Journal of Metals, Materials and Minerals, Vol. 30, No. 3, pp. 101-112, 2020

Observation of structural, spectral characterizations and correlation of physical parameters on VO^{2+} ions doped Cadmium Lithium Sodium Borate glasses

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Received date:
4 April 2020
Revised date:
6 June 2020
Accepted date:
18 June 2020

Keywords:
Oxide ion polarizability ($\propto_{O^{2-}}$) optical basicity (Λ)
3rd order nonlinear optical polarizability ($\chi^{(3)}$)
Interaction parameter (A)

Abstract

A series of quinary 0.1 mol% VO^{2+} doped Cadmium Lithium Sodium Borate (CLNB) glass system with varying alkali (Li_2O/Na_2O) content were prepared by the classical melt quenching technique. The current research was carried out to observe the physical, structural and spectral parameters alter with the variation of alkali content in nonlinear manner. Physical properties such as the oxide ion polarizability ($\propto_{O^{3-}}$), optical basicity of prepared glass (Λ_{th}), Yamashita and Kuroswa's interaction parameter (A) and the third order nonlinear optical polarizability ($\chi^{(3)}$) are calculated by compared with altering the alkali mol% and also correlate them with each other. Physical parameters are varying in non-regular pattern and were substantiated to presence of the mixed alkali effect in glass system. No sharp peaks were exhibited in XRD pattern and suggest that the prepared VO^{2+} doped CLNB glass systems possess the amorphous nature. FTIR spectra of glasses are revealed about the functional groups existed and bonding linkages between them. Optical absorption and EPR spectra of the vanadyl ion doped CLNB glass systems are confirmed the site symmetry of the dopant ion as tetragonally compressed octahedral site symmetry. The evaluated molecular bonding coefficients values are confirming the bonding nature of dopant ion.

1. Introduction

Glass is an assured host, probed the effect of chemical reactions on the optical properties of transition metal ions. They owned high chemical durability, tremendous thermal, electrical and optical properties. Therefore, glasses have been considered as the suitable materials for microelectronics and optical fiber applications. Among the fundamental oxide glass formers, borate is the best glass component owing to its elevated phonon strength, promising choice for enormous technical appliances, holds good solubility and high thermal stability [1,2]. Even though it is well known glass former, pure borate glass is not a stable compound. They have the tendency to undergo through rapid cooling that takes place the structural defects later than heating and have hygroscopic assets which lead to reduce the glass usual applications. Materials that possess good nonlinear optical (NLO) properties have been received much more attention for their potential applications. A wide range of materials such as crystals, nanomaterials, quantum dots, thin films, glasses, glass ceramics, and polymers have been investigating for their nonlinear optical properties. Owing to the excellent adjustability of compositions, glasses can be prepared and explored to tune the desired property for a specific application. Glasses having large nonlinear refractive index, fast response time, and nonlinear absorption coefficient are promising materials for nonlinear optical devices such as ultrafast optical switches and optical power limiters. The nonlinear optical properties can be tailored by choosing the appropriate oxides with large hyperpolarizabilities and large transmittance. In particular glasses containing borate oxide are attracts much attention because of their high refractive indices and large transmission window in the visible and near infrared region [3].

Consequently, to reduce these difficulties and improve the assets of the glass, modifiers like CdO, Na_2O and Li_2O have to merge with the borate. Modifiers can be affecting its physical, structural and spectral characterizations of the B_2O_3 glasses. Glasses doped with transition metal ions (TM) also exhibit the numerous attractive spectral characterizations owing to the different valency states in glassy environment [4]. Transition metal (TM) ions are containing incompletely filled d-shells became attractive dopants for host glass because of their physical properties like low energy excited states and magnetic ground state. These doped ions will change the photo luminescent, magnetic and absorptive properties of the corresponding glasses. Due to their physical properties, TM ions themselves can be used as probes directly by applying different optical, magnetic and structural studies [5]. Borate glasses with alkali and alkaline metal ions doped TM ions are getting more consideration owing to their

DOI: 10.14456/jmmm.2020.43

structural properties and they made uses in the field of electrochemical, solid state lasers and memory devices. Particularly glasses containing Li and Na are the promising materials in solid state battery applications [6-8].

The physical concept of instantaneous relocation of distinct binary itinerant ionic components in mixed alkali glass were led to spread out of dopant ion settled which creates deformation in the neighboring host glass. Corresponding occurred stress of host glass network with mixed alkali oxides is more than or equivalent to binding energy of the glass. The addition of Na and Li ions to the borate glass network creates the non-bridging oxygen (NBOs) and takes place the amendments in structural, physical and spectral characteristics of borate glass. It has been known that the first type of alkali ions can be surrogated with the second type of alkali ions in a mixed alkali glass by maintaining the totality of alkali content constant, variation of numerous properties preceded. This eminent phenomenon known as the mixed alkali effect (MAE). The CdO can be considered as a promising candidate incorporate in to the glass network for host material. because it has the band gap of direct and indirect as 2.5 and 1.98 eV respectively and also working as a good network modifier [9,10].

The V_2O_5 doped glasses with semiconducting properties are add to a large extent in material science and solid-state chemistry due to their appliances as the optical and electrical memory devices, optical switches, cathode ray tubes and condensed tool devices [11-13]. The addition of paramagnetic V_2O_5 to the borate matrix advances the sintering nature of glass network, since the main infrared vibrational band assignments of V_2O_5-based glasses can occupy equivalent state position as of tri borate and tetra borate form of configuration [14], which affords the better industrial applications. Amongst the paramagnetic TM ions, VO^{2+} is better steady cation, and has been widely used as probe to study the local structures and properties in doped glasses through the electronic paramagnetic resonance (EPR) characterization [15]. Vanadium has possessed many valency states such as (+2, +3, +4 and +5) states those are be in corresponding unfilled 3d orbitals. Since carrying mechanism engaged the exchange of electrons in the middle of V^{4+} and V^{5+} states,

$$V^{4+}\text{--}\ O\ \text{--}\ V^{5+} \Leftrightarrow V^{5+}\ \text{--}\ O\ \text{--}\ V^{4+}$$

these V_2O_5 doped glasses are good appliances in the preparation of semiconductors devices [16].

EPR studies furnish the corresponding VO^{2+} ion valance state and describe its occupied site symmetry, besides that generated distortion in the host glass and the kind of structural imperfections rouse. The aim of the present investigations are to observe the effect of mixed alkali on the nonlinear behavior of various physical, structural and spectral parameters of the 0.1 mol% vanadium pentoxide doped $19.9CdO+xLi_2O+(30\text{-}x)Na_2O+50B_2O_3+19.9CdO+xLi_2O+(30\text{-}x)Na_2O+50B_2O_3$ glasses; as an evidence of MAE.

