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Department of Physics

Preparation and Characterization of Glass $60Ba_2O_3.29ZnO.10BaO.CrO_x$

Lab Report

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Abstract

This is our material science project in this we have prepared a glass and had done the characterization and discussed the preparation and application of the glass.

Contents

Chapter 1

Glass

1.1 Introduction

Amorphous materials exhibit a number of unique properties which are not exhibited by the crystalline materials. In the 17^{th} century, glasses transformed the man‘s perception of the universe with the advent of the optical telescope. Today, the uses of glasses are far-ranging with applications in the architectural engineering, electronics, telecommunications and aerospace industries. Glasses are recognized as one of the most important class of amorphous materials known. The mechanical strength of a glass may be increased by introducing certain amount of crystallization by carefully controlled heat treatment.

1.2 Glass

We all know that solids are of two types i.e *Amorphous* and *Crystalline*. An amorphous solid is a solid which lacks high order, repeating arrangement of the atoms that is characterized by a crystal. In amorphous, atoms are arranged in a random or disordered fashion.

An amorphous solid which exhibits glass transition phenomenon is termed as *'glass'*.

1.2.1 Glass Transition Temperature (T_g)

The glass transition is a phenomenon in which an amorphous solid shows abrupt change in heat capacity or thermal expansivity from crystal-like to liquid-like values with change of temperature. In simple words we can say glass transition temperature which is denoted by T_g is a temperature at which a material undergoes a transition from a hard, brittle, glassy state to a softer, more rubbery state.

1.2.2 Glass Formation

The glass formation starts with a molten material. A melt or molten mixture may crystallize at or below the melting temperature, T_m or we may supercooled this molten mixture to form a glass without crystallization. Thus we can obtain the glass by a sufficient fast cooling rate. Figure 1.1[1] shows the specific volume transitions with temperature for crystal, liquids and glass phases.

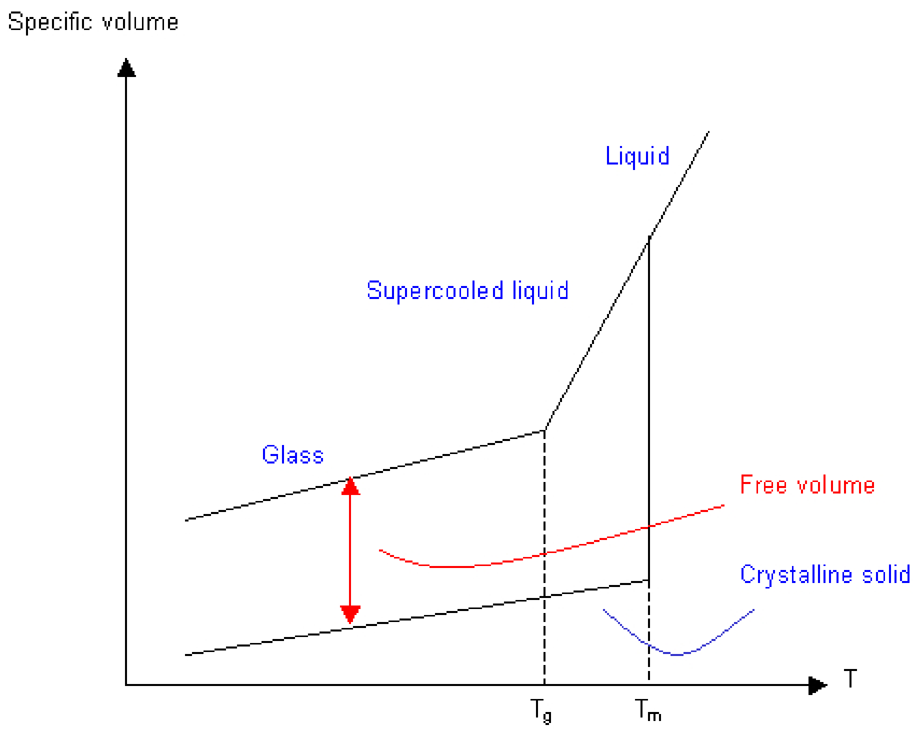

Figure 1.1: Formation of Crystalline and Glass phases ©*DoITPoMS, University of Cambridge*

We can directly see from the Figure1.1 that crystalline and amorphous are characterized by two kind of transition in the cooling curve. In case of the formation of crystalline state, there appears a marked discontinuity in the volume at a well defined temperature called the melting point, T_m of the material. However, if the cooling rate is fast then the crystallization can be avoided and volume of the liquid decreases at about the same rate as above the melting point until there is a decrease in the expansion coefficient in a range of temperature called glass transformation range. In other words, the sharp discontinuity in the liquid – glass cooling curve disappears. The curve, however, shows a change of slope at a temperature called glass transition (transformation) temperature, T_g. Below this temperature the expansion coefficient becomes so low that for all practical purposes the melt can be considered as a solid and the glass structure does not relax further. The expansion coefficient for the glassy state is usually about the same as that for the crystalline solid. Glass transition temperature T_g is not a constant one and is a function of cooling rate. Slower the rate of cooling lower is the value of T_g.

