

ANALYSIS ON THE STRUCTURAL, SPECTROSCOPIC, AND DIELECTRIC PROPERTIES OF BORATE GLASS

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Borate glasses were synthesized by the conventional rapid melt quench method. The XRD pattern confirmed the amorphous nature of borate glass. Optical properties of borate glass were studied using the Photoluminescence spectrum. IR spectrum was analyzed to determine and differentiate the various vibrational modes in the structural changes. Raman spectroscopy of borate glass was also carried out. According to TGA/ DTA and DSC analysis, decomposition pattern had been formulated to account for the weight losses observed. The dielectric properties such as the dielectric constant, the dielectric loss, and AC conductivity of the borate glass were studied in the different frequencies and temperature.

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1. Introduction

The scientific and technological applications of glasses have encouraged researchers to custom-build the novel glasses for the industry. Glasses are receiving considerable attention due to their unique physical properties like hardness, good strength, transparency and excellent corrosion resistance. These properties of glasses to a large extent are controlled by the composition, structure and nature of the bonds of the glasses formed. Studies like X-ray diffraction (XRD), infra-red spectroscopy (IR), differential scanning calorimetry (DSC) studies have been extensively employed over the years to investigate the structure of glasses [1-4]. Borate glasses, in particular, have been the subject of numerous infra-red studies due to their structural peculiarities [5-8]. In B₂O₃ glass structure most of the boron is involved in B₃O₆ (boroxol) ring. Addition of a modifier breaks the boroxol ring, thereby producing BO₃ and BO₄ units [6, 8]. In addition, modifier also changes the physical properties. This paper reports the structural properties of the borate glasses that were determined by X-ray diffraction (XRD) analysis and FTIR and FT-Raman analyses. It was confirmed that the prepared glasses were amorphous. The bonding parameters of the glasses were analyzed by using FTIR and FT Raman analyses and were confirmed to be ionic in nature. The optical and electrical properties of borate glasses were studied.

2. Experimental Procedure

2.1. Preparation of Glass Samples

For the preparation of some glasses silica is not considered as a major component even though it is the basic raw material for glass preparation. Those glasses, which are called network

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glasses, include borate glasses, phosphate glasses, fluoride glasses etc. Among these classifications, borate glasses attract more attention in various industrial applications due to their extremely high refractive index, low thermal expansion, and low electrical conductivity. The desired borate glasses were prepared by melting the appropriate mixtures of boric acid, ZnO, Li_2CO_3 , H_6NO_4 , and Y_2O_3 in the right proportion. All the chemicals were purchased from Aldrich with 99.995% of purity. To get fine powders, the required quantities thoroughly mixed together with mortar and pestle. Finally, the powdered samples kept in a platinum crucible and heated in electric furnace, which operated at 1500°C . After 5-6 hrs time duration of continuous melting, the content was transported into the second furnace for annealing, where it was held at 400°C for 4 hrs. To remove the stress, the prepared samples were allowed to cool at room temperature. The prepared borate glass was polished.

3. Results and Discussion

3.1. XRD characterization

The XRD analysis was used to confirm the amorphous or crystalline state of the materials. The X-ray diffraction pattern of borate glasses were recorded in the range of 20° and 80° . The results showed that the XRD pattern of borate glass exhibited broad diffusion at lower scattering angles indicating the presence of long range structural disorder which is characteristic of amorphous nature as shown in Fig.1. This figure exhibits a broad diffuse scattering at different angles instead of crystalline peaks, confirming a long range structural disorder characteristic of amorphous network.

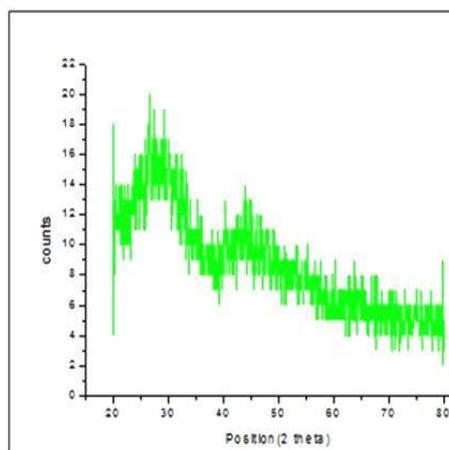


Fig.1. X-ray diffraction pattern of the borate glasses

3.2. Optical Properties

The photoluminescence characterization provided the information about the optical properties of the sample. The fluorescent emission and absorption was studied using Time correlated Single Photon counting instrument (purchased from Horiba Jobin Yvon, USA New Jersey).The Xenon arc lamp was used as an excitation source at 450 Watt Power. The entire system consisted of two separate excitation and emission monochromators and detectors with red sensitive photomultiplier tube (R928p).The excitation spectrum for the samples were recorded from 250 to 500 nm at an emission wavelength of 260 nm. Fig. 2 shows the excitation spectrum of borate glass. The excitation spectrum contains different absorption bands at wavelengths 262 nm, 350 nm and 410nm. Among these absorption wavelengths, energy corresponding to 262 nm wavelength shows more intensity than others, indicating the transition between 4f electronic levels. As a result, it was considered as the excitation wavelength for emission process.

