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FTIR and Optical Absorption Studies of [B2O3]-[Na2O]-[Li2O]-[CuO] Doped with [MgF2] Nanoparticle

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Abstract: The glass system of composition [6$_5$B$_2$O$_3$]-[15Na$_2$O]-[(18-X)Li$_2$O]-[2CuO]-[xMgF$_2$] Where x=0,3,6,9,12,and 15 mol%, has been prepared by conventional melt quenching technique. The density and molar volume (VM) were obtained. The density (p) show almost monotonic increase by increasing MgF2 content the molar volume has opposite trend. Fourier transforms infrared (FTIR) Spectroscopic studies revealed the presence Bo3 triganal and Bo$_2$ tetrahedral structural unit these glass. Show that the ratio the (Bo$_4$/Bo$_3$ + Bo$_4$)follows opposite trend to that of density , recalling that the numbers of Bo4 group ,decrease due to Bo$_4$→Bo$_3$ back diversion and content of (Bos) . The above arguments allow to conclude that the addition MgF$_2$ enhance the format of non-bridging oxygen, this increase the degree of disorder system. Optical transmittance spectra the samples in the range (190-2500) nm was measured and show two important feature .the first is transmission band located at short wave length side which centered at about 500 nm is most likely produced to an octahedral coordination of Cu++in the glass with strong tetragonal distortion. All samples exhibit bond pass filter behavior .the second feature is the absorption edge at the long wave length side . The Urbach energy ΔE increase with increasing MgF$_2$ Content indicate the increases the disorder of glass system. The opposite trend was observed in the value of ΔE is associated with structural disorder in many amorphous solid.

Keywords: Nanoparticle, Density, quenching technique, FTIR spectroscopy, Optical absorption

1 Introduction

Borate glasses constitute an interesting system in which charged network building units can be either borate triangles with non-bridging oxygen atom or borate tetrahedrons with all bridging oxygen atoms. Many studies were reported to elucidate the presence of different structural units in various borate glasses. Based on structure-property relationship many studies on properties such as electrical and optical were reported in these glasses [1-3].Since the incorporation of transition metal ions into glass creates color in the glass, transition metal ions have been used as color centers in glass. Thus, the optical absorption of glasses containing transition metal ions (including Copper ions) has been studied to explore their coloring mechanisms in different glass systems. The electronic structure of the copper atom is $3d^{10}$ $4s^1$, and the usual oxidation states are Cu^0, Cu^{1+} and Cu^{2+} . The Cu^{2+} ion has partially filled d orbitals creating color centers in glass via an absorption band in the visible spectrum. Thus, most glasses which contain Cu^{2+} have a blue to green color [4]. Furthermore the preferences of based-glasses are, eco-friendly Mg is minimum hygroscopics and in symmetry diagonal with lithium, MgF2 acts as GNM at minimum concentration and as a GNF at higher compositions in the g-matrix. So, this work investigates on IR spectra, optical E bands, and basicity optical studies of doped-magnesium - fluoride borate glasses with the formula[65B2O3]-[15Na2O]-[(18-X)Li2O]-[2CuO]-[xMgF2] Where x=0,3,6,9,12,and 15 mol%, are reported. In additions, these glasses display challenging electric, optic and thermal characteristics [5].

2 Experimental Technique

2-1 Glasse Preparations

The glass system with the formula[65B2O3]-[15Na2O]-[(18-X)Li2O]-[2CuO]-[xMgF2] Where x=0,3,6,9,12,and 15 mol % , has been prepared by conventional melt quenching technique. The batches in powder form were mixed and thoroughly in an agate mortar, and melted in porcelain

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*Corresponding author e-mail: khmadina@yahoo.com crucibles in an electric furnace at a temperature range of 1000-1100 C^0 FOR about 1 h in a normal atmosphere. A porcelain crucibles containing the batch was shacked thoroughly to achieve high homogeneity. The crucibles were covered by a porcelain lid to minimize volatilization effect. The resultant melt was then quenched on a pre-heated stainless steel mold to avoid thermal stresses produced by non-uniform rapid cooling of the glass.

The density (p) of the prepared glass samples was measured by Archimedes,s method. (p the corresponding molar volume (V_M) was calculated using the relation, V_M = $M_{W/}p$, where = M_W is the total molecular weight of the multi-component glass system. IR absorption spectra were recorded in the wave number range (400-4000 cm^{-1}) using KBr pellets with a Carl Zeiss Jena spectrometer (UR20 mode).

