CHAPTER 2

EXPERIMENTAL METHODS

2.1. Introduction

In this chapter, the methods of glass preparation and details about techniques used to characterize the samples are described. Glasses are characterized by X-ray Diffraction (XRD), density measurements, UV-visible absorption spectroscopy, Photoluminescence (PL) measurements, Differential Scanning Calorimetry (DSC), Thermo-gravimetric Analysis (TGA), Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR), \(^{11}\)B and \(^{27}\)Al Magic Angle Spinning (MAS) Nuclear Magnetic Resonance (NMR) measurements and high-Q neutron diffraction.

2.2. Glass Preparation

Disk shaped glass samples of all the compositions were prepared by melt quench technique. The starting materials were high purity \(\text{H}_3\text{BO}_3\) (Aldrich, 99%), \(\alpha\)-\(\text{Al}_2\text{O}_3\) (CDH, India, 99.9%) and \(\alpha\)-\(\text{TeO}_2\) (Aldrich, >99%).

\(\text{WO}_3\) (Acros, 99+%), \(\text{Nb}_2\text{O}_5\) (Acros, 99.99+%), \(\text{PbO}\) (Aldrich, 99.9%), \(\text{Nd}_2\text{O}_3\) (CDH, 99.9%), \(\text{Y}_2\text{O}_3\) (Acros, 99.99%) and \(\text{Eu}_2\text{O}_3\) (SD fine Chemicals-AR grade, 99.9%) were used as doping oxides in borotellurite and alumino-borotellurite glass compositions. Appropriate amounts of these materials were weighed and after being milled in an agate mortar and pestle for about half an hour, the batch mixture was transferred to a platinum crucible and slowly heated to 250°C in an electrically heated furnace and sintered at this temperature for 24 hours. The furnace temperature was then slowly raised to 800°C. The temperature was controlled with PID controller with maximum variation of ±5°C. This temperature was sufficient to obtain clear, bubble-free melts for all glass compositions. The platinum crucible containing the melt was occasionally swirled inside the furnace for few times to homogenize the glass melt. Glass samples were prepared by normal quenching in which melt kept at 800°C for about 30 minutes, was poured on a heavy brass block to form disk-shaped glass. This disk shaped sample was quickly transferred to another furnace kept at 300°C for 30 min to reduce thermal stresses generated by rapid cooling.
The composition of glass samples prepared and studied are as follows:

(1) $x\text{B}_2\text{O}_3-(100-x)\text{TeO}_2$

$(x = 15, 20, 25 \text{ and } 30\text{-mol%})$

(2) $y\text{Al}_2\text{O}_3-10\text{B}_2\text{O}_3-(90-y)\text{TeO}_2$

$(y = 5, 10, 20 \text{ and } 30\text{-mol%})$

(3) $z\text{Al}_2\text{O}_3-20\text{B}_2\text{O}_3-(80-z)\text{TeO}_2$

$(z = 5 \text{ and } 10\text{-mol%})$

(4) $5\text{M}_x\text{O}_y-z\text{Al}_2\text{O}_3-20\text{B}_2\text{O}_3-(75-z)\text{TeO}_2$

$(z = 0, 5 \text{ and } 10\text{-mol% and } \text{M}_x\text{O}_y = \text{WO}_3, \text{Nb}_2\text{O}_5, \text{PbO}, \text{Nd}_2\text{O}_5, \text{Y}_2\text{O}_3 \text{ and } \text{Eu}_2\text{O}_3)$.

Alumino-borotellurite glasses required higher quenching rates for the formation of glassy phase so for their preparation, only splat quenching was used. Small amount of melt was poured on heavy stainless steel plate and then pressed by a massive brass block. So, heat was extracted maximally and rapidly because of pressing the melt in-between two metal blocks. Splat quenched samples were not given any annealing treatment. Borotellurite glasses were prepared by both normal and splat quenching to study the effect of quenching rates on the glass properties. The opposite sides of normal quenched glass samples were flattened and polished (thickness ~0.6-3.0 mm) with different grades of emery powders to make them highly transparent for UV-visible absorption measurements.

