

Research Article

# Bright Reddish-Orange emission from Pr<sup>3+</sup> - V<sup>4+</sup> ions co-doped CaO-PbO-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> Glasses for Photonics and Sensor applications

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## Abstract

The synthesized glasses of CaO-PbO-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>: Pr<sub>2</sub>O<sub>3</sub> - V<sub>2</sub>O<sub>5</sub> were prepared by conventional melt-quenching process. The optical absorption spectra exhibit different transition from various energy levels presence of simple Pr<sup>3+</sup> ions and V<sup>4+</sup> ion identities in the UV-vis-NIR region. The EPR spectra exhibited high intense hyperfine splitting of equidistant two sets of eight lines due to presence of VO<sup>2+</sup> paramagnetic ion. The g-factor shows a centred at  $g \approx 1.9857$ . The PL spectra shows seven emission transitions observed intra-configurational  $f^2-f^2$  of Pr<sup>3+</sup> ions. The luminescence spectra of V<sup>4+</sup> ion contain glass exhibited emission transition of  ${}^2E_{2g} \rightarrow {}^2T_{2g}$  of octahedral geometry. The V<sup>4+</sup> - Pr<sup>3+</sup> ions co-doped glass samples exhibited several emission transitions. Among all the emission transitions,  ${}^3P_0 \rightarrow {}^3H_6$  (625 nm) are identified to be prominent emission transitions. With gradual increase of V<sup>4+</sup> ion concentration, the  ${}^3P_0 \rightarrow {}^3H_6$  emission transition intensity to be increased may folds with respect to that of V<sup>4+</sup> ions free glass. The efficient energy transfer from octahedral V<sup>4+</sup>  $\rightarrow$  Pr<sup>3+</sup> ions ( $3d^1 \rightarrow 4f^2$ ). Finally, it is concluded that the preferable PrV1.0 glass for getting highest efficient luminescence of Pr<sup>3+</sup> ions due to energy transfer of metal to metal intervalence charge transfer state ( $d^1 \rightarrow f^2$ ).

**Keywords:** Borosilicate glasses, Optical Absorption, XRD, FTIR, EPR, PL and Energy transfer from  $d^1 \rightarrow f^2$  ions.

## 1. Introduction

Oxide glasses are well known as excellent hosts for co-doped of rare earth and transition metal ions. Borosilicate glasses have the properties of being extremely transparent, physically durable, low thermal expansion, thermally stable by nature and diverse applications. Borosilicate glasses are widely used in many different applications like optical components, sealing materials, chemically resistant containers and the safe storage of radioactive waste. Adding B<sub>2</sub>O<sub>3</sub> to SiO<sub>2</sub> glasses increases their chemical inert, thermal stability and corrosion resistance [1]. Micro-hardness and thermal stability are both improved by adding B<sub>2</sub>O<sub>3</sub> to SiO<sub>2</sub> glass host. The Lead borosilicate glasses are used as radiation hard glasses [2].

Glasses contain V<sub>2</sub>O<sub>5</sub> exhibits a range of colours from green to yellow. Vanadium doped glasses contain different valences develop various colours of the glasses such as V<sup>5+</sup> ions develop yellow to colour less, V<sup>4+</sup> ion blue colour in glasses.

Vanadium metal is one of the important TM oxide that displays excellent properties of electro-chromism of Blue  $\leftrightarrow$  Green  $\leftrightarrow$  Yellow and has unique properties of its semiconducting properties that is the result of electron hopping between the ions.

Vanadium doped glasses shows n-type semiconductor character due to unpaired 3d<sup>1</sup> electron with an energy of  $\sim 2.2$  eV at room temperature. The semiconducting nature of V<sub>2</sub>O<sub>5</sub> is due multivalence of vanadium. V<sub>2</sub>O<sub>5</sub> is the most stable oxide of vanadium atom and conditional glass former which does not form glass on their own. At room temperature V<sub>2</sub>O<sub>5</sub> is insulating phase. The electronic structure of V<sub>2</sub>O<sub>5</sub> is strongly connected with its anisotropy. The degree of anisotropy is in increasing order of vanadium is V<sub>2</sub>O<sub>3</sub> < VO<sub>2</sub> < V<sub>2</sub>O<sub>5</sub>.

Transition metal ions are used in glass science due to their presence in one or more valence states that alters the structural and optical characters. In recent years, vanadium is used as impurity for glass system to understand the orientation, structural and spectroscopic properties of the host glass at different mol %. Transition metals can be used to deduce more information about the local bonding environment in the glass, which negating optical device applications, justifies characterisation of transition metal doped glasses.

Borosilicate glasses are conventional to be good materials for optical devices such as lasers and optical fibres. Silicate glasses are thermally stable, chemically durable and optically transparent towards excitation and lasing wavelengths [3]. Special attention has been

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paid to Pr<sup>3+</sup> ions in silicate glass containing lead [4-6]. The rare earth ions doped glasses have attracted a great deal of attention due to their important physical, optical and chemical properties [7]. The electronic energy levels of rare earth ions determine the lasing characteristics of rare earth ions doped materials and are influenced by the host matrix [8]. Praseodymium doped amorphous glasses, due to several visible and near-infrared absorption and emission transitions are interesting from the spectroscopic point of view. Systematic studies demonstrate that radiative and non-radiative relaxation from the excited states of Pr<sup>3+</sup> ions depend significantly on the glass-host matrices.

The addition of CaO content to the glass composition will accelerates the glass melting and promote the glasses clarification. The most stable and common oxidation state of Lanthanides are trivalent state (Ln<sup>3+</sup>). Ln<sup>3+</sup> ion have unique spectroscopic properties of optical and emission profiles. REI (Rare Earth Ions) and TMI (Transition Metal Ions) were co-doped to the host glass as impurities. Host glasses are easily accept various co-dopants of energy transfer such as TMI to REI (TM → RE). Glasses doped with TMI have a great deal of attention, because of their photoconductivity properties. Introducing the impurity atom in the glass host leads to an increase in the free carrier ion concentration. By co-doped impurities like TMO (V<sub>2</sub>O<sub>5</sub>) and REE (Pr<sub>2</sub>O<sub>3</sub>) into the glass domain change in spectroscopic properties (Optical and Luminescence) of the glass domain with the increasing the dopant concentration.

## 2. Synthesis Reaction of Glasses

The commercial chemicals SiO<sub>2</sub>, B<sub>2</sub>O<sub>3</sub>, CaO, PbO, Pr<sub>2</sub>O<sub>3</sub> and V<sub>2</sub>O<sub>5</sub> are participated in the chemical combination reaction for new glass system. The synthesis reaction of the novel glass system is represented in Figure 1.

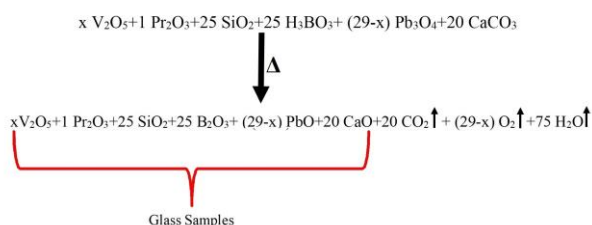


Figure 1: Synthesis Reaction of Glasses

## 3. Experimental Procedure

Commercial Glasses of composition are 20 CaO - (29-x) PbO - 25 B<sub>2</sub>O<sub>3</sub> - 25 SiO<sub>2</sub>: 1Pr<sub>2</sub>O<sub>3</sub> + x V<sub>2</sub>O<sub>5</sub> (where 'x' varies from 0 to 1 mol % with a step of 0.2 mol %) were prepared by conventional melt-quenching technique. The high purity AR-grade (99.9%) commercial chemicals CaO, PbO, B<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, Pr<sub>2</sub>O<sub>3</sub> and V<sub>2</sub>O<sub>5</sub> are oxide powder materials in the appropriate amounts of chemicals are weighed and powders are mixed in the composition ratios. Agate mortar and pestle grinded to obtain homogeneous mixture for de-carbonation. The well mixed powder placed in

procelain crucible heated in an electric furnace at 470 °C for 30 minutes eliminate the carbonate and water vapour residuals. After de-carbonation of the glass powder is removed from furnace again agate mortar and pestle grinded to obtain homogeneous glass mixture for melt quenching process. A 50 ml SiC crucible is used to melt finely mixed powders of chemicals with the use of a programmable furnace. The melting point of glasses were estimated to be at 975 °C. Final transparent bubble-free melt discharged on pre-heated brass plate and pressed quickly with another brass plate to get uniform thickness. These glass samples instantly transferred to another furnace previously kept at 350 °C. Annealing was done in the muffle furnace at 350 °C for 6 hours to remove internal stresses of all the prepared glasses. Finally the Pr<sup>3+</sup> - V<sup>4+</sup> ions co-doped CaO - PbO - B<sub>2</sub>O<sub>3</sub> - SiO<sub>2</sub> glass samples were polished with different grades of emery powder in required shapes for UV-visible-NIR and other spectroscopic measurements. The glass compositions used for the present Investigation are given in Table 1.

