Spectroscopic Studies of Tungsten Ion Doped With Lead-Cadmium-Strontium-Borate Glasses

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Abstract:-PbO-CdO-SrO-B_2O_3 (PCSB) glasses doped with transition metal ion concentration with 0.1mol% WO_3. These glasses are produced by normal melt quenching method. (PCSB) glasses are characterized by various physical properties, optical basicity, X-ray diffraction (XRD), Optical absorption, Electron paramagnetic resonance (EPR) and Fourier transform infrared (FT-IR) spectroscopic studies. Glass formation is recognized by X-ray diffraction spectra. The optical absorption spectra of these glasses shows a relatively small peaks at 421-436nm and 826-857nm is identified due to n–π* , $d_{xy}\rightarrow d_{x2-y2}$ and $d_{xy}\rightarrow$ d_{xz}, d_{yz}transitions of W^{5+} ions. From the optical absorption spectral data, optical band gap (E_{opt}) and Urbach energy (ΔE) are evaluated. From EPR spectra have the strength of the signal is decreased and then increased this is due to paramagnetic O^- ion concentration in the WO_3. The (FT-IR) spectral studies have described the existence of conventional BO_4, B-O-B, Sr^{2+}, Pb-O-B and W-O-B structural units of these glasses.

Key Words: Melt quenching; physical properties; optical basicity; optical absorption; X-ray diffraction; FT-IR.

I. INTRODUCTION

Lead cadmium strontium borate glasses are special applications in the field of laser hosts, lamp phosphors, laser cooling, optical communications in optical fibers, optical filters optoelectronic devices, X- and γ– ray absorbers, photonic devices, radiation shields, surgical lasers, storage, luminescent display devices and up converting optical system [1]. Adding of host metal of transition metal oxides of their glass forming nature compared to all other glass formers. B_2O_3 is a glass forming oxide. It can be considered as having the highest glass formation tendency because molten B_2O_3 does not crystallize by itself even when cooled at the slowest rate. Boron is the first member of the group III in the periodic table and the size of B^{3+} ion is very small. B^{3+} can fit in to the trigonal void created by 3 oxide ions in mutual contact and forming a $[BO_{3/2}]$ unit. $[BO_{3/2}]$ units are the primary building blocks in all borate glasses. Since B in $[BO_{3/2}]$ is electron deficient, it can accept two more electrons in the form of a dative bond. This happens when an oxide ion is available in the glass composition for such additional bonding. $[BO_{4/2}]^-$ units are thus readily formed in borate glass structures. $[BO_{4/2}]^-$ Units are tetrahedral [2]. PbO is a conditional glass former. it has a low rate of crystallization, moisture resistance, stable and transparent glasses could be achieved due to a dual role played by PbO as a glass former and also as a modifier It is well known fact that the effect of introduction of modifiers PbO into B_2O_3 network is to convert the sp^2 planar BO_3 into more stable sp^3 tetrahedral BO_4 units in addition to nonbridging oxygens (NBO's). Each BO_4 unit is linked to two such other units and one oxygen from each unit with a metal ion giving rise to a structure that leads to the formation of long chain tetrahedrons. PbO in general is a glass modifier and enters the glass network by breaking up the B-O-B bonds (normally the oxygens of PbO break the local symmetry while Pb^{2+} ions occupy interstitial positions) and introduces coordinate defects known as dangling bonds along with non-bridging oxygen ions [3]. CdO is a network modifier, its valency II-VI n-type material having the properties are large band gap, low electrical resistivity and high transmission in the visible region. [4-8]. With donor defects, such as Cd interstitials and oxygen vacancies alkaline earth and heavy metal oxides could act as glass network formers (GNF) or glass network modifiers (GNM) depending on their composition in the glass. Mostly at low concentration they occupy network modifier positions and at higher concentration they occupy network former positions, stabilize the glass structure and improve the electrical properties by increasing the dielectric constant [9]. SrO is a modifier adding to the glass matrix which enters the glass network by breaking up the random network. The oxygens of such oxide break the local symmetry while the cation (Sr^{2+} ions) occupy the interstitial positions in the glass system, increases its density as (MgO< CaO< SrO< BaO). The increasing values of density reflect the tightness of the glass structure and the increase of network rigidity. SrO has mostly used as a component ensuring an improvement of a number of physiochemical properties of glasses [10]. Tungsten have oxidation state +2 to +6 oxidation states as trivalent W^{3+}, tetravalent W^{4+}, pentavalent W^{5+} or as hexavalent W^{6+}. The most important states are +5 & +6 with local different sites depending on the host composition and concentration of tungsten ions. Its oxidation +6 state is stable. Tungsten ion built from corner sharing with $WO_{6/2}$ ions formation of octahedral units. It has practical applications as amorphous semiconductors, for waste storage as infrared transmission components, thermal and mechanical sensors, and reflecting windows [11-13].

Now a day's transition metal ions are used to investigate the structure of the glasses, the outer most electronic configuration is $4f^1$, $5d^4$, $6s^2$ because of it has valence d-orbital contain four unpaired electrons, actively participate in bond formation with surrounding ions. Tungsten ion is transition metal ion, it can exhibit in six different oxidation states, 0, +2, +3, +4, +5 and +6 in its compounds [14]. In glasses, tungsten is accepted [15-19]to be found as trivalent W^{3+}, tetravalent W^{4+}, pentavalent W^{5+} or as hexavalent W^{6+}states. Addition of 0-10%WO_3 to PCSB glasses exhibits the modification in the structural properties [3]. Physical properties give the information about the PCSB glass mass, volume, density, transition metal ion concentration, Inter ionic distances, polaron radius, and optical basicity. The study of X-ray diffraction the atomic arrangement and inter atomic distances in a glass are practically the same as in the corresponding crystalline modifications, the essential difference being that the random network which is build up in a vitreous substance does not repeat at regular intervals, and hence the material is non-crystalline. It differentiates the glassy from the crystalline structure. The study of the Optical absorption spectra and in particular the absorption edge is a useful method for the investigation of optically induced transitions and for the provision of information about the band structure and energy gap in non-crystalline materials. The principle involved in this technique is the photon which has more energy than the band gap energy will be absorbed. The Electron Paramagnetic resonance (EPR) is an experimental technique to obtain information on some of the local structure of paramagnetic center and also structural changes in the glasses, dynamic phenomenon of a material and to identify the site symmetry around the transition metal ions in glasses. Fourier Transform Infrared spectroscopy (FT-IR) is an important tool for understanding the structure and dynamics of amorphous materials. It provides structural information about the vibrational modes of the host lattice. And it is used to assign the observed absorption peaks to the proper vibration of the atoms in geometric grouping. The spectra of many molecular group variables can affect the absorption peaks and the assignments of vibration peaks of the atoms are very difficult. FT-IR analysis is used to in order to identify the spectral contribution of each component on the structure and to point out the role of atoms in glass matrix.