2.3. **Density Measurements**

The density ($d$) of samples was measured on an electronic balance having least count of 0.0001g by Archimedes method using dibutylphthalate (DBP) and turpentine oil as the immersion fluids. Measurements were repeated three to four times on each sample to minimize error. The maximum error was in the range of ± 0.001 to 0.005 g/cm$^3$. Density was calculated using the following equation:

$$d = \frac{M_1}{M_2 - M_3} \times \rho_{\text{liquid}}$$  \hspace{1cm} \text{...(2.1)}

$M_1$ = mass of sample in air,

$M_2$ = mass of the (sample + wire) in liquid,

$M_3$ = mass of wire in liquid
\[ \rho_{\text{liquid}} = \text{density of liquid at room temperature.} \]

Density values were used to calculate glass molar volume, \( V_m \):

\[ V_m = \frac{\sum n_i M_i}{d} \quad \ldots (2.2) \]

Where, \( d \) is the glass density, \( n_i \) is the mole fraction of the \( i^{th} \) crystalline oxide component and \( M_i \) is its molecular weight.

### 2.4. X-ray Diffraction

X-ray diffraction measurements were performed on all glass samples on Bruker D8 Focus diffractometer using Cu K\( \alpha \) radiation with \( \lambda = 1.5406 \) Å at room temperature. X-ray tube was operated at 40 kV and 30 mA. Measurements were carried out in detector scan mode with incident angle \( \theta = 10^\circ \) and 20 range from 10-70\(^\circ\) with a step size of 0.02\(^\circ\) at scan rate of 1 sec/step.

### 2.5. Thermal Studies (DSC & TGA)

Thermal studies (DSC & TGA) were performed on SETARAM SETSYS Evolution-1750 system in the temperature range of 200-850\(^\circ\)C at a heating rate of 10\(^\circ\)C min\(^{-1}\). Measurements were done on powdered samples in platinum pans in air flow rate of 20 ml/min. Sample amounts of 20-30 mg were used. Thermo-gravimetric analysis (TGA) measurements were performed simultaneously along with DSC measurements. From DSC thermograms, glass transition temperature (mid-point), crystallization (peak point) and liquidus temperatures (peak point) were determined. The maximum uncertainty in the glass transition, crystallization and liquidus temperatures was \( \pm 1^\circ\)C. From TGA studies, dip in weight loss was observed.

Glass transition temperature values (obtained from DSC curves) were also correlated with average bond enthalpy of glasses. Average bond enthalpy (\( E_B \)) was calculated by following equations [Dimitrov and Komatsu (2010a)] for \( x \)\( \text{B}_2\text{O}_3-(100-x)\text{TeO}_2 \) and \( 5\text{M}_{1}\gamma-20\text{B}_2\text{O}_3-75\text{TeO}_2 \) glasses respectively:
\[
E_B = \frac{x(N_3^{(B)}E_{B-O}^{(3)} + N_4^{(B)}E_{B-O}^{(4)}) + (100-x)(N_3^{(Te)}E_{Te-O}^{(3)} + N_4^{(Te)}E_{Te-O}^{(4)})}{100}
\] …(2.3)

\[
E_B = \frac{5E_{M-O} + 20(N_3^{(B)}E_{B-O}^{(3)} + N_4^{(B)}E_{B-O}^{(4)}) + 75(N_3^{(Te)}E_{Te-O}^{(3)} + N_4^{(Te)}E_{Te-O}^{(4)})}{100}
\] …(2.4)

Where \(E_{M-O}, E_{B-O}\) and \(E_{Te-O}\) are the bond dissociation energies for single bonds: M-O, B-O and Te-O respectively [Sun (1947); Dean (1992); Dimitrov and Komatsu (2010a); Dimitrov and Komatsu (2010b)]. \(N_3^{(B)}, N_4^{(B)}, N_3^{(Te)}\) and \(N_4^{(Te)}\) were determined by FTIR and Raman spectroscopy techniques.