Table 1: Glass Composition of CaO-PbO-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> : Pr<sup>3+</sup> - V<sup>4+</sup> ions co-doped glasses

S. No	Glass Codes	CaO	PbO	B <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Pr <sub>2</sub> O <sub>3</sub>	V <sub>2</sub> O <sub>5</sub>
		mol %	mol %	mol %	mol %	mol %	mol %
1	Pr	20	29	25	25	1	-
2	PrV0.2	20	28.8	25	25	1	0.2
3	PrV0.4	20	28.6	25	25	1	0.4
4	PrV0.6	20	28.4	25	25	1	0.6
5	PrV0.8	20	28.2	25	25	1	0.8
6	PrV1.0	20	28	25	25	1	1.0

Hereafter the host glass coded as CaPbBSi and other glasses coded as Pr, PrV0.2, PrV0.4, PrV0.6, PrV0.8, PrV1.0 glass systems are prepared at melting temperature as 966, 969, 970, 973, 974 and 975 °C respectively. Figure.2 shows the prepared glossy glass samples with different compositions of transparent CaO-PbO-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> : Pr<sup>3+</sup> - V<sup>4+</sup> ions co-doped glasses. The color of the glass samples changes from light blue to thick blue with increasing concentration of V<sub>2</sub>O<sub>5</sub> content.

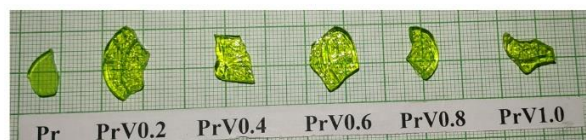


Figure 2. CaO-PbO-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>: Pr<sup>3+</sup> - V<sup>4+</sup> ions co-doped glass samples

### 3.1 Sample Characterization

The mass of the samples is recorded using a scale tech weighing balance. Scale Tech digital weighing balance with a precision of 10<sup>-4</sup> gm/cm<sup>3</sup> recorded the weight of the glasses. The weights of the glasses were used to

obtain the density values using Archimedes' technique. The Refractive index of these glass samples were measured by using Abbe's Refractometer. The X-ray diffraction patterns of the samples were recorded using a Shimadzu XRD-7000. The Optical absorption (UV-Vis-NIR) spectra were recorded JASCO, V-570 spectrophotometer from 200 to 2500 nm with an accuracy of 0.1 nm. The ESR spectra of powder samples were recorded at a room temperature using E11Z Varian X band ( $\nu=9.5\text{GHz}$ ) of ESR spectrometer of 100 kHz field modulation. FTIR spectra were recorded on a JASCO-FTIR-140 spectrophotometer with resolution of 0.2 cm<sup>-1</sup>. The spectral range 400-4000 cm<sup>-1</sup> using KBr pellets (300 mg) containing the pulverized sample (1.5 mg) and the spectra was analyzed in the range of 400-2000 cm<sup>-1</sup>.

The photoluminescence spectra was recorded at room temperature on a Photon Technology International (PTI) spectrofluorometer with excited wavelength ( $\lambda_{\text{excitation}}$ ) 478 nm from 300 to 900 nm.

## 4. Results

### 4.1 Physical Properties

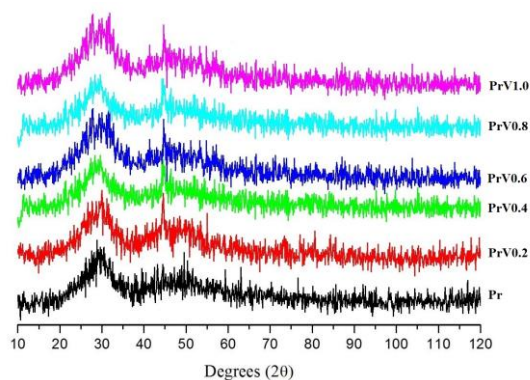
The evaluated values of Density ( $\rho$ ), Refractive Index ( $\mu$ ), Molar Volume ( $V_m$ ), Average molecular weight ( $M$ ), Transition Metal Ion concentration ( $N_i$ ), Inter ionic distance ( $R_i$ ), Polaron radius ( $R_p$ ), Field Strength ( $F_i$ ), Optical Basicity ( $\Delta_{th}$ ) and various other physical parameters of Pr<sup>3+</sup> - V<sup>4+</sup> ions co-doped CaO-PbO -B<sub>2</sub>O<sub>3</sub> - SiO<sub>2</sub> glasses recorded at room temperature are given in Table 2.

**Table 2:** Various Physical properties of CaO-PbO-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>: Pr<sup>3+</sup> - V<sup>4+</sup> ions co-doped glasses

Physical Properties	Pr	PrV0.2	PrV0.4	PrV0.6	PrV0.8	PrV1.0
Thickness ( $t$ ) (mm) ( $\pm 0.001$ )	0.9171	1.0125	1.0136	1.5175	1.0143	1.0116
Density ( $\rho$ ) (gm/cm <sup>3</sup> ) ( $\pm 0.004$ )	4.8002	4.7879	4.7756	4.7632	4.7508	4.7385
Average Molecular Weight ( $M$ ) (g/mol)	111.61	111.53	111.44	111.36	111.28	110.21
Transition Metal Ion Concentration ( $N_i$ ) (10 <sup>22</sup> ions/cm <sup>3</sup> ) ( $\pm 0.005$ )	--	0.5172	1.0324	1.55461	2.0571	2.5672
Inter transition metal ion distance ( $R_i$ ) (Å) ( $\pm 0.005$ )	--	5.7827	4.5925	4.0142	3.6511	3.4006
Polaron radius ( $R_p$ ) (Å) ( $\pm 0.005$ )	--	2.3302	1.8508	1.6177	1.4708	1.3662
Field strength ( $F_i$ ) (10 <sup>15</sup> cm <sup>-2</sup> ) ( $\pm 0.005$ )	--	9.2879	14.5966	19.1061	23.1133	26.7881
Electronic polarizability ( $\alpha_e$ ) (10 <sup>-23</sup> ions/cm <sup>3</sup> ) ( $\pm 0.005$ )	--	1.7538	0.8797	0.5886	0.4430	0.3553
Molar Volume ( $V_m$ ) (x 10 <sup>14</sup> cm <sup>3</sup> mol <sup>-1</sup> )	23.2511	23.2941	23.3358	23.3793	23.4365	23.4675
Refractive index ( $\mu$ ) ( $\pm 0.0001$ )	1.6641	1.6846	1.6858	1.6877	1.6888	1.6895
Refraction losses	0.2203	0.2293	0.2299	0.2307	0.2312	0.2315
Molar Refractivity ( $R_m$ ) ( $\pm 0.0005$ )	8.6253	8.8493	8.8771	8.9128	8.9411	8.9647
Dielectric Constant ( $\epsilon$ ) ( $\pm 0.0005$ )	2.7692	2.83793	2.8419	2.8483	2.8521	2.8544
Specific Volume ( $V_s$ )	0.2087	0.2088	0.2094	0.2099	0.2105	0.2119
Optical Dielectric Constant ( $\epsilon_o$ )	1.7692	1.8379	1.8419	1.8483	1.8521	1.8544
Oxygen Packing Density ( $OPD$ )	80.914	81.412	81.476	81.511	81.545	81.589
Optical Basicity ( $\Delta_{th}$ )	0.6187	0.6229	0.6246	0.6263	0.6285	0.6295

### 4.2 X-Ray Diffraction spectra

X-ray diffraction patterns of Pr<sup>3+</sup>- V<sup>4+</sup> ions co-doped CaO-PbO-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> glasses are displayed in Figure 3.

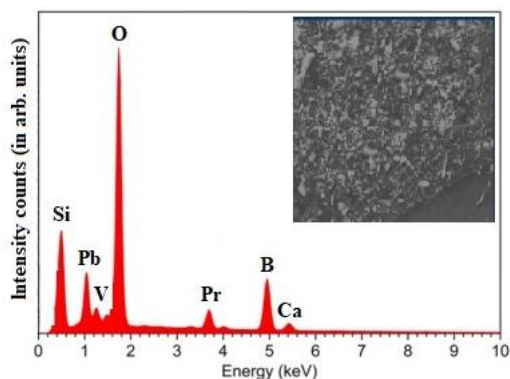


**Figure 3:** X-Ray diffraction pattern of CaO-PbO-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>:Pr<sup>3+</sup> - V<sup>4+</sup> ions co-doped glasses

The diffraction angles are taken up to an accuracy of  $\pm 0.1^\circ$  lines drawn back ground of image only for better view of eye guiding. Two broad humps are observed at around  $\sim 22^\circ$  and  $\sim 45^\circ$  ( $=2\theta$ ) without sharp peaks. XRD analysis suggests glassy behavior of all the prepared glass samples.

### 4.3 EDS Analysis

The Energy Dispersive Spectroscopy the chemical compositions of the glasses were determined as displayed in Figure 4. The Figure.4 shows the Energy Dispersive Spectroscopy of the glass samples of 1 mol% of CaO-PbO-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>: Pr<sup>3+</sup> - V<sup>4+</sup> ions co-doped glasses.



**Figure 4:** EDS of CaO-PbO-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>: Pr<sup>3+</sup> - V<sup>4+</sup> ions co-doped glasses

This analysis indicates the presence of calcium (Ca), silicon (Si), boron (B), lead (Pb), oxygen (O), praseodymium (Pr) and vanadium (V) elements in the glass network.

