INVESTIGATION OF MICROSTRUCTURAL PROPERTIES OF NEW BIOACTIVE GLASS MATERIALS FOR BIOMEDICAL APPLICATIONS

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I certify that in my opinion the thesis submitted by Muftah Shaban Almokhtar Noum titled "INVESTIGATION OF MICROSTRUCTURAL PROPERTIES OF NEW BIOACTIVE GLASS MATERIALS FOR BIOMEDICAL APPLICATIONS " is fully adequate in scope and quality as a thesis for the degree of Master of Science.

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"My dear professor Idris KABALCI, who opened his doors for me to realize my work, which I did not know at first but learned as I walked, enlightened the path I needed to go with patience and faith, always felt professional and personal support regardless of circumstances, and most importantly, knowledge was exalted with labor, patience and love."

Muftah Shaban Almokhtar Noum

ABSTRACT

M.Sc. Thesis

INVESTIGATION OF MICROSTRUCTURAL PROPERTIES OF NEW BIOACTIVE GLASS MATERIALS FOR BIOMEDICAL APPLICATIONS

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In this thesis, biodegradability and bioactivity behaviors of 45S5 bioactive glass materials have been considered for bone-filling therapy in non-load bearing biomedical device applications were investigated. In this study, we examine the effect of synthesis pathway on the microcrystalline structures, surface morphology, and thermal parameters in vitro dissolution and mineral formation on powders produced by traditional sol-gel method of amorphous on crystalline materials. Many reports and articles have shown that crystalline bio-glass ceramics are biologically more effective than their amorphous counterparts, which is measured by the time minerals begin to form. The 45S5 bioactive glass was synthesized using the traditional solvent crystalline method, and then the thermal heat treatment was compared to obtain a semi-crystalline structure and compared to the commercially available amorphous casting powder available 45S5. The prepared gel samples were heated at 700 °C and accounted for more than 80% of the crystal structure. Dissolution in the form of 45S5

ÖZET

BİYOMEDİKAL UYGULAMALAR İÇİN YENİ BİYOAKTİF CAM MALZEMELERİN MİKROYAPISAL ÖZELLİKLERİNİN ARAŞTIRIMASI

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Bu tez çalışmasında, 45S5 biyoaktif cam malzemelerin biyobozunurluk ve biyoaktivite davranışları, dolgu amaçlı olmayan biyomedikal cihaz uygulamalarında kemik doldurma terapisi amaçlı olarak ele alınmıştır. Bu çalışmada, sentez yönteminin mikrokristal yapılar, yüzey morfolojisi ve termal patometrelerin in vitro çözünme ve mineral oluşumu üzerindeki etkilerini kristalin malzemeler üzerinde geleneksel sol-gel yöntemi ile üretilen tozlar üzerindeki etkilerini incelemekteyiz. Birçok rapor ve makale, kristalin biyo-cam yapıların, minerallerin oluşmaya başladığı zaman ölçülen amorf benzerlerinden biyolojik olarak daha etkili olduğunu göstermiştir. 45S5 biyoaktif cam, geleneksel çözücü kristalli usul kullanılarak sentezlendi ve daha sonra ısıl işlem, yarı kristalli bir yapı elde etmek ve ticari olarak temin edilebilen amorf döküm tozu 45S5 ile karşılaştırıldı. Hazırlanan jel numuneleri 700 ° C'de ısıtıldı ve kristal yapının% 80'inden fazlası için oluşturuldu. Çözünme 45S5 biyocam malzemeleri 12 mm çap boyutunda incelenmiştir. Toz haline getirilmiş toz biyoaktif cam malzemeler daha sonra X-ışını difraktometresi (XRD), Taramalı elektron mikroskobu (SEM), enerji dağıtıcı X-ışını analizi (EDS),

diferansiyel termal analiz/taramalı kalorimetre (DTA-DSC) ve kalorimetre (DSC/TGA) kullanılarak analizleri sırasıyla analiz edildi.

Anahtar Kelimeler : Biyo-Cam, Sol-Gel Yöntemi, 45S5, Biyomateryal, Biyomedikal

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SYMBOLS AND ABBREVITIONS INDEX

HCA : Hydroxy Carbon Apatite

FDA : Food and Drug Administration

ACP : Amorphous Calcium Phosphate

SEM : Scanning Electron Microscope

XRF : X-ray fluorescence

XRD : X-ray powder diffraction

DTA : Differential thermal analysis

PART 1

INTRODUCTION

1.1. BIOACTIVE GLASSES

In the late 1970s two new synthetic biomaterials were introduced to search for better biomaterials and materials be situated industrialized independently and nearly concurrently by many material scientists.

Novel synthetic biomaterials were talented to bind and fuse with body tissues among chemical procedures occurring on the superficial of the material, and were named at that time - biologically active ceramics.

By chemical reactions, bioactive glass attaches to the bones and can eventually replace the bones, making them very promising for use in medical claims. In addition, bioglass components are physiological chemicals in the body such as sodium, silicon, magnesium, potassium, oxygen, calcium and phosphorus. As has been stated in numerous studies, the concentration of chemicals never reaches a level that may disrupt neighboring tissues during bone formation and formation.

However, the use of biologically active glass as a material for transplantation or in the manufacture of medical devices with mechanical properties of the glass is incomplete.

New bioactive lenses have become more technically demanding for expanding the bioglass products industry to clinical applications.

Today, new biologically active glasses can be designed to modify clinical applications and to obtain information on different microscopic forms and optimal biomechanical activity under various physical conditions in the human body.

New advances in bioactive glass not only provide precise control of biomechanical activity, but also require detailed knowledge of the effect of glass composition on the production and regulation of various products. Accordingly, glasses-specific applications depend on understanding and mastering a wide range of features important to both the medical and glass industry, and new technologies to produce new types of bio-active lenses such as those derived from sol-gel Are produced. Active glass nanoparticles and bioactive glass nanoparticles. The general structure of the bioactive glass structure is shown in Figure 1.1.[1]

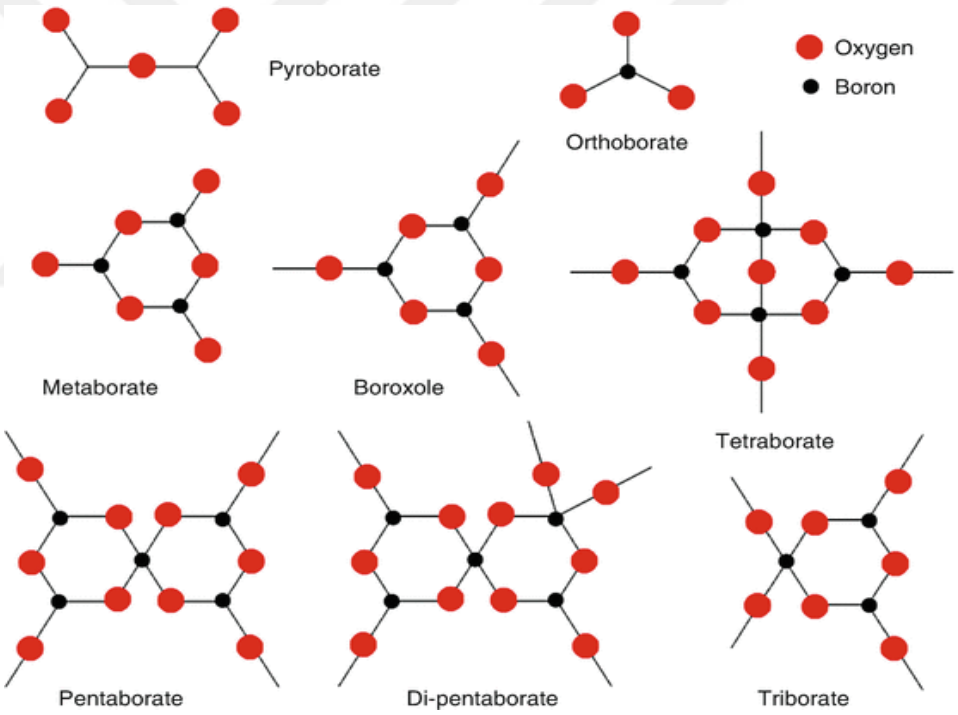


Figure 1.1. The general bioactive glass structure [1].

The bioactive glasses are materials whose properties are retained by the surgery for their use as a bone substitute. Indeed after their insertion in the body, they cover themselves with a layer of carbonate hydroxyapatite, alike to the mineral phase of the natural bone and which allows the establishment of chemical bonds with the bone cells, so a strong attachment of the implant. However, bioactive glasses are little used in surgery because of their poor mechanical possessions. They are however

interesting in thin layers to associate their bioactive characteristics with the interest of other materials.

Two ways of synthesis are possible:

- First one is the conventional route melts the precursor oxides at high temperature (often above 1400 ° C), followed by quenching at room temperature. This route makes it possible to obtain massive bioactive glasses of various sizes, but requires the use of an oven producing these temperatures;
- Second one is the sol-gel process is founded on the use of metal alkoxide, such as silicon, in order to introduce the seeds of the vitreous network. The preformation of the network by the sol-gel process makes it possible to significantly reduce the glass production temperature compared to the melting point. This synthesis is not suitable for obtaining massive glasses, but rather deposits in thin layers, easily exploitable.

1.2. BONE TISSUE (ANATOMY)

A Bone tissue cells are an organic and inorganic matrix but are hardened by calcium in their structure. The bones that make up the skeleton have various tasks. Providing support for the rest of the body, assisting the muscles to move by allowing different postures, maintaining the internal organs, maintaining mineral homeostasis, acid-base balance, providing growth factors reserve with cytokines and creating a suitable environment for hematopoiesis with marrow cavities. There are also physiological tasks [2].

There are two different forms of bone (cortical) and spongious (trabecular). Different regions of the skeletal system have different levels of cortical and trabecular bone content. Compact bone is a tight-form, non-voided tissue. On the other hand, spongous bone tissue has a loose, sponge-like or abundant cavity appearance. The yellow marrow, which consists of red marrow and fat cells where blood cells are produced, is located in these spaces [3].

The compact and spongy bone are both osteons. Osteons in the compact bone are called havers channels. The outer layer of the bone is surrounded by a connective tissue called osteosteum with osteogenic activity. Periosteal surface activity is of great importance in appositional growth and fracture repair [4].

The increased cortical regeneration process leads to an upsurge in cortical porosity and a reduction in bone density. The inner part of the bone is covered with a membrane structure called the endosteum. The endosteum covers the interior of the cortical and trabecular bone, and the interior of the blood vessel channels (Volkman's Channels) found there. The endosteum interacts with the bone marrow cavity, blood vessels channels, osteoblasts and osteoclasts.

Schematic diagram of cortical (compact) and trabecular (spongyous) bone is illustrated in figure 1.2 [5].

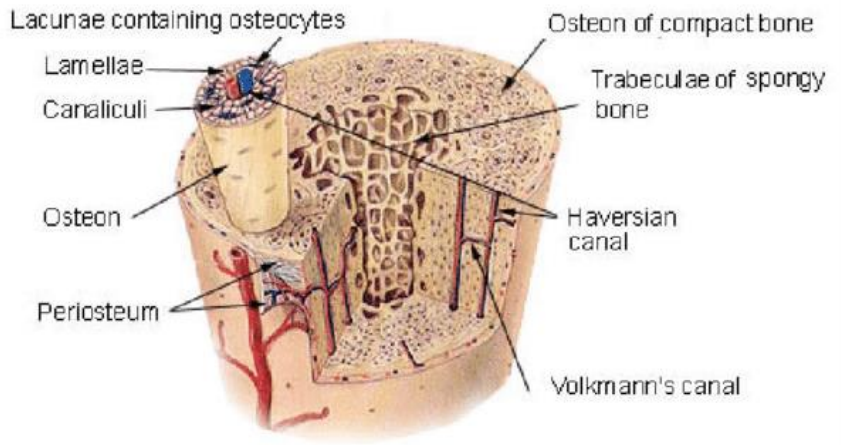


Figure 1.2. Schematic diagram of cortical (compact) and trabecular (spongyous) bone [5].

1.3. NATURE, STRUCTURE AND CHEMISTRY OF BIOACTIVE GLASSES

Bioactive glasses are biomaterials in which chemical attachment occurs among tissues and implants as a outcome of the replacement of silica groups with calcium and phosphorus [6]. The characteristic feature of bioactive glass which belongs to the class of bioactive ceramics is that its surface consists of a layer of bioactive hydroxy

carbon apatite (HCA), which provides the formation of bonds with tissues. Thanks to this feature, bioactive glasses can be chemically bound to the surrounding hard tissue and in some cases to soft tissue [7]. The most important properties of bioactive glasses are; their enzymatic activity is to support the formation of three-dimensional vascular structure, to help differentiation of cells in bone tissue and to connect with organic tissue with bone tissue [8].