For the absorption measurements, were carried out using (JASCO-V570) spectrophotometer in the wavelength range 190-2500 nm. Samples for optical measurements were plate-shaped with a thickness of approximately2.2mm.

2.2. Density Measurements

Density was measured for all glass samples at room temperature using xylene as the immersion liquid. Density is generally measured by the fluid displacement method depending on Archimedes principle. According the Archimedes principle, the buoyancy equals the weight of the displaced fluid. Archimedes Principle using xylene as the buoyant medium evaluated the density of the glass samples. The density was obtained by employing the relation:

$$\rho = W_a \rho_b / (W_a - W_b) \qquad (1)$$

where wa is the weight of glass sample in air, wb is the weight of glass sample in buoyant liquid, (wa-wb) and ρb are buoyancy and buoyant density. Measurements have been madein digital balance. For samples react with water, an inert liquid as toluene, xylene, etc. may be chosen as the immersions medium.

2.3. Calculation of Molar Volumes (MV)

The MV of samples calculated using:

$$V_m = M/\rho. \qquad (2)$$

ρ is sample density and M (molecular weights). All calculations are averages of three independent measure values.

2.4. Ir Measurements

IR absorption spectra recorded in range of (400-4000 cm^{-1}) using KBr pellets with a Carl Zeiss Jena spectrometer (UR20 mode).

For the absorption measurements, (JASCO-V570) spectrophotometer is used in the wavelengths 190-2500 nm. Sample for optical measurement was plate-shaped with a 2.2mm thickness.

3 Results and Discussion

Morphological modifications of glass network and associated in structural units can be given in terms of density and molar volume MV. (6) (simon et al.2003).

The dependence of glass density (p) (g/cm^3) and molar volume M_v (cm^3)) with MgF2 Content (mol %) are shown in fig .(1) and table (1).

The fig reveals non-linear behavior for both density ρ and M_v, however both follow opposite direction, i. e they obey the normal trend. For ranges x= (0-3) ,(9-15) (p) and Mv show opposite trend. On the other in the range x= (3-9), follow common pattern, where both increase with with increasing MF2 concentration. The first case we are dealing with two competing factors the atomic weight of the additives (MF2) and the number of NBOs which responsible for the formation of open structure leading to low density. It seems that in this range, the effect of NBOs is more effective than the increasing density due the replacement of lithium ions by Magnesium ions. Such observed behavior can be accounted for by the replacement of light Li_2O by Heavier MgF_2 and non-bridging oxygen formation. In second case x= (3-9%) the replacement of light lithium ions by heavier Magnesium fluoride ions is responsible for increasing density by Magnesium fluoride addition.

FTIR spectroscopy:

The absorption spectra in infrared region were measured and give Fig (2). For sake of IR band assignment the spectra were deconvoluted and the ratio N4 = BO4/BO3 + BO4 as shown insert fig(3) , The obtained results show that N4 follows opposite trend to that of density . This is expected since the increase of N4 mean's the formation of open structure i.e reduce the density. The above arguments let to hold that the additions MgF2. enhance the formation of non- bridging Oxygen this increase the degree of disorder system .

The investigated glass samples exhibits bonds with intensity and position changes. From this figure, It is well known that the IF spectra of samples are categorized into three main regions [7]. The low wave numbers which observed at 600 – 800 Cm^{-1} and attributed to B – O – B linkage bending the borate network. Intermediate wavenumbers region is at 800 – 1200 Cm^{-1} that denotes the B – O bond stretch for the tetrahedral-BO_4 unit. High region is at 1200 – 1600 Cm^{-1} related to symmetric stretced B – O bond for the trigonal-BO_3 unit [8].

