Republic of Iraq
Ministry of Higher Education and Scientific Research
University of Babylon
College of Materials Engineering
Department of Ceramic Engineering and Building Materials

Preparation and Characterization of 45S5 Bioglass Ceramic at Low Melting temperature

A Thesis

Submitted to the Council of the College of Materials Engineering/University of Babylon in Partial Fulfillment of the Requirements for the master degree in Materials Engineering/ceramic

By

Ahmed Kareem Kadhim Abd Ali

(B.Sc. In Non-metallic Materials Engineering, 2015)

Supervised

By

Prof. Dr. Shaker J. Edrees

2022 A.D **1444 A.H**

بسم الله الرحمن الرحيم

يَرْفَعِ اللَّهُ الَّذِينَ آمَنُوا مِنْكُمْ وَالَّذِينَ أُوتُوا الْعِلْمَ

دَرَجَاتٍ وَاللَّهُ بِمَا تَعْمَلُونَ خَبِيرٌ"

صدق الله العلي العظيم

،

سورة المجادلة: الآية 11

قال رسول الله صلى الله عليه واله

الاطهار

(التفكر ساعة خير من عبادة سنة)

صدق رسول الله

بحار الانوار

Thank you to whoever deserves it

- **Prof. Dr. Shaker J. Edress:-** for his tremendous time and effort spent in leading, supporting and encouraging me during study years. His passion for challenges has given me inspiration; his knowledge of science has given me guidance; his perseverance in research has given me confidence. Without his help and effort, it would be impossible for me even to get close to this point.
- MY FAMILY
- MY FRINDS
- Prof. Dr. Imad Ali Dishar
- Prof. Dr. Mohsin Abbas Aswad
- Assist. Prof. Dr. Firas
- Assist .Prof. Dr. Israa K.Sabree
- Everyone who supported and encouraged me in my research

Abstract

The Manufacture of ceramic materials used in medical applications needs continuous development and the introduction of elements that are beneficial to the human body to serve as fillers for bone damages and regulating the action of insulin or to help eliminate some cancer cells. .

The process of reducing the melting temperature of glass is done by replacing part of the glass components with low-melting oxides without significantly affecting the glass structure. This process is carried out by introducing eutectic compound of (V_2O_5 (39) and K_2O (61) mol%) which was prepared by heating the mixture at 501°C for 2 h. It was suggested that SiO_2 and Na_2O together in the 45S5 bioactive glass to be replaced by the eutectic compound. Three ratios of the compound i.e. (5, 10, 15 mol%) were employed in this study.

The melting was done in two steps. First, the components were calcined at 900 ^{0}C to elimination the carbonates. Then, the temperature was increased up to the melting, which varied from 1100 to 1400 ºC depending on the ratio of replacement. The melt was then held at the melting temperature for 3 h. Finally, then melt was quenched in water to produce an amorphous glass phase. After that, the resulting glass was dried, shaped and sintered at 1000°C for 2 h. The sintered glass was characterized using XRD, SEM, FTIR and EDS. Additionally, the sintered glass was undergone physical and mechanical as well as biological tests to assess its performance with living tissues.

X-ray revealed the presence of the following phases ($Na_4Ca_4Si_6O_{18}$) and a small quantity of ($K_5V_3O_5$) in the sintered glass which pointed out to formation glass-ceramics. The density of the sintered glass increased from 2.451 to 2.489 g/cm^3. While the porosity decreased from 19.88% to 14.83 %, as a result of the eutectic compound. Mechanically, the compressive strength increased from 96 to 137.76 MPa as well as the hardness of the sample raised from 4.23 to 7.76 GPa.

The bioactivity test has shown that a sponge layer of hydroxyapatite ($Ca_5(PO_4)_3OH$) has formed after 2 days of immersion in SBF solution at 37°C as conform by X-ray analyses . SEM images showed the emergence of crystals on the surface of the samples. Examination of EDS showed deposition of elements on the surface of the submerged samples and they were proportions of Ca/P are 1.86: 1.88: 1.07. When Kirby's_Bauer test was done, it was found that the manufactured material is not lethal to bacteria.

TABLE OF CONTENT

LIST Of FIGURE

LIST OF TABLES

Abbreviations and symbols

Seq.	Symbols	Explanation	Unite
1	45S5	Hench bioactive glasses	
2	HA	Hydroxyapatite	
3	HCA	hydroxyl carbonate apatite	
4	BG_S	Bio glasses	
5	I_B	Bioactivity index	
6	F_S	Field strength	
7	BO	Bridge oxygen	
8	NBO	Non Bridge oxygen	
9	T_g	Glass transition temperature	Celsius degree
10	T_M	Melting temperature	Celsius degree
11	$T_{P--}T_X$	peak crystallization temperatures	Celsius degree
12	T_C	crystallization temperature	Celsius degree
13	ACP	Amorphous Calcium Phosphate	
14	SBF	Simulation body fluid	
15	XRD	X-ray Diffraction	
16	FTIR	Fourier Transform Infrared	
17	SEM	scanning electron microscope,	
18	EDS	Energy-dispersive X-ray spectroscopy	
19	B	Bulk density	g/mm^3
20	P %	Apparent porosity	
21	σ_c	compressive strength	Mpa
22	H_V	Vickers Micro Hardness	Gpa

23	σ_f	Three point bending	Mpa
24	E_d	bond dissociation energies	kJ/mol.
25	JCPDS	Joint Committee On Powder Diffraction Standards	
26	PVA	Polyvinyl Alcohol	
27	GC	Glass- ceramic	

Chapter one
Introduction

Chapter one
Introduction

1.1 Overview

The need for replacing damaged parts of the body in order to restore their physiological functionality has always been the driving force which has supported research into the discovery and the design of new materials able to perform this task as efficiently as possible , a bioactive material is one that elicits a specific biological response at the interface of the material which results in the formation of a bond between the tissues and the material **[1]** . Due to the inhibit interfacial mobility in implanted bio-inert ceramics, biologically active glasses and glass_ceramics are now available to achieve a strong hold **[2]**.

The SiO_4 tetrahedron provides the building unit for most glasses and glass-ceramics, which are composed of amorphous silicate , the main components in the majority of BGs and designated as 45S5 are SiO_2, Na_2O, CaO, and P_2O_5, which were created by Hench et al. in 1969 (45S5) and have been shown to be bioactive and osteoconductive **[3]**.

In biological fluid , the implant material should be able to form an HA layer on its surface. Such a material would not be rejected by the body but instead bind directly with the tissue. Glasses within this system would have two essential components of hydroxyapatite ($Ca_5(PO_4)_3OH$) Namely Ca^{2+} and PO_4^{3-} ions . Na^{2+} and Si^{4+} are two other common cations found in the human body **[4].**

Water molecules can permeate the open network of bioactive silicate-glasses far more quickly than they do in conventional glasses, so the bioactive glasses encourage the proliferation of bones cell and result in growth the new bone via the ion release and apatite crystallization on their surface **[5].**

The triangular scheme of effective glass installation is shown in the Figure 1.1.

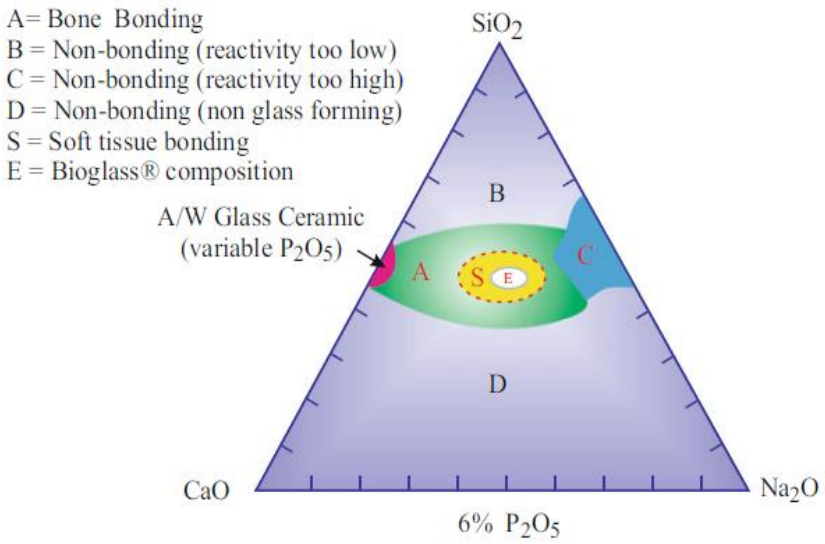


Figure1.1: Triple phase diagram of SiO_2, CaO, Na_2O. It shows the variation of bioactivity with the chemical composition as indicated the colored zones **[6]**.

When using bioactive glass particles to fill a bone deficiency, the rate and quantity of bone regeneration depend upon the nature of the material. The High levels of bioactivity in bio glass induce fast regeneration of trabecular bone with identical amounts, structures, and biomechanical properties to those originally present at the site **[7]**.As indicated below, the bioactive material might be divided into two groups based on the bioactivity indexes

1-Bioactive material class A: materials with I_B(bioactivity index) values of more than 8 are thought to be osteoconductive and osteogenetic substances, such as the bioactive glasses 45S5 **[8]**.

2-Bioactive material class B: materials having an I_B of less than 8 but larger than 0 are only considered to be osteoconductive materials, such as synthetic hydroxyapatites and tri-calcium phosphates, which have

excellent biocompatibilities**[9]**.Bioactive glasses after being subjected to a high-temperature thermal treatment, it can partially crystallize and turn into glass-ceramic. The crystalline phases enhance the strength and fracture toughness of glass-ceramics as compared to parent glass**[10]**. Fracture bridging and crack deflection have been shown to be the most effective mechanisms for toughening glass-ceramic materials. There was no effect on the bioactivity of partly crystallized 45S5 bio glass when the crystallinity of the glasses was at least 40%. This is the primary worry that arises from the use of partially crystallized glasses. The production rate of an apatite layer at a surface is slowed down, but it is not completely inhibited if crystallinity reaches 100 % **[11]**.

One further crucial feature of ceramics and glass is their brittle and low tension strength. Thus, they are often only used in compressive stress settings, such as in an ace tabular cup or the femoral head of a total hip joint replacement **[12]**.

The ideal material for medical uses should not only be compatible with the implanted location but also have physical properties comparable to those of the tissue being replaced or repaired. Ceramics are notoriously brittle, despite their chemical and corrosion-resistant qualities. Researchers, therefore, have been looking for techniques to combine attractive ceramics with other materials in order to modify characteristics like strength and flexibility to match system needs **[13]**.Introducing some oxides to the basic composition of medical glass such as vanadium and potassium can improve some properties like use vanadium oxide in bio glass makes it more effective and rapid interacts with the phosphate solution**.** V_2O_5 are insulin and growth factor mimetic compounds and enhance initial wound healing **[14]**. Potassium was is a commonly used glass additive because it possesses a unique ability to harden the glass **[15]**.

The presence of K_2O improved the stability of the bioactive ceramic system **[16]**.These oxides have a low melting point, so it is possible to find an eutectic point for them **[17]**. The surface of the glass developed a layer of carbonated hydroxyapatite HCA within just a few hours after implantation. This layer regulates the bonding capacity of bone. Consequently, the body cannot reject this substance **[18]**.

Based on Hench's theory, which remains widely accepted today, the silicate BG's bioactivity mechanism consists of eleven reactions split into two macro-stages **[6]**.

1- The first five stages of reactions result in the creation of the hydroxyl carbonate apatite layer, which leads to the crystallization of the a random calcium phosphate stratum **[19]**.
2- The mineralization process begins with the release of ionic compounds from the BG surface and continues with osteogenesis **[19]**.

Aim of The Study

1. Reducing the melting point of bioactive glass by substitution with low-melting eutectic compound ($K_5V_3O_{10}$+ KVO_3) using different weight ratios (5, 10, 15 wt.%).
2. Characterization of the structural, physical, mechanical and biological properties of the resulting glass after sintering.

Chapter two

Theoretical part & Literature survey

Chapter two

Theoretical part and Literature survey

2.1 Introduction

There is a broad range of materials used to prepare medical devices, and each one interacts with the body in a unique way **[20]**. It can be described as' any substance that is employed to replace or restore function to a biological tissue that comes into contact with body fluids on continuously or intermittently **[21]**. Understanding the connections between the characteristics, functions, and design details of biologic materials is crucial since the ultimate objective of biomaterials is to restore the functionality of naturally occurring live tissues and organs in the body **[22]** .

Can be separated the biomaterials into two categories: biological materials having a natural origin and biomedical materials with a man-made origin. Biological materials have a limited collecting capacity and a higher risk of viral and bacterial infections, as well as variability between samples and batches, whereas synthetic materials can be made of a variety of materials and can be sterilized to prevent bacterial infections **[23]**.

Biomaterials have been the most commonly employed in the replacement of body hard tissues, such as knee and hip joint prosthetic, and perhaps in the replacement of dental hard tissues, such as enamel and dentine **[20]**. Ceramics, polymers, metals and their alloys are commonly used in medical applications. as show in Figure2.1 .

The structural, physical, chemical, and mechanical characteristics of these materials which have various atomic arrangements are diverse, and as a result, various qualities allow for various uses in the body**[24]**.

.

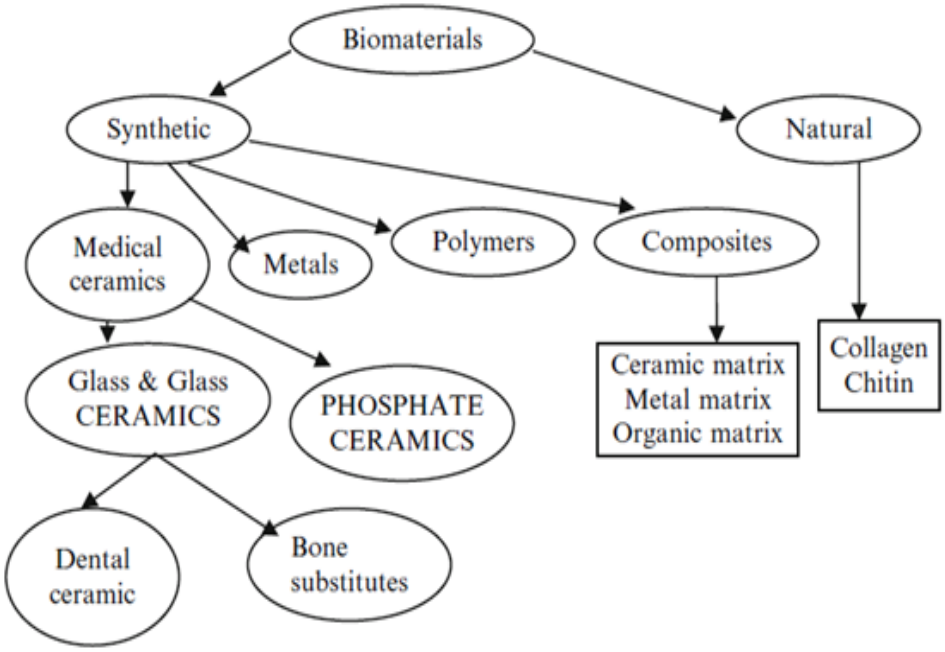


Figure 2.1 Classification of biomaterial **[20]**.

The following is a general summary of biomaterial requirements

a. **Biocompatibility**:- The material should not cause a negative reaction in the host's body but rather promote excellent tissue-implant integration, particularly at the implant-tissue interface. When the material is implanted, however, there is virtually always an initial inflammatory response. If the inflammation persists for a long period, tissue necrosis might occur, which must be avoided. A biocompatible material should only stimulate a modest immune response while without obstructing blood flow **[25,26]**.

b. **Sterilisability**:- The substance must be capable of being sterilized. The most commonly used procedures are ethylene oxide sterilization, gamma ray sterilization, and autoclaving. According to the kind of material being treated, one procedure is favored over another. **[27]**.

c. **Formability**:- This is related to the ability to form the material for a certain purpose in a simple and cost-effective manner. It is dependent on the material's capacity to be molded to meet a specific need. For example, the widespread usage of coronary artery stents is owing to the effectiveness of the manufacturing process, which, via heat treatment and cold working of the material, allows for a product with excellent durability **[25]**.

The word "bio ceramics" refers to ceramics that are used to replace bone in reconstructive procedures. Bio ceramics are necessary to relieve pain and rehabilitate sick or injured body components **[20]** Bio ceramics have developed into a broad and varied class with fundamental types, it is categorized according

1. The composition:- Bio ceramic is categorized according to its composition. The major group is glass, oxide ceramic, glass-ceramics, and calcium phosphates bio ceramic**[28]**.
2. The responses that initiate within the bodies and can It is divided into three types**.**

a) Bio inert material :- Those are Relatively undergo little or no chemical changes when attacked by physiological environments. They preserve their properties (both mechanical and physical) while being in the host. The host form a very thin fibrous tissue (in several micrometers or less) encapsulate the implanted material. Bio inert materials are fixed in the body via mechanically powerful interlock, by growing the tissue within the surface.
The most common examples are: Alumina, Zirconia, Alumina-Zirconia and Pyro lytic Carbon **[29]** .

b) Bioactive material :- The chemical reactions occur only at the surface of bioactive materials inside the body **[30]**. A bioactive substance is described as a material that forms a connection with tissues because it induces certain

biological reactions at the material's interface. Active composites are bioactive glass, bioactive glass-ceramics, and polyethylene-HA, the active substances such as bioactive coatings. It cannot be said that there is an effective and suitable substance for each purpose, as there are factors that determine the bioactivity of the substance, including bonding process, bonding duration, bonding zone thickness, bond strength, material mechanical strength, and fracture toughness **[31]** .

c) Bioresorbable materials :- Are those that dissolve in the body by enzymatic hydrolysis degradation while being replaced by growing organic tissue Hydroxyapatite **[32]**.These materials are perfect implants because the stay in the body during their function and disappear after regeneration, and the result is a very thin interface. The drawback of this implants is that their mechanical strength reduces through the whole time of re-absorption process **[29]**.

A major factor contributing to the demand for bio ceramics is the fact that bone is more prone to fracture in older adults due to bone density and strength reduction with age. Bone density reduces when bone-forming cells (osteoblasts) become less active in generating new bone and mending micro fractures **[20]**.

2.2 Glass Formation

The term "glass" refers to any solid having a non-crystalline structure that undergoes a glass transition when heated to a liquid state **[23]**. Bioactive glasses with varying compositions can be created to meet diverse therapeutic needs utilizing a range of fabrication processes, including the conventional melt-quench method, sol-gel processing, and chemical vapor deposition. They all feature short-range periodic atomic configurations as well as time-dependent glass transition behavior and can be employed in a number of applications, including biological applications**[33]**.

High-temperature "viscous state" glass products are formed by blowing, pressing, drawing, rolling, and casting in order to achieve the desired shape and size. High-temperature annealing (400–500 °C) helps decrease residual stress that has built up during the forming process [**12]**.

Glass have two main features, first, the random structure of the glass and second, the transition temperature (T_g) , which represents the transformation of the glass from the state of a super cooled liquid to solid glass. Glasses, unlike crystalline solids, have no long-range order in their structure. The fact that glasses' viscosity drops by orders of magnitude when heated explains why they can be formed into a variety of various shapes**[5]**.

When bioactive elements or moieties are incorporated into material carriers or structures, they include various compositions of bioactive materials, especially bioactive glass , the ion release profile, the nanostructures of the pores and the surface areas; these elements will determine the bioactivity of the materials upon contact. Furthermore, the bioactivities may be altered by altering the structure. Certain mixtures of BGs can give antibacterial action and/or elicit an anti-inflammatory response. BGs show a lot of promise for regrown bones, delivering drugs, repairing soft tissues, and healing wounds**[34]**.

In 1969, Hench et al. discovered glasses containing bioactive Compounds that can build chemical bonds with bone. This glass composition had a 45% SiO_2 content, in weight percent, together with 24.5% Na_2O and 24.5 % CaO ,additionally, 6 % P_2O_5 was added to the glass composition to imitate the calcium and phosphorus elements of hydroxyapatite, bone's inorganic mineral phase. The glasses did not form interfacial scar tissue, isolating them from the host femoral bone. Instead, the implants bonded to the living bone and could not be removed from their implant site , Bioglasses with the greatest bioactivity

rates promote fast regeneration of trabecular bone via processes known as osteostimulation and osteoconduction **[35]**.

Bioactive glasses that have the ability to connect to live tissues (mainly bone) and encourage new tissue formation while disintegrating over time, making them promising candidates for tissue engineering applications. The strength of the interfacial link between Bioglass and the patient's bone is equivalent to or better than that of the host bone **[36]**.

The ratio of Ca/P in bioactive glass is (1.67), when a molar ratio are lower than this value they do not bind to bone. It has been shown that glass with the highest levels of reactivity forms a stable bond with soft tissues. It is also possible to make glasses with unique characteristics for a specific therapeutic purpose **[21]**. The rise in the percentage of oxides Na_2O and CaO as well as the rise in the percentage of Ca/p is an important factor in increasing the activity and decomposition of the surface of the glass in the SBF solution **[37]**.

Due to ion exchange, BGs have the capacity to increase the PH of the fluid in which they are implanted. Advanced dental biomaterials can enhance these antibacterial properties via certain groupings of these glasses, such as silver-containing BGs. Bioactivity of these glasses is regarding to their mechanism and rate of reaction, making in vivo investigations essential for forecasting the clinical performance of a material **[38]**. Because bioactivity is proportional to the rate at which glass dissolves, it is clear that its form will have an effect. The glass bioactivity increases as the specific surface area, or the contact surface between the material and the physiological fluid, increases **[39]**.

Active glasses are less chemically durable than soda-lime-silica glasses. This is caused by the low silica content and the high sodium oxide component **[4]**.

The ease of penetration of water molecules into the glass networks is due to the open silica networks in the bioactive glass compared to ordinary glass when immersed in water. At the glass/water contact, an ion process happens between modifying ions, mainly Na^+, and solution protons **[40]**.

Strong contact between the active glass surface and liquid seems to be facilitated by the hydrophilic non-bridging oxygen atoms and modified cations, which appear to be the effective agents. In comparison, bridging oxygen atoms are more hydrophobic and have not been seen to interact appreciably **[41]**. The main properties of bioactive glass are shown in the Table2.1.

Table2.1: Properties of 45S5 bioactive glass [**43]**.

Property	**value**
T_M	1350 to 1450°C◦
T_C	677 ˚C
T_g	538 ˚C
ρ	2.7 g/cm^3
Thermal expansion coefficient(Y).	15.1×10^{-6}˚C^{-1}
K_{IC}	0.6MPa m$^{1/2}$
Shear modulus G	30.7GPa
Tensile strength **σ** .	42MPa
Refractive index **n'**	1.59

The degradation of the glass network causes the development of a silica-rich layer on the surface of the glass, and then a layer of calcium phosphate apatite crystals forms. The formation of an apatite layer is affected by a number of criteria, including the surface content, and pore size of the glass, as well as the preparation circumstances **[42]**.

2.3 The Function of Oxides in The Structure of Glass According Zachariasen Theory

1- The network formers:- the components that contribute to the formation of the glass network by creating oxygen tetrahedral and oxygen triangles, also known as network units or structural units. Glass's network-forming components are essential because they can build three-dimensional structures. These units are linked by corner sharing, which results in the formation of oxygen bridges known as bridging oxygen's (BO), (shown in Figure 2.2). SiO_2, B_2O_3, and P_2O_5 are all frequent examples **[44]**.

2- Network modifiers :- These alkali oxides, such as Na_2O, K_2O, Li_2O, CaO, MgO, and PbO, provide more oxygen ions to the system which changes the network's structure so they are referred to as network modifiers. The ratio of oxygen to silicon also rises with an increase in modifiers, which disrupts the three-dimensional network by forming singly-bonded oxygen molecules that don't take part in the network. thereby reducing the chain's length, and formation Non bridge oxygen (NBO). By lowering the viscosity, these modifiers have the main impact of lowering the melting and working temperatures[**45]** .

3- Intermediate oxides:- are the components that depending on the glass composition, act as network formers or network modifiers , MgO and Al_2O_3 are not always desirable in bioactive glasses since they tend to turn the glass into bio-inert, inhibiting bone attachment when the Al_2O_3 level is more than 1.5 weight percent **[3]**. Field strength has been used to classify oxide glass cations. Low cation-oxygen bond energy means low field strength and vice versa. The cations' functions may be summarized as follows **[42]** .

a. F_S >1.3 are Glass former.
b. F_S > 0.4 are Glass modifiers.
c. 0.4< F_S > 1.3 areIntermediates.

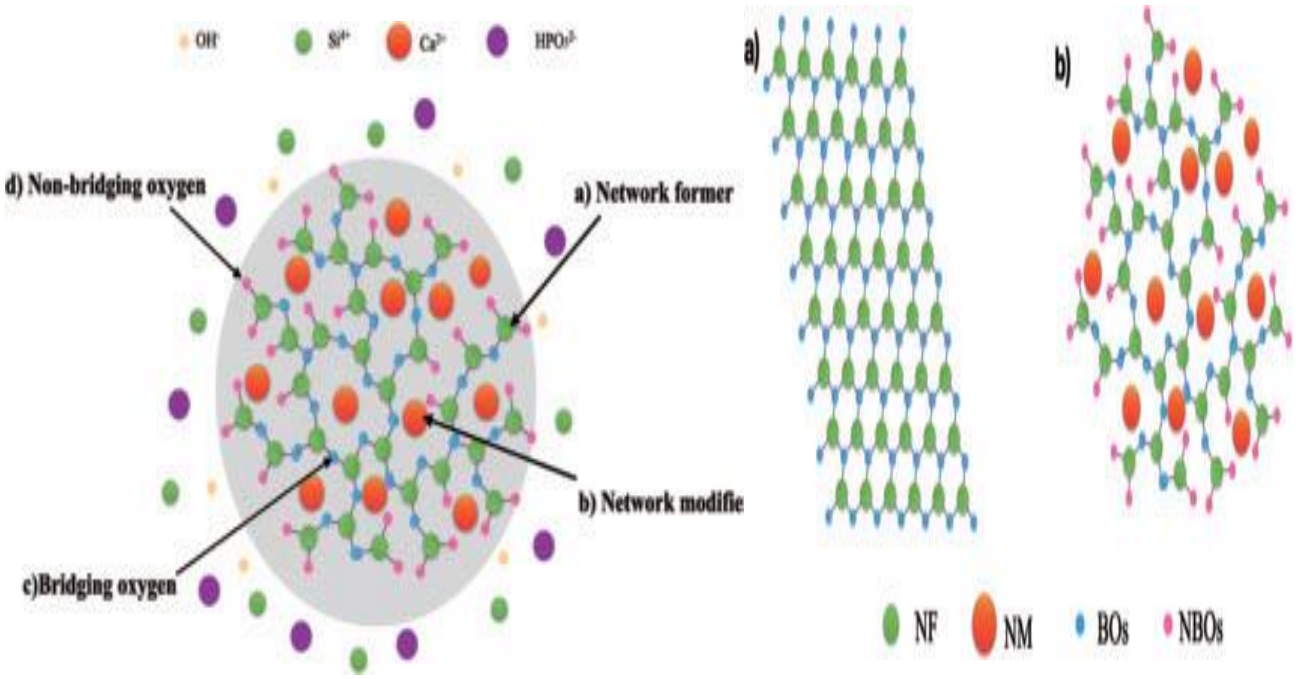


Figure 2.2 illustrates the glass network **[45]**.

2.4 The Effect of Oxides on Structure of Bioactive Glass 45S5

1. Silicon Dioxide (SiO_2)

a. Pure SiO_2 has a three-dimensional structure consisting of SiO_4 tetrahedral, and that each tetrahedron is coupled with one or more bridging oxygen molecules in the structure as shown in Figure 2.2 The oxygen atoms are no longer completely connected to the two silicon atoms and are referred to as non-bridging oxygen Generally, glasses with an network connectivity (NC) of greater than 2.4 are unlikely to be bioactive. During in vivo bone growth, the pace of HCA layer formation and the percentage of new bone formation both decrease fast when the NC value is larger than 2 **[33]**.

b. The silica nets serve as a place to nucleation the apatite layer **[46]**.

2. Phosphorus Pent Oxide (P_2O_5)

a. P_2O_5 increases the surface reactivity , bioactivity and Accelerates the rate of degradation **[44]**.

b. The presence of P_2O_5 accelerates the breakdown of the silicate network, resulting in the rapid crystallization of HA, When water is adsorbing or dissociating on the surface of P-containing bio glasses, it exhibits a strong hydrophilic property. This is in part due to the presence of labile P–O–Si bonds, which can be opened through water adsorption or dissociation **[47]**.