The standard bioactive glass formula is generally known as 45S5 and is permitted by the Food and Drug Administration (FDA). This glass contains predominantly 45% SiO_2, 24.5% Na_2O and CaO and 6% P_2O_5. When changing the composition of the bioactive glass, the SiO_2 component is varied and the P_2O_5 component is kept constant. While keeping the silica content below 60% by weight and keeping the CaO / P_2O_5 ratio high, the material has a highly reactive surface [9]. Furthermore, it is aimed to increase the reactivity of the particles by reducing the size of the glass particles to nano levels after the production process. By reducing the element size of bioactive glasses to nano levels, both the performance of the material is improved and new application areas are gained.

Both faster ion release and high protein adsorption occur from the surface of the glass particles. Thus, it is aimed to increase bioactivity [8].

1.4. USES BIOACTIVE GLASSES IN MEDICAL APPLICATIONS

Although much research has been done about the reactions of bioactive glass with body fluids, there is little information about the behavior of the material in the oral environment, especially the reaction with dentin tubules. Effland et al. Investigated this interaction in vivo. In the study, a mixture was obtained by mixing distilled water and bioactive glass powder. The results show that the applied mixture provides structural integrity with the natural tissue through chemical variations and / or mineralization reaction in contact with the liquid in the dentine tubules. This thesis demonstrated that bioactive glass chemically changes in in-vivo dentine media. The results show hope that bioactive glass could be used as a possible filler. Studies have shown that bioactive glass may exhibit favorable properties for other restorations

outside the implant (eg fillings or crowns) [10]. In another study by Effland et al., It was shown that bioactive glass forms an appetite layer in saliva environment and body temperature [11].

Researchers have shown that bioactive glasses have a significant anti-microbial effect on caries structure pathogens (St. mutans, St. sanguis). Disinfection of infected tissues is one of the most important points in dentistry, especially in endodontics. Microorganisms naturally present in the oral cavity can lead to pathological conditions such as root canal infection. Bioactive glasses lead to an increase in pH. Because of this property, bioactive glass is thought to be used as a regional endodontic disinfection agent [8][12]. Bioactive glass is thought to minimize the inflammatory response and macrophage activity associated with trauma, including surgical operations [13]. Considering all these properties of bioactive glass, the material is used in dentistry; dentin sensitivity and bone remineralization can be used in the studies to be used.

1.4.1. Calcium Phosphate Preparation (Advantage and Disadvantage)

It is called calcium phosphate, through the empirical formula $Ca_3(PO_4)_2$, a intimate of minerals that contain calcium ions (Ca^{2+}) organized with orthophosphates (PO_4^{3-}), metaphosphates or pyrophosphates ($P_2O_7^{4-}$) and infrequently ions of hydrogen or hydroxide [14].

Calcium phosphate is the main way calcium is originate in bovine milk. 70% of the bone is complete up of hydroxyapatite, a calcium phosphate inorganic (called bone mineral). A large proportion of dental enamel is also calcium phosphate [15].

1.4.2. Bioglass As An Alternative To Calcium Phosphate

An attractive alternative to CaPs as bone substitutes is bioactive glass (BG): BGs have bone stimulants and replace the carbonate on their surface by forming a layer such as hydroxyapatite (HCA) carbonate. Bone and surrounding tissues. In addition, BG has been shown to release angiogenic and osteogenic stem cells by releasing

bioactive ions. Therefore, BG properties can be adapted to specific needs: For example, boron may be added to the BG compound to improve angiogenic properties [16].

PART 2

BIOGLASSES AND THEORETICAL CONCEPTS

2.1. BIOMEDICAL APPLICATION AREAS

Over the past 30 years, various bioactive materials have been developed. Because of their osteoconductive and osteoinductive properties, glass-ceramics and bioactive glasses have been the focus of interest in medical applications [17][18]. Bioactive glasses, one of the most important subclasses of bioceramics, have applications in the field of regenerative medicine as filling material in dental applications, bioactive coatings, filling material in BG / polymer composites or as 3-dimensional porous scaffolding.

Bioactive materials; special Na_2O – CaO – MgO – P_2O_5 – SiO_2 composition. All forms are mechanically bonded to the bone. Details were provided by Hench and colleagues. The rate of bone attachment depends on the quality of the material. Glass formulations have high binding rates and are associated with soft tissues. Biologically active glasses have been shown to stimulate bone differentiation in stem cells and promote the spread of bone tumors and mineralization upon examination [19].

One of the important features of bioactive glass in bone tissue engineering is that it supports neovascularization, , enzyme activity , osteoblast adhesion and helps differentiation of osteoprogenitor cells and stem cells [19]. Bioactive glasses are preferred as an alternative coating material to hydroxy-apatite, which is a popular material today because of its excellent bonding to bone. Bioactive glasses were first obtained by Hench as ‘45S5 Bioglass patented’. After a conversation with a US Army colonel on a bus ride, Professor Hench began work to find material that could bind to the bone. The colonel, who has just returned from the Vietnam war, asked the

professor whether materials could be developed to save the human body in the event of an attack from the environment. The problem with all materials available at that time; metals and polymers designed as bioinert, triggered fibrous encapsulation after implantation rather than interfacing or tissue interfacing with tissue. Professor Hench; decided to produce degradable glass with Na_2O – CaO - SiO_2 - P_2O_5 system with its eutectic triple composition in the Na_2O – CaO - SiO_2 diagram containing calcium. 45S5 bioactive glasses have been using to repair the damaged bone in jaw and orthopedic applications in more than one million patients.

Bioactive materials; In orthopedic or dental systems, it is used as an implant for bone and tooth exchange, and it is used as bone grafts to eliminate bone disorders in various ways. The amount and rate of bone regeneration when the bioglass particle is used to correct bone disorder depends on the structure of the material. The bioglass composition, such as 45S5, matches the tissue in the area where it is located, showing the amount, structure, biomechanical quality and high bioactivity of the trabecular bone at the rate of formation.

In general, structure of bioglass is mainly SiO_2 and other metal ions can be added to the glass in different proportions to improve the bioactivity, biodegradability properties. These changes are created by keeping the P_2O_5 component constant.45S5 bioactive glasses contain 45% SiO_2 (S = net forming), 24.5% CaO, 24.5% P_2O_5 and 5: 1 CaO - P_2O_5 [20].

The most important key responsible for the bioactivity of glasses in the composition of 45S5 is the low SiO_2 content (compared to chemically more stable silica glasses), high Na_2O and CaO content (glass network modifiers) and high CaO / P_2O_5 ratio. Those with a ratio of CaO / P_2O_5 less than 5: 1 cannot connect with bone [21]. The silica ratio is below 60%, and the bioactive glass produced has a more reactive surface. Bone binding is simultaneously associated with calcium phosphate and SiO_2-rich film formation on the surface. If the SiO2-rich layer first develops after the calcium phosphate layer (samples containing 46 to 55 mol% SiO_2) or if the phosphate film layer does not develop at all (60 mol% SiO_2), direct bonding with the bone cannot be established [22]. 45S5 bioactive glasses containing 45% by weight of

silicon dioxide have been shown to stimulate osteogenesis by inducing proliferation and osteogenic differentiation of human osteoblasts under in vitro conditions [23].

The Classification of bioactive glasses is shown in figure 2.1.

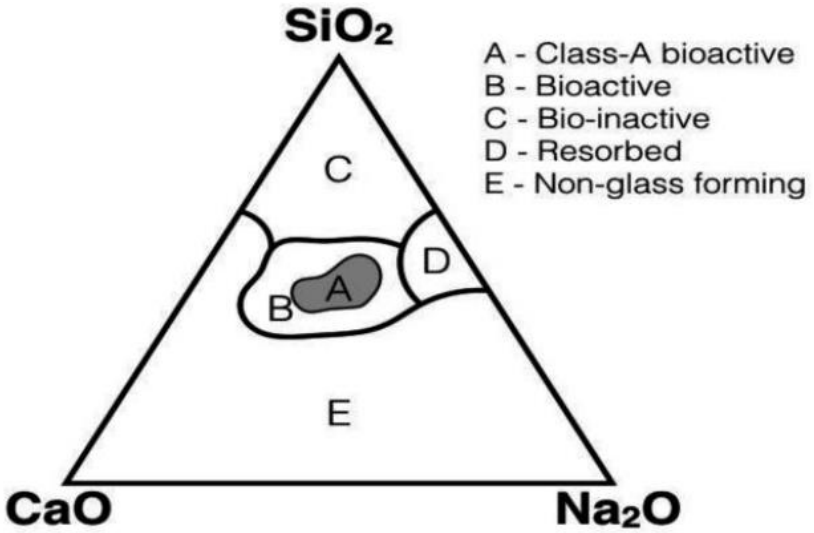


Figure 2.1. Classification of bioactive glasses [24].

The B region is the region of Class A, where bioactive lenses can bind to both soft and hard tissue and enable gene activation [25]. Some formulations of bioglass are given in Table 2.1.

Table 2.1. Composition of various glassware and glass-ceramics [24].

Glass	SiO_2	P_2O_5	CaO	$Ca(PO_3)_2$	CaF_2	Na_2O	Others	Properties
BG 42S5.6	42.1	2.6	29.0			26.3		Mol %
BG 46S5.2	46.1	2.6	26.9			24.4		Mol % best tissue bonding of bioactive glass formulas
BG 49S4.9	49.1	2.6	25.3			23.8		Mol %
BG 55S4.3	55.1	2.6	22.2			21.5		Mol %
BG 60S3.8	60.1	2.6	19.0			17.7		Mol % no phosphate film formed
BG 45S5	45	6	24.5			24.5		The original bioactive glass formulation binds with bone and soft tissues
BG 45S5F	45	6	12.25		12.25	24.5		
BG 45S5.4F5	45	6	14.7		9.8	24.5		
BG 40S5B5	40	6	24.5			24.5	$5B_2O_3$	
BG 52S4.6	52	6	21			21		
BG 55S4.3	55	6	19.5			19.5		
BG 8625	?	?	?			?	Fe_2O_3	Highly compatible, not bound to cells and tissues, coated with fibrous tissue. It has the ability to absorb infrared radiation, can be sealed by laser

Regardless of their composition and uses, the materials used in body repair have to meet both the need for vital functions and tissue compatibility. Biological studies indicate the implant's ability to perform according to the design purpose. What is required at this stage; (1) mechanical properties such as tensile strength, fracture toughness, elongation of fracture, voltage strength, Young's modulus; (2) physical properties such as density in bone implants or thermal expansion in bone fillings; and (3) surface chemistry properties. Such as resistance to decomposition, oxidation, damage, or bone adhesion. Biocompatibility is defined as the ability of a material to form an appropriate good response in a particular application [27].

As bioactive ceramics are used in clinical applications, the detection of limitations in mechanical properties increases. As shown in the Table, even A-W glass-ceramics with higher mechanical properties than other bioactive ceramics, human firm and cancellous bone, cannot be used in the treatment of high-pressure bone fractures such

as femoral or tibial bones, because their fracture strength is low and their elastic modulus is higher than the tight bone. Therefore, there is a need to study improved bioactive materials with bone-like mechanical properties [26]. The Bioactive ceramics and mechanical properties of human bone is shown in Table 2.2.

Table 2.2. Bioactive ceramics and mechanical properties of human bone [26].

		Strength (MPa)		Young's modulus (G Pa)	Fracture toughness. Kic (M Pa m1/2)
		compressive	bending		
BG (45S5)		-	42	35	-
HA		500 - 1000	115 - 200	80 - 110	1.0
Glass-ceramic A-W		1080	220	118	2.0
Human bone	Cancellous	2 - 12	-	0.05 - 0.5	-
	Cortical	100 - 230	50 - 150	7 - 30	2 - 12

Bioactive lenses cannot be used in the loading zones due to their poor mechanical properties, but they have been put into clinical use as a spacer in the iliac wing, vertebra prosthesis and shelf in shoulder-related surgeries [27].

2.2. HYDROXYAPATITE FORMATION STAGES AND BIO CERAMICS

45S5 glasses perform very well in terms of vital activity, compatibility with bone ligation processes. In these studies, the 45S5 glass binding to bones is associated with the formation of an appetite-like layer (HCA) on hydroxy carbon on the glass surface. A biologically active substance is defined as a substance that activates and performs tasks when implanted into the tissues of the body, to a number of specific surface reactions, resulting in the formation of a hydroxyapatite-like layer to form a strong bond with many soft and hard tissues. The ability of a substance to form a HA-like surface layer when deposited in artificial body fluids is an indication of the biological activity of that substance in the laboratory. Because the HCA layer is very similar to the bone mineral composition of the bone, the formation of the HCA allows the bioactive glass to tightly bond with the living bone tissue. Although some

chemical and formal changes have not been clarified to this time, according to Hench's description, it was concluded that the HCA layer on the surface of the bioactive glass results from a series of reactions [30].

