Synthesis, Characterization and Optical Properties of Niobium Doped Silver-Lead-Borate Glasses

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ABSTRACT

Niobium doped silver lead borate glasses with the chemical composition (29-x) PbO-yAg_2O-$70B_2O_3$-xNb_2O_5 (where x= 0.1 to 0.5mol%, y= 1 to 5 mol %) have prepared by conventional melt quenching method.SEM/XRD technique confines glassy nature of the prepared samples. IR and UV optical absorption technique have been used to obtain the information concerning network structure. From the absorption edge studies, the values of optical band gap energies have been evaluated. The density, molar volume, polarizability and glass transition temperature are found to be compositional dependent. The non-linear variations of the above optical parameters are discussed with respect to Nb_2O_5 concentration.

Keywords - DSC, Niobium-doped glasses, SEM, XRD, IR, UV-Optical

1 Introduction

The boric oxide, B_2O_3, acts as one of the most important glass formers and flux materials. Melts with compositions rich in B_2O_3 exhibit rather high viscosity and tend to formation of glasses(for a recent review read e.g.ref [1].Lead borate glasses belong to the unique amorphous solid state materials, which are thermally stable, IR transparency and high refractive index are formed over a wide region of PbO concentration. The large glass forming region is advantageous for manufacture of structurally and optically of different systems, which are strongly depends on PbO / B_2O_3. The borate glasses are important category of glasses, having interesting structural particularity, which are known today as important material for insulation and textile fiber glass. Glasses have been frequently studied from fundamental and industrial points of view in the last few years. That leads to a very different properties and large area of applications [2, 3].The high ionic conductivity and numerous applications such as biomaterials with anti bacterial, HIV therapies, chemical sensors and solid state batteries represent main points of interest on study of glasses containing silver oxide. In the recent years, some authors [4, 5] revealed that the density, molar volume and packing fraction could be directly related to the short range structure of alkali oxide modified borate glasses. The densities prove changes in both short range order and

co-ordination as the modification, while the molar volume is sensible in terms of size and packing. The packing of the borate based glasses with ions having volume smaller than the oxygen is considered to be covalent, controlled by oxygen covalent network, and heavily dependent on the glass former. On the other hand, Nb_2O_5 belongs to the group of transition metal oxides, in which all the d electrons of the transition metal atoms are donated to oxygen atoms. Nb_2O_5 is an n-type semiconducting oxide, these are of great interest, because of their application as non linear photonic materials [6, 7, 8, 9, 10], and as laser hosts having high non linear optical parameters [11]. However, unlike silicate and phosphate-based glasses, very little research has been done on niobium based glasses. The role played by Nb_2O_5 in the glass structure, co-ordination state of Nb^{5+}, and the interaction with other elements in the glass network, is still a subject under study. Nb_2O_5 oxide appeared as non-conventional network formers because of the participation of NbO_6 and NbO_4 groups in the formation of glass network. Therefore, a series of two-component and multi component non conventional glasses with low dielectric constant, and relatively high reflection loss have been synthesized. These glasses exhibit high refractive index, widely adjustable in the range from 2.6 to 2.8 by the appropriate glass composition and have high optical energy gap attributed to the high polarizability of Ag_2O which allows using them in wide range from UV up to infrared [12,13]. In this work, we present a study of the properties of PbO-Ag_2O-B_2O_3-Nb_2O_5 glass system as a function Nb_2O_5 molar ratio, which emphasis on their thermal behavior, structural features and optical durability properties.

2 THEORY

Optical absorption in solids occurs by various mechanisms, in all of which the photon energy will be absorbed by either the lattice or by electrons where the transferred energy is conserved. The lattice (or phonon) absorption will give information about the atomic vibrations involved and this absorption of radiation normally occurs in the infrared region of the spectrum. The higher energy parts of the spectrum particularly those associated with the inter band electronic transition will provide further information about the electron states. In these processes the electrons are excited from a filled to an empty band

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by the photon absorption and, as a consequence of this, a marked sharp increase in the absorption coefficient α (e) will result. The onset of this rapid change in α (e) is called "the fundamental absorption edge", and the corresponding energy is defined as "the optical energy gap". Photons with a certain range of energy could be absorbed by the modifying ions in the oxide glass by two different processes: -
1. The absorption due to internal transitions between the d-shell electrons, and,

2. The absorption due to a transfer of an electron from a neighboring atom to the modifier ion (transition metal ion) and vice versa.