2.6. **UV-visible Absorption Spectroscopy**

UV-visible absorption measurements were recorded on polished samples on a Shimadzu UV-visible double beam spectrophotometer (Model-1601) in the wavelength range of 200-1100 nm. The wavelength accuracy was ± 0.5 nm and the photometric accuracy was ± 0.004 Abs. The light sources were tungsten lamp (300-1100 nm) and deuterium lamp (190-400 nm). Si photodiode was used as detector. The optical absorption coefficient \(\alpha(\lambda)\) was calculated by dividing absorbance \(A\), with sample thickness. Since the glass samples were thick (~ 0.6-3 mm), the true optical bandgap of glasses could not be determined by Tauc plots or by Mott-Davis models which require the measurement of absorption spectra at photon wavelengths where \(\alpha \sim 10^3-10^4\) cm\(^{-1}\) [Tauc et al. (1966); Mott and Davis (1971); Tauc (1974)]. Absorption cut-off wavelength, \(\lambda_o\) was arbitrarily taken as the wavelength at which the absorption coefficient reaches ~12 cm\(^{-1}\). Optical band gap, \(E_g\) of glasses was determined from \(\lambda_o\). The optical bandgap, \(E_g\) was used to calculate the optical electronegativity \(\chi\) [Zhao et al. (2008)], by the following relationship:

\[
\chi = 0.2688E_g
\] …(2.5)

The values of optical electronegativity \(\chi\) were used to determine the refractive index \(n\), by the following relation:

\[
n = 0.73 \ln[0.102\chi] + 0.5511
\] …(2.6)
Electronic polarizability of ions is the ability to easily deform the electronic clouds with application of electromagnetic field. It is closely related with many properties like refraction, conductivity, optical basicity along with optical non-linearity. Oxide ion polarizability, denoted by $\alpha_{O^{2-}}$ and optical basicity $\Lambda$, of glasses were estimated from the following theoretical formulae [Zhao et al. (2008)]:

$$\alpha_{O^{2-}} = -0.9\chi + 3.5 \quad \ldots(2.7)$$

$$\Lambda = -0.5\chi + 1.7 \quad \ldots(2.8)$$

### 2.7. Photoluminescence Spectroscopy

Photoluminescence measurements were performed on PerkinElmer LS-55 luminescence spectrophotometer having Xenon flash lamp as the excitation source. The emission spectra were recorded in the wavelength range of 300-900 nm. Both excitation and emission slit width was kept fixed (5 nm) for all glasses. Excitation was done at wavelengths 394 nm and 360 nm for glass samples containing Eu$^{3+}$ and Nd$^{3+}$ respectively.

### 2.8. Fourier Transform Infrared Spectroscopy

FTIR spectra of samples were recorded in the wavenumber range: 400 cm$^{-1}$ to 1600 cm$^{-1}$ at room temperature on Perkin-Elmer Frontier FT-IR spectrometer using standard KBr disc technique. Samples were ground to fine particles and then mixed with KBr. The mixture was then subjected to a pressure of 10 tons cm$^{-2}$ to prepare thin pellets. The FTIR transmission spectra were measured immediately after preparing the pallets.

FT-IR spectra of all glasses show three absorption bands in the ranges: 450-820 cm$^{-1}$, 820-1130 cm$^{-1}$ and 1130-1550 cm$^{-1}$. These bands are due to vibrations of different Te-O and B-O bond vibrations. Deconvolution of the FTIR spectra were not performed because of several peaks that are fairly arbitrary. $R_{FTIR}$, which is a measure of tetrahedral borons, was calculated by using the integrated area ratios. The area ratio ($R_{FTIR}$) of the second and third bands was calculated by the following relation:

$$R_{FTIR} = \frac{A_{800-1150}}{A_{800-1150} + A_{1150-1550}} \quad \ldots(2.9)$$
2.9. **Raman Spectroscopy**

Raman scattering studies were performed on all powdered glass samples using Renishaw InVia Reflex Micro Raman spectrometer using 488 nm Argon ion laser, 2400 lines/mm diffraction grating, a suitable edge filter and a Peltier cooled CCD detector. Measurements were done in unpolarised mode, at room temperature in the backscattering geometry, in the wave number range of 300 to 1000 cm\(^{-1}\) and at a spectral resolution of 1 cm\(^{-1}\) with incident laser power of 5 mW.