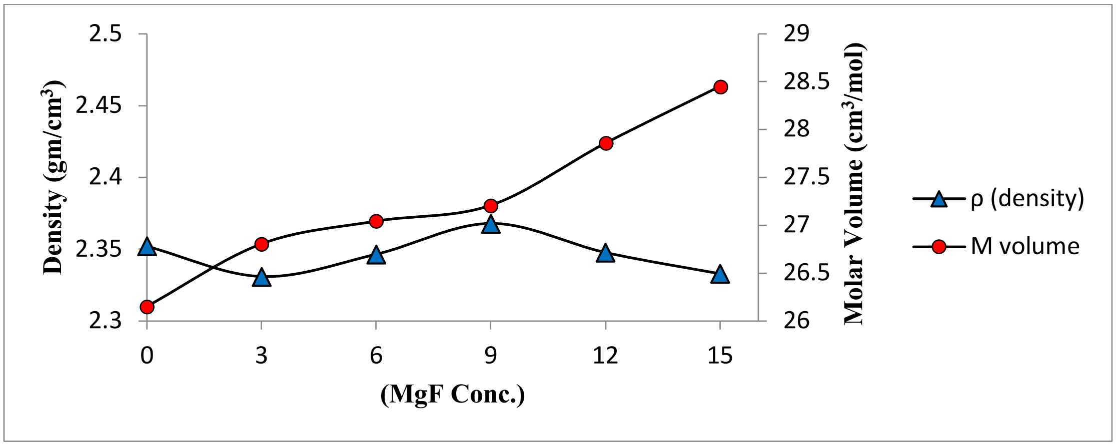


Fig. 1: density and MV dependence on MgF2 contents.

Table 1: Chemical composition (mol%) , density values and molar volume of $65B_2O_3$ – (18-x) Li_2O – $15Na_2$O-2 CuO - xMgF_2 glasses system.

Sample No.	MgF Conc.	Molar mass(m)			Avr M air	Density ρ	Molar volum(V_m)			Density ρ	Mass	Molar volume	ρ liq
1	0	0.349	0.348	0.349	0.348667	2.3520226	61.5144	0.113	0.112	0.113	0.112667	26.1538218	1.592
2	3	0.239	0.239	0.238	0.238667	2.33102658	62.487	0.075	0.076	0.076	0.075667	26.8066458	
3	6	0.377	0.377	0.378	0.377333	2.34654167	63.4596	0.122	0.121	0.121	0.121333	27.0438957	
4	9	0.907	0.907	0.908	0.907333	2.36799126	64.4323	0.297	0.297	0.298	0.297333	27.2096663	
5	12	0.428	0.428	0.427	0.427667	2.34774253	65.4049	0.137	0.138	0.138	0.137667	27.8586238	
6	15	0.418	0.416	0.416	0.416667	2.33294256	66.3775	0.132	0.133	0.132	0.132333	28.4522651	

The infrared absorption spectra of B_2O_3 - Li_2O – Na_2O-CuO -MgF_2 are shown in figure (2).

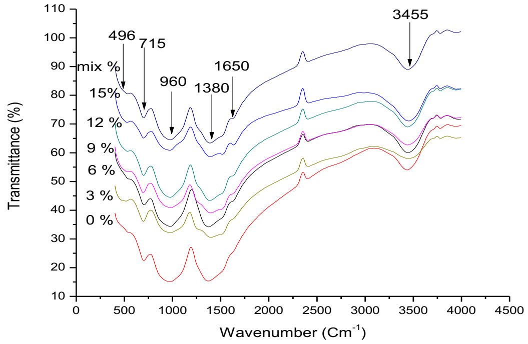


Fig.2: FTIR for B_2O_3 - Li_2O – Na_2O- CuO -MgF_2 glass system.

Fig.(3) exhibits bands at ~ 496, 715, 980, 1380 and 3455cm^{-1} with position and intensity changes in the band. The bands at range 446-453 cm^{-1} showed vibrations of Mg^{2+} ions [9].

Band of absorption at 715 cm^{-1} is a bending vibration of B-O-B in symmetric BO$_3$ triangle [10]. The observed broad bands at 980 cm^{-1} attributed to B-O stretched vibration of tetrahedral BO$_4$ unit in many borate group, like triborate, pentaborate and diborate group [11]. Other band at 1380 cm^{-1} is symmetric B-O stretching vibration of trigonal BO$_3$ unit. This band shifted to higher frequencies with increase in Mg contents which increases the bond lengths of B-O groups. The band with 1650 cm^{-1} report the presence of crystal-water with H-O-H bending mode [9]. Band around 3434cm^{-1} correspond to OH stretched vibrations [9]. The deconvolutions allowed the better identifications of all bands in the FTIR spectra to understand their assignments [12]. The deconvoluted spectra based on Gaussian type functions into the minimum bands to get quantitive informations about the structure groups of the investigated glass samples are shown figure (3).

1. The low frequencies band in the region at ~ 445 - 495 Cm^{-1} can be attributed to / show vibration existence of Mg^{2+} ions [15].

2. The bands at ~ 630 – 690 Cm^{-1} can be attribute to / indicates the bending of B – O – B linkage in the BO_3 triagonal [15]

3. The bands at ~ 700 – 790 Cm^{-1} can be attribute to bending of B – O – B linkage in the BO_3 groups and isolated BO_3^{3-} groups [16, 17].

4. In pure B_2O_3 glasses, the band of absorption at 806 Cm^{-1} is the characteristic of the boroxol ring. The absence of this band in the present IR spectra indicates that the formation of boroxol rings do not occur in the glass systems under study15,16, 17].

5. Bands at ~ 970 - 1100 Cm^{-1} can be attribute to B – O bonds stretching vibrations in BO_4 units [11,14].

6. The bands at ~ 1200 - 1385 Cm^{-1} can be attribute to symmetric stretched vibrations of B – O bonds from pyro and Orth in the BO_3 groups [11].

7. The bands at ~ 1677 - 1813 Cm^{-1} can be attributed to crystal water with H – O – H bending mode [11,18].

8. The bands at ~ 2300 - 2400 Cm^{-1} can be attributed to anti symmetric stretched of water molecules [18].

9. The bands at ~ 3400 - 3600 Cm^{-1} can be attributed to O – H stretched vibrations [18].

The Fractions N_4 is the ratio of [Area related to structural groups containing BO_4 units / Area related to borate units (BO_3+ BO_4)] [8,14]. Hence, Fig.(4). Indicated variation of N_4 with Mg content for B_2O_3 - Li_2O – Na_2O - Cuo_2 glass system. It noted that N_4 shows non linear behavior with Mg content. However also, the N_4 exhibits opposite trend respect to density, indicates that the number of BO_4 groups reduced due to BO_4 BO_3 Back conversion and Creation of (BOs).

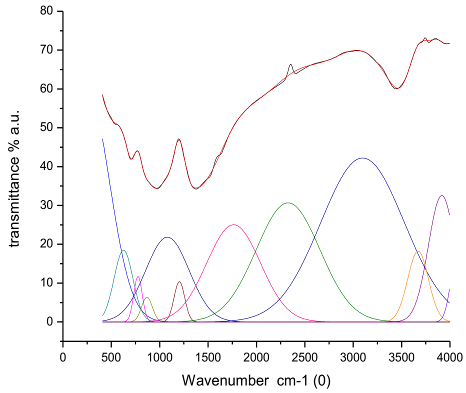
Optical Results:

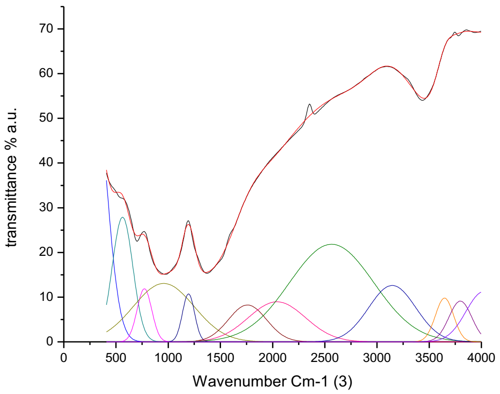
Optical absorption spectra in the range of 200-2500 nm are given fig (5). Two important feature are observaed, the first is transmission band located at short wave-length sides and the second is an absorption edges at long-wave length sides. The former band is most likely due to d-d transition in Cu+2 ions. The copper in glasses can exhibit three different valency states Cu0 ,Cu1 and Cu2 . The colour of copper doped glasses is due to d-d transitions in divalent copper ions . in the latter the ligend field cuvers splitting 3d energy terms and allow d-d transition . As a result of the above d-d transition in Cu2+ two broad absorption bands in near UV and near IR regions should be observed. Between such transmittance allows to use such system as an optical bond pass filter . The observed absorption band can de convoluted according to (Cu) the DE convoluted allows to determine 10 Dq .