The study of optical absorption and particularly the absorption edge is a useful method for the investigation of optically induced transitions and for getting information about the band structure and the energy gap of both crystalline and non crystalline materials. The principle of this technique is that a photon with energy greater than the band gap energy will be absorbed. There are two kinds of optical transitions at the fundamental absorption edge of crystalline and non-crystalline semiconductors, direct and indirect transitions, both of which involve the interaction of an electromagnetic wave with an electron in the valence band. The electron is then raised across the fundamental gap to the conduction band. For the direct optical transition from the valence band to the conduction band, it is essential that the wave vector for the electron be unchanged. In the case of an indirect transition, the interactions with lattice vibrations (phonons) take place; thus the wave vector of the electron can change in the optical transition and the momentum change will be taken or given up by phonons. In other words, if the bottom of the conduction band lies at a different part of K-sub shell from the top of the valence band, a direct optical transition from the top of the valence band to the bottom of the conduction band is forbidden [14].

 From the absorbance data, the absorption co-efficient α (e) was calculated using Lambert Law:

$$Ln(\frac{I_o}{I}) = 2.303.Abs = \alpha(e)d --- (1)$$

Where Abs-Optical density or optical absorbance, I_0 and I are intensities of the incident and transmitted radiation respectively. α(e) is absorption coefficient and thickness of the sample (d).Optical band gap (E_g) was determined by analyzing the optical data with the expression for the optical absorption coefficient α (e) and the photon energy (hυ)using the relation

$$\alpha(e) = k \frac{(h\upsilon - E_g)^n}{h\upsilon} --- (2)$$

Where K is a constant, hυ - the incident photon energy, the value of n is equal to one for direct-gap

material and two for an indirect- gap material and E_g - the optical band gap. It is observed that for many amorphous materials, a reasonable fit of equation (2) with n=2 are achieved.

3 Experimental

3.1 Glass preparation
    The basic glasses with composition (29-x) PbO-yAg_2O-70B_2O_3-xNb_2O_5 (where x= 0.1 to 0.5mol%, y= 1 to 5 mol %) were prepared by melt quenching method. The starting materials Nb_2O_5, B_2O_3,PbO and Ag_2O taken in the appropriate proportion weighed in digital electronic balance and mixed thoroughly in a porcelain crucible, then heated in an electrical furnace by increasing the temperature gradually the mixture was melt at a temperature around 1150^0C. Thus obtained homogeneous melt was quenched between two brass plates. The XRD spectra was obtained by using Bruker D8 Advanced series (Madision,WI) powder technique. Surface morphology is obtained using SEM [model-LEO-440i (U.K)] with Magnification = 5.00KX. DSC measurements were carried out with the commercial Netzsch Simultaneous Thermal Analyzer STA409C with 32-bit controller. The IR spectra of the studied glass samples were recorded using a Perkin-Elmer double beam 598 spectrophotometer over spectral range 400-4000cm^{-1}. The optical absorption spectra in the visible and ultraviolet region were recorded for highly polished-1mm thickness sample using Perkin-Elmer 402 double beam spectrometer in the wavelength range 200-1200nm. The densities (ρ) of all the glasses are determined using the Archimedes method with toluene ($\rho = 0.863 \, g/cm^3$) as an immersion fluid.