First Stage

The rapid exchange of H^+ or H_3O^+ ions in solution with glass network regulators (Na^+ and Ca^+) leads to hydrolysis of silica groups and formation of silanol (Si - OH) groups on the glass surface.

Example

$Si – O – Na+ + H^+ \; Si – OH^+ + Na^+ (aq)$

The consumption of H^+ ions increases the pH of the solution.

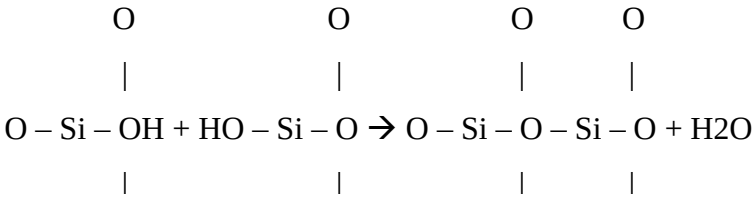
Second Stage

As the pH (or OH^- concentration) increases, silica begins to dissolve in solution in the form of silicic acid (Si (OH) 4) and Si-OH groups form on the surface of the glass.

$Si\text{-}O\text{-}Si + H_2O^- > Si - OH + OH – Si.$

Third Step

Condensation and polymerization of neighboring Si-OH groups results in a layer of silica gel of 1-2 mm thick on the surface;



Forth Step

As the glass dissolves further, the silica-rich layer in the glass and Ca^{2+} $(PO_4)^{3-}$ ions in the solution are coupled, resulting in a layer of amorphous calcium phosphate (ACP) on the surface.

Fifth Step

As the glass continues to dissolve, the $(OH)^-$ and $(CO_3)^{2-}$ and the ACP layer combine to crystallize as the HCA layer. As the HCA layer is formed, osteoprogenitor cells multiply and differentiate into osteoblasts by the attachment of growth factors to form the extracellular matrix.

2.3. 45S5 BIOGLASS

In order to form bioactive glass-ceramics from 45S5 bioactive glass, the replacement of some SiO_2 with 5-15% by weight of B_2O_3 and the addition of 12.5% CaF_2 instead of CaO or increasing the crystalline phase amount by changing the crystallization conditions does not affect the bone bonding properties of the material. Adding low amounts of titanium, tantalum, zirconia, and antimony also reduces the ability of the material to form a bond with other bone [28][29].

2.4. LANTHA NITRATE HEXAHYDRATE

Lantha nitrate is a chemical compound of formula Co $(NO_3)_2$. It occurs most often in the form of hexahydrate Co $(NO_3)_2 \cdot 6H_2O$, which is a deliquescent red-brown salt soluble in water and other polar solvents. It is obtained by reacting carbonate, hydroxide or cobalt oxide with nitric acid HNO_3 [30]:

$CoCO_3 + 2\ HNO_3 + 5H_2O \rightarrow Co\ (NO_3)\ 26H_2O + CO_2$.

There are several degrees of hydration of Lantha nitrate, represented by the generic formula Co $(NO_3)_2 \cdot nH_2O$ where n = 0, 2, 4, 6.

Lantha anhydrous nitrate adopts a three-dimensional polymer structure of the network in which each carbon dioxide (CO2 + cobalt) ion is coordinated into six oxygen atoms in the form of octahedral geometry. The nitrate ion is coordinated with three cobalt ions. Dihydrate is a two-dimensional polymer with nitrate bridges between carbon dioxide centers and hydrogen bridges connecting cobalt nitrate sheets. Tetrahydrates are composed of separate molecules [(H2O) 4Co (NO3) 2] by octahedral geometry. Hexahydrate is best described as hexaaquaLantha nitrate because it consists of [Co (OH 2) 6] 2+ and [NO3] - separate ions.

The main uses of Lantha nitrate generally lead to reducing it to metallic cobalt or to precipitating it on various substrates as part of the catalysis of the Fischer-Tropsch process [30].

2.5. BORON

Boron is a chemical element of the periodic Table of the elements that has the symbol B[1] and atomic number 5, its mass is 10,811. It is a metalloid, semiconductor, trivalent element that exists abundantly in the mineral borax. There are two allotropes of boron; The amorphous boron is a brown powder, but the metallic boron is black. The metallic form is hard (9.5 on the Mohs scale) and is a bad conductor at room temperature. It has not found himself free in nature.

It is used to make borosilicate glasses (eg Pyrex) and enamels, mainly of kitchen utensils. It is also used to obtain special steels, high impact resistance, and other alloys. Due to its high hardness, it is used, in the form of carbide, to make abrasives. Boron has several important applications in the field of atomic energy. It is used in instruments designed to detect and count neutron emissions. Because of its high neutron absorption capacity, it is used as a control buffer in nuclear reactors and as a constituent material of neutron shields. Diluted boric acid is used as an antiseptic for the eyes and nose. In the past, boric acid was used to preserve food, but this use has been banned because of its harmful effects on health. Boron carbide is used as an abrasive and alloying agent.

2.6. SOL-GEL METHOD

The sol-gel processes allow the production of glassy materials, possibly microporous to microporous by polymerization (and optional thermal reprocessing) without resorting to melting. Here, the glass is made directly from a liquid solution (then made colloidal) of silica and other chemical compounds (soda, lime, magnesia, etc.) and catalysts (or in a homogenized medium by ultrasound (sonochemistry) and / or heated by microwaves) [31]. These materials are grouped under the generic name "sol-gel process". Massive materials are available by these methods, but they are especially well suited to the production of films and coatings (for example for surface treatment of glass, metal or plastics (eg anti-corrosion film, anti-UV film), anti-pollutant deposit, anti-abrasion, or anti-scratch and / or "anti-reflective" treatment of spectacle lenses or other glasses or plastics, possibly bi-face) 3. In addition to being able to achieve purely inorganic materials, they are also suitable for the synthesis of organo-mineral (doped) hybrid glasses. The necessary precursors exist for a large number of metals, metalloids and non-metals. They are either liquid or solid, and in the latter in most cases they are soluble in common solvents, so it is possible to prepare homogeneous mixtures of monomers (precursors) or oligomers [32]. The sample sol-gel material is shown in figure 2.2.

Figure 2.2. Prepared sample by sol-gel method.

PART 3

MATERIAL AND METHODS

During the preparation of 45S5 bioactive glass we mixed 33.5 ml TEOS , 2.25 ml of pure nitric acid and 48.6 ml of distilled water. The mixture was stirred for 60 min with the stirrer for 60 min to hydrolyze the precursor. The following reagents were allowed to react separately for 45 minutes. Add triethyl phosphate (2.9 ml) triethyl phosphate (TEP, Sigma Aldrich), (20.13 g) calcium tetrahydrate nitrate (Sigma Aldrich) and (13.52 g) sodium nitrate (Sigma Aldrich) as follows.

The previously isolated transparent solution was then stored at room temperature in a sealed Teflon container for 5 days to form the gel. The gel was kept in a closed container for 1 day at 70 ° C and then dried in the oven for 1 day at 120 ° C. Finally, the dried specimen was dried at 700 ° C in a long bench bottom oven (Thermo Scient, F48055-60, Asheville, NC) for 1 day to remove residual nitrate.

In this research we have add the Boron and Lanthanum doped 45S bioglass which is shown in the Table 3.1.

Table 3.1. Lanthanum/ Borate doped 45S bioglass.

Lanthanum/Borate doped 45S Bioglass							
No	Sample	Si (ml)	Boron (g)	TEP (ml)	Ca (g)	La (g)	Na (g)
1	45SBG	33.5	0	2.9	20.13	0	13.52
2	Bor - BG	29.9	0.93	2.9	20.13	0	13.52
3	1La Bor-BG	29.9	0.93	2.9	19.48	1.08	13.52
4	2La Bor-BG	29.9	0.93	2.9	18.65	2.60	13.52
5	3La Bor-BG	29.9	0.93	2.9	18.07	3.68	13.52

3.1. MATERIALS

During the preparation of bioactive glasses we used the raw material such as:

Distilled water
Nitric acid (Merck - Germany)
TEOS (Merck - Germany)
Triethyl phosphate (Merck - Germany)
Calcium nitrate (Merck - Germany)
Sodium nitrate (Merck - Germany)
Boron (Merck - Germany)
Lanthanitrate-Hexahydrate (Merck - Germany)
The material that used in this study is shown in figure 3.1.

(a) (b)

Figure 3.1. A) The commercial raw materials, b) Ultrasonic cleaning machine (4 Lt).

3.1.1. Preparation of 45S5 Bioglass (45S BG)

During the preparation of 45S4 Bio glasses we used the following step:

Steps:

1. Put 2.25ml Nitric acid + 48.6ml water + 29.9ml TEOS in a beaker and put the beaker on a blender machine for 60 minutes
2. Add 2.9ml triethyl phosphate to the solution and let it blend on the device for 45 minutes
3. Add 20.13gram calcium nitrate to the solution and let it blend on the device for 45 minutes

The device that used in these steps is shown in figure 3.2.

Figure 3.2. Mixer.

1. Add 13.52gram sodium nitrate and let it blend on the device (see Figure 3.2) for 45 minutes.

Note 1: The solution is fully mixed and in a liquid state and transparent in color

2. Leave the solution on temperature of room within 5 days

Note 2: The strength of the solution changed to gel

3. The solution into the oven at 70 c for 24 hours

4. After 24 h at 70 c I raise the heat to 120c and left it in the oven for 24 h
5. Took out the beaker

Note 3: The solution changed from a gel to a solid, white color

6. Grind the material into powder and saved it in a container.

3.1.2. Boron Addition (Bor-BG)

For the preparation of doped bioactive glass – Boron is used that is given in following steps:

Steps:

1. Put 2.25ml Nitric acid + 48.6ml water + 29.9ml TEOS in a beaker and put the beaker on a blender machine for 60 minutes
2. Add 0.93g from Boron to the solution and let it blend on the device for 45 minutes
3. Add 2.9ml triethyl phosphate to the solution and let it blend on the device for 45 minutes
4. Add 20.13gram calcium nitrate to the solution and let it blend on the device for 45 minutes
5. Add 13.52gram sodium nitrate and let it blend on the device for 45 minutes

Note 1: The solution is fully mixed and in a liquid state and transparent in color

6. Leave the solution on temperature of room within 5 days

Note 2: The strength of the solution changed to gel

7. The solution into the oven at 70 c for 24 hours (see figure 3.3)

Figure 3.3. Oven device.

1. After 24 h at 70 c I raise the heat to 120c and left it in the oven for 24 h
2. Took out the beaker

Note 3: The solution changed from a gel to a solid, white color

3. Grind the material into powder and saved it in a container.

3.1.3. Lanthanitrate Hexahydrate Addition (1LaBor-BG)

For the preparation of bioactive glass with Lanthanitrate Hexahydrate Addition following steps are used:

Steps:

1. Put 2.25ml Nitric acid + 48.6ml water + 29.9ml TEOS in a beaker and put the beaker on a blender machine for 60 minutes
2. Add 0.93g from Boron to the solution and let it blend on the device for 45 minutes
3. Add 2.9ml triethyl phosphate to the solution and let it blend on the device for 45 minutes
4. Add 20.13gram calcium nitrate to the solution and let it blend on the device for 45 minutes
5. Add 1.08g La-H to the solution and let it blend on the device for 45 minutes

6. Add 13.52gram sodium nitrate and let it blend on the device for 45 minutes

Note 1: The solution is fully mixed and in a liquid state and transparent in color

7. Leave the solution on temperature of room within 5 days

Note 2: The strength of the solution changed to gel

8. I introduced the solution into the oven at 70 c for 24 hours
9. After 24 h at 70 c I raise the heat to 120c and left it in the oven for 24 h
10. I took out the beaker

Note 3: The solution changed from a gel to a solid, white color this is shown in figure 3.4.

Figure 3.4. Samples after oven.

11. I grind the material into powder and saved it in a container.

3.1.4. Increase Lanthanitrate - Hexahydrate Amount and Decrease Calcium Nitrate Amount (2labor-BG)

For the preparation of bioactive glass with Increase Lanthanitrate - Hexahydrate Amount and Decrease Calcium Nitrate Amount (2labor-BG) following steps are used:

Steps:

1. Put 2.25ml Nitric acid + 48.6ml water + 29.9ml TEOS in a beaker and put the beaker on a blender machine for 60 minutes
2. Add 0.93g from Boron to the solution and let it blend on the device for 45 minutes
3. Add 2.9ml triethyl phosphate to the solution and let it blend on the device for 45 minutes
4. Add 18.65 gram calcium nitrate to the solution and let it blend on the device for 45 minutes
5. Add 2.60 g La-H to the solution and let it blend on the device for 45 minutes
6. Add 13.52gram sodium nitrate and let it blend on the device for 45 minutes

Note 1: The solution is fully mixed and in a liquid state and transparent in color

7. leave the solution on temperature of room within 5 days

Note 2: The strength of the solution changed to gel

8. I introduced the solution into the oven at 70 c for 24 hours
9. After 24 h at 70 c I raise the heat to 120c and left it in the oven for 24 h
10. I took out the beaker

Note 3: The solution changed from a gel to a solid , white color

11- I grind the material into powder and saved it in a container (see figure 3.5).

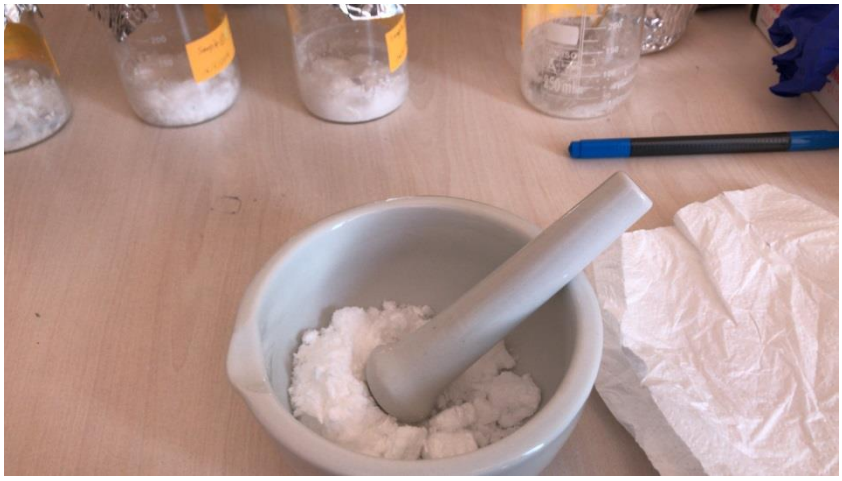


Figure 3.5. Samples after grinding.

3.1.5. Increase Lanthanitrate - Hexahydrate Amount More and Decrease Calcium Nitrate Amount More (3labor-BG)

For the preparation of bioactive glass with Increase Lanthanitrate-Hexahydrate Amount More and Decrease Calci-um Nitrate Amount More (3labor-BG) following steps are used:

Steps:

1. Put 2.25ml Nitric acid + 48.6ml water + 29.9ml TEOS in a beaker and put the beaker on a blender machine for 60 minutes
2. Add 0.93g from Boron to the solution and let it blend on the device for 45 minutes
3. Add 2.9ml triethyl phosphate to the solution and let it blend on the device for 45 minutes
4. Add 18.07gram calcium nitrate to the solution and let it blend on the device for 45 minutes
5. Add 3.68 g La-H to the solution and let it blend on the device for 45 minutes.
6. Add 13.52gram sodium nitrate and let it blend on the device for 45 minutes.

Note1: The solution is fully mixed and in a liquid state and transparent in color (see figure 3.6).

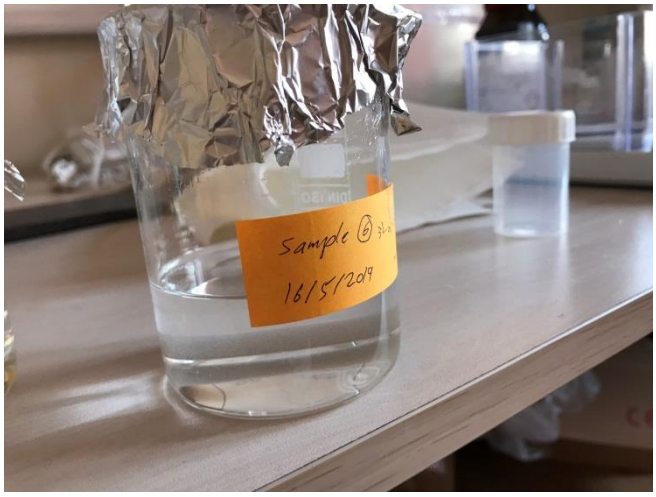


Figure 3.6. Solution after mixed.

7. Leave the solution on temperature of room within 5 days

Note 2: The strength of the solution changed to gel

8. I introduced the solution into the oven at 70 c for 24 hours
9. After 24 h at 70 c I raise the heat to 120c and left it in the oven for 24 h
10. I took out the beaker

Note 3: The solution changed from a gel to a solid , white color

11. I grind the material into powder and saved it in a container.

Upon completion of the preparations I have 5 samples in powder form each sample is placed in ceramic crucible (see figure 3.7).

Figure 3.7. Five samples in ceramic crucible.

I inserted the crucibles in a special oven (see figure 3.8).

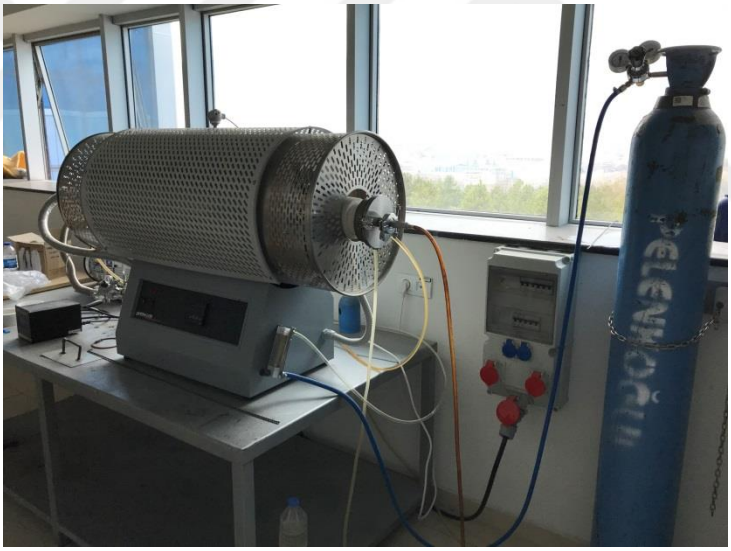


Figure 3.8. Furnace device.

1. The oven begins to rise gradually five degrees per minute up to 700 c
2. The oven stays at 700c for 2 hours and then gradually decreases until room temperature
3. I took the crucibles out of the oven and noticed that the powder had been petrified
4. The samples were grinded and assembled in a container and ready for analysis.

3.2. CHARACTERIZATION

There are different types of characterizations steps that are given in bellow such as:

3.2.1. Differential Thermal Analysis (DTA)

The analysis of differential thermals are a technique of thermoanalysis, a subdivision of physical chemistry for materials exploration. The analysis of differential thermal is to continue recording the temperature difference between sample and inert reference material, as a function of temperature and time, pressure and gas composition. It is similar to calorimetry thermoanalysis. An exothermic reaction in the sample gives a positive temperature difference, while an endothermic reaction gives a negative temperature difference. Therefore differential thermal analysis results in information about transformations that occur, such as glass transformations, crystallization, melting, and sublimation [33]. The device consists of a handle for the sample, with thermocouples, an electric oven, a temperature controller, and a recording device. The handle may be a ceramic block, or a metal block, or a small platter or crucible, such as a platinum, in which the specimen lies. One thermocouple records the temperature and retrieves it to the temperature controller. Two other thermocouples are found in the sample and one in the reference material, most commonly Al_2O_3. These two are connected so that each one cancels the power of the other as they are at the same temperature, but when a reaction occurs, the two temperatures become different. A voltmeter measures the difference a tool records [34]. The DTA machine is shown in figure 3.9.

Figure 3.9. The DTA device.

3.2.2. X-Ray Diffraction

X-ray scattering is an analytical technique based on the diffusion of x-ray waves by a substance. While X-ray diffraction could only be used with crystalline substances, X-ray scattering can be used for crystalline or amorphous substances. X-ray scattering is based on the interaction of X-rays with the electrons of atoms.

X-ray scattering provides information on the shape, size and orientation of materials with dimensions not exceeding the micrometer scale such as:

Large molecules, examples: proteins and polymers; nanoparticles, examples: nanotubes1.

The substances tested can be liquids, solids, foams, gels, etc.

This technique is non-destructive which makes it usable on sensitive substances. The XRD machine is shown in figure 3.10.

Figure 3.10. The X-ray diffractometer.

3.2.3. Scanning Electron Microscope (SEM)

A Scanning Electron Microscope (SEM) is an electron microscope in which an electron beam is guided (screened) in a specific pattern over the object to be magnified and uses interactions of the electrons with the object to produce an image of the object become. The images typically produced by a scanning electron microscope are images of the object surfaces and have a high depth of field. Scattering imaging can also be performed in transmission (scanning transmission electron microscopy, STEM), which requires appropriately equipped transmission electron microscopes or dedicated scanning transmission electron microscopes.

Hans Busch discovered in 1925 that one can use a magnetic field as an electron lens, analogous to the glass lens with light rays. In 1931, Ernst Ruska and Max Knoll built the first electron microscope. However, this was a transmission electron microscope (TEM) and provided no images of the surface, but the distribution of the mass in the object. The resolution of this first electron microscope was initially very limited for technical reasons. Two years later, Ernst Ruska constructed his second electron

microscope with a resolution of 50 nm, far surpassing the resolution with light beam scanning [35][36].

The scanning electron microscope was invented in 1937 by Manfred von Ardenne. He developed and built the first high-resolution scanning electron microscope by high magnification and scanning of a very small raster (side length 10 μm, resolution in the line direction 10 nm) with a two-stage reduced and fine-focused electron beam (probe diameter 10 nm). Von Ardenne used the scanning principle not only to open up another path in electron microscopy, but also purposefully to eliminate the chromatic aberration inherent in electron microscopes. He described and discussed in his publications the theoretical foundations of the Scanning Electron Microscope and the various detection methods and shared his practical execution. Further work came from the Vladimir Zworykin group (1942), later from the Cambridge groups in the 1950s and early 1960s under the direction of Charles Oatley. All of this work eventually led to the commercialization of the first commercial Scanning Electron Microscope "Stereoscan" (1965) by Cambridge Scientific Instruments Company. A report on the early history of SEM was written by McMullan [37]. The SEM machine is shown in figure 3.11.

Figure 3.11. The Scanning Electron Micrsocopy (SEM).

3.2.4. X-Ray Fluorescence (XRF)

X-Ray Fluorescence (XRF) X-ray emission is a secondary (or fluorescent) characteristic of a material emanating from a high-energy beam. The phenomenon is used in X-ray fluorescence analysis to determine the elemental composition of metals, glasses, ceramics and other materials.

Substituting materials of irradiation by short-wave X-rays, the components are ionized by the emission of one or more electrons. If the energy of the radiation is high enough, in addition to the bonding electrons, electrons are also knocked out of the inner shells. As a result, the electronic structure of the atom becomes unstable and electrons of higher shells fall into the resulting gap while emitting radiation characteristic of the element. The XRF machine is shown in figure 3.12.

Figure 3.12. X-Ray Fluorescence (XRF).

PART 4

RESULT AND DISCUSSION

In this section the experimental result will discussion. The measured values indicate that powders show relatively similar median diameter values. This section also presents the measured specific surface areas of the powders. As expected, sol–gel powders exhibited higher surface area. This is because gel-derived powders form by the sintering of particles with the range of 40–100 nm.

4.1. IMPORTANCE OF BIO-ACTIVE GLASSES

In this research we have already realized bio-active glass material by using sol-gel method. From the beginning of 1970s, the melt- quenched method has been applied to get glass-ceramics that crystallize to apatite phases on controlled heat treatment in addition to traditional sol-gel method. Glass-ceramic materials related with bioactive properties could be highly potential materials for various applications such as medical dentistry when improved the bioactive and biocompatible properties by using different compositions and preparation methods. So, to analyze the bioactive glass materials, we need to determine the crystal phases and microstructural properties of the glasses. The Schematic drawing of treatment of dentinal hypersensitivity is shown in figure 4.1. It shows the mineralization of dentinal tubules after treatment with bioactive glass nanoparticles.

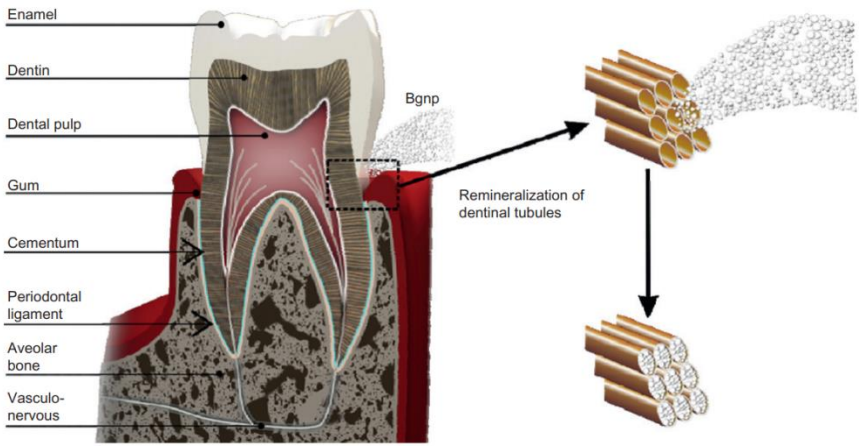


Figure 4.1. Schematic drawing of treatment of dentinal hypersensitivity [38].

4.2. DIFFERENTIAL THERMAL ANALYSIS (DTA) ANALYSIS DATA

According to the obtained bio-active glass materials, differential thermal analysis show that there is a gradually lost of glass compositions during the heat treatment from room temperature to 850 ^{o}C. DTA explain the important parameter for the bio-active glasses, such as glass transition temperature and crystallization temperature and melting points together with decompositions. Fig. 4.2 show the DTA plot related with lost of the glass compositions while increasing the temperature at around the 300 and between the 600-700^{o}C. The lost of glass compositions for 45SBG sample is higher than doped bioactive glass materials that might be based on the dopant compositions effect on the structure. When increase the lanthanum compositions in the bioactive glasses, losing the weight of compositions shifted to low temperature. Moreover, there are related obtained data for the DTA shown in section Appendix.

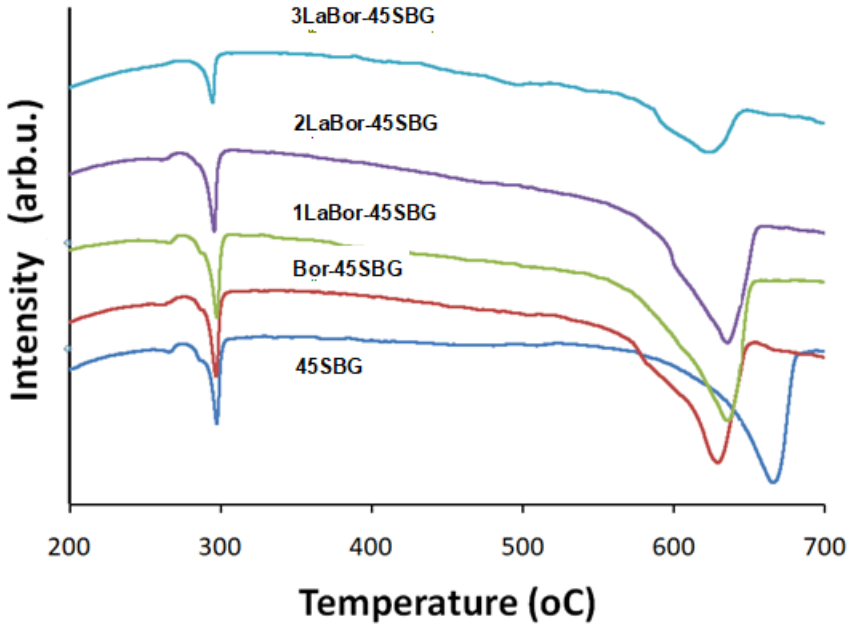


Figure 4.2. Differantial Thermal Analysis thermogram for the prepared bioactive glasses.

4.3. X-RAY DIFFRACTION DATA

The bioactive glass analysis of the crystalline phases was performed by sol-gel method using X-ray diffraction (XRD). The bioactive glass materials prepared were analyzed by X-ray diffraction, 40 kV copper target and accepted as a Rigako brand with 25 mA current. The XRD patterns were recorded from 2θ range of 10° - 60° . The obtained diffraction peaks intensities were determined by comparing with the standardized data which has an angle theta with higher intensity using JCPDS: 075-1687. As seen in Figure 4.3, the peak intensities were Sodium Calcium Silicates.

X-ray diffraction (XRD) technique was used to analyze the crystalline phases present in the samples before and after.

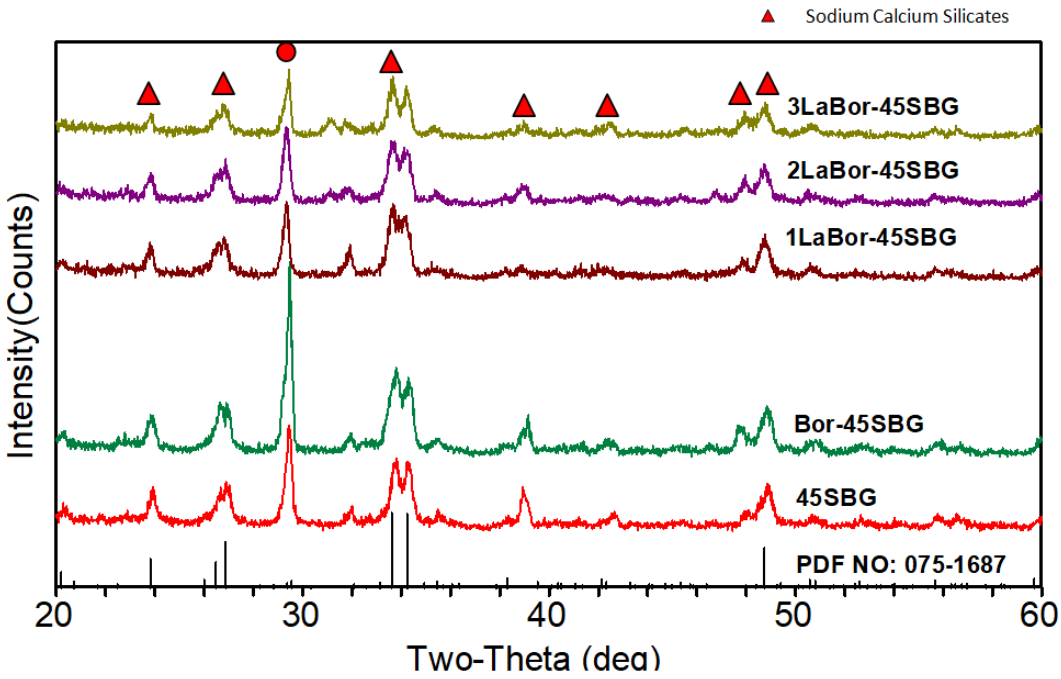


Figure 4.3. XRD results for the bioactive glass samples.

4.4. SCANNING ELECTRON MICROSCOPE DATA (SEM)

The morphology of the bioactive glass materials was deetrmined using Scanning electron microscope (SEM) (ULTRA PLUS-ZEISS). The morphology of the structures of the obtained bioactive glasses was related with tetragonal crystalline as seen figure 4.4. When doped the glass structure with lanthanum compositions, the surface crystalline structure can be seen clearly in Figure 4.5-10. In addition to SEM graph, the local elemental analysis were explained with EDAX measurements for the bioactive glass structures as seen from the Figure 4.6-4.10.

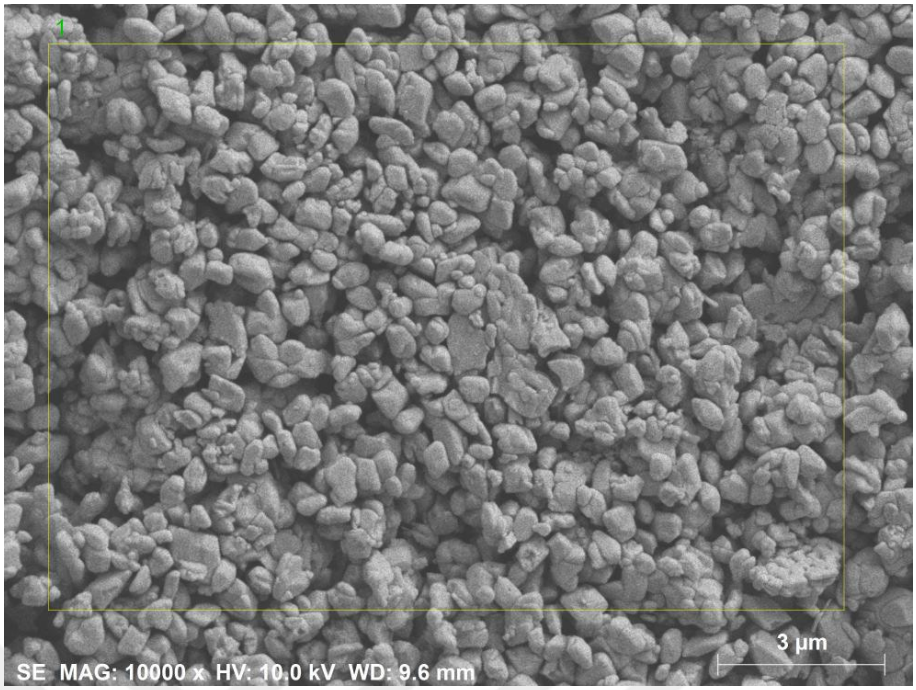


Figure 4.4. SEM morphology of the biactive glass samples for the 45SBG sample.

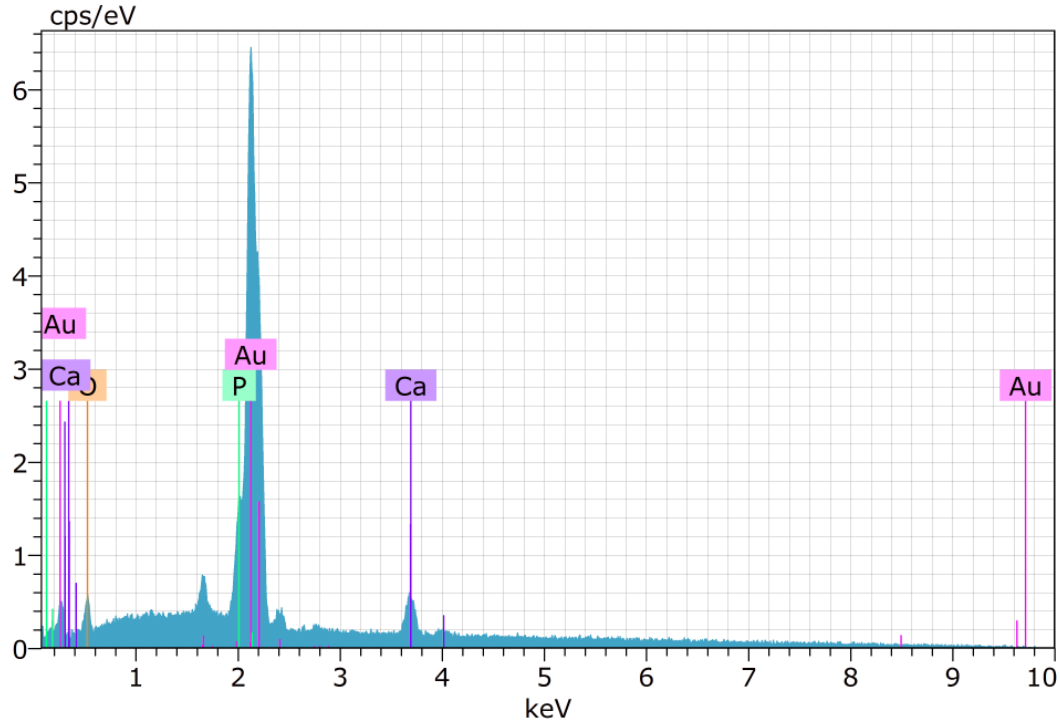


Figure 4.5. SEM/EDAX morphology of the biactive glass samples for the 45SBG sample.