4.4 Differential Thermal Analysis

**Table 3:** Values of glass transition temperature (T<sub>g</sub>), crystallization temperature (T<sub>c</sub>), melting temperature (T<sub>m</sub>), Thermal Stability (ΔT) and Hruby's Parameter (K) of various glass samples

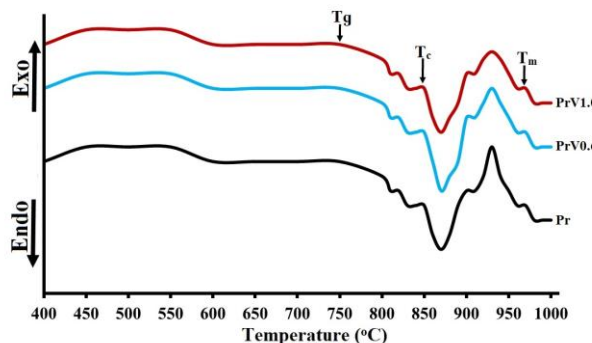
Glass Sample Code	Glass Transition Temperature (T <sub>g</sub> ) °C	Glass Crystallization Temperature (T <sub>c</sub> ) °C	Glass Melting Temperature (T <sub>m</sub> ) °C	Thermal Stability (ΔT) °C	Hruby's Parameter (K)
Pr	744	843	968	99	0.7920
PrV0.6	747	845	973	98	0.7656
PrV1.0	750	847	976	97	0.7519

All the exothermic and endothermic thermograms variations are due to enthalpy change in the 1.0 mol% V<sub>2</sub>O<sub>5</sub> concentration. The thermal stability factor is ΔT=T<sub>c</sub>-T<sub>g</sub> is the difference between glass crystallization temperature (T<sub>c</sub>) and glass transition temperature (T<sub>g</sub>). Each hump is assigned to the glass transition temperature (T<sub>g</sub>), crystallization temperature (T<sub>c</sub>) and melting temperature (T<sub>m</sub>) respectively. From DTA Spectra analysis it was observed that T<sub>g</sub> depends on the strength of chemical bonds in the glass structure and glass composition. Hruby's Parameter (K) gives the information on the stability of the glass against devitrification. The stability of the glass in order of PrV1.0 > PrV0.6 > Pr. Observed DTA results reveal a glass with 1.0 mol % of V<sub>2</sub>O<sub>5</sub> concentration exhibiting the highest thermal stability and from Table.3 observed that PrV1.0 glass have highly stable against devitrification.

4.5 FTIR Spectra

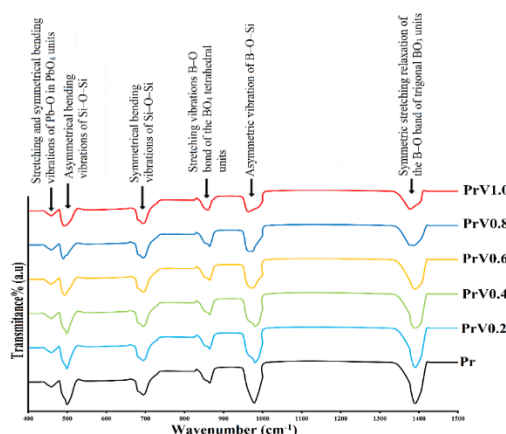
FTIR spectroscopy is used to identify the presence of bond assignments and frequency modes of structural units in the glass composition. FTIR spectra of Pr<sup>3+</sup> - V<sup>4+</sup> ions co-doped CaO-PbO-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> glasses are recorded at room temperature (37 °C) exhibited large, medium, weak and different bands due to the structural frequency modes of Silicate, borate and borosilicate functional groups as shown in Figure 6.

The thermal stability glass defined as the temperature range of the glass more precisely under cooled melt to draw into fiber. The Figure.5 shows DTA curves for Pr, PrV0.6 and PrV1.0 glasses. From the Figure.5 it was observed that the glass transition temperature (T<sub>g</sub>), glass crystallization temperature (T<sub>c</sub>) and glass melting temperature (T<sub>m</sub>) of these glasses are given in Table 3.



**Figure 5:** DTA trace of CaO-PbO-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>: Pr<sup>3+</sup> - V<sup>4+</sup> ions co-doped glasses

According to the lead borosilicate literature survey, the structural vibrations of borosilicate groups are mainly present in the following spectral series of bands, first band at about ν<sub>1</sub> (450 cm<sup>-1</sup>), the second band at ν<sub>2</sub> (495 cm<sup>-1</sup>), third band at ν<sub>3</sub> (698 cm<sup>-1</sup>), fourth band centred at ν<sub>4</sub> (850 cm<sup>-1</sup>), fifth band at ν<sub>5</sub> (990 cm<sup>-1</sup>) and sixth band found at ν<sub>6</sub> (1390 cm<sup>-1</sup>). The summary of data on the spectra band positions in the FT-IR spectra of Pr<sup>3+</sup> - V<sup>4+</sup> ions co-doped CaO-PbO-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> glasses are displayed in Table 4.



**Figure 6:** FTIR spectra of CaO-PbO-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>: Pr<sup>3+</sup>-V<sup>4+</sup> ions co-doped glasses

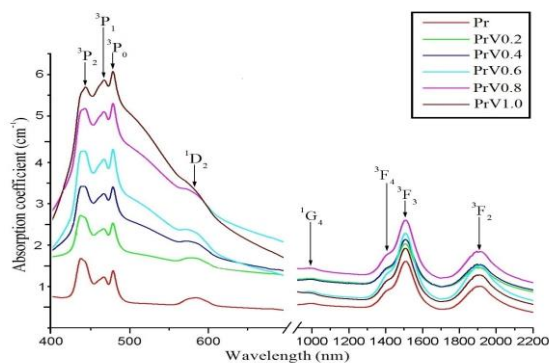
**Table 4:** FTIR band positions CaO-PbO-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>: Pr<sup>3+</sup> - V<sup>4+</sup> ions co-doped glasses

Band Position	Glass Samples						Band Assignments
	Pr	PrV0.2	PrV0.4	PrV0.6	PrV0.8	PrV1.0	
1	450	452	453	459	449	455	Stretching and symmetrical bending vibrations of Pb-O in PbO <sub>4</sub> units
2	499	498	502	505	511	510	Asymmetrical bending vibrations of Si-O-Si
3	698	695	690	695	698	699	Symmetrical bending vibrations of Si-O-Si
4	851	850	855	854	850	852	Stretching vibrations B-O bond of the BO <sub>4</sub> tetrahedral units
5	990	994	995	990	990	991	Asymmetric vibration of B-O-Si units
6	1390	1390	1392	1393	1390	1390	Symmetric stretching relaxation of the B-O band of trigonal BO <sub>3</sub> units

4.6 Optical Absorption Spectra

Optical Absorption Spectra is understanding sensitive tool to study the optical transitions and electronic band structure between TM ions and RE ions co-doped glasses. The optical absorption spectra of CaO-PbO-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>: Pr<sup>3+</sup>- V<sup>4+</sup> ions co-doped glasses in the wavelength range between 200-2500 nm recorded at room temperature is depicts in Figure 7 . This absorption transition spectra exhibit eight absorption transitions corresponding to the 4f<sup>2</sup>-4f<sup>2</sup> intra-configurational electric dipole transitions. All the transition in the absorption spectrum are started from the ground level (<sup>3</sup>H<sub>4</sub>) to various exited levels <sup>3</sup>P<sub>2, 1, 0</sub>, <sup>1</sup>D<sub>2</sub>, <sup>1</sup>G<sub>4</sub>, <sup>3</sup>F<sub>4, 3, 2</sub> and <sup>3</sup>H<sub>6,5</sub> are responsible for Pr<sup>3+</sup> species in the glass matrix [9, 10].

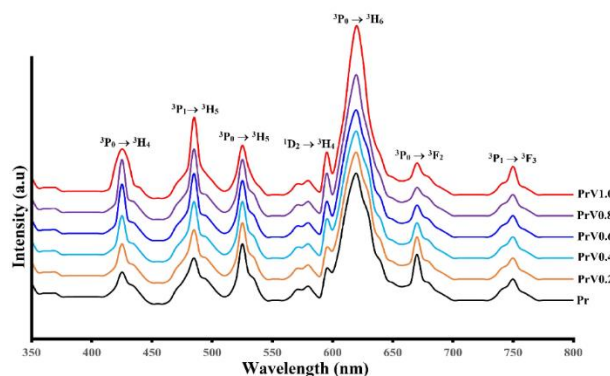
The established prominent hump absorption transition of Pr<sup>3+</sup> ions: <sup>3</sup>H<sub>4</sub> → <sup>3</sup>P<sub>2</sub> (at 445 nm), <sup>3</sup>H<sub>4</sub> → <sup>3</sup>P<sub>1</sub> (at 470 nm), <sup>3</sup>H<sub>4</sub> → <sup>3</sup>P<sub>0</sub> (at 484 nm), <sup>3</sup>H<sub>4</sub> → <sup>1</sup>D<sub>2</sub> (at 587 nm), <sup>3</sup>H<sub>4</sub> → <sup>1</sup>G<sub>4</sub> (at 1015 nm), <sup>3</sup>H<sub>4</sub> → <sup>3</sup>F<sub>4</sub> (at 1430 nm), <sup>3</sup>H<sub>4</sub> → <sup>3</sup>F<sub>3</sub> (at 1529 nm) and <sup>3</sup>H<sub>4</sub> → <sup>3</sup>F<sub>2</sub> (at 1943 nm). From the absorption spectra <sup>3</sup>H<sub>4</sub> → <sup>3</sup>P<sub>2, 1, 0</sub> and <sup>1</sup>D<sub>2</sub> are found in visible region and <sup>3</sup>H<sub>4</sub> → <sup>3</sup>F<sub>4, 3, 2</sub> and <sup>1</sup>G<sub>4</sub> are observed in the infrared region. M. Yamaga, B. Henderson and Y. Yosida reported that, the optical absorption spectra of V<sub>2</sub>O<sub>5</sub> doped glasses exhibited one broad absorption transition at 500 nm corresponding to <sup>2</sup>T<sub>2</sub> → <sup>2</sup>E<sub>2</sub> transition due to isolated V<sup>4+</sup> ions with octahedral symmetry [11].



**Figure 7:** Optical absorption spectra of CaO-PbO-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>: Pr<sup>3+</sup> - V<sup>4+</sup> ions co-doped glasses.

