

ABSTRACT

Alkali oxy borate glasses are well known due to their variety of applications in phosphors, solar energy converters and in a number of electronic devices. These glasses have high mechanical strength when compared with the pure borate glasses. On the other hand heavy metal oxide (Bi₂O₃) glasses owing to high refractive index such glasses exhibit non-linear effects. Besides, high density and transparency of these glasses make them useful for a variety of optical applications such as radiation shielding windows and scintillation counters. Extensive studies on several spectroscopic properties like optical, Electron Spin Resonance and Fourier Transform Infrared of various alkali borate glasses doped with different transition and rare earth metal ions are available. Among various transition metal oxide doped glasses, the MoO₃ doped borate glasses have gained much importance in recent years MoO₃ is known to have a structure composed of Mo pyramids. Glasses show a semi conducting behavior with the electrical conductivity of 10⁻³ to 10⁻⁵ (ohm-cm)⁻¹ which is known to be electron transfer between MO ions, existing in the structure of the glass. Further the conductivity in these glasses can be explained by a small polaron hopping theory. Further vanadium glasses are identified as n-type semiconductor s molybdenum ions are expected to dissolve easily in borate network because some of the infrared vibrational bands lie in the same region as those of BO₃ and BO₄ structural units. Virtually no devoted studies on spectroscopic studies such as optical absorption, electron spin resonance and FTIR on alkali borate glasses doped with MoO₃ transition metal are available. Study on these properties of glasses helps in assessing their structural aspects and can also be used as a tool to throw some light on the insulating/conducting character of the glasses.

The objective of the work incorporated in the dissertation is to have some understanding over the influence of MoO₃ on the structural aspects of Na₂O-Bi₂O₃-B₂O₃ from a systematic study of optical absorption, FTIR spectra. The following composition is chosen for the present study: **10Na₂O-(20-x) Bi₂O₃-70B₂O₃:xMoO₃ with x ranging from 0 to 3.0 wt%.**

I. INTRODUCTION

Materials prepared from a melt quenching are often referred to as glasses. 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 if the glass formation takes place, there will be a gradual break in slope. The region over which the change of slope occurs is known as glass optical absorption 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.

The oxides of the type AO, A₂O should not form glasses, and the rules are satisfied only for oxides of the type A₂O₃, AO₂ and A₂O₅. Presence of oxides such as A⁺ (example Li⁺, Na⁺, K⁺ etc.,) A²⁺ (example Ca²⁺, Pb²⁺, Cd²⁺ etc.,) other than A³⁺ and A⁴⁺ are known as network modifiers. Li₂O, Na₂O, K₂O, PbO, CaO, ZnO, CdO etc., are some of the basic examples of modifiers in glass network. These modifiers break up the continuous network by introducing non-bridging oxygens (A third group of oxides known as intermediate class of oxides also exist which by themselves not readily form glasses but do so when mixed with other oxides; such oxides are known as intermediates. The examples of this group are TeO₂, WO₃, MoO₃, Al₂O₃, Ga₂O₃ and V₂O₅. The applications of the fast-ion conducting glasses in the solid state batteries and electrochemical devices have been examined by many investigators on various types of glasses [1 and refs.1-6 therein]. It is well known that V₂O₅ and MoO₃ oxides are network formers [2]. Ions like Ag⁺, Li⁺ and Na⁺ are well known as charge carriers in ion-conducting glasses with high conductivity in the range of 10⁻¹ – 10⁻² S.cm⁻¹ at room temperature

Vanadium and molybdenum are expected to be the main glass forming substances in a system such as $V_2O_5 - MoO_3 - Fe_2O_3$ with two phases $FeVMoO_7$ and $Fe_4Mo_3O_{20}$ [2]. The Mo-O bond in the molybdenum trioxide MoO_3 may be considered covalent. In mixed former molybdophosphate glasses, MoO_3 provides octahedral structural unit ($MoO_6/2$) that is necessary for the extensive network formation.

Glasses based on heavy-metal oxides such as Bi_2O_3 have received increased attention due to their manifold possible in the field of glass ceramics, layers for optical and optoelectronic devices, thermal and mechanical sensors, reflecting windows, etc., [12-14]. It was also reported that glasses containing Bi_2O_3 are investigated for possible use in scintillation detectors for high-energy physics and the large polarizability of bismuth makes them suitable for possible non-linear optical uses and environmental guide-lines [13, 14]. Binary alkali borate glasses have been studied extensively to elucidate their structures and properties i.e., the nature and relative population of the borate units building the glass network. The aim of those studies was to understand the structural origin of the non-monotonic variation of physical properties with alkaline earth content [15-16]. Addition of alkali oxides like Li_2O , Na_2O , K_2O , etc., in to the borate glass matrices is expected to increase the applications of borate glass network. Spectroscopic studies on alkali metal borate glasses have revealed that the structure of alkali metal borate glasses is dependent not only upon the content of the alkali metal ion but also upon the difference in the alkali metal ions.

The density of the glasses was measured by Archimedes' method, using xylene as the immersion fluid. Measurements were made in duplicate for each glass sample and the averages were taken.

Fourier transform infrared (FTIR) technique is one of the most sought spectroscopic investigations to probe the structural units present in the glass matrix. The structure of borate glass not only depends on the glass forming oxides, but also on the glass modifier oxides and dopant salts present in the glass composition. The present paper reports structural investigations on borate glasses containing three alkali oxide using FTIR technique. We present the action of PbO when the content of alkali oxides remains the same and when it varies in borate glass structure. The paper also reports the structural groups of Bi_2O_3 when the content of alkali oxides remains constant in the borate glass networks.

II. EXPERIMENTAL PROCEDURE

With in the glass-forming region of doped $Na_2O-Bi_2O_3-B_2O_3$ glass system, the following particular compositions with successive increase in the concentration of MoO_3 are chosen for the present study: The present glasses were perfectly colorless and did not show any absorption band in the visible or near infrared region of the spectrum. This confirms that the existence of the copper in the glass is in the monovalent form.

The glasses used for the present study are prepared by the melting and quenching techniques [1-3]. The starting materials used for the preparation of the present glasses were analytical grade reagents (99.9 % pure) of Na_2CO_3 , Bi_2O_3 , H_3BO_3 and MoO_3 . 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. The glasses were melted at about 950 °C for 15 minutes till a bubble free liquid was formed. The samples were subsequently annealed at 300 °C in another furnace. The resultant melt was poured on a rectangular brass mould (containing smooth polished inner surface) held at room temperature. The glasses were then ground and optically polished. The approximate final dimensions of the glasses used for studying optical properties are of 1 mm thickness. The glasses were prepared by the usual melting, quenching and subsequent annealing techniques. The following studies were Infrared spectra. Infrared spectra of all the glasses in the wave number region 400 to 1500 cm^{-1} . Infrared transmission spectra were carried out using the same weight of the glass powder dispersed in KBr pellets. The data were recorded by Perkin Elmer 457 spectrophotometer from 600 cm^{-1} to 4000 cm^{-1} , the spectra were measured at room temperature with about 1 cm^{-1} resolution for the instrument. A 1mg from each sample was mixed with 100 mg of KBr in an agate mortar and pressed into p Density Measurements:

III. RESULTS & CONCLUSIONS

- With increase in MoO_3 concentration BO_4 units are converted into BO_3 units and also the signal intensity of BiO_6 units is increased.
- At higher concentrations of a clear band corresponds to $M=O$ stretching vibrations are resolved along with a new band around 1400 cm^{-1} due to the formation of non bridging oxygens.