II. EXPERIMENTAL

The present glass is prepared from (15-x)PbO-5CdO-(15+x)SrO(65-y)B_2O_3-y(WO_3)where 0<x<8 and y=0.1 system. We have chosen following composition for constant tungsten ion doping concentration chosen for the present study:

Sr1: 15PbO-5CdO-15SrO-65B_2O_3
Sr2: 15PbO-5CdO-15SrO-64.9B_2O_3-0.1WO_3
Sr3: 13PbO-5CdO-17SrO-64.9B_2O_3-0.1WO_3
Sr4: 11PbO-5CdO-19SrO-64.9B_2O_3-0.1WO_3
Sr5: 09PbO-5CdO-21SrO-64.9B_2O_3-0.1WO_3
Sr6: 07PbO-5CdO-23SrO-64.9B_2O_3-0.1WO_3

The starting materials used in the present study are H_3BO_3, PbO, CdO, SrO and WO_3. Appropriate amounts of weighed chemicals are grounded thoroughly in a mortar to produce homogenized mixture is placed in silica crucible and melted in an electrical furnace at 1100°C for 10 min, until a bubble free liquid is formed. The melt is then quenched to room temperature in air by pouring it on a brass slab and annealed at room temperature. As a result transparent and colored glasses are obtained.

In the present work, density (d) of the glass is determined by the standard principle of Archimedes using o-Xylene (99.99% pure) as buoyant liquid. A direct reading balance (capacity 100gm, readability 0.1mg) is used for weighing. The bulk glass is suspended on a very thin copper stand that is set in the immersion liquid container. The density of the samples is determined by weighing them in the liquid and in air. From the measured values of density (d) and calculated average molecular weight (M),transition metal ion concentration (N_i), inter ionic radii (r_i), polaron radii (r_p) and optical basicity ($\wedge_{th}$) of all glass samples are determined.

The crystalline phases in the glass samples are checked by X-ray diffraction spectra recorded on X-ray diffractometer SEIFERT model SODEBYE FLUX 202 fitted with copper target and nickel fitter operated at 40 kV, 30mA at room temperature. JASCO V-670 Spectrophotometer is used for recording the optical absorption spectra range of this instrument is 200-1400nm. for PCSB doped with WO_3 glasses having the thickness 1 mm are used for optical measurement. It is a sophisticated computer controlled spectrophotometer with accuracy of ±0.2nm in UV-VIS and ±1nm in NIR region. The EPR spectra of PCSB doped WO_3glasses are recorded at room temperature using commercial X-band microwave spectrometer Model JEOL JES-FA200 at 100 kHz field modulation. The range of magnetic field is between 0-5000G with a scan speed of 250G/min and the microwave powder used is 5mW. A powdered glass specimen of 100mg has been taken in a quartz tube for EPR measurements. The value of g tensor of the signal is evaluated to an accuracy of ±0.001. The Fourier Transform infrared absorption spectra of the undoped and WO_3 doped PCSB glasses are measured at room temperature in the wave number range 400-2000cm^{-1} by a Fourier Transform infrared spectrometer type, Mattson No.5000 USA. The prepared glasses areused in the form of fine pulverized powders, which aremixed with KBr, in the ratio 1:100 (sample: KBr), respectively. The weighed mixtures are then subjected to a pressure of 5T/cm^2 to produce clear homogenous disks.

III. RESULTS

A. *Physical parameters*

Practically the density (d) and calculated average molecular weight (M), various physical parameters such as tungsten ion concentration (N_i), mean tungsten ion separation (r_i) and the polaron radius (r_p) of the doped and undoped PCSB glasses is determined by standard principle [20]. These values have been furnished in Table 1

B. *Powder XR*

Fig. 1 shows the X-ray diffraction spectra of PCSB glasses. X-ray diffraction is a useful method to detect readily the presence of crystals in a glassy matrix if their dimensions are greater than typically 100nm. The XRD pattern of the present glass system does not reveal any discrete or sharp peaks, and it has been given the characteristic humps of the amorphous material.

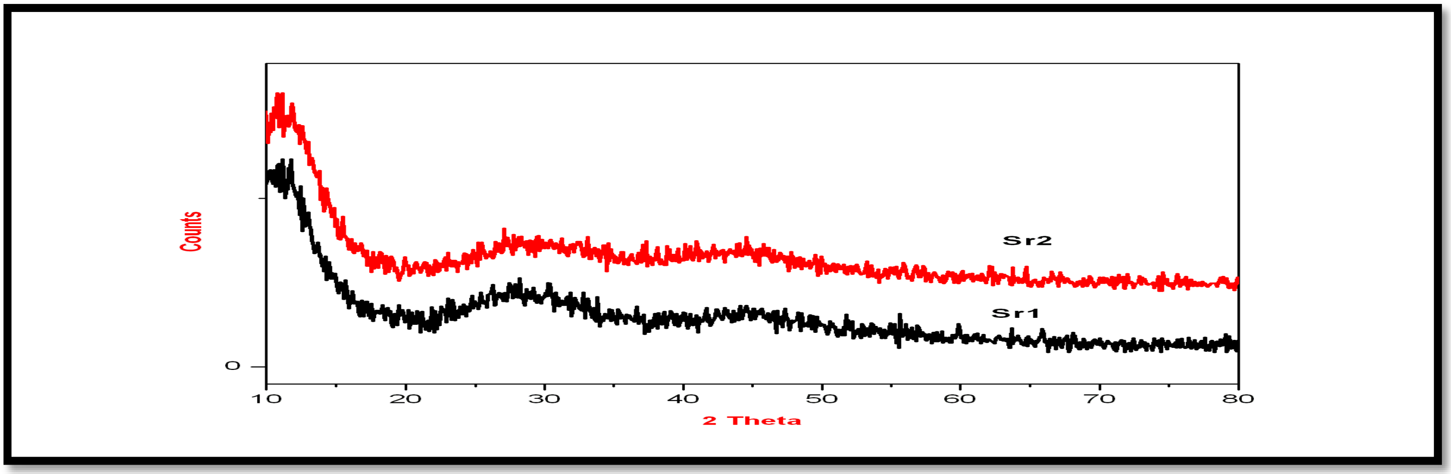

Fig. 1 X-Ray Diffraction Pattern For Undoped, Tungsten Doped PCSB Glasses.

C. *Optical absorption studies*

The optical absorption spectra of tungsten ions in PCSB glass Samples are recorded at room temperature 200-1400nm.

