SPECTROSCOPIC PROPERTIES OF COPPER IONS IN $NA_2O-B_2O_3$ GLASSES

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Abstract:

The physical properties of the glasses are having influence not only in the fundamental process but also in its application. In our study, we have studied the physical properties of three different compositions of CuO doped Na_2O- B_2O_3 glasses such as C_0: 40.0 Na_2O – 60.0 B_2O_3 (Pure), C_1: 39.9 Na_2O – 60.0 B_2O_3 – 0.1 CuO and C_2: 39.8 Na_2O – 60.0 B_2O_3 – 0.2 CuO (all in mol %) using optical absorption in the region 300 to 1600 nm and infrared spectra in the region 400 to 2000 cm^{-1}. We observed that in the Optical absorption spectra of CuO doped Na_2O- B_2O_3 glasses exhibited a broad absorption band peak position at 800 nm; this band is assigned to the $^2B_{1g} \rightarrow {}^2B_{2g}$ transition. An increase in the intensity of this band is observed with increase in the concentration of CuO in the glass matrix. In the infrared spectrum of pure Na_2O-B_2O_3 glasses has exhibited conventional vibrational bands due to BO_3 and BO_4 units in the regions 1200–1600 cm^{-1} and 900–1050 cm^{-1}, respectively. With the introduction of CuO from 0.1 to 0.2 mol% the intensity of the band due to BO_3 structural units is observed to increase at the expense of band due to of BO_4 units.

Key words: Na_2O-B_2O_3 glasses, Optical absorption spectra, Infrared spectra

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Introduction:

The study on the physical properties of the glasses helps us to know the fundamental process-involved in and also its wide application in technology. The main factors that regulate the physical properties of the glasses are the structure, composition, and the nature of the bonds present. The experimenting the changes in the physical properties of glasses by controlled variation of chemical composition, doping etc., is of appreciable interest in wide range of its application. Materials prepared from a melt quenching are often referred to as glasses. These materials possess ionic as well as covalent bonding interaction.

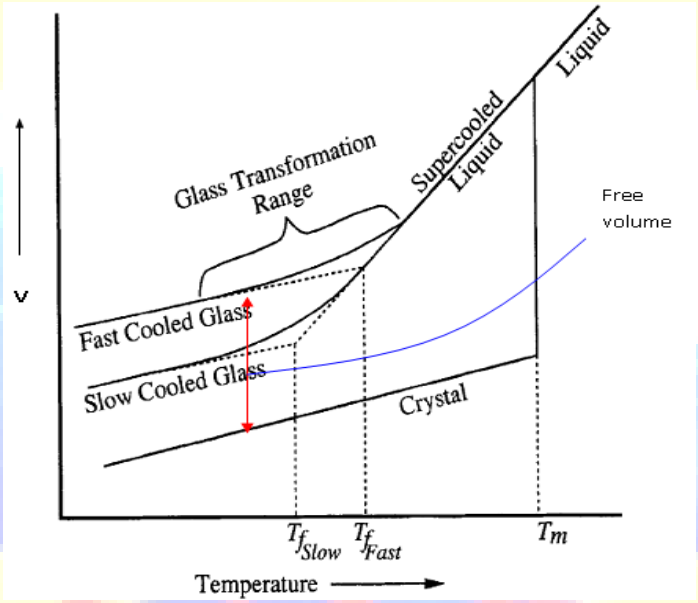

Fig. 1: Schematic illustration of the change in volume with temperature as super cooled liquid is cooled through the glass transition temperature T_g.

When a liquid is cooled from high temperature, crystallization may take place at the melting point T_m. If the crystallization takes place, there will be abrupt change in the volume at T_m and there will be a gradual break in slope if the glass formation takes place. The region over which the change of slope occurs is known as glass transition temperature T_g. This process of changes in volume with temperature as a super cooled liquid is cooled through the glass transition temperature T_g is illustrated Fig. 1.