Optical energy band-gap (E_{gapt}) was calculated see i.e (19). The absorption coefficient ,$\alpha(v^{\cdot})$ and E_{gapt} in several amorphous-materials are given in (20)

$$A(v^{\cdot})=B(\alpha v^{\cdot}-E_g)^n/hv^{\cdot} \qquad (1)$$

B is the parameter of band-tailing, n have the value (1/3,1/2 and 2) corresponding to indirect forbidden, indirect and direct, direct forbidden transitions allowed , $hv^{\cdot}$ the indirect photon energy. Here the optical band gap refer to photons assisting the electron to moves from valance band to conduction bands (19). Refective index n have value range .5and 2 depends on the linear –band electronic transition,





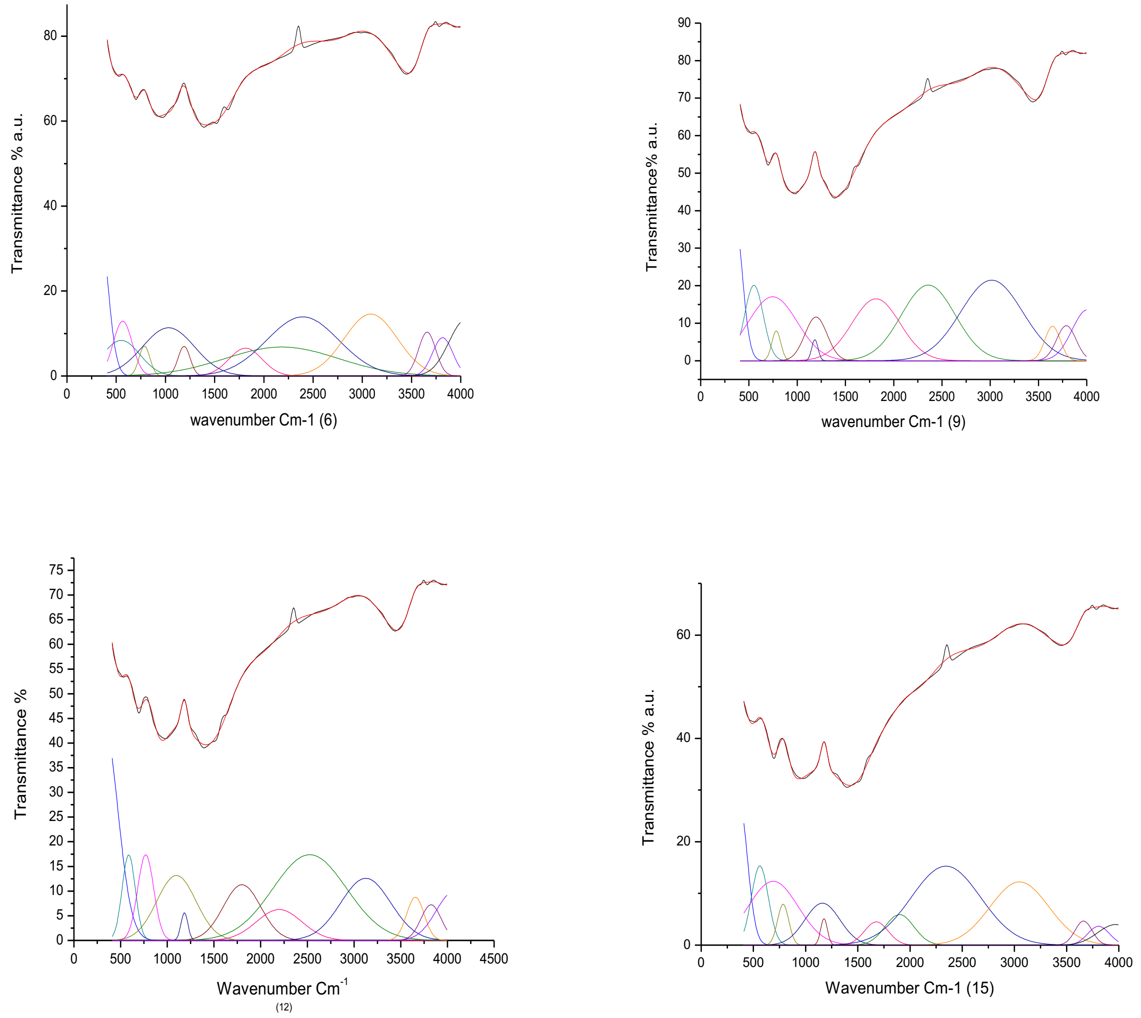


Fig.3: Representative DE convoluted FTIR spectrum for glass system.

