CHAPTER VI

FINAL CONCLUSIONS
6.1 INTRODUCTION

This chapter undertakes the final conclusions drawn from the structural studies conducted on PbO, Bi₂O₃ and Al₂O₃ based borosilicate 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.

6.2 FINAL CONCLUSIONS

Form the whole experimental observation and discussion done in chapters IV and chapter V, the following conclusions can be drawn. In the lead borosilicate glasses, firstly in Pb1 glass with PbO (0.30mole%), the higher number of BO₄ groups shows that PbO act as network modifier in this composition. It modifies the glass network like alkali oxides and because of its strong polarizing nature, it polarizes the two BO₄ tetrahedra and form diborate groups. It changes the BO₃ groups of boroxol rings in the glass network to BO₄ groups and the negative charge is compensated by lead cations. Therefore, it is suggested that at this concentration Pb²⁺ ions are most abundant and are evenly shared by B-O and Si-O networks. These ions must be lying in interstitial space in the voids of glass network.

With the increase of PbO content (0.45 mole%), number of BO₄ groups increases. Again PbO shows the network modifier role and transform BO₃ units to BO₄ groups. It is known that tetrahedral BO₄ groups are relatively strongly bonded as compared to triangular BO₃ groups therefore, the change of BO₃ groups to BO₄ groups results in more compact structure leading to the increase of polymerization of the network. At this concentration most of the voids get filled up by Pb²⁺ ions making the structure compact. It is known that four-coordinated atoms lead to an increase in degree of connectivity of the glass-forming network and plays a significant role in radiation hardness. This could be the reason that Pb2 glass shows no significant changes after their exposure to γ- irradiation hence suggested for radiation shielding or radiation hard glass composition.
When almost all the voids of glass framework gets filled up with Pb$^{2+}$ ions, the further increase of PbO in Pb3 glass (0.60mole%), causes the depolymerisation of the network. The transformation of BO$_4$ groups slows down and BO$_3$↔BO$_4$ equilibrium shifts towards the formation of BO$_3$ units, clearly suggesting that network modifying cations decreases and covalent network forming lead oxide increases. This has been confirmed from the increase of BO$_3$ units at the expense of BO$_4$ species in Pb3 glass. At this concentration PbO starts acting as network former and uses the oxygen of the network to form PbO$_3$ or PbO$_4$ pyramids by showing the covalent character. Also homogeneous incorporation of lead oxide through Si-O-Pb and B-O-Pb bonds occur at this concentration of PbO. The increase of NBOs in this composition made it less stable towards radiation damage.

In Pb4 (0.75mole%) glass, BO$_3$ groups with non-bridging oxygens rises further which can interact easily with irradiation. Therefore, Pb3 and finally Pb4 glass compositions are, having higher and highest number of NBOs in the studied series of lead borosilicate glasses. This highest number of NBOs could be the reason that Pb4 glass is highly affected by irradiation.

A transition of lead oxide from ionic to covalently bound lead species has been observed. Therefore, in our samples PbO clearly shows the dual behaviour from modifier (0.30 mole%-0.45 mole%) to former (≥0.60 mole%). The results are in agreement with the previous work done on lead borosilicate glasses by Kim et al. (1976) and Petrovskaya (1997), where they have shown that PbO below 50mol% acts as network modifier and above 50mol% as network former. For high concentration of PbO, silicate network get destroyed and SiO$_4$ isolated units exist in the network thus making the glass network more susceptible to radiation damage.

With the addition of Al$_2$O$_3$ in lead borosilicate glasses, in PbAl1 with Al$_2$O$_3$ content 0.10mole%, the BO$_3$ groups with non-bridging oxygens rises. With the further increase of Al$_2$O$_3$ content to 0.15mole%, the same pattern persists, that lead towards the conclusion that addition of Al$_2$O$_3$ enhances the transition of PbO from network modifier to network former. Therefore, with the addition of Al$_2$O$_3$, PbO starts behaving as network former at lower concentration as is reported in literature. Thus addition of Al$_2$O$_3$ besides making the glass chemically and
thermally more stable also shifts the transition of PbO from network modifier to network former at much lower PbO concentration.

Also, the increase of NBOs in PbAl1 and PbAl2 compositions leads to depolymerisation of the glass network and reduces structural stability and thus this could be the reason that PbAl1 and PbAl2 are not hard to γ-irradiation.

With Al₂O₃ content of 0.20mole% in PbAl3 glass, BO₄ groups increases. This may be due to the fact that at this composition Al₂O₃ starts bridging the oxygens and constructing AlO₄ or AlO₆ groups. The decrease of BO₃ with non-bridging oxygens and increase of BO₄ groups made the PbAl3 glass more polymerized and hence radiation hard.

In bismuth borosilicate glass series, Bi1 glass has higher number of BO₄ units than BO₃. At this composition of glass Bi₂O₃ transform the structure of borosilicates changing boroxol groups (three-coordinated borons) to the formation of BO₄ tetrahedras. The presence of the band in the region of 800-1150cm⁻¹ centred near 940cm⁻¹ in FTIR spectra, suggests that tetrahedras are mainly tetraborate and diborate groups. Therefore, bismuth oxide act as network modifier at this composition and Bi³⁺ ions fill the vacancies of the glass framework in some interstitial manner just like alkali oxides and also as PbO.

In Bi2 glass, the content of Bi₂O₃ had been increased to 0.45mole%, with the raise of Bi₂O₃ content BO₄ groups rises while BO₃ groups decreases indicating the modifier behaviour of bismuth ions transforming BO₃ to BO₄ units. In this case, the sharpness of the spectra shows the ordered structure of glass and hence more polymerized. The irradiation study of this glass composition suggests it to be a possible candidate for radiation hard glass. Therefore, it can be concluded that in Bi2 glass, Bi³⁺ ions fill up almost all the voids of network making it compact and hence possible composition for radiation hard glass.

With the further increase of bismuth oxide content from 0.45mole% to 0.60mole%, the glass becomes crystalline in nature. As Bi2 glass is more ordered than Bi1, it leads to the conclusion that increase of Bi₂O₃ make the structure ordered and finally, crystallizes it. At this composition, BO₄ groups again rise with
the decrease of BO₃ groups. *This can be suggested due to the destruction of super structural units, the decrease of BO₃ triangles and presence of both BiO₃ pyramidal and BiO₆ octahedral groups. The ordered and hence crystalline structure of Bi₃ also gives a possibility for this to be radiation hard material.*

The addition of Al₂O₃ to the bismuth borosilicate glasses in BiAl1 glass with aluminium content 0.10mole% increases the BO₃ units such as metaborate chains and rings, pyroborate and orthoborate. At this composition BiO₆ octahedral groups are also present, *indicating the incorporation of bismuth into the glass network at lower content.*

With the increase in aluminium content from 0.10mole% to 0.15mole% by replacing bismuth in bismuth borosilicate glasses, both BO₄ and BO₃ groups with non bridging oxygen rises. *But the increase of NBOs is relatively higher than that of BO₄ groups.* This suggests the reason for BiAl2 glass not to be the possible candidate for radiation hard glass. Also, at this composition, BiO₆ start acting as the major component with the presence of BiO₃ groups. These results can be concluded that bismuth plays a role of network former at this composition showing the covalent character and not the ionic.

When 0.20mole% of Al₂O₃ is added to the BiAl3 glass, *the crystalline structure of Bi₃ changes to the amorphous and hence it becomes a glass. Therefore, it is suggested that addition of Al₂O₃ reduces the possibility of devitrification.* It also raises the BO₄ groups present in the glass making it more polymerized and hence possible candidate for radiation hard glass.

At the end of the thesis it is very important to emphasise that although Al₂O₃ has extensively been used in conventional glasses but in case of heavy metal borosilicate glasses, which are used as radiation shielding materials, it increases the BO₃ groups with non-bridging oxygens in the glass matrix at low content. Thus reducing the structural stability of the glass matrix. At moderate concentration of Al₂O₃, it helps in increasing BO₄ groups and also increases polymerisation. Thus making the glass structure more stable towards radiation damage.
Another important advantage of using Al₂O₃ is that by using moderate concentration of Al₂O₃, use of toxic heavy metals can be reduced to have similar level of radiation hardness. Thus making such glasses relatively more environment friendly.