Name of Glass Sample	Density g/cm^3 (±0.004)	Mass (g)	Volume (cm^3)	Avg. Mol. Wt (M)	Transition metal ion conc. N_i(10^{19}ions/cm^3)	Inter ionic distance r_i(Å) (±0.005)	Polaron radius r_p(Å) (±0.005)	Optical Basicity
Sr1	3.752	0.786	0.209	100.697	-	-	-	0.462
Sr2	3.720	0.505	0.135	100.859	2.221	35.570	14.3	0.429
Sr3	3.688	1.010	0.273	98.467	2.255	35.391	14.2	0.431
Sr4	3.649	1.472	0.403	96.076	2.287	35.322	14.1	0.432
Sr5	3.591	1.114	0.310	93.684	2.308	35.119	14.4	0.433
Sr6	3.622	1.206	0.332	91.292	2.389	34.716	13.9	0.435

Table. 1 Physical parameters of tungsten doped PCSB glasses.

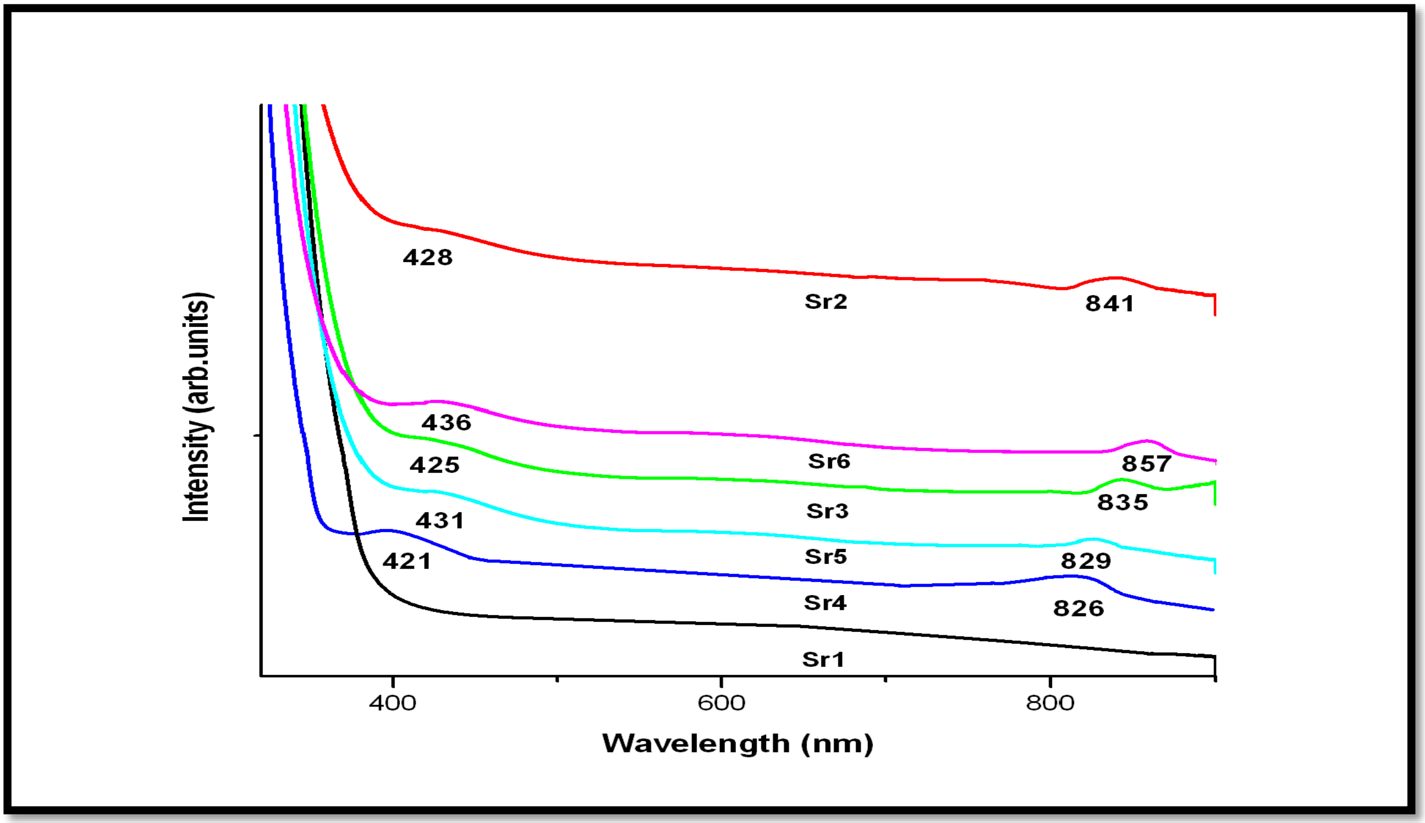

Fig.2 Optical absorption spectra of tungsten doped PCSB glasses.

glass samples, two broad absorption bands in the wavelength regions 421-436nm and 826-857nm are observed for all glass samples. The intensity of the band shifts towards lower wavelength side then shifts higher wavelength side with constant dopant concentration. The absorption bands have been furnished in Table 2. The principle of this technique is that photon energy greater than the band gap energy will be absorbed. The absorption coefficient, below and near the edge of each curve is determined at different wavelengths using the

Formula

$$\alpha(\nu)=(1/d)\ln(I_0/I_t)$$

- Where; I_0 and I_t are intensities of the incident and transmitted beams, respectively and'd' corresponds to the thickness of sample. The factor ln (I_0/I_t) is absorbance [21]. Optical band gaps are calculated using absorption spectra Fig. 3&4 for direct and indirect transitions for Sr2, Sr3, Sr4, Sr5, Sr6. Glass samples from the following equation.For direct transitions

$$\alpha(\nu)=B(h\nu-E_{opt})^n/h\nu$$

- Here n = ½ for allowed transition, B is a constant and E_{opt} is direct optical band gap. Relation (3.2) is also used for indirect transitions. In this equation, where n = 2 for allowed transition, B is a constant and E_{opt} is indirect optical band gap. Ln (α) are plotted as a function of photon energy. Fig. 5 for Urbach energy value (ΔE) are calculated by taking the reciprocal of the slopes of linear portion in the lower photon energy region of the curve as stated with following relation [21].

$$\alpha(\nu)=\alpha_0\exp(h\nu/\Delta E)$$

- using equation (3.2) and (3.3) and by plotting $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^2$ as a function of energy hν, optical band gaps for indirect and direct transitions are obtained. The respective values of E_{opt} are obtained by extrapolating between $(\alpha h\nu)^{1/2}$ and hν for indirect transitions between $(\alpha h\nu)^2$ and hν for direct transitions [22]. Direct, indirect optical band gap values and Urbach energies of Sr2, Sr3, Sr4, Sr5, Sr6 glass samples from Fig. 3-5 are given in Table 2.