3. Calcium Oxide and Sodium Oxide (CaO,Na_2O)

a. Na_2O is added as a fluxing agent, significantly lowering the melting temperatures of the glasses and thereby lowering production costs. It promotes the creation of a silica-rich layer on the glass's surface, which is required for the deposition of Ca^{2+} and P^{5+} ionic species that result in the crystallization of the bonding apatite layer. On the other hand have limited chemical durability. As a result, divalent cation oxides, such as CaO are added to stabilize the glass **[3]**.

b. The Na^+ cations fill the voids between the tetrahedral, allowing oxygen ions to raise the O:Si ratio, resulting in the slow destruction of the SiO2 network. Decreased viscosity is a direct result of network disintegration. The insertion of a divalent cation oxide follows the same principle. In the case of CaO, the two negative charges of the non-bridging oxygen's can be balanced by only one single cation Ca^{2+}. Big cations begin to disintegrate bridges in the basic network resulting in an increase in the mobility of SiO_4 and a drop in viscosity and melting rate **[15]**.

c. The modifier cations working to decreasing network connection **[44]**.

4. Vanadium Pent Oxide V_2O_5

a. A V_2O_5 is referred to as a network former or intermediate. This is because the oxygen coordination number in a crystalline phase is five, which is higher than the coordination number of usual network formers of three and four, making it difficult for this oxide to form glass on its own [**48]** .

b. Vanadium compounds are mostly present in bone. Additionally, numerous Vanadium compounds at low concentrations promote cell proliferation, but at high concentrations they hinder proliferation. Doses of vanadium oxides dissolved in drinking water have been shown to increase wound strength, promote quick and orderly collagen deposition during skin wound healing, and improve tendon and ligament repair [**14]**.

c. The advantage of V_2O_5-containing glasses is that they crystallize easily, as the high crystallinity is achieved by lowering the sintering temperature in comparison to V_2O_5-free glasses. Glasses are typically sintered (between 500and 800 ^{0}C) to induce beneficial transformation reactions inside the glass matrix. Vanadium oxide confers significant advantages to ceramics in the terms of enhanced qualities such as thermal shock resistance, mechanical strength, chemical stability, and bioactivity **[2]**.

d. Pathologic blood sugar levels are reduced by vanadium complexes. They are frequently referred to as insulin mimics, insulin-mimetic, or insulin enhancers due to their insulin-like behavior. Vanadium's anti-diabetic actions are most likely due to its complexes' capacity to exchange ligands or chelators with the surroundings [**49,50,51]**.

e. By lowering the surface energy between the crystal and glassy phases, nucleation agent (V_2O_5) have been shown to enhance the nucleation and growth kinetics of apatite [**2]**.

f. Vanadium oxide is used to treat cancer, as research was conducted on experimental mice, and the result was good to combat this disease. V_2O_5 NPs(Nano particle's) was found to exhibit anti-antigenic properties by inhibiting the growth of endothelial cells **[52]**.

5. Potassium Oxide K_2O

a. K_2O a commonly used glass additive because it possesses a unique ability to harden the glass **[15]**.

b. The introduction of potassium oxide into the composition of the active glass improves its hardness. With the increase in the percentage of oxide in the glass, the crystallization decreases and this leads to an improvement in effectiveness in future in-vitro tests **[16]** .

c. Due to the fact that K_2O is heavier than Na_2O, reducing the sodium content of the glass by substituting it with potassium can result in a little modification in the glass's density and micro hardness values . In general, potassium cations operate as network modifiers, disrupting the glass network's continuity by breaking some Si-O-Si bonds, resulting in the formation of non-bridging oxygen groups, adding a sufficient amount of K_2O disrupts the glass's structure, weakening the molecular network. Increase the amount of K_2O in the glass to further decrease the ultrasonic velocity, elastic modulus, and melting point .In general, the production of an apatite layer is less efficient in potassium-bioactive glass systems than in potassium-free glass systems **[53]**.

2.5 Glass_Ceramics (GCs)

Glass-ceramics (GCs) are polycrystalline materials with one or more crystal phases embedded in a residual glass. They are typically made by melting or sol–gel followed by heat treatment. Heat treatment is frequently (but not always) done in two stages: first, at low temperatures around the glass transition (T_g) to induce internal nucleation, and then at a higher temperature to accelerate the formation of distinct phases(growth) **[54]**.

The first step in the process of growing crystals from nuclei is called nucleation, which refers to the development of small nuclei, often on a Nano scale. The second step is the growth of the nuclei into well-formed crystals. By learning how the two processes involved are affected by temperature, it is possible to control the glass crystallization process and make GC with the right properties **[55,56]**.

Varying heating and cooling rates may be used to generate a phase separation, which can create groups of certain ionic components to be released at different rates, which can be used to control biological response. When it comes to creating multifunctional glass-ceramics, crystallization can play an important role in controlling properties such as resorb ability, cytotoxicity, and bioactivity [**57]**.Glass powders are also formed using a binder and then sintered and crystallized concurrently, which is a less common method. Sintering and crystallization frequently happen at the same time, because the glass frits' free surfaces facilitate crystallization. The kinetics of crystallization also depends on how much T_g there is. Values of $T_g > 0.58–0.60$ indicate surface crystallization, while lower values indicate volume nucleation [**58,59]**.

When bioactive glasses crystallize, their activity decreases due to the ionic exchange between the glasses and the aqueous solution embedded in the crystalline phase [**46]**.

Bioactive glass-ceramics encourage cell proliferation, gene response, and the creation of new cells at the interface between live tissue and the material. Bioactive GCs have a surface layer of physiologically active hydroxyl carbonate apatite (HCA) that attaches to bone. On bioactive glass-ceramics, the HCA phase develops similar to the mineral phase of bone and teeth, This similarity is

essential for interfacial adhesion. The chemical surface reactivity of the remaining glass and crystalline phases in the bodily fluid is the foundation of bioactive glass-ceramics' capacity to attach to bone **[18]**. Another variable that depends on the nature of the material is the time necessary for bond formation, which is related to the bioactivity index (I_B), which is described as

$$I_B = 100/t_{0.5bb} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad 2.1$$

$t_{0.5bb}$ is the time taken for half the material's surface to bond with tissue **[9]**.

2.6 Four Criteria of an Ideal Graft Material in Bone Tissue are as Follows

a. **Osteointegrationis**:regarded as the capacity to develop a chemical connectio n with physiological tissue without forming a fibrous layer surrounding the i mp-lant , Implant stability and long-term clinical success of end osseous dental implants depend on a direct structural and functional link between the surface of a load-carrying implant and the organized, living bone **[60]**.
b. **Osteoconduction**:- or the capability of enabling the establishment of directed blood vessels and the creation of new Haversian networks to encourage bone formation on the grafting material's surface **[61]**.
c. **Osteoinduction**:- induces pluripotent stem cells to differentiate into osteoblasts by stimulating and activating them , TGF- β (transforming growth factor beta) superfamily receptors are involved in this process. The most important belong to the TGF- β superfamily. The cascade that controls this process is called a signaling pathway **[62]**.
d. **Osteogenesis**:which is the production of new bone by osteoblasts existing ins ide the graft (cellseeded biomaterial constructions are utilized) or that have colonized it after implantation **[22]** . The steps of bone regeneration can be in Figure 2.3 .

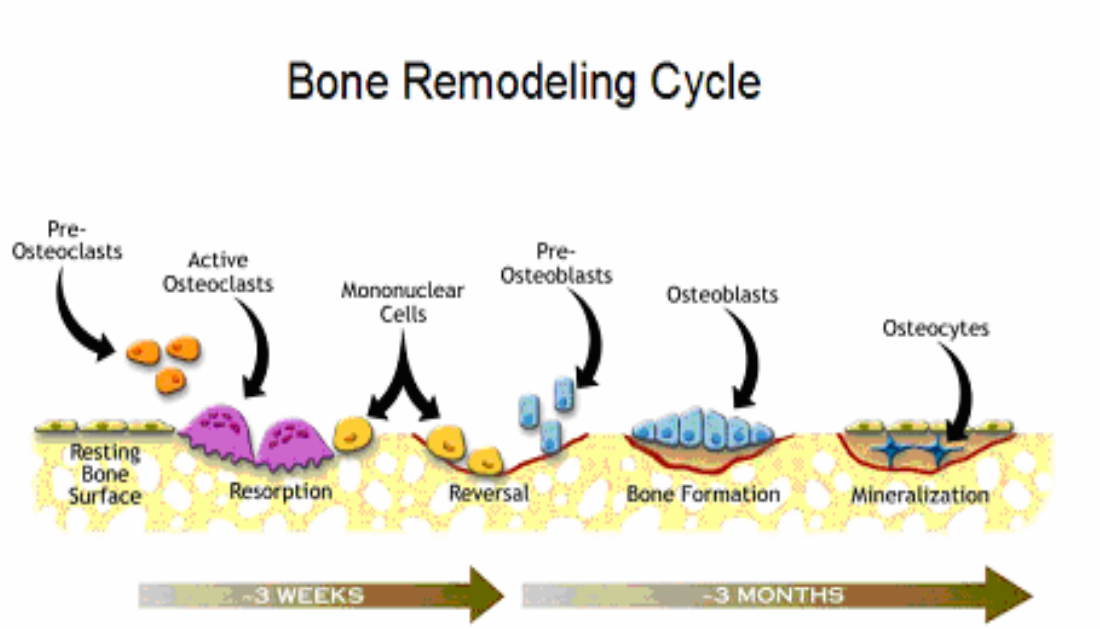


Figure 2.3 Step of remolding bone **[25]**.

2.7 Hydroxyapatite

Hydroxyapatite (HA) is a bio ceramic composed of calcium phosphate. In 1788, Proust and Klaprota reportedly recognized the similarities between these calcium phosphate bio ceramics and the mineral component of bone. Hydroxyapatite is being utilized in a wide variety of orthopedic procedures. It has been utilized to fabricate spacers in a variety of forms, for example, as an iliac bone spacer that is put into the defective iliac bone after iliac bone removal for auto bone grafting **[21]**.

HA may be used to fill in bone deformities caused by the ablation of bone tumors. It may be used alone or in combination with auto graft bone chips. Hip and knee replacements can be coated with HA coatings or HA composite coatings. Additionally, HA is employed in bioactive bone cements[**63]**.The most abundant inorganic biomaterial utilized in biomedical applications is

hydroxyapatite . HA is the primary inorganic component of bones and teeth, accounting for 95–97% of the weight of tooth enamel, 70%–75% of the weight of dentin, and 60%–70% of the weight of compact bone. All calcified tissues (dental enamel, dentin, and bone) are composed of hydroxyapatite crystallites encased in an aqueous-organic matrix **[34]**.

Hydroxyapatite forms crystals that are best described as hexagonal rhombic prisms. HA exists in two different crystal structure, viz. hexagonal a = b= 9.432Å, c=6.881Å, $\gamma = 120^0$ and monoclinic (a=9.42Å, b=2a, and c=6.88Å and $\gamma = 120^o$ (see Figure 2.4) **[64]**.

Tri calcium phosphate ($Ca_3(PO_4)_2$) and hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) are two calcium phosphates that work well with living organisms and help bones grow. Because of their fragility, HA scaffolds are only suitable for applications that are primarily exposed to compressive stress. To overcome this mechanical restriction, polymer matrix hybrids, primarily with HA as the bioactive phase **[65].**

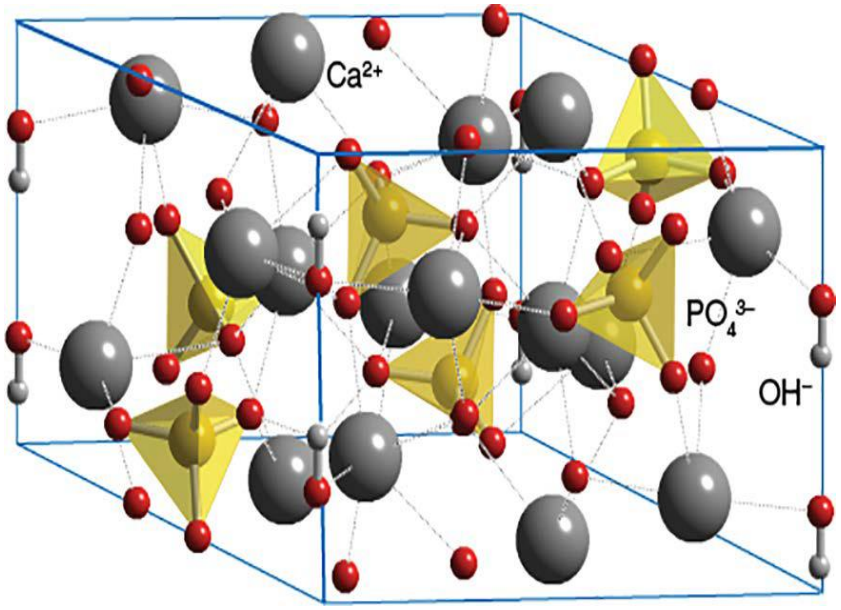


Figure 2.4 : The unit cell of hydroxyapatite**[66]**.

The mechanism of HCA formation has been described by Hench as a series of surface reactions. This can be summarized as

Step 1: Ionic exchange between the material's Ca^{2+} and Na^{+} ions and H^{+} and H3O+ ions from the surrounding environment on the material's surface, silanol linkages (Si–OH) are formed. The solution's pH value increases owing to as a result of the alkaline ion release, the glass surface acquires a silica-rich layer. The $(PO_4)^{3-}$ ions are present in the beginning composition, they are also released. The following is a description of the chemical reaction:

$$Si– O – Na^{+} + H^{+} + OH^{-} \longrightarrow Si – OH^{+} + Na^{+}_{(aq)} + OH^{-}$$

A few minutes after being exposed to body fluids, this response takes place rapidly. Alkaline cations have been removed from the surface layer, so it now has a net surface negative charge of **[6]**.

Step 2: The OH-ion released by the high pH solution attacks the silica glass network, leading to rupturing Si-O-Si connections. Soluble silica is lost to solution as $Si(OH)_4$, resulting in a higher concentration of Si – OH at the boundary between the glass and the solution:

$$H_2O + Si – O – Si \longrightarrow OH – Si + Si – OH$$ **[33]**.

Step 3: Intensification and polymerization of an amorphous SiO_2 rich layer (1-2 microns thick) onto the surface of glass. The Na^{+} and Ca^{2+}-depleted **[67]**.

Step 4: ACP develops on the SiO_2 rich layer as Ca^{2+} and $(PO_4)^{3-}$ ions diffuse from the glass into solution. **[31]**.

Step 5: The layer of ACP crystallizes as an HCA layer after incorporating (OH) and (CO_3) from the solution [**67]**.

The five steps listed above are not tissue-dependent, since they happen on the material side of the interface The glass decomposition steps can be seen in the Figure2.5 .

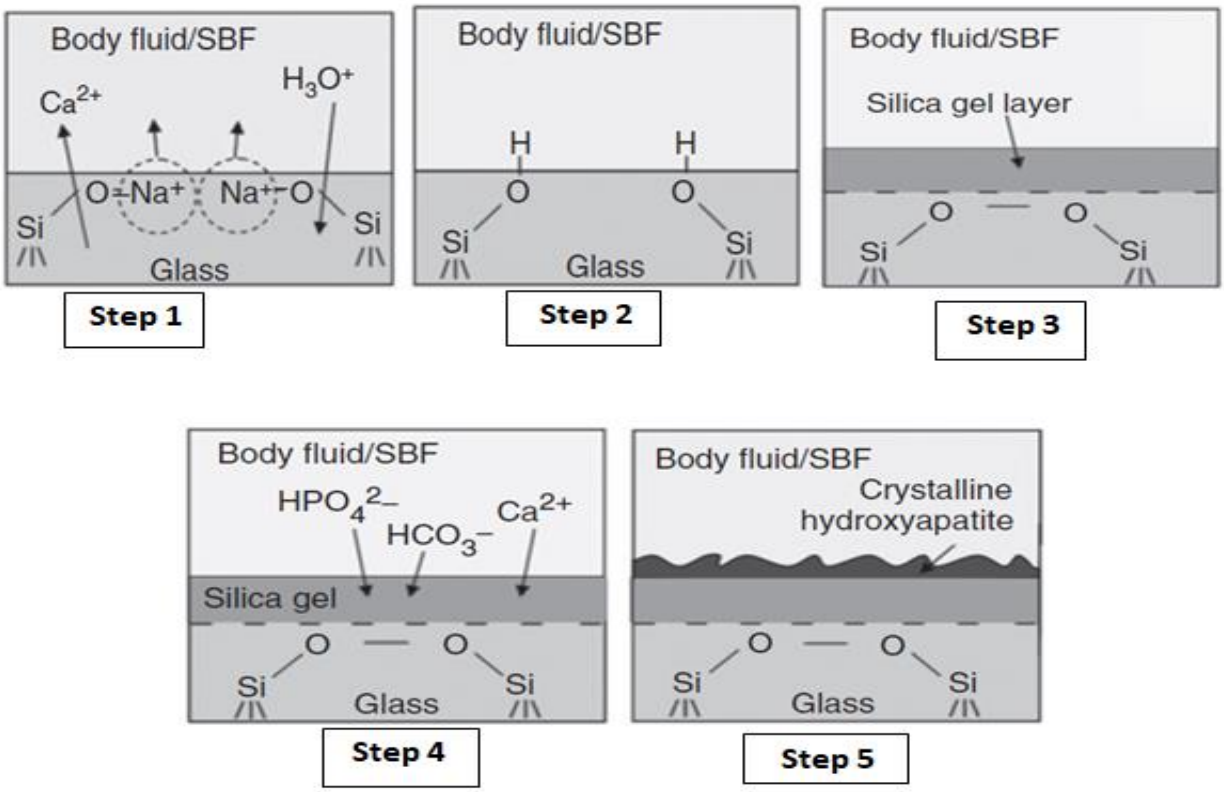


Figure 2.5**:** Schematic representation of bioactivity process steps **[71]**.

In steps 6–11, we'll go over in more detail the reactions that take place in order to form interfacial bonding with bone.

6- Adsorption of blood proteins and wound fluids in SiO_2 _ HCA layer **[68]**.

7- The work of macrophages are white blood cells generated from circulating white blood cells (monocytes) that have the ability to eliminate foreign substances from the wound site (i.e. dead tissue, bacteria, and other particles). During this stage macrophages clean the wound and new blood channels begin to form in the surrounding tissue **[69]**.

8-The mesenchyme cell attachment These are the cells that allow the body to heal itself after a wound. Initially, they are the first kind of cell to come into contact with the graft [**69]**.

9- Mesenchyme cell differentiation At this stage, mesenchyme cells multiply and develop into osteoblasts (bone-growing cells) [**70]**.

10-matrix generation. Osteoblasts synthesize and deposit collagen fibers in an ad hoc manner **[68]**.

11-Matrix mineralization Collagen fibers become more organized and mature, which leads to the growth of new bone [7**1]**.

The reaction steps 1–11 listed above occur in a timeframe that varies according to the bioactive material's index of bioactivity (I_B). The strength of failure diminishes as the thickness of the bonding zone grows because of this index's influence on the thickness.

2.8 Glass Production

2.8.1 Sol-Gel Process

The sol-gel approach is a chemical synthesis procedure in which a solution containing an oxide precursor undergoes a polymerization process, resulting in the gelation of the sol at ambient temperature. Precursors are often selected based on the individual application after an appropriate characterization of the intended final composition **[72]** .When one or more components are combined to produce a sol, a homogeneous and amorphous gel solid is created during the transition from a liquid sol to a solid gel. The sol-gel approach, on the other hand, has a number of drawbacks, including lengthy processing periods, expensive precursor material prices, fast shrinkage rates, and residual carbon and hydroxyl content **[73]**.

By manipulating processing settings in a very flexible manner, the method provides a wide range of products. An alkoxyde precursor (typically tetraethyl orthosilicic acid (TEOS) or tetramethyl orthosilicic acid (TMOS) is hydrolyzed,

poly-condensed, and then aged and dried in ambient air to generate sol–gel glasses for biomedical use **[6]**.

In the case of tetraethyl orthosilicate (TEOS) and other silicate glass alkoxide precursors, hydrolysis results in a colloidal solution (sol). A silicate (–Si–O–Si–) network is generated after poly condensation of silanol (Si–OH) groups. As the (gel) forms, the system's viscosity rises in proportion to the increase in network connectedness. Following that, the gel is dried and solidified at a temperature of around 600–800 °C using a thermal process. Sol-gel produced glasses are mesoporous and have a greater surface area than melt generated glasses, with pores ranging in size from 300 to 800 nm and over all porosities exceeding 60%. Novel bioactive glass compositions incorporating metal oxides may be synthesized by selecting appropriate precursor materials[**13]**.

2.8.2Technique of Melting-Quenching

The melt-quench technique involves melting a mixture of oxide precursors in a furnace at temperatures typically higher than 1000 ^{0}C (the actual melting point depends on the glass composition) and obtaining an amorphous solid by rapidly quenching the melt formed by the fusion of one or more precursors **[23]**.This is followed by either the use of graphite molds to create glass blocks or cooling in water or oil in order to create glass frit. (22 and up)When the cooling rate is high enough to prevent nucleation and crystal formation, the disordered condition of the melt is sustained in the solid state **[3]**.Casting into monoliths and drawing into rods or fibers are the basic forming techniques for bioactive glasses. After forming the glass is annealed at a temperature equivalent to the viscosity (10^{13} Poise) to eliminate residual tensions generated by cooling after forming **[4]**.

Subsequent to the grinding (e.g. in a planetary mill), glass powder may be utilized directly in the treatment of bone fissures, as an additive to polymer-BG

composites or it can be further processed for 3D scaffold production using sintering methods **[74]**. Melting is a versatile method that enables the manufacture of a wide variety of glass compositions simply by adjusting the amount and percentage of raw materials used Additionally, the melt-derived route for manufacturing bioactive glasses has several drawbacks. For instance, high melting temperatures, impurities from the crucible material, and subsequent grinding processes (possible contamination with grinding medium debris particles) might make it challenging to produce glasses-ceramic with high quality **[75]**. The steps for manufacturing glass according to the two methods are shown in the Figure 2.6 These process has many advantages, like easily changing the glass chemistry, cheap raw material prices, fast processing times, and a large output (amount) of glass.

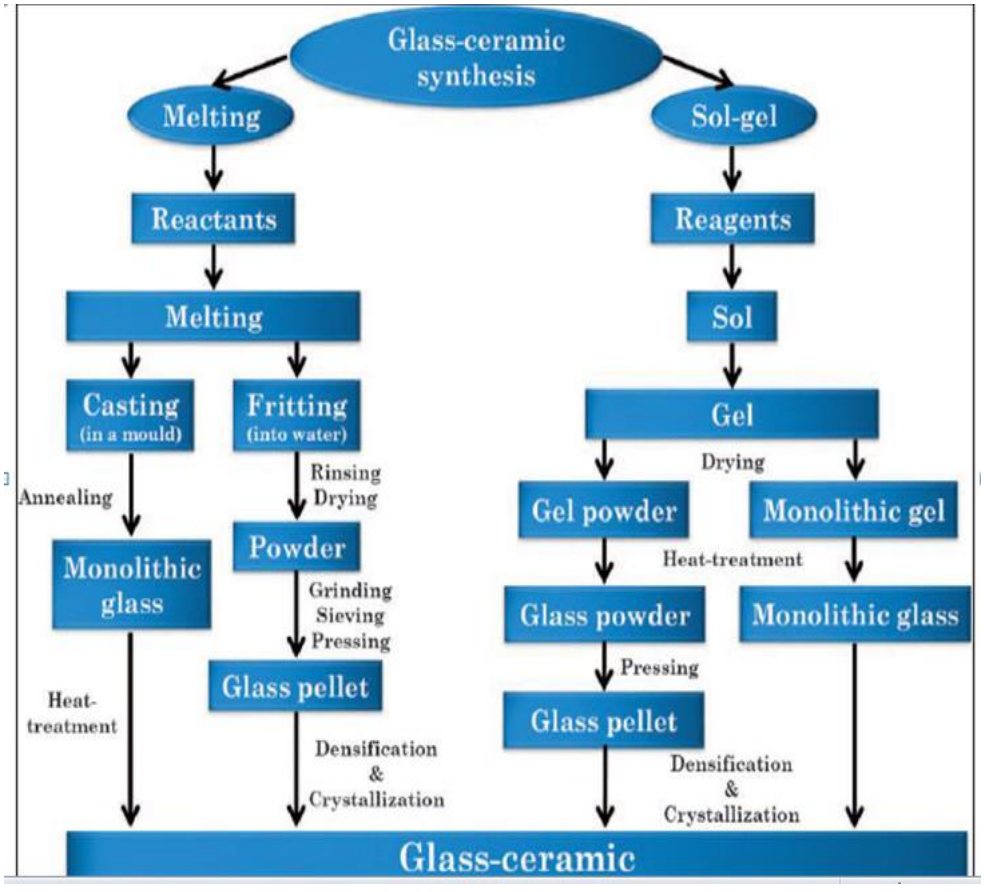


Figure2.6 illustrates the routs of manufacturing glass-ceramic **[76]**.

2.9 Mechanical Properties of Bioactive Glass and Glass-Ceramics

a. Brittleness and low tensile strength are the main drawbacks of using ceramics and glasses as implants. Ceramics and glasses fail with minimal stress under tension or bending loads while having excellent strength under compression. Calcium phosphates and bioactive glasses are not appropriate for use as load-bearing implants **[32]**.

b. The primary benefit of bio glass is its high bioactivity, while its limitations include weakness in construction and poor resistance to fracture related to the a random 2-D glass network. Most bio glass has a bending strength of 40–60 MPa, which is insufficient for loadbearing applications. It has a Young's modulus of 30–35 GPa, which is extremely similar to that of cortical bone **[30]**.

c. Bioactive glasses can partially crystallize after high-temperature thermal treatment, thereby producing glass-ceramic materials with enhanced mechanical behavior over their glass-parent. When compared to their glass parent, glass-ceramics are stronger and more fracture-tough due to the presence of crystalline phases. Therefore, glass-ceramic is used for vertebral replacements when high compressive strength is required, so the most efficient toughening processes were found to be fracture bridging and crack deflection **[11]**.

2.10 Some Applications of Bioactive Glass /Glasses-Ceramic

a. A BGS is effectively employed use as a prosthetic for the middle ear to treat sensory hearing loss, this is the first clinical use of such a material ,Figure (2.7-a) **[8]**.

b. After the extraction of natural teeth, the bioactive glass cones known as End osseous Ridge Maintenance (ERMI) were used as space fillers to restore the roots of the teeth and provide a firm base for dental implants **[25]**.

c. Repairing of the iliac crest after auto graft harvesting and spinal fusion after graft removal have both utilized bioactive glasses [**55**].
d. To fill cysts, flaws caused by injuries, anomalies left by benign tumor excochleation, and to repair significant acetabular defects, BAS-granules and pulverized material are employed as seen in Figure (2.7-b) [**77]**.
e. More contemporary uses of scaffolds for bone repair, composite-based scaffolds, and coatings for metallic orthopedic implants are all examples of applications for bioactive glasses, endodontic and periodontology. Different types of bioactive glass, including particles, putty, dense constructions, or porous scaffolds, may be injected directly into the defect. Figure (2.7-c) shows that **[78]**.
f. Bioglass for pharmaceutical and growth factor administration, using radio - active glass microspheres to eradicate malignant liver or other organ tumors **[70].**

2.11 Two Features of the Material are Essential to its Clinical Success

1. It has the ability to form a strong bond with connective tissues**[71]**.
2. Its capacity to simulate the mechanical performance of the tissue that must be replaced . The technique of tissue attachment has been proven to have a direct relationship with the kind of tissue response at the implant interface**[71]**.