Spectrum: 1

El AN Series unn. C norm. C Atom. C Error (1 Sigma)

[wt.%] [wt.%] [at.%] [wt.%]

O 8 K-series 1.51 1.86 13.08 0.34

P 15 K-series 4.42 5.45 19.74 0.21

Ca 20 K-series 5.22 6.43 18.01 0.23

Au 79 M-series 70.04 86.26 49.17 2.66

Total: 81.20 100.00 100.00

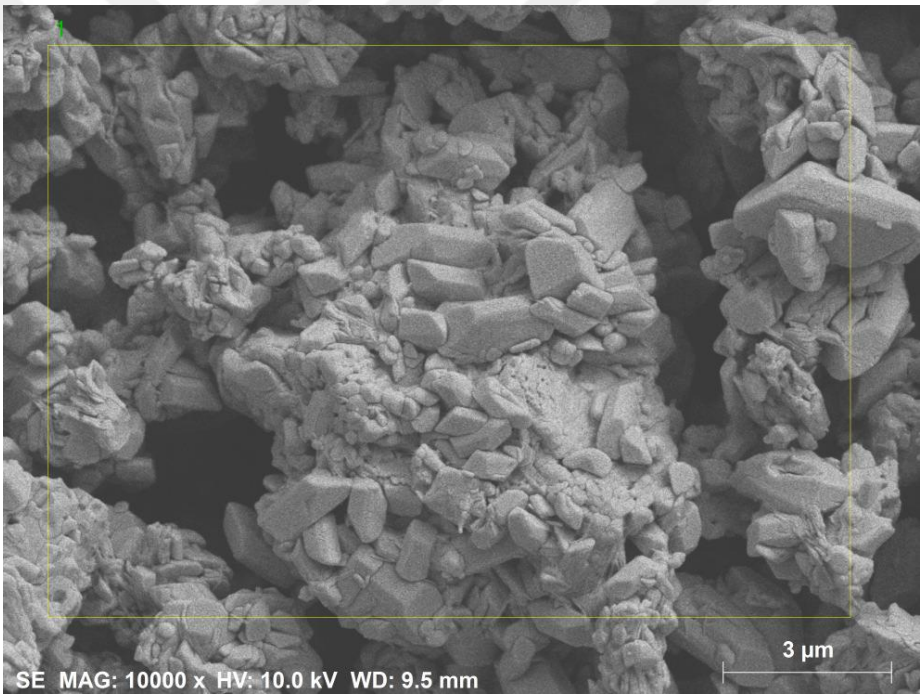


Figure 4.6. SEM morphology of the biactive glass samples for the Bor BG sample.

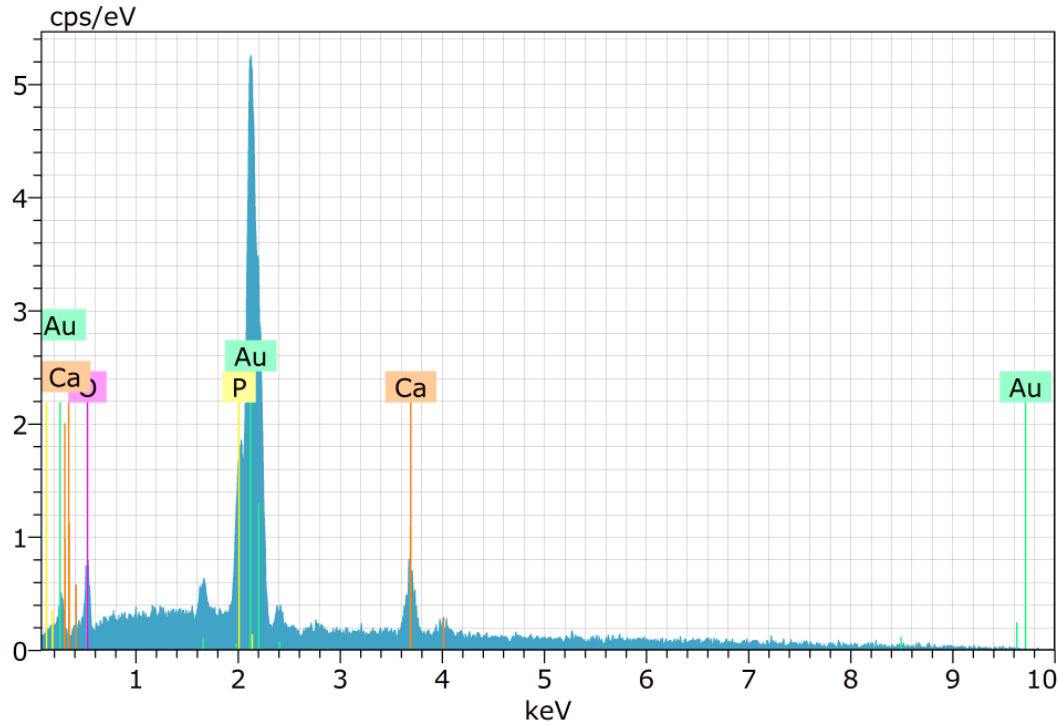


Figure 4.7. SEM/EDAX morphology of the biactive glass samples for the Bor BG sample.

Spectrum: 1

El AN Series unn. C norm. C Atom. C Error (1 Sigma)

[wt.%] [wt.%] [at.%] [wt.%]

O 8 K-series 2.47 3.30 19.09 0.58

P 15 K-series 5.36 7.16 21.42 0.26

Ca 20 K-series 7.06 9.44 21.82 0.33

Au 79 M-series 59.92 80.10 37.67 2.32

Total: 74.81 100.00 100.00

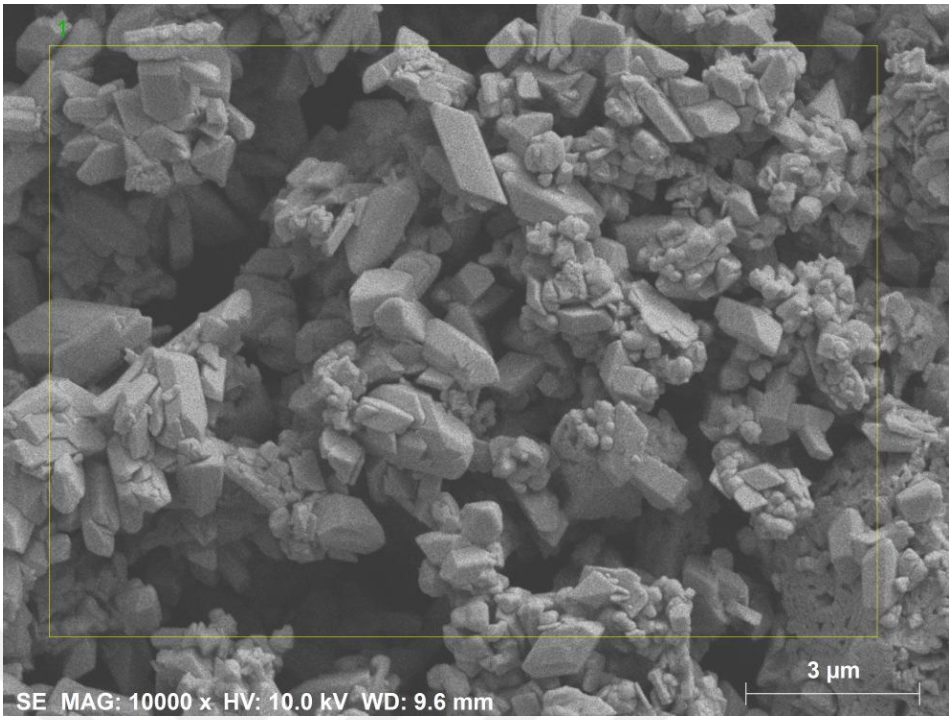


Figure 4.8. SEM morphology of the biactive glass samples for the 1 LaBor BG sample

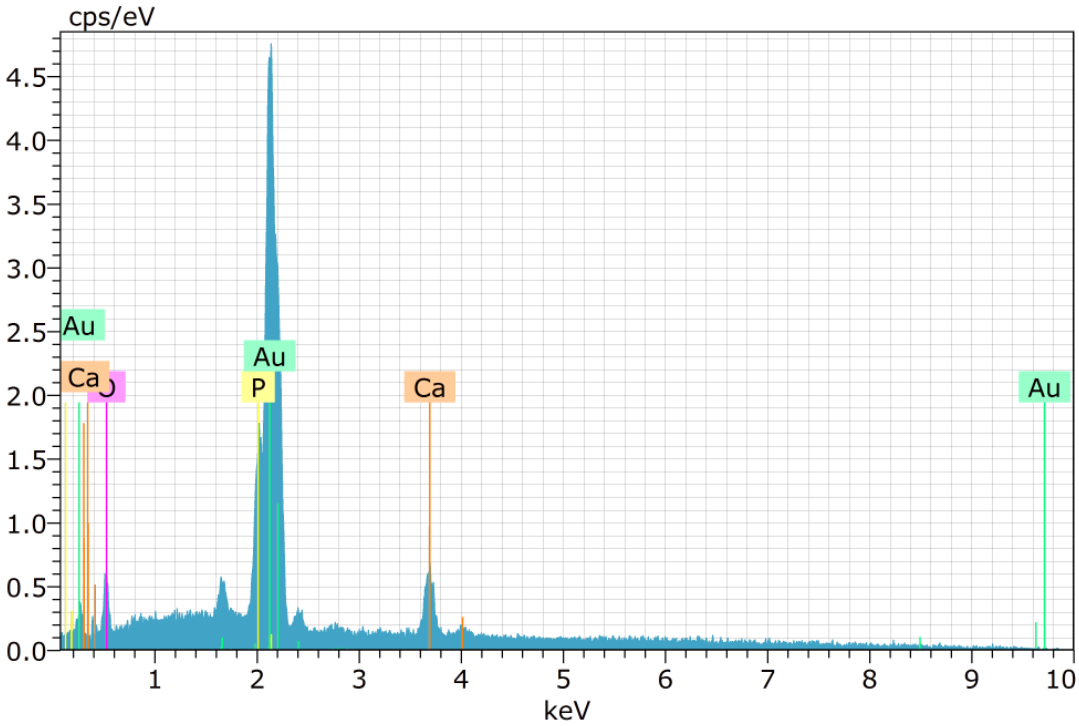


Figure 4.9. SEM/EDAX morphology of the biactive glass samples for the 1 LaBor BG sample.

Spectrum: 1

El AN Series unn. C norm. C Atom. C Error (1 Sigma)

[wt.%] [wt.%] [at.%] [wt.%]

O 8 K-series 2.18 2.78 16.07 0.48

P 15 K-series 6.02 7.66 22.89 0.27

Ca 20 K-series 8.10 10.31 23.80 0.35

Au 79 M-series 62.25 79.25 37.24 2.39

Total: 78.55 100.00 100.00

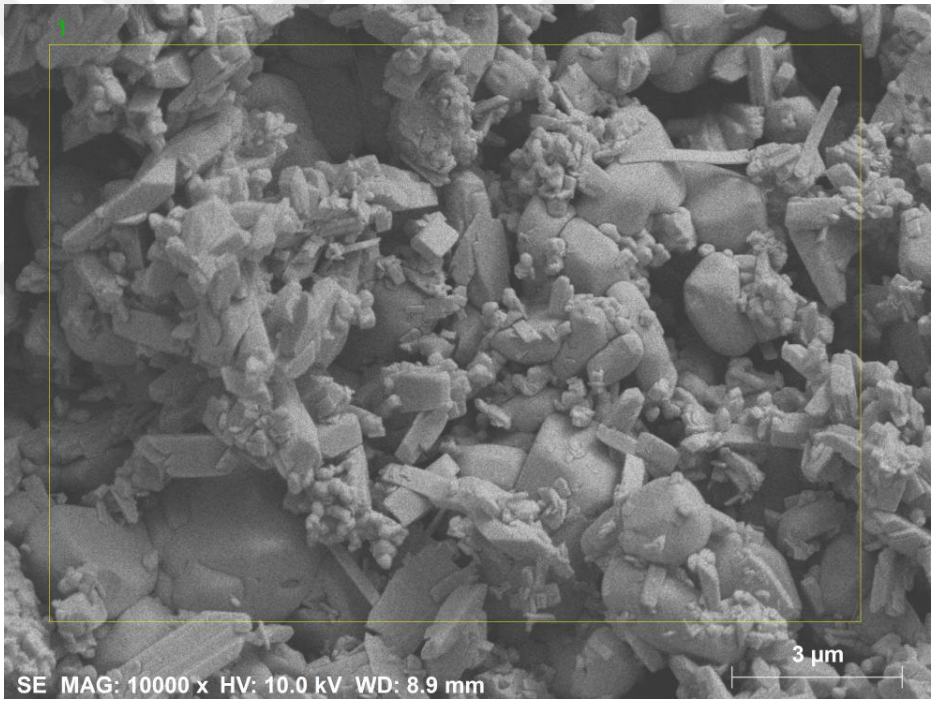


Figure 4.10. SEM morphology of the biactive glass samples for the 2 LaBor BG sample.