4 Results and discussion

4.1 Powder X-ray diffraction studies (XRD)
    Fig.1 shows typical XRD spectra of the sample. The pattern consists of a few broad peaks rather than sharp peaks, which is a sign of amorphous material. All the prepared glass samples confirm the glassy nature.
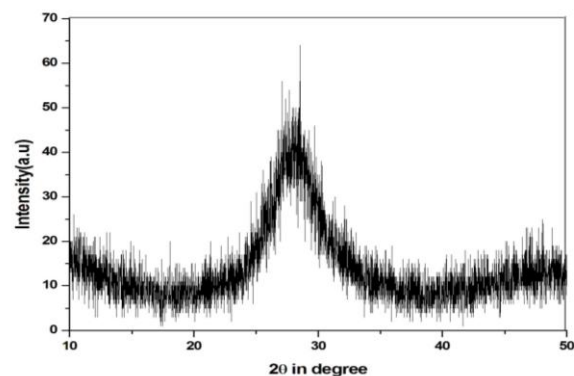

Fig-1: Typical XRD spectra of the glass sample.

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4.2 Scanning electron microscopy (SEM)

Surface morphology of the prepared glass samples was studied by using SEM.
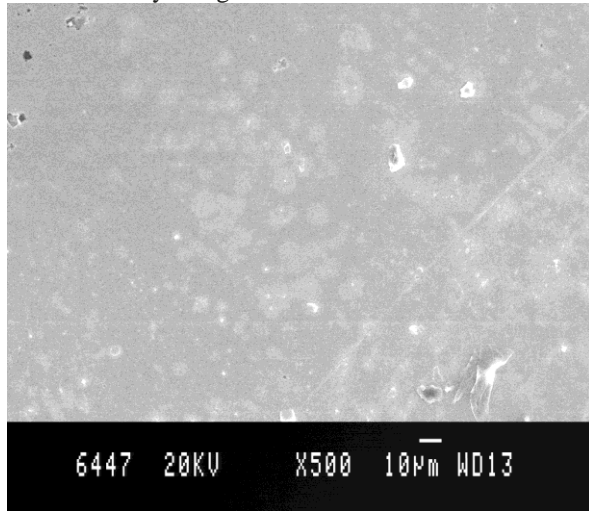

Fig-2: Typical SEM micrograph of the sample.

Typical SEM image is as shown in Fig.2 and one can see almost uniform phase of the glass. This confirms the amorphous nature of the samples.

4.3 Differential scanning calorimetry (DSC)

It is known that T_g is a measure of structural degradation. A typical DSC curve for the glass as shown in Fig.3, a very broad endothermic hump corresponding to the glass transition temperature T_g is 349.46^0C. The glass transition temperature varies with increase of the Nb_2O_5 content. Decrease in T_g is referred to increase in the loose packing and transformation structure [15].In the compositional range 0.3mol%, decrease in the T_g is related to increasing number of non bridging oxygen atoms [16], and to the modification role of both Nb_2O_5 and PbO, which are assumed to interrupt the B-O bond. Furthermore, the oxygen packing density as a measure of tightness of packing of oxide network can be used to explain decrease of T_g as listed in the table 1, the oxygen packing density decreases as impurity increases.

Table 1: Variation of glass transition verses Nb_2O_5.

Nb_2O_5 (mol %)	T_g in ^{0} C
0.1	395
0.2	380
0.3	340
0.4	349
0.5	375

A looser macromolecular structure requires smaller internal energy for chain mobility which is needed for the glass transition. Thus the addition of Nb_2O_5

and PbO indicates the formation of a more open molecular chain in the studied glasses.
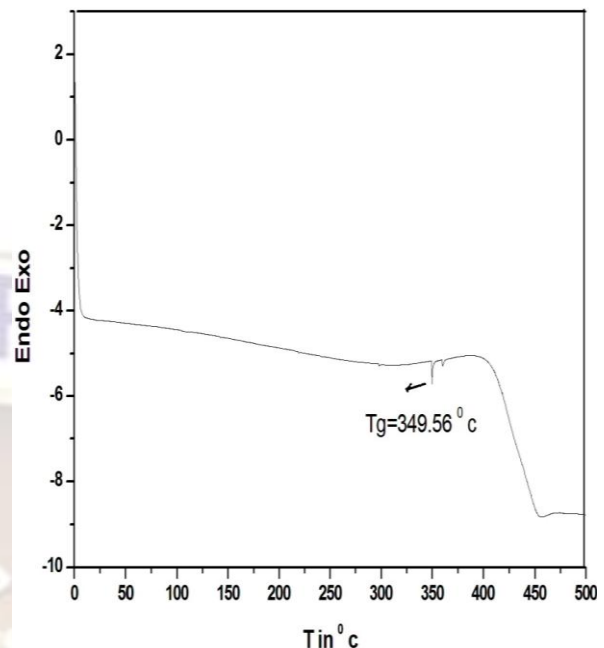

Fig-3: Typical DSC spectrum of the glass.