the measured absorption first well to the above Eq(2) for n=2 and n=1/2. A graphic between $(\alpha h\nu)^n$ and $(h\nu)$ is Tauc's plot (21). A fig of $(\alpha h\nu)^{1/2}$ vs. $(h\nu)$ for indirect allowed transitions is depicted in figure (6). Which explain vary between 2.7 to 2.9 ev .which values are increase with increase MgF_2 contant. The indirect transitions are the most possible transitions mechanism and MgF_2 ions increases the excitation –phonons coupling which results in dynamics this order [22] . It's shown that by increases MgF_2 the optical band energy E_{gapt} firstly increases and then decreases, increase MgF_2 ions causes change in structure in glass network. The forming of non-bridging Mg , that bind excited electron less tightly the bridging Mg increases with

MgF_2 results in the decreases of optical energy bands gap[23].

Urbach energy

Dependence of $\alpha(\nu)$ on the $h\nu$ in amorphous solids is introduced as Urbach rule and can write in (24)

$$\alpha(\nu) = B\exp^{(h\nu/\Delta E)} \qquad (2)$$

B is constant and ΔE is the Urbach energy. ΔE provides a measure of disorder in the amorphous and crystalline ΔE The value of Urbach energy ΔE were calculated using reciprocal of linear portion slopes of ln(α) vs.$h\nu$ curves in the lower energy region as in figure (4) . The value varies between .38 to .41 ev which has nonlinear variations, ΔE decreases with addition MgF_2 content then increase value at .41 ev for Δ with increase MgF_2 at value concentration 15% , this decreasing trend suggest that the degrees of disorder decreases in glasses structure with increases MgF_2 content[25] up ender.

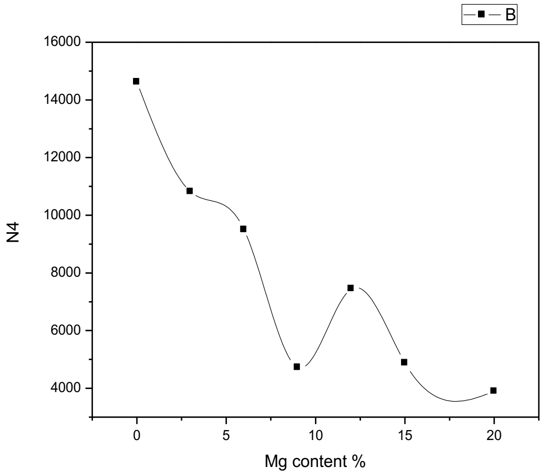


Fig.4: Variation of N_4 with composition of Mg content for B_2O_3 - Li_2O – CuO -Na_2O -MgF_2 glass system.

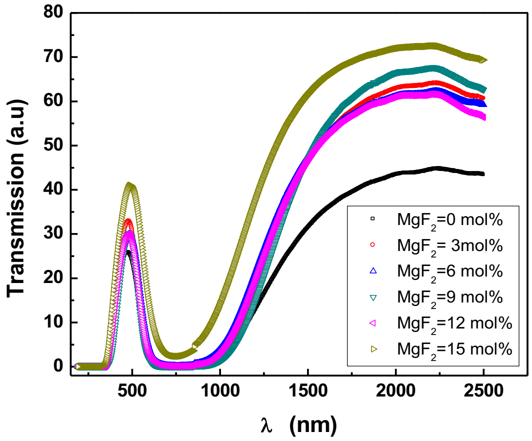


Fig.5: Transmission spectra varies wave length of the glass samples.

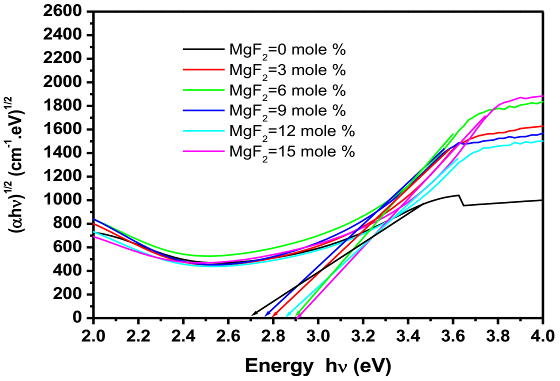


Fig.6: plot of (αhν)$^{\wedge 1/2}$ against hω.