[1] https://www.doitpoms.ac.uk/tlplib/glass-transition/measurement.php

1.2.3 Types of Glass

There are three major types of glasses which are the following:

1. **Chalcogenide glasses** : Chalcogenide glasses are based on chalcogens - elements from Group 16 of the periodic table. These include sulfur(S), selenium(Se), and tellerium(Te). Chalcogenides are often combined with other elements like arsenic(As), germanium(Ge), gallium(Ga) and antimony(Sb) to form stable glasses with a wide range of compositions.The melt of these glasses contains rings and chains of sulphur, selenium and tellurium. These glasses generally have covalently bonded atoms in their structure.

2. **Metallic glasses** : Metallic glasses are are a unique class of materials that bridge the gap between metals and glasses. Metals do not usually form glasses when their melt is cooled at low cooling rate, but they are found to form glasses when their melts are cooled at some higher cooling rates of order of 10^6 to 10^8 K/sec. It is done with the technique called rapid quenching technique. Amorphous form of metals are found to be stronger than the crystalline form.

3. **Oxide glasses** : As name tells oxide glasses are primarily composed of metal oxides with network formers like silicon dioxide, boron oxide, titanium oxide and network modifiers like oxides of sodium, potassium, calcium, magnesium and aluminium. They are most commonly used types of glasses and have wide range of applications.

1.2.4 Glass Network formers and Network Modifiers

1. **Network Formers** : These oxides act as the backbone of the glass structure. They form a covalent bond with the oxygen atoms, creating a 3-D network. Example of network formers are Silicon dioxide, boron oxide ,titanium oxide.

2. **Network Modifiers** : These oxides are added to modify the properties of glass network are known as Network Modifieres. These oxides have lower valence cations. They disrupt the network formed by network formers by introducing ionic bonding. Common network modifiers are alkali oxides such as Na_2O and K_2O and alkaline earth oxides such as CaO and MgO.

The final properties of glass depend on the balance between network formers and modifiers. A higher porportion of the the network formers will result in a high melting point, chemical resistant and more rigid glass whereas greater amount of network modifiers will results to a lower melting pint, low chemical resistivity and higher elctrical conductivity.

1.3 General Method of preparation of Glass

Glass is prepared through a high-temperature melting process followed by quenching, which then rapidly cools the molten material to prevent crystallization. Let's see the steps of preparation of glass.

1. Firstly we will mix the raw material which include network modifiers and network formers which we have discussed before which are weighed according to our desired glass composition.

2. Then the mixed raw material is placed in a crucible and heated to a high temperature(typically 1000°C) in a furnace. During melting, the components react to form a homogenous liquid.

3. After it is melted, the molten glass can be shaped using various techniques depending on the desired final product. For example we can use pressing i.e molten glass is pressed between a mold and plunger to form shapes.

4. After forming, the glass is slowly cooled in a controlled manner to relieve internal stresses and prevent cracking. Rapid cooling can lead to a brittle and unsafe glass product.

This method is also called as **melt quenching** method. There are many methods for glass preparation. We have also prepared our glass sample by this method which we will discuss later. This technique is relatively simpler and also offers a high degree of flexibility in creating glasses with diverse compositions and can be used for various applications.

1.4 Properties of Glass

We all use glass in our daily lives. It possess a unique combination of properties which makes it ideal for diverse applications. Now let's see it's some major properties.

1.4.1 Physical Properties

1. Most of the glasses are **transparent** allowing the light to pass through them which make it valuable for making windows, lenses, containers etc.

2. Glasses can be colourless and also can exhibit color which totally depend on the addition of transition metals in the composition or some colourant.

3. Refractive index of glass is a crucial propety which is used for lenses and optical applications.

4. The density of glass typically falls between 2000 and 4000 kg/m^3, which is higher than most plastics but lower than most metals.

1.4.2 Chemical Properties

1. Oxide glasses, the most common type exhibit **chemical resistance** to many liquids and acids. This makes them suitable for making containers of food, beverages and chemicals.

