Synthesis and Characterization of Glass Ionomer Cement for Dental Fillings

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Certificate

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DEDICATION

This thesis is dedicated to our parents, teachers and colleagues for their support and encouragement.

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Abstract

The title of the project is “Development of Glass Ionomer Cement as Dental Filling material and its characterization”. The aim of the project is local development of Glass Ionomer Cement since they are not manufactured in Pakistan. Glass ionomer cement has two components: Powder Glass and Liquid Acid. Fusion method was used for the production of Hydroxyapatite incorporated Glass using Alumina, Silica, Calcium Fluoride, Calcium Carbonate and Hydroxyapatite. The glass component of Glass ionomer cement was then characterized using XRD, UTM and LIBS. It was reacted in powder form with commercially available acid to produce Glass Ionomer Cement. This product was synthesized for the application of dental filling. The GIC formed by this method provided the required mechanical properties with added benefits of rapid synthesis and low cost processing.

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List of Abbreviations

GIC-Glass Ionomer Cement

HA-Hydroxy Apatite

XRD-X-Ray Diffraction

LIBS-Laser Induced Breakdown Spectroscopy

UTM-Universal Testing Machine

UTS-Ultimate Tensile Strength

HV-Hardness Vickers

DPT-Dye Penetrant Test

SEM-Secondary Electron Microscopy

PSA-Particle Size Analyzer

FE SEM-Field Emission Secondary Electron Microscopy

$Ca(NO_3)_2$-Calcium Nitrate

$(NH_4)_3PO_4.H_2O$-Ammonium Phosphate

NH_4OH-Ammonium Hydroxide

pH-Power of Hydrogen

SiO_2-Silica

Al_2O_3-Alumina

CaF_2-Calcium Fluoride

$CaCO_3$-Calcium Carbonate

ZrO_2-Zirconia

CHAPTER 1

INTRODUCTION

Glass ionomer cement is a dental restorative material that has very good adhesion properties, biocompatibility [1], fluoride release and good compressional strength. Glass ionomers are obtained from the reaction of aqueous polymeric acids and fluoroaluminosilicate glass; they are referred to as acid-base reaction cements. [2]

Tooth decay is a serious health problem. It often leads to development of cavities, which can result in buildup of bacteria colonies in these cavities. These bacteria can attack gums and cause gum diseases. Due to which a human can suffer gum bleeding, bad breath and pain. If left untreated for long times, the bacteria can dissolve in blood stream which can lead to development of cancers. [3]

To solve this problem we have to develop a dental filling material that can remove bacteria and fill the cavity to prevent gum diseases. For a dental filling material to work efficiently, it is required that it has the same properties as teeth, so that it can perform same tasks as the teeth. Moreover, the dental filling material will be subjected to varying environment, for example, Saliva, changing temperature, change in pH and the mastication movements. Therefore, considerable research has to be done to develop these materials. Furthermore, these dental materials should be biocompatible and bioactive. [1]

Glass ionomer cements are traditionally used in low or zero load bearing situations because of their limited mechanical properties. They are not used in molars and premolars. These teeth are used for chewing therefore they experience mechanical forces. When glass ionomer cement was first developed it was classified into various types on the basis of applications. This classification was traditional. A roman numbering system of I to V was given to the types of glass ionomer cements in which I to VI types were auto-cured and type V was light cured. Glass ionomer cement can be used for luting, lining, sealing, bonding and restoration of teeth. [2] [4]

Table 1.1 [4]

Type	Purpose	Film Thickness
Type I	Luting inlays, crowns, bridges and onlays	Less than or equal to 20µm
Type II	Low stress area restorations	Up to 45 µm
Type III	Fissures and pits sealing	25 – 35 µm
Type IV	High stress areas restorations include metal reinforced ionomers	Greater or equal to 45 µm
Type V	Light cured GIC	-

Glass ionomer cements were developed in 1968 by Wilson and Kent. The GIC has been evolved from silicate and polycarboxylate cement and thus acts as a potential replacement for the silicate cement. Due to its adhesion to enamel and dentin and fluoride release for anti-cariogenic effect, it gained popularity widely in dental profession. After that, McLean and Gasser introduced Glass Cermet by sintered glass and metal powders to improve wear resistance and flexural strength in 1985. Resin-modified glass ionomer cement was developed by addition of a hydroxyethyl methacrylate monomer in the polyacrylic acid and their polymerization is initiated along the methacrylate group after exposure of light. Considering the development in dental filling materials since the beginning, one can only imagine how much further development will take place in the future. [5]

1.1 Dental Restorative Materials:

Dental restorative materials are synthetic biomaterials which are used to repair the decayed tooth to restore its original form and functionality or to fill a cavity to avoid disease.

These materials are divided into two groups.

1. Direct restorative materials
2. Indirect restorative materials

1.1.1 Direct Restorative materials: [6]

Direct Restorative materials are those which are directly placed in the cavity of the tooth and then their setting takes place.

Types:

- Gold
- Amalgam
- Composite resin
- Glass ionomer cement

1.1.2 Indirect restorative material: [6]

Indirect restorative materials are mostly used when a large part of the tooth has been lost. These are prepared in laboratory away from the decayed tooth.

Types:

- porcelain
- gold inlays
- crowns

1.2 Requirements of a dental filling material:

- Biologically compatible with the tissue in contact
- Should mimic the tooth in color, stability, hardness, wear resistance
- Should bond to tooth structure efficiently
- Have Mechanical properties enough to withstand masticatory force of mouth
- Not degrade in oral fluids
- Fine particle size
- Should be radiopaque. (white in X-rays)

CHAPTER 2

LITERATURE REVIEW

This chapter discusses the literature review of different direct restorative materials, their history, compositions, properties and their applications. It also discusses the advantages of Glass ionomer cement over other direct restorative materials as well as its manufacturing process.

2.1 Different Direct Restorative Materials:

2.1.1 Gold:

Gold is one of the oldest dental restorative materials. It has been in use for 4000 years. It was used primarily due to the good aesthetics rather than the mechanical properties required for a durable filling material. In those days, it was used to make wires and fixed bridges to bind teeth by the ancient civilizations, such as Etruscans and Romans. This technique was abolished until the middle of nineteenth century; it again rose due to the advancements in the field of dentistry.

Gold is used as a pure metal or in alloyed form with the addition of noble or base metals in the restorative dentistry. The limited use of pure gold is due to its inherent softness (HV 25) and large elongation (45%) which makes it easy to be cold worked, a mandatory requirement for precise filling of a cavity with the absence of any notable standards for applications and properties of direct filling material. [7]

Castings of inlay, onlay and partial crown respectively as examples of conservative dental treatment. (a) Gold inlay in molar 47 (b) Gold onlay on molar 15 (c) Partial crown for molar 36 on the model die. (Pictures courtesy of Hans H. Caesar, Zahntechnikermeister, Ludwigsburg)

Figure 2.1

2.1.2 Amalgam:

Amalgam was developed in 1830 after the formation of a silver paste. It had been in use for 150 years. Amalgam was a great step forward in the field of dentistry due to its good mechanical strength, ease of usability, durability and low cost. Amalgam is an alloy of mercury and has silver, copper as its main constituents.

Due to the presence of excess mercury, dentist refrained from using it because mercury has been known for causing immunotoxicity and cancer. Due to these reasons, amalgam lost its popularity as the go-to dental restorative material. Amalgam does not have good aesthetics. It is yellow or bronze in color, due to which it does not blend with natural tooth color. Researchers used additives or colorants to change its color for better aesthetics. There is not any significant finding to reduce health hazards caused by Amalgam. [8]

Figure 2.2-Amalgam Filling [8]

2.1.2.1 Types:

Different types of amalgams are enlisted below:

- Dental amalgam
- Potassium amalgam
- Sodium amalgam
- Aluminum amalgam
- Ammonium amalgam [9]

2.1.2.2 Composition:

Table 2.1 [9]

Constituent	Amount (%)
Silver	40-60%
Tin	27-30%
Copper	13-30%
Zinc	1%

Amalgam can be used in non-ideal conditions but due to concerns of its toxicity [10] and bad aesthetics it is not commonly used. In some countries it is banned due to its environmental effects. Moreover, due to the presence of Hg it was discarded. [10]

2.1.3 Resin Composite:

In the 1940s, Composite resins were introduced in the field of dentistry to minimize the limitations of acrylic resins in place of silicate cement. Resin based composite has the same aesthetics as tooth. [6] The development in composite has been unceasing, making it necessary to keep it up to date.

For the restoration of caries, material resin (discovered in the 1930s) is of notable interest due to the fact that it allows a wider range of shades which more closely resembles the enamel resulting in an imperceptible look of filling due to the adequate matching of shades. It possesses high compressive strength as compared to most other restorative materials. Through the application of heat, its tensile strength is also enhanced. Moreover, the slight variation in the properties of the resin can give a wider range of uses. [11]

Shrinkage of the composite materials can be reduced by using LED curing lights because their intensity slowly increases during curing. [12]

Light-cured acrylic possesses much longer setting time after it is in application as compared to auto-cured acrylic resin, which starts to set just after the mixing. By the help of same polymerization methods, resin composite (Bisphenol-A Glyceryl Dimethamethacrylate, Bis-GMA or Bowen’s resin) was made and is used in restorative techniques. The use of acrylic resin is limited to applications such as denture bases. Once resin composite was developed, the development of other restorative materials continued as only one material is not capable of successfully restoring all dental problems in each and every type of the situations. [11]

For Example,

- Polyacid modified composites (which has a higher fraction of resin composite and a lesser amount of glass ionomer—GIC added to resin composite)

- Resin-modified glass ionomer cement (which has a higher fraction of glass ionomer and a lesser amount of resin composite – resin composite added to GIC)

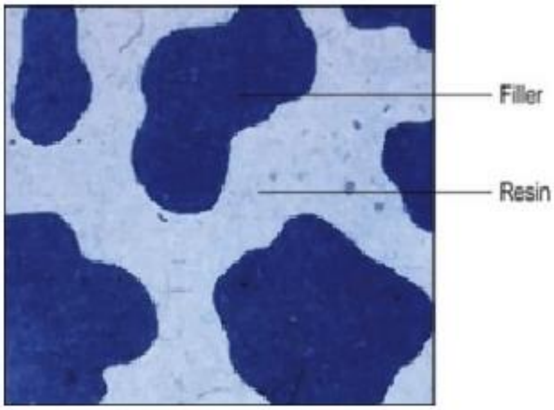


Figure 2.3-Illustration of Resin composite [8]

Resin composite contains several components:

- Organic resin polymer matrix
- Inorganic filler particles
- The silane coupling agent
- Initiators/accelerator
- Pigments. [8]

Type of pigments which are used accounts for the resin composites' improved aesthetic properties as they are available in a wide variety of shades similar to enamel, thus resulting in almost invisible restorations of the teeth.

A decent surface is obtained by these deliberately filled materials which can be finished by the use of fine diamonds burs, sanding discs and abrasive stones to give a reasonably smooth surface. The durable performance is not ideal because the resin surface soon starts to wear away.

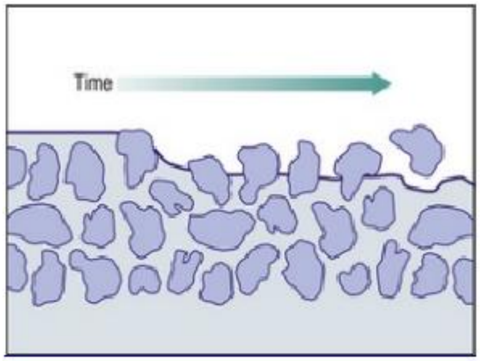


Figure 2.4-Wearing out of resin composite

The effect of finishing a composite preferentially, the resin matrix is wear out and as the greater diameter of filler is exposed so, excessive trimming will mean a loss of filler, and the filler particles are plucked out**.** [8]

2.2 Glass Ionomer Cement:

2.2.1 History:

Glass ionomer cements were synthesized in 1970 by Wilson and Kent. It was derived from silicate cement. Due to its excellent aesthetics and mechanical properties than the available materials of the time, it was the go to material for the anterior segment of the mouth. The first commercial cement was formed by John Mclean, this cement had long setting time of 20 minutes. But the problem was that it had high opacity and poor aesthetics but this cement served the basis of future cements. Between 1979 and 1980, several cements by different commercial names of Fuji Ionomer, and Ketac-fil were produced. ESPE was the first company to use different acids namely copolymers of acrylic and maleic acid, which is a stronger and more reactive acid, to accelerate setting time. With these advancements dentist started to use GIC more regularly. [4] [8]

The invention of the glass-ionomer cement is a series of innovative steps rather than a single act. Finding the alumina/silica ratio of the glass was a major step which controlled the resulting basicity and as a result the readiness with which an acid solution would react with a glass powder. By controlling the alumina/silica ratio allowed the glasses to set much more rapidly than the original glass-poly (acrylic acid) mixture, in which the glass was of relatively low basicity. G200 was the first glass to give at least moderately satisfactory cements. It was designated and contained alumina and silica in the appropriate ratio to give a high basicity; fluoride was also high in ratio. Its composition is given in Table 2.2. [13]

Table 2.2

Constituent	% by mass
SiO_2	30.1
Al_2O_3	19.9
AlF_3	2.6
CaF_2	34.5
NaF	3.7
$AlPO_4$	10.0

After the preliminary reports announcing the development of the glass-ionomer cement, in 1974 detailed scientific publications on these cements began to appear. It covered restoration with glass-ionomers and fissure sealing and was the report of a 2-year clinical study undertaken with the original ASPA formulation of glass-ionomer. The setting reactions of these materials were the part of initial scientific studies.

2.2.1.1 Development of Calcium Aluminosilicates:

Calcium Aluminosilicates with added fluoride were the first practical glasses for use in glass-ionomer cements. To make them sufficiently basic to set on reaction with aqueous poly (acrylic acid) their alumina/ silica ratio was adjusted. The glasses developed by Wilson and Kent remain the basis of all practical glass ionomer cements used clinically even though numerous other glass systems have been investigated since these early studies. The development of strontium-containing ionomer glasses has been one substantial change, where the element strontium is used in place of calcium in the formulation. [13]

2.2.1.2 Development of AluminoSilicates:

Glass structure is considered to be a random assembly of oxygen polyhedral, each comprising a small central cation surrounded by a number of negatively charged oxygen ions, according to this model. A typical polyhedron is (SiO_4). Such glass structures reactivity towards aqueous acids can be increased by including cations such as calcium that can form non-bridging oxygen by breaking up the continuous Si–O–Si structural units.

More complex effects been caused by inclusion of aluminum than the inclusion of simpler chemical species such as calcium or sodium. It can act as a network modifier. The presence of the (AlO_4) tetrahedral has to be balanced by additional cations for example Na^+, Ca^{2+} in the structure close to the main oxide network. According to it we can say that the aluminosilicate glass structure of ionomer glasses can be regarded as consisting of linked (AlO_4) and (SiO_4) tetrahedral, with additional cations to balance the charge deficiency caused by aluminum.

Silica, alumina and fluorite, i.e. SiO_2, Al_2O_3 and CaF_2 were the three essential components of the early glasses for ionomer cements. In practice, in order to improve properties such as the setting rate, translucency and final strength, additional components were added. By fusion of these components, typically in a ceramic crucible, with fusion temperatures varying between 1100 °C and 1500 °C, these glasses were made and the melt was cooled rapidly by pouring it either onto a metal plate or directly into water. As a result, a glass frit consisting of large pieces of glass was produced. It was then ground to a fine powder, typically of 20–50 μm and reacted with acid. [13]

2.2.1.3 G200 GIC:

It was the first successful ionomer glass, reported in 1979. Although it was different from modern ionomer glasses in that it is very high in fluoride and low in sodium, it had some distinctive features that appear to be typical of glasses capable of forming satisfactory glass-ionomer cements. [13]

2.2.1.4 Major Advancements:

With the goal of creating more durable and stronger glass-ionomer materials, In the 1980s, one manufacturer mixed silver amalgam powder to the glass powder. Another combined elemental silver (cermet) with the glass powder by a process of high-heat fusion. Increasing radio-opacity of the cements was the additional advantage of Silver. Furthermore, silver cermet cement's wear resistance was somewhat improved over traditional glass-ionomer restorative materials. But, the fracture toughness and fracture resistance of the metal-modified materials proved to be too low to recommend the materials for stress-bearing regions of teeth and due to the gray color routine use of the cermet in anterior teeth was prohibited. [14]

A resin-modified glass-ionomer was introduced in the late 1980s by the name of Vitrebond which was supplied in a powder/liquid format. The poly-acid component includes a photo-polymerizable resin which hardens with visible light exposure. Upon full cured, the glass-ionomer hardening reaction continues, protected from moisture and over drying. GC America also makes a resin-modified glass-ionomer base/liner by the name of GC Fuji Lining. These materials are known for preventing tooth sensitivity, protecting against bacterial diseases and internal fluoride ion release. [14]

2.2.1.5 Recent Developments in Glass-ionomer Systems:

Encapsulated glass-ionomer restorative cements are now being introduced that harden and sets by the conventional acid/base neutralization reaction, but have improved physical properties compared to other self-hardening GICs. The examples include GC Fuji IX GP EXTRA (and Ketac Molar. By altering the particle size and particle size distribution of the glass powder faster hardening was achieved. These materials are ideal for long-term, non-stress-bearing restorations in permanent teeth, and in the atraumatic restorative technique (ART). [14]

2.2.2 Classification of GIC:

The following table shows the classification of GIC. [4]

Table 2.3

Type	Purpose
Type I	Luting inlays, crowns, bridges and inlays
Type II	Low stress area restorations
Type III	Fissures and pits sealing
Type IV	High stress areas restorations include metal reinforced ionomers

2.2.3 Components of GIC:

Glass Ionomer Cement is synthesized by a polymerization reaction between a glass and an acid, the glass component is soluble in the acid. Glass is mainly alumino-silicate based while acids are polyacrylic or polymaelic acid. After the setting reaction, there is some unreacted glass left which is encased in the matrix. This phenomenon holds the cement together and provides strength to the matrix. The set material forms the cored structure of the GIC in which glass has reacted to permit binding of glass particles together. [8]

2.2.3.1 Glass Component:

Glass component of GIC is basic so that when it reacts with acid salt is formed by the neutralization reaction. Different compositions of glass are reported in literature but in practical applications, only those glass compositions are used which are able to form alumino-silicates glasses, with fluoride and phosphate additions.

In addition to this different elements can be added to impart different properties.

- Strontium and lithium are added to impart radio-opacity
- Altering the aluminum/silica ratio makes cement more translucent
- By changing rate of ion release one can change solubility, setting characteristics and release of fluoride. [8]

2.2.3.1.1 Composition:

The composition which we have chosen for GIC is as follows:

Table 2.4

Component	Weight (g)
SiO_2	45
Al_2O_3	21
CaF_2	12
Hydroxyapatite	10
$CaCO_3$	12

2.2.3.1.2 Manufacturing of Glass Components:

The glass mixture is pelletized and subjected to temperature between 1150°C and 1450°C with different soaking times. The molten mass is then removed from furnace and then quenched in water in a process called thermal shock cooling. Final product is called glass and it is broken to form glass frit. The glass is then wet or dry milled to further produce small particles of glass. By this method, glass of different particles size can be produced depending upon requirement. [8]

2.2.3.1.3 Reactivity:

GIC has basic character because of the presence of alumina and silica. Glasses based on silica alone lack reactivity and also basicity. This is because SiO_4 tetrahedral present in the corners of the structure has no charge. Due to addition of alumina, it adopts 4-fold tetrahedral geometry similar to silicon. Aluminum carries a +3 charge but it does not affect the negatively charged oxygen as effectively as silicon with its +4 charge. Due to this excess negative charge ions are present. So to balance it we have to add Na^+ and Ca^{+2} ions. These ions create basic character and due to this reason glass is attacked by acids. Fluoride is also important in GIC due to its bacterial defense Temperature also plays a vital role in the reactivity of glass. Generally temperature is between 1100℃.to 1300℃ for the quartz, alumina, metal fluorides, and metal phosphates. The total time for this process can range from 40 to 150 minutes.

When the freshly made glass is allowed to mix with polyacid it would set rapidly and the working time for clinical use would be too short. To avoid this problem, passivation method is applied to reduce reactivity of glass. If particle size is small then it becomes of great importance for the passivation of glass because if smaller the size more time it will take to set. [4] Their setting time is 2 to 3 min after the acid-base reaction. [15]

2.2.3.2 Acid Component:

The acid component of the GIC is polyacid which includes:

- Polyacrylic acid
- Polymaleic

- Copolymers of polyacrylic acid

Different manufacturers use different types of homopolymer or copolymer of acrylic acid or maleic acid. Different functional groups of these acids play important role in the reactions. Most important of them all is carboxylate group in which water ionizes into carboxyl and hydrogen ions. Some cement also has phosphate groups due to addition of polyphosphonic acid. These provide some increase in properties of the glass ionomer cement.

Molecular weight is also an important variable and it can change the properties of GIC. Increasing MW can increase the strength of cement but it also increases the viscosity of the acid and makes it difficult to mix. So there should be optimum molecular weight. Optimum properties are achieved when average molecular weights are in the range of 11,000 (number average) to 52,000 (mass average). Working and setting of the cement is inversely proportional to the molecular weight. A small amount of tartaric acid is added to all materials to accelerate the setting phase of the reaction while maintaining the working time [8]

2.2.4 Setting reaction between Glass and Acid:

The stages involved in glass ionomer cement's setting reaction are:

1. Aluminum and calcium ions are liberated by the attack of hydrogen ions from the acid on the glass. There is a release of Sodium and Fluoride ions as well.
2. The rise in pH of the aqueous phase promotes the ionization of the poly-acrylic acid.
3. Relocation of aluminum and calcium cations into the aqueous phase.
4. Unwinding of the polymer chain results from the Ionization of the poly-acrylic acid. As a result, viscosity of the paste increases, and cation concentration increases as well.
5. Condensation of cations on the chains of polymer occurs.
6. In the end, an insoluble salt is formed. [8]

2.2.5 Phases of Glass Ionomer Cement Setting:

There are three discrete and overlapping setting reactions which Glass ionomer undergo. They are as follow:

- ion leaching phase (immediately after mixing)
- hydrogel phase (initial set)
- Poly salt gel phase (final set).

Once set, a glass ionomer consists of three components:

- matrix
- filler
- Salt that attaches the filler to the matrix.

2.2.5.1 Ion-leaching phase:

Powder and liquid are first combined resulting in Ion leaching. The ion-leachable alumino-fluoro-silicate powder is attacked by the aqueous solutions of tartaric accelerators and the polyacid copolymers and dissolves the outer glass surface. Metal cations are released by the tartaric acids and the hydrogen from the polyacid, such as Ca^{2+} and Al^{3+}, from the surface of glass-powder. CaF_2, AlF^{2-}, and larger complexes are formed by the reaction of these cations with fluoride ions. Due to the progressive increase in acidity, the breakdown of unstable CaF_2 occurs resulting in a reaction with the acrylic copolymer which gives a more stable complex. The ratio of powder to liquid decides the liberation of heat between 3° to 7°C by the chemical reaction. More higher the ratio, more vigorous is the reaction and hence more liberation of heat.

2.2.5.1.1 Appearance:

In this phase, adherence of glass ionomer to the tooth structure occurs. It gives a shiny or glossy look as compared to the unreacted matrix. Maximum amount of free polyacid matrix is there for adhesion. So, placement should be completed in the initial part of this phase. As, the material loses its shine at the end of this phase, there is a reaction between free matrix and glass and the material is not much able to bond to the tooth or any other surface. Once the initial gloss is gone, Glass ionomer should not be operated. [4]

2.2.5.2 Hydrogel phase:

After 5 to 10 minutes of mixing, the hydrogel phase is responsible for the initial set. During this phase, there is a rapid release of positively charged calcium ions which react with the negatively charged aqueous poly-anionic poly-acid chains resulting in ionic cross-links. This phase reduces the mobility of the aqueous polymer chains, which is responsible for the initial gelation of the ionomer matrix. Proper protection from moisture and desiccation should be given to the ionomer during this phase.

2.2.5.2.1 Appearance:

A rigid and opaque glass ionomer is formed at this stage. There is a large difference in the refraction index of the glass filler and the matrix due to the opacity. Opacity is brief and should vanish during the final setting reaction. [4]

2.2.5.3 Polysalt gel phase:

When the material reaches its final set, polysalt gel phase is formed, which can continue for several months. Polysalt hydrogel to surround the unreacted glass filler is formed by the aluminum ions, which are released more slowly and hence the matrix matures.

2.2.5.3.1 Appearance:

The index of refraction of the silica gel surrounding the glass filler is more like the matrix. Consequently, the glass ionomer is more tooth-like in appearance. This reduces light scattering and opacity. [4]

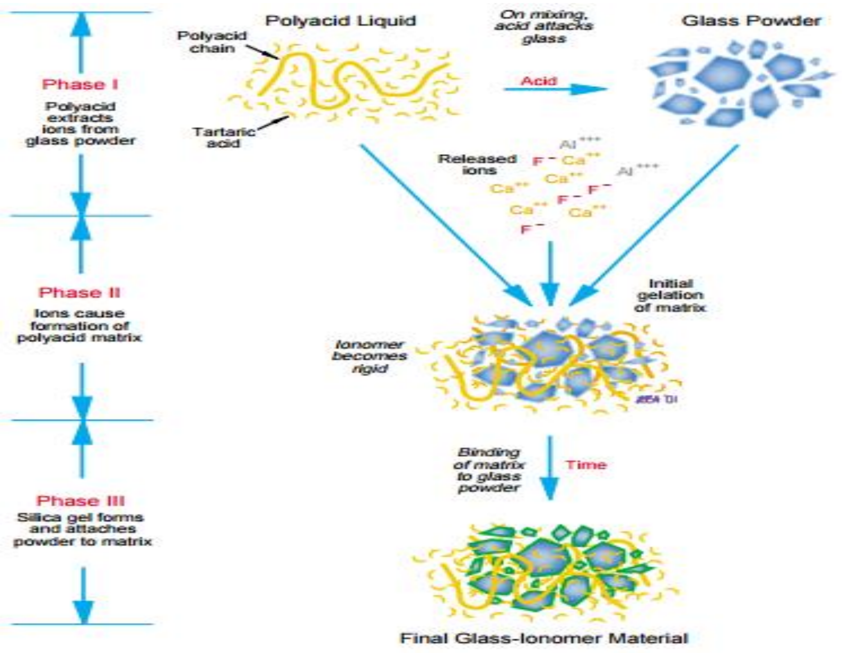


Figure 2.5-Phases of GIC

2.2.6 Properties of GIC: [4]

The attributes of early conventional glass-ionomer materials were slow setting, technique sensitive and reasonably opaque when set, and sensitive to both hydration and desiccation during setting. This results in the early loss of material from the surface. In the newer materials, all of these problems have been lessened. Fast setting and more appealing in looks, are the key attributes of modern glass ionomers, and hydration and sensitivity problems are relatively limited. However, they still should not be used as structural restorations.

Following are the properties of Glass Ionomer Cements.

- Form a rigid substance on setting
- Good fluoride release (bacteriostatic, inhibit, caries)
- Low exothermic reaction on setting
- Tooth colored

- Less shrinkage than polymerizing resins
- Coefficient of thermal expansion similar to dentin
- No free monomers
- Neutral cement is formed
- Dimensional stability at high humidity
- Filler–matrix chemical bonding
- Resistant to micro leakage
- Nonirritating to pulp
- Good marginal integrity
- Adhere chemically to enamel and dentin in the presence of moisture
- Rechargeable fluoride component
- High compressive strength

2.3 Comparison of Dental Filling Materials:

Table 2.5

Material	Cost	Durability	Decay resistance	Aesthetics	Strength
Amalgam	Inexpensive	10 years	High	Not tooth colored	Strong
Composite Resin	Costs more than amalgam	5 years	Moderate	Tooth colored	Strong
Glass Ionomer Cement	Less than composite resin	5 years or less	Fluoride release fights decay	Fairly good	Relatively weak

CHAPTER 3

EXPERIMENTAL METHODOLOGY AND CHARACTERIZATION

All the components were available expect Hydroxyapatite so we had to synthesize it by the assistance of Dr. Aftab. Two experiments were conducted for the synthesis of HA. The precursors used were Ca $(NO_3)_2$ and $(NH_4)_3PO_4.H_2O$. [16]

3.1 Procedure of Synthesis of Hydroxyapatite: [16]

The following procedure was followed:

1. 250ml of distilled water was take in two separate beakers
2. The reactants were completely dissolved in distilled water
3. The pH of Ca $(NO_3)_2$ and $(NH_4)_3PO_4$ solutions were recorded by pH meter in chemistry lab. The pH was reported to be 5.64 and 8.42 respectively
4. The pH of both solutions was adjusted to 10 or above by the addition of NH_4OH
5. After the addition of NH_4OH the pH of the solutions rose to 10.88 and 12.1 respectively
6. Solution of $(NH_4)_3PO_4$ was added to $Ca(NO_3)_2$ at the rate of 30 drops/min through a separating funnel, keeping the pH of the reaction mixture above 10 throughout the reaction
7. After complete addition the reaction solution was stirred for 20 hrs.
8. The pH was recorded to be 10.28
9. Refluxing of the solution was done at 100^oC for 2 hrs.
10. The resulting solution was then filtered by distilled water until its pH dropped below 8
11. The wet powder obtained was dried in a microwave at 80^oC for 22 hrs.
12. Dry pellets were obtained which were crushed to powder in a mortar

13. Resulting powder was annealed for 2 hrs. at 900°C with temperature increasing at 10°C/min in a muffle furnace
14. The powder was characterized through XRD confirming the pure HA powder

3.1.1 Characterization of HA:

The first sample was not refluxed before annealing but the results from XRD confirmed its purity.

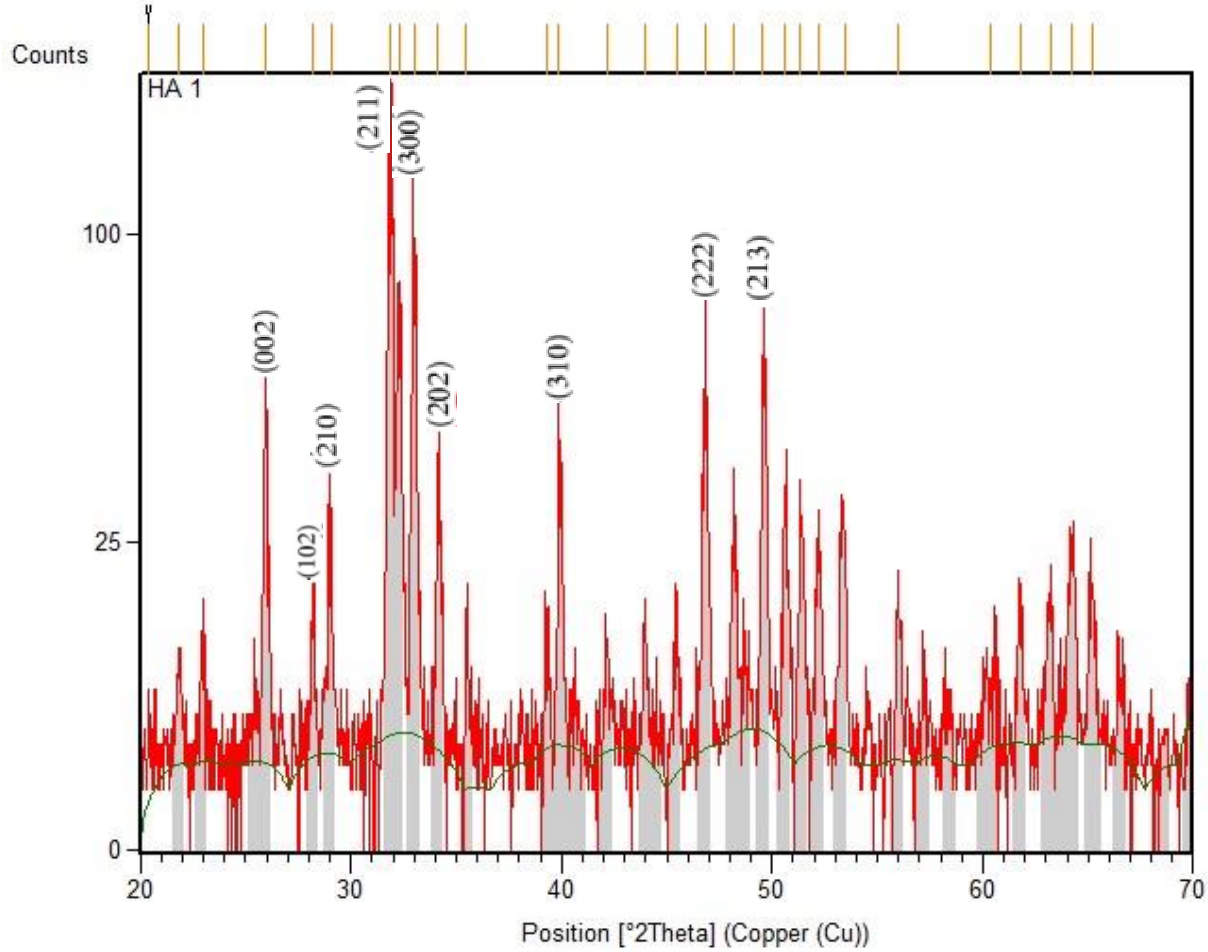


Figure 3.1 XRD of sample 1 of HA

The second sample was refluxed for 2 hours at 100^{o}C. [16] The XRD of this sample shown much sharper peaks and the crystallite size, calculated by the Scherrer Calculator in X'pert HighScore, was in nanometer scale.

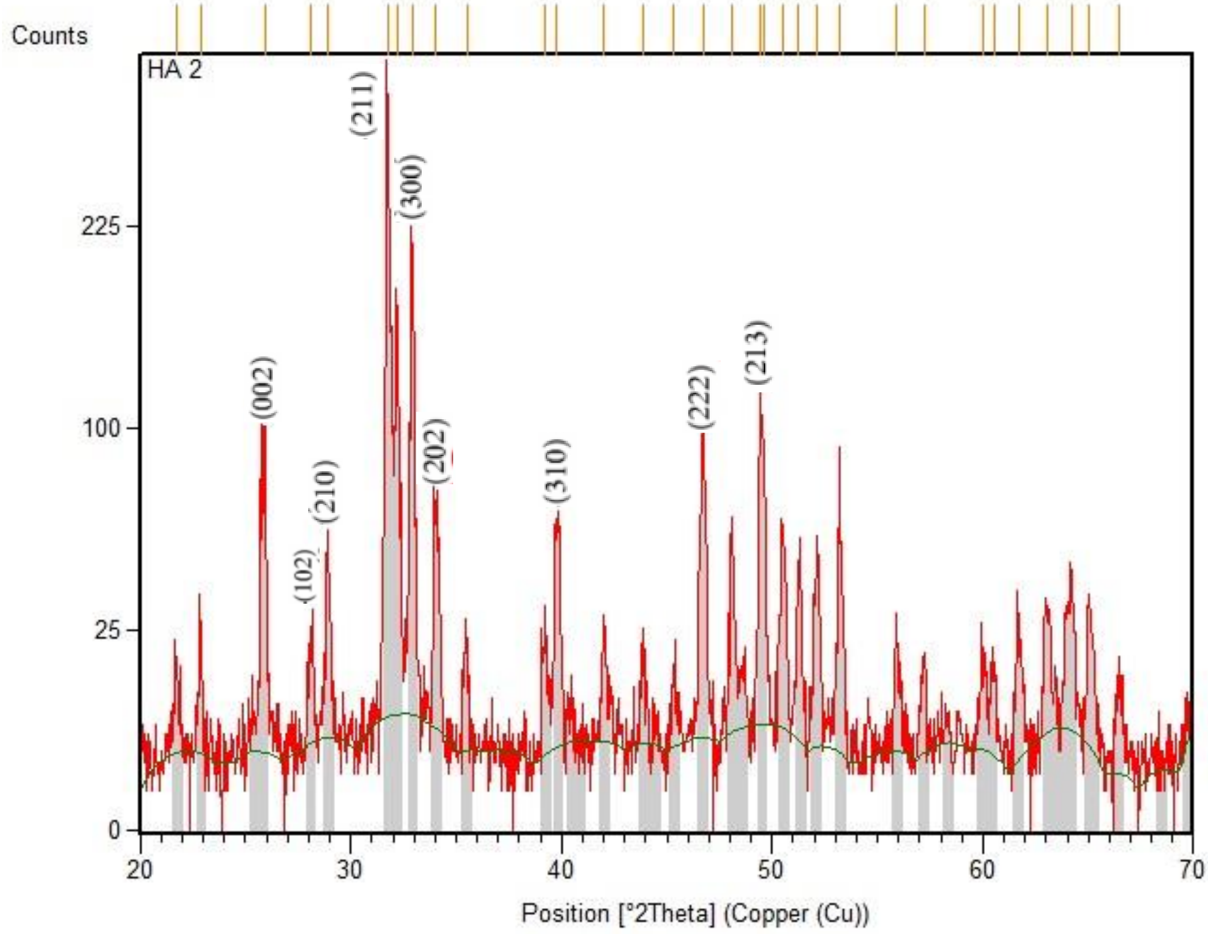


Figure 3.2 XRD of sample 2 of HA

The morphological analysis of HA powder was done using SEM. The micrographs shown in the figure 3.3 represents the particle size of HA. The image is blur because HA is a dielectric bio-material. [17] However, the image can be clearly seen by using FE SEM.

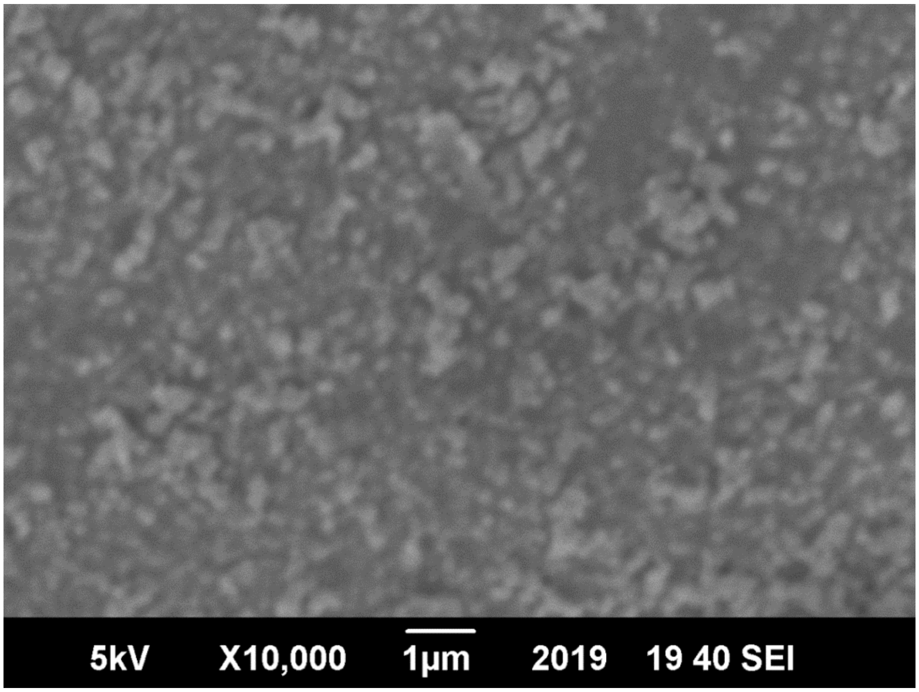


Figure 3.3 SEM of HA

To confirm the chemical analysis of HA we did the Laser Induced Breakdown Spectroscopy. LIBS is an analytical technique which uses high energy short Laser pulse to produce characteristics plasma of the sample. The plasma is collected using lenses by using an optical fiber wire. The plasma collected is transported to a detector and a plot of the chemical composition of the sample is obtained. [18]

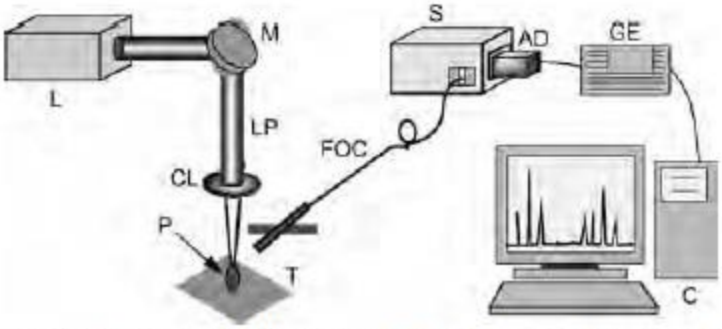


Diagram of a typical laboratory LIBS apparatus. Here: L = laser; M = mirror; LP = laser pulse; CL = lens; P = plasma; T = target; FOC = fiber optic cable; S = spectrograph; AD = array detector; GE = gating electronics; C = computer.

Figure 3.4 Typical setup of LIBS[18]

The LIBS analysis of HA is shown in the following figure 3.5. The range of the detector used was from 200nm due to which the peaks of phosphorous could not be seen because they appear below 200nm. The peaks of Calcium can be seen at different wavelengths.

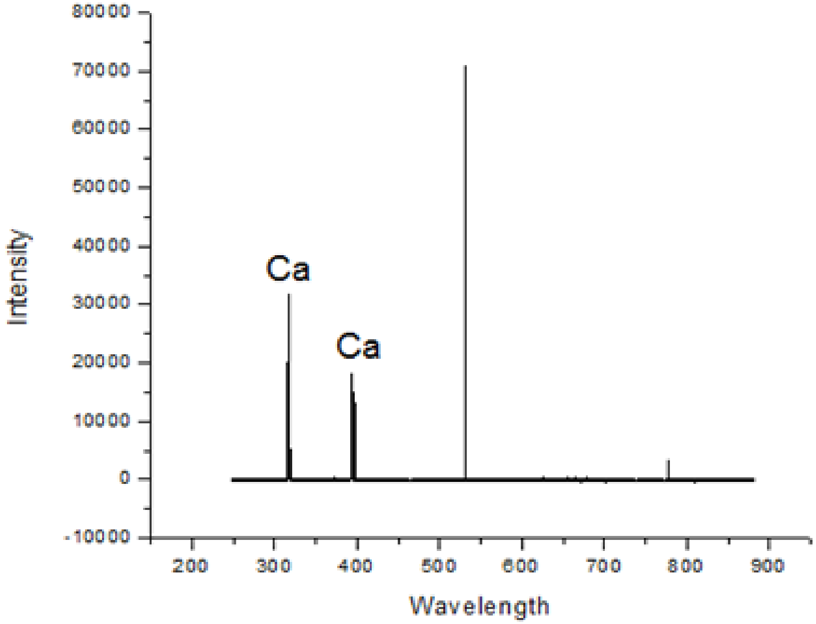


Figure 3.5 LIBS of HA

By using the above obtained HA we took the following proportions of the constituents for the synthesis of glass by Fusion method. [19]

Table 3.1

Component	Weight (g)
SiO_2	45
Al_2O_3	21
CaF_2	12
Hydroxyapatite	10
$CaCO_3$	12

Fusion method was applied because of its feasibility in our department. The sample mixture is placed in a crucible and put into furnace for sintering at a certain temperature for a certain amount of time. The crucible is then quenched in distilled water in order to avoid any crystallization of the glass.

One sample mixture of 70 grams was prepared using the following composition by weighing each component separately on a balance and then mixing them. We did ball milling for 2 hrs. in order to obtain a homogenous mixture. The balls and the bottle were washed with ethanol to prevent any contamination.

Table 3.2

Component	**Weight (g)**
SiO_2	31.5
Al_2O_3	14.7
CaF_2	8.4
Hydroxyapatite	7.0
$CaCO_3$	8.4

The powder was characterized using XRD after conventional ball milling. Peaks of every component can be seen distinctively in the XRD pattern in the figure 3.6. This also indicates that all the components were mixed homogeneously.

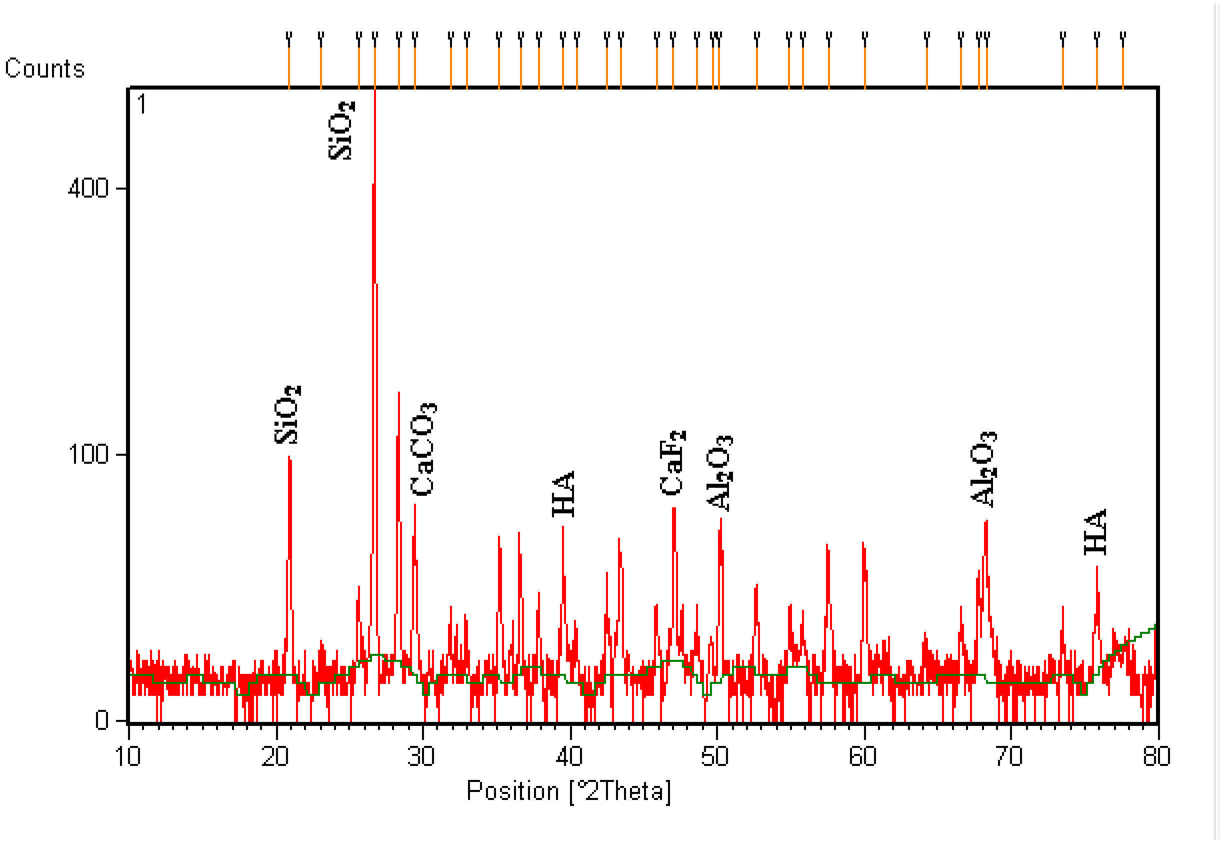


Figure 3.6 Unfused Powders

3.2 Experiment 1:

Pellets of the mixtures were made in the workshop by using the Hydraulic press. A force of 4 tons for 4 minutes was applied on each pellet. The pellets were placed on an alumina boat in muffle furnace at 1300°C with the heating rate of 10°C/min for 8 hrs. The hot alumina boat was handled with metallic tongs, heat resistant gloves and heat resistant helmet during the quenching process in distilled water. [19]

Figure 3.7 Glass Sample 1

The product formed as a result of fusion was very difficult to remove from the alumina boat.

3.2.1 XRD Characterization:

The sample was removed by machining it from the alumina boat. It was then crushed in granite pestle and mortar to avoid any contamination. The XRD pattern of the sample was amorphous as there were no sharp intense peaks in the pattern. This is because the X-Rays were scattered in different directions since there was no crystallinity in the structure.

The broad peaks also indicate the fusion of all the components.

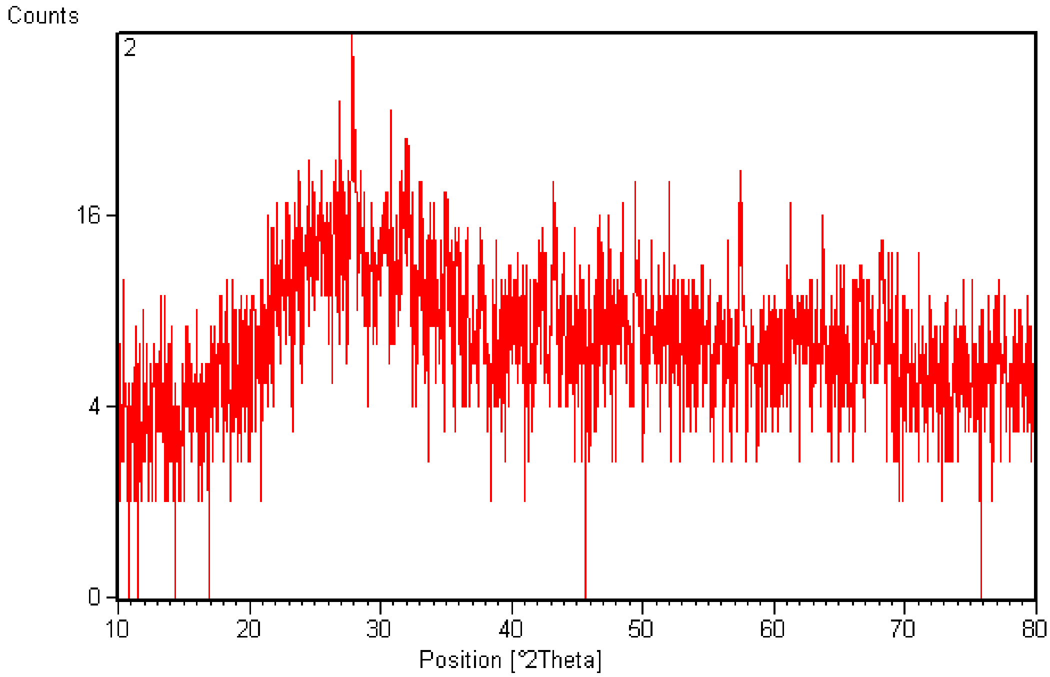


Figure 3.8 XRD of Glass Sample 1

3.3 Experiment 2:

In the 2nd experiment the fusion conditions were the same but we changed the crucible since the fused glass stuck to the alumina boat. This time we used alumina plate. The sample detached from the plate right after quenching because while removing the plate from the furnace the sample accidently touched the tongs.

Figure 3.9 Glass Sample 2

3.3.1 XRD Characterization:

The XRD pattern of the sample also indicates the amorphous structure of the sample.

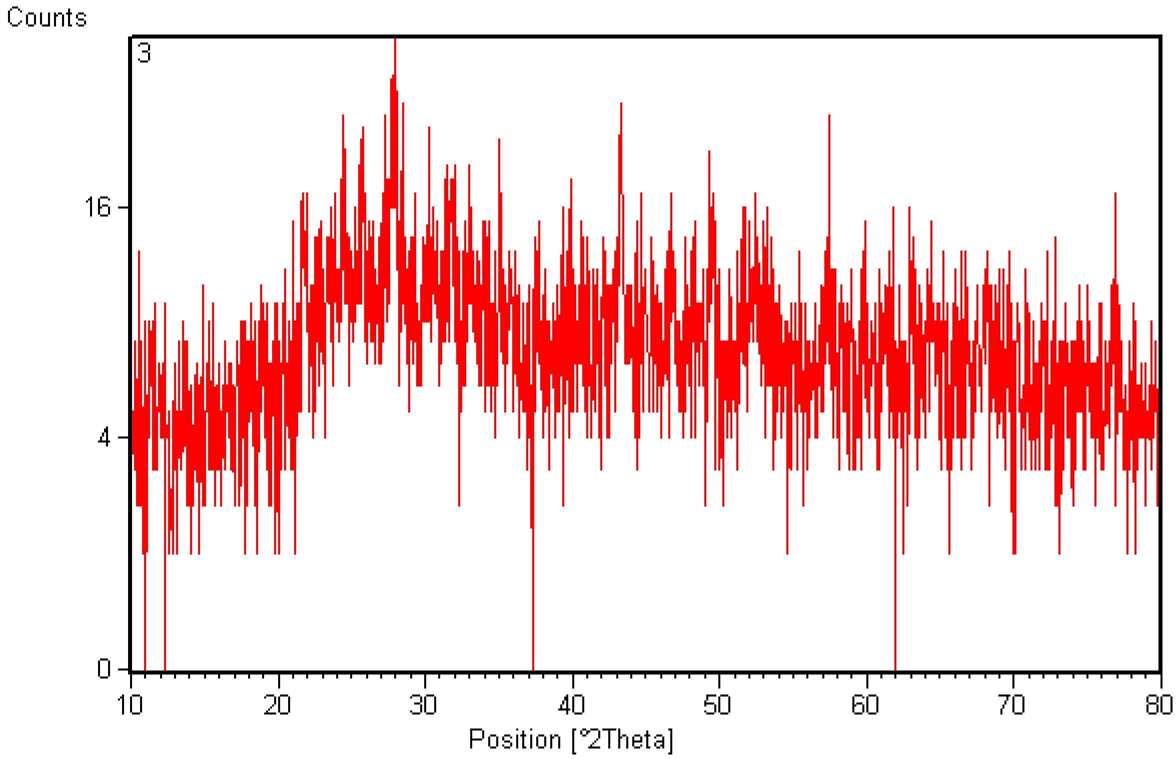


Figure 3.10 XRD of Sample 2 of Glass

3.4 Experiment 3:

In the 3rd experiment all the conditions were again same. We could not increase the fusion temperature due to the limitations of the muffle furnace. This time the sample was detached using a little force applied by the pestle; the alumina plate also broke due to the influence of the force.

Figure 3.11 Glass Sample 3

3.4.1 XRD Characterization:

No sharp and intense peaks in XRD pattern of the sample indicate the lack of crystallinity.

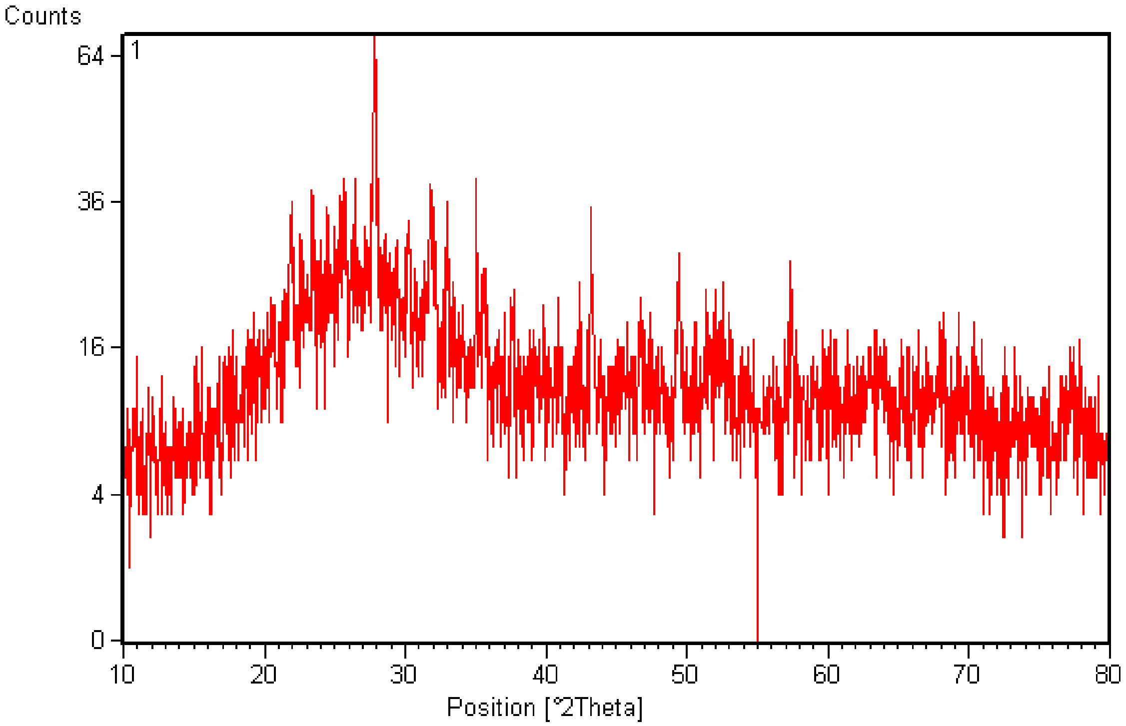


Figure 3.12 XRD of Glass Sample 3

3.5 Experiment 4:

The conditions for this experiment were also same. The milky glass was crushed into powder. Figure 3.13 shows the sample

Figure 3.13 Glass Sample 4

3.5.1 XRD Characterization:

Figure 3.14 shows the XRD pattern of the powdered sample.

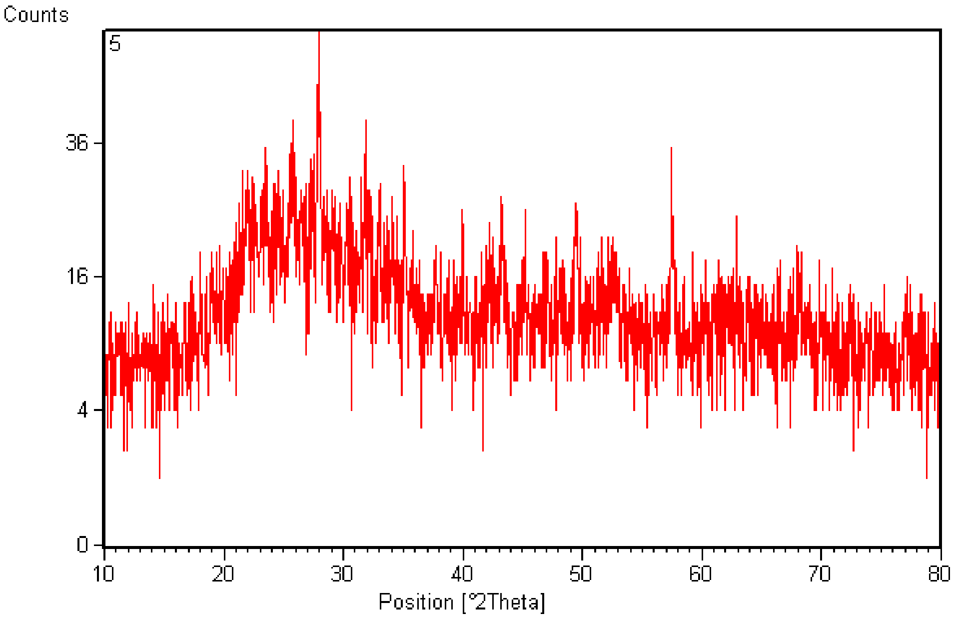


Figure 3.14 XRD of Glass Sample 4

3.6 Experiment 5:

The sample was again prepared in same conditions. This time the sample was accidently touched with the tongs again so it got detached easily without shattering the alumina plate.

Figure 3.15 shows the sample. Its shape is irregular because of the tongs.

Figure 3.15 Glass Sample 5

3.6.1 XRD Characterization:

The XRD pattern of this sample is shown in the figure 3.16.

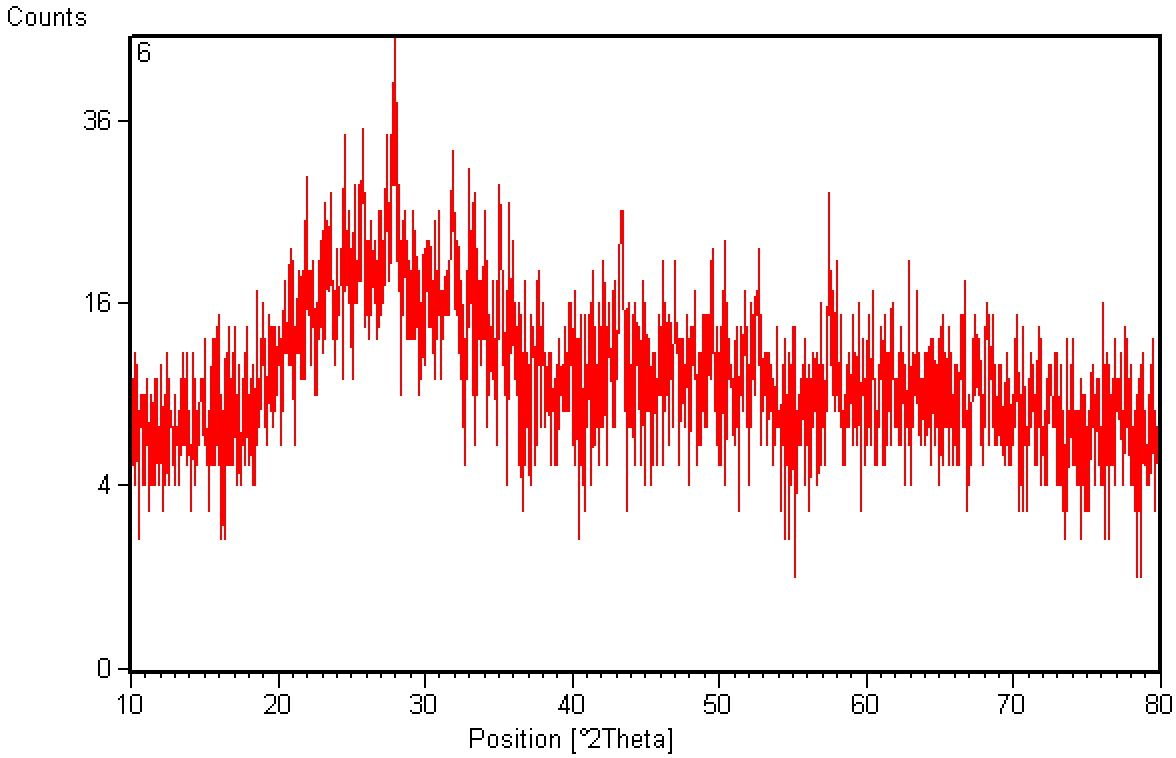


Figure 3.16 XRD of Glass Sample 5

3.7 Experiment 6:

The powder was fused at 1300^0C for 8 hrs. It was quenched in distilled water and crushed in granite pestle and mortar. Figure 3.17 shows the sample and figure 3.18 shows its XRD.

Figure 3.17 Glass Sample 6

3.7.1 XRD Characterization:

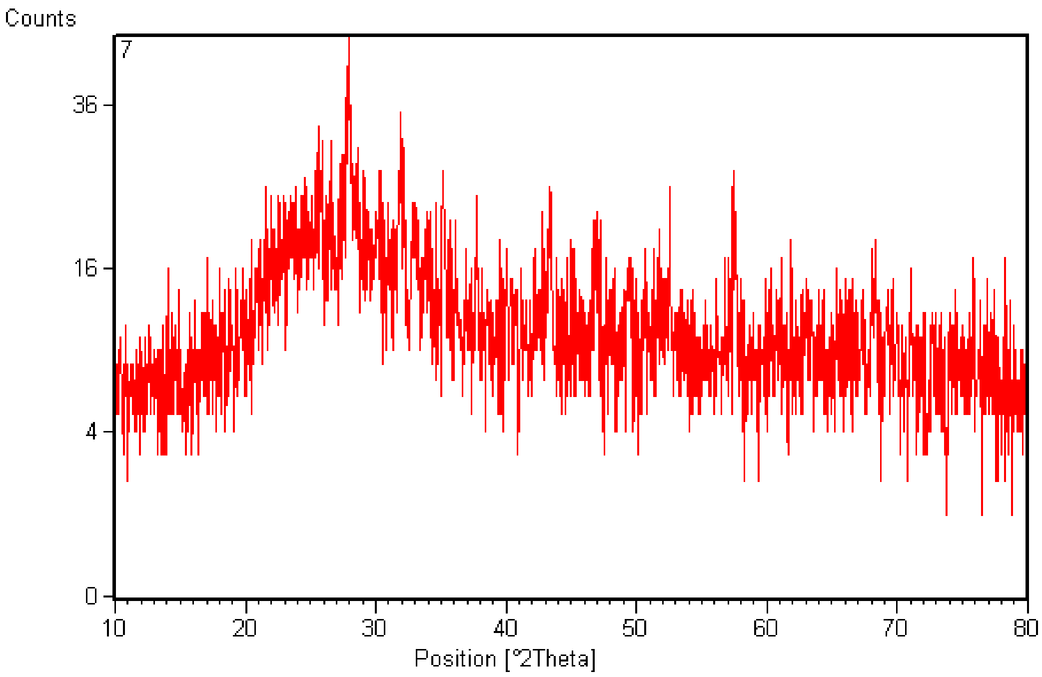


Figure 3.18 XRD of Glass Sample 6

Figure 3.19 shows an XRD of GIC from literature. The hump in the XRD is at 35^0 which is comparable to our sample. [20]

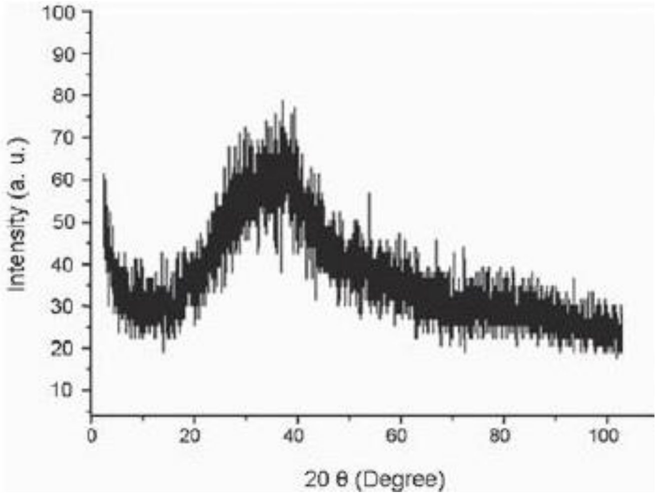


Figure 3.19

3.8 Particle Size Analysis:

Particle size plays a vital role in powders. For glass ionomer cement smaller the particle size is, higher will be the strength of the cement. [21] Particles of mean size 3.34 µm have higher strength than the particles of mean size 9.60 µm. [21]

We did the PSA of the powder crushed manually, the mean size obtained was larger i.e. 30 µm. This powder was reacted with commercially available polyacrylic acid to obtain GIC. As reported in the literature the GIC did not have much strength. The bonds broke by applying manual force by hands. The powder was not also completely wetted by the acid because we did not have the dental spatula required for mixing at that time. The figure 3.20 shows 30 µm powder reacted with acid.

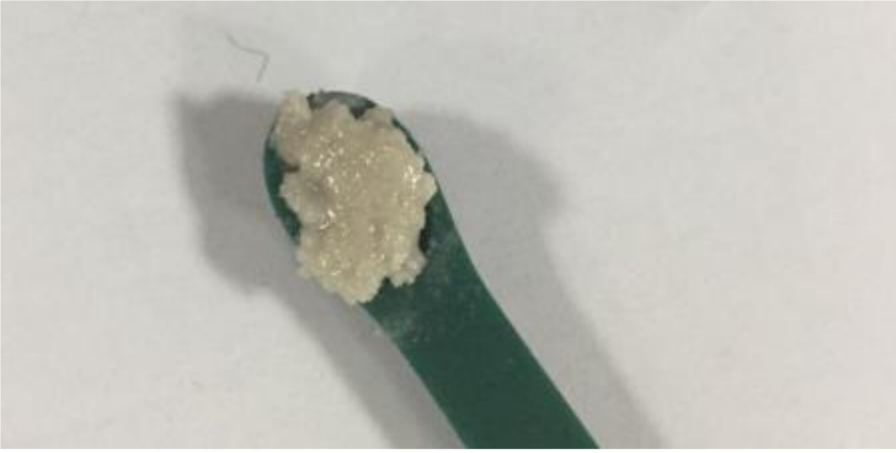


Figure 3.20 Glass Ionomer Cement

The PSA of the powder is shown below. The mean particle size of this powder is 30 µm.

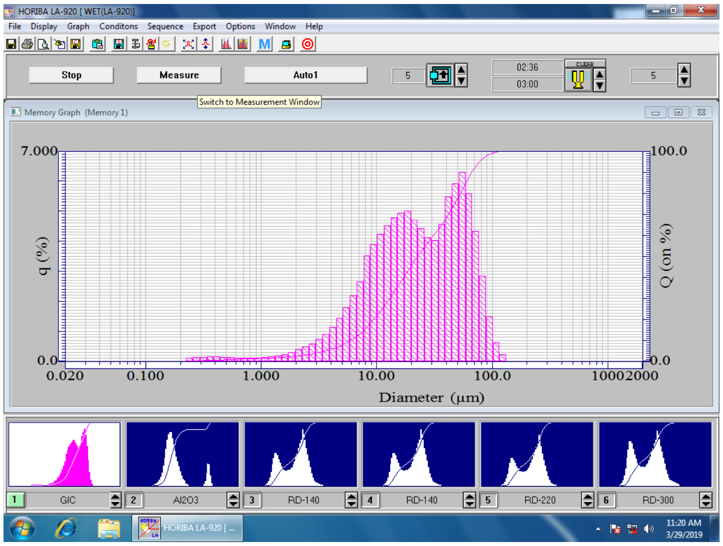


Figure 3.21 PSA before high energy ball milling

The powder was then crushed by high energy ball milling for 3 hourrs to reduce its particle size using ZrO_2 balls. This powder was then reacted with acid to obtain strong cement. Further pallets were made to do the mechanical testing and LIBS of the sample. Figure 3.22 shows the powder after high energy ball milling.

Figure 3.22 Glass Powder after high energy ball milling

The powder was again analyzed using PSA to check its particle size. This time the size reduced to 3 µm. Figure 3.23 shows the particle size after high energy ball milling.

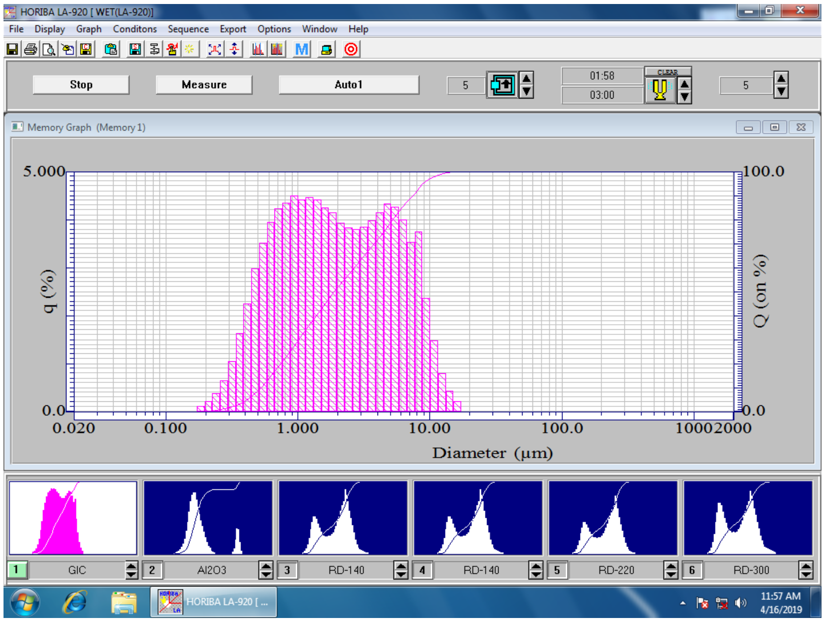


Figure 3.23 PSA after high energy ball milling

3.9 LIBS:

Pellets were made using a dental spatula and 3 µm powders for the chemical compositional analysis of GIC. We did LIBS analysis of the GIC to see the peaks of Fluorine but due to the limitations of the detector and the fact that fluorine ionizes as anion and its less concentration¸ made it difficult for us to see the peaks of fluorine. The detection of halogens is difficult by using conventional techniques. [22] According to literature the peak of Fluorine is obtained at 685.60 nm. [23]

The integration time for the analysis of our sample was 10 µs and the energy of the laser was 90 mj. The figure 3.24 shows the LIBS of our sample. Peaks of Al, Ca and Si can be seen.

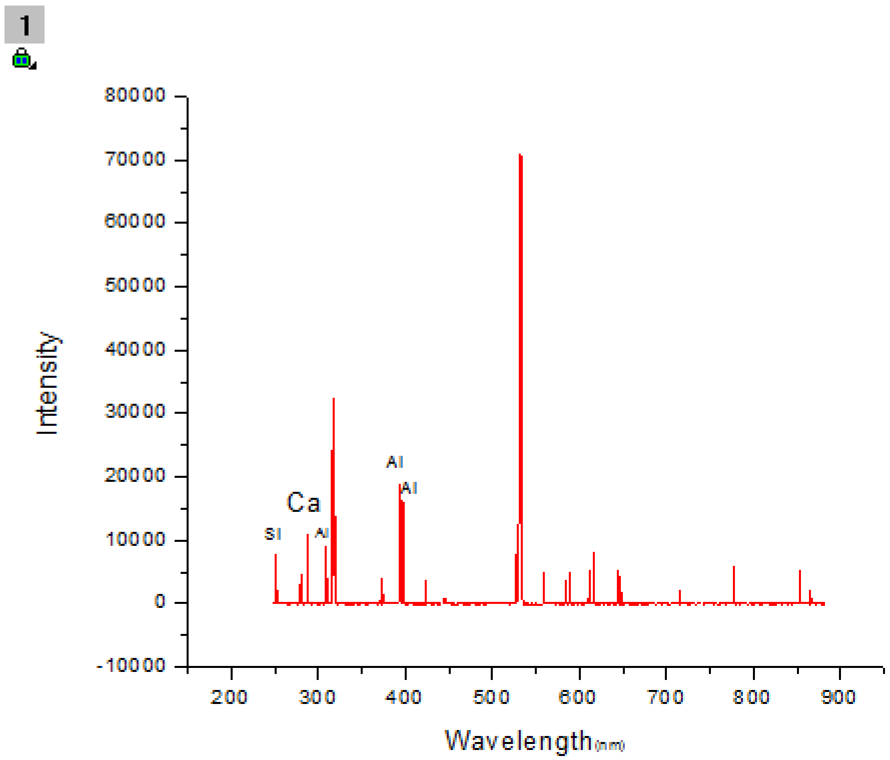


Figure 3.24 LIBS of GIC

3.10 Mechanical Characterization:

3.10.1 Compression test:

For compression test we tried to follow the ISO standard ISO 9917.1.2013. This standard is based on liquid powder dental cements. GIC is a type of liquid powder cement so we tried to follow this standard.

The required parameters for the test were making a pellet of diameter 4mm, height of 6 mm and strain rate of 0.75mm/min.[24] The mold that we used for this test was a glass tube which was lubricated by petroleum jelly to avoid the sticking of the pellet with the glass tube. The pellets were manually pressed by using a steel rod from the upper opening of the glass. The pellets were left to cure for 1 day and then tested by using the UTM machine in Mechanical Testing Lab.

3.10.1.1 Sample 1:

The Yield point of 1st sample was at 12 MPa and its UTS was 4.5 MPa. The quantity of acid in this sample was 1 drop i.e. approximately 80 µL in 300mg of powder.

Figure 3.25 shows the results of compression test.

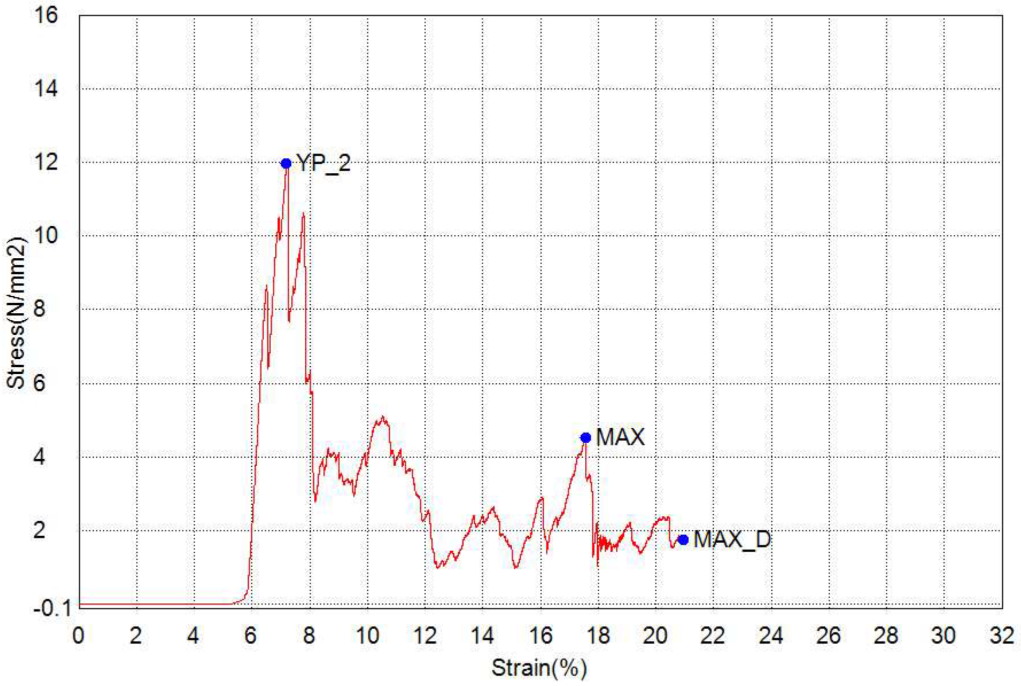


Figure 3.25 Compression test of sample 1

The result is fluctuating because as the pellet was compressed small particles would fall off the sample.

3.10.1.2 Sample 2:

The UTS of this sample was 10.7345 MPa.

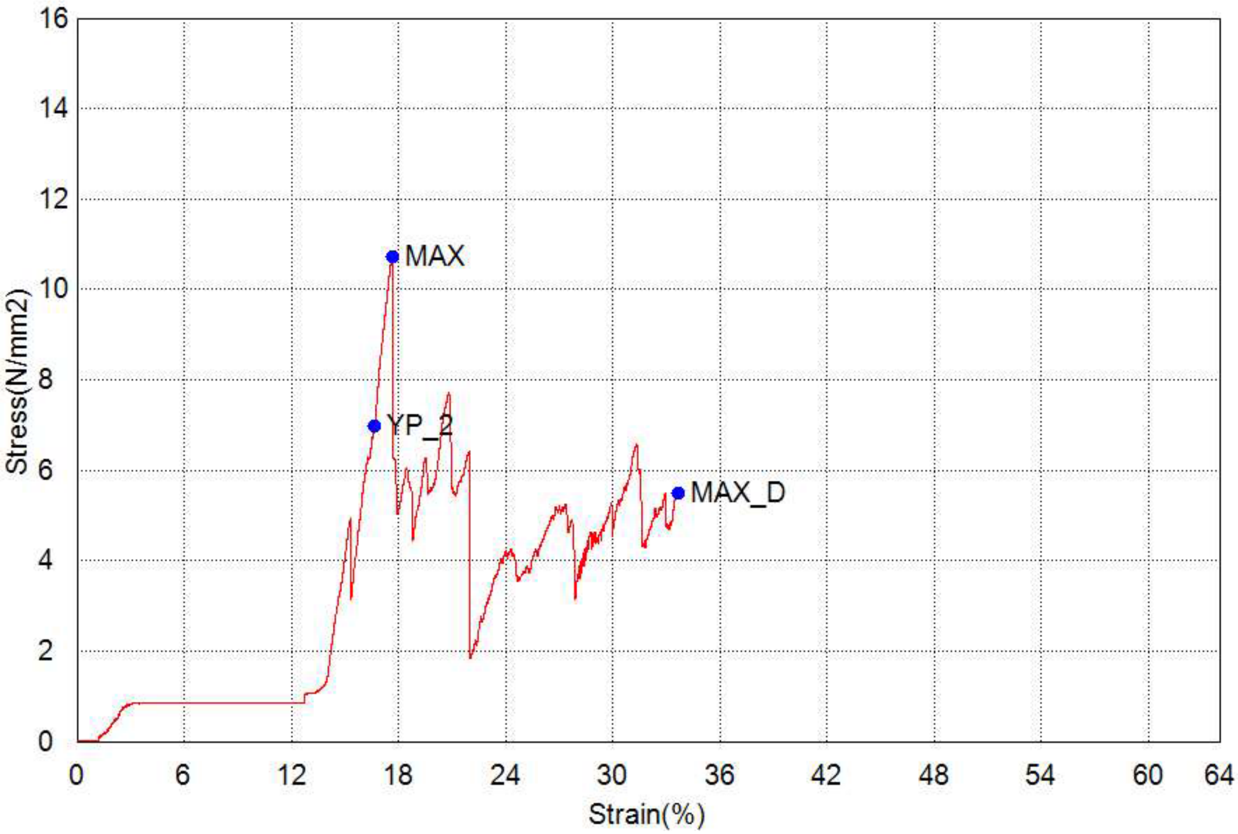


Figure 3.26 Compression test of sample 2

3.10.1.3 Sample 3:

This pellet was prepared by using approximately 150 µL of acid in 300mg of powder. The difference in results is significant. The pellet lost approximately more than half of its strength upon compression. It decreased from 12MPa to 4.19MPa.

The ratio of liquid to powder was changed to obtain the optimum amount of acid required to wet the powder.

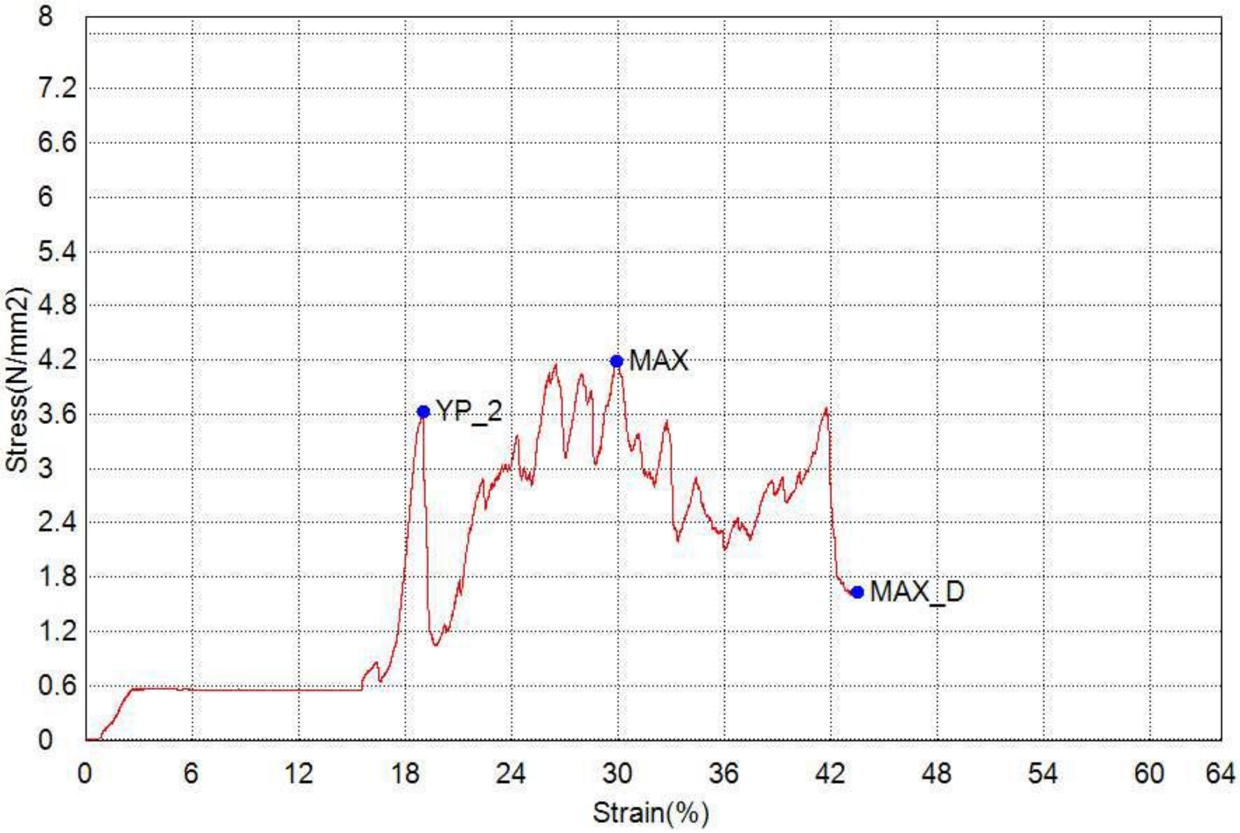


Figure 3.27 Compression test of sample 3

3.10.1.4 Sample 4:

The UTS of this pellet decreased slightly to 8.34MPa.

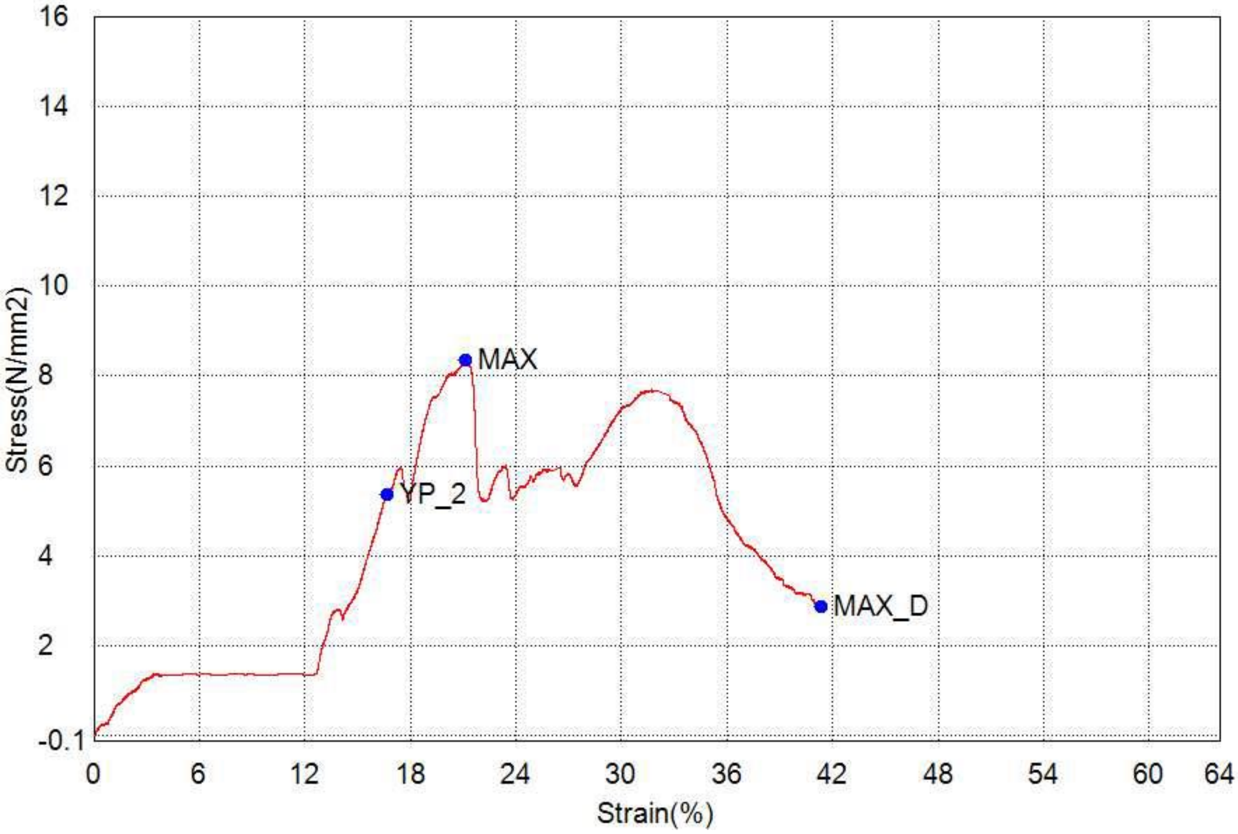


Figure 3.28 Compression test of sample 4

3.10.1.5 Sample 5:

As we were making the pellets manually, they were not compressed completely so the strength of this sample decreased due to porosity in the pellet. The pellet reached a maximum of 5.53MPa before collapsing.

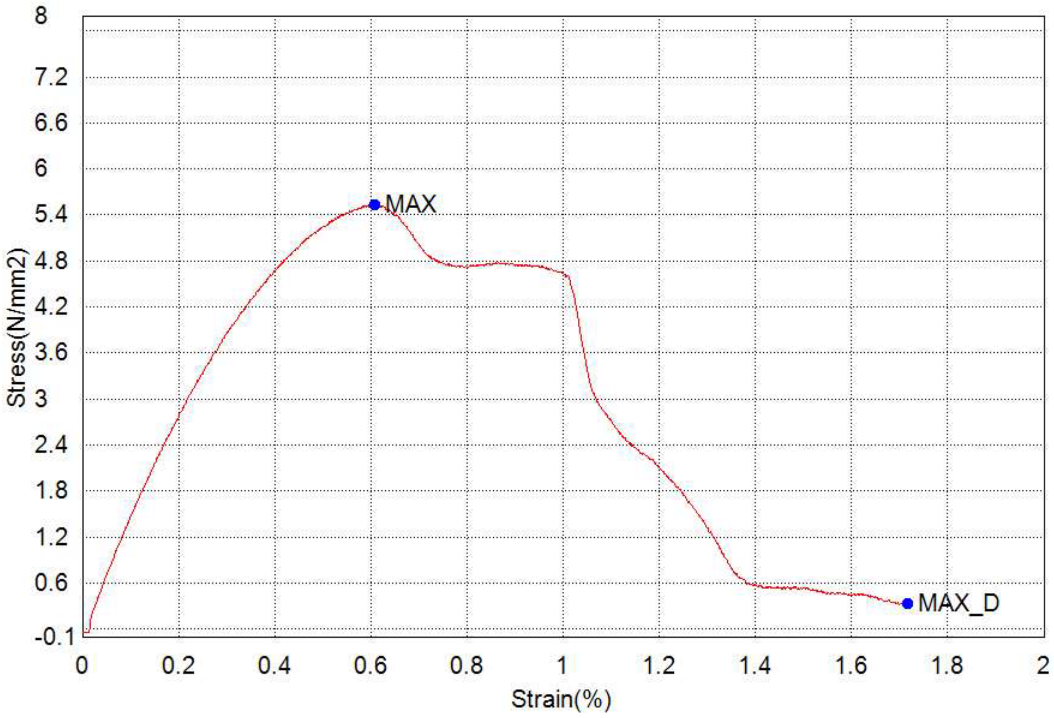


Figure 3.29 Compression test of sample 5

The minimum compressive strength of GIC reported in the literature is 38.90 MPa [25]. Our samples has a maximum of 11 MPa compressive strength, the reasons for such a notable difference are:

1. The pellet was compressed manually before the test
2. The liquid acid was not compatible with the powder
3. The pellet consisted of many pores
4. The liquid acid does not wet the powder completely
5. No proper mold was available for the preparation of pellets
6. The pellets deformed a little after removal from the glass mold

3.10.1.6 Universal Testing Machine:

All the compression tests were carried out using the UTM machine. The pellet mounted in the machine can be seen in figure 3.30.

Figure 3.30 UTM Machine

3.10.2 Hardness Testing:

Hardness test was performed by making a pellet of the GIC. The pellet was made in a mold of height 2mm and diameter of 12mm. The load applied was 50g for a dwell time of 30 secs. [26]

The surface of the pellet was not visible through the microscope of Vickers Hardness machine so we used Dye Penetrant Test sprays to make it visible. Figure 3.31 shows the pellet used for hardness testing.

Figure 3.31 Pellet for Vickers Hardness

The DPT spray was red in color so that is why the pellet has red surface.

Figure 3.32 shows the Vickers indent on the surface of GIC.

Figure 3.32 Vickers Indent

The table below shows the Vickers value of different pellets.

Table 3.3

Serial No.	Hardness (HV)
1	**19.4**
2	**20.7**
3	**17.6**
4	**18.2**
5	**19.2**
Mean	**19.02 ± 0.951**
Error	**0.951**

The minimum hardness reported in literature for Glass Ionomer Cement is 35.08 HV [26] after a curing time of 24 hrs. The maximum hardness obtained by our samples was 19.4 HV even though we cured our pellets for more than a day, the reasons for this difference are:

1. The pellets were compressed manually
2. The liquid acid did not wet the powder completely

3. There were multiple pores in the pellets
4. The pellets were not prepared in a special mold

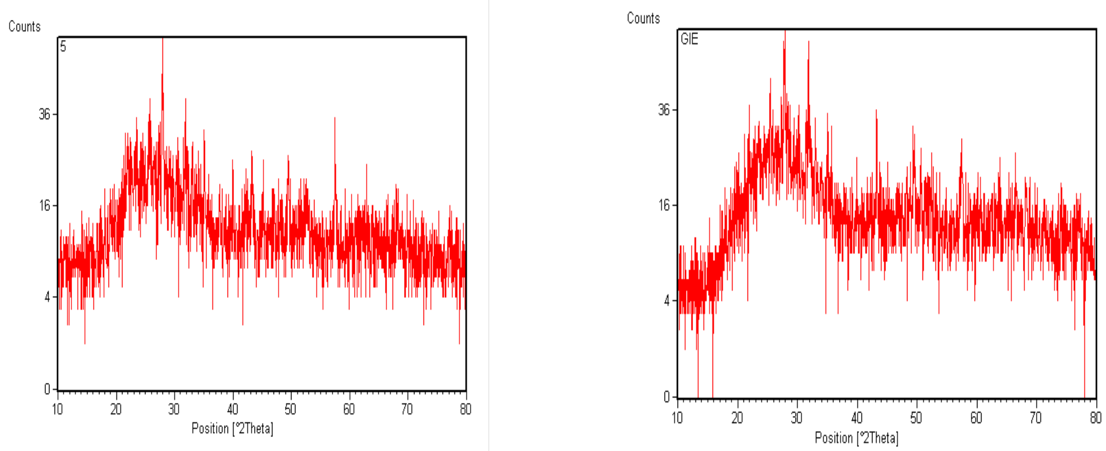
3.11 GIC VS Commercially available (CHINESE) GIC:

We used following characterization techniques to make sure that the GIC synthesized by us is completely compatible with the one being used in local market after importing from foreign countries.

- XRD
- Particle Size Analyzer
- Compressional Testing
- LIBS

3.11.1 XRD:

Results of our sample are totally comparable with the imported one because both appeared to be amorphous in nature and both the samples have the highest peaks at nearly 30 degree position. Moreover the overall pattern of peaks is almost same. [27]



GIC **Chinese GIC**

Figure 3.33 XRD Comparison

3.11.2 Particle Size Analyzer:

Particle size of the two samples under consideration is nearly analogous to each other because in the results we can see that most of the peaks are in range of 1-10 micrometer in our sample, where as in the Chinese sample most of the peaks are in the range of 3-10 micrometers. [21]

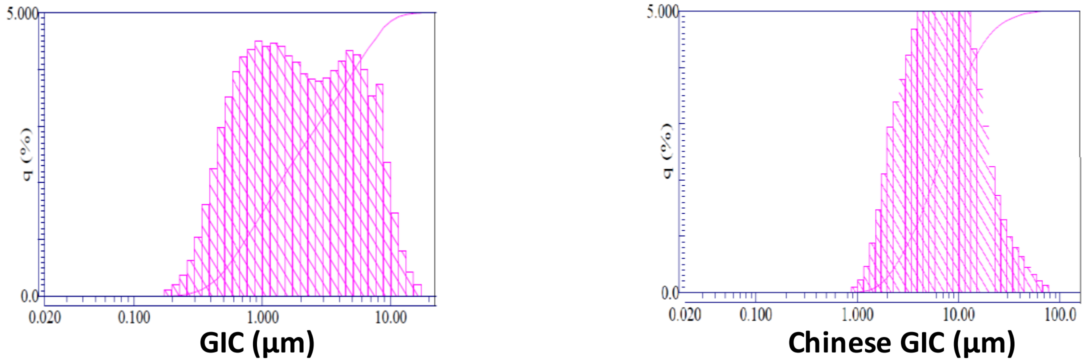


Figure 3.34 Comparison of PSA

3.11.3 Compressional Testing:

Compressional Strength of both the samples is in the same range i.e, 8 to 9 MPa. Moreover, the error for both the readings is also same which means our readings are correct. So, we can claim that our sample can easily bear the mastication movement of our teeth.

The difference from literature is apparently very large but since both the samples were prepared in the same conditions and the same mold so the readings of both glass ionomer cements are comparable.

Comparison Graph is given below:

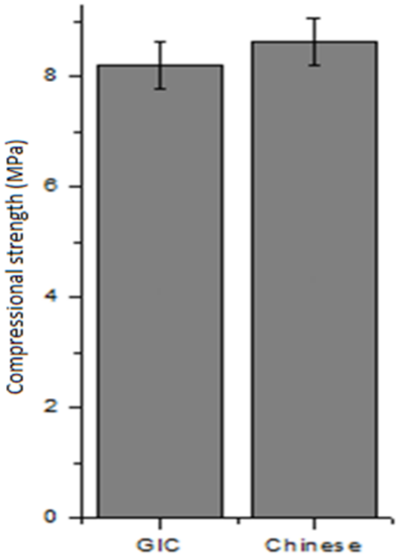
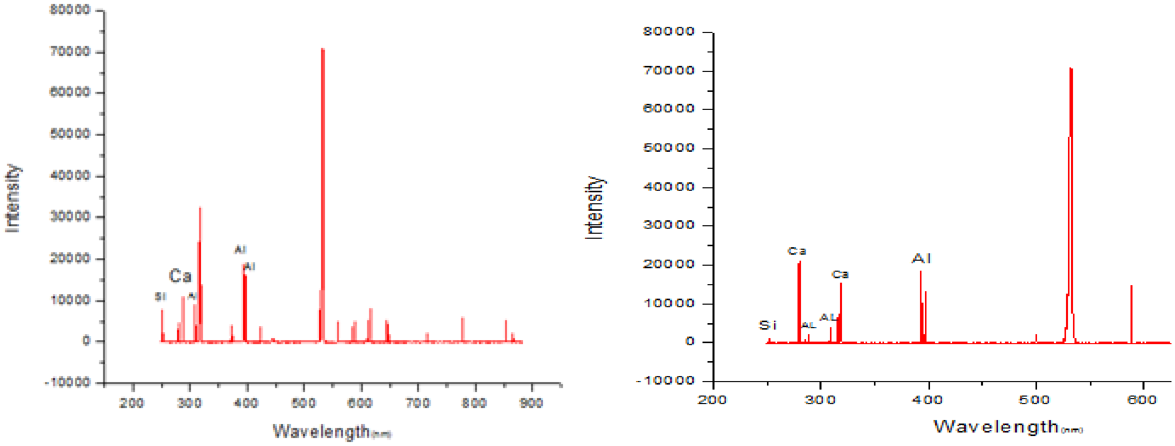


Figure 3.35 Comparison of Compressional Strength

3.11.4 LIBS:

Laser induced breakdown spectrometry confirmed the presence of almost same elements in both samples i.e. Aluminum is present at 400 wavelength (nm) with the same peak intensity in both the samples. Silicon is in both samples but our sample has the higher intensity of it. Moreover, there are 2 peaks of calcium in the Chinese sample and 1 in our sample. It can be concluded that the elemental composition is same. [28]



GIC

Chinese GIC

Figure 3.36 Comparison of LIBS

Conclusion

From the experimentations, it is concluded that the Glass Powder can be formed at temperature of 1300^{0}C with a soaking time of 8 hours followed by quenching in distilled water. By doing high energy ball milling we reduced the particle size in range of 1-10um. This particle size is optimum for complete wetting of glass powder with acid to form GIC. By doing characterization of GIC we found that its particle size was according to the required size given in the literature. GIC mechanical testing also suggested that its hardness and compression were according to the standards. LIBS analysis showed that the elements which we needed in our GIC were present.

We have achieved our defined objectives i.e. synthesis of Glass Ionomer Cement and its characterization. In addition to GIC, we have also synthesized Hydroxyapatite which is also imported in Pakistan and is not commercially available. To conclude, GIC was made successfully. This will enable us to increase research in the field of Biomaterials in Pakistan and it will also help us to create an industry in this field.

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