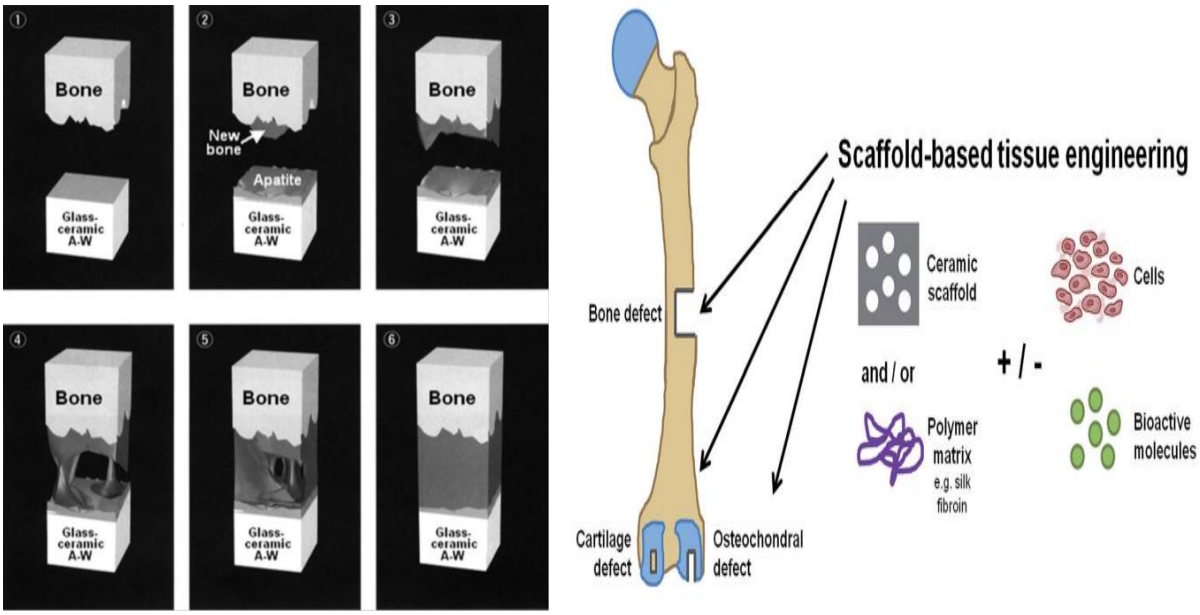


Figure 2.7 : applications of bioactive glass /glasses-ceramic **[78,79]**.

2.12 Literatures Survey

In 1997 Naoki Imayoshi et al: Bioactivity of calcium silicate glasses containing multivalent cations where the Glasses with the following compositions are synthesized using a standard melt-quench method: (V_2O_5, WO_3, Ta_2O_5, or CrO_3) (50-x/2)CaO(50-x/2)SiO_2, where the CaO/SiO ratio was kept constant at 1. The glasses were soaked in SBF with a pH of 7.25 and a temperature of 36.5°C. The formation of apatite changed when transition metal oxides were added to 50CaO-50SiO glass. The addition of 5mol% V_2O_5 and WO_3 had hardily effect on the production of apatite in the SBF, but the addition of 5mol% Ta_2O_5 and CrO_3 suppressed the production of apatite layer. The former increased the amount of calcium and silicon, and the size of the silica gel layer facilitated chemical reactions in the SBF to create apatite layer. On the other hand, the latter improved chemical durability and prevented a silica gel layer from forming **[80]**.

1n 2009 V. Cannillo *, A. Sola et al. BG-45S5, SiO_2 (46.1%), P_2O_5 (2.6%), CaO (26.9%), and K_2O (which replaced Na_2O) (24.4%) were melted in a platinum crucible at 1450 ^{0}C. Melt was quickly cooled in water. A new glass that reduces BG-45S5's crystalline tendency. The addition of potassium oxide did not impact the thermo-mechanical properties, and the potassium-containing glass was better than BG-45S5 for enameling since it did not crystallize during heating. Potassium oxide seems to help in the usage of bioactive glasses without affecting their thermo mechanical characteristics or bioactivity **[81]**.

In 2011 M.R. Majhi et al: The bioactive glass 45S5 (Hench glass), having composition 45 SiO_2 - 24.5 Na_2O - 24.5 CaO - 6 P_2O_5 (wt %) were prepared by substituted with Li_2O, K_2O, ZnO, MgO, and B_2O_3. using a typical melting procedure in an electric globar furnace at 1400 ^{0}C. Increases in the concentration of Li_2O and K_2O in the place of Na_2O in bio-glass mixture improve density and compressive strength, while the influence of K_2O in place of Na_2O in the bioactive glass 45S5 causes a drop in both glass transition and crystallization temperatures. The fourier transform infrared (FTIR) absorption spectroscopy reveals that the effect of introduction of B_2O_3 in place of SiO_2, in the bioactive glass 45S5 has decreasing of bioactivity, a minor change of bioactivity in an introduction of Li_2O and K_2O in place of Na_2O, while the effect of introduction of MgO and ZnO in place of CaO, in the bioactive glass 45S5 cause a decrease in bioactivity **[82]**.

In 2012 Taehee Kim et al: Effects of using K_2O instead of Na_2O in the Glasses composition 24.5CaO-(24.5-x)Na_2O-45SiO_2- 6P_2O_5-xK_2O (where X is 0, 8, 16, and 24.5) % mol. was created by melting a homogeneous mixture in a Pt-Rh crucible at 1400°C for 60 minutes. The molten is quenched in a stainless steel mold. In-vitro tests demonstrated that substituting Na_2O with K_2O decreases the Tg and density of 45S5 Bioglass while increasing the molar

volume. might anticipate crystalline apatite layer growth by FT-IR changes (bioactivity). Form and composition of sample surfaces were confirmed using FESEM photos and EDX data. The capacity of the glass to form a calcium phosphate layer on SBF-exposed surfaces enhanced when Na_2O was substituted with K_2O **[83]**.

1n 2014 A. M. Deliormanli et al . After one hour at 1100 ^{0}C in a platinum crucible, the components of $CaCO_3$, Na_2CO_3, $MgCO_3$, K_2CO_3, H_3BO_3, $CaHPO_4.{}_2H_2O$, and V_2O_5(0.15,1,3)% were melted in the air and cooled between stainless steel plates. Results showed that that vanadium-containing scaffolds degraded at a faster rate compared to the bare borate glass scaffolds. Based on the FTIR analysis and SEM observations a decrease was not observed in vitro bioactivity of the vanadium containing borate glass scaffolds and powders even at high substitution levels. The converted layer on the 3% vanadium-containing glass was crystalline HA after 20 days of immersion in SBF. Results revealed that the incorporation of this ion caused a decrease in density and the Vickers micro hardness of the bare borate glass samples was higher compared to the substituted samples at high indentation loads. It was concluded that vanadium presumably acted as an intermediate ion and loosen the borate glass network by formation of triangular BO_3 groups. The V_2O_5-containing borate based bioactive glasses are suitable candidate materials for biomedical applications **[84]**.

In 2016 G. El-Damrawi1 et al. showed that by using the traditional melting method and according to the composition of glasses 24.5Na_2O, 24.5CaO, 6 P_2O_5- x$V_2O_5$and(45-xSiO_2) mol% (x =0, 3, 6, 9, 12&15 mole %), The batches melted at 1250°C for 2 hour. and casted into preheated stainless steel molds. The latter turned into white opaque glass in the crystalline structure at proportions(<6 moles %) under sintering temperature of 660 ^{0}C. The advantage of V_2O_5 containing glasses is that it can easily be crystallized,Low-V_2O_5 glass networks

remained amorphous and transparent after heating. Sintering process produces apatite (A), wollastonite (W), and modified vanadate phase. Sintered glasses have different structure and morphology than as-prepared glasses. The well-formed species generated in thermally treated glass have a needle-like structure as their most prominent feature. The presence of vanadium in the glass network acted as a crystallization agent, which accelerated the reaction of the material when soaked in body fluid **[2]**.

In 2016 Rehana Zia et al: The solid state technique was utilized to make bio glass and examine the influence of K_2O on the microstructure. TGA-DSC, Fourier transform IR, X-Ray Diffraction, and Scanning electron Microscopy were used to study the effects of sintering temperature at 900 ^{0}C and partial replacement of Na_2O with K_2O on the thermal and structural properties of the system. Adding K_2O to the bioactive ceramic system made it more stable. Combeite, Sodium Calcium Silicate, and Wollastonite were the main phases in all of the samples. Also when the amount of K_2O went up the amount of crystallization went down, which suggests that bioactivity was greatly increased for in-vitro testing **[16]**.

In 2016 Siti Hafizah Mohamed et al: The influence of adding Na_2O on the solubility of phosphate glass with the following concentrations: (34-x)K_2O , 45P_2O_5, 18CaO, xNa_2O,Al_2O_3, x= 0, 5, 10, 15, and 20 % wt. The glasses were made by melting the mixture in an alumina crucible at 1300 °C for 2 minutes and then cooling to room temperature. The glass samples were crushed and sieved to 2.0 mm–3.9 mm in size. The glass composition has a massive effect on the solubility of phosphate glass due to the presence of K_2O which has a stronger solubility. the phosphate glass structure is disrupted and weakened by the larger ionic radius of K^+, which increases glass solubility **[85]**.

In 2020 Konstantinos Dimitriadis et al. Fine powders of SiO_2, $CaCO_3$, $Mg(NO_3)26H_2O$, $(NH_4)2HPO_4$, Na_2CO_3, K_2CO_3, and CaF_2 were melted in a Pt crucible at 1400 ^{0}C for 1 hour in air. Grinding glass-frit (used in the thermal analysis experiments as well as to produce the glass-ceramics). T_g and T_p of glasses with K^+ for Na^+ substitution shifted to high temperatures, but there were no significant changes in glasses with Mg^+ for Ca^+ substitution. When GCs immersed in SBF at 37°C for one week, exhibited bioactivity characteristics related to wollastonite or-PMS (alpha-potassium magnesium silicate crystalline phases) Their surface can develop hydroxyapatite (HA). The phase assembly produced well-sintered, well-crystallized GCs with dense microstructures, affecting their mechanical properties, Reduces elastic modulus, increases fracture toughness, and reduces micro hardness **[86]**.

In 2021 Laís D. Silva et al. Bioactive glass mix result from using 26.9CaO , $46.1SiO_2$,$2.6P_2O_5$,$24.4K_2O$ and with different particle sizes and heating rates, a sintered GC with excellent fracture strength, low elastic modulus, and bioactivity was created. The mixture was melted in a platinum crucible for 4 hours at 1350°C. It was put in graphite tubes. The glassy samples were annealed at 50 °C below the glass transition temp . increased densification due to particle size reduction. Replacing Na^+ by K^+ enlarged the processing window, T_X - T_g which increased from 138 to 172 K when Na^+ was entirely replaced, resulting in a denser material using two-step sintering. Due to glasses' weak mechanical properties, most sintering research focuses on scaffolds, sintering additives in ceramic composites, and bioactive coatings. The new GC generates an HCA layer after 8 hours in the SBF solution and as can be seen sintering and crystallization improve bioactivity **[87]**.

Summary of Literatures Survey

Many of the previous studies preparing bioactive glass-ceramic and worked on improving the properties and reduce the melting temperature by using many additives, such as potassium oxide. There is a difference in literature that shows the K_2O effect on the crystallization process, where glass can be treated at high temperatures without crystallization, in addition to the process of improving density, as well as fracture toughness and compressive resistance, and some of them show that it has an effect on reducing hardness or reducing density. When using potassium with lithium oxide, it works to drop in both glass transition and crystallization, In addition to its effect on rise the dissolution of glass in the SBF solution and little effect on bioactivity, as for glass-ceramic it increases stability. The other additive is V_2O_5, as it works to increase crystallization at relatively low temperatures above 600 ^{0}C, also it has an effect on improving the mechanical properties and accelerated the reaction of the sample when soaked in body fluid. However, there is no research using a compound resulting from finding a eutectic point between two oxides and adding or replacing it with glass components.

chapter Three

Experimental work

Chapter Three

Experimental work

This chapter explains the materials , processes and apparatus used to manufacture bioactive glasses and glasses_ceramic with eutectic compound .

3.1 Materials

The chemical formula, purity and source of the materials that used in this work are illustrated in Tables 3.1 and Table 3.2.

Tables 3.1.The chemical formula, purity, form, and origin of the materials utilized in this study are shown in the.

Materials	**Chemical formula**	**Purity**	**form**	**Source**
Silica foam	SiO_2	98%	Powder	India
Sodium carbonate	Na_2CO_3	98%	Powder	India
Calcium carbonate	$CaCO_3$	98%	Powder	India
Phosphor pent oxide	P_2O_5	98%	Powder	Merck Germany
Potassium carbonate	K_2CO_3	98%	Powder	England
Vanadium pent oxide	V_2O_5	N/A	Powder	England

Table 3.2 : Chemical formula, source and purity of the materials used in the prepare of Simulated Body Fluid (**SBF**).

Materials	**Chemical formula**	**Source**	**Purity**
Sodium chloride	NaCl	India	99.9%
Sodium bicarbonate	$NaHCO_3$	China	99.9%
Potassium chloride	KCl	Belgium	99.5%
Sodium hydrogen phosphate	$Na_2HPO_4.2H_2O$	India	99.8%
Magnesium chloride hex hydrate	$MgCl_2.6H_2O$	Italy	99.5%
Calcium chloride dehydrate	$CaCl_2 .2H_2O$	Spain	99%
Sodium sulfate	Na_2SO_4	Spain	99%
Tris	$(CH_2OH)_3CNH_2$	Spain	99%

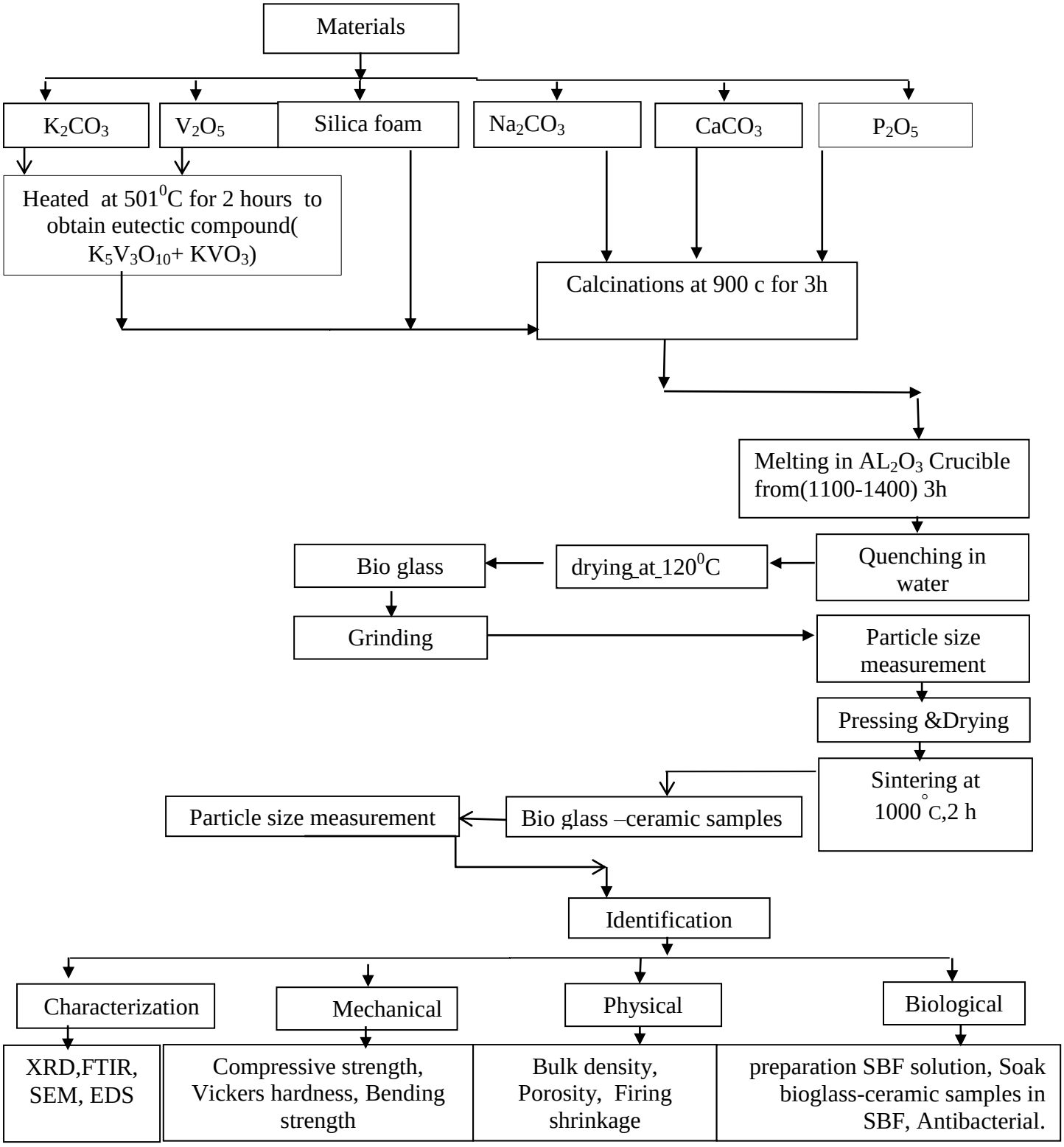


Figure 3.1 Schematic diagram of the glass- ceramic preparation process.

3.2 Preparation of Eutectic Component :

Eutectic compound of 39% V_2O_5 - 61%K_2O was prepared according to the phase diagram shown in Figure (3.2). A mixture of the two oxides with the above proportions was heated at 501 °C for 2 hours**.** The required amounts were calculated according the equation 3.1.

n = m/M ……3.1 **[88]**.

Where,

- n is the number of moles,
- m is the mass of substance,
- M is the mass of one mole of that substance .

Heating at 501^0c
at 3 hours

$$V_2O_5 + K_2O \longrightarrow K_5V_3O_{10} + KVO_3$$

39% mole . 61% mole

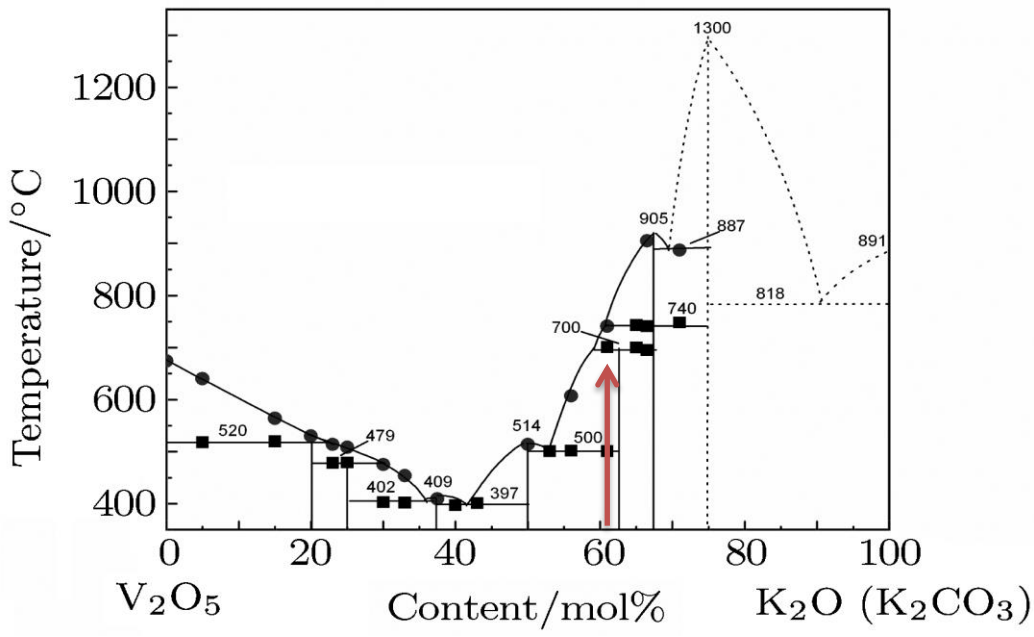


Figure 3.2 Phase diagram of binary system of V_2O_5, K_2O.

3.3 Preparation of Bioactive Glasses- ceramic

The conventional melt-quench technique was used to prepare 45S5 bioactive glass, which is composed of 45wt% SiO_2, 24.5wt% Na_2O, 6wt% P_2O_5, and 24.5wt% CaO, Three weight percentages (5, 10, 15 wt%) of the eutectic compound ($K_5V_3O_{10}$+ KVO_3) was replaced by SiO_2 and Na_2O together as shown in Table 3.3. The detailed scheme of the glass-ceramic preparation process as well as the devices used for the examination are shown in the Figure 3.1.

Table 3.3 The weight percentage of bioactive glasses.

No.	**SiO_2** (wt %)	**CaO** (wt %)	**Na_2O** (wt %)	**P_2O_5** (wt %)	**Eutectic component** ($K_5V_3O_{10}$+ KVO_3)wt%
A	45 %	24.5 %	24.5%	6 %	0%
B	42.5%	24.5 %	22 %	6 %	5%
C	42.5%	24.5 %	17 %	6 %	10%
D	40 %	24.5 %	14.5 %	6 %	15%

Four batches as shown in Table 3.3 was calcined at 900 °C to elimination Carbonate as in reaction below. Then rising the temperature until melting at 1400 °C, 1130 °C, and 1100 °C for 3 hours, respectively, according to the proportions used. The melt was quenched in water to obtain an amorphous glass phase, the produced glasses are shown in the Figure 3.3 , After that, it was dried for 24 hours at 120 °C and ground to a fine particle size and sieved in a mesh No. 200 .The obtained powder was examined by X-Ray diffraction dives. The resulting powder is pressed with the required shape according to the standard specifications to producing excellent compact samples and less than two hours of sintering at 1000 ^{0}C lead to turns it into glass-ceramic. The chemical composition ,structural and morphological of the samples were

characterized by X-ray diffract meters, Scanning electron microscope, FT-IR instrument and X-Ray Energy-Dispersive Spectroscopy (EDS) in order to identified the resulting phases and understand the characteristics of glass-ceramic Structure .To simulate the conditions to which the sample are exposed when implanted in vivo, physical, mechanical and biological tests are conducted for them .

$$CaCO_{3(s)} \xrightarrow[\text{at } 900^0C]{\text{Calcination}} CaO_{(s)} + CO_{2(g.)}$$

$$Na_2CO_{3(s)} \xrightarrow[\text{at } 900^0C]{\text{Calcination}} Na_2O_{(s)} + CO_{2(g.)}$$

Figure 3.3 The yield glass granules after quenching in water.

3.4 Preparation of Compact Samples

3.4.1Pressing Process

Before the pressing process, 2 % PVA liquid is added to the powder of glasses and mixed well to provide ease of pressing and good cohesion of the sample. This process is done under the settings of cold die pressing with a uniaxial pressure device (CT340-CT440) at 150 MPa to produce a well pressed sample.

3.4.2 Drying Process

The samples are dried at a temperature of 120 ^{0}C for 24 hours to get rid of moisture and to prevent cracking in the sample resulting from the rapid release of moisture when sintering This process takes place in an electric oven (WG43 Electric Blast Dry Box) in the department of ceramics labs / College of Material Engineering / University of Babylon.

3.4.3 Sintering Process

The glass samples are sintered at different temperatures (600, 700, 850, and 1000) ^{0}C as it was found that at 600 ^{0}C crystallization occurs in the glass and turns into glasses_ceramic, The selection of the sintering temperature is important to achieve high compaction and strong cohesion. The sintering temperature was adopted at 1000 ^{0}C. Figure 3.4 show the samples after donning preparation process .

Figure3.4 The compacted bioactive glasses-ceramic samples.

3.5 Characterization and morphology of Bioactive glass-Ceramic Samples

3.5.1 The Particle Size Analyzer

The bioglass-ceramic is produced after the melting , drying and sintering process, its grinded and measured its particle size by using a device (bettersize2000,Babylon University/College of Materials/Ceramic and Building Materials Engineering). This process depends on its theory the Mie

scattering which means dissolving a quantity of the powder in distilled water to form a dilute solution, The device emits a laser beam of a specific wavelength that passes through the suspended solution.

3.5.2X-ray Diffraction (XRD) Test

The fundamental purpose of the XRD approach is to determine the chemical composition of materials. In this work, specimens were finely ground before and after sintering to achieve a particle size below 75 microns and scanned at ambient temperature, An x-ray detector (XRD 6000, Shimadzo, Japan) in the University of Babylon/ College of Material Engineering/ ceramics laboratories. was used with a scanning rate of 5 degrees per minute from 10° to 60° (Bragg angle) and a Cuk, radiation (λ= 1.5405) and a power of 40 kV / 30 mA to determine if the structure is random or crystallized . Can calculation the crystals size from scherrer equation 3.3 **[89]**.

$$n\lambda = 2d\sin\theta \quad \text{……. 3.2 .}$$

$$D=K\lambda/\beta.\cos\theta \quad \text{…….. 3.3}$$

Where the Distance between adjacent planes is (d) , Integer (n) , Bragg's angle (θ), (D) is the Nano crystallite size , (β) full width at half maximum of peaks , λ is wavelength, K is the shape factor (0.89).

3.5.3 Infrared Analysis (FTIR) Test

After sintering at 1000 ^{0}C,the FTIR was utilized to evaluate the bonds in the bioglass-ceramic . It was carried out with the aid of an FTIR-8300 spectrometer, Bruker, Germany. It is situated in the Laboratories of the University of Babylon's/College of Material Engineering/ Department of Polymer .The test sample is made by combining 0.001 g of the sample with (0.1) g of KBR(potassium bromide), pressing the mixture to create a thin film enough to achieve a suitable spectrum, and then inserting it into the instrument.

3.5.4 Scanning Electron Microscope (SEM) Test

A SEM apparatus was utilized to characterize the microstructure of the bioglass-ceramic samples surface before and after immersion in SBF and to observe the phases in it, as well as other details such as pores and crystalline . Prior to scanning using a SEM device, The surface of bio glass-ceramic samples was coated with very thin layer of gold using a sputtering deposition process, SEM equipment (EMITEC k350 UK) (VEGA3.TESCAN) University of Babylon/Engineering materials/ Ceramic Department. Additionally, the chemical composition of the elements deposited on the surface of a glass-ceramic sample after immersing it in a SBF solution find by the means of Energy-Dispersive X-Ray Spectroscopy (EDS).

3.5.5 Physical Characterization

The Archimedes technique (ASTM C373-88) can be used to calculate bulk density and apparent porosity **[90]**.

1. To make sure the sample is dry and remove moisture ,The test sample is placed in a drying oven for 24 hours at a temperature of 120 ^{0}C , after which the dry mass (D) is measured
2. poling the sample for 5h and let it in distilled water for 24h then measuring the suspended mass (S),
3. The saturated mass (M) of specimen is calculated by softly blotting the surface with a damp cotton towel to remove any surplus water .

Bulk density can be expressed as follows:

$$B = \frac{D}{M-S} \quad \text{..... 3.4}$$

Where

B: is bulk density

Apparent porosity can be measure by use the equation 3.5

$$P\,\% = \frac{M-D}{M-S} * 100 \quad \text{.....3.5}$$

and Firing shrinkage can be measure by use the equation 3.6 **[91]**.

$$\text{Shrinkage}(\%) = \frac{D1-D2}{D1} * 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots .3.6$$

where:

D1 :diameter of sample before sintering process

D2 : diameter of the sample after sintering.

3.5.6 Mechanical Characterizations

3.5.6.1 Compression Strength

The compressive strength test is the most popular and widely used method of describing the mechanical properties of bone to simulate the pressure to which the bone is exposed as a result of the weight of the body itself and other loads. Under the same circumstances, three samples are tested for each ratio. The computerized universal testing equipment was used based on the ASTM standard C-773. The test was carried out at a speed of 0.5 mm/min **[92]**.

$$\sigma c = \frac{Pf}{A0} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ 3.7$$

Where: $\boldsymbol{\sigma_c}$ is the compressive strength of the cylinder sample MPa

P_f is the fracture load (N)

A_0 is Cross-sectional area of the sample (mm^2).

3.5.6.2 Vickers micro Hardness

Under the same circumstances, three samples are chosen for each batch ; disc samples are formed in a steel die, all samples are suitably polish before tested . In conformity with ASTM standard C1327-90, the test is conducted using a digitally Vickers micro hardness meter (TH-717) (In the laboratories of the Faculty of Materials Engineering/ Ceramic Department). At 1000 g_f with a dwell duration of 15 seconds .Figure 2.5 show the work of micro hardness device.

$$Hv = 1.854 \left(p / d^2 \right) \ldots\ldots\ldots\ldots\ldots\ 3.8$$

Where Hv : which means Vickers hardness in Gpa . P : load . d: The diameter of the hole as a result of shedding the load in (μ m) **[93]**.

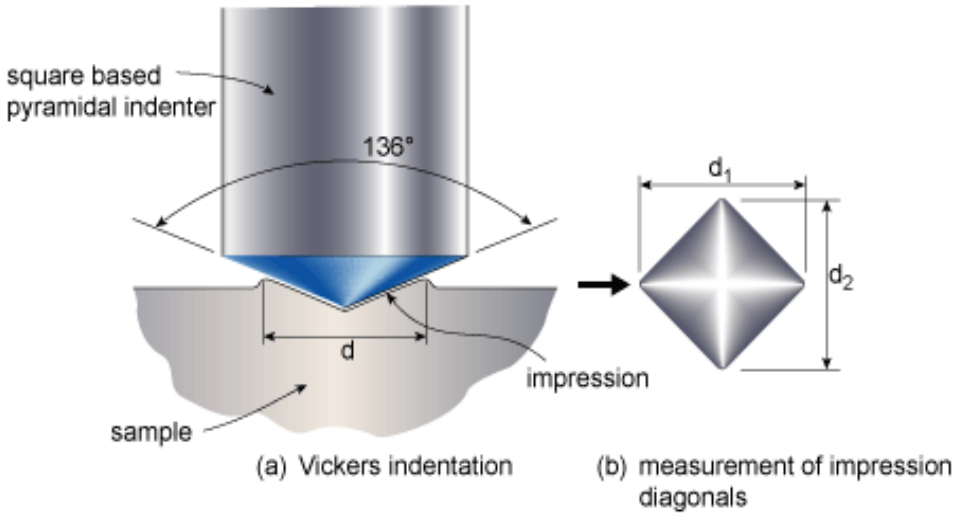


Figure 3.5 An illustration of how the device Vickers works.

3.5.6.3 Three Point Bending

The bending test is conducted after the process of molding the glass in a rectangular shape with suitable dimensions and according to ASTMC1161 specification. After sintering at a temperature of 1000 °C, the samples are ready for examination using the WDW-5E electronic device located in the laboratories of the polymer department . Figure 2.6 illustration the works of three point bending device. The bending strength is calculated as follows at a motion of 0.5 mm/min **[20]**. Dimension of samples are listed in Table3.4.

$$\sigma_f = \frac{3PfL}{2wt^2} \ldots\ldots\ldots\ldots\ldots\ldots 3.9$$

Where :

$\sigma_{f:}$ the bending strength in megapascals. P_f : the fracture load in newton's

W: sample width in millimeters. t: sample thickness in millimeters

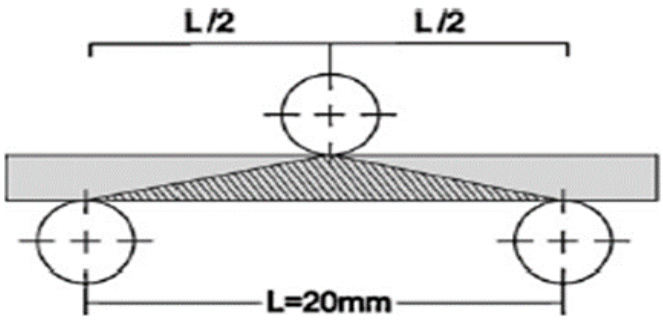


Figure 3.6 An illustration of how the device three point bending works.

Table 3.4: Samples dimensions that were used for conducting above examinations.

Test name	Dimension in mm	ASTM
1- compression test	D=12 , H=20	C-773
2- Vickers Hardness	D=12 , H=5	C1327-90
3-Three point bending	L=60,W=4,H= 6	C1161
4- Density and porosity	D= 12 , H= 10	C373-88
5- Shrinkage	D=16.67, H= 10	
6- Biological test sample	D= 20 , H=5	

3.6 Preparation Simulation Body Fluid (SBF)

The SBF was prepared as follows **[94]**. and according to the components mentioned in the Table 3.5

1. First, the bottle and other tools are wash using one molar of hydrochloric acid and distilled water.
2. Adding 700 ml of distilled water to a 1000 ml glass container, and was rapidly swirled with a magnetic stirrer.

3. The raw materials used in the preparation of SBF as shown in the Table3.5 below, they are added one by one after it is completely dissolved according to the order, It must be ensured that the temperature of the solution is set when preparing at 37^0C.
4. Another note, the pH of the solution must be set to 7.4 by adding one mol/dm3 of HCl, as most of the additives are basics, so it causes the pH to rise.
5. Distilled water is added to the solution until it reaches 1000 ml.
6. The resulting solution is put in a polyethylene or polystyrene bottle and stored in the freezer at a temperature of 5_10°C.
7. This fluid has been proven to accurately mimic in vitro apatite growth on the surfaces of various bioactive glasses and glass-ceramics in vivo.

Table 3.5 The substances involved in the preparation of a simulated solution for body fluid **[67].**

Chemical Formula	Quantity in Gram
NaCl	6.547
$NaHCO_3$	2.268
KCl	0.373
$MgCl_2.6H_2O$	0.305
$CaCl_2.2H_2O$	0.368
$Na_2HPO_4.2H_2O$	0.178
Na_2SO_4	0.071
$CH_2OH)_3CNH_2$	6.057

3.7 Formation of the Hydroxyapatite Layer

After preparing the SBF solution, the samples of bioactive glasses- ceramic are immersed in it for 21 days and under standard conditions at a temperature of 37 using incubators (blender, Germany, in the College of science

/University of Babylon) to examine the resulting layer that formed on sample surface , X-ray diffraction used device in addition to the scanning electron microscope and the Energy-Dispersive Spectroscopy (EDS).

3.8 Anti- Bacterial Test

To evaluate the effect of samples made of bioactive glass-ceramic in the media containing bacteria, the Kirby_Bauer test is conducted by using bacteria present in urine . The basis of this test is based on the use of an agar tablet containing bacteria, then the samples to be tested as the antibiotic are placed in these tablets for 24 hours . The effect of the samples as an antibacterial can be seen through forming an area in the form of a circular ring around the sample. As the diameter of the ring increases, this means that the sample is more effective as an antibiotic **[95]**. This test was carried out in the laboratories of Al-Kifl Hospital.

Chapter four

Results & discussion

Chapter four

Results and discussion

This chapter will present the results obtained after preparing bioactive glass/ Glass.ceramic and explain physical, mechanical and biological examinations **.**

4.1 The result of the X-ray analysis for the primary powders

The materials used in the preparation of the bioactive glass-ceramic must be examined and ensured of their chemical formula and that they are free from other impurities. This process is carried out using x-ray diffraction. We notice the analysis of silica In the Figure 4.1 as it appears in a random phase. In Figure 4.2 the result analysis is $CaCO_3$ agree with Card No .01-086-2334.In Figure 4.3 the result analysis is Na_2CO_3 agree with Card No .01-086-0287.In Figure 4.3 the result analysis is P_2O_5 agree with Card No 01-085-1120.In Figure 4.3 the result analysis is K_2CO agree with Card No, 00-049-1093.In Figure 4.3 the result analysis is V_2O_5 agree with Card No .01-089-0611.

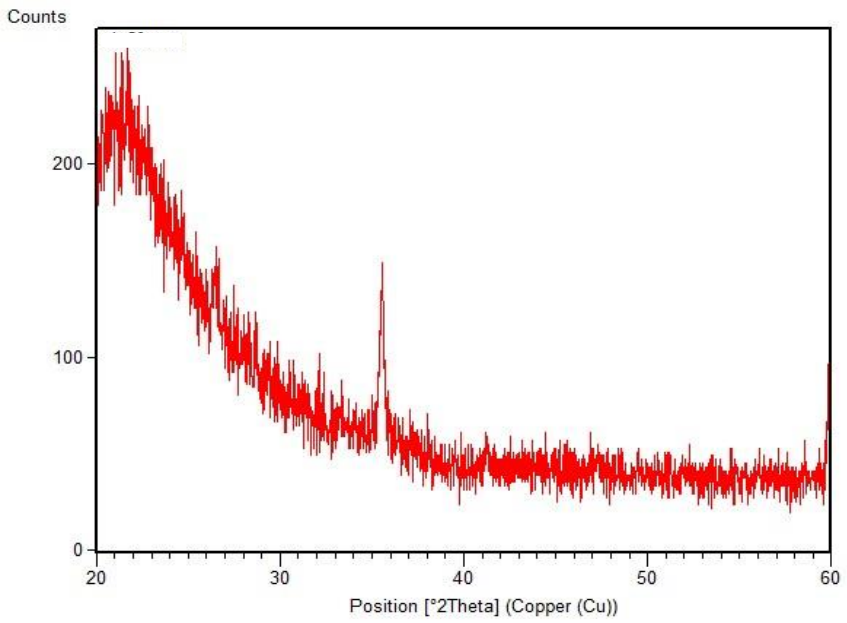


Figure 4.1:X.ray analysis of silicon dioxide.

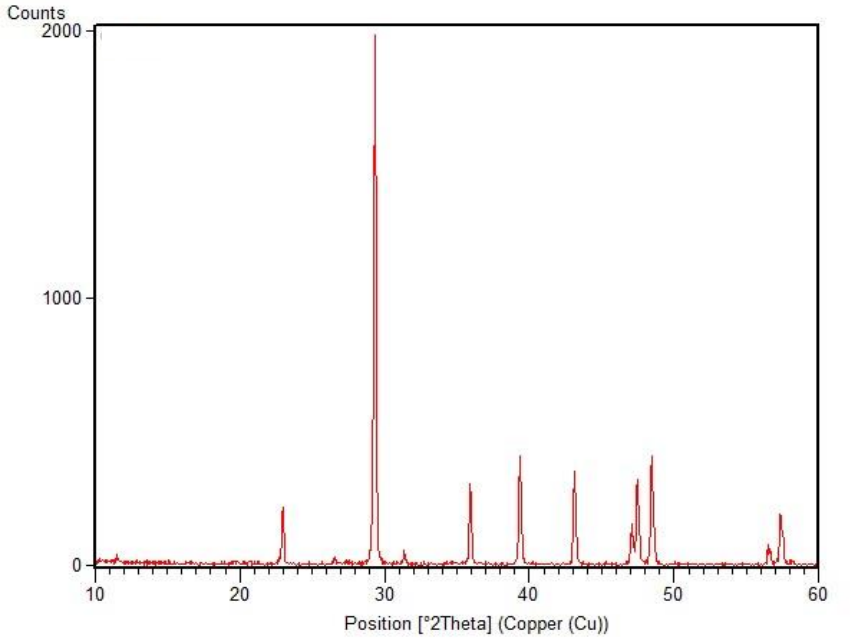


Figure 4.2**:** X-rays analysis of calcium carbonate.

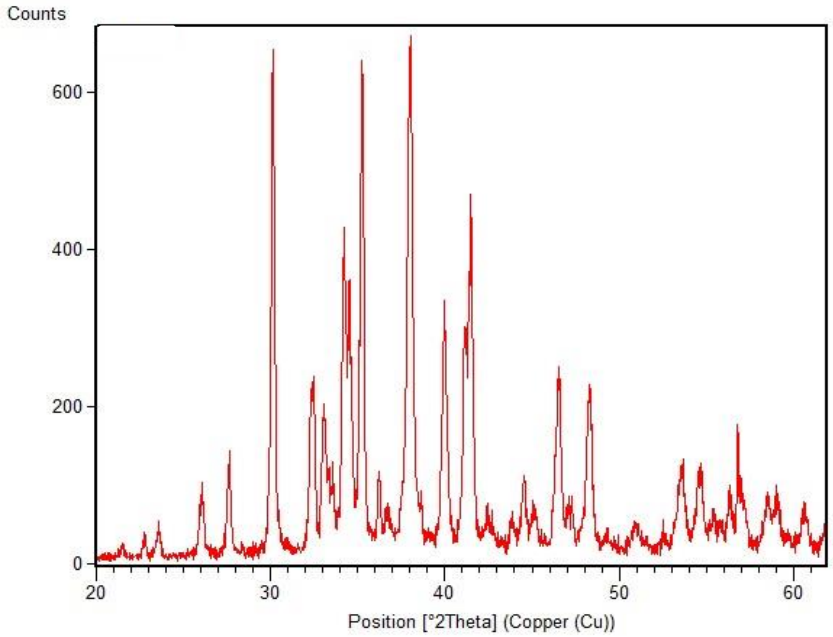


Figure 4.3: X-rays analysis of sodium carbonate.

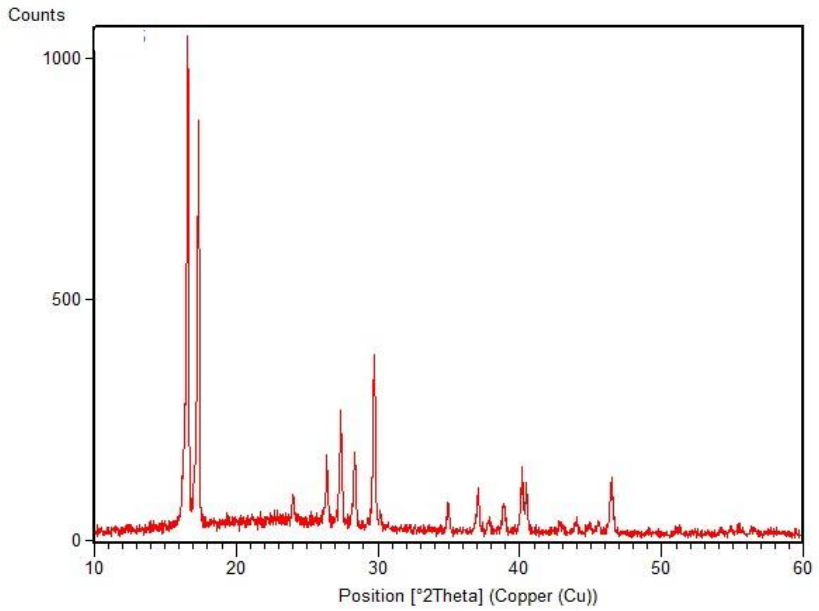


Figure 4.4: X-rays analysis of phosphorous pent oxide.

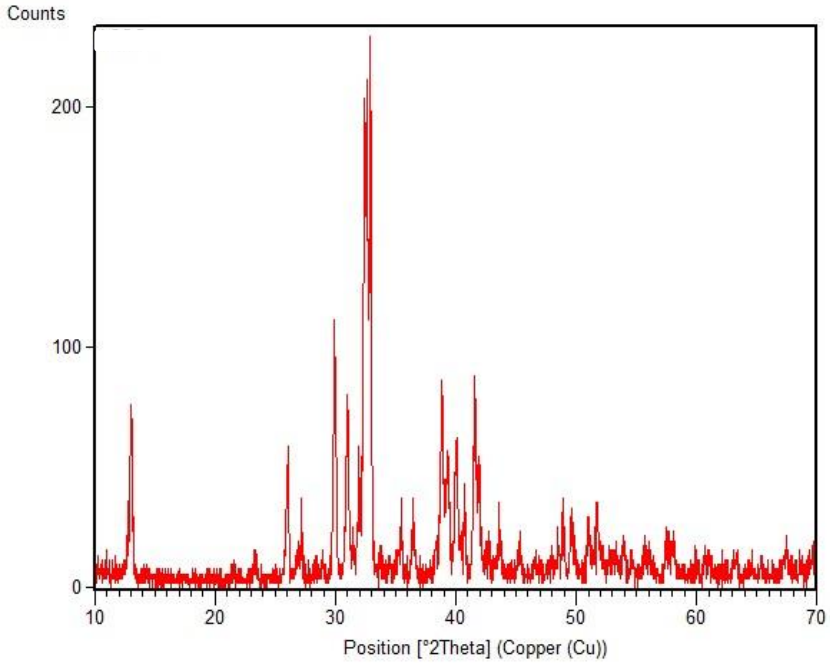


Figure 4.5: X-rays analysis of potassium carbonate .

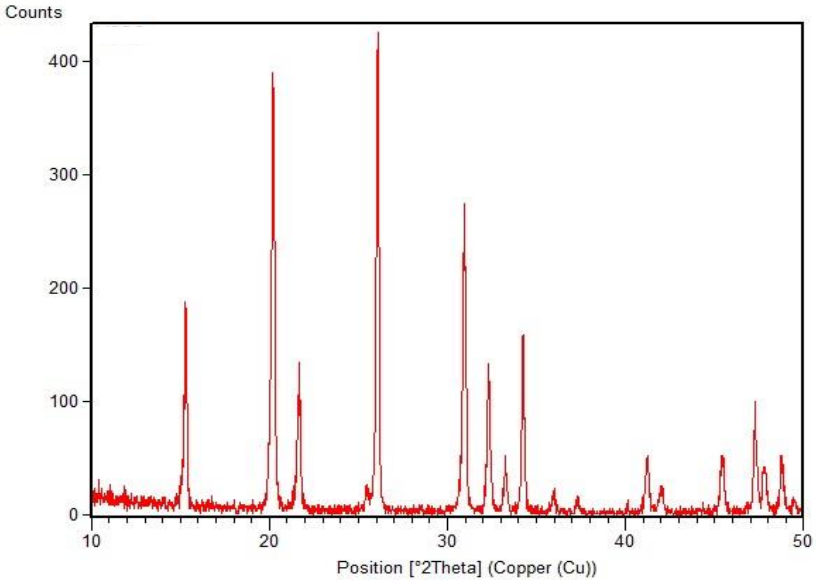
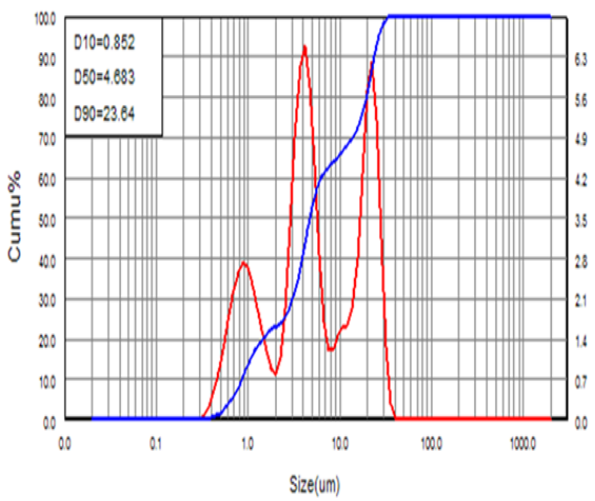


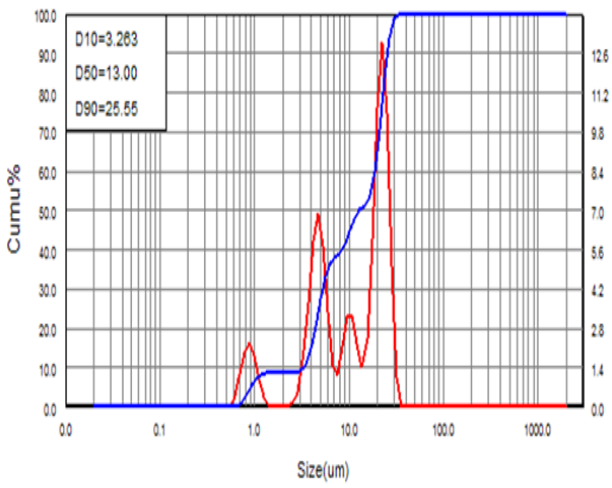
Figure 4.6: X-rays analysis of vanadium pent oxide.

4.2 Result of Particle Size Analysis

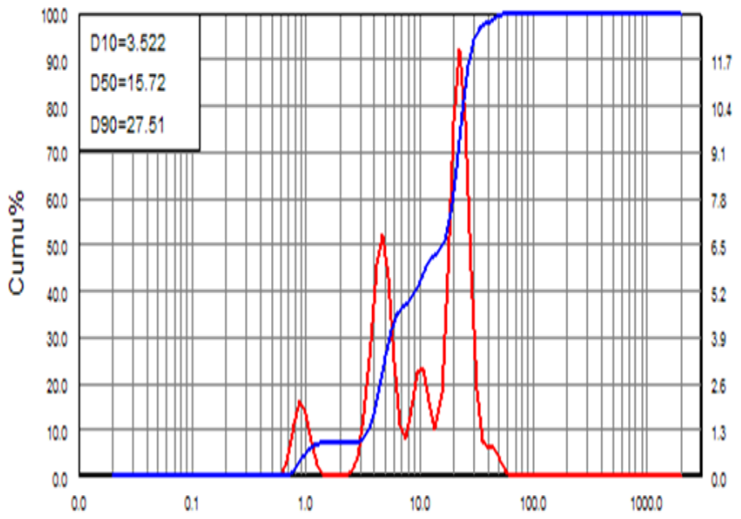
Figure (4.1)shows the result of the analysis for measuring the particle size of the bioactive glasses-ceramic powders, Under the same conditions and simultaneously using the laboratory mill where the particles sizes for powder with 0% addition are(D_{10}= 0.852,D_{50}=4.683, D_{90}=23.64) and the particle size of sample with 10 % addition are (D_{10}= 3.263,D_{50}=13.00, D_{90}=25.55) , and the particle size of sample with 15% addition are (D_{10}= 3.522,D_{50}=15.72, D_{90}=27.51), the increase in granular size are noticed with the addition of this eutectic compound and increase the hardness of bioactive glasses –ceramic .



- a -



- b -



- c -

Figure .4.7: The particle size distribution of the bioactive glass-ceramic powders (0,10.15 %) after the grinding process .

4.3 X-Rays Diffractions (XRD) Analysis

The result of the X-ray diffraction analysis of the eutectic compound as shown in Figure(4.8) the compounds were obtained are (KVO_3) agree with (JCPDS, card No-01-070-0677) and ($K_5V_3O_{10}$) agree with (JCPDS, card No 01-077-1454), where a scanning with angle (2Ɵ) from 10º to 80 º .

After grinding the glass produced from the process of quenching the molten in water, it was examined by X-ray device and scanned in the range from 10 º to 60 º (2 Ɵ), as shown in Figure(4.9), where the peaks are random due to the silica bonds (Si – O – Si) and sudden quenching which prevents the atoms from being arranged in a three-dimensional manner. We notice a slight change and crystallization of some peak slightly resulting from the addition of the eutectic compound as shown in Figure(4.10-4.11) and the appearance of a phase ($Na_2Ca_3Si_2O_8$) which agree with (Card .No. 00-023-0670) shown in Figure(4.12).

As in Figure(4.13) scanning with angle (2Ɵ) from 10º - 60 º shows the crystallization occurs in the glass without any addition and its transformation into

glass- ceramic when sintered at a temperature of 1000 °C, the main compound are ($Na_4 Ca_4 Si_6 O_{18}$) is a bio phase agree with (JCPDS, card No-01-079-1089) .When adding the eutectic compound in the following proportions (5,10,15)% as shown in the Figure (4.14-4.15-4.16) , its noticed an increase in the crystallization of the glass and this is due to the presence of vanadium oxide, which acts as a nucleation agent in glass, the main phase is the combeite ($Na_4 Ca_4$ ($Si_6 O_{18}$) which is a bio phase agree with card number (01-079-1089) and ($K_{.5}V_3O_5$) agree with (JCPDS, card No-01-080-0686) which is a powders coupled with increase in the crystallization rate . it's also noticed a decrease in the intensity of the main beak with the increase in the percentage of adding the eutectic compound to the glass until it reaches the most low with addition ratio 15%, as in Figure(4.16) . By using the Scherrer equation from (high score plus) program to calculate the crystal size, the results were (56.5, 69.7, 75.45) nm, notice an increase in size with the addition of the compound due to the effect of vanadium oxide who works as a catalyst for nucleation at low temperature from early time .

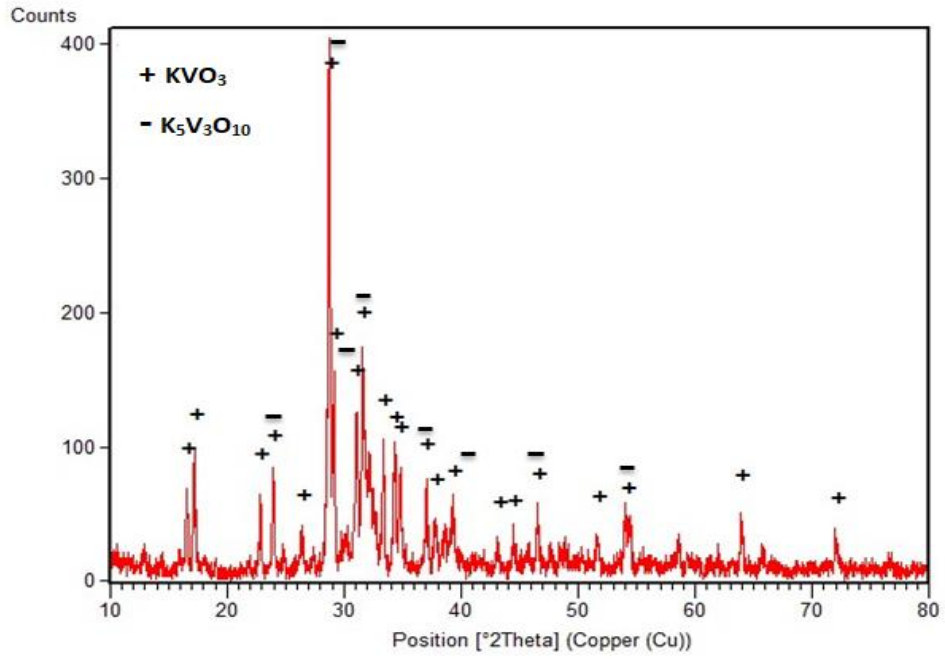


Figure .4.8: X-ray diffraction analysis of eutectic component ($K_5V_3O_{10}$+ KVO_3).

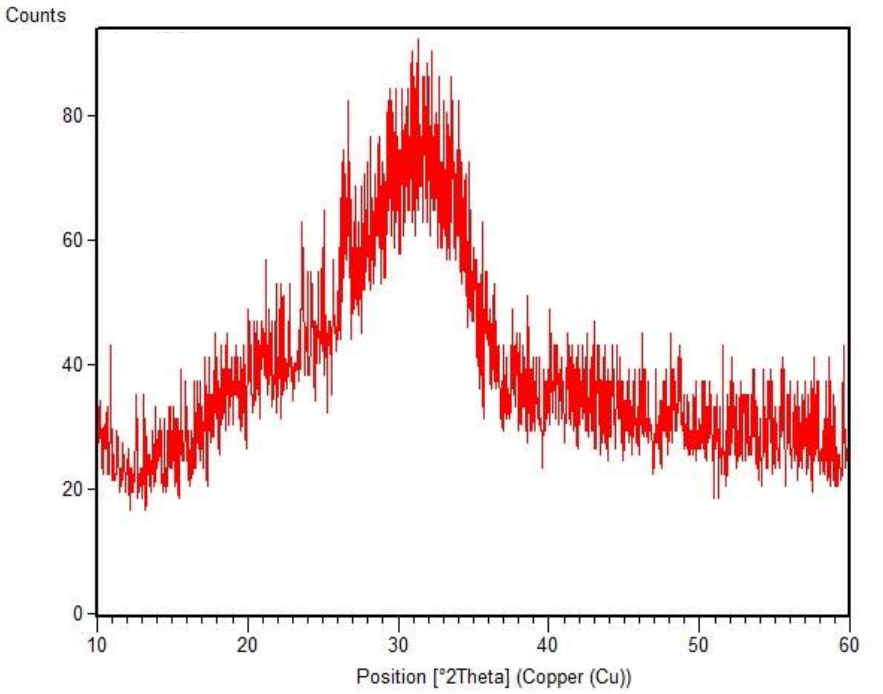


Figure 4.9: X.ray analyses of bioactive glass sample (A) .

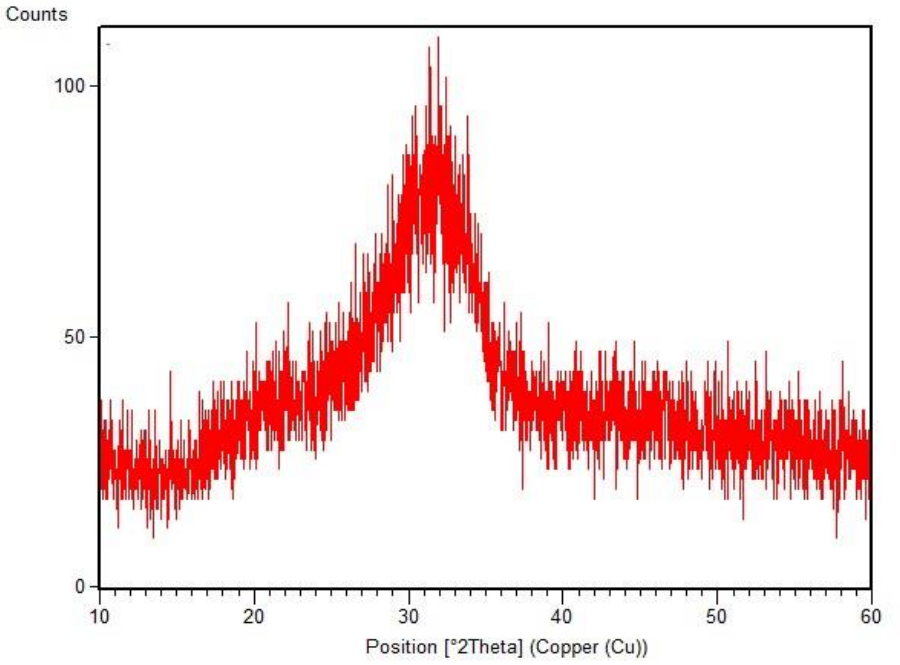


Figure 4.10: X.ray analyses of bioactive glass sample (B).

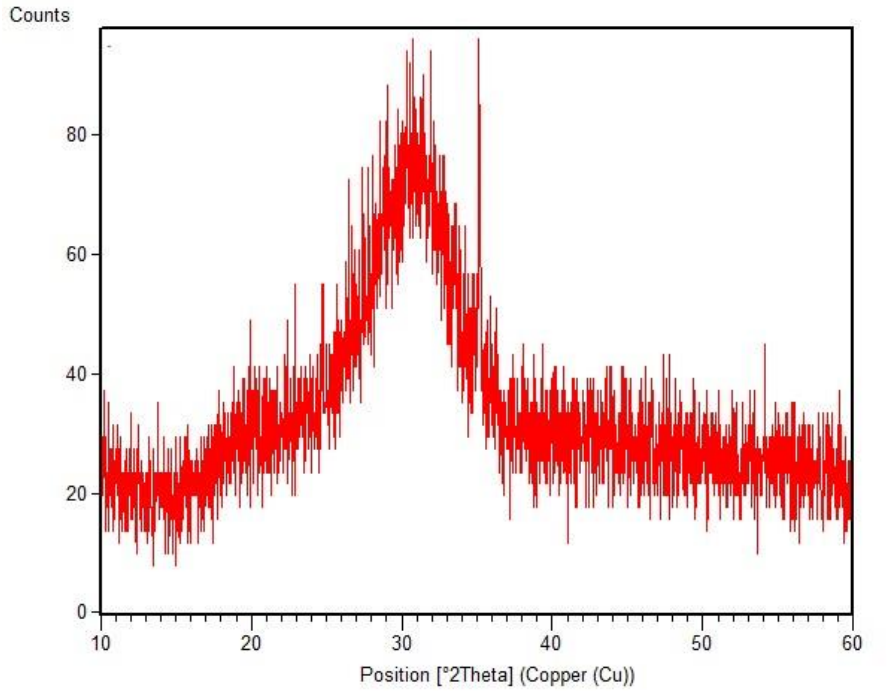


Figure 4.11: X.ray analyses of bioactive glass sample (C).

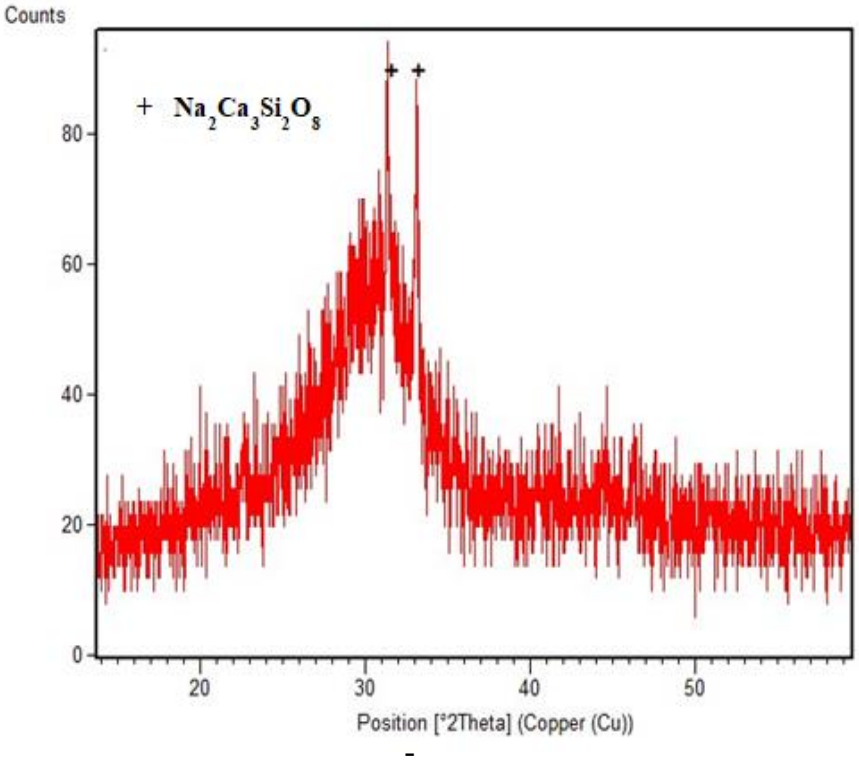


Figure 4.12: X-ray analyses of bioactive glass sample (D).

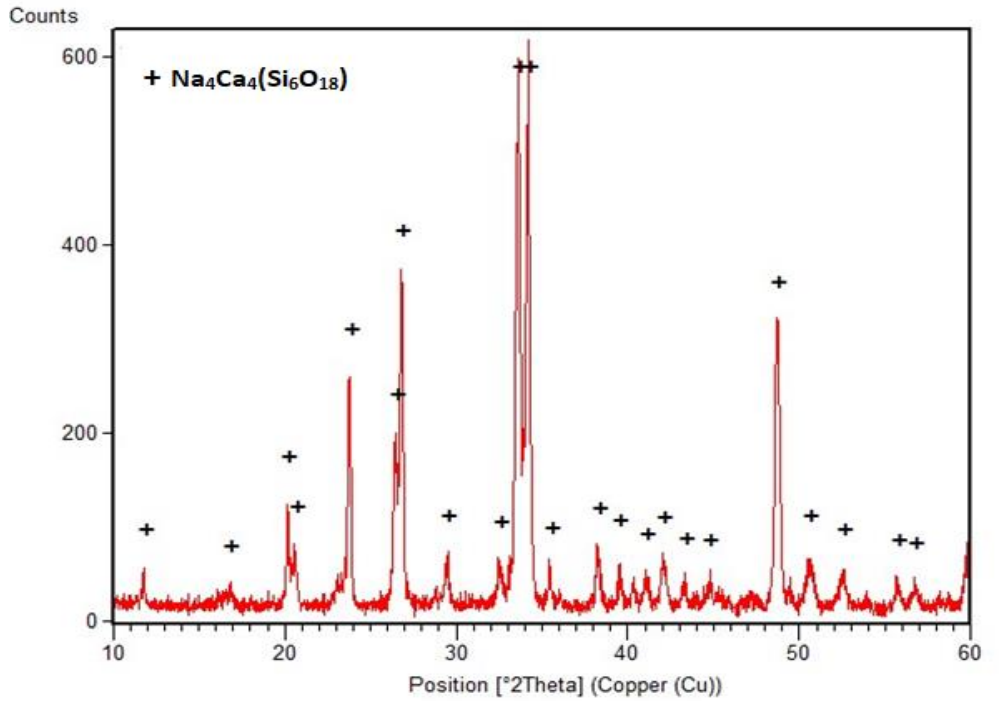


Figure 4.13: X.ray analyses of bioactive glass-ceramic sample (A).

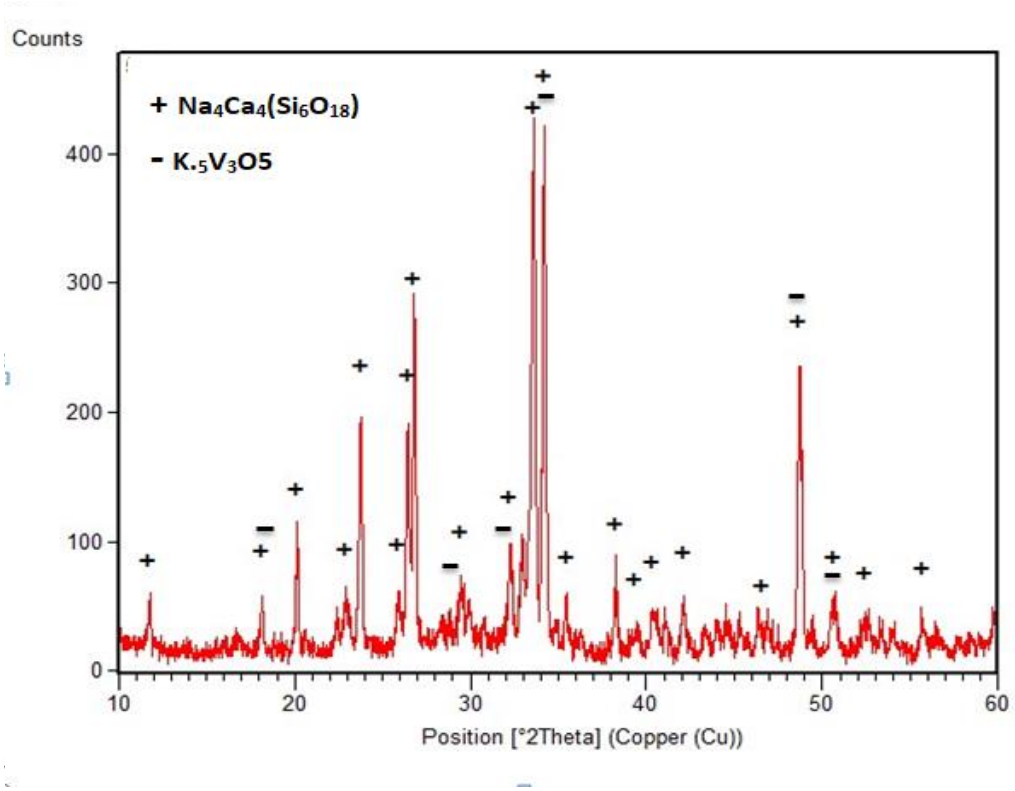


Figure 4.14: X.ray analyses of bioactive glass-ceramic sample (B).

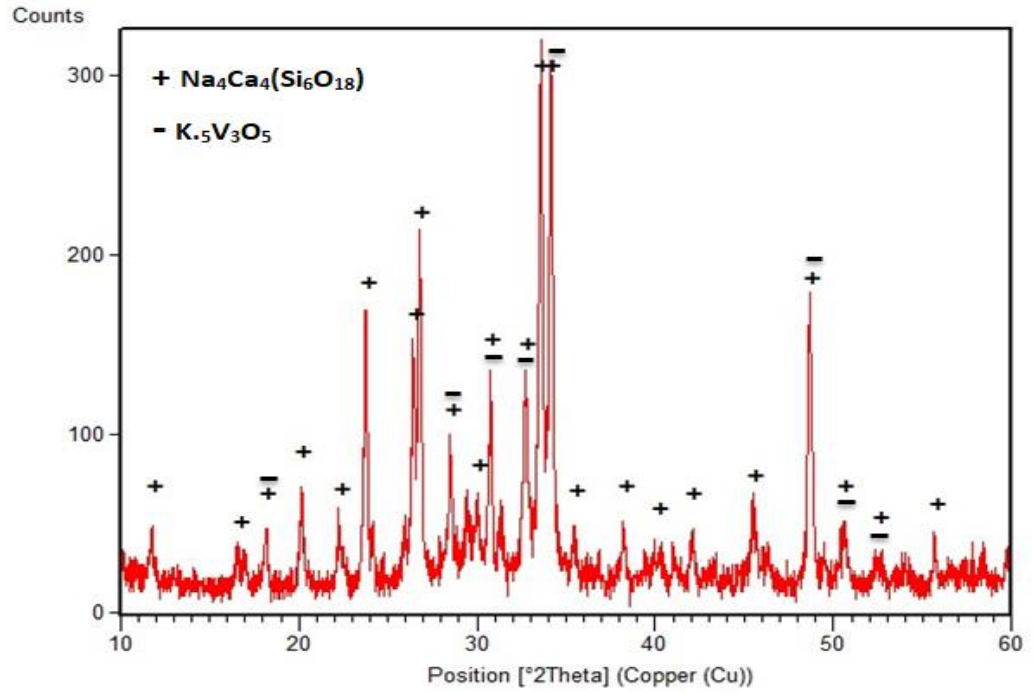


Figure 4.15: X.ray analyses of bioactive glass-ceramic sample (C).

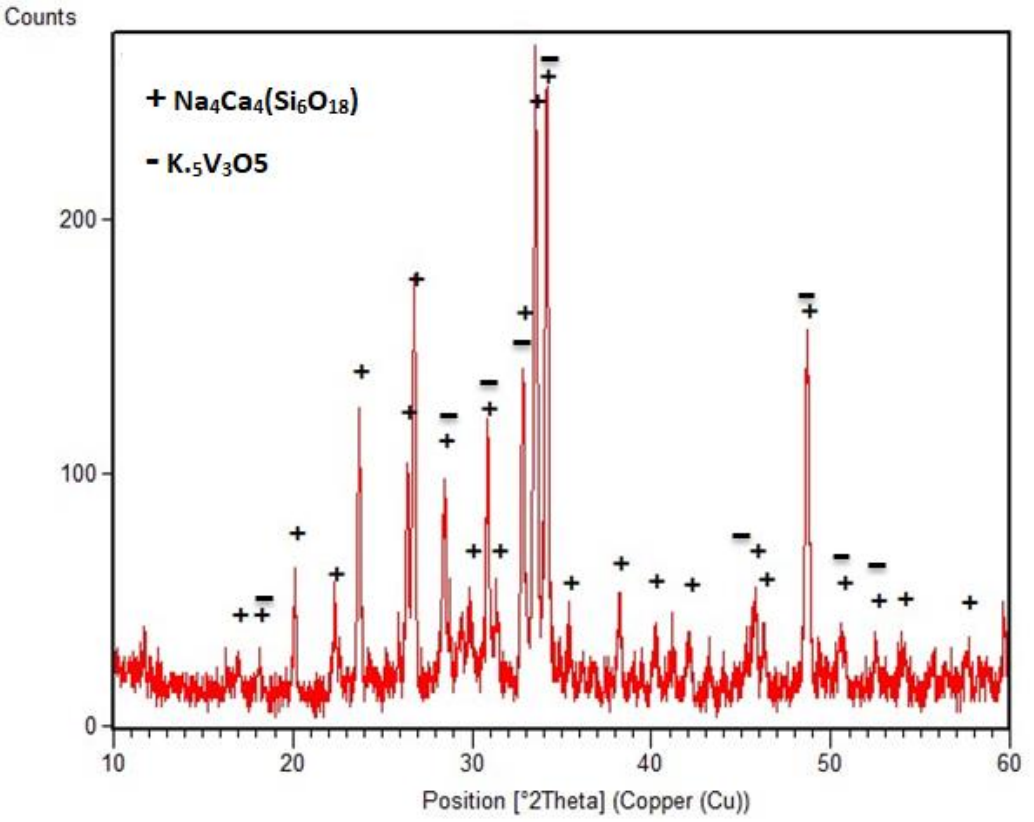
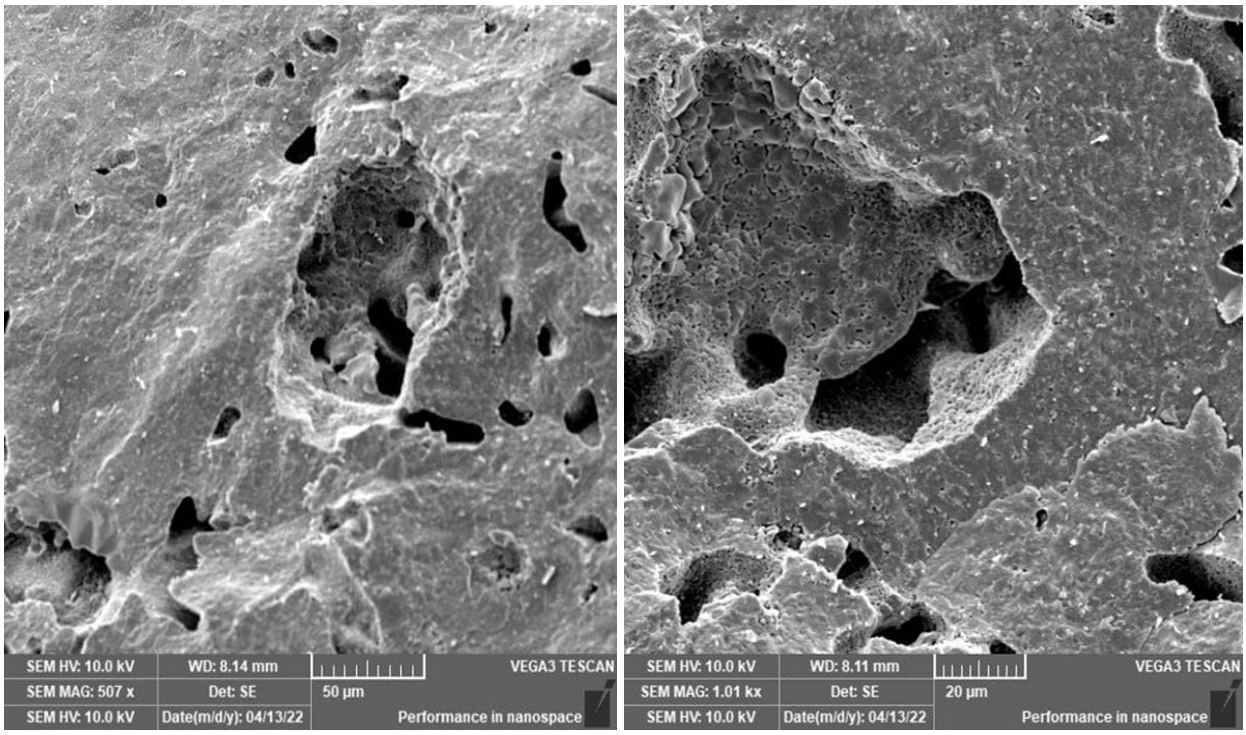


Figure 4.16: X.ray analyses of bioactive glass-ceramic sample (D).

4.4 Scanning Electron Microscope (SEM)

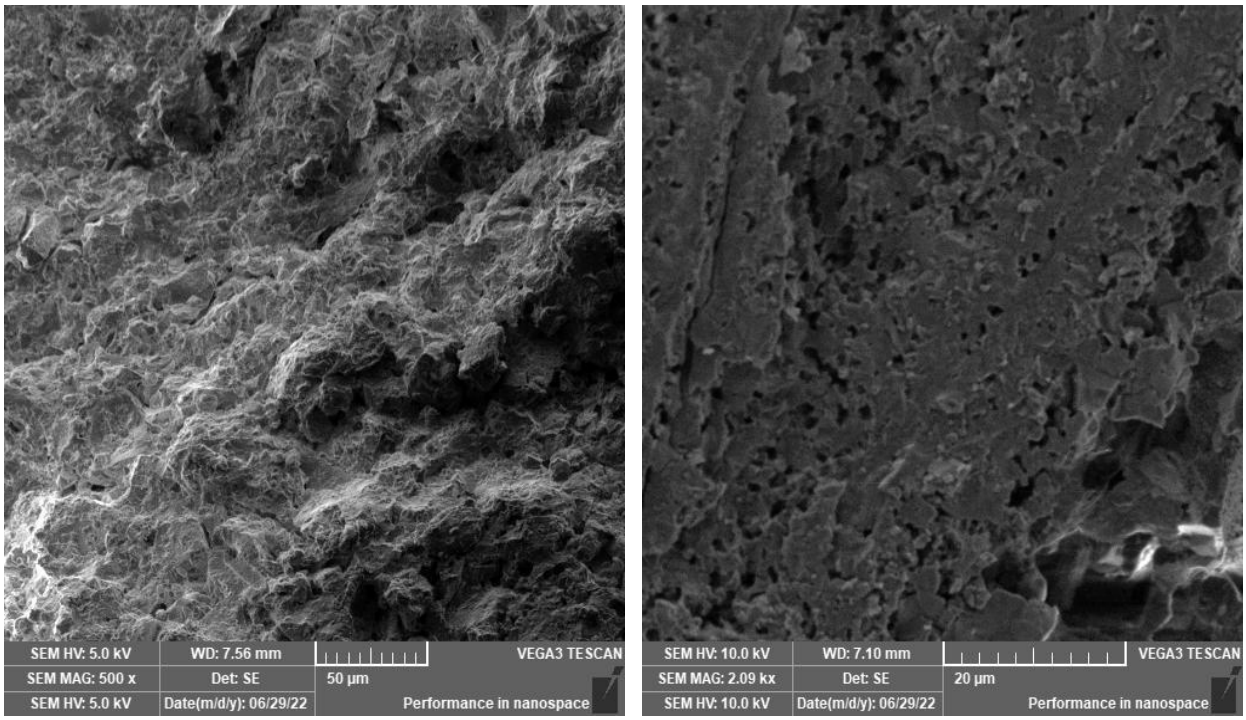
The SEM device located in the laboratories of the Faculty of Materials Engineering/the Ceramic Department (VEG3) .was used with powerful magnification (500X, 1KX, and 2.36KX) to analyze the fracture surface of glass-ceramic after sintering at temperature 1000 ^{0}C. Figure (4.17-a) shows the images of sample With a porous microstructure where the pores are connected or permeable to the inside, they enhance the connection with living tissue by creating a path for traveling blood and cells. Figure (4.17-b) demonstrates the crystallization that occurred in the sample as a result of heat treatment .Figure (4.18) shows a slight change in the structure due to the little addition.

Figure (4.19-a) at magnification of 500X shows a decrease in porosity were found as a result of adding a compound of 10% ($K_5V_3O_{10}$+KVO_3) which leads to Increasing the phase ($K_{.5}V_3O_5$) as shown by X-ray diffraction analysis and Couse a high and uniform grain growth and crystallization in the structure of the sample as can be seen in the Figure (4.19-b) , In the Figure (4.20-a) there is a decrease in the porosity and high densification surface as a result of the increase in the percentage of the added compound of 15%. While in Figure (4.20-b) its noted the presence of a continuous prismatic phase throughout the sample in addition to the crystal phase and verification due to partial melting of the sample as a result of the approach of the sintering temperature to the melting of the sample.



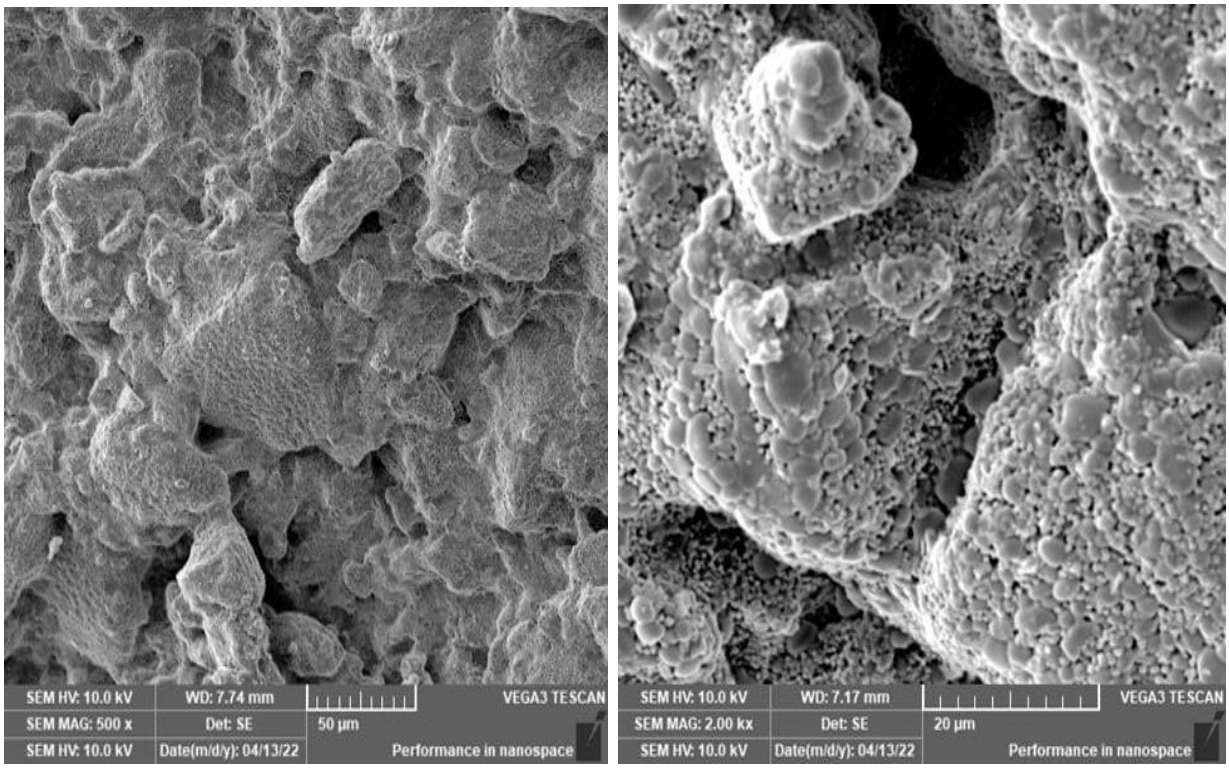
-a - - b-

Figure 4.17:(a ,b) SEM photo of sample (A) without replacement .



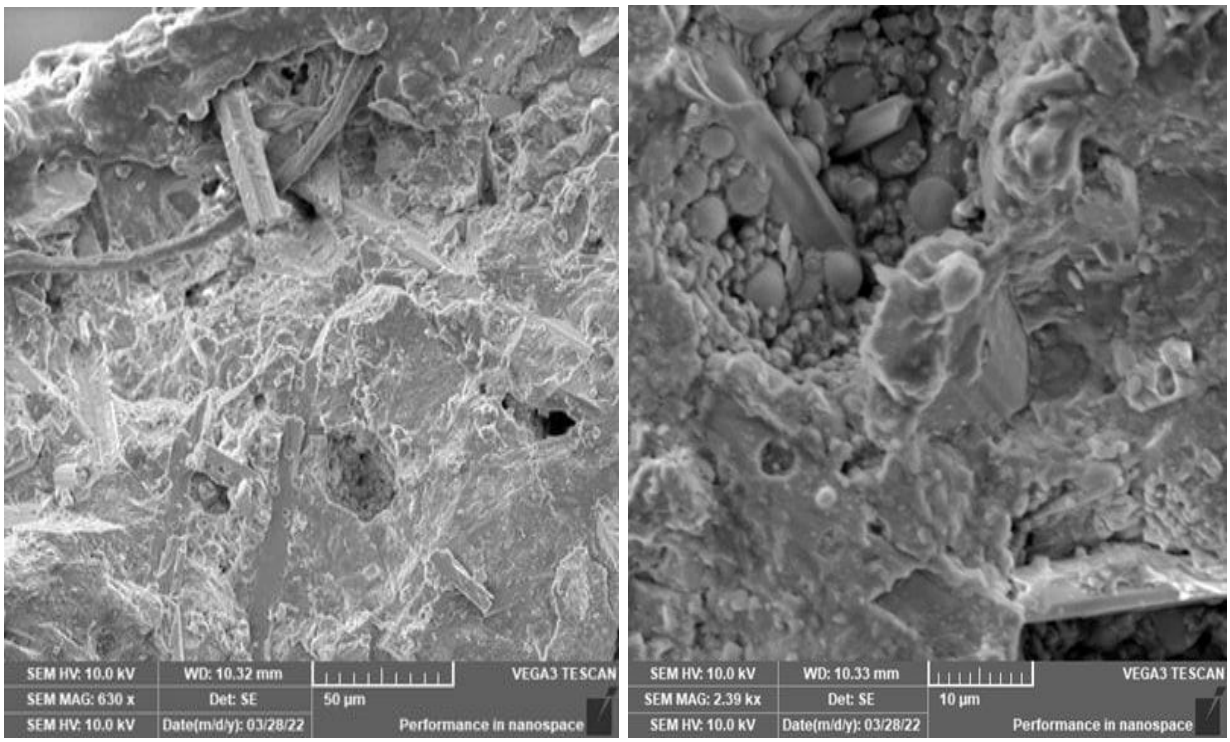
- a- -b-

Figure 4.18:(a ,b) SEM photo of sample (B) with replacement 5 % .



- e - - f –

Figure 4.19:(a ,b) SEM photo of sample **(**C) with 10% replacement.



- g - - h –

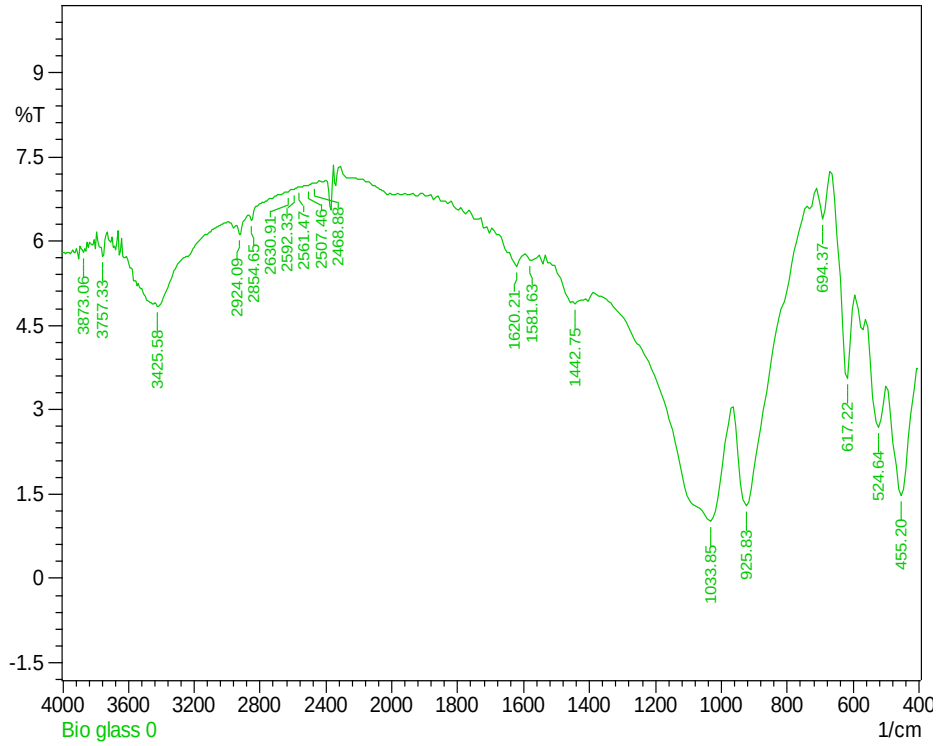
Figure 4.20:(a ,b) The SEM photo of sample (D) with 15% replacement .

4.5 Fourier-Transform Infrared Spectroscopy

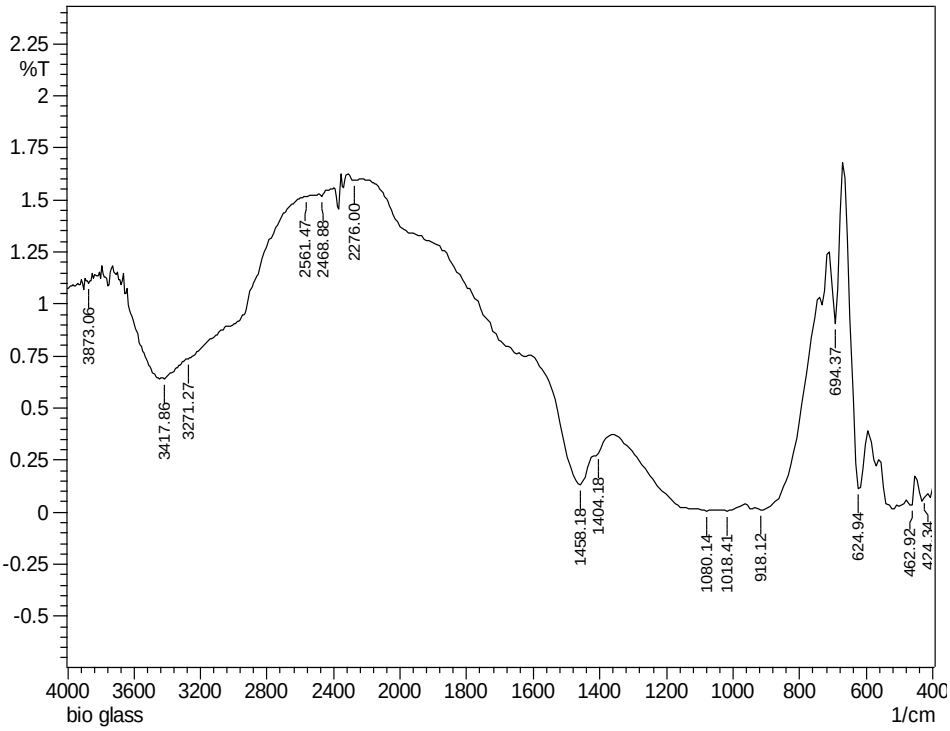
The samples' FTIR spectra were examined in the wave length range of 400 to 4000 cm^{-1}, which detects the chemical bonds and functional groups in the substance.

Figures(4.21) show correspondingly, the IR spectra of the bioglasses- ceramic . The absorption bands for the silicates can be seen in the area 1033-1041 cm^{-1} and at 995 cm^{-1} in the spectra of the as-prepared materials. In addition there are bands at 570 cm^{-1} and within 788-794 cm^{-1}, which are attributed to the bending vibration of P–O in amorphous calcium phosphate and the symmetric stretching of the Si-O-Si bond, respectively. Additionally, a broad OH absorption band at 3330 cm1 and a weak adsorbed water band in the produced ceramic powder is shown by the presence of two peaks at 2364 and 2334 cm^{-1} attributed to the O-H stretch vibration of hydrogen-bonded O-H groups, and a peak, at 1638 cm^{-1} attributed to the O-H bending mode.

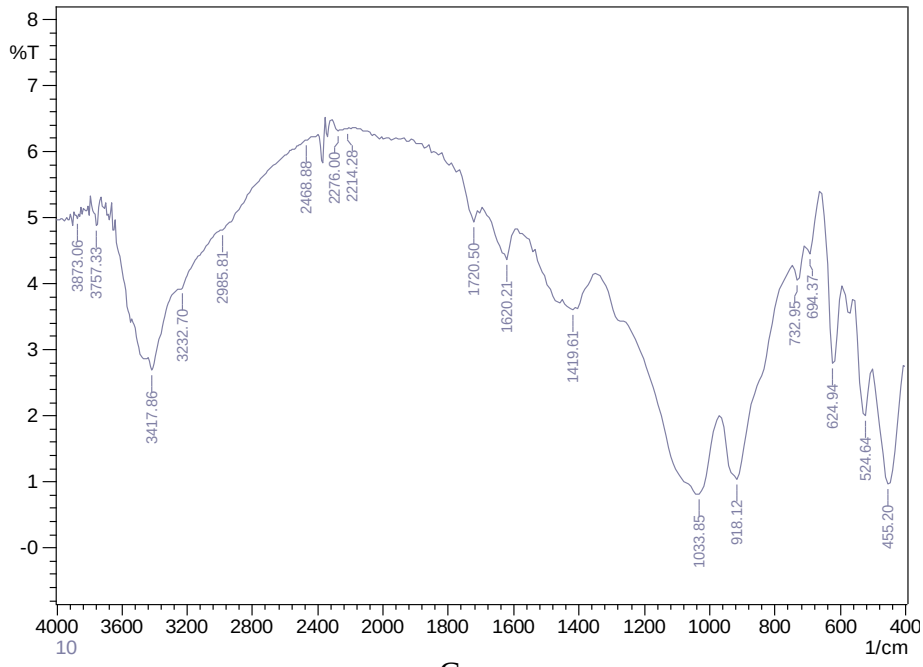
Carbonate group absorption is attributed to the band between 1404 and 1465 cm^{-1}. The signal at 720 cm^{-1} reveals the existence of K_2O in the glass structure of the current series. The FTIR spectrum of pure V_2O_5 reveals a low frequency band about 516 cm-1, that can be ascribed to the symmetric stretching vibrations of the V-O-V group. Bands around 726 cm-1 and about 800 cm-1 were also seen in the FTIR spectra of V_2O_5, which could have been ascribed to the asymmetric stretching vibrations of the V-O-V group, The existence of a crystalline phase is further supported by the FT-IR spectrum, which exhibits a peak at 524,624cm^{-1}, corroborated by the XRD result.


%T
9
7.5
6
4.5
3
1.5
0
-1.5
3873.06
3757.33
3425.58
2924.09
2854.65
2630.91
2592.33
2561.47
2507.46
2468.88
1620.21
1581.63
1442.75
1033.85
925.83
694.37
617.22
524.64
455.20
4000 3600 3200 2800 2400 2000 1800 1600 1400 1200 1000 800 600 400
Bio glass 0
1/cm

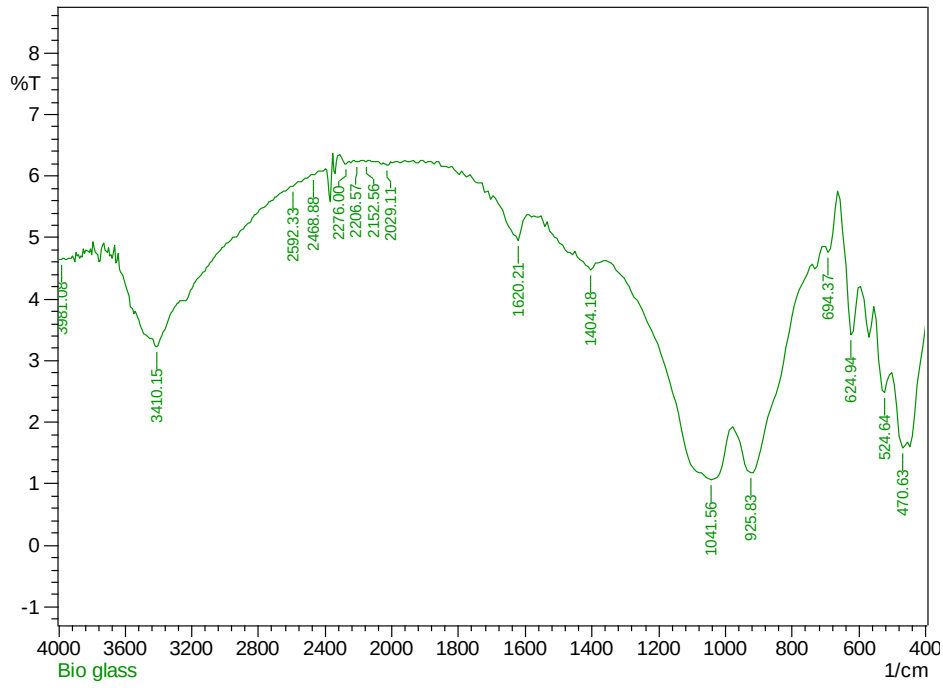
-A -


%T
2.25
2
1.75
1.5
1.25
1
0.75
0.5
0.25
0
-0.25
-0.5
3873.06
3417.86
3271.27
2561.47
2468.88
2276.00
1458.18
1404.18
1080.14
1018.41
918.12
694.37
624.94
462.92
424.34
4000 3600 3200 2800 2400 2000 1800 1600 1400 1200 1000 800 600 400
bio glass
1/cm

- B -



- C -



- D -

Figure 4.21: Analysis of the infrared spectrum of bioactive glasses – ceramic samples A,B,C,D with substitution eutectic compound (5,10,15)% respectively .

4.6 Physical Properties of Manufactured Bioactive Glass_Ceramic Samples

Making a number of bioglass_ceramic samples and conducting physical examinations for them gives an approximate indication of the true values of the material as the samples manufactured with the substitution (0,5,10,15)% eutectic component ratio gave satisfactory results as noticed there is a slight decrease in porosity coming from the addition ($K_5V_3O_{10}$+ KVO_3) as shown in Figure (4.22) , The density of the sample improved after the eutectic compound was introduced into the glass composition, and this can be seen in the Figure (4.23) ,This is due to the fact that the density of the added oxides is higher than that of the substituted oxides whereas the density of K_2O (2.32 g/cm3) is higher than Na_2O (2.27 g/cm3) and the density of V_2O_5 (3.35 g/cm3) is higher than the density of SiO_2 (2.65 g/cm3) **[96]**.

Perhaps and due to the difference in the diameters of their ionic radiuses, the radii of ions K^+ is larger than Na^+ **[97]**. and the radii of ions V^+ is larger than Si^+ **[98]**. It could lead to a disturbance in the network arrangement. Since this replacement in a glass system can result in a slight change in the physical and mechanical properties of the glass. The nucleation and granular growth occur as a result of the increase in vanadium oxide because it has the property of giving the glass a high crystallization with heat.

After decreasing the melting point as a result of substitution with the eutectic component and the sintering process for samples at a 1000 ^{0}C, which is close to the melting point, led to the disappearance or smallness of some pores and make the samples with high condensation , which is can be observed in the images of the scanning electron microscope analysis.

The substitution of oxides that have a low melting point and the formation of a eutectic compound between them has contributed to reducing the melting point and this is explained by the bond dissociation energies (E_d) of K_2O and V_2O_5 are less than those of SiO_2 and Na_2O (239, 644, 798, and 257) kJ/mol, respectively **[99]**. which leads to breaking down the bonds when the temperature rises and lower melting temperatures. When added to a material, K_2O acts as a network modifier, causing non-bridge oxygen ions and point defects, all of which weaken the bonds as the temperature rises. Both sodium Na^+ and potassium K^+ ions have the same charge (**+1**), but since the potassium ion is bigger, the electrostatic forces of attraction in potassium oxide are weaker. As a result, less energy is needed to separate the ions, resulting in a less endothermic enthalpy of lattice dissociation**[100]**.Vanadium serves as an efficient crystallization agent during the heat treatment of glasses. Some of these reasons have led to a slight increase in shrinkage in the manufactured samples as can see in Figure (4.24) .

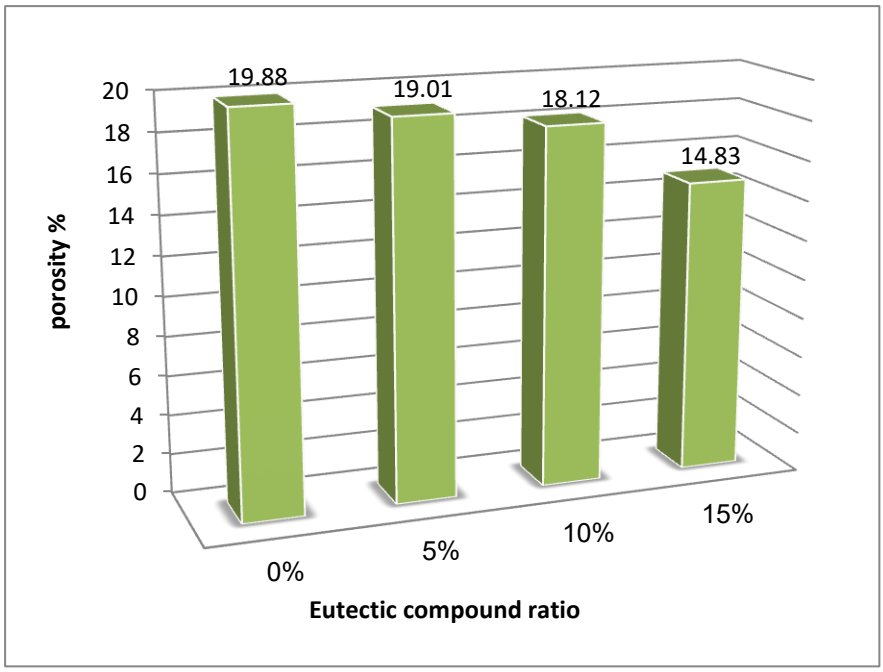


Figure 4.22 : The effect of eutectic component ($K_5V_3O_{10}$+ KVO_3) on porosity of bioactive glasses-ceramic samples A,B,C,D.

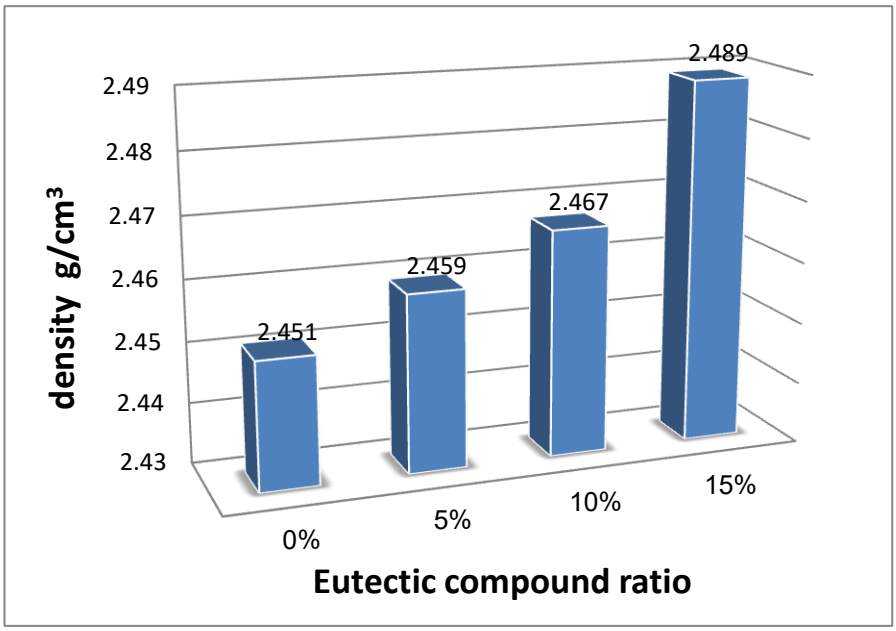


Figure 4.23 : The effect of eutectic component ($K_5V_3O_{10}$+ KVO_3) on density of bioactive glasses-ceramic samples A,B,C,D.

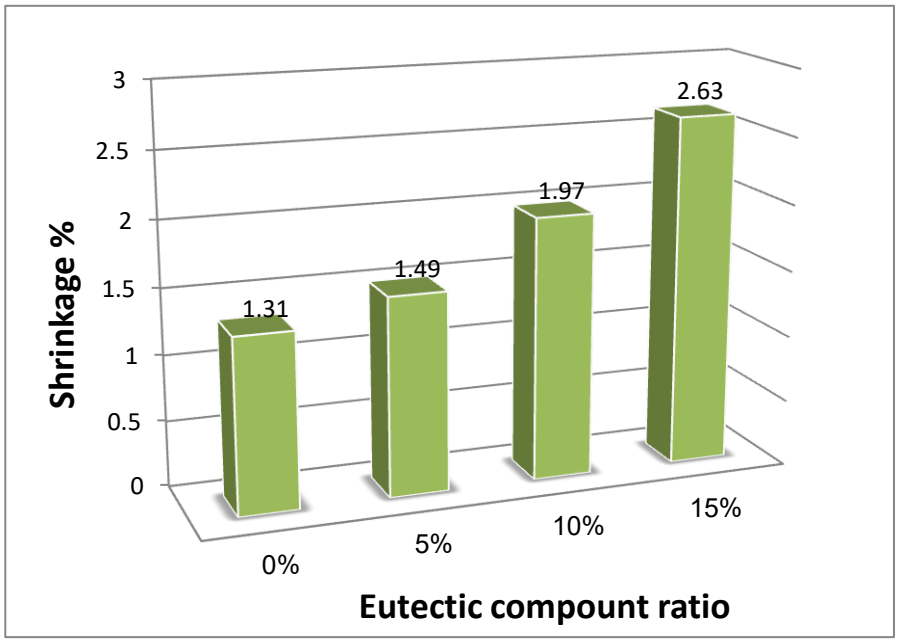


Figure 4.24 The effect of eutectic component ($K_5V_3O_{10}$+ KVO_3) on shrinkage of bioactive glasses-ceramic samples A,B,C,D.

4.7 Mechanical Properties

A clear improvement in the mechanical properties of bioactive glass-ceramic samples with an the substitution eutectic compound (0,5 ,10,15) %, this is due to improvement and a rise in the density of the manufactured glass-ceramic and the diminution in its porosity ratio lead to an increase in compaction and a decrease in areas of weakness resulting from the random distribution and irregular shape of the pores that represent stress concentrate points, as can be seen above in the images of the scanning electron microscope analysis.

The heat treatment of the glass, where it was sintered at a temperature of 1000 ^{0}C, led to its transformation into glass-ceramic and obtaining high crystallization ,the sintering degree approached the melting point of the samples, so there was a closeness between the grains and partial melting, which led to high condensation. The long-range order of the crystal can impede the crack progression and improve the mechanical properties. Adding potassium oxide, which can give glass more hardness .The K_2O/Na_2O substitution improves the chemical durability of the glass-ceramic **[53]**.

Incorporating vanadium oxide into the ceramics' composition increased mechanical strength **[2]**. As can see in Figure(4.25) the compression strength of the bioactive glass- ceramic rise from 96 to 137.76 mpa when replacement with ($K_5V_3O_{10}$+ KVO_3) compound in samples A,B,C,D. height value obtained at substitution ratio 15% because the sintering temperature approaching the melting point, so a slight melting occurred and prismatic phases formed as shown in the SEM images for the sample (D). this value is more than the compression strength of cortical bone so it can be used in application that undergo to compression load. Ceramic materials are characterized by their hardness, and this is result from the strength of the covalent bonds and the crystalline alignment after the thermal treatment of the glass,

where most of the pores have disappeared or their size is small, in Figure(2.26) an increase in the Vickers hardness from 4.23 to 7.76 Gpa as resulted of replacement with eutectic compound. The improvement in bending strength from 24.54 to 32.5 mpa results from the replacement with an eutectic compound. As shown in the Figure**(**2.27)It is known that ceramic materials are weak under the influence of bending load, and when compared this value of glass-ceramic samples with cortical bone, note that the values that have been reached are much less than the bending strength value of bone. In the Table4.1 is a comparison between the results obtained for glass-ceramic samples and natural bones .

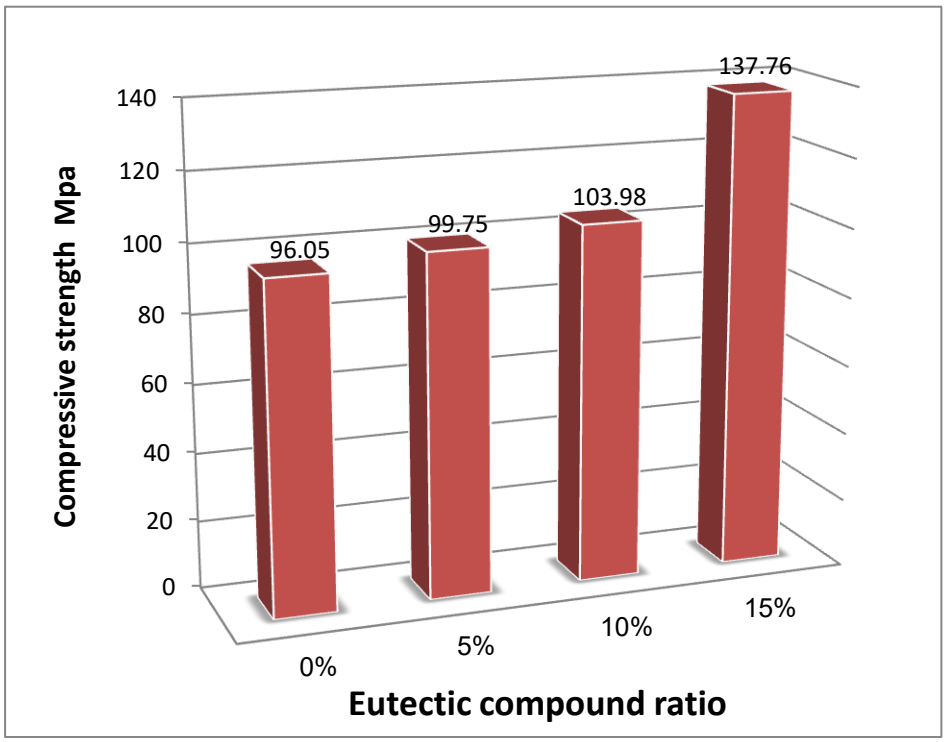


Figure4.25:The effect of eutectic component($K_5V_3O_{10}$+ KVO_3) on compression strength of bioactive glasses-ceramic samples A,B,C,D.

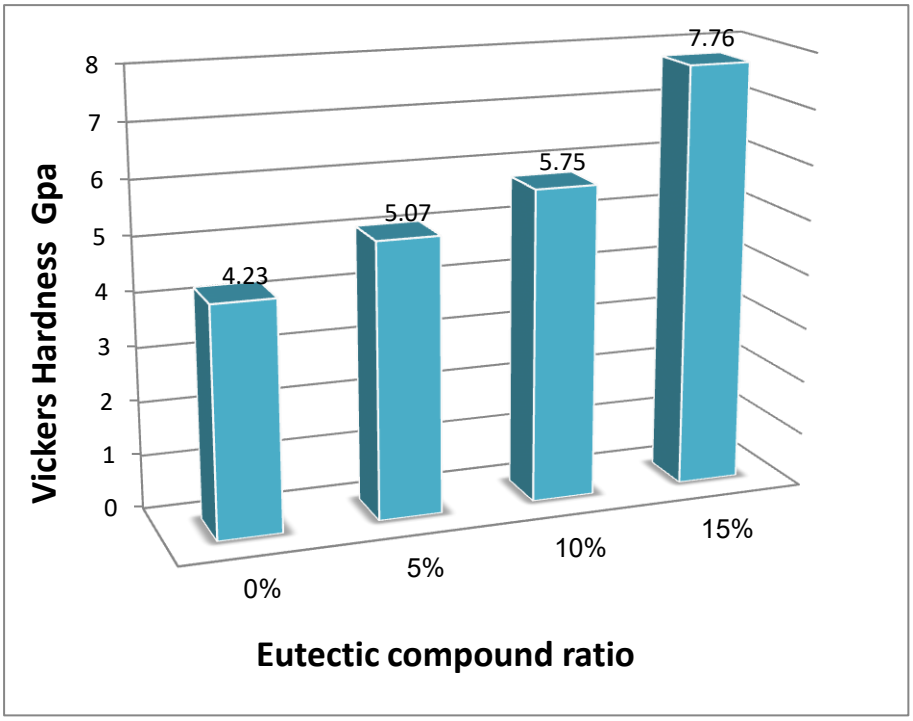


Figure4.26: The effect of eutectic component($K_5V_3O_{10}$+ KVO_3) on Vickers micro hardness of bioactive glasses-ceramic samples A,B,C,D -

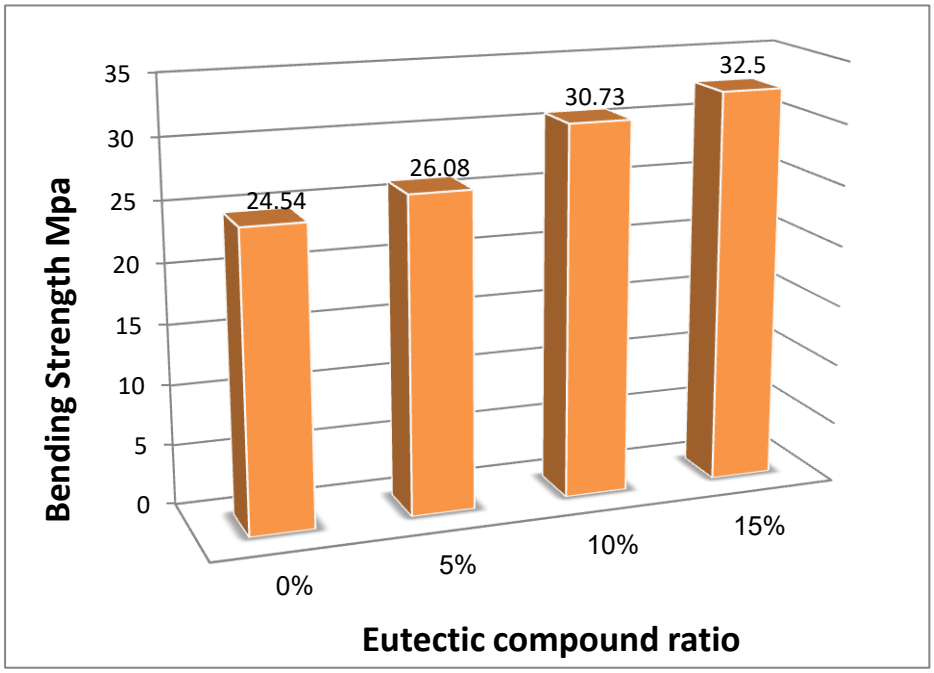


Figure4.27The effect of eutectic component($K_5V_3O_{10}$+ KVO_3) on bending strength of bioactive glasses-ceramic samples A,B,C,D.

Table 4.1 : Comparison of values for the physical-mechanical properties of bone **[11,21,101]** and bioactive glass-ceramic samples produced.

Properties	**Cortical bone**	**Cancellous bone**	**Bioactive glass- ceramic**			
			0%	**5%**	**10%**	**15%**
Density (g/cm^3)	1.6–2.1	1.0	2.451	2.459	2.467	2.489
Porosity (%)	5-30	30-90	19.88	19.01	18.12	14.83
Compression strength .MPa	100-135	23	96.05	99.75	103.98	137.76
Vickers hardness (Gpa)	---	---	4.23	5.07	5.75	7.76
Bending strength (Mpa)	50-150	10-20	24.54	26.08	30.73	32.5

4.8 Biological Response of Bioactive glasses-Ceramic Samples after Immersion in SBF

Growth of hydroxyapatite in the form of a layer on the surface of the implanted material in the body indicates that the material is active and has the ability to adhere to the bone tissue. The ion exchange occurred between Ca^{2+} and Na^{2+} from manufacturer glass_ceramic samples and H_3O^+ in simulating fluid SBF and breaking the silica bond Si – O – Si When immersing the samples in a solution for 21 days at a temperature of 37^0C and PH = 7.4 and after two days emergence of a sponge-like layer that can be seen by the eye was deposited on the surface of the sample with a percentage 10% addition , as well as a thin layer on the sample without addition, and successively during the immersion period, a layer was formed on all the samples. Then we carefully extract the samples from the solution and put it in the drying oven for 48 hours at a temperature of 120 °C the confirmation of the following tests indicates that this layer is hydroxyapatite.

4.8.1 X-ray Diffraction Analysis of Bioactive glass-Ceramic Samples After Immersion in SBF Solution

For the purpose of knowing the chemical composition of the sponge-like layer formed on the samples after drying, an X-ray diffraction device was used at scanning angle from 30 to 50 degrees for all proportions of the manufactured samples with the eutectic compound (0,5,10,15)% respectively and as shown in Figure 4.11, the results compound are ($Ca_5(PO_4)_3OH$) corresponding to the (ICSD, Card No. 01-084-1998).) and all peaks that belong to the metasilicates phase was disappeared. By using the High Score analysis program, we extracted the crystallographic parameters which is: the crystal system is hexagonal , a= 9.4166Å , b= 9.4166Å, c= 6.8745Å and the miller indices (h, k, l) through the levels of plan reflections (121),(112) ,(300) (202),(002), (111), space group P63/m also the density about 3.16 g/cm$^{3)}$ and it is confirmed that is apatite layer . Its Also noted that the intensity of the pick decreases with the percentage of addition and reaches less level at 10% in the Figur4.30 .

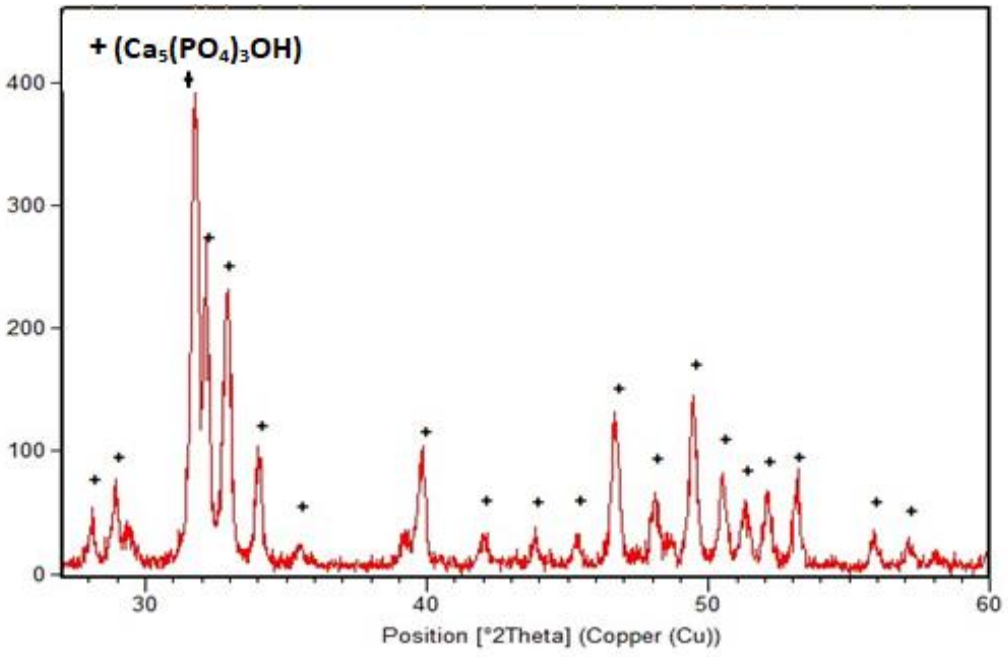


Figure 4.28: The X-ray diffraction analysis of bioactive glass-ceramic sample (A) after immersion in SBF and the formation of hydroxyapatite on the outer layer of the sample.

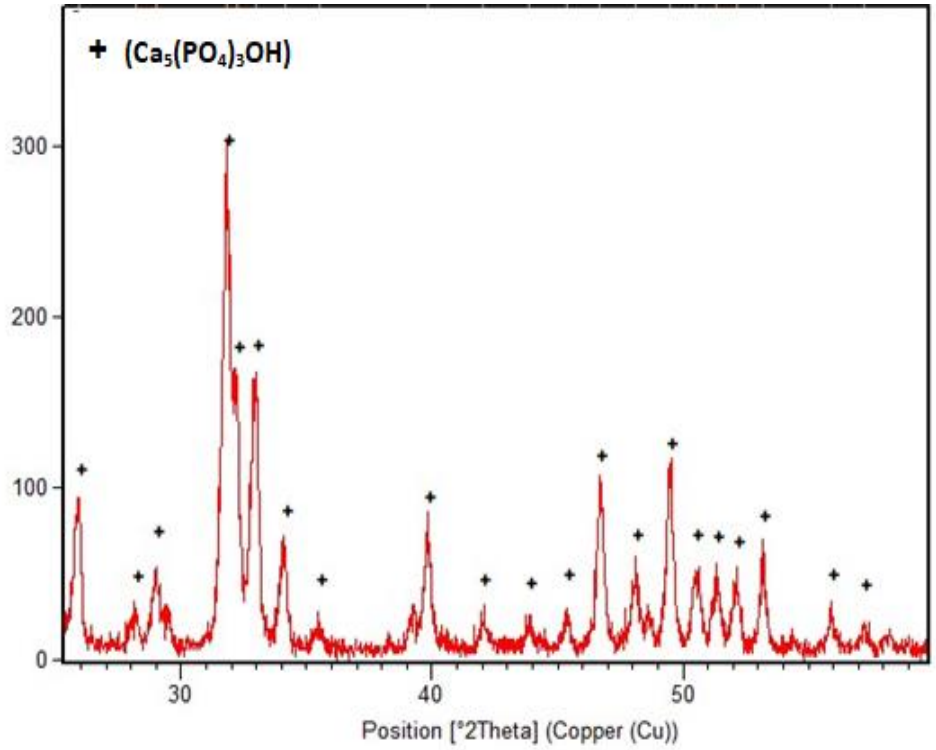


Figure 4.29: The X-ray diffraction analysis of bioactive glass-ceramic sample (B) after immersion in SBF and the formation of hydroxyapatite on the outer layer of the sample.

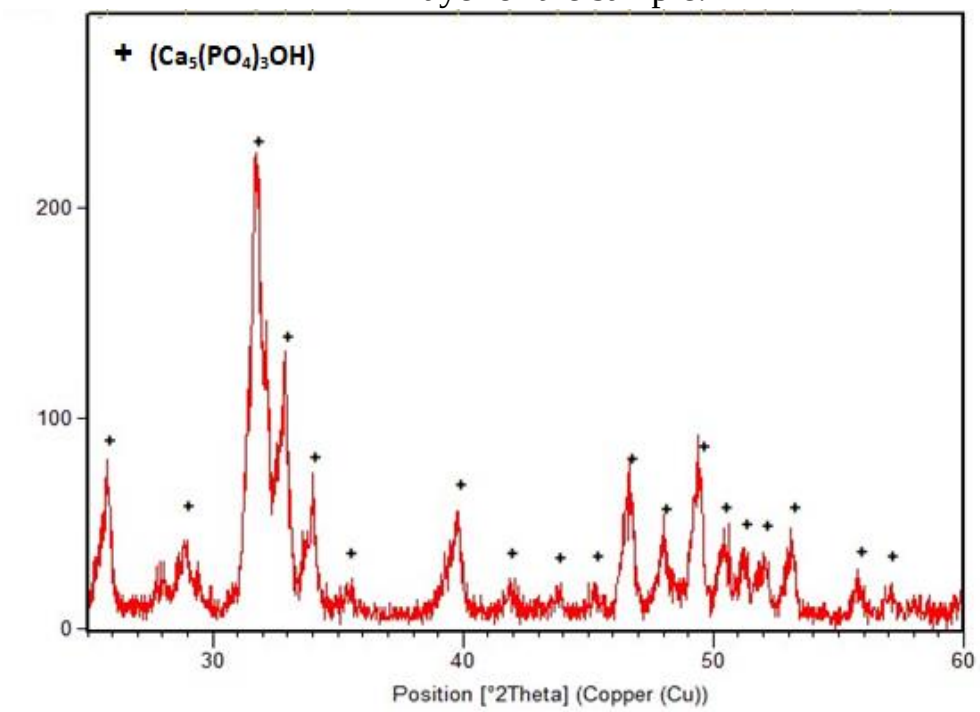


Figure 4.30: The X-ray diffraction analysis of bioactive glass-ceramic sample (C) after immersion in SBF and the formation of hydroxyapatite on the outer layer of the sample.

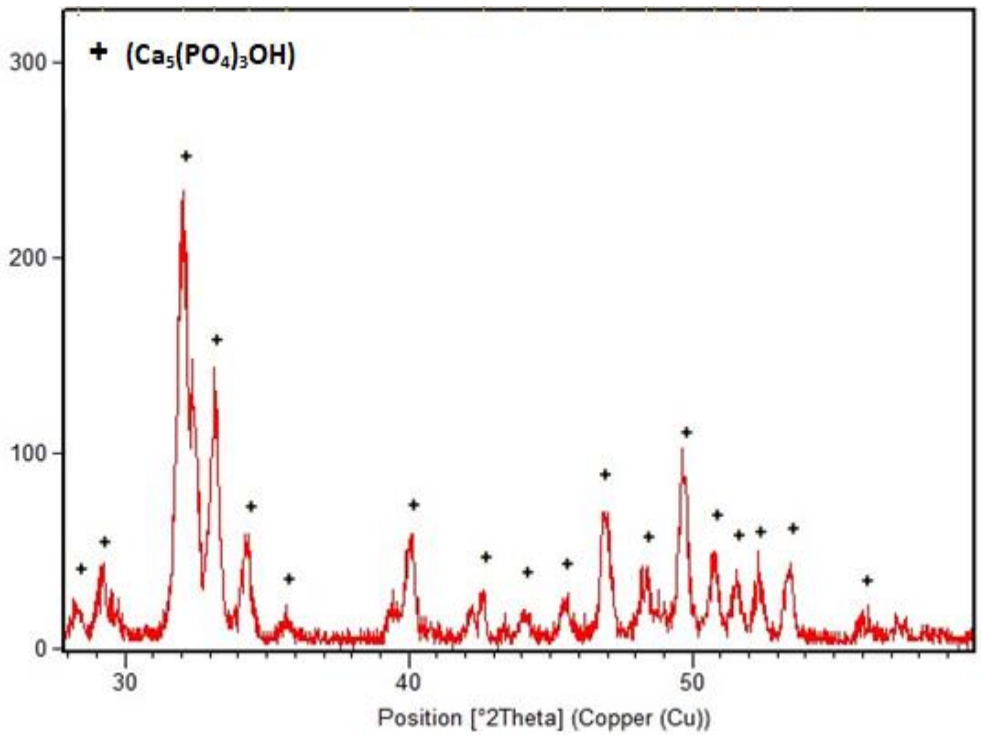
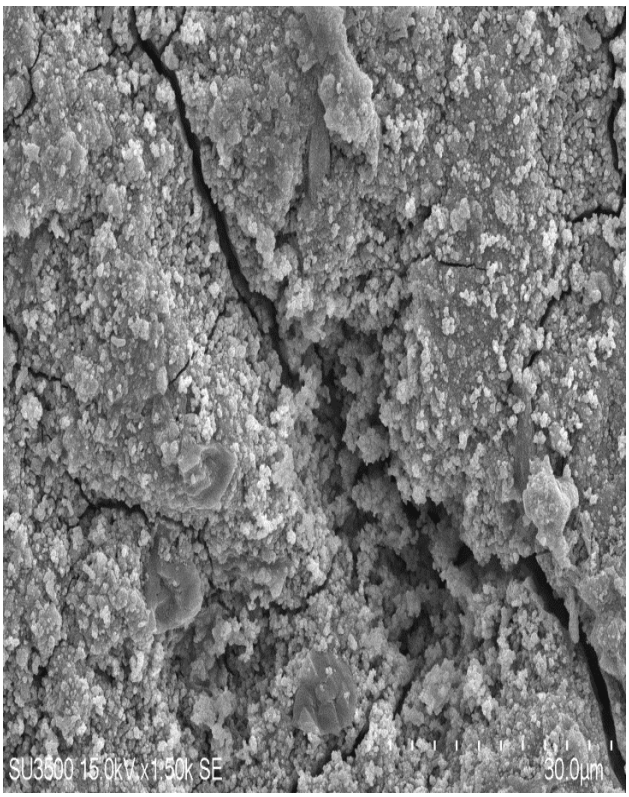


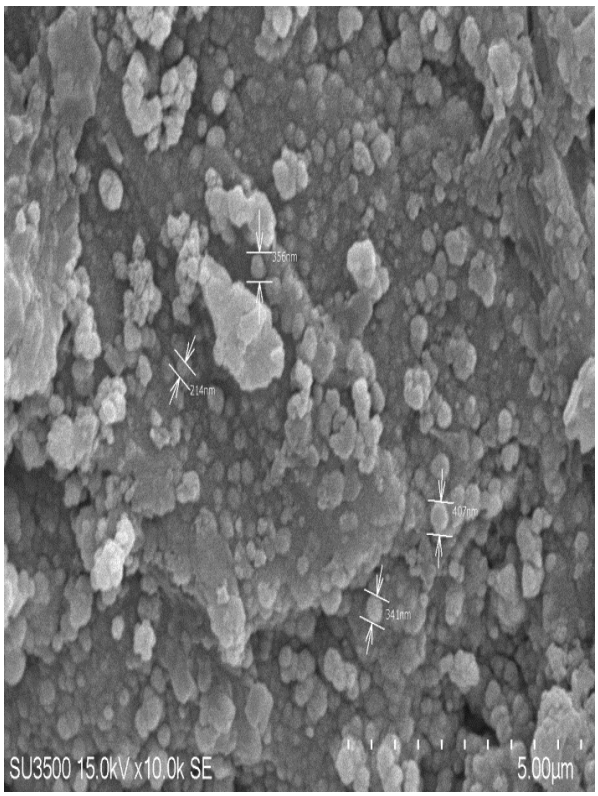
Figure 4.31: The X-ray diffraction analysis of bioactive glass-ceramic sample (D) after immersion in SBF and the formation of hydroxyapatite on the outer layer of the sample.

4.8.2 SEM and EDS Analysis's of Samples after Immersion in SBF Solution

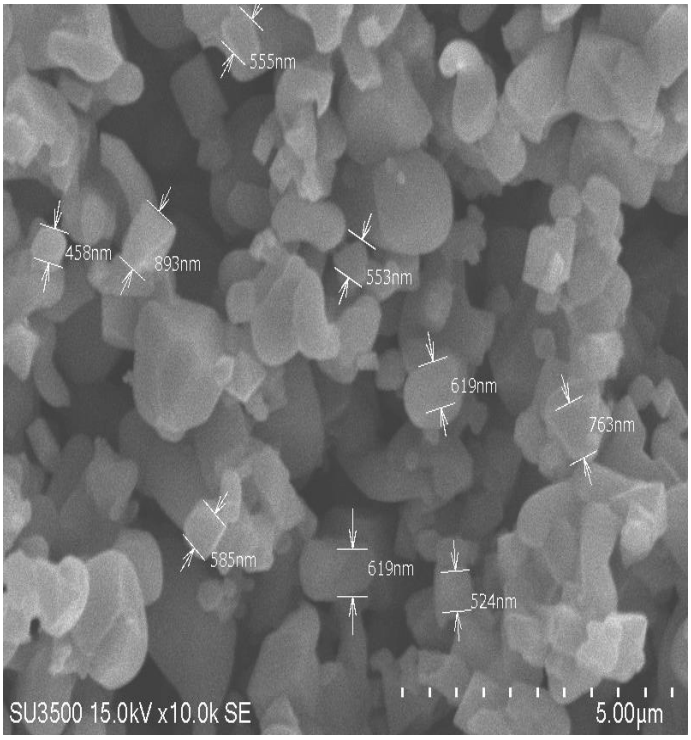
After drying the samples, they are prepared for examination using the SEM device (SU3500, Iran) with high magnification power up to Nano in order to see the changes that take place in the microstructure and morphology of the sample and the growth of crystals on the surface resulting from the process of the dissolution the sample in SBF solution. The formation of ($Ca_5(PO_4)_3OH$) was confirmed by X-ray analysis and the pictures in Figure (4.32-4.33-4.34) below show the growth of the hydroxyapatite layer in the form of small balls ,Fibrous bushes, or irregular gatherings. Through the result of the analysis of the EDS apparatus for the glasses_ceramic samples , its noted the deposition of elements

on the surface of the sample, as well as other elements from the SBF solution such as Mg, Cl. Can calculate the ratio of calcium to phosphorous deposited on the samples as Ca/p = 1.86 : 1.88 : 1.07 For the percentage of addition 0 % . 10 % .15% . because of the increase in the percentage of a compound($K_5V_3O_{10}$+ KVO_3) led to a decrease in the activity of the implanted material and a decrease in its percentage of Ca/p .

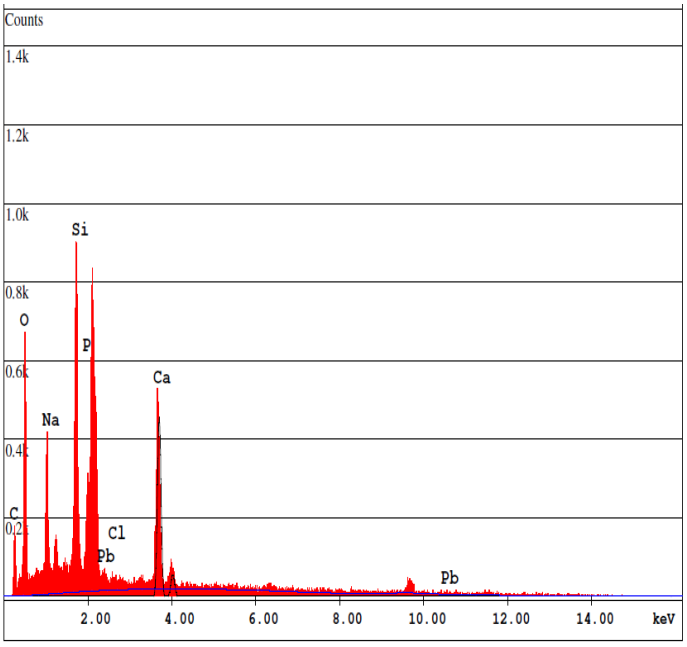




- a - - b -



- c -



- d -

Figure4.32 : (a ,b ,c , d)Result of analyzing bioactive glass-ceramic sample (A) without substitution using SEM and EDS device .

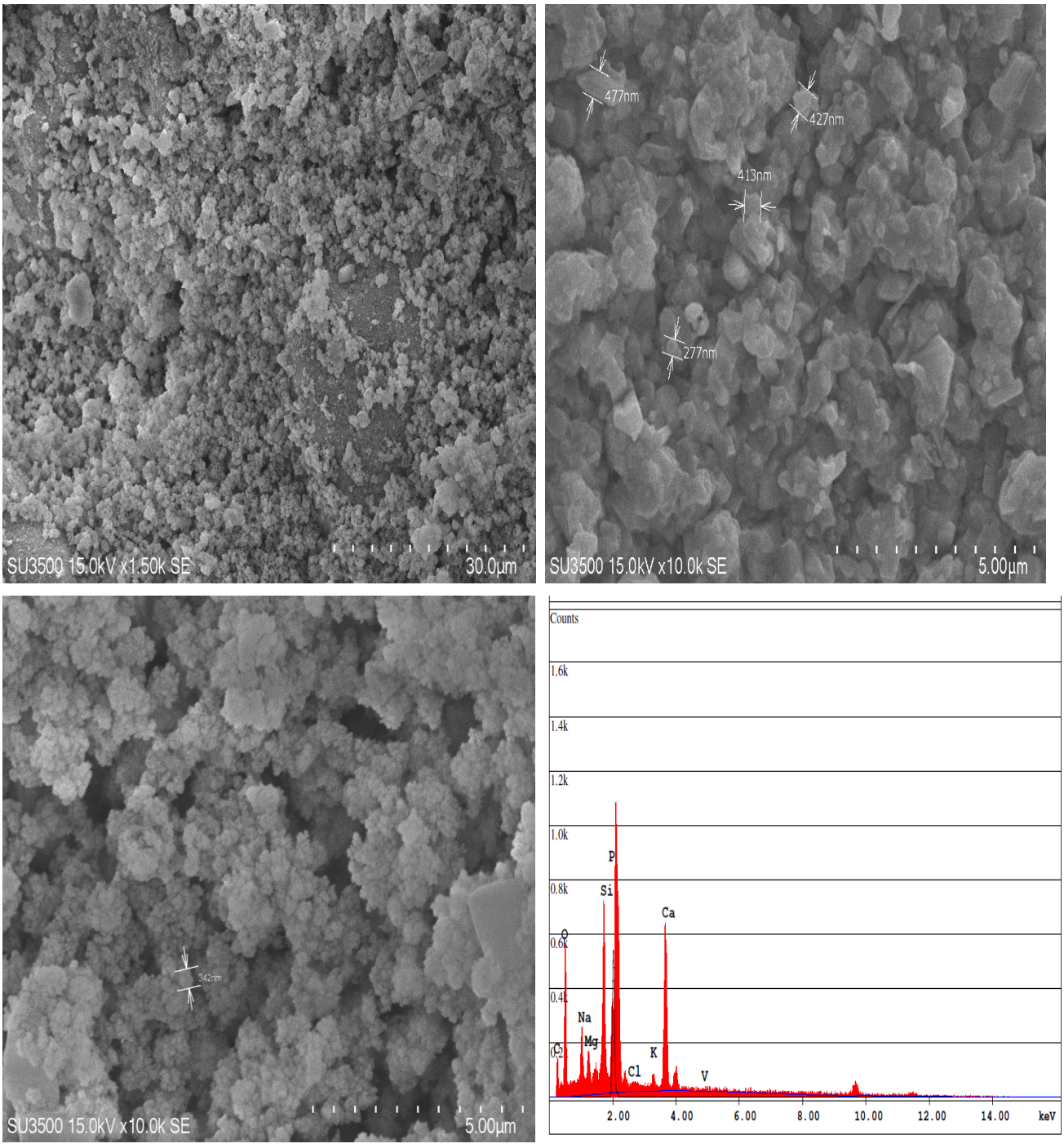


Figure4.33 : Result of analyzing bioactive glass-ceramic sample (C) with 10 % substitution using SEM and EDS device .

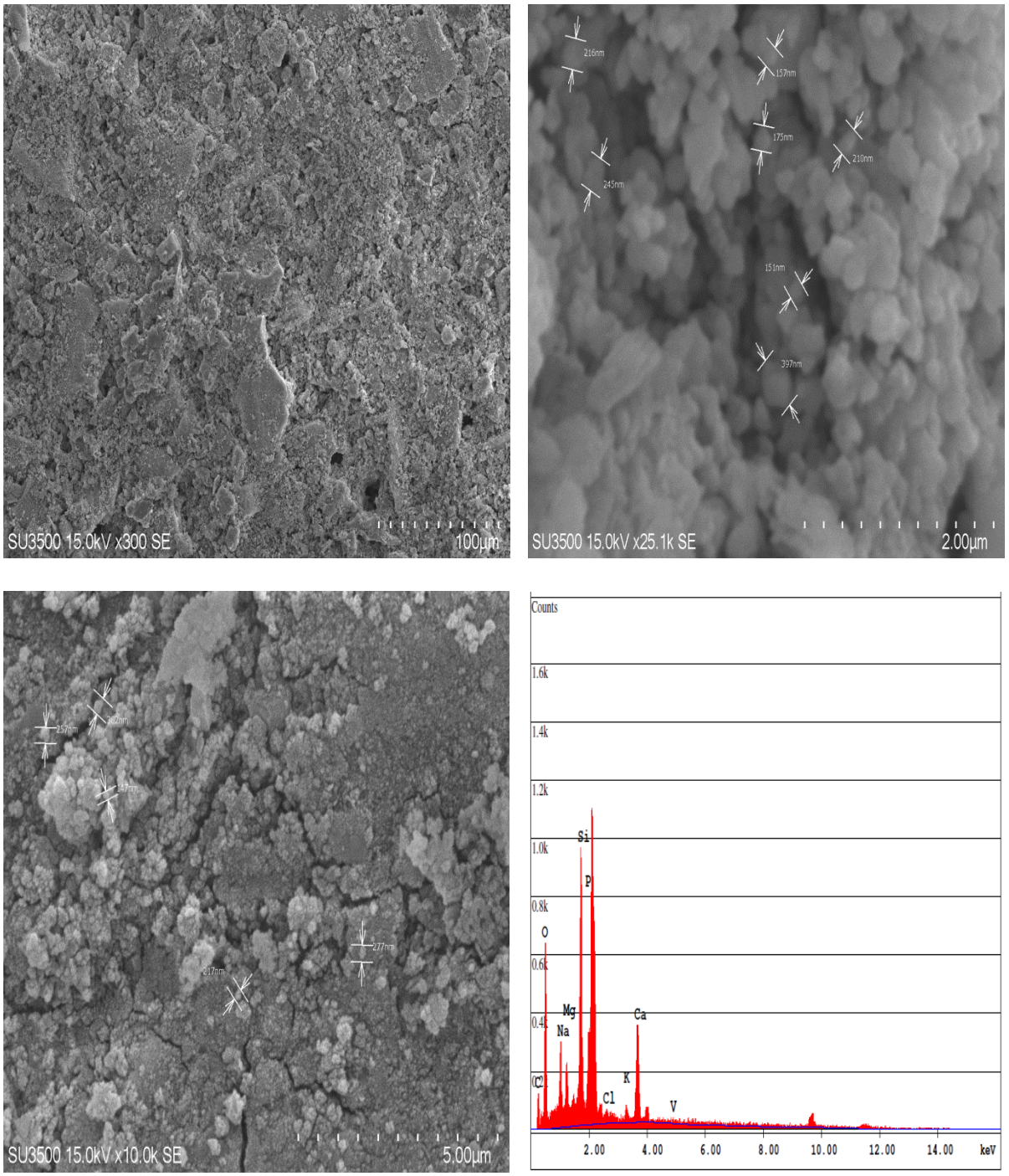


Figure 4.34 : Result of analyzing bioactive glass-ceramic sample (D) with 15% substitution using SEM and EDS device .

4.9 Antibacterial efficacy of bioactive glass-ceramic samples (Kirby_Bauer test)

Three samples of bioactive glass-ceramic with dimension(H =5 mm, D =12mm) were placed in an agar disc, and this disc contains bacteria of the type(E-coli bacteria, Urine culture) , which are found in the vivo. After that, the disc was placed in an incubator at a temperature of 37 °C, and after 24 hours of cultivation, the samples were taken out of the incubator to know the effect of bacteria on them. During the formation of a circular dark ring around the samples with a diameter that varies according to its bactericidal effect (inhibition zone diameter (IZD)) . However, as can be seen in the Figure(4.35), the bioactive glass-ceramic samples do not have a ring around them, indicating that they have a bactericidal action, even in bioactive glass-ceramic samples that contain an eutectic compound. Where there is no effect of vanadium oxide or potassium oxide on this type of bacteria.

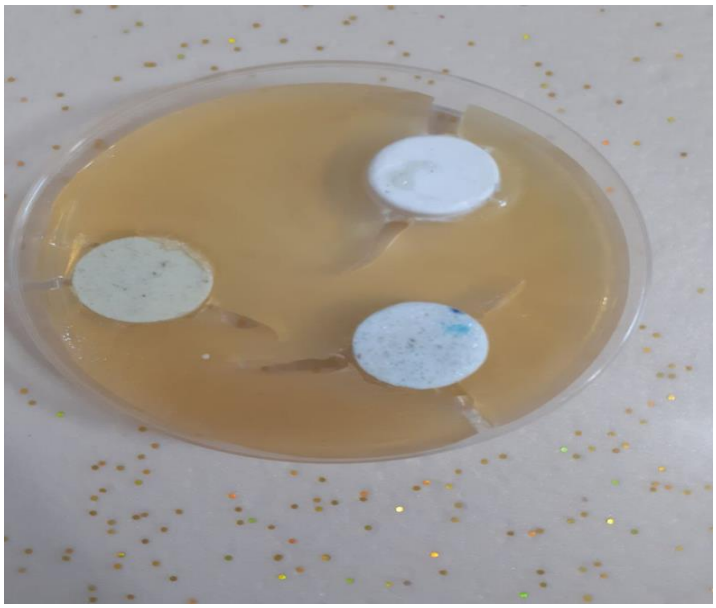


Figure4.35: Bioactive glass-ceramic Samples (A,C,D)placed in the agar disc containing bacteria (E- Coli).

Chapter Five

Conclusions and recommendations

Chapter Five

Conclusions and recommendations

The process of manufacturing bioactive glass-ceramic with the addition of an eutectic compound led to

1- The ($K_5V_3O_{10}$+ KVO_3) compound was obtained from finding eutectic point between the binary system V_2O_5 39%:K_2O 61% at 501^{0}C for 2 hours.
2- The melting point of the glass was decrease from 1400 °C to 1100 °C because the effect of the substitution with the eutectic compound ($K_5V_3O_{10}$+ KVO_3) at ratio 15 %.
3- In the process of sintering glass, it was found that above 600°C crystallizes and turns into glass- ceramic , but to make the structure cohesive and well sintered, it was sintered at a temperature of 1000°C .The main phase formed in the glass-ceramic without substitution is (Na_4Ca_4 Si_6 O_{18}) where was detected by X-ray diffraction analysis,with the substitution of the eutectic compound to the mixture, it led to the formation of a phase ($Na_4Ca_4Si_6O_{18}$) in addition to ($K_{.5}V_3O_5$) in all proportions 5%,10%,15%.
4- Through the results of the scanning electron microscope examination of the samples, the highest crystallization rate was shown with the percentage 10%.
5- An improvement in the physical and mechanical properties of bioactive glass-ceramic , where a rise in density with an increase in the percentage of addition and a decrease in porosity led to an improvement in the mechanical properties, as a significant increase in the compressive strength, bending strength and Vickers micro hardness.

6- Cultivation of samples in a solution of SBF that forms a layer of hydroxyapatite on the surface of the sample after two days of immersion on the surface of the sample with 10% substitution in also to formed a very thin layer on the surface of the sample without additives, After a few days, a layer formed on the surface of the other samples.

7- The presence of a compound ($Ca_5(PO_4)_3OH$) is detected by used X-ray for the surface of the samples .

8- SEM pictures showed a good growth of hydroxyapatite on the surface of the samples , The EDS examination of the surface of the submerged samples showed the precipitate of calcium and phosphorus elements in a percentage 1.86 : 1.88 : 1.07.

9- The samples placed in an Agar disc for the purpose of Kirby's test showed that they were not lethal to bacteria.

5.2 Recommendations

1- Use different sintering temperatures and times, and study its effect on the physical , mechanical and biological properties.

2-The use of other oxides with a low melting point and good properties and the formation of a eutectic compound to reduce the melting point to a large extent for example, boron oxide with potassium oxide.

3- Synthesis glass-ceramic scaffold with the same composition that used in this work and increase the porosity by adding any volatile substance without effect on structure .

Reference

1. dos Santos, V ,Brandalise, R.N, & Savaris, M. (2017). Biomaterials: characteristics and properties. In Engineering of Biomaterials (pp. 5-15). Springer, Cham.
2. El Damrawi, G, Hassan, A. K, Kamal, H., Aboelez, M, & Labeeb, S. (2016). Structural Investigations on Na2O-CaO-V2O5-SiO2 Bioglass Ceramics. British Journal of Applied Science & Technology, 16, 1-9.
3. Fernandes, H. R, Gaddam, A, Rebelo, A, Brazete, D., Stan, G. E, & Ferreira, J. M. (2018). Bioactive glasses and glass-ceramics for healthcare applications in bone regeneration and tissue engineering. Materials, 11(12), 2530.
4. Ylänen, H. (Ed.). (2017). Bioactive glasses: materials, properties and applications. Woodhead Publishing.
5. Brauer, D. S. (2015). Bioactive glasses-structure and properties. Angewandte Chemie International Edition, 54(14), 4160-4181.
6. Fiume, E, Barberi, J, Verné, E, & Baino, F. (2018). Bioactive glasses: from parent 45S5 composition to scaffold-assisted tissue-healing therapies. Journal of functional biomaterials, 9(1), 24.
7. Hench, L. L. (2013). Chronology of bioactive glass development and clinical applications.
8. Strnad, Z, & Sestak, J. (1999, July). Bio-compatible ceramics as mimetic material for bone tissue substitution. In Proceedings of the Second International Conference on Intelligent Processing and Manufacturing of Materials. IPMM'99 (Cat. No. 99EX296)(Vol. 1, pp. 431-436). IEEE.
9. Krishnan. V, & Lakshmi, T. (2013). Bioglass: A novel biocompatible innovation. Journal of advanced pharmaceutical technology & research, 4(2), 78.

Reference

10. Peitl. O, Zanotto, E. D, Serbena, F. C, & Hench, L. L. (2012). Compositional and microstructural design of highly bioactive P2O5–Na2O–CaO–SiO2 glass-ceramics. Acta biomaterialia, 8(1), 321-332.

11. Kaur, G, Kumar, V, Baino, F., Mauro, J. C., Pickrell, G., Evans, I., & Bretcanu, O. (2019). Mechanical properties of bioactive glasses, ceramics, glass-ceramics and composites: State-of-the-art review and future challenges. Materials science and engineering: C, 104, 109895.

12. Park, J. (2009). Bioceramics: properties, characterizations, and applications (Vol. 741). Springer Science & Business Media.

13. Saad, R, Edrees, S. J, & Hadi, A. Fabrication of Zinc calcium phosphate for antibacterial applications.

14. Deliormanli, A. M. (2014). In vitro assessment of degradation and mineralisation of V2O5 substituted borate bioactive glass scaffolds. Materials Technology, 29(6), 358-365.

15. Arstila, H. (2008). Crystallization characteristics of bioactive glasses.

16. R., Riaz, M., Hameed, I., & Afifa, A. (2017). The effect of K2O on the microstructure of Na2O-CaO-P2O5-SiO2 based ceramic system. Optik, 129, 15-20.

17. Ye-Qing, Chen, et al. "Phase relations in the ZnO-V2O5-K2O system." Chinese Physics B 20.7 (2011): 076402.

18. Abdalwahad, M. S. R. I., & Edrees, A. P. D. S. J. Preparation of Hydroxyapatite and Bioactive Glass Ceramic to Get Biocomposite by Using a Genetic Algorithm Method.

19. Julian R. Jones. “Bio-Glasses: an introduction”.2012. John Wiley & Sons

20. El-Meliegy, E., & Noort, R. V. (2012). Theoretical Estimation of Glass Properties. In Glasses and Glass Ceramics for Medical Applications (pp. 79-93). Springer, New York, NY.

Reference

21. Levingstone, Tanya J. (2008).Ceramics for medical applications.

22. Park, J, & Lakes, R. S. (2007). Biomaterials: an introduction. Springer Science & Business Media.

23. Foroutan, F. (2015). Sol-gel synthesis of phosphate-based glasses for biomedical applications (Doctoral dissertation, UCL (University College London)).

24. Raghavendra, G. M., Varaprasad, K, & Jayaramudu, T. (2015). Biomaterials: design, development and biomedical applications. In Nanotechnology applications for tissue engineering (pp. 21-44). William Andrew Publishing.

25. Bovo, N. (2007). Structure-properties relationships in bioactive glasses for PAA-based polyalkenoate cements.

26. Anderson, J. M. (2001). Biological responses to materials. Annual review of materials research, 31(1), 81-110.

27. Pruitt, L, & Chakravartula, A. (2011). Biocompatibility, sterilization, and materials selection for implant design. In Mechanics of Biomaterials: Fundamental Principles for Implant Design(Cambridge Texts in Biomedical Engineering, pp. 3-25). Cambridge: Cambridge University Press.

28. Abd Aladel, B, Sabree, I. K., & Edrees, S. J. (2019). Effects of MgO wt.% on the structure, mechanical, and biological properties of bioactive glass-ceramics in the SiO2, Na2O, CaO, P2O5, MgO system. Int J Mechanical Engineer Technol, 10(1), 97-106.

29. Aza Moya, A. H. D, Aza, P. N. D., & Aza Pendas, S. D. (2005). Crystalline Bioceramic Materials.

Reference

30. Patel, N. R, & Gohil, P. P. (2012). A review on biomaterials: scope, applications & human anatomy significance. International Journal of Emerging Technology and Advanced Engineering, 2(4), 91-101.

31. Hench, L. L. (1991). Bioceramics: from concept to clinic. Journal of the american ceramic society, 74(7), 1487-1510.

32. Dee, K. C, Puleo, D. A., & Bizios, R. (2003). An introduction to tissue-biomaterial interactions. John Wiley & Sons.

33. Li, Y. (2014). Investigating the Structure, Solubility and Bioactivity of Na/Sr Bioactive Glasses/Glass-Ceramics (Doctoral dissertation, New York State College of Ceramics at Alfred University. Kazuo Inamori School of Engineering).

34. Pantulap, U, Arango-Ospina, M., & Boccaccini, A. R. (2022). Bioactive glasses incorporating less-common ions to improve biological and physical properties. Journal of Materials Science: Materials in Medicine, 33(1), 1-41.

35. Hench, L. L, Day, D. E., Höland, W, & Rheinberger, V. M. (2010). Glass and medicine. International Journal of Applied Glass Science, 1(1), 104-117.

36. Baino, F., Novajra, G., Miguez-Pacheco, V., Boccaccini, A. R., & Vitale-Brovarone, C. (2016). Bioactive glasses: Special applications outside the skeletal system. Journal of Non-Crystalline Solids, 432, 15-30.

37. Nandi, S. K., Kundu, B., & Datta, S. (2011). Development and applications of varieties of bioactive glass compositions in dental surgery, third generation tissue engineering, orthopaedic surgery and as drug delivery system. Biomaterials applications for nanomedicine, 4, 69-116.

Reference

38. Farooq, I, Ali, S, Husain, S., Khan, E, & Hill, R. G. (2019). Bioactive glasses—structure and applications. In Advanced Dental Biomaterials (pp. 453-476). Woodhead Publishing.

39. Vichery, C, & Nedelec, J. M. (2016). Bioactive glass nanoparticles: from synthesis to materials design for biomedical applications. Materials, 9(4), 288.

40. Tilocca, A, & Cormack, A. N. (2010). Surface signatures of bioactivity: MD simulations of 45S and 65S silicate glasses. Langmuir, 26(1), 545-551

41. Tilocca, A, & Cormack, A. N. (2009). Modeling the water– bioglass interface by ab initio molecular dynamics simulations. ACS Applied Materials & Interfaces, 1(6), 1324-1333.

42. Kaur, G. (2017). Biomaterials influencing human lives. In Bioactive glasses (pp. 1-20). Springer, Cham.

43. O'Donnell, M. D. (2012). Melt-derived bioactive glass. Bio-glasses. Chichester (UK): Wiley, 13-28.

44. Hampshire, S. (2015) Bioglasses Bioglasses and Bioglass-ceramics. University of Limerick, Ireland, Madrid, Spain, 17-19 .

45. ZUNIGA-HEREDIA, E. E, NAGASAKI, R, KAWAMURA, N., & IIJIMA, M. (2021). Network modifiers of bioactive glasses.

46. Farooq, I, Imran, Z, Farooq, U, Leghari, A, & Ali, H. (2012). Bioactive glass: a material for the future. World J Dent, 3(2), 199-201.

47. Tilocca, A, & Cormack, A. N. (2007). Structural effects of phosphorus inclusion in bioactive silicate glasses. The Journal of Physical Chemistry B, 111(51), 14256-14264.

48. Aoyagi, T, Kohara, S, Naito, T, Onodera, Y, Kodama, M, Onodera, T& Takizawa, H. (2020). Controlling oxygen coordination and valence of network forming cations. Scientific reports, 10(1), 1-12.

Reference

49. Heyliger, Clayton E, Arun G. Tahiliani, and John H. McNeill. "Effect of vanadate on elevated blood glucose and depressed cardiac performance of diabetic rats." Science 227.4693 (1985): 1474-1477.

50. Cohen, Neil, et al. "Oral vanadyl sulfate improves hepatic and peripheral insulin sensitivity in patients with non-insulin-dependent diabetes mellitus." The Journal of clinical investigation 95.6 (1995): 2501-2509.

51. Scior, T, Antonio Guevara-Garcia, J, Do, Q. T, Bernard, P, & Laufer, S. (2016). Why antidiabetic vanadium complexes are not in the pipeline of "big pharma" drug research? A critical review. Current medicinal chemistry, 23(25), 2874-2891.

52. Das, S., Roy, A., Barui, A. K., Alabbasi, M. M. A., Kuncha, M., Sistla, R. & Patra, C. R. (2020). Anti-angiogenic vanadium pentoxide nanoparticles for the treatment of melanoma and their in vivo toxicity study. Nanoscale, 12(14), 7604-7621.

53. Rabiee, S. M, Nazparvar, N, Azizian, M, Vashaee, D, & Tayebi, L. (2015). Effect of ion substitution on properties of bioactive glasses: A review. Ceramics International, 41(6), 7241-7251.

54. Montazerian, M., & Dutra Zanotto, E. (2016). History and trends of bioactive glass-ceramics. Journal of Biomedical Materials Research Part A, 104(5), 1231-1249.

55. Karpukhina, N, Hill, R. G, & Law, R. V. (2014). Crystallisation in oxide glasses–a tutorial review. Chemical Society Reviews, 43(7), 2174-2186.

56. Hasanuzzaman, M, Rafferty, A, Sajjia, M, & Olabi, A. G. (2016). Properties of glass materials.

57. Fernandes, J. S, Gentile, P, Pires, R. A., Reis, R. L., & Hatton, P. V. (2017). Multifunctional bioactive glass and glass-ceramic biomaterials

with antibacterial properties for repair and regeneration of bone tissue. Acta biomaterialia, 59, 2-11.

58. Fokin, V. M, Zanotto, E. D, & Schmelzer, J. W. (2003). Homogeneous nucleation versus glass transition temperature of silicate glasses. Journal of Non-Crystalline Solids, 321(1-2), 52-65.

59. Zanotto, E. D, & Fokin, V. M. (2003). Recent studies of internal and surface nucleation in silicate glasses. Philosophical Transactions of the Royal Society of London. Series A: Mathematical, Physical and Engineering Sciences, 361(1804), 591-613.

60. Parithimarkalaignan, S., & Padmanabhan, T. V. (2013). Osseointegration: an update. The Journal of Indian Prosthodontic Society, 13(1), 2-6.

61. Giannoudis, P. V, Dinopoulos, H, & Tsiridis, E. (2005). Bone substitutes: an update. Injury, 36(3), S20-S27.

62. Janicki, P, & Schmidmaier, G. (2011). What should be the characteristics of the ideal bone graft substitute? Combining scaffolds with growth factors and/or stem cells. Injury, 42, S77-S81.

63. Sheikh, Z, Najeeb, S, Khurshid, Z, Verma, V, Rashid, H., & Glogauer, M. (2015). Biodegradable materials for bone repair and tissue engineering applications. Materials, 8(9), 5744-5794.

64. Dash, S. R. (2015). Effect of Fabrication Methods on the Porosity, Microstructure, Strength and In-Vitro Bioactivity of Porous Hydroxyapatite Scaffolds (Doctoral dissertation).

65. Fu, Q. (2009). Freeze casting of bioactive glass and ceramic scaffolds for bone tissue engineering. Missouri University of Science and Technology.

66. Dashevskiy, I, Balueva, A, Todebush, P, Campbell, C, Magana, J, & Clement, N. (2019). On estimation of adhesive strength of implants

bioactive coating with titanium by density functional theory and molecular dynamics simulations. Materials Research, 22.

67. Murty, H. P. (2012). Development of Porous Bioactive SiO2-Na2O-CaO-P2O5 Glass Ceramic Scaffold (Doctoral dissertation).

68. Hench, L. L. (1997). Sol-gel materials for bioceramic applications. Current Opinion in Solid State and Materials Science, 2(5), 604-610.

69. Fitzgerald, V. (2007). Structural Characterisation of Bioactive Glasses. University of Kent (United Kingdom).

70. Alsultani, Hawraa Oday, and Shaker Jahil Almohna. "Manufacturing and characterization of bioglass for bio application." Advances in natural and applied sciences 10.17 (2016): 135-143.

71. Boccaccini, A. R, Brauer, D. S, & Hupa, L. (Eds.). (2016). Bioactive glasses: fundamentals, technology and applications. Royal Society of Chemistry

72. Owens, G. J, Singh, R. K, Foroutan, F, Alqaysi, M, Han, C. M., Mahapatra, C, & Knowles, J. C. (2016). Sol–gel based materials for biomedical applications. Progress in materials science, 77, 1-79.

73. Carter, C. B, & Norton, M. G. (2013). Sols, gels, and organic chemistry. In Ceramic Materials (pp. 411-422). Springer, New York, NY.

74. Fagerlund, S, & Hupa, L. (2016). Melt-derived bioactive silicate glasses.

75. Grumezescu, A. M, & Grumezescu, V. (Eds.). (2019). Materials for Biomedical Engineering: Bioactive Materials, Properties, and Applications. Elsevier.

76. Kaur, G, Pickrell, G, Sriranganathan, N, Kumar, V, & Homa, D. (2016). Review and the state of the art: sol–gel and melt quenched bioactive glasses for tissue engineering. Journal of Biomedical Materials Research Part B: Applied Biomaterials, 104(6), 1248-1275.

Reference

77. Kokubo, T. (Ed.). (2008). Bioceramics and their clinical applications. Elsevier.

78. Li, J. J, Kaplan, D. L, & Zreiqat, H. (2014). Scaffold-based regeneration of skeletal tissues to meet clinical challenges. Journal of materials chemistry B, 2(42), 7272-7306.

79. Wu, X. Walsh, K, Hoff, B. L, & Camci-Unal, G. (2020). Mineralization of biomaterials for bone tissue engineering. Bioengineering, 7(4), 132.

80. Sedel, Laurent, and Christian Rey, eds. *(*1997) *Bioceramics Volume 10*. Vol. 10. Elsevier.

81. Cannillo, V, & Sola, A. (2009). Potassium-based composition for a bioactive glass. Ceramics international, 35(8), 3389-3393.

82. Majhi MR, Pyare R, Singh SP. (2011).Studies on preparation and characterizations of CaO–Na 2145 2O–SiO2–P2O5 bioglass ceramics substituted with Li2O, K2O, ZnO, MgO, and B2O3. Int J Sci Eng Res.

83. Kim, T, Hwang, C, Gwoo, D, Park, H, & Ryu, B. K. (2012). Effects of substitution of K2O for Na2O on the bioactivity of CaO-Na2O-SiO2-P2O5 glasses. Electronic Materials Letters, 8(5), 541-544.

84. Deliormanli, A. M. (2014). In vitro assessment of degradation and mineralisation of V2O5 substituted borate bioactive glass scaffolds. Materials Technology, 29(6), 358-365.

85. Mohamad, S. H, & Muhamad Nor, M. A. A. (2017). Effect of Na2O and K2O on the Solubility and Chemical Properties of P2O5-CaO-Na2O-K2OAl2O3 Glass. In Materials Science Forum (Vol. 888, pp. 146-150). Trans Tech Publications Ltd.

86. Dimitriadis, K, Moschovas, D, Tulyaganov, D. U, & Agathopoulos, S.(2020). Development of novel bioactive glass-ceramics in the Na2O /

K2O CaO-MgO-SiO2-P2O5-CaF2 system. Journal of Non-Crystalline Solids, 533,119936.

87. Silva, L. D, Puosso, F. C, Soares, V. O, Peitl Filho, O., do RF Sabino, S.Serbena, F. C, & Zanotto, E. D. (2021).Two-step sinter crystallization of K2O-CaO-P2O5–SiO2(45S5-K) bioactive glass. Ceramics International , 47(13), 18720-18731.

88. Lowell, S, & Shields, J. E. (1991). Powder surface area and porosity (Vol. 2). Springer Science & Business Media.

89. Mitchell, B. S. (2004). An introduction to materials engineering and science for chemical and materials engineers. John Wiley & Sons.

90.ASTM standards: C373-88, 1999. "standard test method for water absorption, bulk density, apparent porosity and apparent specific gravity of fired white ware products".

91.J. Martin-Marquez, J. Ma. Rincon, M. Romero, 2008, " Effect of firing temperature on sintering of porcelain stoneware tiles " Ceramics International Vol 34, p 1867-1873.

92. Heness, G., Booth, N, & Ben-Nissan, B. (2014). Specimen Size Effects on the Compressive Strength of Porous, Open Cell Ceramics-Size Matters. Journal of the Australian Ceramics Society Volume, 50(2), 176-179.

93. Sadighpour, L, F. Geramipanah, and B. Raeisi. "In vitro mechanical tests for modern dental ceramics." (2006): 143-152.

94.Müller, L, & Müller, F. A. (2006). Preparation of SBF with different HCO3-content and its influence on the composition of biomimetic apatites. Acta biomaterialia, 2(2), 181-189.

Reference

95. Giuliano, C, Patel, C. R, & Kale-Pradhan, P. B. (2019). A guide to bacterial culture identification and results interpretation. Pharmacy and Therapeutics, 44(4), 192.

96. Sukumar, N. (2012). A matter of density: exploring the electron density concept in the chemical, biological, and materials sciences. John Wiley & Sons.

97. Miliou, Amalia N., Ramakant Srivastava, and Ramu V. Ramaswamy. "Modeling of the index change in K+–Na+ ion-exchanged glass." Applied optics 30.6 (1991): 674-681.

98. Slater, John C. "Atomic radii in crystals." The Journal of Chemical Physics 41.10 (1964): 3199-3204.

99. Cottrell, T. L. (1958). The strengths of chemical bonds. Butterworths Scientific Publications.

100. Riley, J. F. (1968). STUDIES OF THE THERMAL DECOMPOSITION OF THE POTASSIUM OXIDES IN THE TEMPERATURE RANGE 300--480 DEGREES C. University of Rhode Island.

101. Thompson, I. D., & Hench, L. L. (1998). Mechanical properties of bioactive glasses, glass-ceramics and composites. Proceedings of the Institution of Mechanical Engineers, Part H: Journal of Engineering in Medicine, 212(2), 127-136.

جمهوريـة العراق
وزارة التعليم العالي والبحث العلمي
جامعــة بــابل
كليــة هندسة المواد
قسم هندسة السيراميك ومواد البناء

تحضير وتوصيف زجاج سيراميك حيوي 45S5 في درجات انصهار منخفضه

رسالة

مقدمة الى كلية هندسة المواد/جامعة بابل وهي جزء من متطلبات نيل شهادته

الماجستير في هندسة المواد/السيراميك

من قبل

احمد كريم كاظم عبد علي

(بكالوريوس هندسة المواد اللامعدنية 2015)

واشراف

أ.د. شاكر جاهل ادريس

ميلادي 2022 **هجري 1444**

الملخص

صناعة المواد السيراميكة المستخدمة في التطبيقات الطبية تحتاج إلى تطوير مستمر وإدخال عناصر مفيدة لجسم الإنسان حيث يمكن استخدامها لمليء الفجوات في العظام او ينظم عمل الأنسولين أو للمساعدة في القضاء على بعض الخلايا السرطانية.

تتم عملية تقليل درجة حرارة انصهار الزجاج عن طريق استبدال جزء من مكونات الزجاج بمركب يوتكتك ذو درجة انصهار منخفضة دون التأثير بشكل كبير على بنية الزجاج. تم تحضير مركب اليوتكتك من خلط K_2O (61 mol%) بالإضافة الى V_2O_5 (39 mol%). حيث تم تسخين الخليط عند 501 درجة مئوية لمدة ساعتين. المركب الناتج عبارة عن خليط من اكاسيد البوتاسيوم و الفناديوم ($K_5V_3O1_0$+KVO_3). اما الزجاج فتم تحضيره بالاعتماد على تركيب زجاج Hench (45S5) مع استبدال SiO_2 و Na_2O معا" بمركب اليوتكتك عل ثلاث نسب وزنية (5، 10، 15 wt%). حيث بعد مزج الاكاسيد، تم كلسنتها بدرجة حرارة 900 م° للتخلص من الكربونات في الخليط. بعدها تم رفع درجة الحرارة حتى الانصهار لمدة h 3 بمدى من (1100- 1400) مئوية حسب نسبة الاستبدال. تم اخماد المنصهر في الماء لإنتاج طور زجاجي. وبعد ذلك تم طحن الزجاج و كبسه ثم تلبيده عند 1000 م° لمدة 2 h.

لتوصيف بنية عينات الزجاج-سيراميك الحياتي ، تم استخدام الاختبارات التالية XRD، SEM، FTIR، EDS. كما اجريت الاختبارات الفيزيائية والميكانيكية والبيولوجية لتقييم اداء الزجاج لمحاكاة الظروف التي تتعرض لها المواد المصنعة عند غمرها في الانسجة الحية. كشفت الأشعة السينية عن وجود الاطوار التالية (Na_4Ca_4 Si_6O_{18}) وكمية صغيرة من ($K_5V_3O_5$) في العينات الاخرى. أظهر مقياس فورييه الطيفي الروابط المتكونة في السيراميك الزجاجي والامتصاص بينهما.

أظهرت نتائج الفحوصات الفيزيائية بعد الكبس والتلبيد زيادة في كثافة الزجاج الملبد من 2.451 إلى 2.489 g/cm^3 وانخفاض في كمية المسامية من 19.88٪ إلى 14.83٪ نتيجة تأثير مركب اليوتكتك أيضًا ارتفاع طفيف في الانكماش بعد التلبيد. التحسن في الخواص الميكانيكية للعينة كزيادة مقاومة الانضغاط من 96 إلى 137.76 MPa وكذلك صلادة العينة من (4.23 إلى 7.76) GPa نتج عن تحسن الخواص الفيزيائية والتبلور العالي الذي حصل في العينات نتيجة لتأثير المركب المستبدل. أظهر اختبار النشاط الحيوي أن طبقة إسفنجية من هيدروكسيباتيت ($Ca_5(PO_4)_3OH$) قد تشكلت بعد يومين من الغمر في محلول SBF عند 37 درجة مئوية كما مؤكد بتحليل X-ray وأظهرت صور SEM تكون بلورات على سطح العينات. بينما نتيجة فحص EDS بينت ترسب العناصر على سطح العينات المغمورة وكانت نسب Ca / P هي 1.86: 1.88: 1.07. وعند اجراء اختبار Kirby's_Bauer لعينات الزجاج سيراميك المصنعة تبين انها غير قاتله للبكتريا.