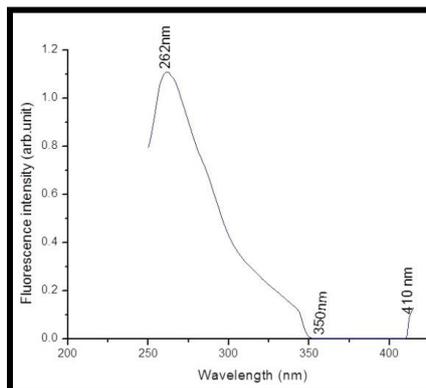


Fig.2 The excited spectrum of borate glass

Fig.3 shows the emission spectrum of borate glass when it was excited at 260 nm. The emission spectrum contains different peaks 282 nm, 388nm, 413 nm, 437nm, and 453nm. The emission band corresponding to wavelength 437 nm is sharper and also is hypersensitive. Photoluminescence theory predicts that sharp emission wavelength is associated with more intense energy. As a result, it can suggest that the borate glasses emit broad band of light in the visible region. Hence, this type of borate glasses finds much importance in fluorescence spectroscopy.

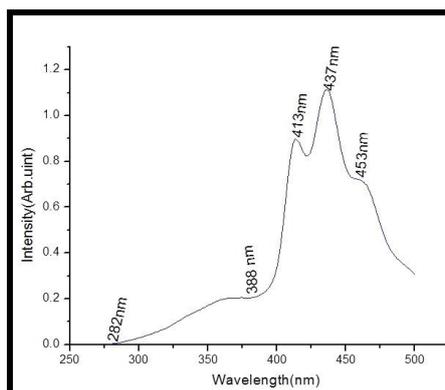


Fig3.Emission spectrum of borate glass

3.3. Spectral Analysis

3.3.1 FTIR analysis

Fig.4 shows the Infra red spectrum of borate glass in the range of 500- 4500 cm^{-1} . FTIR characteristics of the sample give the information about the various vibrations involved at different wavelengths. In this region of spectrum, bands are connected with vibrations of borate network. The IR spectrum also exhibits the characteristics of H_2O (OH – stretching vibration). Due to this reason, borate glasses show strong luminescence quenching. The IR spectrum consists of spectral bands located at 760cm^{-1} , 1048cm^{-1} , 1581cm^{-1} , 1738cm^{-1} , 3699cm^{-1} , and 3782cm^{-1} . In addition to these bands, it contains large number of small peaks corresponding to weak transitions. The region at $650\text{--}800\text{cm}^{-1}$ represents the BO_3 bending, and stretching vibration of tetrahedral BO_4 group at $950\text{--}1050\text{cm}^{-1}$. The region near ($1200\text{--}1600\text{cm}^{-1}$) shows stretching of trigonal BO_3 and tetrahedral BO_4 groups. The additional bands appearing in the spectral range $1700\text{--}4500\text{cm}^{-1}$ predicts the presence of both ionic and covalent bonds in the prepared sample and also implies the properties of different additives.

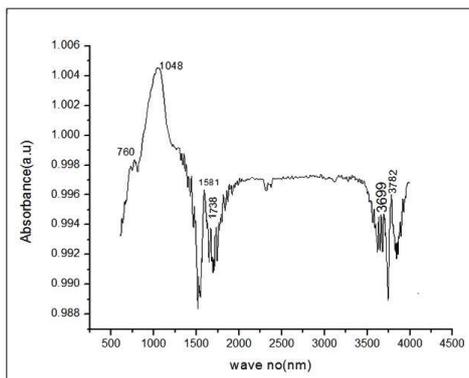


Fig.4 FT-IR spectrum of borate glass.