Name of Glass sample	**Cut-off wavelength (nm)**	**Band position (nm)**		**Direct band gap (eV)**	**Indirect band gap (eV)**	**Urbach Energy (eV)**
		n–π*	**$d_{xy} \rightarrow d_{x2-y2}$**			
Sr1	**322**	**-**	**-**	**-**	**-**	**-**
Sr2	**313**	**428**	**841**	**3.810**	**3.694**	**0.285**
Sr3	**317**	**425**	**835**	**3.742**	**3.584**	**0.298**
Sr4	**308**	**421**	**826**	**3.706**	**3.489**	**0.331**
Sr5	**316**	**431**	**829**	**3.757**	**3.505**	**0.330**
Sr6	**309**	**425**	**857**	**3.801**	**3.530**	**0.278**

Table 2. Summary of the numerical on optical absorption spectra of tungsten doped PCSB glasses.

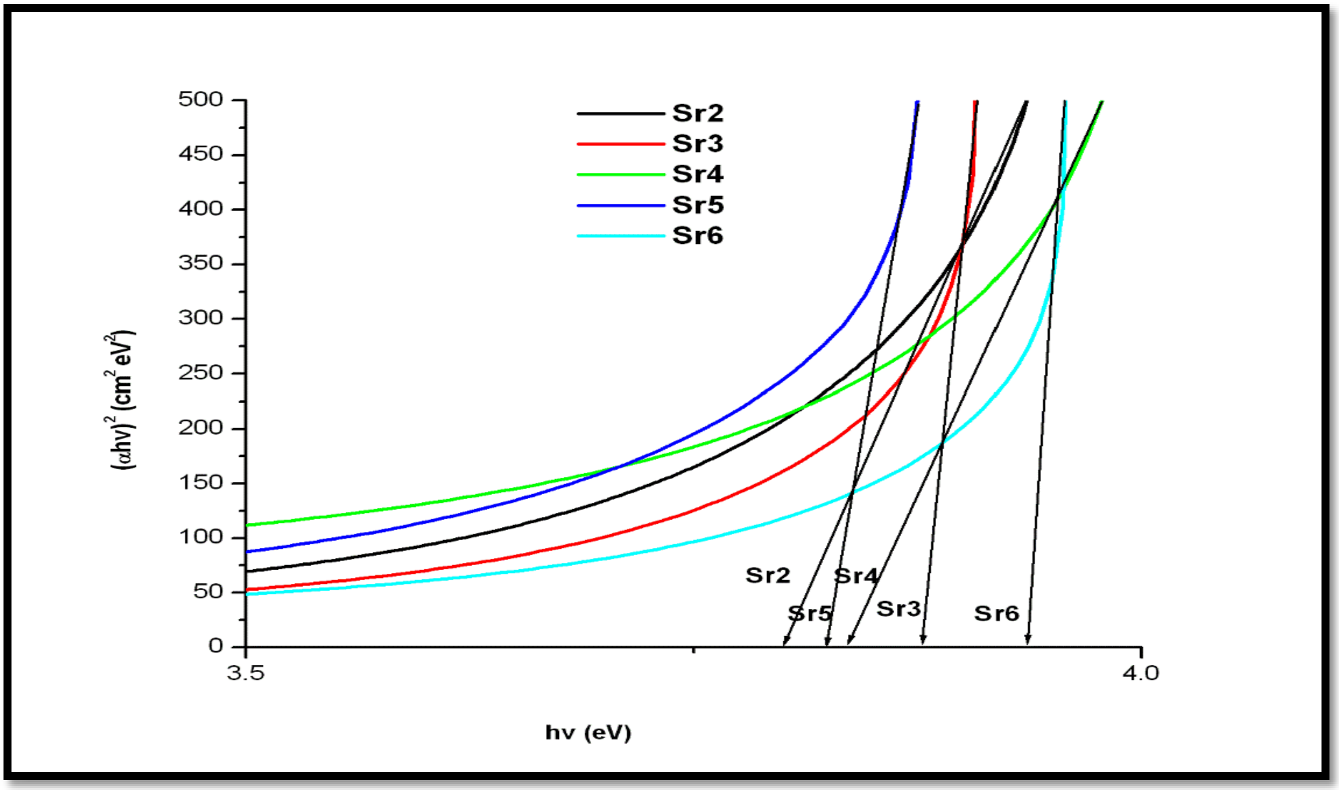

Fig. 3A plot between $(\alpha h\nu)^2$ and hν for tungsten doped PCSB glass samples

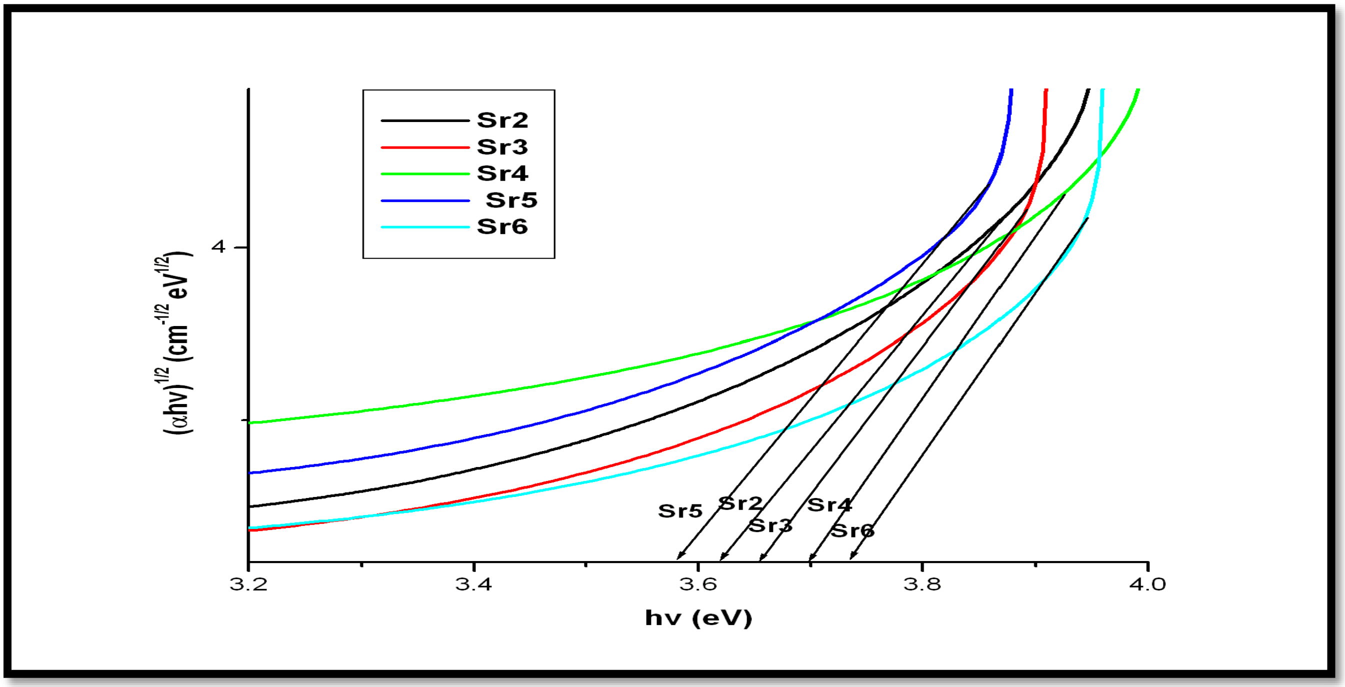

Fig. 4 A plot between $(\alpha h\nu)^{1/2}$ and hν for tungsten doped PCSB glass samples.

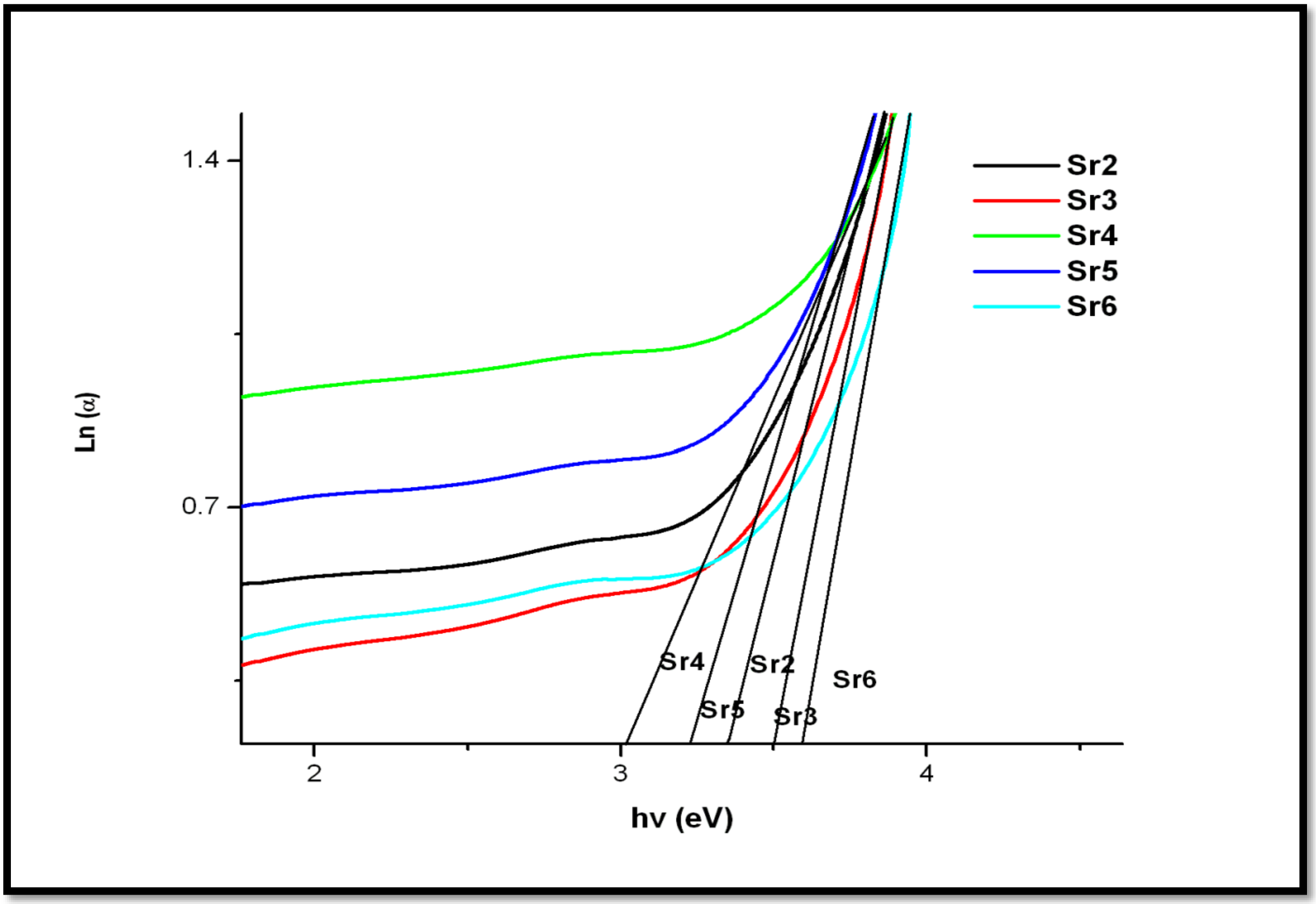

Fig. 5 A plot between Ln (α) and hν for PCSB glass samples.

- *EPR Spectra*

No EPR signal has been detected in the Sr1 glass. 0.1mol% WO_3 introduced into the PCSB glasses, all samples (Sr2, Sr3, Sr4, Sr5, Sr6) has exhibited significant signals. Fig. 6 shows a typical EPR spectrum of glass samples. The spectra of glass PCSB exhibited an asymmetric signal at $g_\perp$ =1.71 identified due to W^{5+} ions [23], and symmetric signal at $g_\parallel$ =1.61 identified due to oxygen (paramagnetic O^- ions) [24]. The signal is found to be feeble in the glass sample Sr4, and highest for glass sample Sr1 among the five samples. The values of g obtained five glass samples doped with 0.1mol% of WO_3 are furnished in Table3.