Also, the bond strength plays a competitive role in decreasing T_g. So decrease in T_g, is referred to the replacement of B-O linkages by the Nb-O and weaker Pb-O linkages. In the compositional range of 0.4mol% the T_g increases. This behavior is affected by the transformation of the structural unit NbO_6 into NbO_4 which acts as a former and tighten the borate network.

4.4 Physical properties

The mean atomic volume (V_M) of each glass was obtained from the values of densities (ρ) and mean atomic weights. The calculated values are given in Table 2, along with other physical parameters.

Refractive index (n) of samples was calculated by using the following relation [17].

$$\frac{n^2-1}{n^2+1} = 1 - \sqrt{E_g / 20} - (3)$$

The dielectric constant (ε) was calculated from the refractive index of the glass using [18].

$$\varepsilon = n^2 - - - - - - - - (4)$$

The reflection loss (R) from the glass surface was computed from the refractive index by using the Fresnel's formula as [19].

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$$R = \left(\frac{n-1}{n+1}\right)^2 - - - - -(5)$$

The molar refractivity (R_m) for each glass was evaluated using equation [20].

$$R_m = \frac{(n^2-1)M}{(n^2+2)\rho} - - - -(6)$$

Where M is the average molecular weight and ρ is the density in gm/cm^3.

The electronic polarizability (α_e) was calculated using the formula [21].

$$\alpha_e = \frac{3(n^2-1)}{4\Pi N(n^2+2)} (7)$$

Where N - is the Avogadro number.

The measured and calculated values of densities, molar volumes and polirizability of oxide ions of Nb_2O_5 doped silver lead borate glasses are listed in the table 2.

Table2: Density (ρ), Molar volume (V_m) and polarizability (α_e) of the prepared samples.

Mol %				ρ g/cm^3	V_m cm^3	α_ex10^{-24} cm^3
B_2O_3	Ag_2O	PbO	Nb_2O_5			
70	1	28.9	0.1	4.8	18.8	3.04
70	2	27.8	0.2	4.0	22.9	5.27
70	3	26.7	0.3	4.7	19.4	4.46
70	4	25.6	0.4	4.6	18.8	4.55
70	5	24.5	0.5	4.9	18.4	4.24

The measured and calculated values of molar refractivity, dielectric constant and reflection loss of oxide ions of Nb_2O_5 doped silver lead borate glasses are depicted in the table 3.

Table 3: Molar refractivity (R_m), dielectric constant (ε), and reflection loss (R) of the prepared samples

Mol %				R_m cm^3	ε	R
B_2O_3	Ag_2O	PbO	Nb_2O_5			
70	1	28.9	0.1	13.23	0.231	8.1
70	2	27.8	0.2	15.72	0.217	7.5
70	3	26.7	0.3	13.09	0.209	7.2
70	4	25.6	0.4	13.34	0.208	7.1
70	5	24.5	0.5	12.30	0.204	7.0

Density is one of the powerful tools capable of exploring the changes in the structure of glass and variation of density verses mol% of Nb_2O_5 as shown in Fig 4.
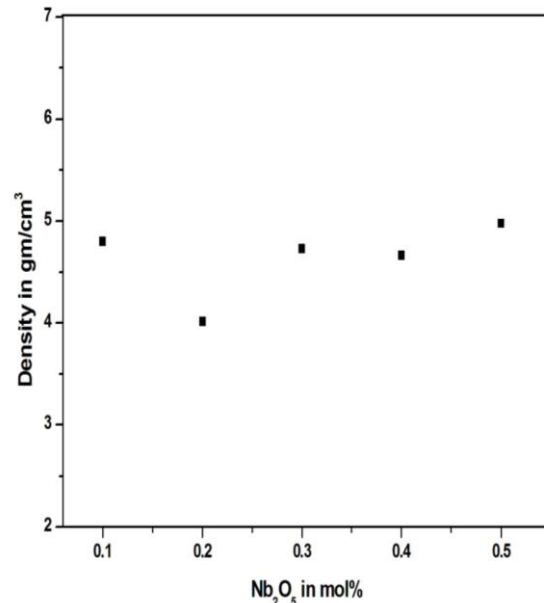

Fig-4: Variation of density verses Nb_2O_5 mol%

There is a sudden drop in density at 0.2mol% due to less number of non bridging oxygen atoms. Then there is a creation of more number of non bridging oxygen atoms on other mol% of Nb_2O_5. The Density is also affected by the structural softening/compactness, change in geometrical configuration, co-ordination number, cross link density and dimension of interstitial spaces of the glasses.
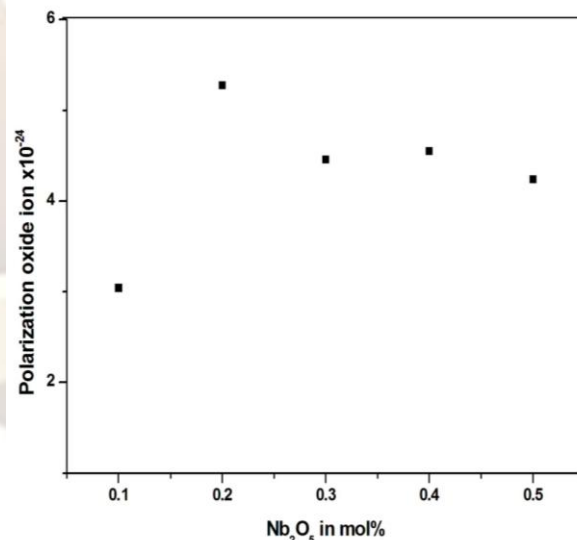

Fig-5: Variation of polarizability of oxide ions verses Nb_2O_5 mol%

Fig.5 shows the variation polirizability of oxide ions versus mol% of Nb_2O_5. The behavior of polarizability is exactly apposite to that of density is expected. This indicates that may be due to break down of borate

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bonds to create non bridging oxygen atoms at 0.2mol% of Nb_2O_5. The trend of dielectric constant and reflection loss decreases with increase of Nb_2O_5, where as the molar refractivity behavior same as that of polarizability.

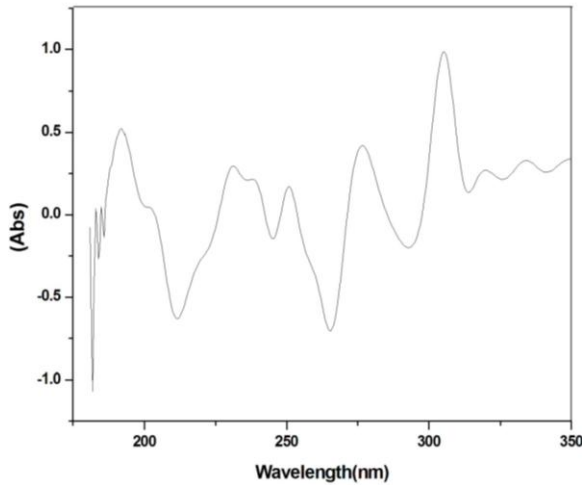### 4.5 Optical band gap (E_g) and refractive index (n) studies

Fig-6: Typical UV spectra of the sample.