4.8 Photoluminescence Spectra

Figure 10: shows the luminescence spectra of CaO-PbO-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>: Pr<sup>3+</sup> - V<sup>4+</sup> ions co-doped glasses. The photoluminescence spectra is recorded at room temperature with an excitation wavelength (λ<sub>excitation</sub>) of 478 nm. The luminescence spectra of CaO-PbO-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> glasses contain Pr<sup>3+</sup> ions shows seven emission transitions [12, 13]. They are assigned as <sup>3</sup>P<sub>0</sub> → <sup>3</sup>H<sub>4</sub> (at 440 nm), <sup>3</sup>P<sub>1</sub> → <sup>3</sup>H<sub>5</sub> (at 490 nm), <sup>3</sup>P<sub>0</sub> → <sup>3</sup>H<sub>5</sub> (at 530 nm), <sup>1</sup>D<sub>2</sub> → <sup>3</sup>H<sub>4</sub> (at 595nm), <sup>3</sup>P<sub>0</sub> → <sup>3</sup>H<sub>6</sub> (at 625 nm), <sup>3</sup>P<sub>0</sub> → <sup>3</sup>F<sub>2</sub> (at 655 nm) and <sup>3</sup>P<sub>1</sub> → <sup>3</sup>F<sub>3</sub> (at 755 nm). K. Vera Prabhu and other researchers investigated that the emission spectra of V<sup>4+</sup> ions exhibited a band at around 619 nm with transition of <sup>2</sup>E → <sup>2</sup>T<sub>2</sub> [14]. By increasing concentration of V<sub>2</sub>O<sub>5</sub> in the glass system the hyper intense emission transition was observed at 625 nm due to <sup>3</sup>P<sub>0</sub> → <sup>3</sup>H<sub>6</sub> of Pr<sup>3+</sup> ions.



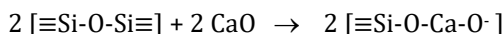
**Figure 10:** Photoluminescence spectra of CaO-PbO-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>: Pr<sup>3+</sup> - V<sup>4+</sup> ions co-doped glasses

5. Discussion

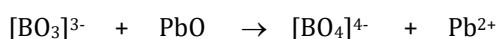
Glasses are randomly neutral network because all the metallic, non-metallic cations and non-metal anions are stabilized by connecting with bonding oxygen (BO) and NBO's. Glasses are combination of cation-oxygen-cation order with long geometrical symmetry and irregular linkers. NBO's act as charge balancing centres in the glass layout. In the present study of co-doped glasses, SiO<sub>2</sub> and B<sub>2</sub>O<sub>3</sub> are well known strong glass formers. SiO<sub>2</sub> is the primary glass former and B<sub>2</sub>O<sub>3</sub> is binary

glass former. In the borosilicate network SiO<sub>2</sub> is fundamental glass network former with SiO<sub>4</sub> tetrahedral structural units.

Borosilicate glasses contain ordered SiO<sub>4</sub>, BO<sub>3</sub> and BO<sub>4</sub> super-structural units are the back bones of the borosilicate network. The [SiO<sub>4</sub>]<sup>4-</sup>, [BO<sub>3</sub>]<sup>3-</sup> and [BO<sub>4</sub>]<sup>4-</sup> are super-structural units of silicate and borate in borosilicate glasses are fused to form borosilicate ordered long chains. Borosilicate glass structure consists of alternating pairs of silicate and borate tetrahedrons. Silicon atom has the ability to form longest chains containing millions of silicon atoms (Si<sup>4+</sup> cations). Borosilicate glasses having extensive ≡Si-O-Si≡ strong linkages in the silicon chain with silicon atom undergo *sp*<sup>3</sup> hybridization for 4-fold structural units. The *sp*<sup>3</sup> hybridization of silicon atom with oxygen atom is forming tetrahedron orientation along with the four corners of a tetrahedron having minimum repulsion between their electrons. The Si<sup>4+</sup> cation is at the centre of the tetrahedron. All these bonds are equal energies, tetrahedral SiO<sub>4</sub> in OSiO bond angle is 109° 05' and Si-O bond length is 162 pm. The Si-O-Si bonding angle between tetrahedrons varies from 120° to 180° and maximum at 144°. The Si-O-Si bonding angle distribution is the main key element in eliminating the three-dimensional periodicity of the glass structure and is comparable with Si-O bonding distances in the glass and glass environment. Borosilicate glasses are complex structure with 3D layout. The modifier CaO enters into the silicate network and depolymerizes to form meta, pyro and ortho silicates.



The modifier Ca<sup>2+</sup> cations creates NBO's and occupies interstitial position. B<sub>2</sub>O<sub>3</sub> is binary glass network former in the borosilicate glasses with 3-fold [BO<sub>3</sub>]<sup>3-</sup> and 4-fold [BO<sub>4</sub>]<sup>4-</sup> structural units. Addition of heavy metal modifier oxide (PbO) enters into borosilicate glasses, the glass samples became highly stable against devitrification and chemical inert. At low mol % of PbO (> 50 mol %) act as glass modifier. In the borosilicate glass layout the silicate and borate structural units in the network strongly interact without PbO modifier with its structural unit PbO<sub>4</sub> by creating NBO's. In borosilicate glasses it is generally agreed that addition of modifier oxide PbO converted [BO<sub>3</sub>] to [BO<sub>4</sub>] units.



In borosilicate glasses, the effect of silica on the boron-oxygen coordination and the possible inter-tetrahedral avoidance that exist between BO<sub>4</sub> and SiO<sub>4</sub> structural units. The 4-fold BO<sub>4</sub> entities dominate in the silicate-rich domain, whereas 3-fold boron entities prevail in the borate-rich hand and forms easily B-O-Si (Borosilicate Bridge) linkage. Each SiO<sub>4</sub> structural unit linked with one SiO<sub>4</sub> one BO<sub>4</sub> structural units and one oxygen from each unit linked with a metal ion and

leads the structural formation of long tetrahedral (4-fold) chains [15, 16]. Depolymerisation of glass network modifiers take up the interstitial space between networking polyhedral, breaking up the periodicity of bonding oxygen and forming more NBO's in the glass environment.

To study the structural evolution of prepared co-doped glasses Density ( $\rho$ ), Refractive Index ( $\mu$ ) and Molar Volume ( $V_m$ ) are the crucial physical parameters of the glass samples. The synthesized oxide glasses, the study of Density ( $\rho$ ), Refractive Index ( $\mu$ ) and Molar Volume ( $V_m$ ) of glasses becomes important to provide excellent information about structural bonding units, network forming units and network modifying units. The density of a glass sample is an important property of evaluating the compactness and short range structure of glasses. The refractive index of a glass sample is used to determine the suitability of glassy materials to be optical devices.

Decreasing density with decreasing trend in optical direct and indirect band gaps energy by increasing mol % of V<sub>2</sub>O<sub>5</sub> contribution in the glass layout. Average molecular weights (M) of glasses from Pr to PrV1.0 are in decreasing order, while the molar volume ( $V_m$ ) is increasing trend with V<sub>2</sub>O<sub>5</sub> content. Molar Volume ( $V_m$ ) of glass samples reciprocal to Average molecular weights (M) and density of the prepared glasses that indicating change in the geometrical configuration of glassy network is observed. The increasing V<sup>4+</sup> ion Concentration ( $N_i$ ) influence the variation intensity of ESR spectra of co-doped glassy network and increase free carrier absorption behaviour in the prepared glasses. The increasing refractive index of glasses verses with increasing quite trend in Urbach Energy ( $\Delta E$ ) is observed with increasing mol% of V<sub>2</sub>O<sub>5</sub>. The modification of structural compactness of glasses was observed from various other physical parameters like Polaron radius, field strength, and electronic polarizability values. Increase oxygen packing density (OPD) values of glasses indicates that increase distribution of oxide ions (O<sup>2-</sup>) in the prepared glass environment. The optical basicity value increase with V<sub>2</sub>O<sub>5</sub> content reveals with high electron donor ability of oxide ions to cations. Addition of Pr<sup>3+</sup> - V<sup>4+</sup> ions co-doped to the CaO-PbO-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> glass system causes strongly influenced the increase of NBOs, electron density carried by oxygen and decrease optical band gaps of these glasses with varying V<sub>2</sub>O<sub>5</sub> content was observed from calculated physical parameters.

The melt-quenching technique is a very simple method for the preparation of the transparent and stable glasses. Glasses were having randomly disordered structure and they don't have long range order. In borosilicate glasses the small molecular structural units like SiO<sub>4</sub> and BO<sub>4</sub> are monomer units. The borosilicate glasses have same type of arrangement of monomer structural units and it is arranged linearly like borosilicate monomers. The monomers of borosilicate structural units are joined together to form long straight chains like polymer

molecules. Borosilicate glasses contain arrangement of long, linear and cross-linked SiO<sub>4</sub> and BO<sub>4</sub> identical small borosilicate structural units to form borosilicate polymer glass network. Borosilicate glass structure is like danburite type structure.

The monomer units of borosilicate glasses which continually repeating the units in these glasses were observed from FT-IR vibrational spectra. At the glass formation SiO<sub>4</sub>, [BO<sub>3</sub>]<sup>3-</sup> and [BO<sub>4</sub>]<sup>4-</sup> structural units initially formed linear long chains are joined together to form a three dimensional geometric network. Borosilicate glasses are considered to be a composite glass composed of three network forming units namely SiO<sub>4</sub>, BO<sub>3</sub> and BO<sub>4</sub> groups in different proportions depending upon the glass composition. Silicon and Boron are typical non-metals forms only covalent bonds to form more bridging oxygens in the glass network and instantly react with more electropositive elements like Ca<sup>2+</sup> and Pb<sup>2+</sup> to form NBOs in the glass network. CaO and PbO acts as stabilizers in the glass system.