3.3.2 FT-Raman analysis

Raman measurements were performed at room temperature in the wave number range from 200 to 2000 cm^{-1} with a T64000 Jobin-Yvon confocal micro-Raman spectrometer using a 514.5 nm excitation line of a Coherent 70C₅ Ar⁺ laser at 2.8 W. Fig.5 shows the Raman spectrum of the prepared sample. From the spectrum, it can be seen that each Raman band represents either borate groups or modifier (i.e., Li) [9]. In this spectrum the most intense Raman band is associated with 1231 cm^{-1} which is due to (B-O⁻/B- \emptyset -B) stretching in diborate units. The remaining bands arise due to Li-O/Y-O stretching (335 cm^{-1}), (B- \emptyset -B) stretching in B₄ units (450-500 cm^{-1}), (B- \emptyset -B) stretching in metaborate rings (613-700 cm^{-1}), symmetric breathing in rings with BO₄ unity (774 cm^{-1}), (B- \emptyset -B) stretching in pyroborate units (850-900 cm^{-1}), (B-O⁻) stretching (930-960 cm^{-1}), B-O⁻ stretching in metaborate rings and chains (1300-1800 cm^{-1}). Here \emptyset indicates the presence of bridging oxygen. From this, it is clear that the region near (850-1200 cm^{-1}) is due to the various types of stretching involved in BO₄ group like diborate, triborate, tetraborate, and pentaborate groups [10]. These observed values agreed with previous studies.

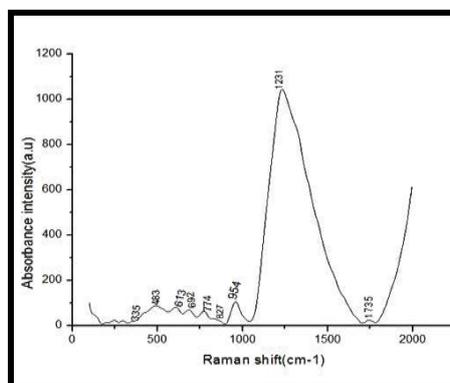


Fig.5 Raman spectrum of borate glass

3.3 Thermal analysis

Thermogravimetric analysis is a technique to assess the stability of various substances. Fig.6 shows the simultaneously recorded thermo gravimetric analysis (TGA) and differential thermogravimetric analysis (DTA) curves for borate glass. These TGA and DTA thermo grams of the present glasses also show, like XRD, the amorphous nature of the glasses. The endothermic peaks corresponding to the glass transition temperature (T_g) is clearly observed. No appreciable weight loss was detected in the TGA measurements in the glass sample studied as shown in Fig.6. From the DTA scans, it is also observed that the lack of sharp endothermic and exothermic peaks evidently indicate the formation of homogeneous glass. Fig.7 shows the differential thermal analysis traces of the glasses under investigation. The borate glasses exhibit the glass transition temperature (T_g) at 639.4°C.