Fig.6 shows the typical absorption intensity in arbitrary units as a function of wavelength for the glass with impurity 0.1 mol%. It is clear from the figure there is no sharp absorption edge and this is the characteristic of glassy nature. In addition, absorption edge occurs near ultraviolet region. In the Present work, absorption edge in the samples determined by oxygen bond strength in the glass forming network [22].
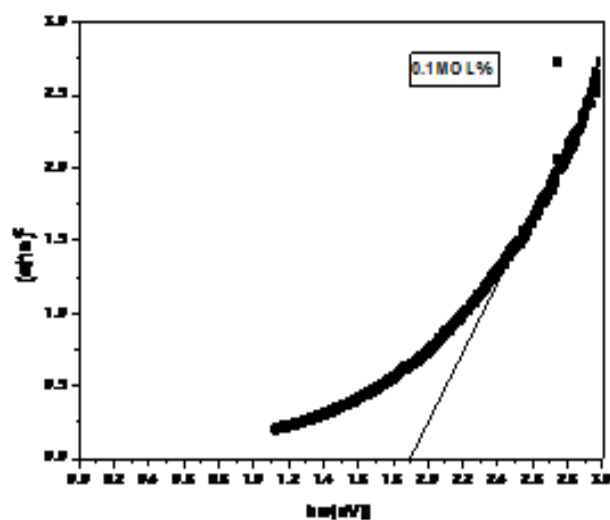

Fig-7: A typical plot of $(\alpha h\upsilon)^2$ as a function of energy $(h\upsilon)$ in $PbO-Ag_2O-B_2O_3-Nb_2O_5$.

Table 4. Optical band gap (E_g) and refractive index (n) of the prepared samples.

Mol %				E_g eV	n
B_2O_3	Ag_2O	PbO	Nb_2O_5		
70	1	28.9	0.1	1.75	2.852
70	2	27.8	0.2	1.95	2.75
70	3	26.7	0.3	2.1	2.689
70	4	25.6	0.4	2.125	2.683
70	5	24.5	0.5	2.215	2.648

It has been observed that for indirect allowed transitions, the measured absorption data fits for n=2 in the equation 2, therefore the results were plotted $(\alpha h\upsilon)^2$ versus photon energy $(h\upsilon)$, a typical plot is as shown in Fig. 7.
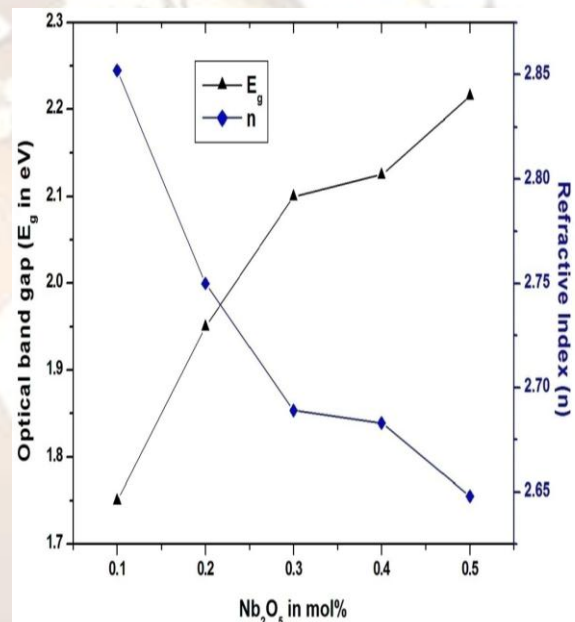

Fig-8: Variation of optical band gap and refractive index of oxide ions verses Nb_2O_5 mol%

It is observed from Fig. 8 and the values depicted in the table 4, that the optical band gap increases and refractive index decreases with increasing Nb_2O_5.

4.6 Infrared spectra (IR)

The experimental IR spectra of these glasses are presented in the Fig.9 and assignments of the bands detected are summarized in the table 5.The mid infrared region (400-1600cm^{-1}), where the vibrations of the B-O arrangements are dominant, is only consider. In particular, three domains could be separated in the IR spectra of borate glasses: the wave number profile in the range 400-780cm^{-1} is assigned to bending vibrations of various borate