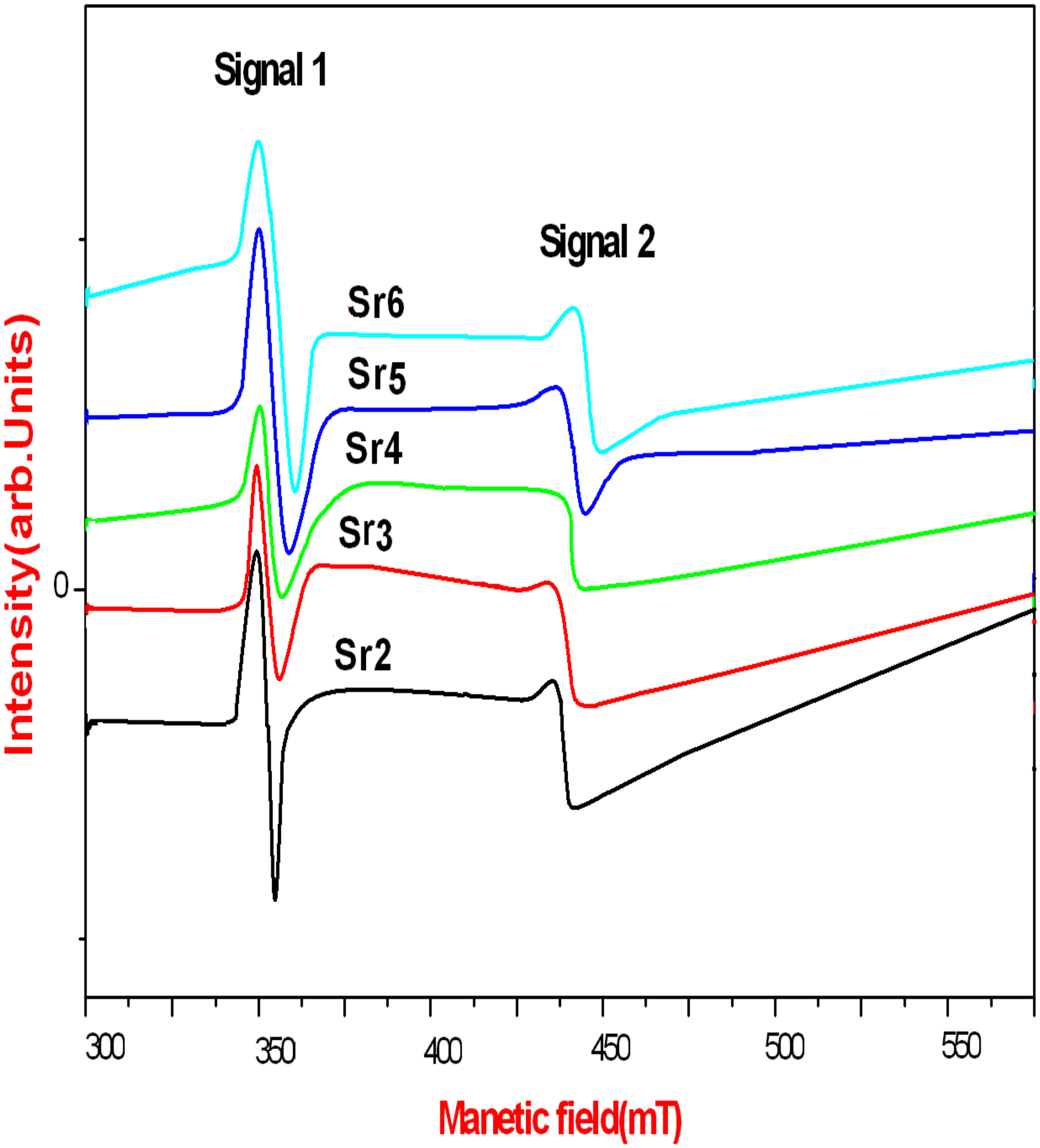

Fig.6 EPR Spectra of WO_3 Ion Doped PCSB Glasses.

Name of Glass sample	g∥	g⊥	K∥	K⊥	A∥	A⊥
Sr2	**1.616**	**1.719**	**0.171**	**0.145**	**97**	**55**
Sr3	**1.614**	**1.715**	**0.173**	**0.147**	**95**	**57**
Sr4	**1.612**	**1.711**	**0.175**	**0.149**	**93**	**59**
Sr5	**1.613**	**1.712**	**0.174**	**0.148**	**94**	**58**
Sr6	**1.615**	**1.713**	**0.172**	**0.146**	**96**	**56**

Table. 3 Summary Of EPR Spectra Of WO_3 Ion Doped PCSB Glasses.

- *FT-IR Studies*

The Fourier Transform Infrared (FT-IR) spectra of PCSB glasses are recorded at room temperature are shown in Fig. 7. (FT-IR) spectra of host (Sr1) glass sample show four main bands. Two conventional bands are originated from borate groups. 1171cm^{-1} is due to symmetric bending of the B-O band of tetragonal BO_4 units [25], 716 cm^{-1} is due to bending vibrations of B-O-B linkage [26] , 513 cm^{-1} is due to stretching vibrations of SrO [27], 458 cm^{-1} is due to stretching vibrations of PbO [28]. In 0.1mol% WO_3 doped to the base one additional band has formed. It is around 935 cm^{-1} is identified due to WO_6 groups [29]. The summary of data on the position of various vibrational bands in the WO_3 doped PCSB glasses are presented in Table 4.

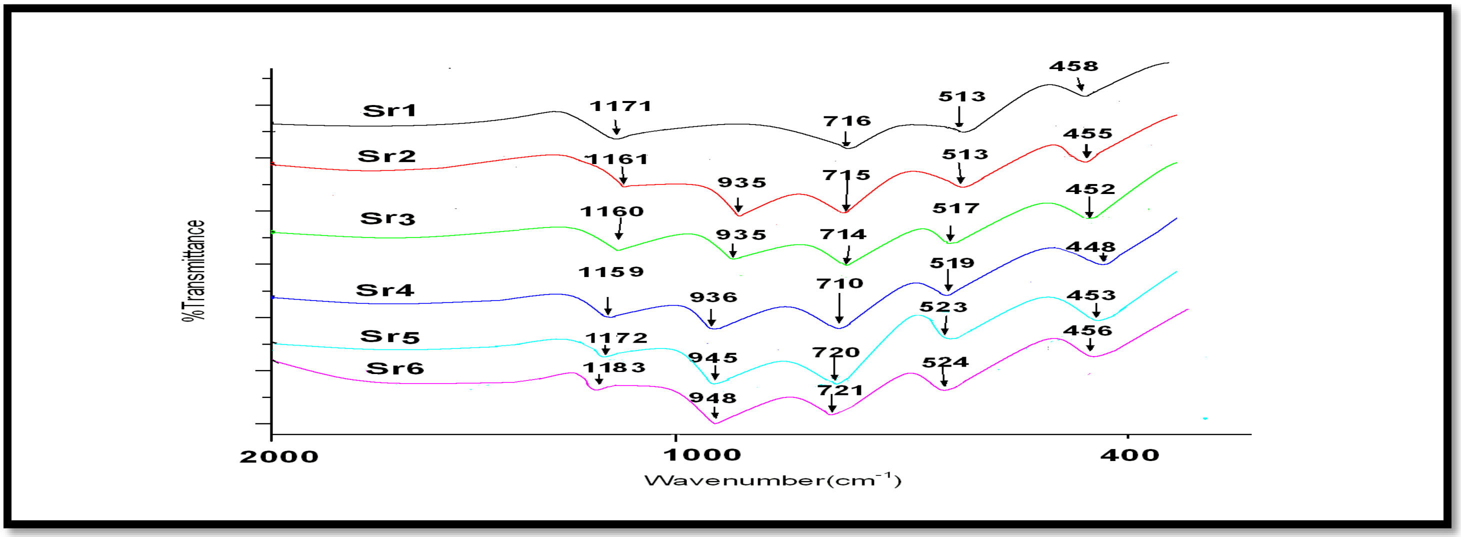

Fig. 7 FT-IR Spectra Of Tungsten Doped PCSB Glass Samples.

