2.1 **Bismuth Borate Glasses**

Bi$_2$O$_3$ containing glasses and crystals are technologically important materials due to their high density, refractive index, large transparency in UV-visible region of electromagnetic spectrum, and outstanding third order nonlinear optical susceptibility that increases with Bi$_2$O$_3$ content. Bismuth borate glasses have a very wide glass formation range of 20 to 80 mol % Bi$_2$O$_3$. The phase diagram of Bi$_2$O$_3$-B$_2$O$_3$ system was first investigated by Levin and Daniel (1962) and is shown below in Fig. 2.1. Five stable crystalline phases: Bi$_{24}$B$_{12}$O$_{39}$ (boron sillenite), Bi$_4$B$_2$O$_9$, Bi$_3$B$_5$O$_{12}$, BiB$_3$O$_6$ (bismuth triborate), Bi$_2$B$_8$O$_{15}$ (bismuth octaborate) and one metastable phase: BiBO$_3$ (bismuth orthoborate), and its two polymorphs (BiBO$_3$-I and BiBO$_3$-II) are known to exist.

![Phase diagram of Bi$_2$O$_3$-B$_2$O$_3$ system](image)

*Fig. 2.1 Phase diagram of Bi$_2$O$_3$-B$_2$O$_3$ system [Levin and McDaniel (1962)].*
Out of these crystalline bismuth borate phases, Bi$_2$B$_8$O$_{15}$ has all boron atoms in tetrahedral co-ordination with oxygen. BiB$_3$O$_6$ has layers of alternating BO$_3$ triangles and BO$_4$ tetrahedra, in the ratio of two triangles to one tetrahedron [Teng et al. (2001)]. Bi$_3$B$_5$O$_{12}$ contains superstructural units in the form of isolated dipentaborate groups [Kityk and Majchrowski (2004)] and has 40 % of boron atoms in tetrahedral co-ordination. Bi$_4$B$_2$O$_9$ has only isolated triangularly co-ordinated, BO$_3$ structural units [Levin and Daniel (1962)], in other words it contains all boron atoms in triangular co-ordination with oxygens. Recently, single crystals of all these bismuth borate phases were prepared and characterized by mid-infrared spectroscopy. The IR spectroscopic data like X-ray diffraction patterns for different phases is characteristic and is very useful for the identification of crystalline phases [Egorysheva et al. (2005)].

The structure, density, thermal and optical properties of bismuth borate glasses has been investigated by several authors. George et al. (1999) extended the glass formation range of Bi$_2$O$_3$-B$_2$O$_3$ system to 88 mol % Bi$_2$O$_3$ by using roller quenching method and reported very density values ~9 g cm$^{-3}$ at high Bi$_2$O$_3$ concentration. These authors found a maximum in glass transition temperature, T$_g$, at Bi$_2$O$_3$ concentration of 23 mol% (Fig. 2.2).

A very interesting glass matrix effect on the optical absorption and fluorescence properties of bismuth borate glasses has been reported recently [Murata and Mouri (2007)]. It has been found that Bi ion containing borate glasses show an optical absorption band around 440 nm, which is completely missing in silicate glasses. It is further reported that there is a large influence of melting conditions like highest melting temperature, on the optical properties of oxide glasses containing Bi$_2$O$_3$ [Sanz et al. (2006)]. Transmission electron microscopy (TEM) studies concluded that at high bismuth oxide concentration, Bi$^{3+}$ ions reduce to Bi$^{2+}$. The oxidation state of Bi ions can critically influence the optical absorption and fluorescence properties of bismuth borate glasses.
One of the early structural studies of Bi$_2$O$_3$-B$_2$O$_3$ glasses was by Bishay and Maghrabi (1969) who measured the vibrational spectra of several bismuth borate glasses, and calculated the fraction of tetrahedral borons (N$_4$) as a function of Bi$_2$O$_3$ concentration. These authors reported maxima in N$_4$ at 45 mol% of Bi$_2$O$_3$. However Bishay and Maghrabi studies had one major drawback that they prepared glasses by melting the batch mixture in a porcelain crucible, which reacts unkindly with the melt and drastically reduces N$_4$. The best direct method to determine N$_4$ in borate glasses is high magnetic field $^{11}$B Magic Angle Spinning (MAS) Nuclear Magnetic Resonance (NMR) spectroscopy. Tersashima et al. (1997) reported that N$_4$ maximizes around 50 mol % of Bi$_2$O$_3$. These conclusions were however in contradiction to N$_4$ values calculated from the high resolution neutron diffraction measurements on bismuth borate glasses [Stone et al. (2000)].
Stone et al. (2000), concluded from neutron diffraction measurements that the B-O bond distributions for the BO$_3$ triangles and/or BO$_4$ tetrahedra present in Bi$_2$O$_3$-B$_2$O$_3$ glasses are asymmetric, and that N$_4$ increases from 0.38 ± 0.07 at 31 mol% Bi$_2$O$_3$ to 0.48 ± 0.07 at 67 mol% Bi$_2$O$_3$. These authors therefore concluded that N$_4$ increases uniformly in the Bi$_2$O$_3$ range of 31 to 67 mol%. All bismuth borate glasses showed a peak at 3.6 Å in the real space correlation function, suggesting the presence of superstructural units.