Raman spectra of all glasses show two broad bands in the ranges: 350 to 550 cm\(^{-1}\) and 550 to 900 cm\(^{-1}\). The spectra were deconvoluted to give peaks centered at 451, 507, 618, 665, 719, 764 and 904 cm\(^{-1}\). Area ratio of the peaks originating from TeO\(_4\) and TeO\(_3\) units was calculated. Barney *et al.* also employed area ratio under Raman bands to calculate coordination number of tellurium with oxygen by and their result was found to match well with the values obtained from neutron diffraction studies [Barney *et al.* (2013)]. Coordination number of Te with O (N\(_{Te-O}\)) is calculated by employing area ratio of the Raman bands as:

\[
N_{Te-O} = 3 + \frac{(A_{614} + A_{660})}{(A_{717} + A_{762}) + (A_{614} + A_{660})} \quad \ldots(2.10)
\]

2.10. **\(^{11}\)B and \(^{27}\)Al MAS-NMR Spectroscopy**

All solid-state NMR experiments were performed at room temperature on a Varian 500 MHz spectrometer (11.7 T) at a Larmor frequency of 130.3 MHz and 160.3 MHz for \(^{27}\)Al and \(^{11}\)B respectively. Glass samples were crushed into powder and packed in 4-mm silicon nitride rotors and spun at the magic angle at 13 kHz. A short pulse (0.3 μs) was applied and the recycle delay was 0.5 s. The chemical shifts were referenced to 1.0 M Al(NO\(_3\))\(_3\) and BF\(_3\).O(CH\(_2\)CH\(_3\))\(_2\) at δ = 0 ppm.

2.11. **Neutron Diffraction**

High-Q neutron diffraction studies were performed using monochromatized thermal neutrons with λ\(=\) 0.783 Å in Q range from 0.3 to 15 Å\(^{-1}\) at the Dhruva reactor of Bhabha Atomic Research Centre (BARC), Mumbai. Flux on the sample was \(3\times10^5\) cm\(^{-2}\) s\(^{-1}\). Five one dimensional position sensitive detectors were used to the cover entire Q range [Fig. 2.1].
Experimental data was collected on four powdered glass samples (i) \(0.20\text{B}_2\text{O}_3-0.80\text{TeO}_2\), (ii) \(0.05\text{M}_x\text{O}_y-0.20\text{B}_2\text{O}_3-0.75\text{TeO}_2\) where \(\text{M}_x\text{O}_y = \text{WO}_3, \text{Al}_2\text{O}_3, \text{PbO}\) in vanadium containers. The difficulty in studying the boron containing samples by neutron diffraction is the extremely high neutron absorption cross-section of \(^{10}\text{B}\) isotope (2134 barns at 1 Å neutron wavelength) [Johnson et al. (1982)]. Therefore, boron isotopically enriched in \(^{11}\text{B}\) (99\%) was used in order to minimize the influence of high neutron absorption of \(^{10}\text{B}\) present in natural boric acid [Sears (1992)].

The mathematical relationships between the pair correlation function, \(g(r)\) and the structure factor, \(S(Q)\) for any isotropic system like a liquid or a glass can be given as:

\[
g(r) = 1 + \frac{1}{2\pi^2 r \rho} \int_0^\infty Q(S(Q) - 1) \sin Qr \, dQ \tag{2.11}
\]

where \(\rho\) is the total number density of sample.

Fig. 2.1: Experimental set-up for high-Q neutron diffractometer at Dhruva reactor, BARC.

