha(\omega) = A(\hbar\omega - E_{opt})^2/\hbar\omega$$

Two fundamental equations are used for the analysis

$(\alpha h\nu)^2 = A(h\nu - E_{opt})^2$, for direct electron transition from valence band to conduction band and $(\alpha h\nu)^{1/2} = A_1(h\nu - E_{opt})$, for indirect electron transition from valence to conduction band where, α is the absorption co-efficient, ω is angular frequency, A is a constant and E_{opt} is the optical energy gap Here we applied the Mott and Davis theory [41] to evaluate the optical band gap of Neodymium doped and Neodymium: Chromium co doped samples. Direct and Indirect band gaps are determined from the linear regions of the plots. The results show that direct band gap values are larger than that of the indirect band gap and both are decreasing with increasing concentration of the Cr³⁺ ions.

1.6.2. Effect of Gamma Irradiation

With Gamma radiation a decrease in band gap is observed in all the prepared samples, which may be due to the displacement of the ions and breaking of bonds. The decrease in E_{opt} is related to the increase in the Nd³⁺ ions; content. It may be caused by the tendency of the transition atoms to form chemical disordering and to create localized centers in band gap. Table 3 shows the values of band gap energy before and after Irradiation.

Table :3. Direct and Indirect Band gaps of the samples before and after Gamma Irradiation

Sl.No	Sample	Before Gamma		After Gamma	
		Direct Band Gap (eV)	Indirect Band Gap (eV)	Direct Band Gap (eV)	Indirect Band Gap (eV)
1	A	3.90	3.45	3.8	3.40
2	B	3.80	3.40	3.75	3.35
3	C	3.75	3.30	3.70	3.25
4	D	3.70	3.25	3.65	3.20

IV. CONCLUSIONS

Sol gel method was successfully used for the preparation of pure silica gel derived glasses doped with Nd³⁺: Cr³⁺. The amorphous nature of gel glasses have been confirmed by XRD spectra at room temperature. The FTIR spectra elucidate the bonding system of the constituent atoms and groups such as Si-O, and OH that throw light to the expected structure. The UV/VIS absorption spectra lead to the study of the structure of the samples. Hence the absorption and structural properties could be enhanced by co doping with transition metal. The d- orbital of transition metal ions or atoms is very sensitive to the surroundings and hence they influence the neighboring atoms and ions. Conversely, 4f – electrons are located deep inside the shell of the rare earth atoms or ions are strongly shielded by the

5s and 5p – electrons. In many applications, interactions between the rare earth ion and the electronic states of the host material can enhance or inhibit performance and provide mechanisms for manipulating the material's optical properties [42]. The substitution of Nd³⁺: Cr³⁺ ion in the samples influences the structural, infrared properties and optical band gap values of neodymium doped silicate glasses.

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