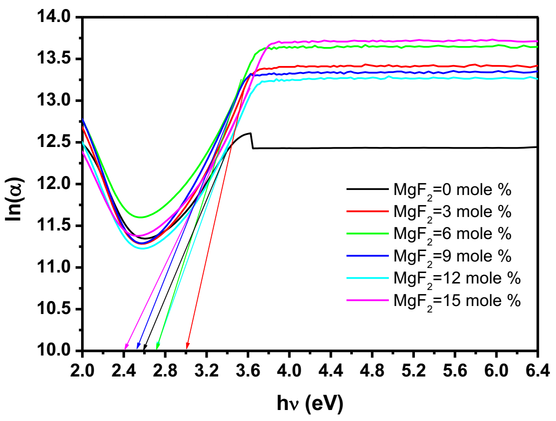
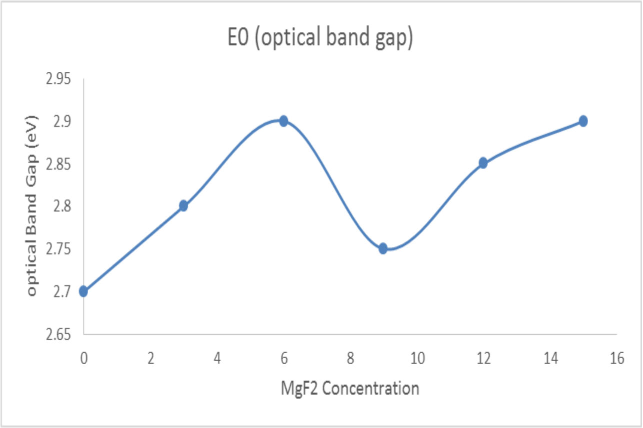


Fig.7: plot of lnα against hω variation of energy band gap in samples glasses with concentration.



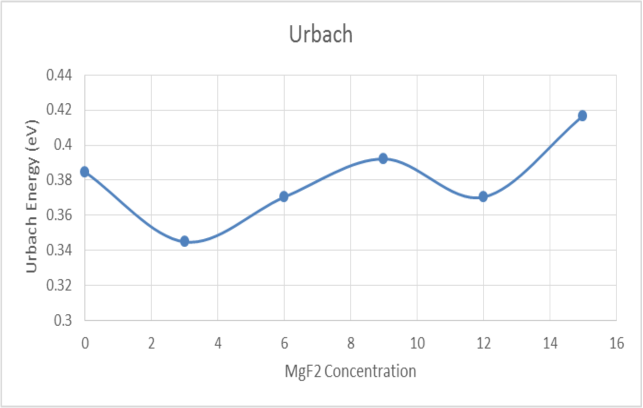


Fig.8: Variation of Urbach energy in samples glasses with concentration.

Table 2: Optical band gap energy (E_{gapt}) and Urbach energies (ΔE) of [65B2O3]-[15Na2O]-[(18X)Li2O]-[2CuO]-[xMgF2] Where x=0,3,6,9,12,and 15 mol%.

MgF2	E0 (optical band gap)	Urbach
0	2.7	0.384615
3	2.8	0.344828
6	2.9	0.37037
9	2.75	0.392157
12	2.85	0.37037
15	2.9	0.416667

4 Concluding Remarks

Physical and optical glass sample properties dependent on the glass compositions. The density and molar volume (V_M) were obtained. The density (ρ) show almost monotonic increase by increasing MgF_2 content the molar volume has opposite trend. FTIR Spectroscopic studies exposed the countenance of Bo3-trigonal and Bo2-tetrahedral structure unit these glass. Show that the ratio the ($Bo_4/Bo_3 + Bo_4$)follows opposite trend to that of density, from above we can say that addition MgF_2 of non-bridging oxygen, this increase the degree of disorder system. Optical transmittance spectra the samples in (190-2500)nm range was measured and show two important feature. The ΔE increase with increasing MgF_2 Content indicate the increases the disorder of glass system. The opposite trend was observed in the value of ΔE is associated with structural disorder in many amorphous solid. Inspected glasses find their implementations in both photonic and optoelectronic fields.

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