2. It also has **corrosive resistance** properties making it good for outdoor applications.

1.4.3 Mechanical Properties

1. Glass is known for it's **hardness** and **strength**. It has resistant to scratching and abrasion. However this property depends on the composition and processing

2. Glass exhibits very **low elasticity**, this means it will not deform significantly under stress and will break instead of bending.

3. Glass is a **poor conductor** of heat, making it a good insulator for thermal applications. However, it can withstand high temperatures before softening or melting.

1.4.4 Additional Properties

1. Glasses also show electrical properties. The electrical conductivity of glass depends on the composition. Modifier with mobile cations can increase the electrical conductivity.

2. By changing the composition and processing techniques, manufacturers can enhance or change the properties of glass to meet specific needs.

So these were some properties shown by the glass. By understanding these properties we can choose right type of glass for various applications.

1.5 Applications

Glass is a surprisingly versatile material with a wide range of applications in our daily lives. Here are some of the most common uses of glass:

1. Containers are made from glass and are used for storing a large variety of food and beverage products. Glass is chemically inert and doesn't leach chemicals into the contents, making it a safe and reliable packaging material.

2. Glasshouses and greenhouses are structures with walls and roofs made of glass. They are used to create a controlled environment for growing plants.

3. Glasses are transparent that's make them ideal in making windows not only of home also of space shuttle.

4. Glass can also be used to create beautiful works of art and decorative objects.

5. High-purity silica glass is used in optical fibers due to its low light absorption and excellent light transmission properties.

Chapter 2

Characterization Technique

2.1 Introduction

There are numerous of techniques which are used to analyze and understand the properties of glass. There is no single technique for studying all the properties of the glass structure. A combination of techniques is used for a comprehensive study of the glass structure and properties. Now we will discuss these techniques one by one.

2.2 X-Ray Diffraction(XRD)

XRD technique is a powerful non destructive which is widely used to analyze the crystallographic structure of materials, including glasses. It tells information about the arrangement of atoms within the glass network. It also tells the presence of any crystalline phases due to incomplete melting or introduction of network formers that can crystallize.

2.2.1 X-Rays

X-rays are a form of electromagnetic radiation. They have high energy and can pass through most material.

Importance

- X-Rays is used to study the crystal structure including glasses.
- It is widely used as a tool in material science research.
- They are used in the field of medical science. They are used to detect bone fracture, detection in many types of injuries.

2.2.2 Generation of X-Rays

Generation of X-Rays can be undestand by arrangement shown in Figure 2.1[1] and can be summarized in the points given below

- Heating filaments emit electrons by thermionic emission.
- Electrons are accelerated by high voltage.
- X-Rays produced when high voltage speed e's hit the metal target.

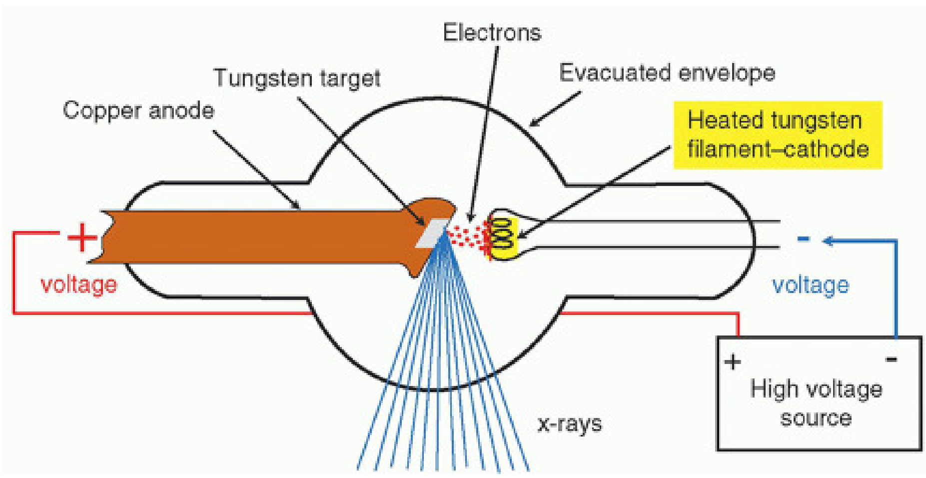

Figure 2.1: Production of X-Rays

Types of X-Rays

1. *Continuous X-Rays* : They are emitted when high speed electrons lose their energy when electrostatic interaction with the nucleus of the target atom.
2. *Characteristic X-Rays* : When a high energy electron collides with an inner shell elecron both are ejected from the atom leaving a 'hole' in the inner layer. This is filled by an outershell electron with a loss of energy emitted as an X-ray photon.