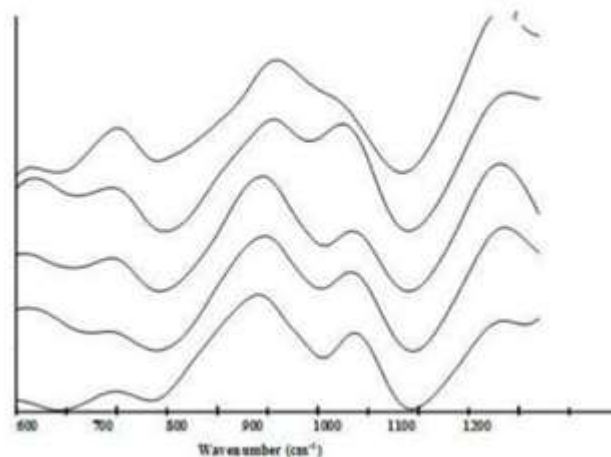
- The increase in MoO₃ content in the present glass system enhances the octahedral structural units of [BiO₆] and [MoO₃] groups. It clearly indicates that the bismuth as well as molybdenum ions act as modifiers in the present glass network at higher concentrations. The IR transmission spectra of pure MoO₃ and doped Na₂O-Bi₂O₃-B₂O₃ glasses are shown in Fig. 3.6 and the observed bands and their corresponding assignments are given in Table 3.3. The spectra exhibit three conventional broad bands originated from borate groups at about 1356 cm⁻¹ (due to BO₃ units), 1023 cm⁻¹ due to BO₄ units and at 687 cm⁻¹ due to bending vibrations of B-O-B linkages. These broad bands are the result of convolution of individual bands with each other. In the spectrum of pure MoO₃ sample a feeble band is appeared at 460 cm⁻¹. However with the doping of V₂O₅ a small new band at 553 cm⁻¹ is appeared and is broadened with increase in concentration of MoO₃. Interestingly, with increasing in the concentration of MoO₃, the intensity of the bands at around 1356 cm⁻¹ is increased and red shifted as the expense of BO₄ vibrational units and at higher concentrations new bands around 1385 and 800 cm⁻¹ are formed

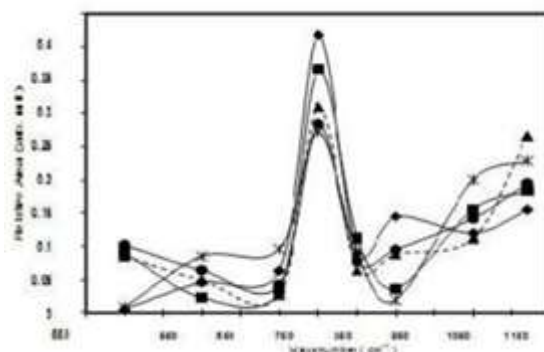
Summing up the results on the spectroscopic studies of Na₂O-Bi₂O₃- B₂O₃ glasses concludes that the rigidity/insulating strength of glass network is decreasing due increase of MoO₃, BiO₆ octahedral structural units and non bridging oxygens in the network..

The infrared results of the glasses under investigation are shown in Fig.(1), where the spectra are shifted for the sake of clarity. The data have been drowning in such a way to get an idea about the replacement of MoO₃ by In order to analyze the IR absorption spectra, many trials have been done to deconvolute them using the Peak Fit computer program [18], at last it was found that the Gaussian band is the best fit. The only input for fitting program was the number of bands and the initial values for the parameters describing the intensity, position and width of each band. Subsequently, the program using a least-squares fitting procedure adjusted these parameters

Figure (3) shows, for example, the IR spectra for glass 35 mole % of B₂O₃ along with the Peak Fit computer fitting in the wave number range from

1120 – 600 cm⁻¹. There were no characteristic absorption bands in the region >1120 cm⁻¹. From this figure the band deconvolution of IR spectra for the studied glass yielded the central position, amplitude, area and the full width at half maximum (FWHM) of each peak. The glasses show quite similar IR spectra with slightly shifting to the position of the main peaks this due to the borate ions The main peaks were centered in the following absorption regions at 600 The results led to the conclusion that the glass is composed of discrete ions of barium ions and MoO₄²⁻ and condensed units of MoO₄, probably Mo₂O₇²⁻ ions. The condensed units of MoO₄ must be large.





The effect of borate content on the centre of the IR absorption bands for the studied glass

IV. REFERENCES

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