Sr1	**Sr2**	**Sr3**	**Sr4**	**Sr5**	**Sr6**	**FT-IR Assignments**
1171	1161	1160	1159	1172	1183	B-O stretching vibrations of tetrahedral BO_4 diborate, triborate and pentaborate structural groups
-	953	953	986	988	988	Vibrations of asymmetric of W-O-W bridges and stretching vibrations associated with WO_6
716	715	714	710	720	721	Vibrational modes of B-O-B bending linkage
513	513	517	519	523	542	Vibrations of metal cation such as Sr^{2+}
458	455	452	448	453	456	Vibration modes of Pb-O-B or W-O-B with more non-bridging oxygen ions.

Table. 4 FT-IR Vibrational Bands Observed (Wave Number Cm^{-1}) In The Tungsten Doped PCSB Glasses

IV. DISCUSSION

PbO-CdO-SrO-B_2O_3 glass system is an admixture of glass formers, modifiers and intermediates. Among various constituents of the composition, PbO is a conditional glass former. It has a low rate of crystallization, moisture resistance, stable and transparent glass could be achieved due to dual role played by PbO as a glass former and also as a modifier. PbO acts as a modifier at low concentration (15-20mol%) Pb^{2+} cations occupy interstices forming [PbO_6] structural units. These structural units promote the conversion of [BO_3] units to [BO_4] tetrahedral. PbO At high concentration (above 20mol%) PbO enters the structure as network former in the form of [PbO_4] units [30]. Borate is the glass former. It combines with the metal oxides like CdO, PbO and SrO modifies the conversion of sp^2planar BO_3 units to sp^3 tetrahedral BO_4 units and making bonds with non bridging oxygens. Bray et al [31].

$$(PbO_6) + 2(BO_3) \leftrightarrow (PbO_4) + 2(BO_4)$$

WO_3 is a glass former, it exist pentavalent W^{5+} state, which exhibit paramagnetic resonance and involves WO_4 and WO_6 structural units [32]. W^{5+} state is present in PCSB glasses doped with WO_3 are expected to occupy the interstitial positions; results are confirmed by the optical absorption, EPR and FT-IR studies.

A. *Physical parameters*

The change in geometrical configuration, co-ordination number, cross-link density and dimensions of interstitial space of glass decide the density and dimensions interstitial space of glass decide the density values; density is a tool which reveals the degree of change in structure with change in composition of glasses. Density values have been decreased gradually from Sr1 to Sr5 and then increase in Sr6 respectively. The increase in the density is attributed to molecular weight of the added transition metal oxides (231.83g/mol) which is higher than that of B_2O_3 (69.62g/mol) [33]. The molar volume of 0.20-0.33 cm^3 increases non-linearly this may be due to increase in the bond length or the inter-atomic spacing between the tungsten and oxygen atoms are furnished in Table 1.

B. XRD

X-ray diffraction is useful method to conform the amorphous nature of glass matrix. The atoms are neither regularly spaced nor uniform as in the case of crystals. Because of variations in inter atomic distances of glasses. The peaks are wider range.

4.3 Optical absorption studies Duffy and Ingram [34] have given the theoretical formula of optical basicity is

$$\sum_{i=1}^{n} \frac{z_i r_i}{2\gamma_i}$$

- Where n is the total number of cations present, z_i is oxidation number of the i^{th} cation, r_i is the ratio of number of i^{th} cations to the oxides present and γ_i is the basicity moderating parameter of the i^{th} cation. The basicity moderating parameter γ_i can be calculated from the following equation [35].

$$\gamma_i = 1.36(x_i - 0.26)$$

- Where x_i is the Pauling's electro negativity of the cation. Pauling's electro negativity of boron, lead, cadmium, strontium and tungsten ions is 2.04, 2.33, 1.69, 0.95, and 2.36respectively. Theoretical values of optical basicity (Λ_{th}) are presented in Table 1. In PCSB doped with WO_3 glasses optical basicity increases from Sr2 to Sr6 with the constant dopant concentration. It suggests that ability of oxide ion donate electrons to surrounding captions increases [36]. Optical absorption spectra of PCSB glasses doped with WO_3 two absorption bands are observed for Sr2 glass sample, one at 428nm is due to n-π*(15-x)PbO-5CdO-(15+X)SrO-(65-y)B_2O_3y(WO_3)where 0<x<8 and y=0.1 system have large deformation of the basic structure in the lead part of the glass network modifications are related mainly to the formation of [PbO_3] and [WO_4] structural units that contributes to the increase of the number of n-π* electronic transitions in the optical absorption spectrum and the formation of Pb^{2+} ionsand other at 841nm band is due to $d_{xy} \rightarrow d_{xz,}$ d_{yz} and $d_{xy} \rightarrow$ d_{x2-y2} transitions [37].This band is identified due to the excitation of lower valance state W^{5+} ions from ground state the next state with crystal field parameters around Δ=16000cm^{-1}& δ=13000cm^{-1}[38].

From Table 2 shows that the direct, indirect optical band gap energy values are slightly decreases from Sr2-Sr4 and slightly increases Sr5 & Sr6. The optical band gaps for direct 3.810-3.706, 3.757& 3.801eV, for indirect 3.694-3.489, 3.505 & 3.530eV. The Urbach energy values are increases from 0.285-0.331, decreases from 0.330 & 0.278eV. The decrease in the optical band gap can be explained as the trapped electron at this W^{5+} site is transferred to the neighboring new W^{6+} site by absorbing a photon energy. Sr2-Sr4 the position of band lower wave length modifies to higher wave length in the W^{5+} octahedron geometry. This observation indicates a gradual migration of the tungsten ions from tetrahedral to octahedral positions and an increasing modifying action of tungsten ions in the glass.