2.2.3 XRD Technique

XRD analysis is a non destructive technique that provides detailed information about the crystallographic structure, chemical compostition, and a physical properties of a material. It is based on the constructive interference of monochromatic X-rays and a crystalline samples including glasses. X-ray diffraction diagram is shown in Figure[2] 2.2

In XRD, the generated X-rays are collimated and directed to a sample, where the interaction of the incident rays with the sample produces a diffracted ray, which is then detected, processed and counted. The intensity of the diffracted angles of material are plotted to display a diffraction pattern as shown in Figure 2.3.It is a graph between the Intensity vs 2θ

[1]https://radiologykey.com/x-ray-production-tubes-and-generators/

[2]https://wiki.anton-paar.com/se-en/x-ray-diffraction-xrd/

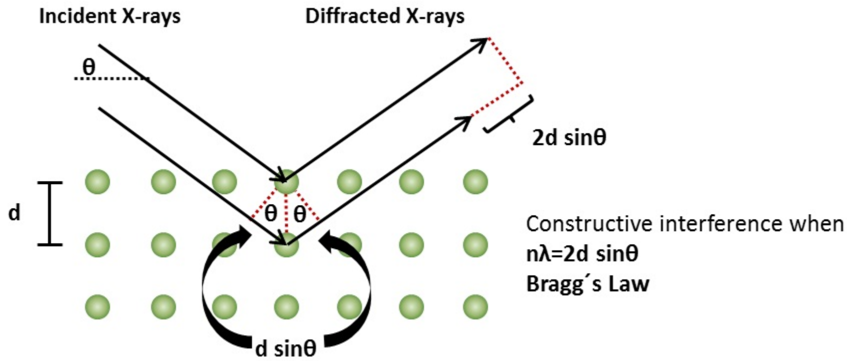

Figure 2.2: Bragg's Law reflection.

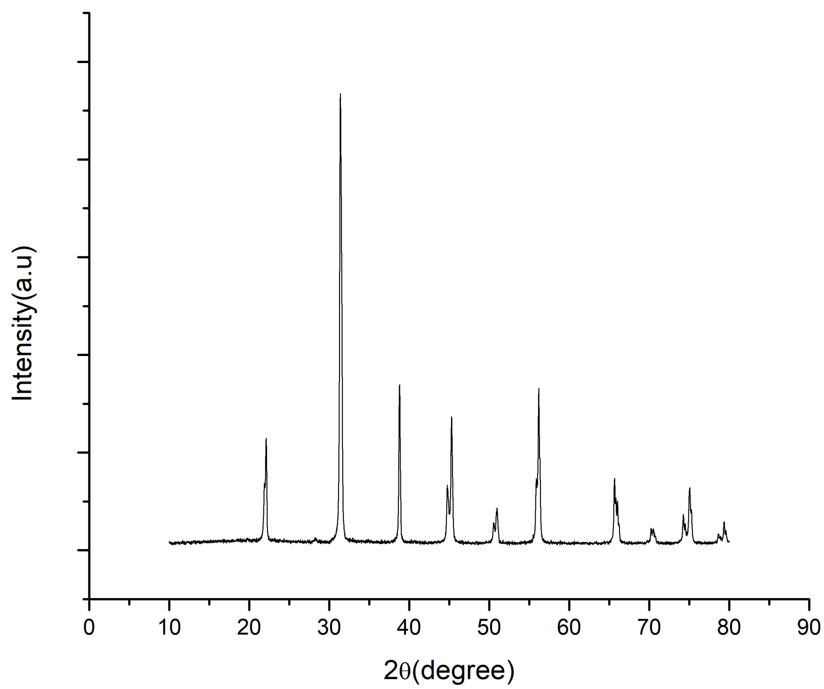

Figure 2.3: X-Ray Diffraction pattern

Xrd pattern provides information on the crystalline phase, amorphous phase, defects, while the peak relative intensities provide insight into the atomic distribution in the unit cell.

2.3 Differential Scanning Calorimetry(DSC)

Differential scanning calorimetry (DSC) is a technique used to measure the heat flow into or out of a sample as a function of temperature. This technique is also helpful for understanding the working range and behaviour of the glass. It can be used to

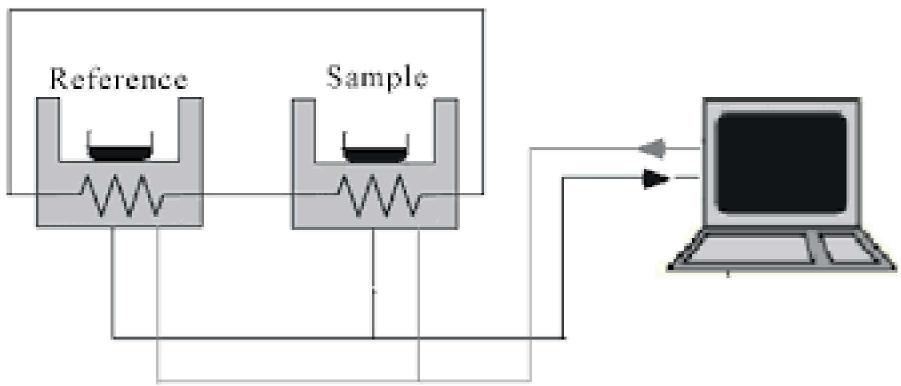

Figure 2.4: Schemetic diagram of DSC instrument

determine the glass transition temperature(T_g). DSC schemetic diagram is shown in [1] Figure2.4

2.3.1 Working Principle

1. In a DSC instrument we have haouses two crucible.

   (a) **Sample pan** which contains the material of interest (for e.g., our glass sample).

   (a) **Reference Pan** which is filled with an inert material like empty pan or a well defined material with a known heat capacity.

2. Then the both pans are heated or cooled at a constant rate. The instrument will continuously monitors the difference in temperature ΔT between the sample and reference pans.

3. So now any difference in ΔT reflects the heat absorbed or released by the sample as its temperature changes.

2.3.2 Information from DSC

As we have shown in the [3]Figure 2.5 we can directly see the result that are following

- When the sample absorbs heat(endothermic process) the sample pan lags behind the temperature in temperature, resulting in a positive ΔT peak in the DSC scan. This gives us many information which includes the T_g, *melting and Evaporation.*

- When the sample releases heat(exothermic process) the sample pan outpaces the reference pan, leading to a negative ΔT peak. This indicate us about the *crystallization* if a supercooled liquid crystallizes upon cooling, it releases heat, resulting in a negative peak.

[3]https://www.shimadzu.com/an/service-support/technical-support/thermal/overview/whatis$_d$*sc.html*

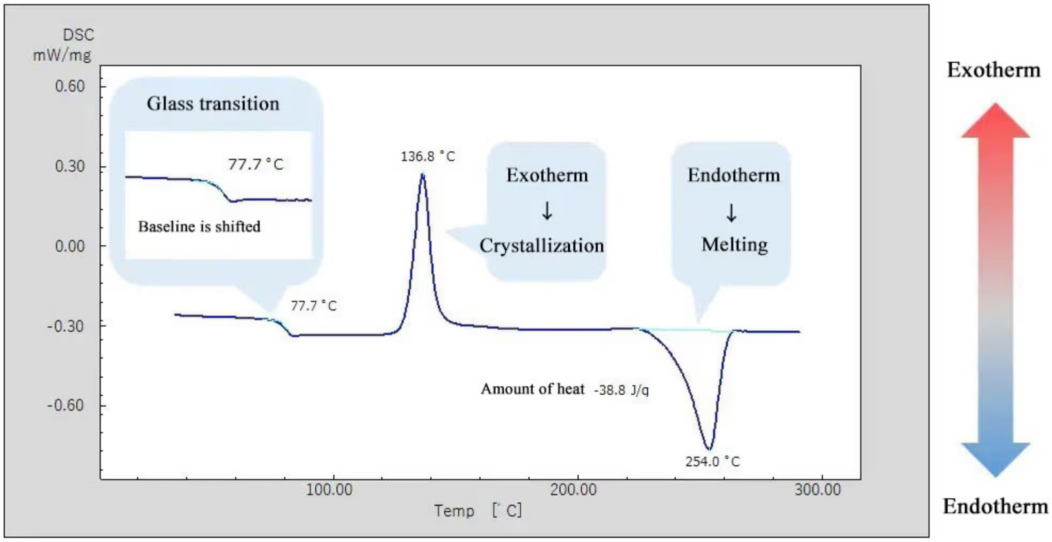

Figure 2.5: DSC curve

2.4 Fourier Transform Infrared Spectroscopy(FTIR)

This technique analyzes the vibrational modes of the bonds within the glass network. It helps identigying the type of bond present i.e covalent or ionic. In glass science FTIR plays a role in characterizing the types of bonds present and understanding the glass structure. Now we will discuss the working principle and the information obtained from FTIT spectroscopy.

2.4.1 Working Principle

1. In FTIR, we first irradiate a sample with Infrared light.
2. Then the different functional groups present within the sample molecule or material absorb specific frequencies of light.
3. Then the absorbed frequencies correspond to the vibrational modes of bonds within the molecules.
4. Then by measuring the intensity of light absorbed at different frequencies, FTIR spectrum is generated, which acts as a unique "fingerprint" of the sample.

2.4.2 Information Obtained from FTIR

1. We can identify the functional groups based on characteristic absorption peaks.
2. The relative intensity and postion of specific peaks can provide information about the network structure of the glass.
3. We can also detect the presence of impurities of minor components within the galss by identifying their characteristic absorption peaks.

2.5 RAMAN Spectroscopy

It is a powerful characterization tehnique which tells us about the vibrational and rotational modes of molecules within a material. In the glass science RAMAN spectroscopy helps us to study the influence of network formers and modifiers on the glass structure. Now we will discuss the working principle.

2.5.1 Working Principle

1. RAMAN uses monochromatic light. When the light interacts with the sample molecules, a small portion is scattered inelastically.

2. This means that scattered light has a slightly differenced frequency than the incoming light.

3. This shift in frequency is known as Raman shift, it provides us a information about the vibrational modes of the molecules and the chemical bonds present.

2.5.2 Information obtained from RAMAN Spectroscopy

1. Similar to FTIR, raman spectrum also identify the presence of various functional groups based on the characteristic Raman Shift peaks.

2. The intensity and position of specific of Raman peaks will gives us insights into the network structure.

3. Also, we can sometime detect the presence of crystalline phases due to the differences in their Raman scattering behaviour when compared to the amorphpus glass network

Chapter 3

Sample Preparation

So far we have discussed about the glass, it's types, properties and it's general method of preparation of glass. From now onwards, we will be discussing how we prepared the glass in our lab and will do the analysis of the glass by using the characterization technique which we had discussed before. We have prepared a glass by using melt quenching method, which is a very simple process and we had discussed in previous chapter.

3.1 Preparation

So we will now discuss the preparation of the glass. First we will see the composition we have taken for our glass then we will move on to the procedure.

3.1.1 Composition

We have taken the compound and the raw material listed below :

- Boric acid : $H_3BO_3 = 9.5207g$
- Zinc Oxide : $ZnO = 3.0378g$
- Barium Oxide: $BaO = 1.98341g$
- Hydrated Chromium Nitrate : $Cr(NO_3)_3 \cdot 9\,H_2O = 0.5228g$

$$60\,H_3BO_3 + 29\,ZnO + 10\,BaO + Cr(NO_3)_3 \cdot 9\,H_2O \xrightarrow{\Delta} 60\,B_2O_3 \cdot 29\,ZnO \cdot 10\,Ba \cdot CrO_3$$

3.1.2 Procedure

1. The starting material for the glass which we have mentioned aboved are weighed and grinded them to the powdered form and mixed.
2. The weighed material is placed in a crucible and it is then placed in a high temperature furnace and heated to $1200°C$.
3. Once it was melted the molten glass was rapidly cooled. This was achieved by pouring the melt onto a metal mold or plate at room temperature. Thus how we prepared the glass sample.

Chapter 4

Sample Analysis

Prepared glass sample is shown below and it's name is given as BZC-1. We will now analyze the glass which we have made by using the characterization technique one by one.

Figure 4.1: Prepared sample of glass : BZC-1

4.1 X-Ray Diffraction(XRD)

The XRD analysis was performed using a Multipurpose Versatile XRD System (XRD)[SmartLab 3kW/ Rigak]equipped with a Cu Kα radiation source.