Various factors play a significant role in determining the ease of glass formation, for example, chemical, structural properties, thermodynamic or free volume aspects of the materials, etc. Zachariasen was the first to categorize the materials into glass formers and non-glass formers

[17]. He used five oxides such as SiO_2, GeO_2, B_2O_3, As_2O_3, P_2O_5 and that were the only known glass formers to prepare glasses. The advantages of these oxides are these can also form glasses when mixed up to certain percentage with other oxides, which were not glass formers by themselves. Based on these, Zachariasen proposed the rules that an oxide should obey if it has to form a glass. Cooper has some limitations on the original rules [2]. The latest rules after objections are

1. A high proportion of glass network forming cat ions is surrounded by oxygen tetrahedra or triangles.
2. The oxygen polyhedra share only corners with each other.
3. Some oxygen atoms are linked to only two cat ions, and do not form additional bonds with any other cations.

Excellent reviews on the topology of the glass by Vanvotert [15], Elliott [3], Polk [5], Ingram [12], gives more and useful information on construction of continuous random network for a glass. As per these rules stated above, the oxides of the type AO, A_2O should not form glasses. The rules are satisfied only for oxides of the type A_2O_3, AO_2 and A_2O_5. Presence of oxides such as A^+ (example Li^+, Na^+, K^+ etc.,) A^{2+} (example Ca^{2+}, Pb^{2+}, Cd^{2+} etc.,) other than A^{3+} and A^{4+} are known as network modifiers. Li_2O, Na_2O, K_2O, PbO, CaO, CdO are some of the basic examples of modifiers since these modifiers break-up the network by introducing non-bridging oxygens. The third group of oxides which are known as intermediate glass modifiers are the class of oxides which are not readily form glasses by themselves but form glasses when they are mixed with other oxides such as TeO_2, WO_3, MoO_3, Al_2O_3, Ga_2O_3 and V_2O_5 etc [8, 11].

In the last few decades, there is a significant development in developing a large variety of inorganic glasses which has suitable electrical, mechanical, optical characteristics along with the improved physical properties such as electrical resistance, mechanical strength, glass transparency, IR transmission performance and ability to accept more transition metal ions for their use in solid-state ionic devices [16, 6]. Experimental work on these areas was carried out on a number of glasses yields valuable information. Investigations on the spectroscopic properties

such as optical absorption, IR spectra and electron spin resonance can be used as probes to throw some light on the structural aspects of these glasses [14].

B_2O_3 acts as one of the most important glass formers and can be incorporated into various kinds of glass systems as a flux material to attain materials with specific physical and chemical properties. Boron can exist in three and four oxygen co-ordinate environments having high strengths of covalent BO bonds which enable borates to form a stable glass. B_2O_3 glasses have attracted extensive investigation in recent years, in view of their potential applications in a number of solid state ionic devices [10].

The origin of the properties of borate glasses has been strongly correlated to the local order around boron atoms. Studies shows that the coordination geometry of boron atoms strongly dependent on not only the composition of the glasses but also the chemical nature of the network modifier. For example, the addition of sodium oxide, in to the borate glass network, changes the coordination of boron atom from BO_4 tetrahedral units to BO_3 trigonal units. Basic characteristics of borate glass structures are generally agreed upon. The fundamental building block in vitreous B_2O_3 is the BO_3 groups which exist either as a random network of boroxol rings or some fraction of BO_3 triangles connected by B-O-B linkages [9]. The boroxol group is composed of three corner–sharing BO_3 triangles, which form a very highly planar ring.

Alkali oxy borate glasses have simple and well-understood glass structure. Several physical properties viz., electrical, optical and mechanical properties of pure and various transition metal ions doped alkali borate glasses have been under extensive investigation in recent years in view of their technological applications especially in phosphors, lasers, solar energy converters and in a number of electronic devices. Alkali fluoro borate glasses are transparent from the near UV to the middle infrared region. They are resistant to atmospheric moisture and are capable of accepting large concentrations of transition metal ions [13].