2. Experimental

2.1 Synthesis of glass

For the synthesis of vanadyl ions doped cadmium lithium sodium borate glass samples, analar grade chemicals of CdO (99.9%), B_2O_3 (99.9%), Li_2CO_3 (99.9%) and Na_2CO_3 (99.9%) were used. These mixtures are grinded in an agate mortar with pestle after added 0.1 mol% of V_2O_5, finally total mixture is grinded for 1 h. The final composition was sintered at 750 K and melted at 1250 K for 1 h. The homogenized melt was quenched to room temperature by pouring it onto a brass plate and quickly pressed by another one to obtain disks having a thickness of 1-2 mm and annealed at 700 K for 1 h to diminish the structural deformations. The glass composition taken as $(19.9)\ CdO + xLi_2O + (30\text{-}x)\ Na_2O + 50\ B_2O_3 + 0.1\ V_2O_5$ $(5 \leq x \leq 25)$ and hereafter named as VO^{2+} doped CLNB glass system.

2.2. Characterization techniques

The XRD pattern of VO^{2+} doped CLNB glass systems were characterized by PANalytical Xpert Pro diffractometer with CuKα (1.5406 Å). Molar volume (V_m) and density was measured for the prepared glasses with the principle of Archimedes by using xylene solution as captivate liquid. Abbe's refractometer was used to determine the refractive indices values. The electron paramagnetic resonance spectra of synthesized glasses are recorded at RT with JEOL JESTE100 EPR spectrometer. The location of doped ions was identified with JASCO V-670 spectrophotometer by taking the optical spectra. The functional groups in the prepared glass samples were verified by Shimadzu IR Affinity 1S spectro-photometer.

3. Results and discussions

3.1 Physical parameters

One of the important parameters, density plays a vital role to produce numerous varieties of glass samples. Also provide information about interstitial space, structural and conduction mechanism. The variation of alkali content (both Li_2O and Na_2O) in prepared glass systems lead to slight variation in density of the glass samples due to the amendment of interstitial volume in glass network with formation of the non-bridging oxygen (NBOs) [17]. Figure 1 shows the comparison between density and molar volume values with varying alkali mol%. Both parameters are varying nonlinearly and opposite in direction as inversely proportional relation due to addition of Li^+ ions, which confirms the presence of MAE for the respective physical properties. Figure 1 clearly indicates the density is altering the non-regularly with increasing x mol% of lithium content featuring three maxima and two minimal values w.r.t the alkali content variation, which shows the indication of MAE. As a consequence of MAE density reduced in pure alkali borate glasses [18]. The density is increases and decreases with increasing the Li_2O contentment. The density can be related to be the type of structural units that form when Li_2O is incorporated into the glass structure. Li_2O converts symmetric BO_3 triangles into BO_4 tetrahedra or converts the latter into asymmetric BO_3 triangles. A compensation of the negative charge on the BO_4 tetrahedra would come from positively charges of Li^+ or Cd^{2+} and V^{4+} cations for each BO_4 tetrahedron. It is also suggested that when a smaller cation substitutes for a larger one the mean size of the sites for the larger one increases and vice versa. The effect is related to the cation field strength and is due to a competition of cations for the negative sites of oxygen ions. However, it is accepted that the presence of dissimilar alkali ions affects both the local and intermediate range orders of the glass network [19].

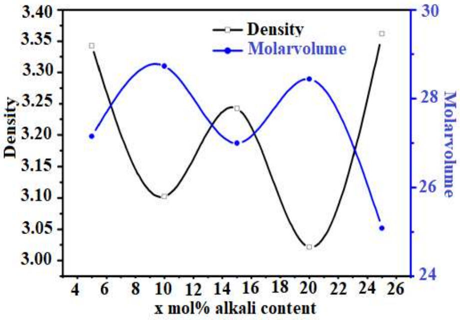

Figure 1. Effect of alkali content on Density vs Molar volume.

The correlation exists between ionic concentration and ionic polarizability as shown in Figure 2 with Li_2O content. With increasing the Li_2O content both ionic concentration and ionic polarizability vary nonlinearly but opposite in direction and these parameters are inversely proportional with each other. The ionic polarizability curve appears just like a mirror image of the ionic concentration curve. The physical parameters like dielectric constant (ε), reflection loss, molar refractivity (R_M) electronic polarizability (α_e), polaron radius (r_p) and inter-ionic separation (r_i) are calculated using the formulae reported earlier [20,21]. The evaluated these physical parameters are listed in Table 1. With increasing Li_2O content, the above all constraint parameters are varying non-linearly. In borate glasses, the electronic polarizability (α_e) possess less value when the ionic concentration is high which lead to increase in the ionic conductivity.

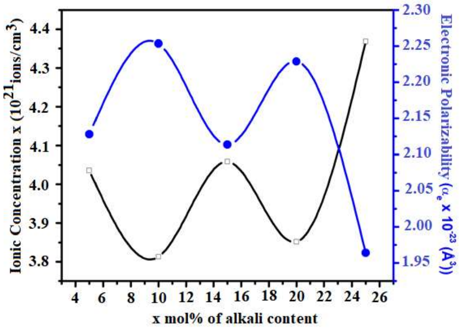

Figure 2. Effect of alkali content on Ionic concentration vs Electronic polarizability

Table 1. Physical properties of VO^{2+} doped CLNB glass system at room temperature.

S.No.	Physical parameter	CLNB1	CLNB2	CLNB3	CLNB4	CLNB5
1	Average molecular weight (g·mol^{-1})	90.7373	89.1324	87.5275	85.9227	84.3178
2	Molar volume (V_m) (cm^3·mol^{-1})	27.1460	28.7310	26.9930	28.4370	25.0810
3	Density (ρ) (g·cm^{-3}) (±0.004)	3.3425	2.1023	3.2425	3.0215	3.3618
4	Refractive index (n_d) (±0.0001)	1.6387	1.6452	1.6359	1.6584	1.6380
5	Dielectric constant (ε) (±0.005)	2.6853	2.7067	2.6762	2.7503	2.6830
6	Optical dielectric constant	1.6853	1.7066	1.6761	1.7502	1.6830
7	Reflection loss (R%)	0.0586	0.0595	0.0582	0.0613	0.0585
8	Molar refractivity (R_m) (cm^3) (±0.05)	9.7647	10.4180	9.6759	10.4780	9.0139
9	VO^{2+} concentration (N) (10^{21} ions·cm^{-3}) (±0.005)	4.0336	3.8111	4.0564	3.8505	4.3658
10	Electronic polarizability (α_e) (Å^3) 10^{-23}	2.1300	2.2726	2.1107	2.2856	1.9663
11	Inter ionic distance (r_i) (Å) (±0005) 10^{-8}	6.2821	6.4020	6.2703	6.3801	6.1185
12	Polaron radius (r_p) (±0.005) (Å) 10^{-8}	2.5312	2.5796	2.5265	2.5707	2.4653
13	Oxygen packing density (O) (g-atm·l^{-1})	73.6742	69.6110	74.0910	70.3306	79.7411
14	Optical energy gap (E_g) (±0.0004) (Å) eV	4.0998	4.0627	4.1159	3.9884	4.1038
15	Field strength (×10^{14} cm^{-2})	0.2097	0.1842	0.2136	0.1821	0.2461
16	Theoretical optical basicity (Λ)	0.4356	0.4354	0.4352	0.4350	0.4346
17	Optical basicity (Λ)	0.3297	0.4560	0.3104	0.4664	0.1476
18	Oxide electronic polarizability ($\propto_{O^{2-}}$) (Å^3)	1.2459	1.3756	1.2283	1.3875	1.0970
19	Metallization criterion (M)	0.6403	0.6373	0.6416	0.6315	0.6406
20	Interaction parameter (A) Å^{-3}	0.0747	0.0688	0.0772	0.0695	0.0865
21	3rd Order NLO susceptibility χ ×10^{-10} esu	3.0674	3.2258	3.0012	3.5683	3.0508