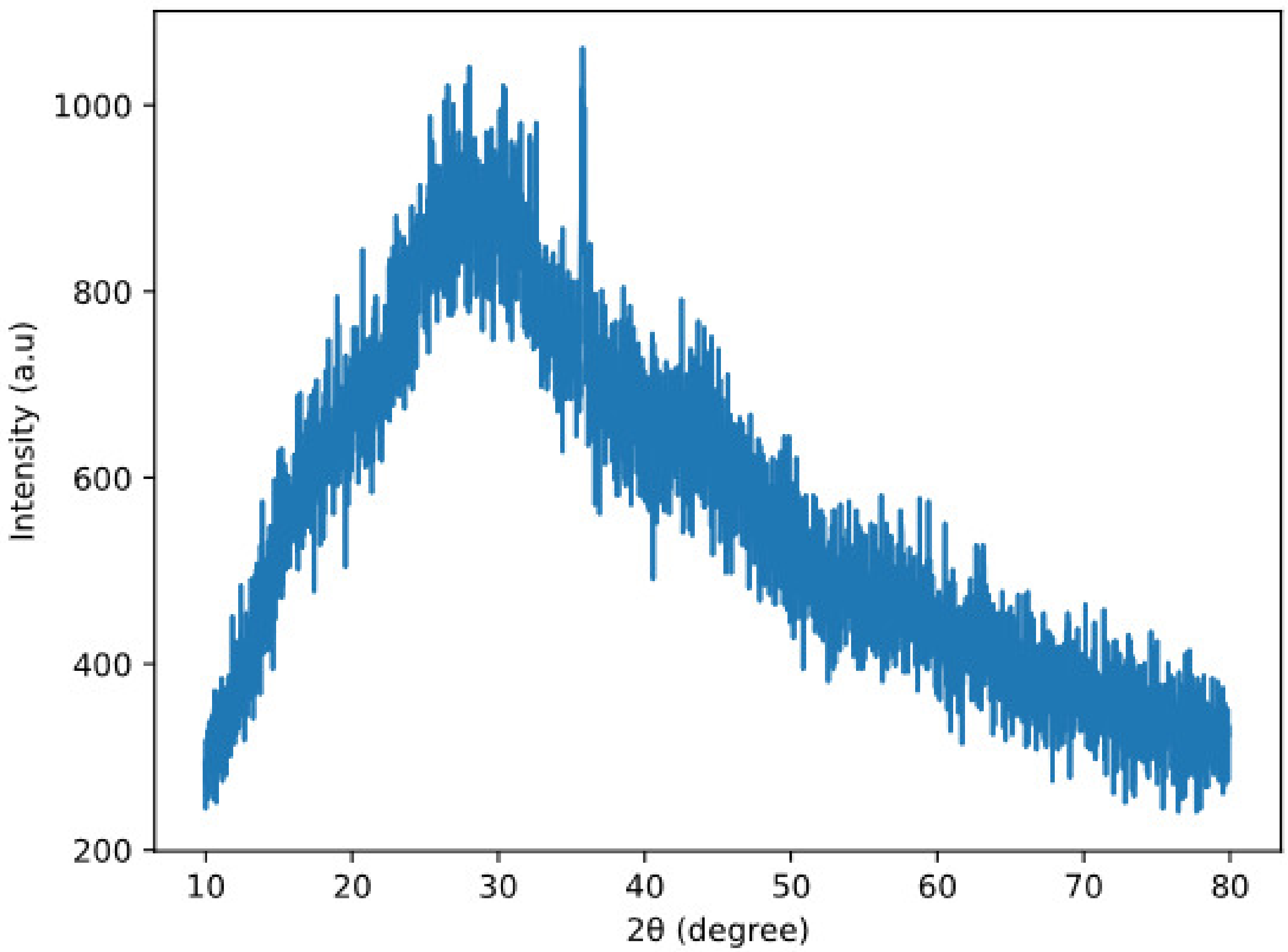

Figure 4.2: XRD pattern

The XRD pattern obtained from the glass sample is presented in Figure 4.2. The absence of sharp peaks in the XRD pattern suggests that the glass sample is largely amorphous, with no significant presence of crystalline phases.

4.2 Differential Scanning Calorimetry(DSC)

A DSC analysis of the sample was performed. The DSC scan obtained from the glass sample is presented in Figure 4.3

The DSC curve shows a shift of the baseline around $^{\circ}C$, indicating "glass transition". which can be attributed to the glass transition (Δg) of the material. The glass transition marks the transition from the rigid, glassy state to a rubbery state where the molecular mobility increases.