The origin of the properties of alkali oxy borate glasses has been strongly co-related to the local order around boron atoms. The coordination geometry of boron atoms has been shown to be strongly dependent on the composition of the glasses and on the chemical nature of the network

modifier. For example, the addition of alkali oxide in to the borate glass network changes the coordination of boron atom from BO_4 tetrahedral units to BO_3 trigonal units.

Recently much attention has been paid to research in inorganic glasses doped with transition metal ions because of their technological importance in the development of tunable solid state lasers, new luminescence materials, solar energy converters and fiber optic communication devices. Copper is being extensively used in several commercial glasses, such as red glass hematite, aventurine and rubies. CuO containing glasses are also important in technological point of view, because of their semiconducting properties and due to other potential applications. In glasses, copper ions exist in two stable ionic states viz., monovalent Cu^{+} ions, divalent Cu^{2+} ions and may also exist as metallic copper. The electronic structure of the copper atom is [Ar] $3d^{10}$ $4s^{1}$ [10]. Though considerable number of studies is available on some CuO containing glasses most of them are restricted to spectroscopic studies.

Though extensive recent studies on certain physical properties of alkali oxy borate glasses are available, the thorough survey of the literature on these glasses show detailed investigations on spectroscopic properties of copper doped Na_2O-B_2O_3 glasses in particular, are not extensively investigated. Detailed studies on spectroscopic properties viz., optical absorption and infrared spectra of copper ions doped Na_2O-B_2O_3 glasses is expected to throw some light on the possible use of these glasses in lasers, solar energy converters and in a number of electronic devices. Thus, the aim of our present work is to prepare, characterize and to investigate various spectroscopic properties (optical absorption and infrared spectra) of Na_2O-B_2O_3 glasses doped with different concentrations CuO [1].

Materials and methods:

Composition of glasses:

The details of compositions of the glasses investigated are:

C_0: 40.0 Na_2O – 60.0 B_2O_3 (Pure)

C_1: 39.9 Na_2O – 60.0 B_2O_3 – 0.1 CuO and

C_2: 39.8 Na_2O – 60.0 B_2O_3 – 0.2 CuO

Range of infrared spectra and Optical absorption spectra:

The present study is devoted to have a comprehensive understanding over the influence of copper ions on the structure of Na_2O – B_2O_3 glass system from a systematic study of the following physical properties:

Infrared spectral studies in the wave number range 400-2000 cm^{-1} and the study on the effect of concentration of copper metal ions on the position and intensity of various vibrational bands;

Optical absorption studies in the wavelength range 300-1600 nm, identification of various electronic transitions of copper ions

Methods of preparation of glasses

The glasses used for the present study are prepared by the melting and quenching techniques. The starting materials used for the preparation of the present glasses were Analytical grade reagents (99.9 % pure) of Na_2CO_3, H_3BO_3 and CuO. The compounds of required compositions were thoroughly mixed in an agate mortar and melted in a platinum crucible. The furnace used was a PID temperature controlled furnace (Fig.2). The glasses were melted at about 700 - 900^oC for an hour till a bubble free liquid was formed. The resultant melt was poured on a rectangular brass mould (containing smooth polished inner surface) held at room temperature. The samples were subsequently annealed at 300^oC in another furnace. The glasses were then ground and optically polished. The approximate final dimensions of the glasses used for studying the electrical and optical properties are 1cm x 1cm x 0.2cm. For the present work the thickness of the sample is approximately 0.15cm only.

Fig.2: Schematic sketch of furnace used for melting the samples

Physical parameters:

The density (*d*) of the glasses was determined by the standard principle of Archimedes' using o-xylene (99.99 % pure) as the buoyant liquid. A direct reading balance (capacity 100 gm, readability 0.1 mg) was used for weighing. The bulk glass was suspended on a very thin copper stand that was set in the immersion liquid container; the density of the samples was determined by weighing them in the liquid and in air. From the measured values of density *d* and calculated average molecular weight $\overline{M}$, various physical parameters such as metal ion concentration N_i, mean ion separation r_i and polaron radius r_p which are useful for understanding the physical properties of these glasses were evaluated using standard formulae.