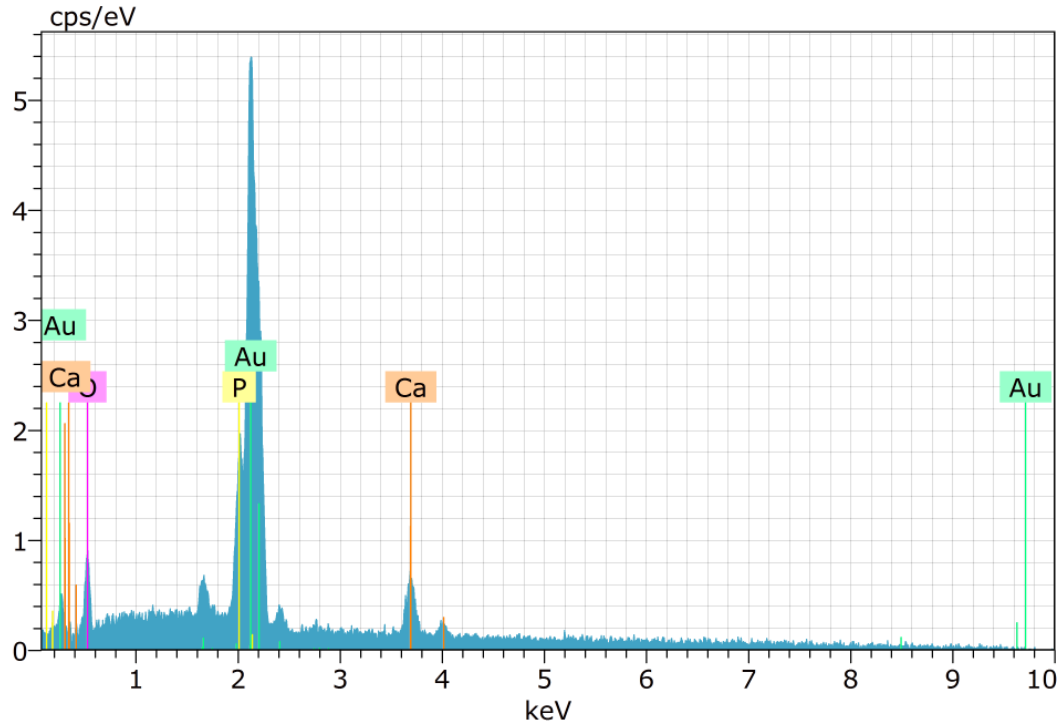


Figure 4.11. SEM/EDAX morphology of the biactive glass samples for the 4 LaBor BG sample.

Spectrum: 1

El AN Series unn. C norm. C Atom. C Error (1 Sigma)

[wt.%] [wt.%] [at.%] [wt.%]

O 8 K-series 2.97 3.89 22.00 0.67

P 15 K-series 5.40 7.09 20.68 0.26

Ca 20 K-series 6.98 9.16 20.66 0.34

Au 79 M-series 60.87 79.86 36.66 2.36

Total: 76.21 100.00 100.00

4.5. XRD RESULTS

The XRD data of the bioactive glass composites were measured at room temperature using powder diffractometer (Cu Ka radiation) operating at a voltage of 40 kV. XRD was taken at 2 tetha angle range of 5–60◦ as seen from Figure 4.11. Depends on the

dopant ratios in the bioactive glass samples, the dominant crystalline phases were determined as a Sodium Calcium Silicate from JCPDS catalogue.

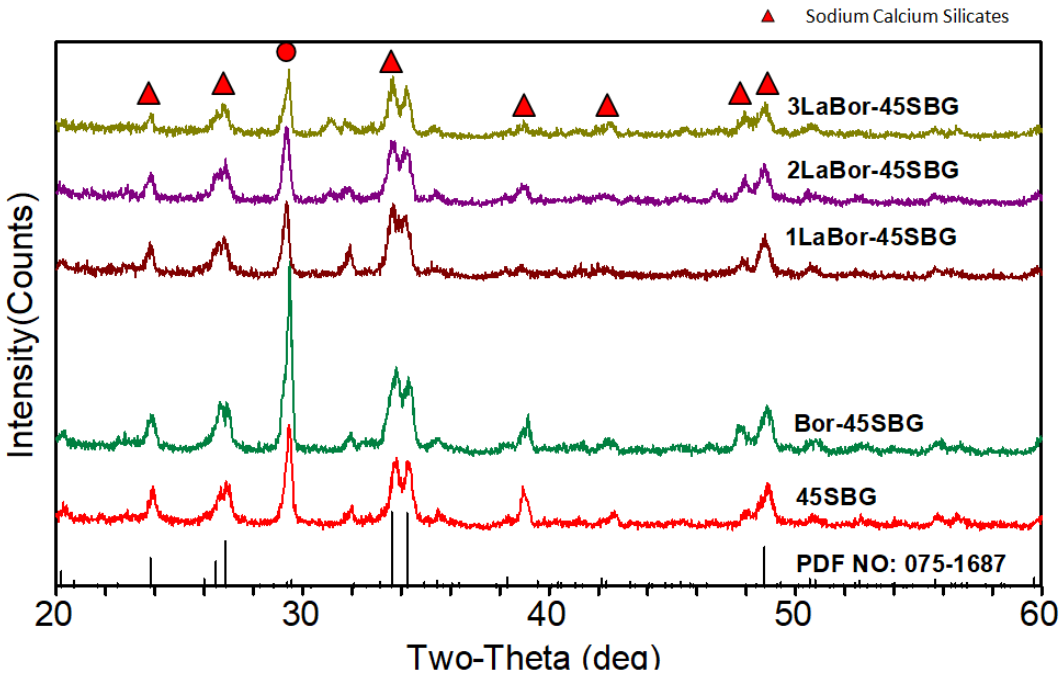


Figure 4.12. The XRD data for the various glass compositions.

4.6. XRF SPECTROMETER

The XRF spectrometer is usually applied to obtain a preliminary synthesis of bioactive glass samples that are prepared by sol-yield methods as powder.

Table 4.1.4.5 shows the preliminary structural analysis of bioactive glass materials of lanthanum and boron. The structural changes to the initial analysis of materials produced in different combinations are explained after the completion of the heat treatment process. Biologically active boron-containing glass materials, which are prepared at certain equivalent proportions according to XRF results, show that the molar ratios of the chemical elements are preserved in an equal manner at the end of the different stimulant ratios.

Table 4.1. The analysis of element with using XRF for the 45S BG sample.

Sample : S-1 Date analyzed : 2019-11- 5 12:49

Sample type : Metal & Alloy Component type : Metal Matching library :

Sample film corr. : P.P.F-12u Impurity corr. :

Component	Result	Unit	Det. limit	El. line	Intensity	w/o normal	Analyzing depth(mm)
Na	17.6858	mass%	0.65411	Na-KA	0.8623	7.2585	0.0057
Si	28.7810	mass%	0.03932	Si-KA	88.4569	11.8121	0.0122
P	3.1585	mass%	0.01433	P -KA	21.0411	1.2963	0.0099
K	0.4042	mass%	0.01119	K -KA	1.7242	0.1659	0.0377
Ca	49.9706	mass%	0.03595	Ca-KA	203.1059	20.5085	0.0486

Table 4.2. The analysis of element with using XRF for the Bor BG sample.

Sample : S-2 Date analyzed : 2019-11- 5 12:55

Sample type : Metal & Alloy Component type : Metal Matching library :

Sample film corr. : P.P.F-12u Impurity corr. :

Component	Result	Unit	Det. limit	El. line	Intensity	w/o normal	Analyzing depth(mm)
Na	22.0611	mass%	0.77370	Na-KA	1.1740	9.7066	0.0060
Si	24.9495	mass%	0.04666	Si-KA	79.2170	10.9775	0.0121
P	3.7328	mass%	0.01498	P -KA	27.4565	1.6424	0.0105
Cl	0.2533	mass%	0.05032	Cl-KA	0.5614	0.1114	0.0180
K	0.4977	mass%	0.01024	K -KA	2.3123	0.2190	0.0398
Ca	48.5057	mass%	0.03303	Ca-KA	214.8623	21.3419	0.0512

Table 4.3. The analysis of element with using XRF for the 1 Labor BG sample.

Sample : S-3 Date analyzed : 2019-11- 5 13:01

Sample type : Metal & Alloy Component type : Metal Matching library :

Sample film corr. : P.P.F-12u Impurity corr. :

Component	Result	Unit	Det. limit	El. line	Intensity	w/o normal	Analyzing depth(mm)
Na	17.7045	mass%	0.85610	Na-KA	1.0013	9.3133	0.0049
Al	0.1820	mass%	0.02636	Al-KA	0.4521	0.0957	0.0075
Si	26.4101	mass%	0.04902	Si-KA	92.2860	13.8929	0.0103
P	3.2409	mass%	0.01595	P -KA	26.3454	1.7048	0.0090
Cl	0.2128	mass%	0.05136	Cl-KA	0.5220	0.1119	0.0154
K	0.4106	mass%	0.01154	K -KA	2.0679	0.2160	0.0336
Ca	45.3122	mass%	0.03976	Ca-KA	223.2207	23.8362	0.0431
La	6.5270	mass%	0.23642	La-LA	2.4655	3.4335	0.0327

Table 4.4. The analysis of element with using XRF for the 2 Labor BG sample.

Sample : S-4 Date analyzed : 2019-11- 5 13:08

Sample type : Metal & Alloy Component type : Metal Matching library :

Sample film corr. : P.P.F-12u Impurity corr. :

Component	Result	Unit	Det. limit	El. line	Intensity	w/o normal	Analyzing depth(mm)
Na	18.6558	mass%	0.88241	Na-KA	0.9598	9.8227	0.0043
Si	23.7223	mass%	0.05537	Si-KA	73.8884	12.4903	0.0088
P	3.0694	mass%	0.01695	P -KA	23.7892	1.6161	0.0083
K	0.5441	mass%	0.01287	K -KA	2.5665	0.2865	0.0305
Ca	40.5048	mass%	0.03870	Ca-KA	190.6834	21.3266	0.0389
La	13.5035	mass%	0.17398	La-LA	5.2234	7.1099	0.0325

Table 4.5. The analysis of element with using XRF for the 3 Labor BG sample.

Sample : S-5 Date analyzed : 2019-11- 5 13:14

Sample type : Metal & Alloy Component type : Metal Matching library :

Sample film corr. : P.P.F-12u Impurity corr. :

Component	Result	Unit	Det. limit	El. line	Intensity	w/o normal	Analyzing depth(mm)
Na	23.7138	mass%	1.07051	Na-KA	1.0929	11.4767	0.0044
Si	18.0904	mass%	0.05356	Si-KA	47.9082	8.7552	0.0083
P	3.7964	mass%	0.01635	P -KA	27.3375	1.8373	0.0086
K	0.5948	mass%	0.01279	K -KA	2.5576	0.2878	0.0312
Ca	37.2203	mass%	0.03008	Ca-KA	161.3536	18.0134	0.0397
La	16.5843	mass%	0.15945	La-LA	6.1100	8.0263	0.0347

PART 5

CONCLUSION

In this systematic experimental researches, doped and undoped bioactive glass materials were prepared by traditional sol-gel methods for various lanthanum ratios.

1. The 45S5 bioactive glass materials initially prepared as a precursor to be able to compare the dopants effect on the bioactive glass structurers.
2. Secondly, boron based bioactive glass materials prepared by following the sol-gel method.
3. In addition to the prepared the 45S5 and boron BG materials, lanthanum based bioactive glass samples also prepared by sol-gel processes at room temperature.
4. Prepared bioactive glass materials were sintered at 850^{o}C in air atmosphere, then very well powdered.
5. The microstructural analysis were realized by usuing systematic experimental steps such Differential Thermal Analysis (DTA), X-ray diffraction (XRD), Scanning Electron Microscope(SEM/EDAX) and X-ray fluoroscence spectrometer (XRF), respectively.
6. In this research, we obtained the bioactive glass materials that has a Sodium Calcium Silicate crystalline phases was dominant on the structures.

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APPENDIX A.

DIFFERENTIAL THERMAL ANALYSIS (DTA) ANALYSIS DATA

Module : TG/DTA

Data Name : 1LaBor-BG(3).tgd

Measurement Date : 7/2/2019

The name of sample : 1LaBor-BG(3)

The weight of sample : 13.524 mg

The name of reference : Bos

The weight reference : 0.000 mg

The program of temperature :

Cel	Cel	Cel/min	min	s
1*	57	700	5	0 0.5

Comment:

Operator: asus

Gas1: Azot

Gas2: Oksijen

Pan: Seramik

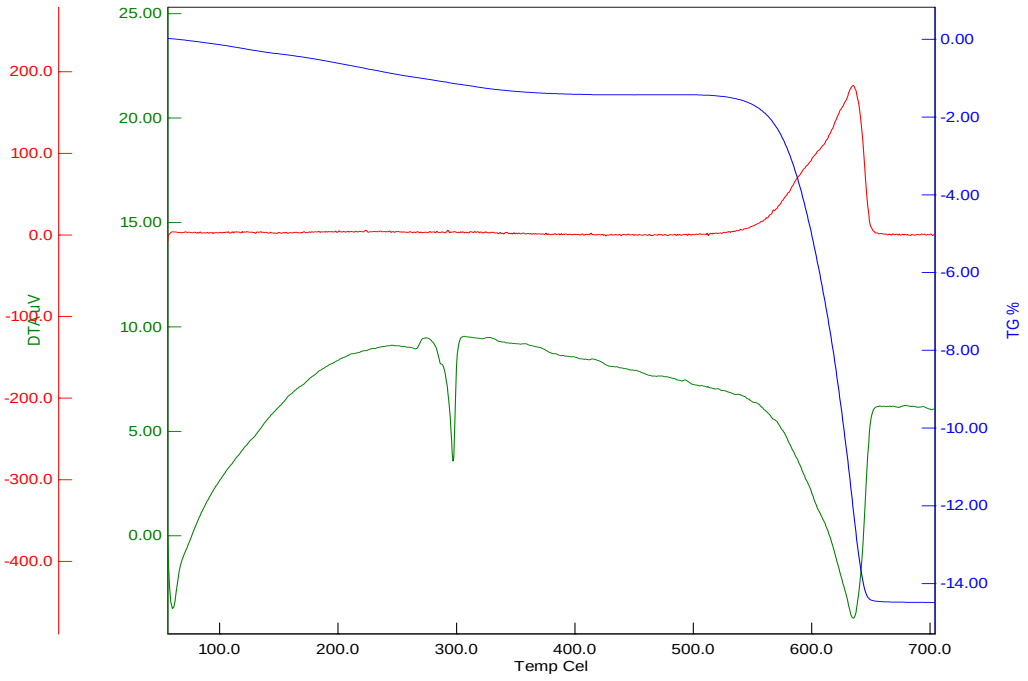

Figure Appendix A.1 The DTA thermogram for the 1 LaBor BG sample.