To describe the structure of the prepared glassy system, oxygen packing density (OPD) is one of the essential parameters. The OPD resolves the strength of the array of oxygen atoms in the oxide-based glass systems and it can be measured using the relation [22]:

$$\text{OPD} = (1000 \times \text{O})/V_m \ (\text{g. atom}\cdot\text{l}^{-1}) \quad (1)$$

Where, O is the quantity of oxygen present in the oxide-based glass system. Non regular variation in the OPD depends upon the rate of NBOs released due to the structural deformation caused by the alkali metal ions in these glasses and these OPD values are varies in irregular manner. Figure 3 depicts the correlation between the molar volume and oxygen packing density. It clearly represents the molar volume of the VO^{2+} doped CLNB glasses follows the contrary relation with oxygen packing density in nonlinear manner just like the mirror image with each other.

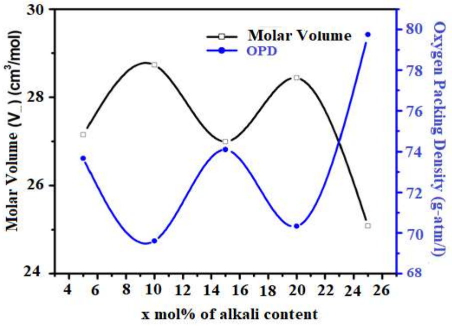

Figure 3. Effect of alkali content on Molar volume vs Oxygen packing density.

3.1.1 Oxide ion polarizability, optical basicity, Interaction parameter and 3rd order non linear optical susceptibility

Since polarizability of every cation and anions exhibit consistent values when mixed stoichiometrically rather than oxygen ions, for its peculiar behaviour that it performs different values in different oxide elements. So, the inference of oxide ion polarizability($\propto_{O^{2-}}$) would be helpful reliant in the preparation of crystalline and glassy materials, which provides technical assistance in the synthesizing various electronic and optical resourcing materials. Dimitrov and Komatsu resolved an expression for the average oxide polarizability by means of the optical energy gap and refractive index of the present glass system [23].

Numerous nonlinear responses oxide ion electronic polarizability is

$$\propto_{O^{2-}} (n_o) = [\frac{R_m}{2.52} - \sum \propto_{Cat}]/N_{o^{2-}} \quad (2)$$

Where $\propto_{Cat}$ is the cation electronic polarizability and $N_{o^{2-}}$ referring to the quantity of oxygen in the synthesized glass composition. To evaluate these ($\propto_{O^{2-}}$) values, the required $\propto_{Cat}$ data for the chemical constituents' cations of the glass were taken from work reported by Dimitrov and Komatsu [24]. The escalation or diminish in the polarizability and refractive index can be predictable because of growth or reduction of the NBOs in glass sample with varying the alkali content ($\propto_{O^{2-}}$) and the refractive index maintains proportionality relation with varying the alkali content.

The theoretical optical basicity of prepared glass Λ_{th}, constituted with several components including dopant supposed by Ingram along with Duffy [25]

$$\Lambda_{th} = x_1\Lambda_1 + x_2\Lambda_2 + x_3\Lambda_3 + \ldots\ldots\ldots \quad (3)$$

where Λ_1, Λ_2 and Λ_3 was the optical basicity of the individual constituents of oxides of the glass and x_1, x_2 and x_3 are corresponding equivalent mole fractions in the present glass. Here each one of the glass sample possess slight variation in the theoretical optical basicity values. Increased values of optical basicity mean glass oxide ions possess more capability to transfer electrons to the neighboring cations [26], it represents also the increase of covalence bond between cations and oxygen relating to glass system. The experimental optical basicity values of VO^{2+} doped CLNB glasses estimated by an equation that setup an inherent relation between oxide electronic polarizability ($\propto_{O^{2-}}$) and optical basicity proposed by Duffy [25] as

$$\Lambda = 1.67(1 - \frac{1}{\propto_{O^{2-}}}) \quad (4)$$

Here the calculated optical basicity values Λ_{th} of the prepared glass samples are close to the theoretical values but varies in non-regular manner and exhibit relation with the refractive index, tending to basic nature increases with increasing the refractive index. Also, VO^{2+} doped CLNB glasses posses ($\propto_{O^{2-}}$) over 2 Å^3 and optical basicity values below 0.5 suggest that transition metal ions exhibit less optical basicity values. Comparison of oxide ion polarizability ($\propto_{O^{2-}}$) and optical basicity Λ_{th} of the prepared glass samples illustrated in the Figure 4. It is suggesting that both these values vary in proportional manner. It describes that, if the oxide polarizability increases corresponding basic character also increases that means the ability of transfer the electrons between oxide ions and cations decreases. By increasing the alkali content these polarizability values vary in nonlinear pattern advised existence of MAE in the present glass system.