### 2.2 Lead Borate Glasses

Lead borate glasses like bismuth borates have a very wide glass formation range of 20 to 80 mol% PbO. These glasses have very high densities (upto 7 g cm$^{-3}$), large transparency in the UV-visible region and find use as glass to metal seals, porcelain glazes and nuclear radiation shielding windows. PbO is often added in glass forming melts like silicates and borosilicates to lower the melting temperatures, increase glass forming ability (GFA), increase glass density and refractive index values. Lead borate glasses show highest glass transition temperature at PbO concentration of 27 mol% [Mazurin et al. (1985)], while the highest microhardness values are reported at 40 mol% of PbO [Shaw et al. (2006); Shinkai et al. (1983)]. The phase diagram of PbO-B$_2$O$_3$ system is shown in Fig. 2.3 below. The two well known crystalline phases of this system are PbB$_4$O$_7$ (lead tetraborate) and Pb$_6$B$_{10}$O$_{21}$, the former is a promising material in non-linear optics [Bartwal et al. (2001)] and has all boron atoms in tetrahedral co-ordination.

Several authors have prepared lead borate glasses and characterized them by density measurements [Pan et al. (1995), George et al. (1999)], thermal analysis [Mazurin et al. (1985); Zahra et al. (1993)] and UV-visible optical absorption spectroscopy [George et al. (1999)]. Doweidar and Oraby (1997) used lead borate glass density and N$_4$ values to calculate the volume and packing fraction of symmetrical BO$_3$, asymmetrical BO$_3$ and BO$_4$ units as a function of PbO concentration.
Brekhovskich and Cheremisinov (1960) studied lead borate glasses containing 39 to 90.8 wt % PbO (from PbO.5B₂O₃ to 3PbO.B₂O₃) by infrared spectroscopy. All these glasses gave spectra which contained bands produced by the vibrations of boric anhydrides; these bands were strongest in the spectra given by glasses containing 86.3 and 90.8 wt % PbO [Brekhovskich and Cheremisinov (1960)]. This seems to indicate that the molecular structure of B₂O₃ was retained even at high lead oxide concentration.

Bray and co-workers, who studied the structures of vitreous boric oxide and of lead borate glasses by nuclear magnetic resonance (NMR), arrived at different conclusions [Leventhal. and Bray (1965); Bray et al. (1963)]. In their view, the boron atoms are situated in BO₃ triangles. If PbO content is low, the Pb-O bond is ionic, and the Pb²⁺ ions must be considered as modifiers, while the formation of BO₄ groups proceeds at the rate of two boron tetrahedral units for each added oxygen. Above 15 to 20 mol % PbO, the formation rate of tetrahedral units is reduced, because some of the lead atoms now participate in the network as PbO₄ pyramids, with the Pb atom forming...
the apex. These pyramids preferentially bridge to BO$_3$ rather than BO$_4$ units. The corresponding NMR spectra become similar to those of orthorhombic and tetragonal PbO, the nature of the bond becoming much more strongly covalent.

A noticeable change in the BO$_3$ units appears at about 30 mol % PbO. This is due to a change in the electron distribution in the B$_3$-O bonds, which probably results from the replacement of B$_3$-O-B$_4$ by B$_3$-O-Pb bonds. The fractional content of four-coordinated boron (N$_4$) attains its maximum value of about 0.5 when the PbO and B$_2$O$_3$ contents are approximately equimolar. It would seem that the content of the N$_4$ fraction cannot become higher, because the modified BO$_3$ units containing one or more B$_3$-O-Pb bonds are unable to accept a fourth oxygen atom.

A more recent structural study of PbO-B$_2$O$_3$ glasses containing 25 to 75 mol % PbO was reported by Shaw et al. (2006). These authors carried out high magnetic field (16.44 T) $^{11}$B MAS-NMR and $^{207}$Pb static NMR experiments. Their investigation found that N$_4$ maximizes around 50 mol % of PbO, a result which agrees with earlier studies by Bray et al. (1963). $^{207}$Pb static NMR experiments found that the average Pb-O coordination number decreases from a value of 7 to 8 in low PbO content glasses (upto 25 mol % PbO) to 3-4 as PbO content was increased to 65 mol %. These results show that PbO acts as network modifier at high PbO concentration. $^{207}$Pb NMR measurements by other investigators also concluded that both PbO$_3$ trigonal and PbO$_4$ pyramids exist in lead borate glasses [Takaishi et al. (2000)].

Several early studies report a very curious phase separation phenomenon and the existence of some type of inhomogeneities in lead borate glasses in composition range where they are known to form single phase glasses [Liedberg et al. (1966)]. Small angle x-ray scattering experiments revealed that there exist some sort of inhomogeneities of size 200 to 300 nm in optically transparent lead borate glasses with 25 to 35 mol % of PbO. The size of these inhomogeneities decreased with increase in PbO concentration. SAXS measurements could not elucidate the nature of these inhomogeneities, and whether these were compositional or structural. Composition inhomogeneities would imply usual liquid-liquid phase separation often observed in glasses, while structural inhomogeneities with same composition would point to
existence of unusual liquid-liquid phase separation in which a liquid separates into two phases with same composition but with different short range structure and thermodynamic properties. The latter phenomenon is known as polyamorphism and is of special interest in this thesis. It will be very fruitful to investigate the size, shape, distribution and nature of these inhomogeneities that are reported to exist in lead borate glasses by present day state-of-art small angle X-ray and neutron scattering techniques. We plan to do these studies in the future.
Bibliography