The FTIR frequency spectra of CaO-PbO-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>: Pr<sup>3+</sup>- V<sup>4+</sup> ions co-doped glasses exhibits various modes of bands with their structural frequencies. The first band ( $\nu_1$ ) at 450 cm<sup>-1</sup> attributed due to the stretching and symmetrical bending vibrations of Pb-O in PbO<sub>4</sub> units [17], the second band ( $\nu_2$ ) at 495 cm<sup>-1</sup> is due to the asymmetrical bending vibrations of ≡Si-O-Si≡ (strong, di-silicate linkage, Si<sub>2</sub>O<sub>7</sub>) associated with two SiO<sub>4</sub> structural units connected by one bridging oxygen, the third band ( $\nu_3$ ) at 698 cm<sup>-1</sup> due to the Symmetrical bending vibrations of ≡Si-O-Si≡ (strong, di-silicate linkage, Si<sub>2</sub>O<sub>7</sub>), the fourth band ( $\nu_4$ ) at 851cm<sup>-1</sup> due to Stretching Vibrations B-O bond of the BO<sub>4</sub> tetrahedral units, the fifth band ( $\nu_5$ ) at 990 cm<sup>-1</sup> due to Asymmetric vibration of B-O-Si≡ (Borosilicate Bridge, weak linkage) linkage units [18- 20] and the final band ( $\nu_6$ ) at 1390 cm<sup>-1</sup> due to due to Symmetric stretching relaxation of the B-O band of trigonal BO<sub>3</sub> structural units [21].

Borosilicate glass exhibits energy barrier order of breaking cation-oxygen-cation linkages strength sequence of ≡Si-O-Si≡ > B-O-Si≡ > B-O-B depend on introduction of the network modifiers like CaO, PbO, V<sub>2</sub>O<sub>5</sub> and Pr<sub>2</sub>O<sub>3</sub>. The mixing of the borate and silicate through sub-network formation of Si-O-B Bridge. The width of FTIR bands decrease with varying mol % of V<sub>2</sub>O<sub>5</sub> content. The gradual increase of mol% of V<sub>2</sub>O<sub>5</sub> content in these glasses, the FT-IR line intensities of the frequency bands decreased due to increase of structural modifications and compactness of the glass layout. Vanadium cations like Ca<sup>2+</sup> and Pb<sup>2+</sup> ions are expected to depolymerize in the glass network by producing more donor centres defects and NBO's. By increase mol % of V<sub>2</sub>O<sub>5</sub> in the glass matrix, it was identified that the formation of large number of NBO's thus it indicates creation of more NBO's reduces the

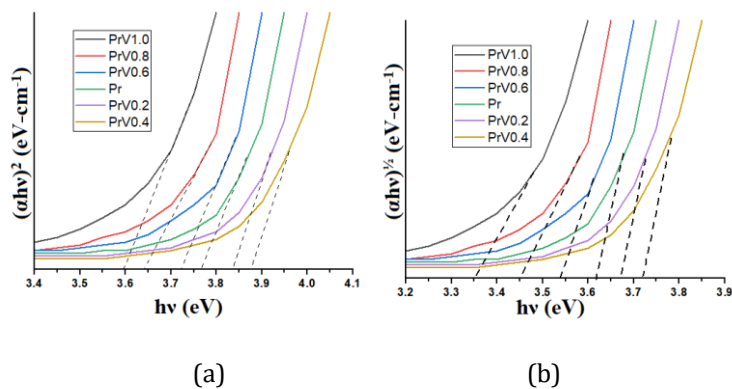
connectivity of the glass network. Addition of CaO, PbO, Pr<sub>2</sub>O<sub>3</sub> and V<sub>2</sub>O<sub>5</sub> into borosilicate network, the linear ordered long chains are transformed to randomly and cross-linked network give well packed structure due to formation of more NBO's and more metal ion centres. The isolated V<sup>4+</sup> cations are standard modifiers enters into the glass network occupies interstitial position like Pb<sup>2+</sup> cation. The isolated V<sup>4+</sup> octahedral cations (O<sub>h</sub>) in the glass network the creation of more V<sup>4+</sup> donor centres is expected.

The most favours of glasses where depends on optical transparency in the visible region in a designed range of wavelength. In the Calcium lead borosilicate glasses, the Pr<sup>3+</sup> and V<sup>4+</sup> cations are easily enters into the glass network and distributed randomly entire glass layout. Optical absorption spectra of glasses is a technical tool, to study the optical transition and electronic band structure between Pr<sup>3+</sup> and V<sup>4+</sup> ions co-doped CaO-PbO-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> glasses. While gradual increase of V<sub>2</sub>O<sub>5</sub> content the area of the absorption transition of <sup>3</sup>H<sub>4</sub>→<sup>3</sup>P<sub>2</sub> decreases instantly the area of the absorption transition of <sup>3</sup>H<sub>4</sub> →<sup>3</sup>P<sub>0</sub> increase is observed form the Figure 7. Among all the transitions a notable <sup>3</sup>H<sub>4</sub> → <sup>3</sup>P<sub>0</sub> is identified hypersensitive transition and highest intense. The V<sup>4+</sup> cation has 3d<sup>1</sup> electronic configuration which means there is only one excited E<sub>g</sub> state [22]. The octahedral V<sup>4+</sup> (3d<sup>1</sup>) cations in the CaO-PbO-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-Pr<sub>2</sub>O<sub>3</sub> glass network, the <sup>2</sup>D ground state (Russell-Saunders) splits into a lower energy <sup>2</sup>T<sub>2g</sub> and higher energy <sup>2</sup>E<sub>2g</sub>. There are no higher laying terms and levels for a d<sup>1</sup> ion, so the only one possible transitions are from <sup>2</sup>T<sub>2g</sub> → <sup>2</sup>E<sub>2g</sub> giving rise to a single transition in the UV-vis wavelength region.

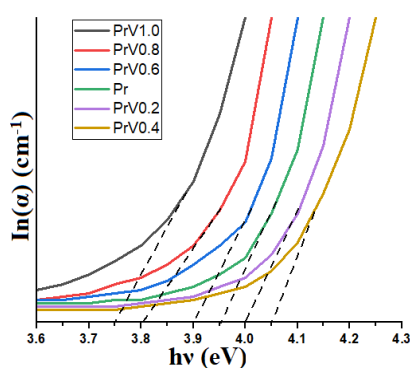
From the observed absorption edges, we have evaluated the optical band gaps (E<sub>o</sub>) of these glasses by drawing Tauc plots between (αhv)<sup>1/2</sup> and hv as per the following equation

$$\alpha(v) hv = C (hv - E_o)^n \quad \dots\dots\dots (1)$$

Here the exponent (n) can take values 1/2 and 2 for indirect, direct transitions and C is a constant in glasses respectively [23]. Tauc plots for direct transition are shown in Figure.11 (a) and indirect transitions are shown in Figure 11 (b). Extrapolating the linear portion of these plots as (αhv)<sup>1/2</sup> = 0, (αhv)<sup>2</sup> = 0 gives optical band gap, the theoretical band gap energy is calculated using the equation E=hc/λ. Urbach Energy (ΔE) was evaluated from the slopes of the linear regions of the curves and taking their reciprocals. Urbach Energy (ΔE) that indicates a measure of a disorder in glassy environment are shown in Figure 12. The cut-off wavelength (λ<sub>c</sub>), direct and indirect band energy gaps and Urbach Energy (ΔE) data is given in Table 5.



**Figure 11** (a) & 11 (b): Tauc plots to evaluate (a) direct band gap (b) In-direct band gap of CaO-PbO-B<sub>2</sub>O<sub>3</sub>- SiO<sub>2</sub>: Pr<sup>3+</sup>- V<sup>4+</sup> ions co-doped glasses



**Figure 12:** A plots of  $\ln(\alpha)$  and  $h\nu$  for CaO-PbO-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>: Pr<sup>3+</sup>- V<sup>4+</sup> Ions co-doped glasses

**Table 5:** The cut-off wavelength ( $\lambda_c$ ), Optical band gaps ( $E_g$ ) and Urbach energy of CaO-PbO-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>: Pr<sup>3+</sup> - V<sup>4+</sup> ions co-doped glasses

Glass Sample	Cut-off wavelength ( $\lambda_c$ ) (nm)	Theoretical Band gap (eV)	Direct Band gap (eV)	Indirect Band gap (eV)	Urbach energy ( $\Delta E$ ) (eV)
Pr	324	3.689	3.739	3.592	0.2879
PrV0.2	331	3.752	3.845	3.604	0.2966
PrV0.4	339	3.681	3.879	3.649	0.2897
PrV0.6	342	3.644	3.696	3.534	0.3336
PrV0.8	345	3.581	3.606	3.456	0.3556
PrV1.0	348	3.543	3.589	3.357	0.3573

From the Table.5 It was observed that direct and indirect optical band gaps energy decreasing trend while increasing mol% of V<sub>2</sub>O<sub>5</sub> content. The cut-off wavelength ( $\lambda_c$ ) of all prepared glass samples were shifted towards higher wavelength region in absorption spectra and at the same instant Urbach Energy ( $\Delta E$ ) values increasing trend with introduction of V<sub>2</sub>O<sub>5</sub> was observed from Table 5.

