PREFACE

Glasses containing heavy metal oxides (HMO) such as PbO and Bi₂O₃ are of much interest due to their manifold applications. Glasses containing Bi₂O₃ have been investigated for their possible use in scintillation detectors, wave guides, radiation shielding windows, optical transmission devices etc. On the other hand PbO based glasses are popular for being widely used for enamels, optical lenses and electronic device applications.

The addition of Al₂O₃ in the glass network has a significant effect on the structure of glasses and hence in their properties. It is known to reduce the number of NBOs in glass network and hence becoming popular to modify and improve the properties of these glasses for different requirements. Their potential application lies in the field of mixed oxide dielectrics, and host for fluorescence centers in optical devices, nuclear waste materials etc.

A small change in composition or processing can have changes on physical, electrical and other material properties of amorphous material. When radiant energy interact with glass, profound change in structure of the glass take place, which result in change in structural and hence in other properties. This change in structure depends on the type of radiation and radiation dose also. For this reason it is important to study the influence of various external factors on the glass system.

The main objective for the current work is to investigate the changes in the structural properties before and after gamma irradiation of heavy metal oxide borosilicate glasses with and without the addition of Al₂O₃ to explore these glasses for there possible role in industrial use and as gamma ray shielding material, host for scintillation detectors and other applications involving high radiation fields.

The thesis consisting of six chapters embodies the description of the aforesaid investigation and the results obtained there from. The content of each chapter is outlined briefly in the following paragraphs.
Chapter I: This chapter presents a brief introduction and objective of work done in present thesis. The different aspects of glasses viz. general introduction, history of glasses, glass components, glass forming networks along with the structural theories of glass formation proposed by various scientists and groups have been discussed in detail with pictorial illustrations. Further their uses and applications in different areas of technology, engineering electronics, telecommunications etc. with special emphasis of radiation hard glasses widely used in nuclear radiation shielding applications, scintillation host materials etc. is discussed. The chapter also throws light on idea behind the chosen compositions of glass series.

Chapter II: This chapter presents the review of research work done by various scientists and groups on structure determination of heavy metal oxide especially PbO and Bi$_2$O$_3$ based glasses. The change in structure and hence properties of glasses with the change in both; the composition and effect of irradiation has been made in detail. The chapter also covers the general criterion of radiation interaction with glasses along with the special attention to work done so far on radiation effects on lead and bismuth borosilicate glasses.

Chapter III: This chapter is focused on the details of experimental techniques used for the characterization of the prepared glasses. The samples under study are classified mainly in four series: Lead Borosilicate, Lead Aluminium Borosilicate, Bismuth Borosilicate and Bismuth Aluminium Borosilicate with borate and silicate as the essential constituents. In Lead Borosilicate series PbO has been added with the variation of 0.30 mole% to 0.75 mole%, while in the Lead Aluminium Borosilicate glasses PbO has been partially replaced by Al$_2$O$_3$ to insight the role of Al$_2$O$_3$ in glass network. The same has been done for Bismuth and Bismuth Aluminium Borosilicate glasses. The sample preparation, and the characterizing techniques used like X-Ray diffraction, Raman spectroscopy, Fourier Transform Infrared (FTIR)) has been discussed in detail with their physical principles and experimental details. The samples were investigated before and after gamma ray irradiation using $^{60}$Co source at different gamma ray doses.
Chapter IV: In this chapter the structural investigation of PbO-B$_2$O$_3$-SiO$_2$ and PbO-Al$_2$O$_3$-B$_2$O$_3$-SiO$_2$ glass series before and after $\gamma$-irradiation has been made using FTIR and Raman spectroscopic techniques. Amorphous nature of samples has been confirmed by XRD analysis. From the spectroscopic studies it is concluded that for both the series of glasses the BO$_3$ and BO$_4$ are the main groups that act as network structural groups. It is found that BO$_4$ groups play a dominant role when the PbO content varies from 0.30 mole % to 0.45 mole % whereas BO$_3$ groups form the major part at higher concentration of PbO. This compositional change of PbO from 0.30mole% to 0.75mole% reveals the dual role played by PbO. i.e. at low concentration it shows the ionic behavior (Pb$^{2+}$ ions) and acts as network modifier while at higher concentration it shows the covalent character and works as network former. The increase of PbO shows the incorporation of PbO into glass network via a transition from ionic to covalent behavior. Comparison of both the series with the addition of Al$_2$O$_3$ in lead borosilicate glasses increases the number of non-bridging oxygens and the transition of lead species resulting from ionic to covalent bonding is enhanced. The results obtained from the FTIR and Raman spectroscopy are in agreement with each other and give approximately the similar information about the present glasses. $\gamma$-irradiation effects with different doses show pronounced effects on both the series. But two compositions one from each series seems to be irradiation hard composition.

Chapter V: In this chapter another heavy metal oxide glass series, where PbO has been replaced with Bi$_2$O$_3$ is discussed. The chapter deals with the structural analysis of Bi$_2$O$_3$-B$_2$O$_3$-SiO$_2$ and Bi$_2$O$_3$-Al$_2$O$_3$-B$_2$O$_3$-SiO$_2$ series. The effect of composition and irradiation with different doses of gamma rays on structural properties has been discussed using FTIR and Raman Spectroscopic techniques. The main emphasis has been given on the role of Aluminium on Bismuth Borosilicate glasses. XRD pattern reveals the crystalline nature of one of the Bismuth Borosilicate glass with 0.60 mole% of Bi$_2$O$_3$ content. A significant change in structural properties has been observed with systematic variation in composition and with the effect of $\gamma$-irradiation on the prepared glasses. Analysis of compositional dependence of both the series indicate towards the increased number of BO$_4$ groups with the increase of Bismuth content. The comparison between Bismuth Borosilicate and Bismuth Aluminium Borosilicate series shows the presence of Bi$^{3+}$ cations as BiO$_3$ pyramidal units and
BiO$_6$ units. The XRD analysis also verifies that addition of Al$_2$O$_3$ in glasses prevents the crystallization of glass.

**Chapter VI:** This chapter undertakes the final conclusions drawn from the structural studies conducted on PbO, Bi$_2$O$_3$ and Al$_2$O$_3$ based glasses by considering the relation between NBOs, radiation hardness and polymerization of the glass structure. In this chapter the results of structural change with gamma irradiation has been used to suggest promising candidates for radiation hard glasses among the studied glass compositions.