The transition metal ion concentration (N*i*) could be obtained from:

$$N_i\ (10^{21}\ \text{ions}/\text{cm}^3) = \frac{N_A M(\text{mol}\,\%)d}{\overline{M}} \qquad (1)$$

from the N_i values obtained, the polaron radius (r_p) and inter – ionic distance (r_i) of transition metal ions could be evaluated:

$$\text{Inter – ionic distance } r_i\ (\text{Å}) = \left[\frac{1}{N_i}\right]^{1/3} \qquad (2)$$

$$\text{Polaron radius } r_p\ (\text{Å}) = \frac{1}{2}\left[\frac{\pi}{6N_i}\right]^{1/3} \qquad (3)$$

Optical absorption spectra

The optical absorption spectra of the glasses were recorded using a JASCO Model V-670 Spectrophotometer (Fig.3) in the wavelength range 300-1600 nm.

Fig. 3: JASCO Model V-670 UV–vis–NIR spectrophotometer

Infrared transmission spectra

Infrared transmission spectra were recorded on a (Fig.4) with a resolution of 0.1 cm^{-1} in the spectral range 400–2000 cm^{-1} using potassium bromide pellets (300 mg) containing pulverized

sample (1.5 mg). These pellets were pressed in a vacuum die at ~680MPa. The spectra were recorded on Jasco-FT/IR-5300 spectrophotometer.

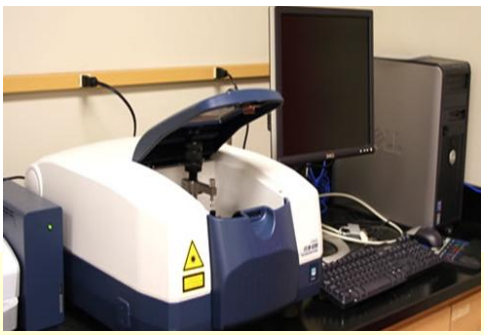

Fig.4: JASCO-FT/IR–5300 spectrophotometer

Results

Physical parameters

Various physical parameters such as total copper ion concentration Ni, mean Cu2+ ion separation ri, have been evaluated with the measured values of density d and the calculated average molecular weight $\overline{M}$ for the present these glasses and are presented in Table.1.

Physical parameter	**Glass**		
	C_0	C_1	C_2
Density *d* (g/cm^3)	3.468	3.487	3.494
Dopant ion conc. N_i (x10^{21} ions/cm^3)	-	2.25	4.48
Interionic distance of Cu^{2+} ions r_i (Å)	-	7.63	3.07
Polaron radius r_p (Å)	-	6.06	2.44

Table.1: Various physical parameters of Na_2O-B_2O_3: CuO glasses

Optical absorption studies

Fig. 5(a), 6(a) and 7(a) represents the optical absorption spectra of Na_2O-B_2O_3: CuO glasses recorded at room temperature in the wavelength region 300-1600 nm. The spectrum of CuO free glass has not exhibited any absorption bands. The spectra of glasses containing CuO exhibited a broad absorption band at 800 nm identified due to the transition $^2B_{1g} \rightarrow {}^2B_{2g}$ of Cu^{2+} ions. The intensity of this band is observed to increase with increase in the concentration of CuO. With increasing concentration of CuO up to 0.2 mol %, the peak position slightly changed but the intensity is observed to increase.