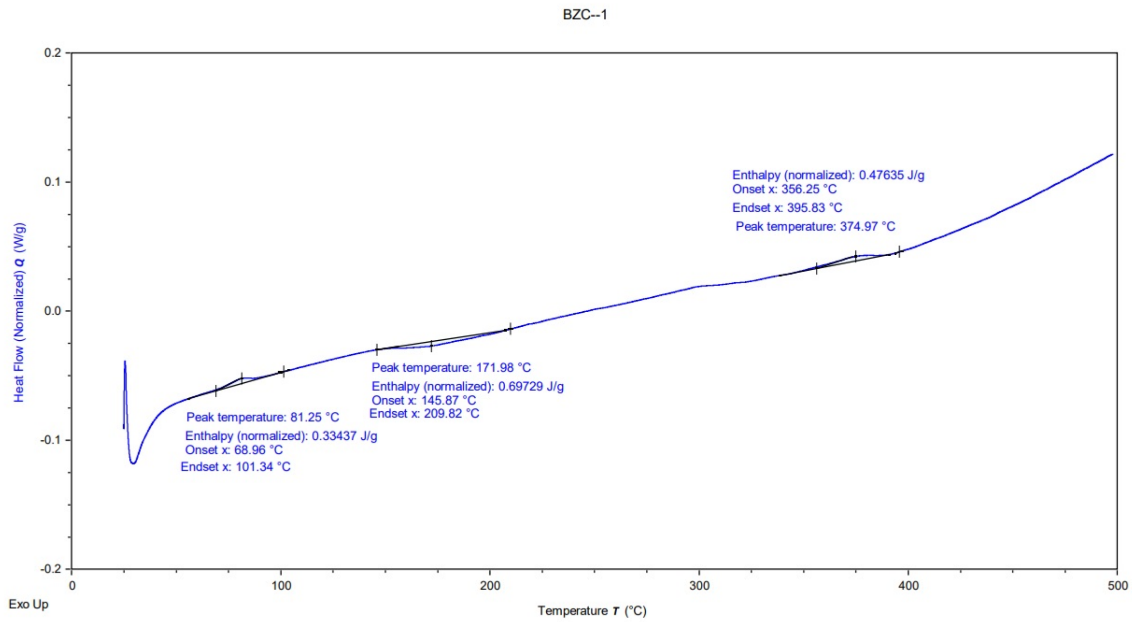

Figure 4.3: DSC curve

4.3 Fourier Transform Infrared Spectroscopy(FTIR)

The FTIR spectrum was acquired of the glass sample. It is shown in Figure4.4

It is seen from the spectrum there is a broad peak at 3148.28 $cm^{-}1$ It tells us the presence of Water -OH strech group.

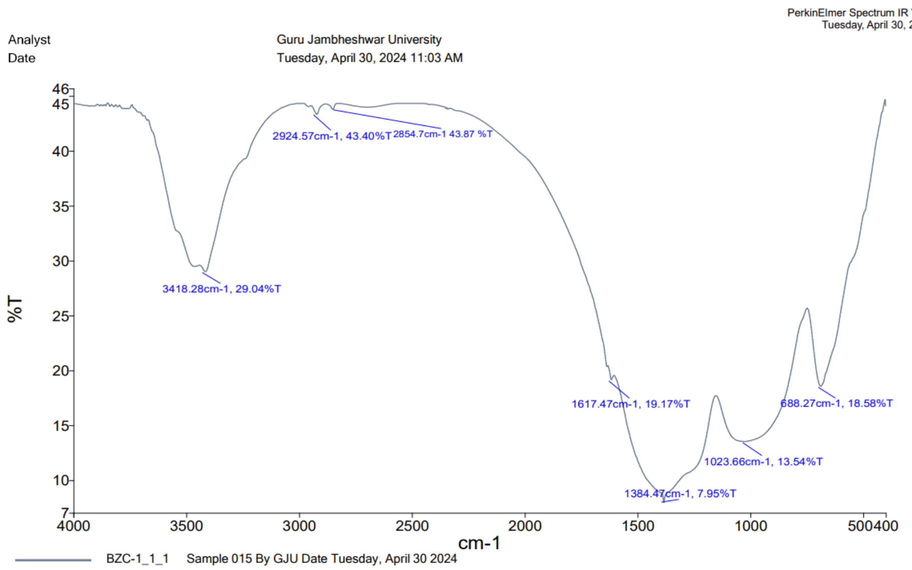

Figure 4.4: FTIR spectrum

4.4 RAMAN Spectroscopy

Raman spectroscopy was done on the sample. Raman spectrum was obtained as shown in the Figure4.5.

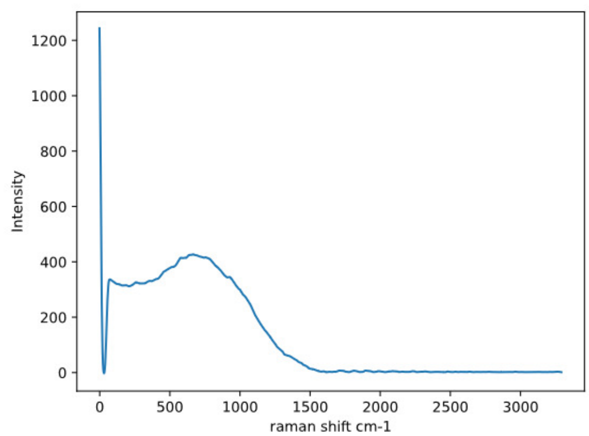

Figure 4.5: Raman spectrum

4.5 Result

Sample is confirmed as glass. It's density was measured 3.6 g/cc. Colour of the sample was green and it is due to the presence of transition metal 'Cr'. Glass Transition temperature is

Bibliography

[1] Khashayar Ghandi. A review of ionic liquids, their limits and applications. *Green and Sustainable Chemistry*, 04, 01 2013.