Yamashita and Kuroswa's interaction parameter A is one of the vital tools to express the kind of polarizability and optical basicity of the prepared glass system constituted with multi oxide glass modifiers. Interaction parameter (A) can also give an idea about the capability of type of bonding nature type existed between the cations and the oxide modifiers. Generally, rise in oxide electronic polarizability and optical basicity values indicates when the down falls occurs in the interaction parameter. In accordance with the supposition of Yamashita and Kuroswa, Dikshit and Kumar [27] proposed interaction parameter relation as

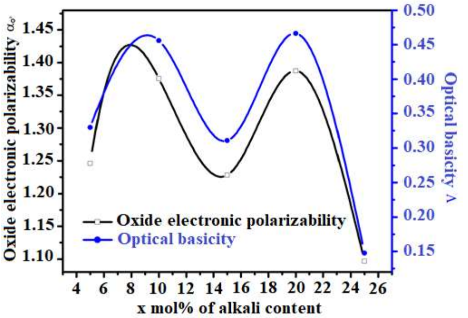

Figure. 4. Effect of alkali content on correlation between OPD vs Optical basicity.

$$A=\frac{(\alpha_f^{+}+\alpha_f^{-})-(\alpha_c^{+}+\alpha_c^{-})}{2(\alpha_f^{+}+\alpha_f^{-})(\alpha_c^{+}+\alpha_c^{-})} \tag{5}$$

Where, $\alpha_f^{+}, \alpha_f^{-}$ were the free state electronic polarizabilities of the +ve and -ve ions and $\alpha_c^{+}, \alpha_c^{-}$ were the related electronic polarizabilities of the individual ions in the constituted glass samples under consideration respectively.

By considering the approximation ($\alpha_f^{+} \approx \alpha_c^{+}$), Dimitrov and Komatsu modified the above equation with substitution of α_c^{+} with $\propto_{O^{2-}}$ as following expression

$$A=\frac{(\alpha_f^{-}-\propto_{O^{2-}})}{2(\alpha_f^{+}+\alpha_f^{-})(\alpha_c^{+}+\propto_{O^{2-}})} \tag{6}$$

The overall interaction parameter of each sample can be calculated by taking the summation of individual interaction parameters of the glass oxide constituents to prepare the VO^{2+} doped CLNB glass systems. Using the value of free state oxide ion α_f^{-}= 3.921 Å (Pauling value) the interaction parameter A can calculated as

$$A = X_{CdO}\frac{(3.921-\propto_{O^{2-}})}{2(\alpha_{Cd^{2+}}^{+}+3.921)(\alpha_{Cd^{2+}}^{+}+\propto_{O^{2-}})}$$

$$+X_{Na_2O}\frac{(3.921-\propto_{O^{2-}})}{2(\alpha_{Na^{2+}}^{+}+3.921)(\alpha_{Na^{2+}}^{+}+\propto_{O^{2-}})}$$

$$+X_{Li_2O}\frac{(3.921-\propto_{O^{2-}})}{2(\alpha_{Li^{2+}}^{+}+3.921)(\alpha_{Li^{2+}}^{+}+\propto_{O^{2-}})}$$

$$+X_{B_2O_3}\frac{(3.921-\propto_{O^{2-}})}{2(\alpha_{B^{3+}}^{+}+3.921)(\alpha_{B^{3+}}^{+}+\propto_{O^{2-}})}$$

$$+X_{V_2O_5}\frac{(3.921-\propto_{O^{2-}})}{2(\alpha_{VO^{2+}}^{+}+3.921)(\alpha_{VO^{2+}}^{+}+\propto_{O^{2-}})} \tag{7a}$$

Here, the individual values of $\alpha_{Cd^{2+}}^{+}, \alpha_{Na^{2+}}^{+}, \alpha_{Li^{2+}}^{+}, \alpha_{B^{3+}}^{+}$ and $\alpha_{VO^{2+}}^{+}$ can be taken from the research work reported by Dimitrov and Komastu [23] and the estimated interaction parameter values are tabulated in the Table 1. From these calculated interaction parameters of the VO^{2+} doped CLNB glass sample values, it is noticed that these values vary nonlinearly with altering the alkali ions content in the glass system. The interaction parameter also evidences the presence MAE. A plot has drawn between oxide electronic polarizability ($\propto_{O^{2-}}$) against interaction parameter with altering the Li and Na is shown in Figure 5. It is noticed that the electronic polarizability increases, interaction parameter decreases and the electronic polarizability, interaction parameter of oxides increases with the neighboring molecules. The graph appears for both parameters just like a mirror image with each other.

On taking account into the refractive index based on molar refraction R_M, Duffy proposed a pragmatic relation to find the E_g (optical energy gap) of the glass system from the following relation for a glass constituted with multi number of simple oxides as,

$$Eg=\left(1-\frac{R_M}{V_m}\right)^2 \tag{7b}$$

Using the above equation energy gap of VO^{2+} doped CLNB glass samples are evaluated and reported in Table 2. The E_g values are vary nonlinearly with changing the alkali content in the range from 3.8 to 4.2 eV. On seen these E_g values of the prepared glass samples exhibit wide band gap, that is suitable for the preparation of multi-functional semi conducting materials.

Table 2. FTIR spectra of VO^{2+} doped CLNB glass system.

Glass code	Vibrational bands (cm^{-1})					Vibrational band assignments
CLNB1	425	423	425	422	425	Specific vibrations of Li–O bonds
CLNB2	506	487	494	475	472	Vibrations corresponding to the Li-O bond
CLNB3	716	712	717	713	710	B-O-B bending vibrations of BO_3 triangles with NBOs
CLNB4	984	989	989	978	987	B–O bond symmetric stretching vibrations of BO_4 containing groups
CLNB5	1382	1379	1383	1385	1380	B–O symmetric stretching vibrations of trigonal BO_3 units

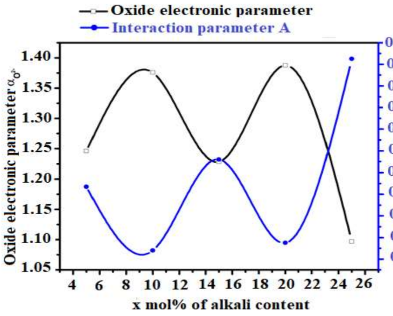

Figure 5. Effect of alkali content on Oxide electronic polarizability vs Interaction parameter.

One of the significant parameters, that provides information concerning about the strength of the chemical bonds among the elements of glass constituents is 3rd order nonlinear optical polarizability $\chi^{(3)}$ seeming to be nonlinear optical susceptibility (NLOS). The 3rd order NLOS $\chi^{(3)}$ of the VO^{2+} doped CLNB glasses were evaluated form the following formulae [28]

$$\chi^{(3)}=[\chi^{(1)}]^4 \times 10^{-10} \text{ esu.} \tag{8}$$

Where, $\chi^{(1)}$ is the linear optical susceptibility (LOS) in esu evaluated by

$$\chi^{(1)}= \frac{n_o^2-1}{4\pi} \tag{9}$$

The enormity of LOS strongly affected by the covalent and ionic chemical bonds. The calculated $\chi^{(3)}$ values vary in the range from 3 to 3.6 x 10^{-10} esu and these values are presented in the Table 1. The obtained $\chi^{(3)}$ values maintain proportionality relation with the corresponding refractive indices of the VO^{2+} doped CLNB glasses and pursuing nonlinear dissimilarity. A graph plotted between 3rd order NLOS ($\chi^{(3)}$) verses optical energy gap (E_g) with the variation of alkali content is depicted in Figure 6. It is observed that, with increasing the $\chi^{(3)}$ values E_g values decreases and decreasing the $\chi^{(3)}$ values E_g values increases and hold both the parameters nonlinear variance pattern with the altering of alkali content in the VO^{2+} doped CLNB glasses to the existence of MAE followed by these parameters and which may use better candidates for nonlinear optical applications.