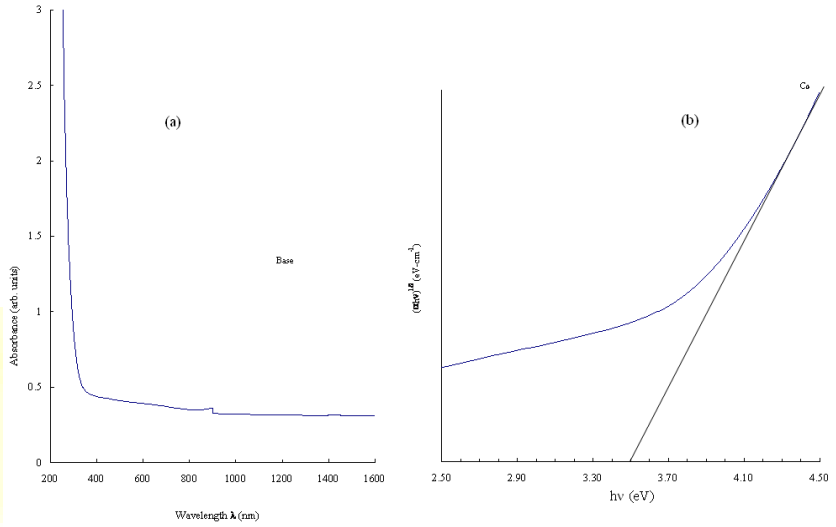

Fig. 5 (a) Optical absorption spectra and (b) Tauc plots of $Na_2O–B_2O_3$ base glasses

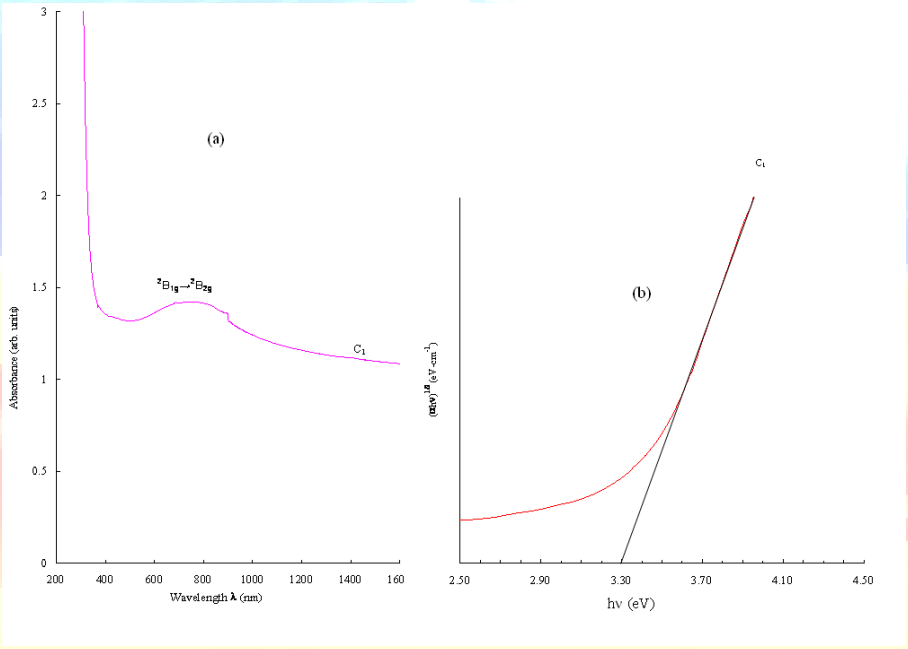

Fig. 6 (a) Optical absorption spectra and (b) Tauc plots of $Na_2O–B_2O_3$: 0.1 CuO glasses