In the present study of co-doped glasses, while gradual increase of V<sub>2</sub>O<sub>5</sub> content, the decreasing density with the increasing molar volume indicates the successive replacement of Pb<sup>2+</sup> by V<sup>4+</sup> cations. The total number of Pr<sup>3+</sup> (4f<sup>2</sup>) ion exhibits 91 quantum states. Pr<sub>2</sub>O<sub>3</sub> enters into the glass network as a modifier and Pr<sup>3+</sup> ions occupy interstitial positions with 6-fold coordination in the glass environment [24]. The V<sup>4+</sup> ions has 3d<sup>1</sup> electronic configuration and exist as Oxo-Cation (VO<sup>2+</sup>- Vanadyl) exhibit d-d transitions

reach absorption band in the glass samples. The free carrier concentration of the different composition changes in the different manner with the varying of V<sub>2</sub>O<sub>5</sub> content. As V<sup>4+</sup> ions is usually coordinated to six oxygen ligands forming an octahedral complex and with one oxygen as ligand, one V-O band becomes very distant which is termed as Vanadyl ion (VO<sup>2+</sup>) [25]. The vanadyl oxygen which leads in an increased bond length of vanadyl oxygen thereby improving the octahedral nature of the V<sup>4+</sup> (O<sub>6</sub>) complexes [26]. The Optical absorption spectra was identified presence of the isolated VO<sup>2+</sup> species in the prepared glasses.

The lowest optical band gap is observed for PrV1.0 glass due to large formation oxygen sensing response influences the degree of localization of electrons by creating more donor centres in the glass matrices increasing V<sub>2</sub>O<sub>5</sub> content. The higher values of Urbach Energy ( $\Delta E$ ) in the present study of co-doped glasses



suggests that modification of geometrical configuration of glassy network which turns increase degree of distortion of glasses, increase of NBO's and formation of V<sup>4+</sup> - V<sup>4+</sup> donor centres while increasing V<sub>2</sub>O<sub>5</sub> mol % content. The isolated V<sup>4+</sup> cations obviously present in these prepared glasses and occupy interstitial positions like Pr<sup>3+</sup> simple ion.

The quantitatively comprehend Optical phenomena of rare earth ions in glasses, it is of great importance to evaluate radiative and non-radiative decay process of related 4f levels. The Judd-Ofelt theory is usually adopted to obtain the transition probabilities including radiative decay rate by utilizing the data of absorption cross sections of several f-f electric-dipole transitions. From the optical absorption spectra, the calculated and experimental oscillator strengths of the absorption transitions are estimated in terms of the area under an absorption peak.

$$f_{exp} = 4.32 \times 10^{-9} \int \epsilon(\nu) d\nu \quad \text{----- (2)}$$

Where  $\epsilon(\nu)$  denotes the molar extinction coefficient at a wave number  $\nu$  in cm<sup>-1</sup>.

According to the J-O theory [27, 28] the oscillator strength of electric-dipole f-f transition of trivalent rare earth ions from a level ( $\psi_j$ ) to a particular final state ( $\psi'_j$ ) is given as

$$f(\psi_j; \psi'_j) = \frac{v}{(2j+1)} \left[ \frac{8\pi^2 m c (n^2 + 2)^2}{3h(9n)} \right] \sum_{\lambda=2,4,6} \Omega_{\lambda} \langle (\psi_j || U^{\lambda} || \psi'_j) \rangle^2 \quad \text{--- (3)}$$

where 'm' refer to the mass of the electron, 'c' is the velocity of light in vacuum, 'h' is the plank's constant, J and J' are the total angular moment of the initial and final levels, n is the refractive index of refraction of the glass,  $\Omega_{\lambda}$  ( $\lambda=2, 4, 6$ ) are the material parameters and  $\langle U_{\lambda} \rangle^2$  are the doubly reduced matrix elements of the unit tensor operator of the rank  $\lambda=2, 4$  and 6. The rms deviations between the experimental and calculated energy value are very small, indicating the validity of the full matrix diagonalization.

$$\delta_{rms} = \sqrt{\left[ \frac{\sum (f_{exp} - f_{cal})^2}{N} \right]} \quad \text{----- (4)}$$

Where N is the total number of transitions involved in the fitting

Applied J-O intensity parameters  $\Omega_{\lambda}$  ( $\lambda=2, 4, 6$ ) are evaluated from the least square fitting procedure using experimentally measured oscillator strength for Pr<sup>3+</sup> - V<sup>4+</sup> ions co-doped CaO-PbO-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> glasses, the obtained values are given in Table 6. Applied J-O intensity parameters determined in the present glass network are observed to be in the trend  $\Omega_4 > \Omega_6 > \Omega_2$  as shown in Table 7.

**Table 6:** Theoretical and experimental oscillator strength of CaO-PbO-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>: Pr<sup>3+</sup> - V<sup>4+</sup> ions co-doped glasses

Transition from	GLASS SAMPLES											
	Pr	PrV0.2		PrV0.4		PrV0.6		PrV0.8		PrV1.0		
$f_{cal}$ (x10 <sup>-6</sup> )	$f_{exp}$ (x10 <sup>-6</sup> )	$f_{cal}$ (x10 <sup>-6</sup> )	$f_{exp}$ (x10 <sup>-6</sup> )	$f_{cal}$ (x10 <sup>-6</sup> )	$f_{exp}$ (x10 <sup>-6</sup> )	$f_{cal}$ (x10 <sup>-6</sup> )	$f_{exp}$ (x10 <sup>-6</sup> )	$f_{cal}$ (x10 <sup>-6</sup> )	$f_{exp}$ (x10 <sup>-6</sup> )	$f_{cal}$ (x10 <sup>-6</sup> )	$f_{exp}$ (x10 <sup>-6</sup> )	
<sup>3</sup> H <sub>4</sub>	5.7613	5.7849	5.8554	5.8917	5.8431	5.8769	5.8116	5.8291	5.7518	5.7613	5.5912	5.6119
<sup>3</sup> P <sub>2</sub>	3.8416	3.8637	3.9029	3.9359	3.8645	3.8921	3.8579	3.8816	3.8376	3.8792	3.8389	3.8593
<sup>3</sup> P <sub>1</sub>	4.0256	4.0478	4.1468	4.2309	4.3359	4.2116	4.4871	4.4941	4.5024	4.5359	4.5994	4.6246
<sup>1</sup> D <sub>2</sub>	1.5071	1.5286	1.6245	1.6355	1.6007	1.6209	1.5469	1.5718	1.5194	1.5364	1.4934	1.5167
<sup>1</sup> G <sub>4</sub>	0.9567	0.9651	0.9861	0.9985	0.9729	0.9825	0.9671	0.9746	0.9506	0.9685	0.9419	0.9522
<sup>3</sup> F <sub>4</sub>	1.8763	1.9121	1.9397	1.9426	1.8971	1.9351	1.8821	1.9297	1.8868	1.9217	1.8652	1.8919
<sup>3</sup> F <sub>3</sub>	3.3915	3.4768	3.4198	3.5251	3.2178	3.5116	3.9112	3.4912	3.8611	3.4837	3.2116	3.4619
<sup>3</sup> F <sub>2</sub>	2.3576	2.3615	2.3819	2.4791	2.2237	2.4354	2.1573	2.3909	2.1947	2.3793	2.1436	2.3415
Rms deviation	0.0394		0.0656		0.0594		0.0612		0.0532		0.0469	

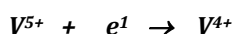
**Table 7:** J-O Parameters of CaO-PbO-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>: Pr<sup>3+</sup> - V<sup>4+</sup> ions co-doped glasses

Glasses Samples	$\Omega_2 \times 10^{-20}$ (cm <sup>-2</sup> )	$\Omega_4 \times 10^{-20}$ (cm <sup>-2</sup> )	$\Omega_6 \times 10^{-20}$ (cm <sup>-2</sup> )	Trend
Pr	0.69	4.65	3.78	$\Omega_4 > \Omega_6 > \Omega_2$
PrV0.2	0.54	4.41	3.72	$\Omega_4 > \Omega_6 > \Omega_2$
PrV0.4	0.65	4.69	3.76	$\Omega_4 > \Omega_6 > \Omega_2$
PrV0.6	0.61	4.67	3.79	$\Omega_4 > \Omega_6 > \Omega_2$
PrV0.8	0.51	4.62	3.75	$\Omega_4 > \Omega_6 > \Omega_2$
PrV1.0	0.49	4.74	3.89	$\Omega_4 > \Omega_6 > \Omega_2$

The J-O parameter of  $\Omega_2$  is sensitive to the symmetry of the rare-earth ion site and strongly affected by covalence between rare-earth ion and ligand ions, moreover  $\Omega_4$  and  $\Omega_6$  of J-O parameters are related to the rigidity of the host medium in which the ions are situated [29, 30].

The vanadium metal is versatile neutral atom (V) contains 23 electrons and electronic configuration is presented as [Ar] 3d<sup>3</sup> 4s<sup>2</sup> (ground state) and [Ar] 3d<sup>5</sup> 4s<sup>0</sup> (excited state). Vanadium is a d-block element that forms different compounds with oxygen atom. They are VO (Vanadium monoxide), VO<sub>2</sub> (Vanadium

dioxide), V<sub>2</sub>O<sub>3</sub> (Vanadium trioxide) and V<sub>2</sub>O<sub>5</sub> (Vanadium Pentoxide). Among all these V<sub>2</sub>O<sub>5</sub> is most stable phase of forming oxygen vacancies (V<sub>o</sub>) are the most common defect in V<sub>2</sub>O<sub>5</sub> doped Glasses [31]. The vanadium ion exhibits different oxidation states such as +3 (Trivalent), +4 (Tetraivalent) and +5 (Pentavalent) depending on the addition of vanadium compound and mol % in the glass composition. The V<sup>5+</sup> ions has 3d<sup>0</sup> electronic configuration and as such it will not give rise to d-transitions and no EPR signal since it contains no d-electrons. During the melting process, the reduction of V<sup>5+</sup> ions to V<sup>4+</sup> ions to balance the electric charges in CaO-PbO-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-Pr<sub>2</sub>O<sub>3</sub> glasses. The isolated V<sup>4+</sup> ions are stabilized in these glasses according to the following equilibria.