Module : TG/DTA

Data Name : 2LaBor.tgd

Measurement Date : 7/3/2019

The name of sample : 2LaBor

The weight of sample : 11.473 mg

The name of reference : Bos

The weight reference : 0.000 mg

The program of temperature :

Cel	Cel	Cel/min	min	s
1*	57	700	5	0 0.5

Comment:

Operator: asus

Gas1: Azot

Gas2: Oksijen

Pan: Seramik

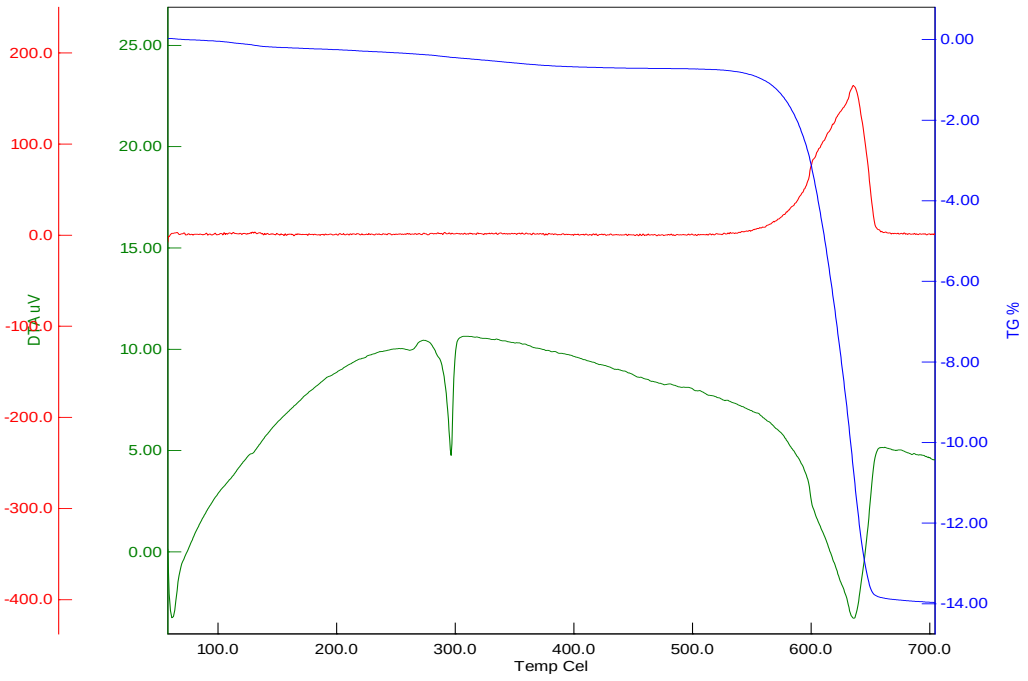

Figure Appendix A.2 The DTA thermogram for the 2 LaBor BG sample.

Module : TG/DTA

Data Name : 3LaBor-BG.tgd

Measurement Date : 7/5/2019

The name of sample : 3LaBor-BG

The weight of sample : 6.586 mg

The name of reference : Bos

The weight reference : 0.000 mg

The program of temperature :

Cel	Cel	Cel/min	min	s
1*	57	700	5 0	0.5

Comment:

Operator: asus

Gas1: Azot

Gas2: Oksijen

Pan: Seramik

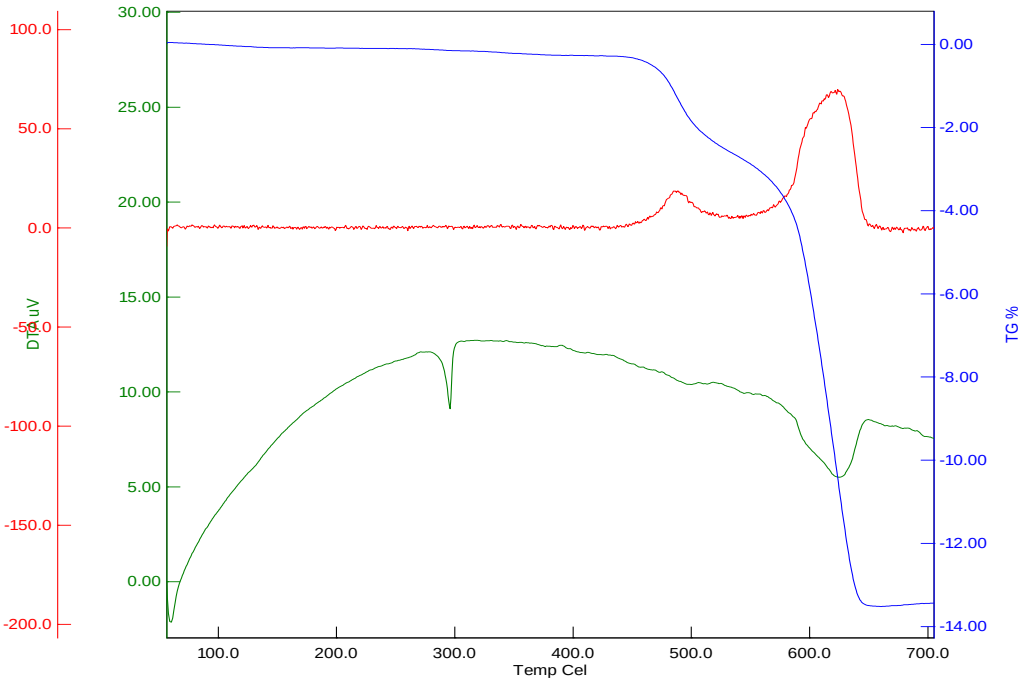

Figure Appendix A.3 The DTA thermogram for the 3 LaBor BG sample.

Module : TG/DTA

Data Name : 45SBG.tgd

Measurement Date : 7/1/2019

The name of sample : 45SBG

The weight of sample : 8.464 mg

The name of reference : Bos

The weight reference : 0.000 mg

The program of temperature :

Cel	Cel	Cel/min	min	s
1*	57	700	5	0 0.5

Comment:

Operator: asus

Gas1: Azot

Gas2: Oksijen

Pan: Seramik

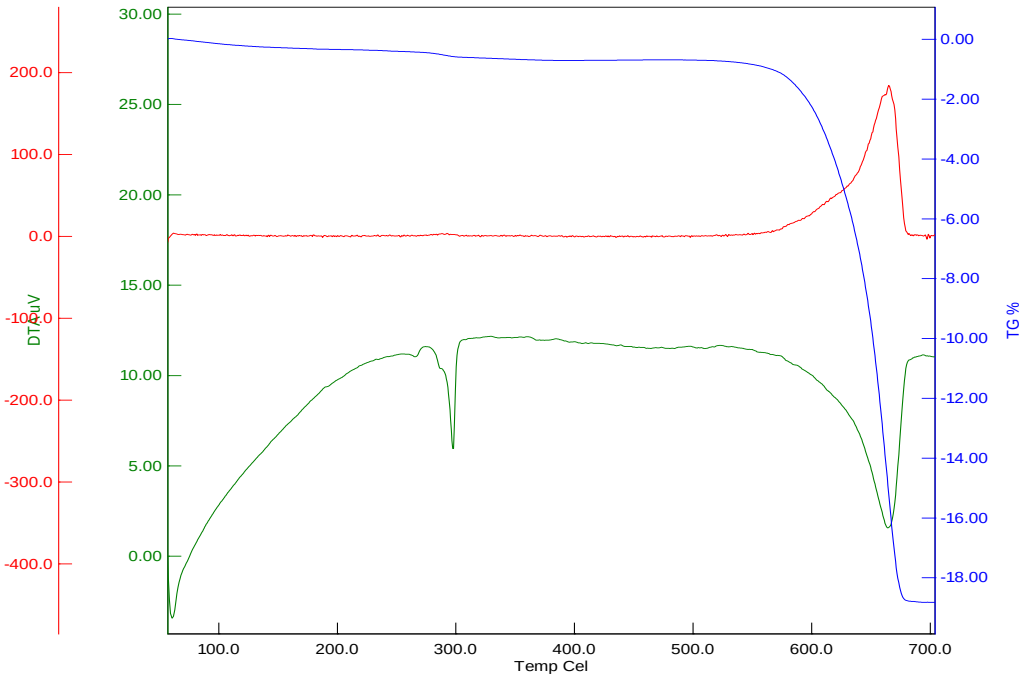

Figure Appendix A.4 The DTA thermogram for the 1 Bor BG sample.

Module : TG/DTA

Data Name : Bor-BG(2).tgd

Measurement Date : 7/5/2019

The name of sample : Bor-BG(2)

The weight of sample : 8.921 mg

The name of reference : Bos

The weight reference : 0.000 mg

The program of temperature :

	Cel	Cel/min	min	s
1*	57	700	5 0	0.5

Comment:

Operator: asus

Gas1: Azot

Gas2: Oksijen

Pan: Seramik

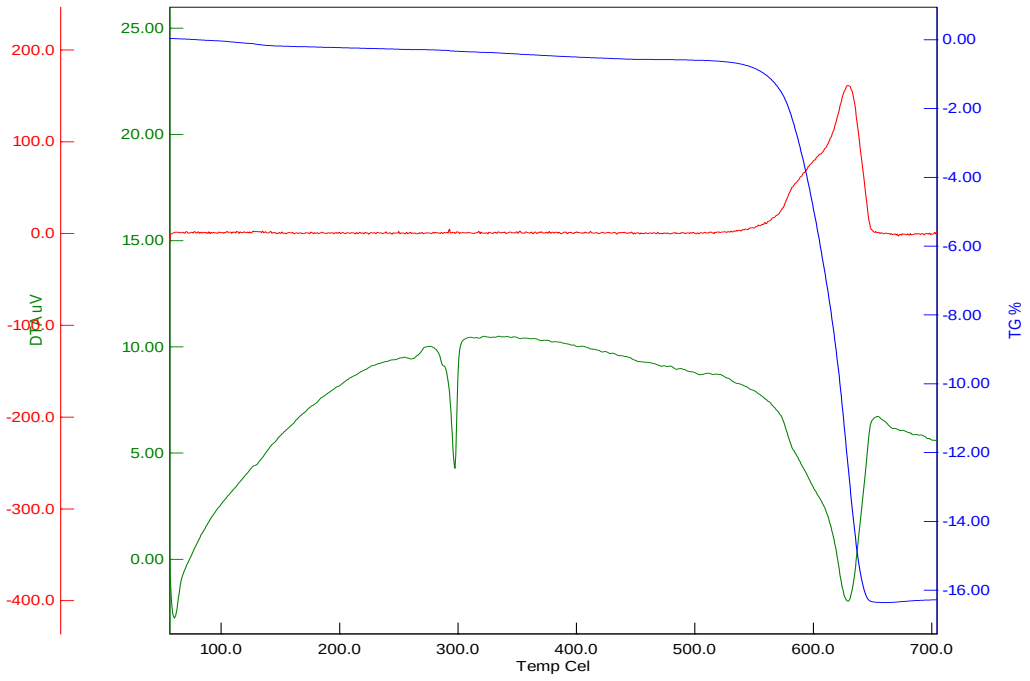

Figure Appendix A.5 The DTA thermogram for the 45S5 BG sample.

RESUME

Muftah Noum was born in 1988 and he graduated elementary and high school education in Mesallatah / Libya. Then he started to study at Tripoli University, department of medical sciences from 2007 to 2012. Then in 2016 he started studying Master Degree in Karabük University – Biomedical Engineering Department and completed in 2019.

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