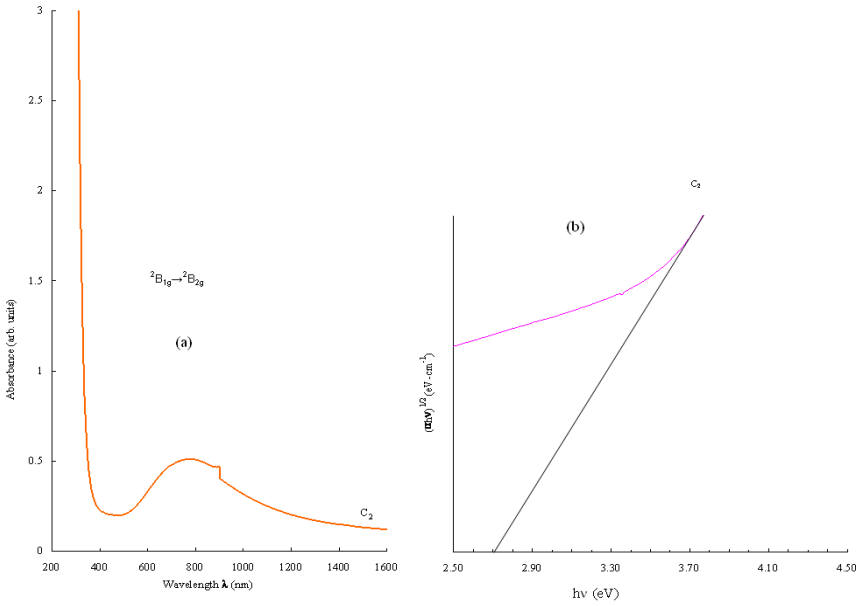

Fig. 7 (a) Optical absorption spectra and (b) Tauc plots of $Na_2O–B_2O_3$: 0.2 CuO glasses

From the observed absorption edges, we have evaluated the optical band gaps (E_o) of these glasses by drawing Tauc plot between $(\alpha \hbar \omega)^{1/2}$ and $\hbar \omega$ as per the equation:

$$\alpha (\alpha \cdot \hbar \omega) = C (\hbar \omega - E_o)^2$$

where α represents absorption coefficient.

Fig. 5(b), 6(b) and 7(b) represents Tauc plots of all glasses in which a considerable part of each curve is observed to be linear.

From the extrapolation of the linear portion of these curves, the values of optical band gap (E_o) obtained from these plots for Na_2O-B_2O_3: CuO glasses and are presented in Table.2. The value of E_o is found to increase with the increase in concentration of CuO.

Glass	C_0	C_1	C_2
Absorption Edge (nm)	267	319	329
Optical band gap E_o	3.50	3.30	2.70
$^2B_{1g}\rightarrow{}^2B_{2g}$	-	800	808

Table.2 Summary of data on optical absorption spectra of $Na_2O–B_2O_3$: CuO glasses.

Infrared transmission spectra

Fig.8, 9 and 10 represents the IR spectra of Na_2O-B_2O_3: CuO glasses recorded at room temperature in the region of 400-2000 cm^{-1} The infrared transmission spectra have exhibited three conventional bands at 1354 cm^{-1} (due to BO_3 units), 1013 cm^{-1} (due to BO_4 units) and band at 718 cm^{-1} due to bending vibrations of B-O-B linkages. With increase in the concentration of CuO the intensity of band due to BO_3 structural units increases at the expense of band due to BO_4 units in the glass matrix.