**Table 8:** The Spin-Hamiltonian Parameters of VO<sup>2+</sup> - Pr<sup>3+</sup> ions co-doped CaO-PbO-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> glasses

Glass Sample	g <sub>  </sub>	g <sub>⊥</sub>	A <sub>  </sub>  x10 <sup>-4</sup> cm <sup>-1</sup>	A <sub>⊥</sub>   x10 <sup>-4</sup> cm <sup>-1</sup>	P x10 <sup>-4</sup> cm <sup>-1</sup>	k
PrV0.2	1.9672	1.9711	171.41	64.79	141	0.75
PrV0.4	1.9665	1.9743	173.66	67.65	143	0.76
PrV0.6	1.9654	1.9761	176.58	71.26	144	0.78
PrV0.8	1.9643	1.9782	178.35	73.58	147	0.79
PrV1.0	1.9636	1.9795	183.47	75.89	149	0.81

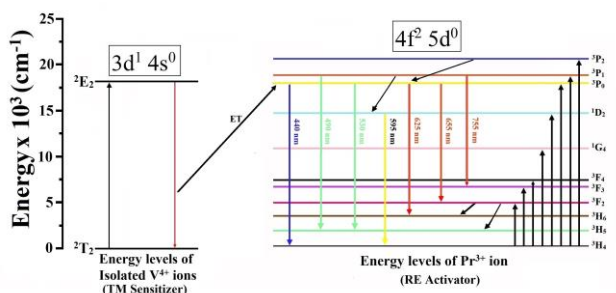
The spin-Hamiltonian parameters in order to know the site symmetry around VO<sup>2+</sup> ions in these glasses. The spin-Hamiltonian parameters are very sensitive ligands present around the transition metal ion and also the glass composition. The variation of g<sub>||</sub> and g<sub>⊥</sub> depends critically on the local symmetry of this field. From Spin-Hamiltonian calculations, it was clearly observed that the value of g<sub>||</sub> decrease while g<sub>⊥</sub> increase with increasing concentration of V<sub>2</sub>O<sub>5</sub> in these co-doped glasses. From the Table: 8 the experimental EPR results it is clearly observed that the g-factor was found increasing in the relation of g<sub>||</sub> < g<sub>⊥</sub> < g<sub>e</sub> and |A<sub>||</sub>| > |A<sub>⊥</sub>| confirmed would give paramagnetic cation V<sup>4+</sup> (3d<sup>1</sup>, S=+1/2) occupy octahedral geometry with tetragonal compression with contribute to the many magnetic interactions. From Spin-Hamiltonian parameters calculations, it was observed that exist of VO<sup>2+</sup> ions [35-37] in octahedral geometry with tetragonal compression and have C<sub>4v</sub> symmetry. Hyperfine interactions between the electron spin and remote magnetic nuclei present the surroundings of the paramagnetic V<sup>4+</sup> species. Isotropic EPR spectra of isolated V<sup>4+</sup> paramagnetic ion is expected to show a hyperfine structure composed of eight lines resulting from the dipole-dipole interaction between the magnetic moment of the <sup>51</sup>V nuclei (I=±7/2) and the electronic moment of the V<sup>4+</sup> metal ion [38]. The electron in 3d<sup>1</sup> configuration (V<sup>4+</sup> ion), either the d<sub>z<sup>2</sup></sub> or d<sub>xy</sub> orbital is concluded to hold the unpaired electrons [39]. The ESR spectrum of all the glass samples are investigated and exhibited a single resonance signal at g= 1.9857 which are responsible of isolated V<sup>4+</sup> ions [40].

The vanadium impurity is homogeneously distributed into the glassy environment as paramagnetic V<sup>4+</sup> metal centres like Oxo-Cations. The V<sup>4+</sup> ion (3d<sup>1</sup>) (s=1/2) exhibits 10 quantum-states. The EPR spectra shows between first derivation of absorbance verses magnetic field (mT). The V<sup>4+</sup> ions are arranged in low dimensional structure in the prepared glasses. From the EPR spectra, it is a notable highest intense of equidistant two sets of eight lines are observed (sixteen-line hyperfine pattern) [32-34]. The V<sub>2</sub>O<sub>5</sub> content gradually increase in the glass composition the increase EPR line intensities proving that V<sup>4+</sup> paramagnetic metal centres. From the EPR spectra data, the spin-Hamiltonian parameters evaluated are presented in the Table 8.

Optical absorption spectra and photoluminescence spectra are the function of co-dopants of REI, TMI and wavelength. Photoluminescence spectroscopy gives information only the low lying energy levels of the investigated co-doped glass systems. Emission transitions of Pr<sup>3+</sup> ions execute different colour transitions with radiative and non-radiative transitions. The Pr<sup>3+</sup> ions have the ability to show four level laser action associated with transitions from <sup>3</sup>P<sub>0</sub> state in certain host systems and are potentially active ions for visible laser generation. Emission quantity efficiency from a given energy level strongly depend upon the phonon energy of the host medium. The intensity of the emission spectra was found to be dependent on the both types of glass composition and co-dopants of TMI and REI. The change in radiative emission life time depends on the refractive index of the surround medium of the glass composition. Pr<sup>3+</sup> ions exhibits very different visible spectra emission transitions contribution of V<sup>4+</sup> ions in the glass system. The period between absorption and emission transitions are typically short.

All these bands occurred within the 4f<sup>2</sup>-4f<sup>2</sup> transitions of the Pr<sup>3+</sup> simple ions. Under an excitation wavelength of 478 nm the Pr<sup>3+</sup> simple ion are quickly excited from the ground state <sup>3</sup>H<sub>4</sub> level to the higher <sup>3</sup>P<sub>2</sub> excited level. The non-radiative emission takes place from <sup>3</sup>P<sub>2</sub> excited level to the <sup>3</sup>P<sub>1</sub> and <sup>3</sup>P<sub>0</sub> lower excited levels. Upon excitation with 478 nm <sup>3</sup>P<sub>2</sub>, 1, 0 depopulation form higher energy bands occurred to the metastable <sup>3</sup>P<sub>0</sub> energy level. From PL spectra analysis hyper intense of <sup>3</sup>P<sub>0</sub> → <sup>3</sup>H<sub>6</sub> emission transition of Pr<sup>3+</sup> ions spectral overlaps with <sup>2</sup>E → <sup>2</sup>T<sub>2</sub> transition

of V<sup>4+</sup> metal ions, since there is a chance of non-radiative energy transfer through multi-pole interaction. In this present study, the energy of V<sup>4+</sup> emission transition <sup>2</sup>E → <sup>2</sup>T<sub>2</sub> is transformed to <sup>3</sup>P<sub>0</sub> → <sup>3</sup>H<sub>6</sub> transitions of Pr<sup>3+</sup> ion that is represented in the simplified energy level diagram of Figure: 13.



**Figure 13:** Simplified Energy level diagram of CaO-PbO-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>: Pr<sup>3+</sup> - V<sup>4+</sup> ions co-doped glasses

The significant high intense emission transition of Pr<sup>3+</sup> ion through the addition of V<sup>4+</sup> ion suggests that <sup>3</sup>P<sub>0</sub> → <sup>3</sup>H<sub>6</sub> level of Pr<sup>3+</sup> ions are populated due to energy transfer from V<sup>4+</sup> ions (V<sup>4+</sup> → Pr<sup>3+</sup>). All the observed emission transitions originated mostly from the <sup>3</sup>P<sub>0</sub> populated energy level. The non-radiative transition probability was found to increasing in the order of <sup>1</sup>D<sub>2</sub> < <sup>3</sup>P<sub>1</sub> < <sup>3</sup>P<sub>0</sub> in all prepared glasses. Here <sup>3</sup>P<sub>2, 1, 0</sub> and

<sup>1</sup>D<sub>2</sub> are populated energy levels of Pr<sup>3+</sup> ions for emission of visible (Blue, Green, Yellow or Red) color. The energy transfer efficiency of sensitizer –activator between TM and RE ions of the glass system depends on the chemical composition, mol % co-dopants, glass melting temperature and chemical nature of the co-dopants.

The mechanism of photoluminescence is that, after excitation of Pr<sup>3+</sup> ions to <sup>3</sup>P<sub>2</sub> states, non-radiative de excitation occurred from <sup>3</sup>P<sub>2</sub> to <sup>3</sup>P<sub>1</sub>, <sup>3</sup>P<sub>0</sub> and <sup>1</sup>D<sub>2</sub> states. Finally, the photon emission takes place from <sup>3</sup>P<sub>1</sub>, <sup>3</sup>P<sub>0</sub> and <sup>1</sup>D<sub>2</sub> states to lower lying states. Figure.13 significantly reveals that, the intense de-excitations are occurred mainly from <sup>3</sup>P<sub>0</sub> and <sup>1</sup>D<sub>2</sub> excited bands. V<sup>4+</sup> ions give emission due to <sup>2</sup>E<sub>2g</sub> → <sup>2</sup>T<sub>2g</sub> transition and this spectrum of V<sup>4+</sup> overlaps with <sup>3</sup>P<sub>0</sub> → <sup>3</sup>H<sub>6</sub> absorption of Pr<sup>3+</sup> simple ion. Hence the charge transfer and change of non-radiative energy transfer through multi-pole interaction. The remarkable strengthening of the emission band of the Pr<sup>3+</sup> ions through the introduction of V<sup>4+</sup> ion suggests that <sup>3</sup>P<sub>0</sub> → <sup>3</sup>H<sub>6</sub> level of Pr<sup>3+</sup> ions is also populated due to energy transfer from V<sup>4+</sup> ions. Applying J-O intensity parameters Branching ratio “β” (that defines the luminescence efficiency of the transition) of orange emission due to <sup>3</sup>P<sub>0</sub> → <sup>3</sup>H<sub>6</sub> transition is calculated and shown in Table: 9.