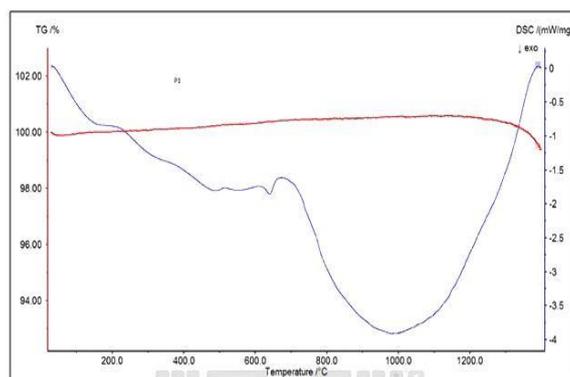


Fig.6 TGA of borate glass

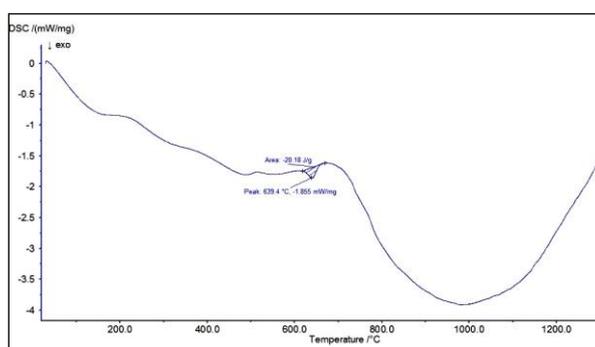


Fig.7 DSC of borate glass

3.4 Dielectric Studies

The dielectric analysis is an important tool used to know the details about the electrical properties of material at different frequencies. Analysis on the dielectric behaviour of glasses gives information about the electric field distribution within the glass. Dielectric properties are correlated with the electro-optic property of the glasses. The dielectric constant of the sample was measured using HIOKI 3532 - 50 LCR meter in the frequency ranging from 50 Hz to 5 MHz. The frequency dependence of dielectric constant at different temperatures is shown in Fig.8. It can be seen that with an increase in frequency and decrease in temperature the dielectric constant and the dielectric loss gradually decreases. Increase in the dielectric constant and the dielectric loss is more at lower frequencies. This behavior can be attributed to the electron hopping between two different sites in glasses due to the applied electric field. The jump frequency of the charge carrier becomes large and comparable with the frequency of the applied field at high temperatures. Accordingly, at low frequency the charge carriers hop easily out of the sites with low free energy and tend to accumulate the sites with high free energy barriers. This leads to a net polarization and gives an increase in the dielectric constant and the dielectric loss. However, at high frequency, the charge carriers will no longer be able to rotate sufficiently rapidly, so their oscillation will begin to lag behind this field resulting in a decrease of the dielectric constant and the dielectric loss. At low temperatures, jump frequency of the charge carriers becomes smaller than the frequency of the applied field. The periodic reversal of the applied field takes place so rapidly that there are no excess charge carrier jumping in the field direction and the polarization due to the disappearance of charges piling up at high free energy barrier sites and this leads to a decrease in the values of the dielectric constant and the dielectric loss [11-13]. At low frequencies, all the polarization mechanisms are active and with increasing frequency the contribution from different polarization starts decreasing. As the frequency increases, the dipoles do not comply with the varying external field, thereby decreasing the value of the dielectric constant at low frequency region. The dependence of the dielectric loss with frequency is shown in Fig.9. The dielectric loss is high at low frequency and is found to decrease in the higher frequency region.

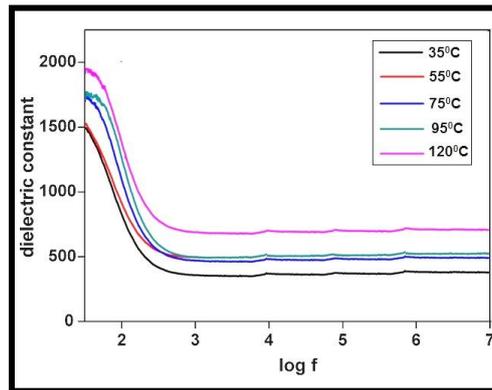


Fig.8 Dependence of dielectric constant on various frequencies and temperatures

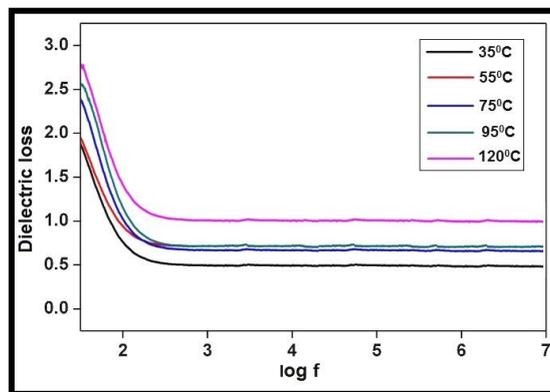


Fig.9 Dependence of dielectric loss on various frequencies and temperatures

The frequency dependence of the ac conductivity for various temperatures is shown Fig.10. It is observed that the conductivity increases with increasing frequency. The conductivity is high for higher frequencies confirm polaron hopping at a given temperature. It is clear from the figure that conductivity increases as the temperature increases. At higher frequencies this increase in conductivity could be due to the reduction in the space charge polarization. The frequency dependence of the ac conductivity behavior bears an evidence for the poly-dispersive behaviour. Further, as the frequency decreases, more and more charge accumulation occurs at the interface between the electrode and the electrolyte, which leads to a drop in conductivity at low frequencies.

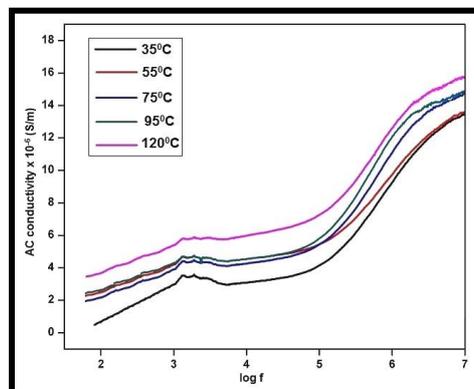


Fig.10 Variation of conductivity with frequency for glass

4. Conclusion

Borate glass was prepared by the conventional melt quenching method. The XRD spectrum revealed that the borate glass was amorphous in nature. Photoluminescence properties of borate glass were analyzed. FTIR and FT Raman studies were carried out of borate glass. Thermal analyses of the glasses were done to see the structure of the glasses. The variations of the dielectric constant, the dielectric loss, and the AC conductivity with frequency and temperature for borate glass were analyzed. The dielectric studies revealed that both the dielectric constant and the dielectric loss decreased with an increase in the frequency.

Acknowledgements

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