C. EPR spectral studies

PCSB doped with WO_3 consisting the local symmetry and interaction between paramagnetic ions investigated by EPR spectroscopy. EPR spectra of these glass samples are analyzed by an axial Spin-Hamiltonian [39] in which the quadrupole and nuclear Zeeman interaction terms are ignored.

$$H = g_{\parallel}\beta H_z S_z + g_{\perp}\beta(H_x S_x + H_y S_y) + A_{\parallel} S_z I_z + A_{\perp}(S_x I_x + S_y I_y)$$

- Where β is Bohr magneton, $g_{\parallel}$& $g_{\perp}$ are the parallel and perpendicular principal components of g tensor, H_x, H_y, H_z are components of the magnetic field, S_x, S_y, S_z, I_x, I_y, I_z are components of the electron and nucleus spin operator, $A_{\parallel}$& $A_{\perp}$ are principal components of the hyperfine coupling tensor. The possibility of tungsten ions reduce to W^{5+} state during the melting at temperature. The Spin-Hamiltonian parameters of the W^{5+} ions are determined summarized in Table 3. The g factor values are observed in the range $1.713 < g_{\perp} < 1.719$ and $1.615 < g_{\parallel} < 1.616$, indicate that W^{5+} ions present in axially distorted positions with a short W-O bond and opposite long W-O bond along the symmetry axis of oxygen ions [24].
- These values indicating the presence of W^{5+} centers, having nd^1 electronic configuration with C_{4v} local symmetry in oxide glasses [40]. ^{177}W nucleus whose nuclear spin I=1/2 resulting values are good agreement with reported values [41]. The shape of the EPR spectra depends on the WO_3 content of glasses. The signal intensity is approximately invariant, $g_{\perp}$ values increases from 1.713-1.719 which indicates the paramagnetic nature of W^{5+} ion. The amount of W^{5+} centers remains constant and the values of g remains unaffected when the 0.1mol% WO_3 concentration. This behaviour of the intensity and width of EPR signal suggests that there is a constant proportion in the reduction of W^{6+} to W^{5+} ions. When the WO_3 content is 0.1mol% tungsten ions remain mostly in their higher valance state as W^{6+} ions and only a few are reduced to the W^{5+} state [41]. W^{5+} state acting as glass modifier adding of tungsten is expected to decrease the life time of the $^4I_{11/2}$ level by multi phonon relaxation. Hence an increase in the pumping and amplifier gain for the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition at 1.5μm is possible.

$2Pb^{+2} \leftrightarrow Pb^0 + Pb^{+4}Pb^{+2} + 2W^{+6} \leftrightarrow Pb^{+4} + 2W^{+5}$The values of $K_{\parallel}$ & $K_{\perp}$ covalent reduction factors of W-O bands are along the z-axis and in the (x, y) plane respectively. Values evaluated using the following formulae

$$g_{\parallel} = g_e - \frac{8k_{\parallel}^2 \lambda}{\Delta}$$

$$g_{\perp}=g_e-\frac{8k_{\perp}^2\lambda}{\delta}$$

- where; g_e is the free electron g-factor, $\boldsymbol{\lambda}$ is the spin orbit coupling constant, Δ is the energy of $d_{xy}\rightarrow d_{x2-y2}$ transition and δ is the splitting due to tetragonal distortion. Covalency factor $k_{\parallel}$ is high for Sr4 glass sample and low for Sr2 glass sample it indicating that the W-O bond in the Z-direction becomes more covalent nature. Similarly the covalency factor $k_{\perp}$ describes W-O bonds located in (x, y) plane these bonds are more ionic than those in parallel direction and the degree of ionic nature appears to be more Sr4 glasses in this plane also. Thus the analysis of the EPR spectra indicates that the legend environment of W^{5+} ions experiences different degree of distortion with the modifier particularly, the axial distortion stretches the WO_6 octahedron along the Z-axis. This signal indicates that W^{5+} ions are located in axially tetragon ally elongated octahedral position with a short W-O bond along the symmetry axis of oxygen ions [24].

D. FT-IR

FT-IR gives the information about functional group and molecular structure of the system. FT-IR studies on borate glasses, the infrared absorption spectra of various borate groups are classified and interpreted as follows [42-44].

- The IR absorption in the region 800-1200cm^{-1} can be assigned to BO_4 groups.
- The IR absorption in the region 1200-1600cm^{-1} can be related to BO_3 groups.
- The infrared bands in the region 530-630 & 690-770cm^{-1} are due to bending vibrations of B-O-B (BO_3) groups.
- The near-infrared bands in the region 3000-4000cm^{-1} are related to vibrations of water, OH or B-OH groups.

The different structural groups in PCSB glasses doped with WO_3 exhibits from the Fig. 7 IR spectra recorded at room temperature. In undoped glasses this spectra exhibit vibrational bands at 1171cm^{-1} is assigned due to BO_4 tetrahedral units, at 716cm^{-1} is assigned due to B-O-B bending vibrations, at 458cm^{-1} is assigned due to stretching vibrations of PbO [45] and at 513cm^{-1} is assigned due to stretching vibrations of SrO [46], are observed. The bands are shifted when the tungsten is added to the PCSB glasses and additional vibrational bands are observed in the region 950-980cm^{-1}. These bands are assigned due to vibrations of W^{5+} ions due to the WO_4 groups. More over the bands in the region 440-460cm^{-1} are also assigned to either WO_4 groups are PbO bonds. The decrement of position of bands Sr2-Sr4 is due to decrement of NBO in the glasses, while the increment of position of bands Sr5-Sr6 is due to increment of NBO in the tungsten doped PCSB glasses. The bands at a 950cm^{-1} and 450 cm^{-1} due to vibration of W^{5+} is present in the two bands due to the vibrations of WO_4 groups expected in the region 920-950cm^{-1} and 420-450cm^{-1} respectively [47]. The appearance of vibration band at about 950cm^{-1} suggest that there is gradual transformation of W^{5+} ions from tetrahedral position to Octahedral positions.

V. CONCLUSIONS

- Density values of the samples are found to be decrease from Sr1-Sr4 then Sr5 and Sr6 increases with the concentration of WO_3.
- Average molecular weight (M),Inter ionic distance (r_i) and Polaron radius (r_p)values are found to be decrease continuously with the concentration of WO_3. Optical basicity has increases from Sr2 to Sr6 with the constant dopant concentration. It suggests that ability of oxide ion to donate electrons to surrounding cations increases.
- Amorphous nature of the undoped and WO_3 doped PCSB sample is confirmed by the broad bands in XRD studies.
- Two absorption bands appeared around 436, 857cm^{-1} in all the glass samples. The band position seems to be non-linear variation. This is due to transformation of W^{5+} tetrahedral positions to octahedral positions. The Optical band gaps of PCSB glass samples varied from 3.81 to 3.66 eV for direct transition and from 3.69 to 3.53 eV for indirect transitions. The Urbach energies varied from 0.28 to 0.27 eV.
- The spin-Hamiltonian parameters $g_{\parallel}<g_{\perp}<g_e$ and $K_{\parallel}>K_{\perp}$ conforms in the glass tungsten ions in exists in W^{5+} octahedral environment with tetragonal distortion.
- FT-IR absorption spectra of tungsten ion doped PCSB glasses shows; the system contains BO_4, B-O-B, Sr^{2+}, Pb-O-B/W-O-B & WO_6 structural groups are observed in the glass matrix.

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