**Table 9:** Various radiative properties of CaO-PbO-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>: Pr<sup>3+</sup> - V<sup>4+</sup> ions co-doped glasses

Transitions	GLASS SAMPLES											
	Pr		PrV0.2		PrV0.4		PrV0.6		PrV0.8		PrV1.0	
	A(s <sup>-1</sup> )	β%	A(s <sup>-1</sup> )	β%	A(s <sup>-1</sup> )	β%	A(s <sup>-1</sup> )	β%	A(s <sup>-1</sup> )	β%	A(s <sup>-1</sup> )	β%
<sup>3</sup> P <sub>0</sub> → <sup>3</sup> H <sub>4</sub>	2316	14.15	2443	15.24	2386	14.57	2348	42.29	2291	13.68	2258	13.72
<sup>3</sup> P <sub>1</sub> → <sup>3</sup> H <sub>5</sub>	2756	42.51	2896	44.24	2843	43.76	2731	43.26	2694	41.36	2651	40.11
<sup>3</sup> P <sub>0</sub> → <sup>3</sup> H <sub>5</sub>	921	11.69	1019	11.96	1006	11.75	966	10.64	929	10.21	904	10.09
<sup>1</sup> D <sub>2</sub> → <sup>3</sup> H <sub>4</sub>	608	6.54	712	7.19	694	6.78	675	6.51	645	6.31	591	6.13
<sup>3</sup> P <sub>0</sub> → <sup>3</sup> H <sub>6</sub>	2946	49.63	3122	53.43	3077	51.68	3010	60.12	2981	58.76	2914	48.46
<sup>3</sup> P <sub>0</sub> → <sup>3</sup> F <sub>2</sub>	1542	13.42	1610	2.87	1570	13.87	1556	14.49	1516	13.78	1381	13.46
<sup>3</sup> P <sub>1</sub> → <sup>3</sup> F <sub>3</sub>	1361	14.44	1390	16.34	1381	15.96	1373	14.84	1350	24.76	1339	13.21
At (s <sup>-1</sup> )	7451.33		9564.87		8296.87		8067.59		5234.27		7109.94	

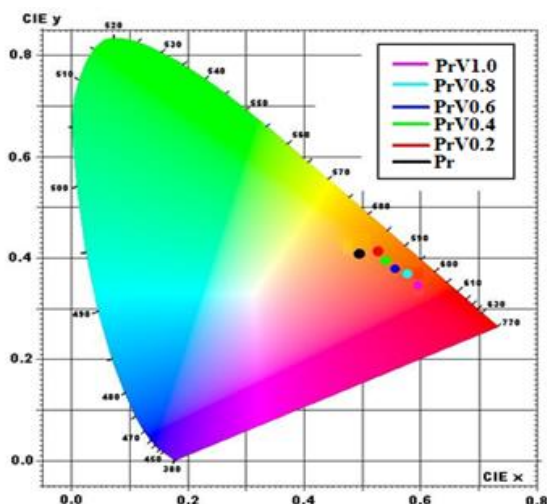
The comparison of “β” for all prepared glass samples, suggests good value for the glass PrV1.0. From this observations suggests that, 1.0 mol% of V<sub>2</sub>O<sub>5</sub> is more optimal concentration in this glass matrix to produce high luminescence efficiency. The energy level of Pr<sup>3+</sup> close to the V<sup>4+</sup> emitting state, indicates that possibility of energy transfer takes place from tetravalent vanadium to trivalent praseodymium ion. This energy transfer mechanism suggests dipole-dipole in nature. The large value of energy transfer probabilities and transfer efficiencies suggest that V<sup>4+</sup> ions acts as good sensitizer for Pr<sup>3+</sup> ions acts as good activator in CaO-PbO-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> glasses. CIE chromaticity coordinates for all co-doped glass samples are evaluated and the results are shown Figure: 14 and Table: 10.

**Table 10:** The color coordinates of CaO-PbO-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>: Pr<sup>3+</sup> - V<sup>4+</sup> ions co-doped glasses.

Glasses Samples	X	Y
Pr	0.49784	0.42375
PrV0.2	0.52894	0.41357
PrV0.4	0.54326	0.39561
PrV0.6	0.55641	0.37548
PrV0.8	0.57916	0.37014
PrV1.0	0.59501	0.35786

The emitting colors of the glasses varies from orange to orange red with an increasing concentrations of V<sub>2</sub>O<sub>5</sub>. The CIE chromaticity coordinates for PrV0.8, PrV1.0

lies in orange-red region. This glass can be recommended as a good host that can emit bright reddish-orange laser [41]. From this reason, CaO-PbO-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>: Pr<sup>3+</sup> - V<sup>4+</sup> ions co-doped glasses have high potential applications in the field of optical fibers, LED displays, glass probes and optical applications.



**Figure 14:** The color space chromaticity diagram of CaO-PbO-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>: Pr<sup>3+</sup> - V<sup>4+</sup> ions co-doped glasses

## Conclusion

The synthesized series of CaO - PbO - B<sub>2</sub>O<sub>3</sub> - SiO<sub>2</sub> glasses were co-doped with Pr<sup>3+</sup> - V<sup>4+</sup> ions by conventional melt-quenching technique. The glasses were characterized by XRD, FTIR, Optical Absorption, EPR and Photoluminescence spectra. The main conclusion of this present paper are as follows:

1. Various physical parameters of all glass samples were evaluated. The transition metal ions concentration, density and molar volume of all the studied glasses were strongly influenced the modification in the structural alteration of glasses, structural compactness and decrease of bridging oxygen atoms (BO) with increasing V<sub>2</sub>O<sub>5</sub> concentration.
2. The Refractive index of Pr<sup>3+</sup>- V<sup>4+</sup> ions co-doped CaO-PbO-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> glasses are function of wavelength ( $\lambda$ ). While refractive index (n) increase with wavelength ( $\lambda$ ) by increasing mol% of V<sub>2</sub>O<sub>5</sub> content.
3. From the XRD spectra, it is clear indication and confirm co-doped glassy samples was amorphous nature without sharp peaks. From DTA analysis of all the glasses reveal PrV1.0 glass is highly stable against devitrification.
4. From FTIR studies reveals the beneficial of SiO<sub>4</sub>, BO<sub>3</sub> and BO<sub>4</sub> local structural oscillators in CaO-PbO-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> glasses co-doped with Pr<sub>2</sub>O<sub>3</sub> and V<sub>2</sub>O<sub>5</sub>.
5. The Optical Absorption measurements like cut-off wavelength ( $\lambda_c$ ), direct and indirect band gaps energy values are evaluated for all glass samples.

The lower value of optical band gap of PrV1.0 indicates higher degrees of disorder of this glass.

6. The Pr<sup>3+</sup> ions exhibits in several absorption and emission transitions in the contained glass network. In the present paper study, the Optical absorption spectra and Luminescence spectra were characterized by applied J-O parameters.
7. From the PL spectra of CaO-PbO-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>: V<sup>4+</sup> - Pr<sup>3+</sup> ions co-doped glasses, it is observed that <sup>3</sup>P<sub>0</sub> → <sup>3</sup>H<sub>6</sub> significant a notable transition falls in bright reddish-orange region at 625 nm (1.98 eV) due to energy transfer from <sup>2</sup>E<sub>2g</sub> → <sup>2</sup>T<sub>2g</sub> transition of V<sup>4+</sup> ions to <sup>3</sup>P<sub>0</sub> → <sup>3</sup>H<sub>6</sub> levels of Pr<sup>3+</sup> ions.
8. From the Optical Absorption spectra and Photoluminescence spectra results V<sup>4+</sup> ions occupy higher coordination of octahedral (O<sub>h</sub>) symmetry of these co-doped all glass samples.
9. From the EPR Spectra results all the prepared and co-doped glasses exhibited strong hyperfine intense resonance signals in presence of isolated VO<sup>2+</sup> paramagnetic molecular ions. Analysis of EPR spectra shows relation of g<sub>||</sub> < g<sub>⊥</sub> < g<sub>e</sub> and |A<sub>||</sub>| > |A<sub>⊥</sub>| indicating VO<sup>2+</sup> molecular ions are stabilized in octahedral geometry with tetragonal compression. The resolved hyperfine structure and centering of signal around **g=1.9857**.
10. Calcium lead borosilicate glass co-doped with V<sup>4+</sup> and Pr<sup>3+</sup> ions because of the spectroscopic properties of 3d<sup>1</sup> → 4f<sup>2</sup> transfer of electron (Isolated energy transfer of d<sup>1</sup> → f<sup>2</sup>) which are great interest for application in laser and have high novel luminescent efficiency.
11. The isolated d<sup>1</sup> → f<sup>2</sup> charge transfer is type of metal to metal intervalence charge transfer state levels of the d → f transition of V<sup>4+</sup> - Pr<sup>3+</sup> ions co-doped CaO-PbO-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> glass system.
12. From the CIE chromaticity coordinates, it was identified that PrV1.0 glass fall in bright reddish-orange. The PrV1.0 glass have wide range potential technological applications in optical components, optoelectronic devices, optical temperature sensors, memory devices and sensors.

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