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segments and Pb-O bonds, the medium bond between 780 and 1145cm^{-1} is due to the B-O asymmetric stretching of tetrahedral BO_4 units and, usually strong bands that appeared in the 1145-1500cm^{-1} are generated by stretching vibrations of borate units in which boron atoms are connected to three oxygen atoms(BO_3)[23,24,25,26].
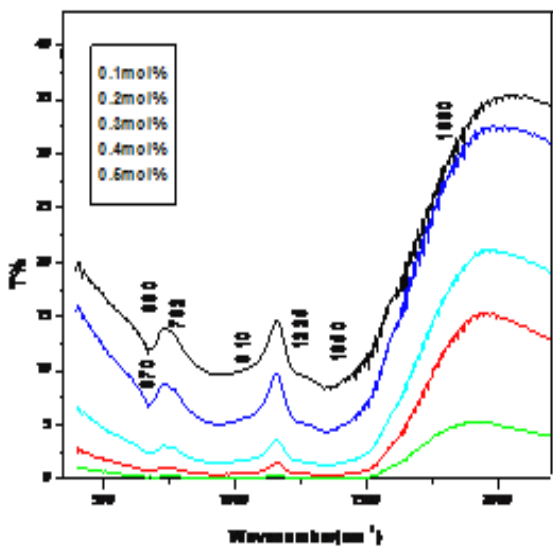

Fig.9: IR spectra of the glasses.

From the Fig. 9, increasing Nb_2O_5 and decreasing of PbO show wave numbers slightly shift towards longer wave number side. For the studied glasses, these experimental data indicate a structure built by: di-($B_4O^{2-}_7$), tri-($B_3O_5^-$), tetra-($B_8O_{13}^-$), penta - ($B_5O_8^-$) and ortho-($B_3O^{3-}_3$) borate groups (**O⁻ :** non-bridging atom) [3, 13]. No characteristic vibration modes of bonds from Nb_2O_5 and Ag_2O oxides were detected in the IR spectra. The 400-780cm^{-1} spectral domain is dominated by the band centered at 670cm^{-1}.

Table 5: Wave numbers and their assignments for IR spectra of glasses.

Wavenumber (cm^{-1})	Assignment
~670	O-B-O bond bending vibrations.
~680	O-B-O bond bending vibrations from pentaborate groups.
~762	BO_3-B-BO_4 bonds bending vibrations.
~910	B-O stretching vibrations in BO_4 units from diborate groups.
~1225	B-O asymmetric stretching vibrations of BO_3 units in pyro and ortho-borate groups and stretching vibrations of the B-O bonds $(BO_3)^{3-}$ involving mainly the linkage oxygen connecting different groups.
~1350	Asymmetric stretching modes of borate triangles BO_3 and BO_2^- and stretching vibrations of B-O of triangle $(BO_3)^{3-}$ units in metaborates, pyroboratyes and orthoborates.
>1630	O-H bond vibrations

IR spectra as shown in Fig.9 appear small shoulder attributed to the O-B-O bond bending vibrations [3].The band at centered dominate ~680cm^{-1}, the 400-760cm^{-1} spectral domain, being assigned to O-B-O bond bending vibrations from pentaborate groups [3, 27].The bond situated at ~762cm^{-1} is ascribed to the BO_3-B-BO_4 bonds bending vibrations and has approximately the same small amplitude for all other compositions. The band around ~910cm^{-1} were assigned to B-O stretching vibrations in BO_4 units from diborate groups[3,21].The band around ~1225cm^{-1} can be attributed to the B-O asymmetric stretching vibrations of BO_3 units in pyro and ortho-borate groups and stretching vibrations of the B-O bonds(BO_3)$^{3-}$ involving mainly the linkage oxygen connecting different groups[23]. The band around ~1350cm^{-1} was ascribed to asymmetric stretching modes of borate triangles BO_3 and BO_2^- and stretching vibrations of B-O of triangle $(BO_3)^{3-}$ units in metaborates, pyroboratyes and orthoborates [3, 24].

5. Conclusions

SEM/XRD shows that the samples are amorphous in nature. DSC reveals that the T_g variation. The IR data revealed the presence of boron atoms in both three and four coordinate states. Detected the presence of new structural groups namely Boroxol rings, Pyro and Dipent-Borate. The variation of molar volume and polarizability versus mol% of Nb_2O_5 is exactly opposite to that of density variation is expected. The addition of Nb_2O_5 and Ag_2O supports formation of BO_3 units with non bridging oxygen atoms. The optical properties of prepared glasses have been investigated. The calculated optical band gap of glass samples increase in accordance with Nb_2O_5 and is of indirect type. The trend of refractive index is opposite to that of band gap.

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