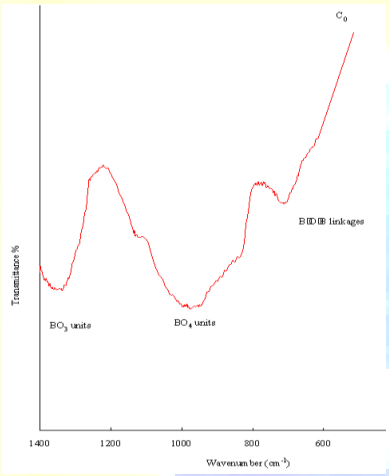

Fig. 8 IR spectra of $Na_2O–B_2O_3$ base glass

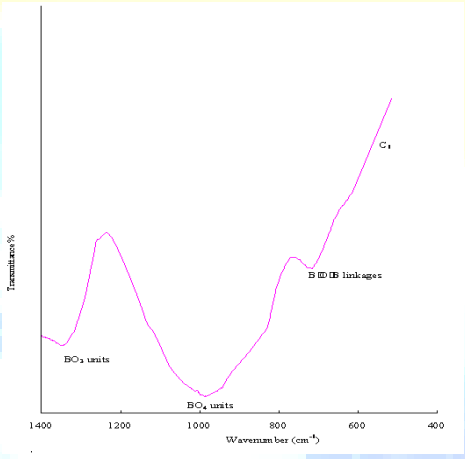

Fig.9. IR spectra of $Na_2O–B_2O_3$: 0.1 CuO glass

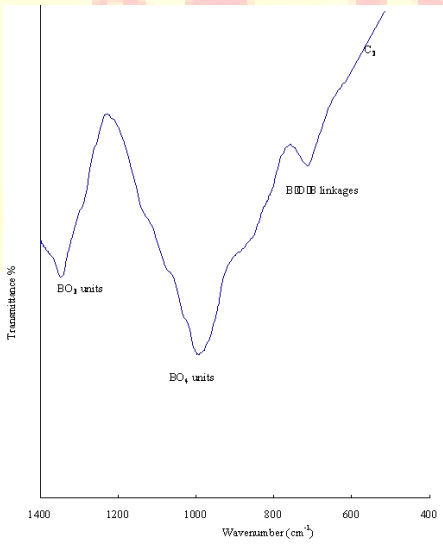

Fig.10: IR spectra of $Na_2O–B_2O_3$:0.2 CuO glasses

Discussion

It is well known that the B_2O_3 glasses network consists of sp^2 planar BO_3 units and more stable sp^3 tetrahedral BO_4 units. The presence of such units in the borate glasses was proved earlier from the IR spectral studies. The BO_4 unit in the glass network linked to two such other units and one oxygen from each unit with a metal ion and the structure leads to the formation of long chain tetrahedron.

The free ion term Cu^{2+} (d^9) is ^2D. In octahedral crystal field it splits into ^2E_g and $^2T_{2g}$ with ^2E_g being the lower level. ^2E_g generally splits due to Jahn- Teller effect. Therefore Cu^{2+} is rarely found in regular octahedral site. Accordingly, in the present investigation, Cu^{2+} is taken to be octahedrally coordinated by six oxygen atoms and octahedron is tetragonally distorted. Hence in the tetragonally distorted octahedrtal environment, the ^2E_g level splits into $^2A_1$ and $^2B_1$, and $^2T_{2g}$ level into ^2E and $^2B_2$, the ground state being $^2B_1$. The broad absorption band observed in the optical absorption spectra of titled glass is assigned to $^2B_{1g} \rightarrow {}^2B_{2g}$ transition of octahedral Cu^{2+} ions [5].

With increase of CuO content, there is a gradual increase in the intensity of this band. This observation indicates there is an increase in the concentration of octahedral Cu2+ ions in the glass network. The increase of such octahedral ions increases the de-polymerization of the glass network. The observed increase in the intensity of the band due to BO_3 structural units with increase of CuO content supports this view point.

Conclusions

The main conclusions drawn from the results of above studies are summarized below:

Optical absorption spectra of CuO doped Na_2O- B_2O_3 glasses exhibited a broad absorption band peak position at 800 nm; this band is assigned to the $^2B_{1g} \rightarrow {}^2B_{2g}$ transition. An increase in the intensity of this band is observed with increase in the concentration of CuO in the glass matrix.

The infrared spectrum of pure Na_2O-B_2O_3 glasses has exhibited conventional vibrational bands due to BO_3 and BO_4 units in the regions 1200 – 1600 cm^{-1} and 900 -1050 cm^{-1}, respectively.

With the introduction of CuO from 0.1 to 0.2 mol% the intensity of the band due to BO_3 structural units is observed to increase at the expense of band due to of BO_4 units.

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