To estimate the metallic or insulating nature of the glass samples in the solid state, précised parameter metallization criterion (M) expressed as [29]

$$M = 1-\frac{R_m}{V_m} \tag{10}$$

In consistent with the theory of metallization of the solid state materials supposed by Herzfeld, if $\frac{R_m}{V_m} = 1$, the corresponding refractive index (RI) converted to immeasurable which means the electron of the solid state materials nomadic and glass acquires the metallic nature. The necessary condition to predict the glass material is metal or non-metal the values of $\frac{R_m}{V_m} < 1$ is possess non-metal whereas the value $\frac{R_m}{V_m} > 1$ possess metallic nature. In the present VO^{2+} doped CLNB glass exhibited M values around 0.6 which is less than 1 and implied to the present synthesized glasses as non-metallic. A plot has drawn between metallization criterion and OPD with altering the alkali content is shown in Figure 7 and it reveals that the OPD increase in metallic nature increases when OPD decreases metallic nature also decreases. Both the OPD and metallization criterion parameters varies in linear pattern with varying the alkali content.

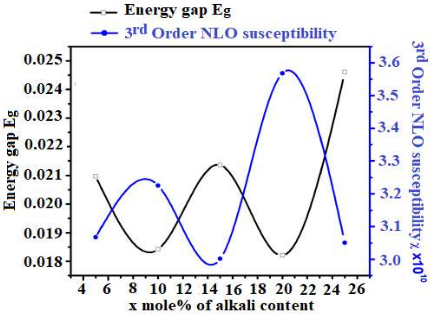

Figure 6. Effect of alkali content on optical energy gap vs 3rd order NLO susceptibility.

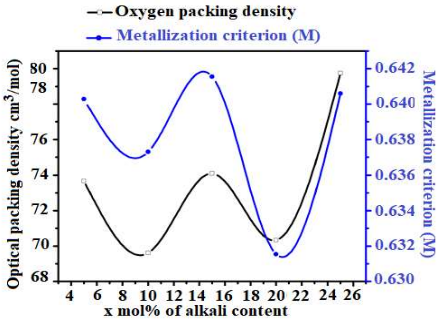

Figure 7. Effect of alkali content on OPD vs Metallization criterion.

3.2 XRD studies

Figure 8 shows the typical XRD pattern of VO^{2+} doped CLNB3 glass system at x = 15 mol%. No sharp peaks are present in the XRD pattern of the prepared glass, it is evident that the amorphous nature of glass material. A large hump located within 20°-40° for all prepared glass samples are evident. The lack of sharp peaks and the presence of a broad peak confirm the amorphous nature [30].

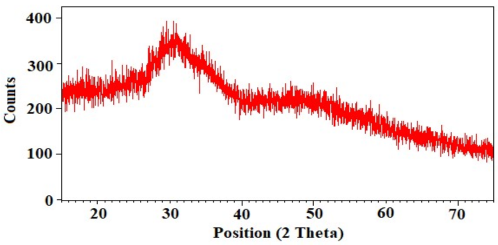

Figure 8. XRD pattern of VO^{2+} doped CLNB3 glass system.

3.3 FTIR studies

FT-IR spectra of VO^{2+} doped CLNB glasses depicted in Figure 9. Generally, B-O-B bending vibrations are observed in the range of 600 to 800 cm^{-1} for the both BO_3 and BO_4 units. B-O symmetric stretching vibrations of tetrahedral BO_4 units are observed in the region 800-1200 cm^{-1}. Asymmetric stretching vibrations of B-O bonds in BO_3 units are observed in the region 1200-1500 cm^{-1} [31]. The obtained absorption bands and their assignments are summarized in Table 2. The prescribed vibrations corresponding to the Li-O bond absorption band assignments are in the region 425-506 cm^{-1} [32].

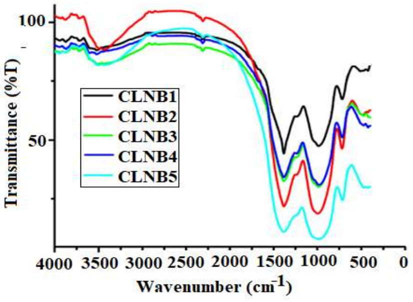

Figure 9. FTIR spectra of VO^{2+} doped CLNB glass system.

The current IR spectra of VO^{2+} doped CLNB glass system is depicted the orderly modifications around 700, 900 and 1300 cm^{-1}. These variations occurred with increasing of the lithium oxide up to 25 mol% exhibited several vibrational bands of BO_4 groups. The absorption vibrational band assignments at 506, 487, 494, 475 and 472 cm^{-1} are attributed to the Li-O bond. The absorption bands around 710 cm^{-1} is assigned to the B-O-B bending vibrations of BO_3 triangles with non-bridging oxygen (NBOs). The absorption bands obtained at 984, 994, 989, 978 and 987 cm^{-1} are assigned to the B–O bond symmetric stretching vibrations of BO_4 containing groups. The bonds attained in the region 1350-1400 cm^{-1} are consigned to the B–O symmetric stretching vibrations of trigonal BO_3 units. The bonds arrived above the 1600 cm^{-1} is being owed to the water molecule H-O-H. Figure 9 depicts the vibrational band peaks are varied with increasing the lithium mol% in the all regions supported the present glass system exhibits MAE. From the FT-IR spectra the formation of bridging oxygen ions in the borate matrix is expected due to the former role of V_2O_5.

3.4 Optical studies

The lower lying state of VO^{2+} free ion with d^1 configuration is ^2D. In this state d^1 electron reside in $^2T_{2g}$ and excited subsequently occupied $^2E_{2g}$. If VO^{2+} attains the pure octahedral site symmetry (O_h), singlet band can expect through the transition $^2T_{2g} \rightarrow {}^2E_{2g}$ only. On the other hand, VO^{2+} not at all being in O_h state rather than that it reduced its symmetry from O_h to C_{4v} (Tetragonal site symmetry). In this symmetry of C_{4v} the ground state $^2T_{2g}$ splits as $^2B_{2g}$ and ^2E_g while the $^2E_{2g}$ splitting as $^2B_{1g}$ and $^2A_{1g}$. Figure 10 have been depicted the optical absorption spectra of VO^{2+} doped CLNB glasses. The optical absorption spectra of VO^{2+} doped CLNB glass samples consists of three considerable bands, first one around 838 nm (11933 cm^{-1}), second one is a broad band around 694 nm (14409 cm^{-1}) and third one is a weak resolved band around 456 nm (21929 cm^{-1}) in the order of ascending of energy. The consigned relative electron transitions are $^2B_{2g} \rightarrow {}^2E_g$ ($d_{xy} \rightarrow d_{xz}, d_{yz}$), $^2B_{2g} \rightarrow {}^2B_{1g}$ ($d_{xy} \rightarrow d_{x^2-y^2}$) and $^2B_{2g} \rightarrow {}^2A_{1g}$ ($d_{xy} \rightarrow d_{z^2}$) respectively. The consign of these energy bands originated through the energy levels of molecular orbital's of VO^{2+} in tetragonal symmetry of the CLNB glasses [4]. The corresponding cubic (Dq) and tetragonal field (Ds and Dt) field parameters are estimated using the subsequent expressions.

$$-3Ds + 5Dt: {}^2B_{2g} \rightarrow {}^2E_g \tag{11}$$

$$10Dq: {}^2B_{2g} \rightarrow {}^2B_{1g} \tag{12}$$

$$10Dq - 4Ds - 5Dt: {}^2B_{2g} \rightarrow {}^2A_{1g} \tag{13}$$

The estimated values of (Dq, Ds and Dt) are reported in the Table 3. The obtained energy transitions and the evaluated Dq, Ds and Dt values put forward the arrangement of VO^{2+} ions in the CLNB host glassy system in tetragonally distorted octahedral site symmetry and the negative sign of tetragonal field parameters recommended the distortion would be compression along the V-O axis [33].

3.4.1 Optical direct, indirect band gaps and Urbach energy

To comprehend the formation of optically induced transitions of crystalline and amorphous materials, optical absorption spectrum is an advantageous technique. Especially in the spectra, absorption edge is examined in order to assess energy band gap, form of the band structure and optical absorption coefficient $\alpha(\nu)$ as a function of photon energy [34]. In general, there exists a pair of optical transitions takes place at absorption edge, direct and indirect transitions. In glassy materials, anions directly affect the conduction band then cations play indirect key role. For direct transitions, absorption coefficient

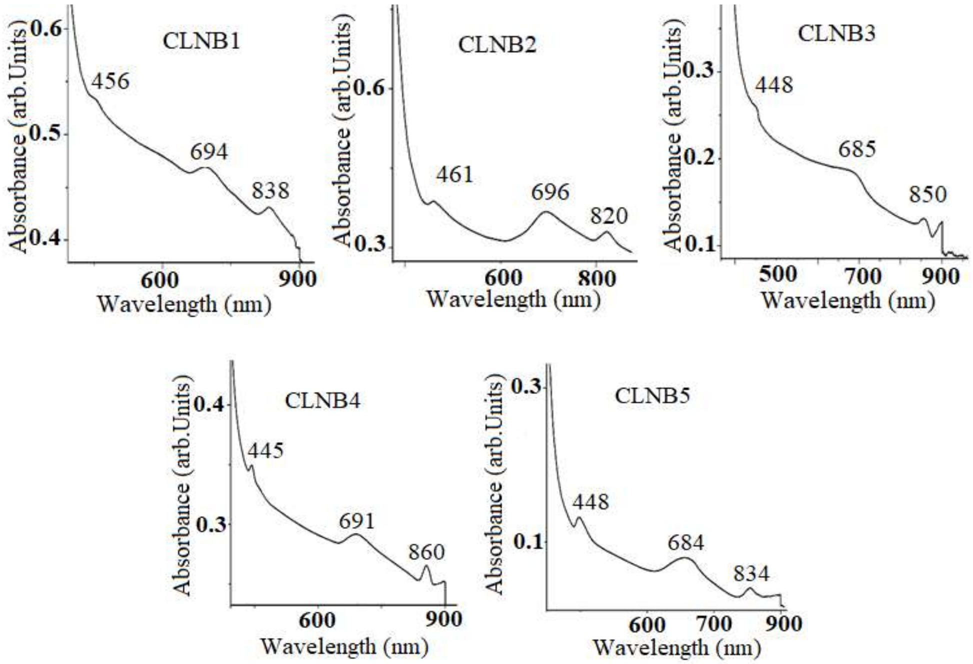

Figure 10. Optical absorption spectra of VO^{2+} doped CLNB glass system

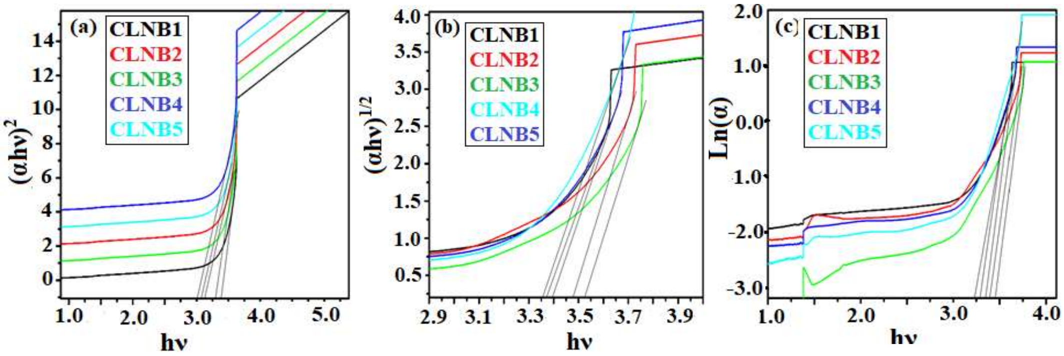

Figure 11. (a) Direct bandgap energy, (b) Indirect bandgap energy, and (c) Urbach energy of VO^{2+} doped CLNB glass system.

$$\alpha(\nu) = A(h\nu - E_{opt})^n/h\nu \tag{14}$$

Where, A is a constant, E_{opt} is energy band gap, h is Plank's constant, ν is the frequency of corresponding energy band gap and n = 1/2 for direct allowed transitions, n = 2 for indirect allowed transitions.

Optical band gaps are obtained for the direct and indirect transitions by drawing graphs for $(\alpha h\nu)^2$, $(\alpha h\nu)^{1/2}$ against the function of photon energy $h\nu$. The E_{opt} values gives direct and indirect transitions, got through extrapolating $(\alpha h\nu))^2 = 0$ for direct and $(\alpha h\nu)^{1/2} = 0$ for indirect transitions depicted in Figure 11(a) and Figure 11(b) respectively. To obtain Urbach energy values, plot a graph ln(α) vs $h\nu$ and is shown in Figure 11(c). By taking the reciprocals of slope of the linear segment in the photon energy section, Urbach energy values (ΔE) would be measured. Urbach energy (ΔE) value provides the information related to the structural defects present in the glass sample. If a glassy system comprised with lesser Urbach energy (ΔE), it would have the better structural stability. Smaller value of Urbach energy gives the better structural stability of the glass system. The obtained E_{opt} values of corresponding direct, indirect and Urbach energy values are tabulated in Table 4. It is observed that the values of E_{opt} for direct and indirect band gap energies are varies between 3 to 3.5 eV supposed to have the wide band gap energies and may be used in semiconducting devices. Lesser Urbach energy values suggesting the synthesized VO^{2+} doped CLNB glass system have the greater stability. The direct, indirect and Urbach band gap energies slightly varies in nonlinear manner may due to the variation of alkali content which also supported the MAE in the present glass system.

Table 3. Optical band positions, crystal field and inter-electronic repulsion parameters of VO^{2+} doped CLNB glass system.

Glass code	Transitions form $^2B_{2g}$	Wavelength (nm)	Wavenumber (cm^{-1})		Dq (cm^{-1})	Ds (cm^{-1})	Dt (cm^{-1})
			Observed	Calculated			
CLNB1		456	21929	21923	1441	-2779	719
		694	14409	14405			
		838	11933	11929			
CLNB1		461	21692	21686	1436	-2788	765
		696	14367	14364			
		820	12195	12191			
CLNB3		448	22321	22315	1459	-2784	682
		685	14598	14594			
		850	11765	11761			
CLNB4		445	22472	22465	1447	-2803	642
		691	14472	14467			
		860	11627	11624			
CLNB5		448	22321	22315	1461	-2813	710
		684	14619	14615			
		834	11990	11987			

Table 4. Optical band gaps and direct, indirect and Urbach energy values of VO^{2+} doped CLNB glass system.

Glass system	Absorption edge (nm)	Thickness	Optical band gap energy (eV)		Urbach energy (eV)
			Direct	Indirect	
CLNB1	397	2.39	3.38	3.37	0.3039
CLNB2	394	2.01	3.13	3.40	0.2906
CLNB3	396	2.37	3.29	3.52	0.2949
CLNB4	390	1.81	2.99	3.35	0.3095
CLNB5	386	1.01	3.06	3.39	0.2994

3.5 EPR studies

Electron paramagnetic resonance spectrum is a perceptive tool to observe transition metal ions in solids. It affords the information about the internal surroundings with host lattice, kind of attachment between them and valance state of the transition metal ions. The Electron paramagnetic resonance (EPR) spectra of VO^{2+} (0.1 mol%) doped CLNB glass systems are recorded at room temperature and depicted in the Figure 12. A sixteen line well resolved hyperfine components of EPR spectra determined eight lines parallel and eight lines perpendicular each obtained by a typical isolated vanadium ion existed as VO^{2+} in C_{4V} symmetry for the unpaired $3d^1$ electron with ^{51}V isotope (I = 7/2, found 99.8% by large quantity in nature). The corresponding magnetic quantum numbers of these eight lines are associated with the ±7/2, ±5/2, ±3/2 and ±1/2 respectively [35]. Since the glass samples are synthesized at higher temperatures there exists a prospect of modification of V^{5+} ions as V^{4+} ions shown in the following equation

The obtained V^{4+} ions lead to constitute VO^{2+} complexes, act as modifiers and distort the glass network. Generally, V^{4+} ion is pertained to 6-fold coordination and not in pure octahedral site symmetry but the tetragonal distortion (C_{4V}) existed along the axis due to the Jahn-Teller effect. The distinct spectral parameters are primarily authorized the tetragonal distortion in the octahedral site symmetry. The octet EPR spectra contain eight lines associated with the eight magnetic quantum numbers. The sharp and maximum intensity resonance peaks in each spectrum suggests the isolated V^{4+} ions which can be extant as VO^{2+} ions in the CLNB glass systems [36].

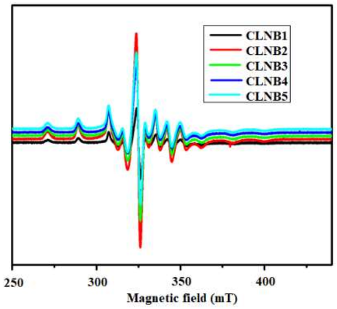

Figure 12. EPR spectra of VO^{2+} doped CLNB glass system.

To assess the spin Hamiltonian parameters the EPR spectra of VO^{2+} doped CLNB glass system can be construed with the following spin Hamiltonian

$$2V^{5+} + O^{2-} \rightarrow 2V^{4+} + \frac{1}{2}O_2 \uparrow \tag{15}$$

$$\begin{aligned} H = {} & \beta[(g_{\|}B_zS_z + g_{\perp}(B_xS_x + B_yS_y)] \\ & + A_{\|}S_zI_z + A_{\perp}(S_xI_x + S_yI_y) \end{aligned} \tag{16}$$

Where, β is the Bohr's magnetron; $g_{\|}$, $g_{\perp}$, $A_{\|}$ and $A_{\perp}$ are the horizontal and vertical components of gyro magnetic tensor g and hyperfine coupling tensor A; B_x, B_y and B_z are the three components of the applied magnetic field while S_x, S_y, S_z and I_x, I_y, I_z are the components associated to the electron spin and nucleus spin respectively.

The spin-Hamiltonian parameters are elucidated using the typical formulae

$$H_{\|}(m) = H_{\|}(O) - A_{\|}(m) - \left(\frac{63}{4} - m^2\right)\frac{A_{\perp}^2}{2H_{\perp}(O)} \tag{17}$$

$$H_{\perp}(m) = H_{\perp}(O) - A_{\perp}(m) - \left(\frac{63}{4} - m^2\right)\frac{A_{\|}^2 + A_{\perp}^2}{4H_{\perp}(O)} \tag{18}$$

To overcome the defects originated by the overlapping between hyperfine components, Muncaster and Parke put forward a recitation method for the analysis of the spectra [37]. With the help of this iterative method the evaluated spin Hamiltonian parameters of VO^{2+} doped CLNB glasses are tabulated in the Table 5.

Tetragonal compression in the octahedral sites would gratifies the condition $g_{\|} < g_{\perp} < g_e$. Here the calculated $g_{\|}$ values are in the range of 1.9440 to a maximum at 1.9683 for CLNB1 glass and $g_{\perp}$ values are in the range from 1.9791 to 1.9980 for CLNB1 glass, which is less than g_e (2.0023). The values of $A_{\|}$ vary in the range from 179.792 to a maximum value 175.604 cm^{-1} for CLNB3 glass and $A_{\perp}$ varies 67.3176 to a maximum value 71.6161 for CLNB3 glass. In this juncture both gyromagnetic tensors $g_{\|}$ and $g_{\perp}$ pursuing the inversely proportional relation and in nonlinear manner as well as in the case of $A_{\|}$ and $A_{\perp}$ also. The attained gyromagnetic tensor ($g_{\|}$ and $g_{\perp}$) values are well agreed with the above said condition and followed the supplementary condition $A_{\|} > A_{\perp}$ by the hyperfine coupling tensors ($A_{\|}$ and $A_{\perp}$). The assessed parallel components of g and A illustrated the non collinear nature allocated leading distortion of octahedral symmetry where these components located in the spectra and the obtained distortion subjected to V=O bond directions [37].

Table 5. Spin Hamiltonian parameters of VO^{2+} doped CLNB glass system.

Glass code	$g_{\|}$	$A_{\|}$ (10^{-4} cm^{-1})	$g_{\perp}$	$A_{\perp}$ (10^{-4}cm^{-1})	$\Delta g_{\|}$	$\Delta g_{\perp}$	P	κ	β_1^2	ε_π^2
CLNB1	1.9683	175.604	1.9879	70.2686	0.0340	0.0144	125.2152	0.8151	0.3728	0.1561
CLNB2	1.9527	175.817	1.9980	67.9605	0.3496	0.0043	123.5051	0.8277	0.5537	0.5458
CLNB3	1.9677	179.792	1.9885	67.3176	0.0346	0.0138	126.5738	0.8298	0.3853	0.4954
CLNB4	1.9440	176.714	1.9899	71.6161	0.0583	0.0124	127.7368	0.7796	0.6509	0.6361
CLNB5	1.9664	177.050	1.9791	70.3393	0.0359	0.0232	124.8591	0.8280	0.4013	0.4547

By correlating spin Hamiltonian parameters ($g_{\|}$, $g_{\perp}$, $A_{\|}$ and $A_{\perp}$) and the energy separation between ground state to nearby higher energy values ($\Delta_{\|}, \Delta_{\perp}$) w.r.t. the corresponding transitions taken from the optical absorption data the molecular bonding coefficient β_1^2, β_2^2, ε_π^2, Fermi contact term κ and hyperfine coupling constant P are estimated using the following formulae.

$$\beta_1^2 = \frac{(g_e - g_{\|})\Delta_{\|}}{8\lambda\beta_2^2} \tag{19}$$

$$\varepsilon_\pi^2 = \frac{(g_e - g_{\perp})\Delta_{\perp}}{2\lambda\beta_2^2} \tag{20}$$

$$A_{\|} = P\left\{-\frac{4}{7}\beta_2^2 - \kappa + (\Delta g_{\|}) + \frac{3}{7}(\Delta g_{\perp})\right\} \tag{21}$$

$$A_{\perp} = P\left\{\frac{2}{7}\beta_2^2 - \kappa + \frac{11}{14}(\Delta g_{\perp})\right\} \tag{22}$$

where λ is the spin orbit coupling constant (170 cm^{-1}); β_1^2, β_2^2 and ε_π^2 are the assessment of the in-plane σ-bonding and π–bonding and out of plane π–bonding parameters of V–O respectively; $\Delta_{\|}, \Delta_{\perp}$ are the energy differentiation corresponding to the transitions $^2B_{2g} \rightarrow {}^2E_g$ and $^2B_{2g} \rightarrow {}^2B_{1g}$ respectively. The calculated β_1^2, β_2^2, ε_π^2, P and κ values are specified in Table 5. The measured values of β_1^2 and ε_π^2 are between 0.3 to 0.6 and 0.2 to 0.6 respectively. Usually if $\beta_1^2 = 1$ the bond should be purely ionic, if $\beta_1^2 = 0.5$ the bond should be covalent. In this exertion the evaluated values of β_1^2 and ε_π^2 implied the in plane σ-bonding and out of plane π -bonding are covalent or moderately covalent and β_2^2 is assumed to be 1 for the in-plane π-bonding with the equilateral field ligands [38]. κ is Fermi interaction parameter which is a unit less and dimension less invariable, portrayed core ***s*** polarization corresponding single electron density of vanadium nucleus and P is a dipolar coupling constant determine radial distribution of single electron wave function.

$$P = 7(A_{\|} - A_{\perp})/6 + (3\lambda/2\Delta_{\perp}) \tag{23}$$

The free ion P = 160 x 10^{-4} cm^{-1} and the computed P values for the current glass samples lie in between 123 x10^{-4} cm^{-1} to 127 x10^{-4} cm^{-1} in an irregular manner which substantiate that all the vanadyl doped CLNB glass systems literally acquired the covalent nature. From the calculated isotropic and anisotropic parameters (g and A), Fermi interaction parameter κ is determined by the equation

$$\kappa = -(A_{iso}/P)-(g_e-g_{iso}) \quad (24)$$

The estimated κ values are lie in the range from 0.7 to 0.85 and these values are less than unity means the assimilation of 4s orbital into d_{xy} orbital due to a lower symmetry of the ligand field. Higher the value of κ supposed that a huge part of this hyperfine invariant by the single ***s***-electrons [39]. All the measured molecular orbital coefficients, P and κ varies in non-linear pattern supported the existence of MAE in the present glass system may be due to rearrangement of alkali metal ions.

4. Conclusions

A sequence of quinary VO^{2+} doped CLNB glass systems are prepared by typical melt quenching mode and they have been explored for their physical, structural and spectral properties. The comparison of physical properties such as OPD with molar volume, oxide electronic polarizability with optical basicity, oxide electronic polarizability with interaction parameter, third order nonlinear optical susceptibility with optical energy gap and OPD with metallization criterion have been observed and correlated. No sharp peaks obtained in XRD pattern suggest the prepared VO^{2+} doped CLNB glass system acquired the amorphous nature. FT-IR spectra afford information; concern functional groups existed and bond linkages between them. The prepared glasses microstructure was determined by optical absorption spectra the vanadyl ion resided in the host glass as tetragonally compressed octahedral site symmetry. Traced Urbach energy values implied the present glass system was more stable and has the high chemical durability. The obtained direct and indirect band gap energies vary in nonlinear pattern and evidence the MAE in the glass system corresponding to the band gap energies. EPR spectra confirms the site symmetry of the present glass system and give the provision of oxidation state of vanadyl in the host glassy system. The molecular bonding coefficients confirm the nature of bonding of the dopant ion is merely covalent or partial covalent nature

5. Acknowledgements

One of the authors M. Avinash would like to thank CSIR for providing financial support all the way through SRF and R.V.S.S.N. Ravikumar would like thank DSA-1, DST-FIST New Delhi for funding to the department of Physics, Acharya Nagarjuna University, Guntur for carryout this research work.

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