The experimental data was collected up to the limit, \(Q_{\text{max}}\) (15 Å\(^{-1}\) in our case). The \(Q_{\text{max}}\) is limited either by the instrumental capability or by relatively large wavelength. These limitations impose uncertainties in the deduced \(g(r)\), since integration used in deriving \(g(r)\) requires \(Q\) values upto infinity. This limitation can be accounted for by introducing a modification function. The most straightforward modification function is step function, which yields the best real-space resolution but at the expense of relatively large number of...
termination ripples. So, experimentally obtained structure factor, \( S(Q) \) was Fourier transformed using most commonly used Lorch modification function to obtain pair correlation function, \( g(r) \) [Lorch (1969)]. The use of Lorch function reduces termination ripples to a large extent and is very useful. The total correlation function, \( T(r) \) and the radial distribution function, \( N(r) \) can be obtained from \( g(r) \) with the following equations as:

\[
T(r) = 4\pi r \rho g(r) \quad \text{...}(2.12)
\]

\[
N(r) = rT(r) = 4\pi r^2 \rho g(r) \quad \text{...}(2.13)
\]

\( N(r) \) is used to define the average number of atoms lying within a range \( r \) to \( r + dr \), of a given atom [Umesaki et al. (1995); Rao et al. (1998); Hoppe et al. (2004); Hoppe et al. (2005); Gulenko et al. (2014)]. The area of peak in \( N(r) \) can be used to determine the average coordination number, \( C_e \) which is related to partial coordination numbers \( N_{ij} \), that expresses the average number of j-type atoms around i-type atom within the range of integration, as:

\[
C_e = \frac{1}{\langle b \rangle^2} \sum_{ij} c_i \bar{b}_i \bar{b}_j N_{ij} \quad \text{...}(2.14)
\]

\[
C_e = W_{11}N_{11} + W_{12}N_{12} + W_{22}N_{22} \quad \text{...}(2.15)
\]

\[
W_{11} = c_1 \left| \langle \bar{b}_1 \rangle \right|^2 ; W_{12} = 2c_1 \text{Re} \left( \frac{\bar{b}_1 \bar{b}_2}{\langle \bar{b} \rangle^2} \right) ; W_{22} = c_2 \left| \frac{\bar{b}_2}{\langle \bar{b} \rangle} \right|^2 \quad \text{...}(2.16)
\]

\[
\langle \bar{b} \rangle = \left| \sum_i c_i \bar{b}_i \right| \quad \text{...}(2.17)
\]

where \( W_{ij} \) are the weight factors defining the contributions of partials, \( N_{ij} \) to average coordination number, \( C_e \). The variables \( C_i, b_i, \langle \bar{b} \rangle \) represent the concentration, coherent scattering length and average scattering length from all components in the sample, respectively [Rao et al. (1998)].

### 2.12. Chemical Stability

The chemical stability of one normally quenched borotellurite glasses was studied by crushing the samples into a fine powder and exposing it to laboratory ambient conditions for about one month. One of the glass containing 30-mol% of \( \text{B}_2\text{O}_3 \) (Sample: 30BTe) and sample after exposure to ambient conditions (Sample: 30BTe*) was analysed by XRD and Raman spectroscopy to study the effect of atmosphere on the glass short-range structure.
2.13. **Effects of Gamma Irradiation**

Normally quenched borotellurite glass of composition: 30B$_2$O$_3$-70TeO$_2$ (Sample: 30BTe) was irradiated with Co-60 gamma rays to a total dosage of 88 kGy. After irradiation, the sample (named as 30BTe-γ) was analyzed by density, XRD, DSC, UV-visible and Raman spectroscopy and chemical stability studies.

Chemical stability of gamma irradiated samples was compared with that of original un-irradiated glass by keeping both of them in laboratory ambient conditions for about one month. Exposed gamma irradiated glass (30BTe-γ*) and unirradiated sample after exposure to ambient (30BTe*) were analysed by XRD and Raman spectroscopy to study the changes in glass structure.
References:


