

REPUBLIC OF TURKEY
FIRAT UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES



**PREPARATION AND CHARACTERIZATION OF
HYDROXYAPATITE BIOCERAMIC BY
HYDROTHERMAL METHOD**

HIMDAD IBRAHIM MUSTAFA

Master's Thesis

Department of Physics

General Physics

Supervisor: Assoc. Prof. Dr. Canan AKSU CANBAY

MARCH, 2017

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SUMMARY

In this master thesis, we prepared hydroxyapatite (HAP) by hydrothermal method. The structural analysis, thermal analysis and electrical characteristics of HAP sample have been investigated. The structural analysis was performed to determine the crystal structure and to observe the surface morphology of the sample. The thermal analysis was made from room temperature to 925 °C, to determine the mass loss according to temperature and phase transitions or decomposition in the sample. TG-DTA analysis was done to determine the thermal stability. The mass loss is 8.583% . The compositional analysis was done by EDX. I-V analysis was made to calculate the electrical conductivity value of the sample. The electrical conductivity calculated for the sample is 1.2×10^{-10} S/cm.

Keywords: Hydroxyapatite (HAP), hydrothermal method, electrical conductivity.

ÖZET

HİDROKSIAPATİT BİOSERAMİKİN HİDROTHERMAL YÖNTEMİYLE HAZIRLANMASI VE KARAKTERİZASYONU

Bu yüksek lisans çalışmasında, hidrotermal metot ile hidroksiapatit (HAP) üretilmiştir. Üretilen HAP numunesinin karakterizasyonu için yapısal analiz, termal analiz ve I-V HAP özellikleri incelendi. Yapısal analizler difraksiyon veren düzlemleri belirlemek ve yüzey morfolojisini incelemek için yapıldı. Sıcaklığa bağlı kütle kaybını belirlemek ve faz geçişleri yada bozunmayı gözlemlemek için termal analiz oda sıcaklığından 925 °C ye kadar yapıldı. Malzemenin elektriksel iletkenliğini belirlemek için termal kararlılığı belirlemek için TGA/DTA analizi yapıldı. Kütle kaybı 8.583% olarak bulundu. Kompozisyon analizi EDX ile yapıldı. I-V karakterizasyonu yapıldı. Numunenin elektriksel iletkenliğini 1.2×10^{-10} S /cm olarak hesaplandı.

Anahtar Kelimeler: Hidroksiapatit (HAP), hidrotermal metod, elektriksel iletkenlik.

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ABBREVIATIONS

HAP	: Hydroxyapatite powder
SEM	: Scanning Electron Microscope
FTIR	: Fourier Transform Infrared
XRD	: X-ray Diffraction
I-V	: Current-Voltage
EDX	: Energy Dispersive X-ray
DTA	: Differential Thermal Analysis
TGA	: Thermogravimetric Analysis
DCPA	: Dicalcium phosphate anhydrous
OCP	: Octa calcium phosphate
CaO	: Calcium oxide
CTAB	: Cetyl Trimethyl Ammonium Bromide

1. INTRODUCTION

Nanotechnology which is a science, engineering, and technology conducted at the nanoscale and also about (1-100) nanometers. Nanoscience and nanotechnology are the study and application of extremely small things and can be used across all the other science fields, such as chemistry, biology, physics, materials science, and engineering. The ideas and concepts behind nanoscience and nanotechnology started with a talk entitled “There’s Plenty of Room at the Bottom” by physicist Richard Feynman at an American Physical Society meeting at the California Institute of Technology (CalTech) on December 29, 1959, long before the term nanotechnology was used. In his talk, Feynman described a process in which scientists would be able to manipulate and control individual atoms and molecules. Over a decade later, in his explorations of ultraprecision machining, Professor Norio Taniguchi coined the term nanotechnology. It wasn't until 1981, with the development of the scanning tunneling microscope that could individual atoms, that modern nanotechnology began [1]. Nanotechnology, the generally critical innovation of our century, has turned into an essential field of logical research, and its preparations are presently being utilised as a part of everyday life primarily, of the advanced and evolving nations make essential interests to the nanotechnology and nanoscience researchers. The good comprehension of physical properties of the nanoscale structures can partake to both the growth of nanotechnology and to the usage of them in daily life. By structure, the examination fields of the nanoscale materials are digestion like Nanocrystals, Nanoparticles, Nanotubes, Nanowires, Nanorods or Nanoscale thin films. These structures have numerous magnificent physical behaviours that aren't yet completely comprehended in atomic level. So, the explorations on these material behaviours in nanoscale have been sustained by theoretical and experimental educations. Nanotechnology is the science and technology that deals with very tiny those things of particular, things that are less than 100nm in size. One nanometer is about three atoms long or equal 10^{-9} meters also we can say for comparison, a hair of human is about 60000-80000 nanometers wide. Scientists have found that small materials at dimension, small particles, thin films, etc, can have importantly different properties than the same materials at a larger scale. There are thus infinite possibilities for improved equipment. Materials and structures if we can learn how

to control the assembly of small structures and understand these differences [2]. We can see that there are many different views of precisely what is included in nanotechnology. The important properties are as:

1. Small size, measured in 100 of nanometers or less
2. Unique properties, Because of the small size
3. Control the composition and the structure of the nm scale so as to control the properties [2].



2. NANOMATERIALS

2.1. What Are Nanomaterials?

Nanoscale materials are a set of materials, one dimension where at least is less than approximately hundred nanometers. A nanometer is 1 millionth of a millimetre-approximately 80000 times smaller than the diameter of a human hair [3]. Nanoscience primarily deals with synthesis, characterization, exploration, and exploitation of nanostructured materials. These materials are characterized by at least one dimension in the nanometer range. A nanometer (nm) is one billionth of a meter, or 10^{-9} m. One nanometer is approximately the length equivalent to 10 hydrogen or 5 silicon atoms aligned in a line [4]. Nanomaterials are of significance because at this scale unique optical, electrical, magnetic, also other properties appear. These emergent properties have the potential for enormous effects in electronics, medicine, and another field in life [3]. Types of nanomaterials and classification of nanomaterials ,carbon nanotubes , fullerenes and buckyballs, dendrimers, fine and ultrafine Particulates in air , quantum dots and nanocrystals, titanium dioxide nanoparticles , silver nanoparticles , silver nanowire etc. carbon-based nanomaterials, nanocomposites metals and alloys, biological nanomaterials, nano-polymers, nano-glasses, nano-ceramics [3].

2.2. Nanomaterial Synthesis and Processing

Nanomaterials manage with very well structures; a nanometer is a billionth of a meter. This, in reality, permits us to think of both the ‘bottom up’ or the ‘top down’ approaches figure 2.1 to synthesise nanomaterials, that is either to collect atoms together or to disassemble bulk solids into finer pieces until they are constituted of just a few atoms. This field is a pure case of interdisciplinary work between physics, chemistry, and engineering to medicine [3, 4].

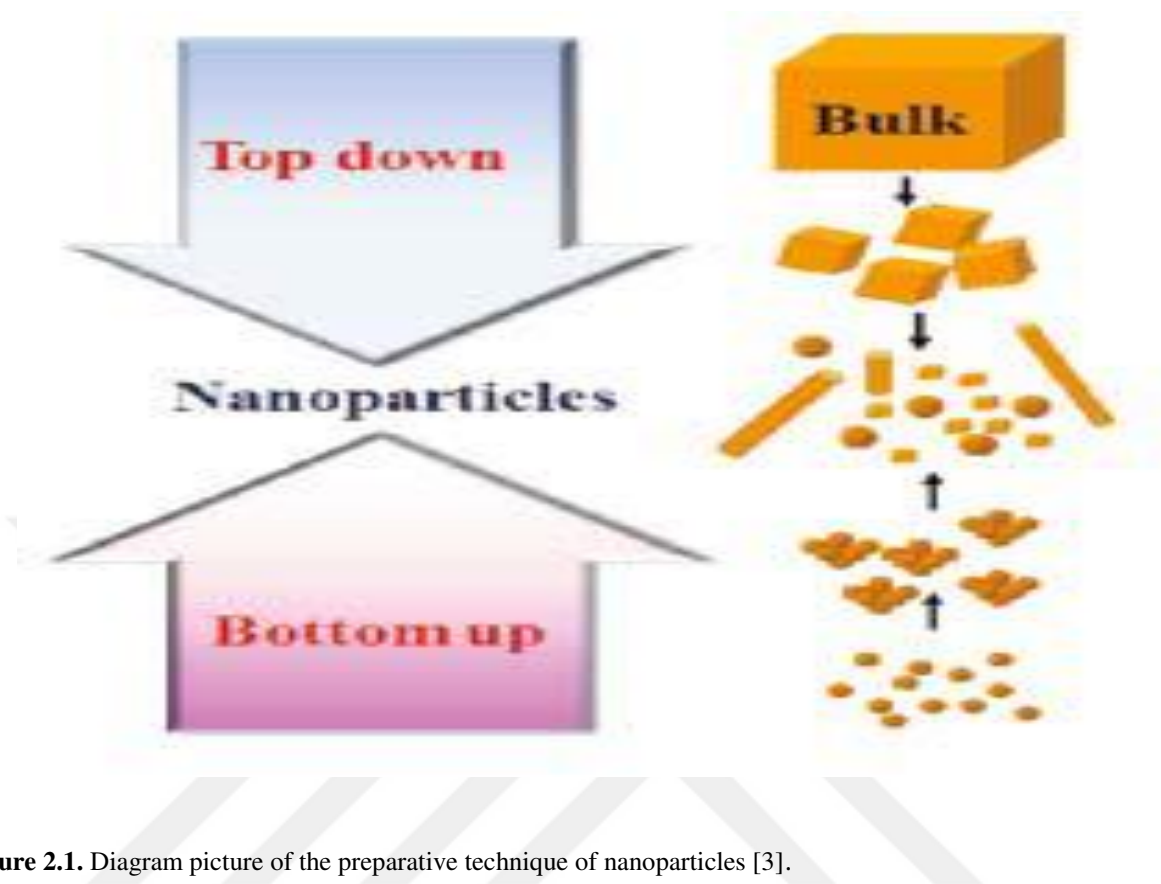


Figure 2.1. Diagram picture of the preparative technique of nanoparticles [3].

Nanomaterials have an enormously small size which having at least 1D (100 nm or less). Nanomaterials can be nanoscale in 1D, 2D for or 3D as surface films, strands or fibres and particles, respectively [3].

3. BIO CERAMICS

3.1. Hydroxyapatite

Hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, HAP), as the major mineral constituents of vertebrate bone and tooth. Hydroxyapatite powder (HAP) is an actually happening phosphate mineral, the crystal unit cell of HAP contains two entity and hence for the generally written as formula $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$. Also the OH^- ions of the HAP crystal can be put in place by chloride carbonate or fluoride creating fluorapatite or chlorapatite. The HAP crystallises in the hexagonal crystal system. Immaculate HAP is white in colour and normally happening apatite has diverse colours for example yellow, brown, or green colorations due to the incorporation a diversity of metal ions into the HAP crystal lattice. It has been very much reported that HAP nanoparticles can essentially add to the bioactivity and biocompatibility of made biomaterials [5, 6]. Hydroxyapatite (HAP) is a biologically dynamic calcium phosphate ceramic that is utilised in a surgical procedure to supplant and mimic bone. Although HAP powder bioactivity means it has a major attitude to advance bone development alongside its surface, its mechanical properties are inadequate to significant load bearing instruments [7]. The mineral component in the living bone is also a hydroxyapatite, the so-called biological apatite. The amount of the biological apatite in bone is approximately 70% by weight [7]. Hydroxyapatite (HAP) we can say is hexagonal by means space group $\text{P6}_3/\text{m}$, lattice with parameters ($a=b=9.4214 \text{ \AA}$, $c=6.8814 \text{ \AA}$, $\alpha=\beta=90^\circ$, $\gamma=120^\circ$). The hexagonal structure is characterised with the 6 fold over c-axis perpendicular for 3 equivalents a-axis at 120° angles to every other. Calcium ions Ca^{2+} and phosphate anion PO_4^{3-} are approved around columns of monovalent hydroxyl anion OH^- , which is appeared in figure 3.1 [8].

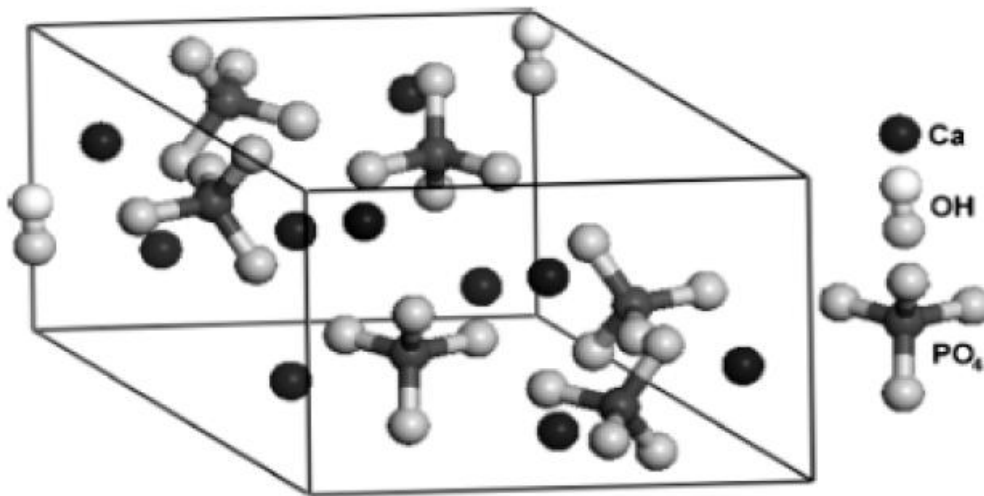


Figure 3.1. Crystal structure of hydroxyapatite [8].

Bone is a composite, consisting mainly of calcium phosphate (69%), collagen (20%), with water (9%), other organic material, for instance, polysaccharides, proteins, are present in little amounts. Calcium phosphate in the shape with crystallised HAP confirms bone inflexibility. The HAP crystals are in the form of needles 40–60 nm in length, 1.5-5 nm thickness and 20 nm in width. The mineral component of bone is alike to HAP but includes fluoride, magnesium, and sodium, with other ions like impurity [9].

Nowadays, an increasing importance and application of biocompatible, reliable and active biomaterials, human to the function of living organs or tissue in the body or used to support the materials, are continuously or periodically in contact with body fluids [10]. Since the birth of a variety of people is facing a stay with disease and accidents. Both diseases and accidents as well as tissues and organs in the human body it leads to destruction. Therefore it needs renewal and replacement of damaged tissues and organs. This area has two main points to be considered in the material to be used; to fulfill their biological function and body compatibility. Biomaterials sometimes mechanically, sometimes it does not meet the natural properties of the tissues and organs of the body in terms of compatibility. The researchers carried out by 60 % of bone hydroxyapatite and collagen fibres by 20% show that comprises [11].

The main feature is expected from the use of biomaterials material is biocompatible with the structure. The biocompatibility of the material itself, as well as the surrounding tissue, should all be based on the principles adopted by the body.

Biocompatible materials do not damage the structure of the environment, will not interfere with the normal change does not cause abnormal inflammatory response forms do not trigger allergic reactions that affect the immune system and cause cancer or cost. Biomaterial surface structural and compatibility can be expressed separately. Surface compatibility, a biomaterial to body tissues physical, chemical and biological whilst being in accordance with the structural integrity of the material is provided for optimum adaptation to the mechanical behaviour of body tissue. Despite this approach, there is a very precise definition of biocompatibility. Because of where the body of the material used and determine the definitions to be used for what purpose. The material in direct contact with blood is very different definitions from each other biocompatibility of the material in direct contact bone. So both biomaterials, the biomaterial placed both body environment should be examined [12-14].

They millions of years before, clay ceramic pottery to be converted, resident human communities from nomadic hunting of the biggest factors in the agricultural legislative passage there has been [12-15]. The ceramic materials many evident properties, for instance, the resistance to corrosion, chemical stability, thermal conductivity with low electrical. These materials, we can say have been broadly utilised as a part of biotechnology and medical fields due to of the attractive properties [15-19]. Usually, the ceramics available in medical applications are known as bioceramics [19]. Without a doubt, hydroxyapatite (HAP), which is an associate from calcium phosphate family members, business one of the most popular bioceramic materials, also its chemical recipe is $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$. It is the main inorganic component of human bones and teeth [20-22]. Bioceramics, made of polycrystalline ceramic materials (alumina and hydroxyapatite), bioactive glass, bioactive glass ceramic or bioactive composites in the form may be prepared [12]. There are more than a few different ways to synthesising HAP, counting hydrothermal, spray pyrolysis, solid-state reactions, sol-gel methods and wet chemical [23, 24]. The preparation method and the states of synthesis are vital parameters for manufacturing procedure, moreover, they can influence the chemical, structural and morphological properties of HAP. In contrast with the other manufacturing techniques, sol-gel method has many benefits, counting high creation purity and low synthesis temperature. Moreover, this method is extremely helpful to the synthesis of nanocrystalline HAP powders [25, 26]. An important group of such materials that form the inorganic material, it is utilised in a broad diversity of applications in the health sector. For example,

glasses, diagnostic devices, thermometers, tissue culture plates, used in endoscopic fiber optics, among others. Insoluble porous glass, enzymes, antibodies and antigen are used as the carrier.

Microorganisms, temperature, solvents, pH great changes and resistance to high pressures, which in terms of applications it is providing benefits [12]. When bioinert ceramics examined, although not quite in the body, which is a challenging environment as they arise rather chemically stable and are in contact it seems to be concerned any chemical bonding. Their response encountered in the body, stick around, and touch filamentous material forming a shell. In this case, the body may result in the material being covered and insulated all time emerges as a defence mechanism. Non-bioactive, such as alumina and zirconia oxide ceramic, this kind shows a shell formation. Alumina hip prosthesis and the bone filling material; chemical inertness, biocompatibility of high strength, high wear resistance, low friction coefficient, is preferred due to its outstanding properties like corrosion resistance and causing less scarring. The zirconium oxide ceramics are being used mainly in the hip joint prosthesis. Zirconium oxide is mechanically stronger than a good addition to the biocompatibility of aluminium oxide and zirconium so HAP can be strengthened by adding mechanical properties of the coating. General as in clinical practice is made of alumina or zirconia material implants arranged to allow a movement of the interface has been very successful [25-27]. As a result; ceramics, glass and glass-ceramics have very good chemical properties for use in many biomedical applications because of the material suitable for the human body. Phase or phases are determined by the application needs to be used. In particular, hydroxyapatite, bioglass and glass-ceramic with hydroxyapatite crystals, do not cause a strange reaction in the body and binds chemically to the bone generally cause minimal; tissue reaction, hard and surround themselves by creating a reliable bone-implant interface leads to loss of cells in the tissue. The vast majority of them are hydrophilic.

Corrosion problems can be found in some biomaterials such as metals it can be observed in ceramics. However, the fracture toughness of the material, fatigue resistance and so on. Their use in load-bearing prosthesis implants is not suitable due to such mechanical properties. Therefore, in such applications are typically used as coatings on the metallic material. Repair of tough connective tissue in the skeleton or use, in particular, is emerging as age-related progressive renewal. Considering the average life expectancy is 80 years, the average need of replacement material to living tissue begins around age 60.

Because reduced bone density and strength and bone producing cells, i.e. the productivity of the production of new bone by osteoblasts and the closing of microcracks formed in the bone are reduced. Today bioceramics are being used successfully in many parts of the body, and the ongoing question as a result of research areas are increasing every day [12, 26, 27].

3.2. Preparation methods of HAP

There are several methods mentioned in the literature about the production of HAP materials [28].

3.2.1. Dry methods

The dry method doesn't utilise a solvent, not at all like wet methods. Pursuant the literature, the attributes of a powder synthesised by a dry method aren't strongly affected by the procedure parameters, therefore the majority dry methods not need exactly control conditions, building them appropriate for mass production of powders. Also, a number of researchers hence modified famous dry methods, counting solid-state synthesis and the mechanochemical procedure, for the readiness of HAP particles [28].

3.2.2. Solid – State Synthesis

The solid-state reaction, as a comparatively simple process, could employ in the mass fabrication of HAP powder [29-31]. In a representative procedure, antecedents are initial milled and then calcined at a high temperature, for instance, 1000°C [29]. The precursors will be calcium and phosphate including chemicals several types or basically a formerly prepared CaP salt. The high temperature of calcination's prompts to the configuration of a well-crystallized formation. The general procedure is seen in figure 3.2. As a drawback, the powder synthesised by a solid-state reaction frequently displays heterogeneity in its stage composition, due to the small diffusion coefficients of ions inside the solid stage [30, 31].

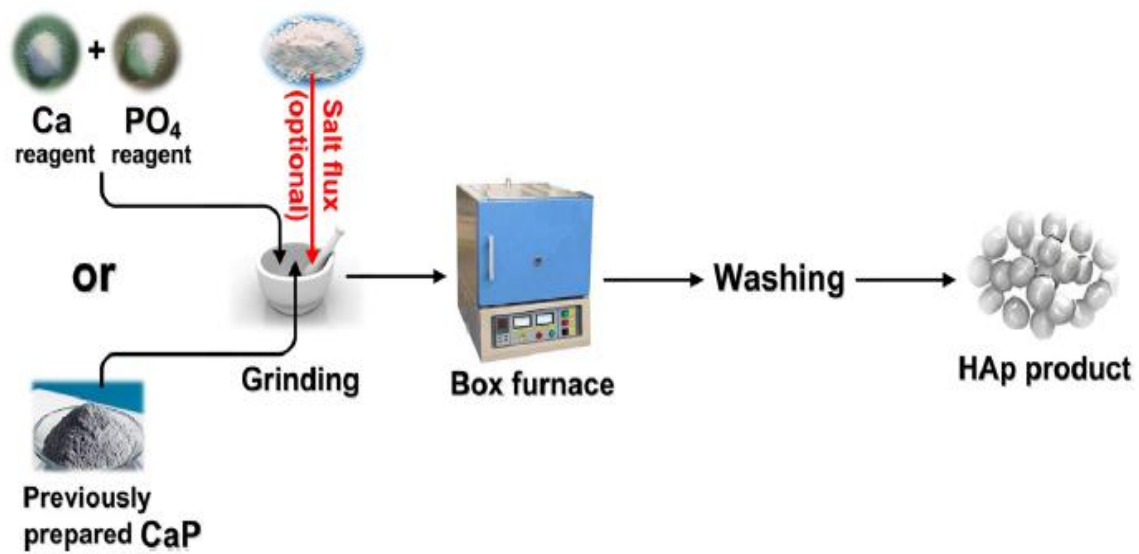


Figure 3.2. Preparation of HAP powder via solid-state method [28].

3.2.3. Mechanochemical Method

The mechanochemical procedure, in some cases, recognised as mechanical alloying, is an easy dry method for production variety of advanced materials, for instance, ceramics and nanocrystalline alloys [32, 33]. As opposed to the solid-state method by which heterogeneous particles with sporadic shape are typically created, powder synthesised utilising a mechanochemical course usually possesses a definite structure. This is owing to the perturbation of surface-bonded species as an effect of pressure, improving the thermodynamic and kinetic reactions between solids [34-38]. In fact, the mechanochemical procedure has the benefit of effortlessness and reproducibility of a solid-state process to do mass fabrication and the basic characteristics of an ordinary wet reaction to make a powder with a suitable microstructure. As seen in figure 3.3, in a typical procedure, the materials are ground on a planetary mill whereas the molar ratio of the reagents is reserved at the stoichiometric ratio [35, 36].



Figure 3.3. Preparation of HAP nanoparticles using Mechanochemical Method [28].

3.3. Wet methods

As declared before, HAP produced from a representative dry method is usually great in size and asymmetrical in the form. So wet methods have traditionally been functional to the preparation of HAP particles. Also, from a basic viewpoint aimed to understand the *Vivo* biomineralization method, the expansion pathway with HAP crystals in answer have been the subject of increasing attention on top of the past decade [39,40]. Wet chemical responses have benefits in their capability to controlling a morphology and the indicate size of powder, and, based on the numerous experimental data, they are the majority promising systems for the production of nanosized HAP. In fact, wet methods are normally simple to conduct and development conditions will be in a straight line controlled by adjusting the response parameters. The basic potential one of the drawbacks, be that as it may, is the low planning temperature contrasted to the dry techniques, performing in the production of CaP stages other than HAP (Table 3.1) [39, 40].

Table 3.1. A range of HAP powder nanostructures among modulated shapes[28].

Shape	Name(s) in literature	Approx. size range	Method(s) of synthesis*
	irregular, formless, sphere	5 nm–200 μm	ss, mch, cc, hl, sg, hth, em, sch, ht, bs, cp
	sphere, microsphere, nanosphere, ball	10 nm–1000 μm	mch, cc, sg, hth, em, sch, ht, bs, cp
	rod, needle, tube, filament, fiber, wire, whisker, prism, worm, hexagonal prism, platelet, lath, strip	length: 10 nm–150 μm , diameter: 3 nm–50 μm , aspect ratio: 2–1200	ss, mch, cc, hl, sg, hth, em, sch, ht, bs, cp
	plate, flake, sheet	length: 40 nm–50 μm , width: 20 nm–35 μm , thickness: 5 nm–3 μm	cc, hth, bs, cp
	self-assembled nanorods, bundles of nanorods, oriented bundle, oriented raft, enamel prism-like structures, clusters of nanotubes, oriented array of bundled needles, packed nanorods	length: 200 nm–80 μm , width: 100 nm–50 μm (organized nanorods of 10 nm–13 μm diameter and 200 nm–75 μm length)	cc, hl, hth, bs, cp
	dandelion, chrysanthemum, flower, feathery structure, bundle of fibers, self-assembled nanorods, rosette	1–8 μm (organized nanorods of 80–500 nm diameter and 600 nm–5 μm length)	hth, em, bs, cp
			
	leaf, flake, sheet, plate	800 nm–10 μm (organized nanoplates of 20–100 nm thickness)	cc, hl, cp
	flower	700 nm–60 μm (organized petals of 20 nm–10 μm width and 180 nm–50 μm length)	cc, hth, bs
	porous microsphere, mesoporous sphere	0.5–7 μm (pores of 20–150 nm)	hth, cp
	bowknot, self-assembled nanorods	1.5–2.5 μm (organized nanorods of 100–150 nm diameter and 1–2 μm length)	cp
	dumbbell	2–3 μm (organized nanoparticles of ~50 nm size)	cc

- ss: solid-state synthesis, mch: mechanochemical method, cc: conventional chemical precipitation, hl: hydrolysis method, sg: sol–gel method, hth: hydrothermal method, em: emulsion method, sch: sonochemical method, ht: high-temperature processes, bs: a synthesis from biogenic sources, cp: combination procedures.

3.3.1. Conventional Chemical Precipitation

Along with the several wet processing techniques, the simplest way for the synthesis of nanosized HAP is customary chemical precipitation. The chemical precipitation is supported on the actuality that, at room temperature and pH 4.2, HAP is the smallest amount soluble and regularly the most steady CaP stage in a watery solution [41]. The precipitation response is, though, normally conducted at pH principles higher than 4.2 and temperatures scoring from room temperature to temperatures close to the boiling point of water [42-43]. Figure 3.4, shows a schematic graph of the stepladder occupied in the chemical precipitation of HAP, straight with the parameters projected to influence the powder characteristics. To create HAP nanoparticles, chemical precipitation would be proficient utilising different calcium and phosphate including reagents, for instance, calcium nitrate or calcium hydroxide as the Ca^{2+} resource and orthophosphoric acid or diammonium hydrogen phosphate as the PO_4^{3-} source. A distinctive procedure includes the dropwise adding up of one reagent to one more under continuous and tender stirring, while the molar ratio of components Ca/P is reserved at stoichiometry indicated to Ca/P ratio in HAP powder 1.67 [44,45]. As a final, the resulting deferment might be matured off the atmospheric under pressure or at once washed, dried, filtered and smashed into a powder [46, 47]. A lot of factors are stated to cause this disadvantage, counting the high chemical affinity of HAP to some ions, the compound environment of the CaP crystals, hydrogen bonded interactive through the HAP particles and the kinetic parameters role, which, according to the experimental conditions, win through over the thermodynamic parameters [48, 49]. The non-stoichiometric attribution can happen as a consequence of opportunities in the crystal lattice, the exchange of diverse ions like carbonate, chloride and potassium or the attendance of extrastages [48-51]. Hence, an exact control over the processing conditions is forever recommended for the readiness of a powder with insignificant defects. The production of a single crystal HAP with high phase purity, the precipitation reaction is typically conducted at a high temperature or a high pH. At any time the pH worth should be lowered, the temperature must be moved up and vice versa [52, 53]. This prompts to a dramatic lessening in the production of stage impurities, for instance, octacalcium phosphate (OCP), and dicalcium phosphate anhydrous (DCPA) resultant in HAP as a dominant stage [54-56].

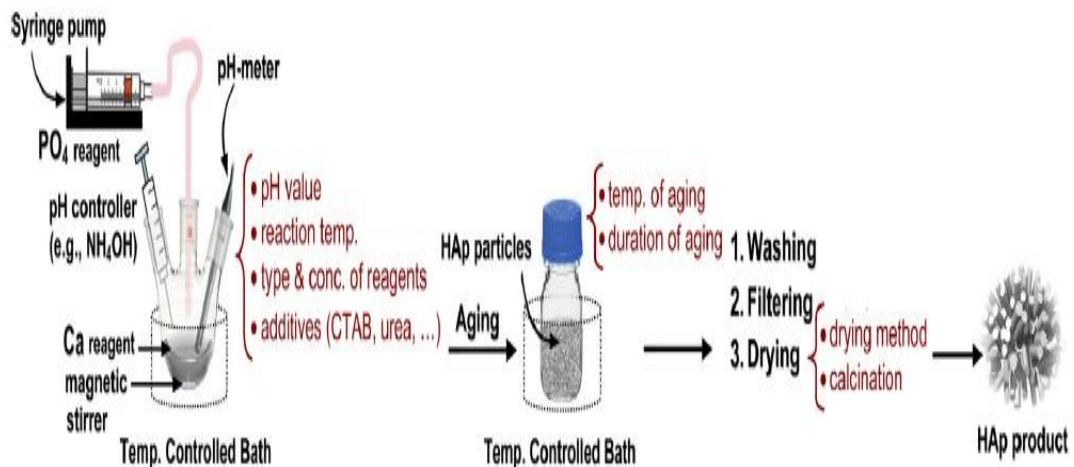


Figure 3.4. Preparation of HAP nanoparticles using Conventional Chemical Precipitation [28].

3.3.2. Hydrolysis method

Can be set up by the hydrolysis of other CaP stages of the HAP nanoparticles, containing dicalcium phosphate anhydrous, tricalcium phosphate and dicalcium phosphate dehydrate, hydrolysis octacalcium phosphate though. In the final decade has not been of enormous attention to the preparation of HAP particles, perhaps of the slow rate of octacalcium phosphate hydrolysis or the capability of octacalcium phosphate to integrate impurity species, containing added substance and strange ions utilized for its conversion to HAP. Fluid hydrolysis of CaP stages into HAP commonly profits by dissolution and precipitation procedures [57-59].

3.3.3. Sol-gel method

The conformist sol-gel procedure includes the readiness of a three dimension inorganic system by integration alkoxides in whichever and or a watery organic stage, trailed by old age at room temperature, gelation, drying on a hot plate and lastly take aways of organic residues as of the resultant dried gel by utilizing post heat up treatment instrument calcination [60-63]. The in general method is showed in figure 3.5. In the solution stage, the response to the calcium and phosphorus precursor or happens gradually,

this is why a long time of old age is normally necessary for the apatitic stage to shape. Also, the thermal treatment stride was established to be critical in the production of pure HAP and the expulsion of residual organic parts, water molecules and gaseous products from the porous gel [64-65]. In fact, insufficient old age or; and uncontrolled gelatin and heat treatment might reason the production of several impurities, basically CaO , $\text{Ca}_3(\text{PO}_4)_2$, CaCO_3 and $\text{Ca}_2\text{P}_2\text{O}_7$. The gelation rate, the life of the solvent, temperature and pH employed during the process depend on the chemical structure of the reagents usanced in the sol-gel synthesis. Addition allow-temperature methods, for instance, wet chemical precipitation and sol-gel combination need post heat treatment to the crystallise the HAP; while crystalline HAP could be formed in one stride using hydrothermal synthesis. The initial stage is mixing the phosphorus-calcium and precursors following maintaining the Ca/P ratio at a constant valuerate of 1.67. The solution is heated in a sealed vessel autoclave. The mixing is then permitted to age, and subsequently washed and filtered. Finally, it is dried in an oven and calcined. The amount of HAP is limited to the size of the reaction vessel. The starting reagents and H_2O should occupy 50-60% of the autoclave volume. Main drawbacks contain the production of the secondary stage and the high cost of some of the beginning materials, specially alkoxide supported precursors. Secondary CaO stage was showed to be damaging to the biocompatibility of HAP and then efforts have been made to take out the coexisting CaO, also during washing of the calcined powder via a dilute acid solution or alteration of the basic process, for example, during growing the old age time [68].

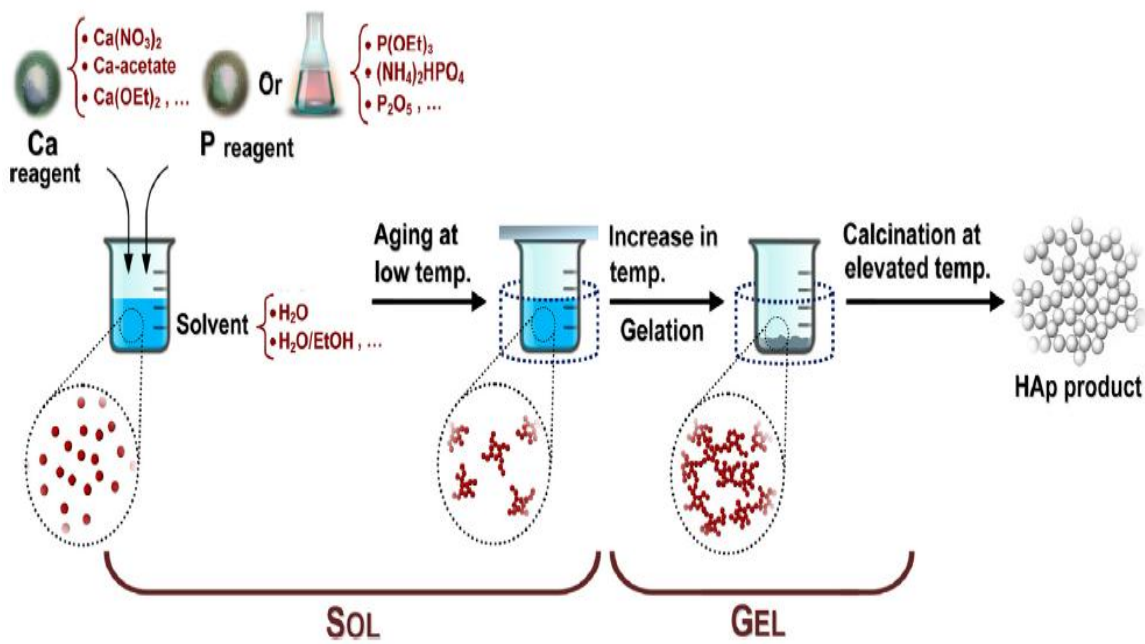


Figure 3.5. Preparation of HAP nanoparticles using sol-gel process [28].

3.3.4. Emulsion method

The exact controlling over morphology and size division of particles or grains are quite significant and surely hard, particularly when one intends to create nanoscopic substance by means of least agglomeration. Emulsion processing to the HAP particles has been first acquainted with the process the bunch and to limit the forming of rigid agglomerates [69]; while this procedure is at the present an interesting subject not merely to get ready an agglomerate gratis ceramic powder, other than too to control the microstructure and morphology of particles resultant. Besides this, unlike wet procedures created for HAP production, emulsion technique is optional to be extra efficient to decrease the particle size, for manage the morphology, with to boundary the agglomeration of HAP particles [70, 71]. Furthermore, effortlessness and mild synthesis state devoid of any high-temperature necessity for the duration of the major procedure make the emulsion system to be a suitable technique. A microemulsion is a thermodynamically steady, isotropic clear dispersion of two immiscible fluids, like organic and water, formed through the attendance of surface active operators. Surfactants because amphiphilic molecules by a hydrophilic head linked to a hydrophobic can decrease the surface pressure of the immiscible fluids, resultant in a dispersed stage limited in nanometer regimes; the

produced emulsion is, therefore, able of carrying nano-sized particles while the feedback is limited in the nanosized fields. Emulsion procedure relies powerfully on the kind of surfactant utilised and focus of the surfactant exists in the fluid medium [69, 70, 72].

3.3.5. Sonochemical method

Sonochemical methods, which every time yield nanosized produces, are depended on the chemical reactions stimulated by means of influential ultrasound radiation [73, 74]. In reality, the reactivity of chemicals is stirred to accelerate the heterogeneous reactions amid and solid and liquid reactants [75]. It has also been notified that HAP nanoparticles synthesised by a so no chemical procedure possess more regular, lesser, and purer crystals with negligible agglomeration [76-79]. These nanoparticles could considerably improve the sintering kinetics, because of the higher surface region, and for this the mechanical properties of last product. CaO et al. with urea as organic modifier [80]. They exhibited that adding of urea favors the creation of HAP nanoparticles. They found an Arrhenius connection between the rate of HAP construction and the reaction temperature [28].

3.4. High-Temperature Processes

Combustion and pyrolysis are two procedures in high-temperature processes which can be used to burn or partially burn the precursors [28].

3.4.1. Combustion

This method is also called solution combustion method, it is measured as a common and most capable way in preparation of a conventional process to prepare several oxide ceramics, and CaP nanocrystals [81-83]. Furthermore, low price of materials which is used as raw material and it is identified as a simple preparation process by comparing with another process, as well as good chemical uniformity of synthesised powder as a result of the intimate blending of his constituents make this method very powerful and popular [84,85]. As shown in figure 3.6, solution combustion processing of HAP involves a very fast exothermic and self-sustaining redox reaction between oxidants (calcium nitrate and HNO_3) and an appropriate organic fuel in an aqueous phase [86, 87]. Firstly, mixing the aqueous stock solutions of $\text{Ca}(\text{NO}_3)_2$ and $(\text{NH}_4)_2\text{HPO}_4$, and then adding the concentrated HNO_3 to dissolve the resulting white precipitate; a single or a mixture of two or more fuels

are subsequently incorporated into the resulting solution. Secondly, by heating the mixture to the proper temperature, for example, 300°C in a furnace, the reaction started, and then increase in temperature rapidly, as a result of the combustion, to a maximum value. Finally, to avoid any more particle growth and making extreme nucleation the solution should cool down very rapidly. Many studies are being issued recently in using the combustion for preparing of nanosized HAP using, for example, Ghosh et al. A vigorous exothermic reaction occurs between the fuel and oxidizer; the gaseous products of this reaction spontaneously combust. This produces a very high local temperature that causes the formation of solid calcium phosphate powder. By using a proper fuel, makes the process very fast and does not take a long time to complete (less than 20min.). The formed product may be either crystalline or amorphous. Both require a calcination step; to remove organic residues and crystallise the phase formed, respectively [88, 89].

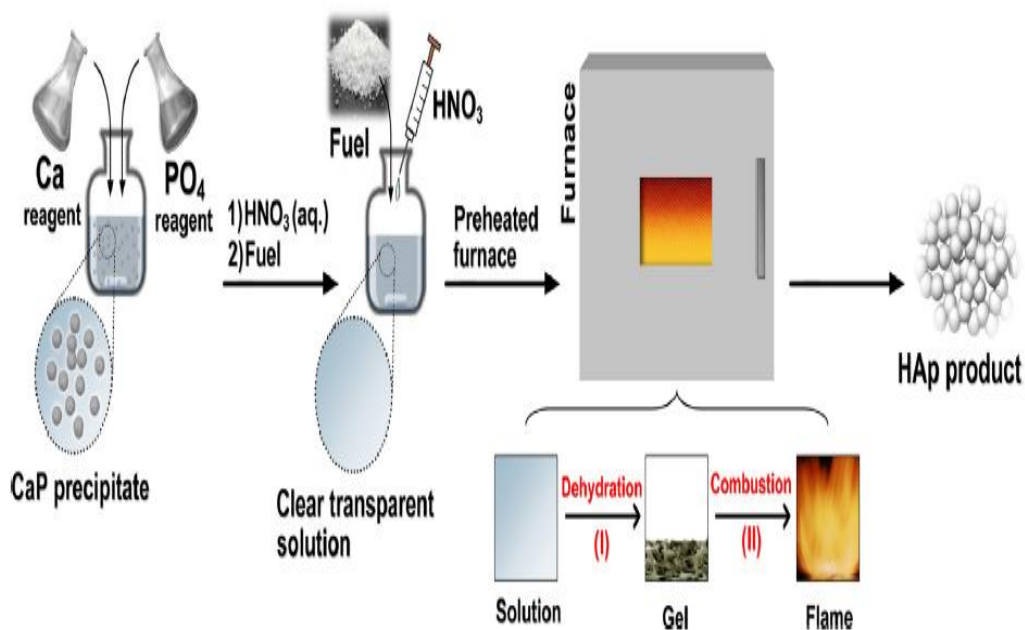


Figure 3.6. Preparation of HAP powder nanoparticles by the use of solution Combustion process [86].

3.4.2. Pyrolysis (SprayPyrolysis)

The process of getting a stoichiometric single-crystal HAP should be controlled very firmly and prepare some in advance high-temperature conditions to get a high crystalline product. In the other hand, the HAP particles which fabricated directly by a rapid pyrolysis-based method have been classified as a well crystalline, homogeneous, and stoichiometric [90, 91]. The process of producing HAP particles is continuous and not stopping in this method. This is referred from particles to reactants in a gas stage produced by physical evaporation of liquid precursors. In comparison with the combustion technique, no fuel mixed with the reactants is required in the pyrolysis synthesis and the procedure can be effortlessly scaled up for the continuous creation of HAP particles. The pyrolysis method sometimes named as an aerosol method due to transferring gas-to-particle or liquid to-particle aerosol decomposition process. As well as ‘spray pyrolysis’ is another name of pyrolysis method, because of spraying the precursor solutions into a flame or a hot zone of an electric furnace using an ultrasonic generator. Then final powder was produced by the reaction of the generated vapours and gases at high temperatures. Figure 3.7 depicts the schematic illustration of the tools. According to the shape, then the size of the droplets produced during the process; are very significant and it has an enormous effect on the size of the particles so that, some attempts have been prepared to reduce particle size by the formation of fine droplets [92, 93].

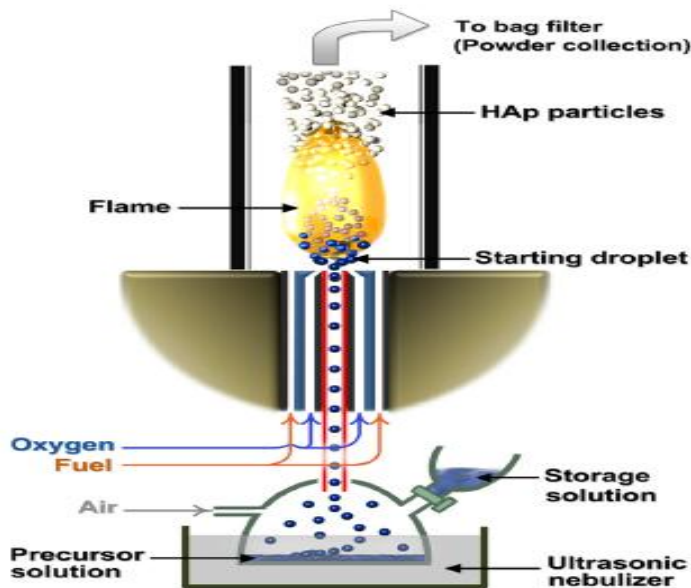


Figure 3.7. Graphic diagram illustrating the equipment system for the preparation of HAP powder nanoparticles using Flame Spray Pyrolysis [28].

3.5. Combination Procedures

Over the past decade, there have been many efforts to enhance the properties of the final outcomes, such as combining of two or more different methods to produce a synergistic strategy [94, 95]. Both the hydrothermal–hydrolysis and hydrothermal–microemulsion combinations can be given as example [96,97]. Combining the mechanochemical method with the hydrothermal process through the incorporation of an aqueous stage into the system is still the most important approach. Combinations of hydrothermal-mechanochemical, hydrothermal-hydrolysis and hydrothermal-emulsion have received more attention. Combinations of the microwave irradiation with different methods e.g. solid-state and sonochemical methods have been reported. Combination procedures may develop the characteristics of HAP nanoparticles [28, 98].

3.6. Hydrothermal Synthesis

The hydrothermal technique is turning out to be one of the most crucial tools for advanced materials processing, especially in the processing of nanostructural materials for a broad variety of technological applications such as electronics, optoelectronics, catalysis, ceramics, magnetic data storage, biomedical, biophotonics, etc [99, 100]. Hydrothermal synthesis involves the several techniques of crystallising substances from high-temperature aqueous solutions at high vapor pressures; also named "hydrothermal method". Hydrothermal synthesis can be defined as a method of synthesis of single crystals that depends on the solubility of minerals in hot water under high pressure. The definition of the word hydrothermal has undergone several changes from the original Greek meaning of the words 'hydros' meaning water and 'thermos' meaning heat. The crystal growth is performed in an apparatus consisting of a steel pressure vessel called an autoclave[100].

3.7. Electrical properties of Hydroxyapatite

In contrast to a massive body of text that exists in the field of chemical synthesis, processing and functionalization of HAP and related materials and devices. In the past ten years, there has been increasing in the interest towards electrical properties of a biomaterial, hydroxyapatite (HAP), $\text{Ca}_5(\text{PO}_4)_6(\text{OH})_2$ widely used in cementless implant coatings and bone graft substitutes. Both bone and dentine present the ability to generate electrical charge the surface when stressed [101, 102]. This pressure induces surface charge has been considered to be connected with the functional form generation of bone by the Wolff's law. Due to its pyroelectric property bone also has a spontaneous electrical polarisation which again is believed to have functional distribution and purposes. Since the 1960s until the end of the 1980s, there are strong investigations of the electrical properties due to bone piezoelectricity and observing rare electrical properties of bone originates from its organic constitute, collagen. Collagen is a fibrillar protein and has been found to display both piezoelectricity [101,103, 104] and pyroelectricity. The attendance of apatite in bone was measured to create bone stiff because of its mechanical strength and to do something as a reservoir for calcium to maintain calcium homoeostasis. The electrical influence of apatite in bone's piezoelectric behaviour had been clarified as a natural composite between apatite as a non-piezoelectric dielectric inside a piezoelectric collagen matrix [105]. Further studies of electrical properties of hydroxyapatite have been developed after discovering both two significant features piezoelectric hydroxyapatite stages [106, 107], and the aptitude of making discrete domains of electrostatic charges [108].

4. MATERIALS AND METHOD

4.1. The Synthesis Method of HAP

For the preparation of nanostructured hydroxyapatite bioceramic (10mmol) calcium nitrate tetrahydrate $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ is dissolved in 30mL distilled water (2.3615g) and mixed on a magnetic stirred for 30 min at 60°C , and (6mmol) ammonium hydrogen phosphate $(\text{NH}_4)_2\text{HPO}_4$ is dissolved in 30mL distilled water, 0.79236 g, was added to the above solution. Both solutions separately sonicated for 10 min. After the addition of 40 mg of cetyl trimethyl ammonium bromide (CTAB) to the solution and sonicated 60 min, the ratio of Ca/P in the solution was maintained 1.67. Also, put hydrothermal 24 hours at 180°C and at 140°C in 100 mL water in an autoclave. After 24 hours filtering, the solution cleaned then washed in ethanol then drying the powder in the oven at 50°C . We make calcinations at 700°C in a furnace to evaporate the nitrates and hydrates from the structure. Because the structure is complex and we must tend off nitrates and hydrates from the structure so calcination is required to get pure hydroxyapatite. In this section, the design and working of the experimental setup used for preparation and characterization of hydroxyapatite have been described. In addition, the detailed sample preparation procedure and the crystalline phases of synthesised nanostructured hydroxyapatite bioceramic were determined by X-ray diffraction (XRD) analysis on the RigakuRadB-DMAX II diffractometer with $\text{CuK}\alpha$ radiation at room temperature. Morphological features of hydroxyapatite bioceramic coatings were observed by scanning electron microscopy (SEM) executed on a scanning electron microscope JEOL-7001 and EDX performed on Energy Dispersive X-ray analysis JEOL-7001. Fourier transform infrared (FTIR) spectroscopy was taken (Thermo scientific Nicole IS 5) and we to used Keithley 4200 semiconductor characterization system for current-voltage (I-V) analysis. The weight loss measurements made by thermogravimetric analysis (TGA) and the phase transitions occurred in the sample was analysed by differential thermal analysis (DTA) by SHIMADZU DTG-60AH equipment.

4.2. Scanning Electron Microscopy (SEM) Analysis

The SEM is a kind of electron microscope images that the surface by scanning sample with a high-energy beam of electrons in a raster scan pattern. The electrons interface with the atoms that make up the specimen generates signals that include data about the taster's surface topography, composition and for the other properties like electrical conductivity (σ) [109]. SEM are scientific tools that utilisation a beam of highly energetic electrons to check objects on a very fine scale. This examination of the electron microscopy gives us information about the (Morphology, Topography, Composition and Crystallographic Information of the nature of any objects).

An ordinary SEM operates at a high vacuum. The basic principle is that a beam of electrons is produced by an appropriate source, regularly a tungsten filament or a field ejection gun. The electron beam is accelerated through a great voltage for example 25 kV and permits through an arrangement of apertures, also magnetic lenses to produce a thin beam of electrons, then the beam scans the surface of the sample by means of scan coils. Electrons are released from the sample by the action of the scanning beam and composed by an appropriately situated finder [110].

4.3. Energy Dispersive X-ray (EDX) Analysis

Energy dispersive X-ray analysis (EDXA), Energy dispersive X-ray spectroscopy (EDS) or (EDX). It is sometimes known as energy dispersive X-ray microanalysis (EDXMA), an analytical procedure we utilised for the recognising elemental analysis or chemical characterization of the specimen. The Energy dispersive X-ray examination system works as an integrated feature of a SEM and can't operate on shave without the last. It depends on an interaction little source of X-ray excitation and a specimen. Its characterization capabilities are due in large part to the fundamental principle that every element has a single atomic structure permitting a unique set of peaks on its X-ray emission spectrum. For stimulating the release of typical X-rays after a specimen, by the higher-energy beam of charged particles like electrons of X-rays is concentrated into the specimen being studied. At relax, of the atoms within the specimen contains ground state electrons in separate energy levels. Them is hap beam can excite the electron in an internal shell, expelling the internal shell from the shell while making an electron-hole where the electron. An electron as of an outside, higher-energy shell then become full

the hole and the difference in energy difference the higher-energy shell and the lower energy shell perhaps free in the form of an X-ray. The number and energy of the X-rays give out from a specimen can be measured by an EDS. Also, energies to the X-rays are characteristic of the difference in energy between the two shells and of an atomic structure of a releasing element, EDS permits of the elemental composition of the sample to be measured [111, 112].

4.4. Fourier Transform Infrared (FT-IR) Spectroscopy Analysis

FT-IR is a method which is utilised to get an infrared spectrum of emission or absorption or of a solid, gas or liquid. A Fourier transform infrared spectrometer at the same time gathers high spectral resolution data over a wide spectral range. FTIR refer to Fourier Transform Infra-Red, the favoured technique of infrared spectroscopy. In IR spectroscopy, infrared radiation is moved into through a specimen. A few to the IR radiation is occupied through the specimen and a few of it is transmitted. The out coming spectrum substitutes the molecular transmission and absorption, making a molecular fingerprint of the specimen. Similar to a fingerprint no two unique molecular structures generate a like infrared spectrum. This creates infrared spectroscopy helpful for more than a fewkind of analysis.

Therefore, what database able to Fourier transform infrared grave?

- It can identify unfamiliar substances
- It can find out the quality or consistency of a specimen
- It can find out a number of segments in a blend

IR lies amid the visible light and microwave portions of the electromagnetic spectrum. Infrared waves have shorter than microwaves and wavelengths longer than visible with shaving frequencies also are lower than visible and higher than microwave. The IR sections is divided into near, far and mid region primary source of IR is thermal radiation(heat) Any object radiates in infrared. Even an ice cube emits infrared [113].

Light falls on a light source some of the light is reflected some transmitted The reflected light goes to the stable mirror and it reflected back to beam splitter and the transmitted light also reflected to beam splitter , both goes to the detector and both interfere

constructively and destructively and generate a sinusoidal signal and generate an interferogram. The IR area ($10-14000\text{ cm}^{-1}$) to the electromagnetic radiation is distributed into three districts: near, mid, and far-infrared. The mid-infrared ($400-4000\text{ cm}^{-1}$) is the greatest ordinarily used district to an analysis by way of complete molecules possesses characteristic absorbance frequencies and essential molecular vibration in that area. Mid-IR spectroscopy techniques are established on the studying communication of infrared radiation through the specimen. By way of infrared radiation is moved into a specimen, particular wavelengths are absorbed reasoning the chemical bonds in the substance to go through vibrations like stretching, bending, and constricting. Functional groups there in a molecule be inclined to absorb infrared radiation in the similar wave number range despite additional structures in the molecule, and spectral peaks are resulting from the absorption of bond vibrational energy become in the infrared region, therefore there is a relationship among infrared band position and chemical construction of the molecule. As well to as long as qualitative knowledge concerning functional groups, the infrared spectrum is able to give quantitative information, for instance, the concentration of bacteria in a development average [114-117].

4.5. X-ray Diffraction (XRD) Analysis

XRD powder possibly the many broadly utilised XRD method for characterising materials. As the name proposes, the specimen is normally in a powdery shape, consisting of fine grains of unique crystalline material to be explained. The method is utilised also broadly for reviewing particles in liquid suspension furthermore thin film or bulk materials. The peak pattern in an XRD is exactly associated with the atomic distances. consign us look an event X-ray beam interacting with the atoms organised in a periodic comportment as appeared in two dimensions in the subsequent illustrations show in figure 4.1. The atoms, represented as green spheres in the graph, can be viewed as forming different sets of planes in the crystal. For a particular set of lattice planes with an inter-plane distance of (d), the state for a diffraction to happen can be basically written as

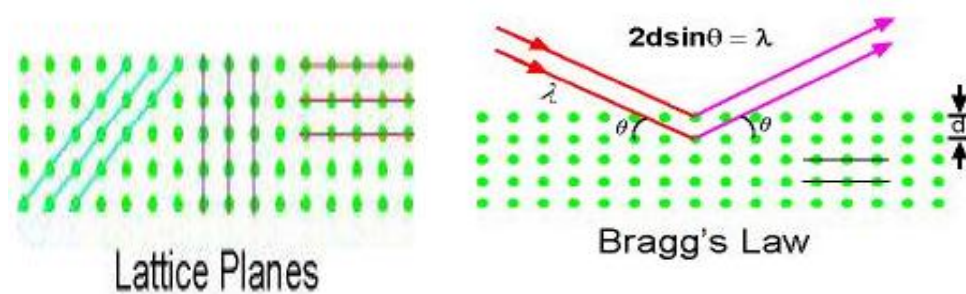


Figure 4.1. Illustration of Bragg's law [118].

which is identified like the Bragg law, who first offered it. In the equation, the wavelength of the X-ray is (λ), the scattering angle (θ), and (n) is an integer indicating the order of the diffraction peak. The Bragg's Law is one of the very significant rules utilised for interpreting X-ray diffraction data Bragg's Law refers to the straight forward equation:

$$n\lambda = 2d \sin \theta \quad (4.1)$$

derived by the English physicists (W.L. Bragg in 1913) to make clear why the cleavage faces of crystals emerge to reflect X-ray beams at sure angles of incidence (θ , λ). The changeable d is the distance between atomic layers in a crystal, and also the variable is the (λ) wavelength X-ray beam of the incident so (n) is an integer [118].

4.6. Thermogravimetric (TG) Analysis and Differential Thermal (DT) Analysis

4.6.1. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis is a system whereby the weight of the material, in around heated or cooled at a controlled rate is registered as an element of time or temperature. A TG is the department of thermal analysis which examines the mass vary of a specimen as a function of temperature in the scanning mode. Thermogravimetric analysis is a way of thermal analysis in which very in property physical and chemical of any materials are measured as an element by increasing temperature with constant heating rate [119-121]. Changes in the mass of a specimen are examined while the specimen is subjected to a package and changes in temperature influence the specimen. Not everyone

thermal changes-incidents get a change in mass of specimen that is(Melting, Crystallisation) but some thermal events a (absorption, desorption, vaporisation, reduction, sublimation, oxidation, and decomposition) get a drastic change in mass of the sample. It is utilised in the analysis of (Volatile products, Gaseous products lost for the period of the reaction in Thermoplastics, Thermosets, Elastomers, Composites, Films, Fibres, Coatings, and Paints). [122].

4.6.2. Differential Thermal Analysis (DTA)

DTA includes cool or heat (emitted, absorbed) by a test sample and an inert-reference undergo to similar conditions, whilst for any temperature contrast between that the sample (T_s) and the reference (T_r) compound is recorded($\Delta T = T_s - T_r$). The differential temperature is then plotted against temperature or time. Change in the example which prompt to the development or absorption of heat is able to detect aspect to the inert reference. Differential Thermal Analysis can, in this way, be utilised to study thermal properties and stage changes which not prompt for an adjustment in enthalpy. The pattern of the Differential Thermal Analysis curve necessary at that time show distinguishing at the transition temperatures and the slope of the curve at any point will depend on the microstructural constitution at that temperature. Differential temperatures can also arise between two inert samples when their response for the practical heat management is not identical. A Differential Thermal Analysis curve can be utilised like a fingerprint to identification purpose. The range under a differential Thermal Analysis peak can be to the enthalpy change and is not influenced by the heat capacity of a sample. Differential thermal analysis perhaps cleared officially as a system for recording the difference in temperature between a matter and a reference substance against either temperature or time like the cooled two samples are subjected to the indistinguishable temperature administrations in a situation heated at the limited rate [123].

A system of which the temperature difference between is measured as a function of temperature and a substance, while the substance and reference are subjected to the same controlled temperature programme. The difference of temperature is named since differential temperature conspires against temperature. Physical changes frequently produce into an Endothermic peak, whereas chemical reactions these of an oxidative nature are exothermic. Exothermic reaction comprises oxidation and catalytic reaction gives

upward peak. Endothermic reaction comprises vaporisation and absorption also give downward peak [123].

4.7. Current-Voltage (I-V) Characterization

The current-voltage characteristic curves, which are short to the I-V Characteristic Curves or basically current-voltage bends with an electrical gadget or component, are a group of graphic curves which are utilised to categorise its operation inside the electrical circuit. Current-voltage characteristic curves prove a rapport between the current flowing through to the electronic gadget and apply a voltage to its terminal. Current-voltage characteristic is usually utilised as an instrument to decide and comprehend fundamental parameters of the constituent or tool and which can also be used to the scientifically demonstrate its behaviour within an electronic circuit. But as with the majority electronic devices, there is an infinite number of current-voltage characteristic curves representing a variety of inputs or parameters and like we can show a family or else a collection of curves on the same graph to represent the various values. We say, e.g., the I-V characteristics of the bipolar transistor can be shown by various amount with base propel. Also, the motionless I-V characteristics of a constituent or tool necessary are not the straight line. Get such as the characteristics of the static worth resistor, we would wait for them to be reasonably straight and constant within sure varieties of current, voltage and power as it is a linear or ohmic tool. But the electrical supply voltage, (V) applied to the stations of the resistive component (R) above was unlike, and the subsequent current, (I) quantified, this current would be characterised like;

$$I = \frac{V}{R} \quad (4.2)$$

A creature one of the Ohms Law equation. We recognise after Ohms Law this of the voltage across the resistor increases so too does a current coursing through it, it should be possible of concept the graph to explain a relation between the voltage and current as shown in the diagram indicating the volt-ampere attributes of the resistive element [124].

5. RESULTS AND DISCUSSION

5.1. X-Ray Analysis

X-ray is utilised to analyse the structural properties of any material. Qualities of individual crystal structure comprise diffraction angle (θ) and to the diffracted beam intensity. The intensity of diffracted beam for each matter will be unique as of the dissimilar physical attributes of each atom. That uniqueness benefits to recognises the structure and determine the structural parameters of the substance. XRD spectra of the HAP taken within a 2θ range of $20-80^\circ$ are shown in figure 5.1. The mean crystallite size D of the sample was computed by analysing the XRD data using the Debye - Scherrer formula:

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (5.1)$$

where D represents average crystalline size, λ is the wavelength of X-ray (0.1540559 nm), θ is the peak angle of diffraction degree (Bragg's angle) and β is the full width of the peak at the half-maximum intensity in radian (FWHM), also Scherrer constant defined as the crystallite shape and is around equal to 0.9. Sharp peaks appeared in the XRD patterns of the calcined HAP powders revealed their good crystallinity. The characteristic peak of the sample appears at $2\theta = 29.08$, corresponding to (210) plane of HAP, which confirms the presence of HAP crystallite. The average crystalline size of all samples scaffold were estimated using Debye-Scherrer equation confirming the nanostructure of the nano-composite and was found to be 12.2 nm, This range confirms that all the studied composites are nanostructured materials [125, 126].

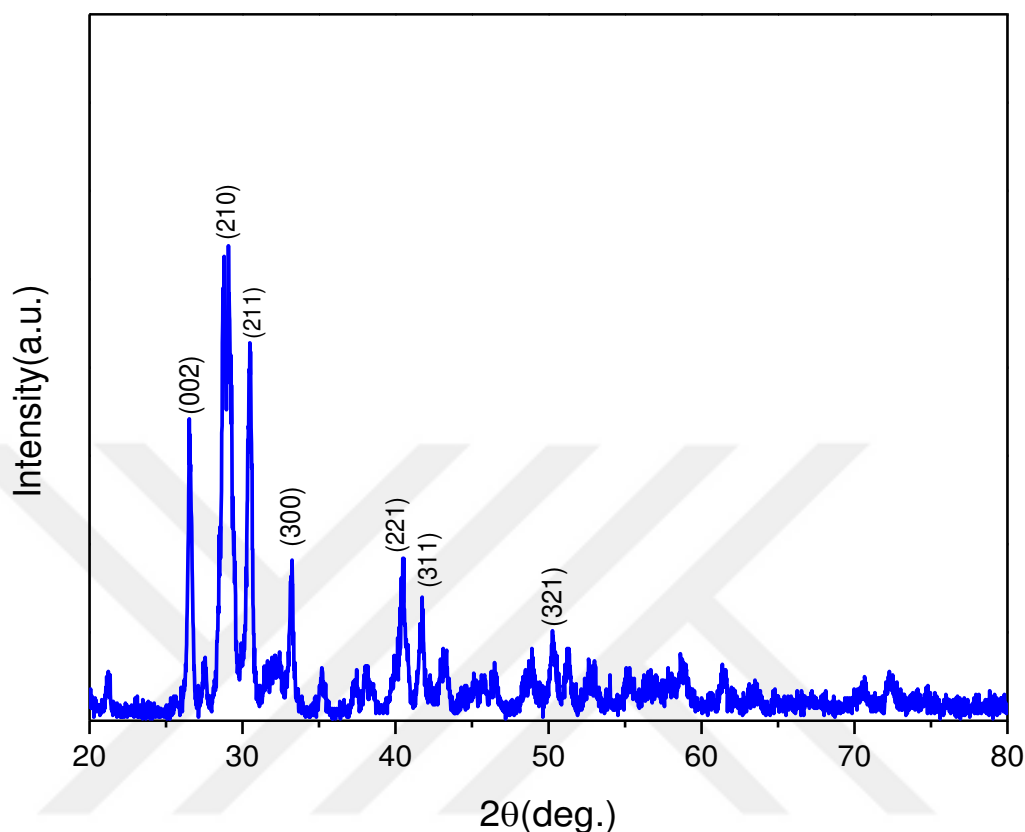


Figure 5.1. XRD patterns of HAP powder in the sample.

5.2. FTIR Analysis

FTIR is a way utilised for chemical identification, principled on the actuality that the selective absorption of material happens in the infrared domain. The molecule of chemical substance vibrates in numerous modes later absorption of Infrared giving fourier transform infrared spectroscopy absorption spectrum, above broad wavelength scope. FTIR analyses helped us to reveal the chemical bonding characteristics with the powder samples. FTIR spectra of the HAP are shown in figure 5.2. All the bands corresponding to HAP structure were observed in FTIR spectrums. The observed bands correspond to the bands of hydroxyl and absorbed water phosphate species [230]. Characteristic bands for phosphate stretching vibrations and phosphate banding appeared in the region (950 cm^{-1} – 1250 cm^{-1}). The bands at (903 cm^{-1} – 962 cm^{-1}) correspond to ν_1 stretching mode of PO_4^{3-} group while the bands at (1032 cm^{-1} – 1092 cm^{-1}) correspond to ν_3 stretching mode

[127,128]. PO_4 bands at (1091cm^{-1} – 962 cm^{-1}) confirm the formation of HAP structure. The most intense peak among the phosphate group was observed in the region of $\sim 720\text{cm}^{-1}$ [129, 130]. The obtained all FTIR bands are in good agreement by the bands of HAP [130]. The appearance of the sharp peaks associated with the stretching vibration in investigated samples indicates to the formation of crystalline HAP.

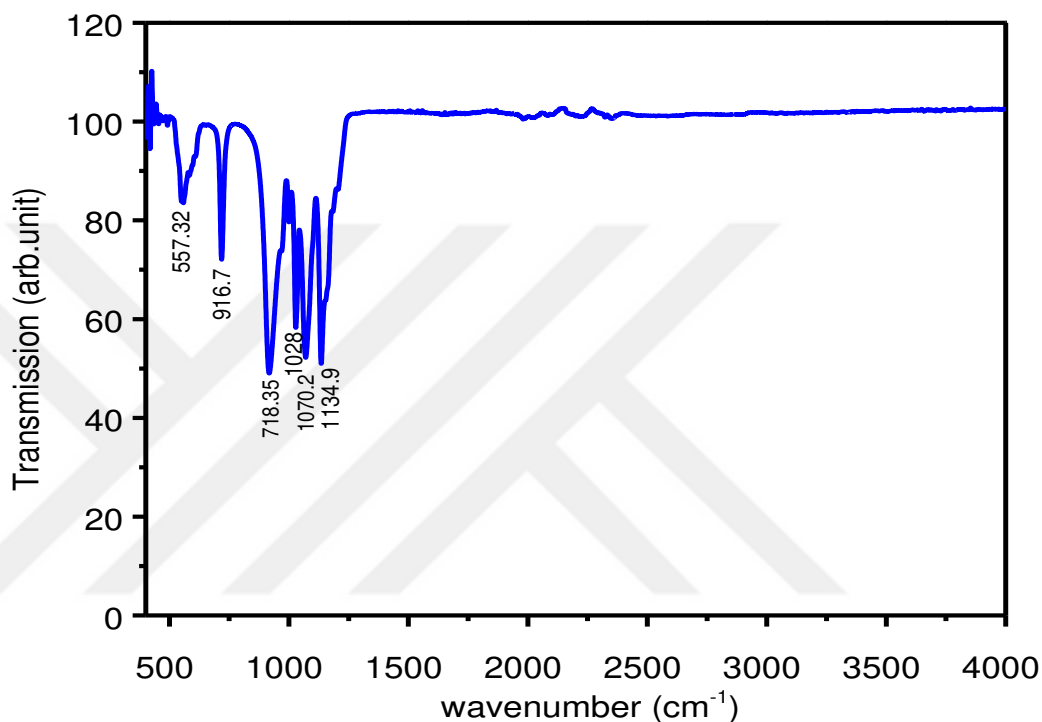


Figure 5.2. FTIR spectra of HAP in the sample.

5. 3. SEM and EDX Analysis

Scanning electron microscopy instrument has been invoked to know the morphology of the obtained HAP. The SEM images of the HAP in the range microparticle are shown in figure 5.3. The morphology of HAP sample exhibit shape plate-like structure with a smooth surface. Also, we can say generally HAP sample from (figure 5.3.(a-d)) morphology obtained plate-like, but when size at x 6000 magnification clearly exhibited shape plate-like structure. The elemental analysis with the HAP sample was performed by X-ray Energy Dispersive spectroscopy (EDS). The phosphorus, calcium and oxygen were observed only in obtained EDS spectra of the HAP sample. The elemental composition and homogeneity of particles have major effects on biocompatibility and bioactivity properties

of bioceramic materials. To know the inter relationship between materials properties, the composition of the material should be known. This technique was utilised to analyse HAP specimen. An EDS spectrum of this sample is exhibited in figure 5.4. Organic reactions of a HAP sample are powerfully depend on its chemical composition, energy dispersive spectroscopy (EDS) result uncovers that HAP specimen contains Ca, P and O. The best Ca/P ratio for synthesised specimen was observed to be 1.65, which is somewhat smaller than 1.67 theoretical worth and the similar was usually reported [131, 132].

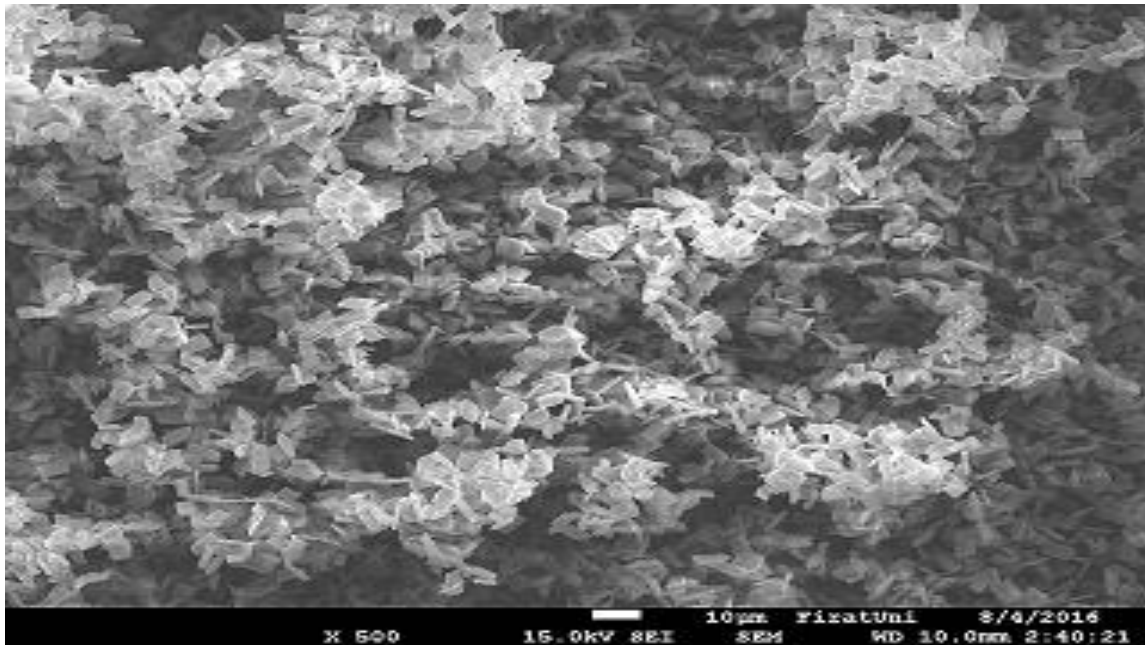


Figure 5.3.a) SEM (10µm) of HAP in the sample at 500x magnification.

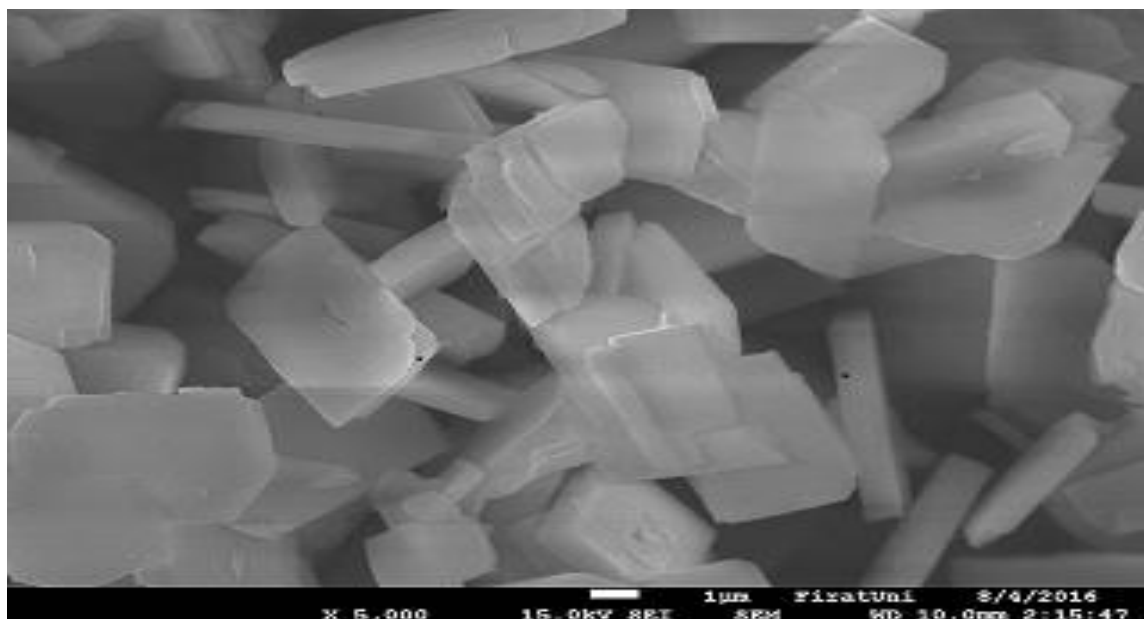


Figure 5.3.b) SEM (1 μ m) of HAP sample at 6000 x magnification.

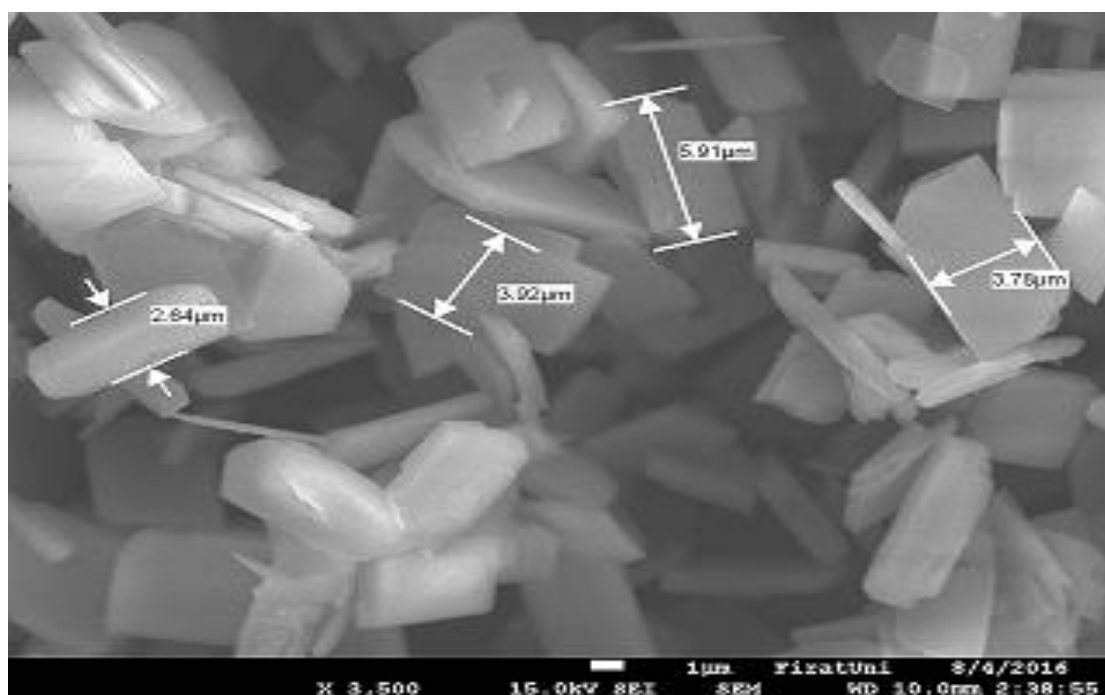


Figure 5.3.c) SEM (1 μ m) of HAP in the sample at 3500x magnification.

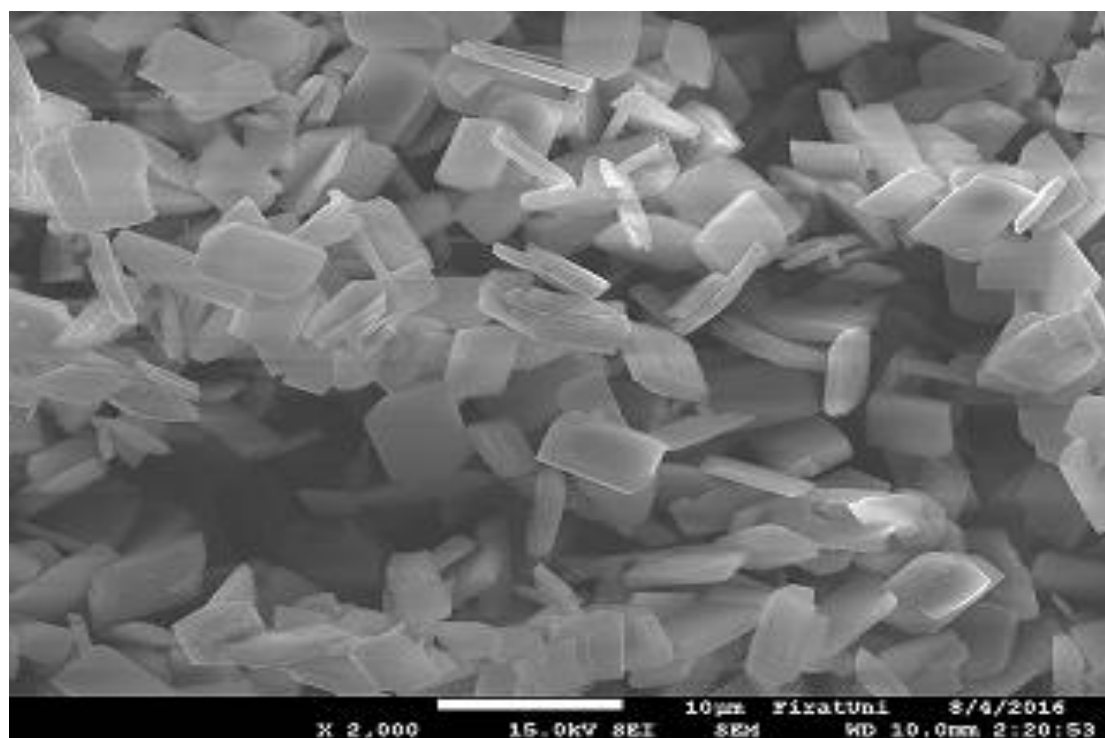
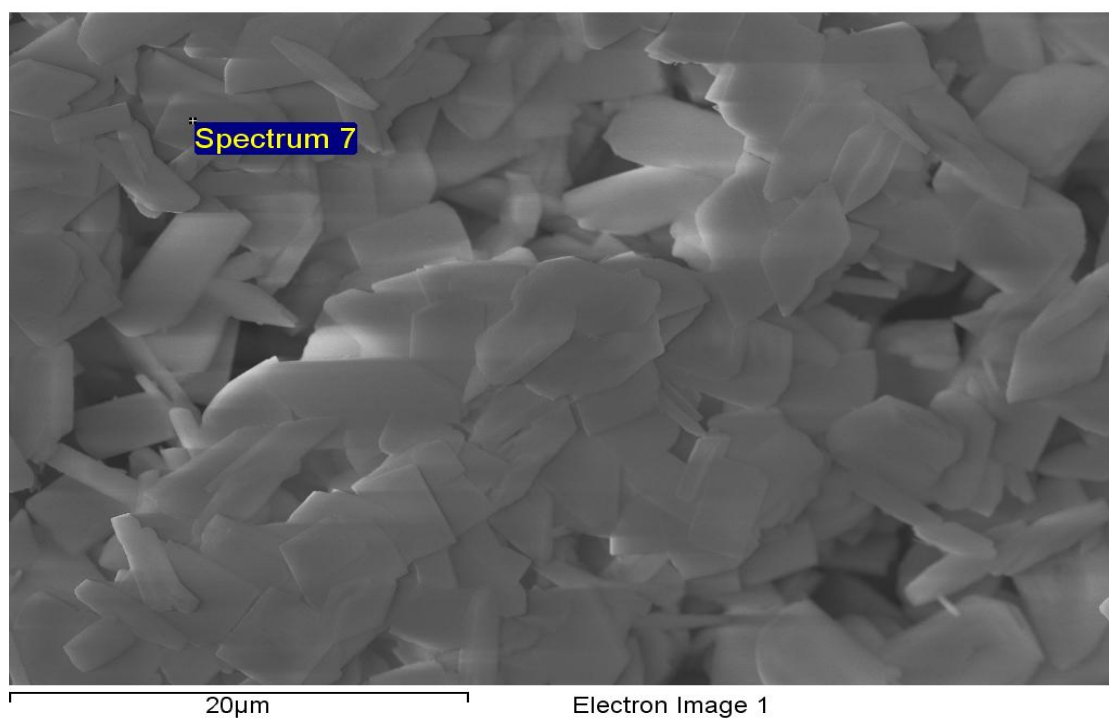
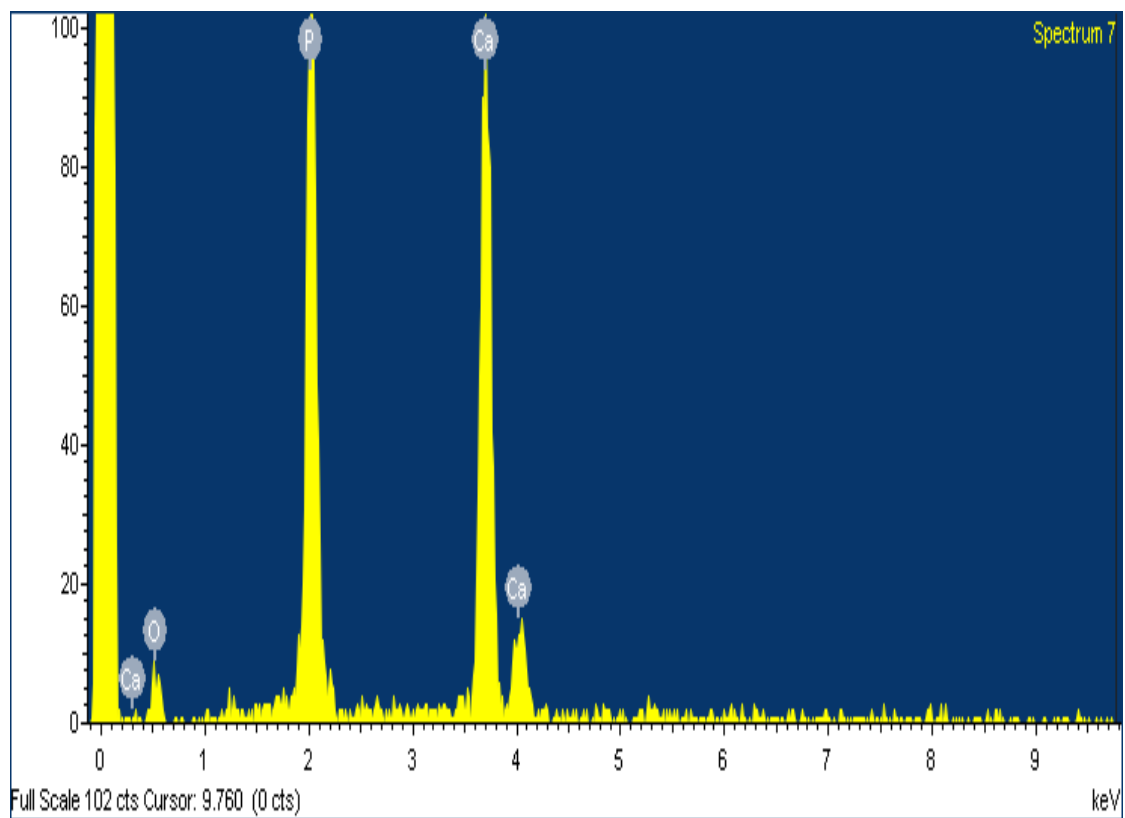


Figure 5.3.d) SEM (10 μ m) of HAP in the sample at 2000x magnification.



Element	Weight%	Atomic%
O K	11.49	22.63
P K	33.66	34.24
Ca K	54.85	43.12
Totals	100.00	

Figure 5.4. EDX analysis of the sample.

5. 4.TGA/DTA Analysis

Thermogravimetric analysis (TGA) and Differential thermal analysis (DTA) for hydroxyapatite sample was made from room temperature to 925°C. Thermal stability of HAP sample was examined by thermal decomposition of the powder. The TGA/DTA results are shown in figure 5.5. The TGA (thermogravimetric analysis) demonstrates total weight loss is 8.583% in the temperature range from room temperature to 925°C that the decomposition of HAP sample due to evaporation of physically adsorbed water is given in figure 5.6. DTA (differential thermal analysis) curve shows that thermal decomposition of HAP sample at 290.76°C with an endothermic peak and this peak is alone due to degradation of residual water from the sample shown in figure 5.7. The result of thermal decomposition is useful for optimisation of conditions to obtain monophasic biomaterial.

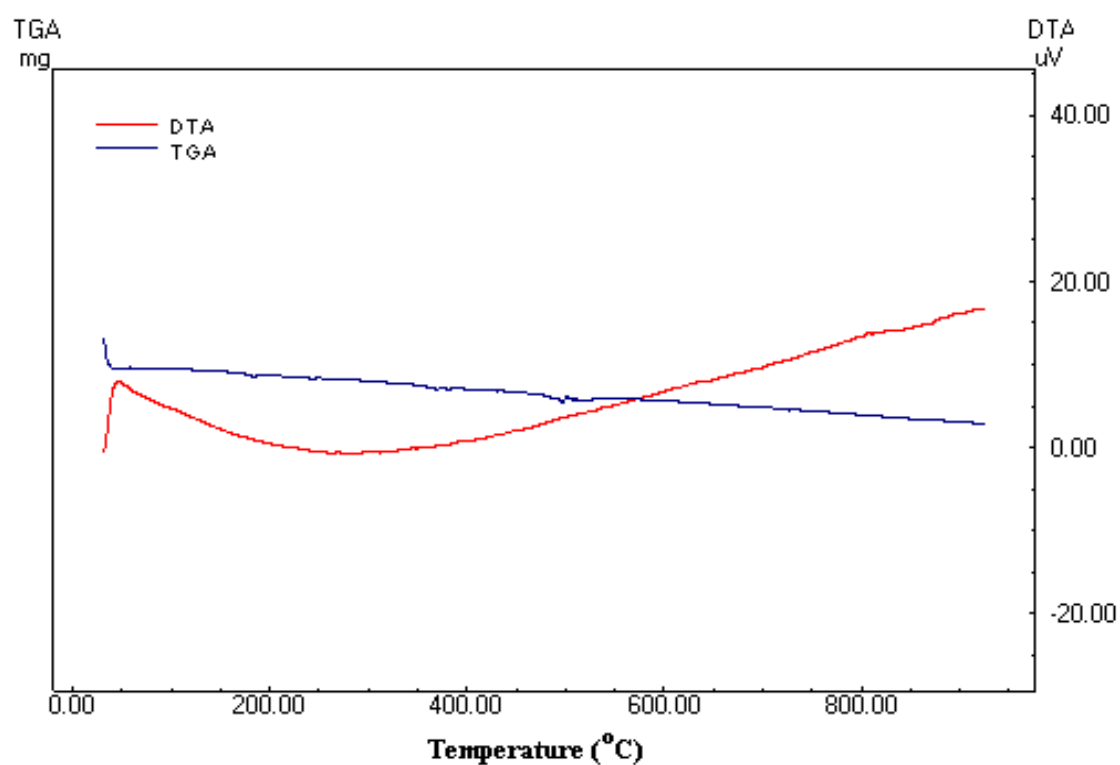


Figure 5.5. Both TG/DTA curve of the sample.

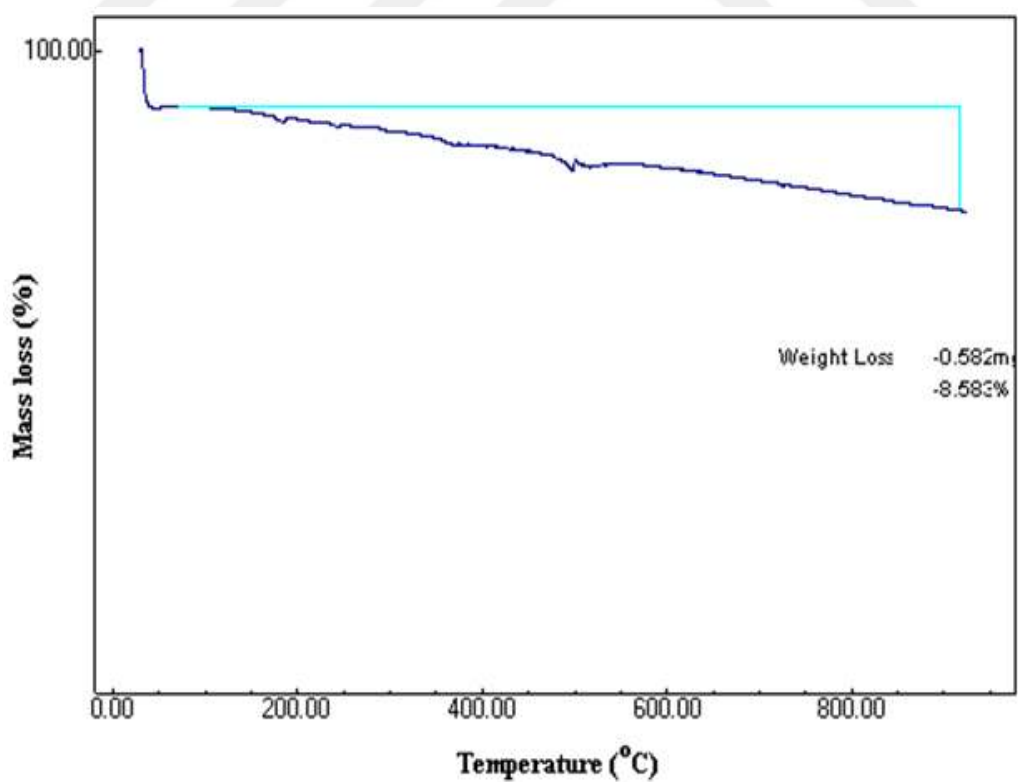


Figure 5.6. TG curve of the sample.

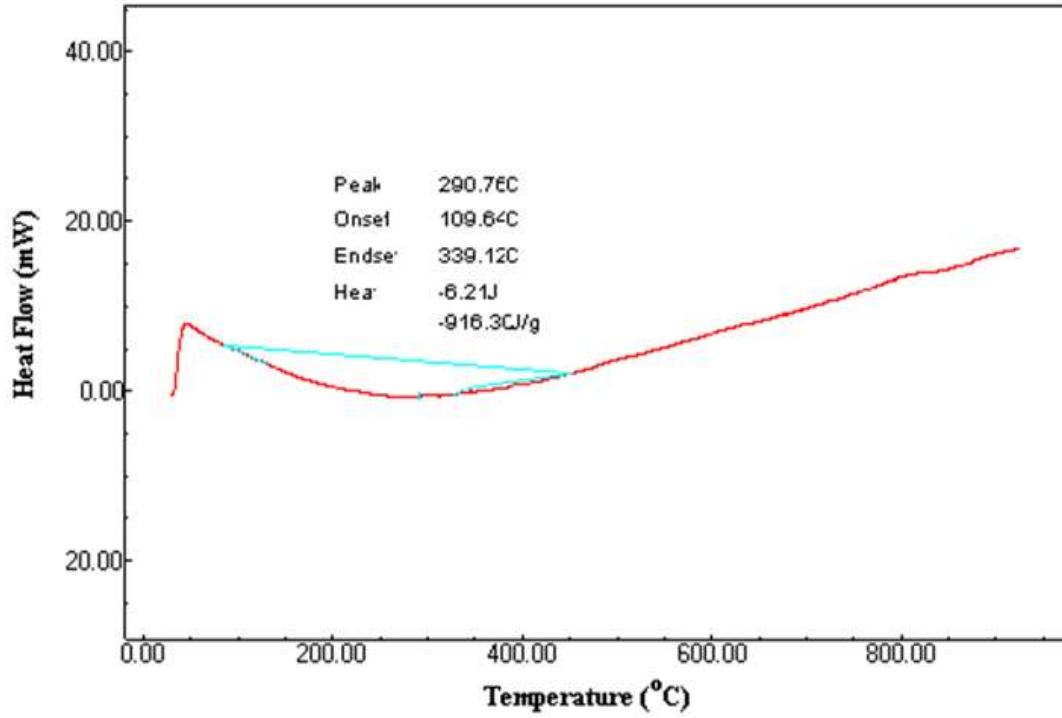


Figure 5.7. DTA curve of the sample.

5. 5. I-V Characterisation

In I-V characterization we get the current slope of the sample according to the voltage value. So we draw the graph of current versus voltage value. In this graph, we find the resistivity of the sample. From this point, we can find the slope ($3.9756 \times 10^{-10} \text{S}$) of the sample as seen in figure 5.8, and then we use the slope of the graph to calculate the electrical conductivity by the help of the following equation:

$$\sigma = \frac{I}{V} \cdot \frac{d}{A} \quad (5.2)$$

where (I) am current, (V) is the voltage, (d) is the thickness of the sample and (A) is the surface area of the sample. As we calculated the electrical conductivity as $1.2 \times 10^{-10} \text{S/cm}$. The electrical conductivity value calculated for our sample is really good for HAP as compared in literature. Also generally we can say insulators are materials having an electrical conductivity $\sigma < 10^{-8} \text{S/cm}$.

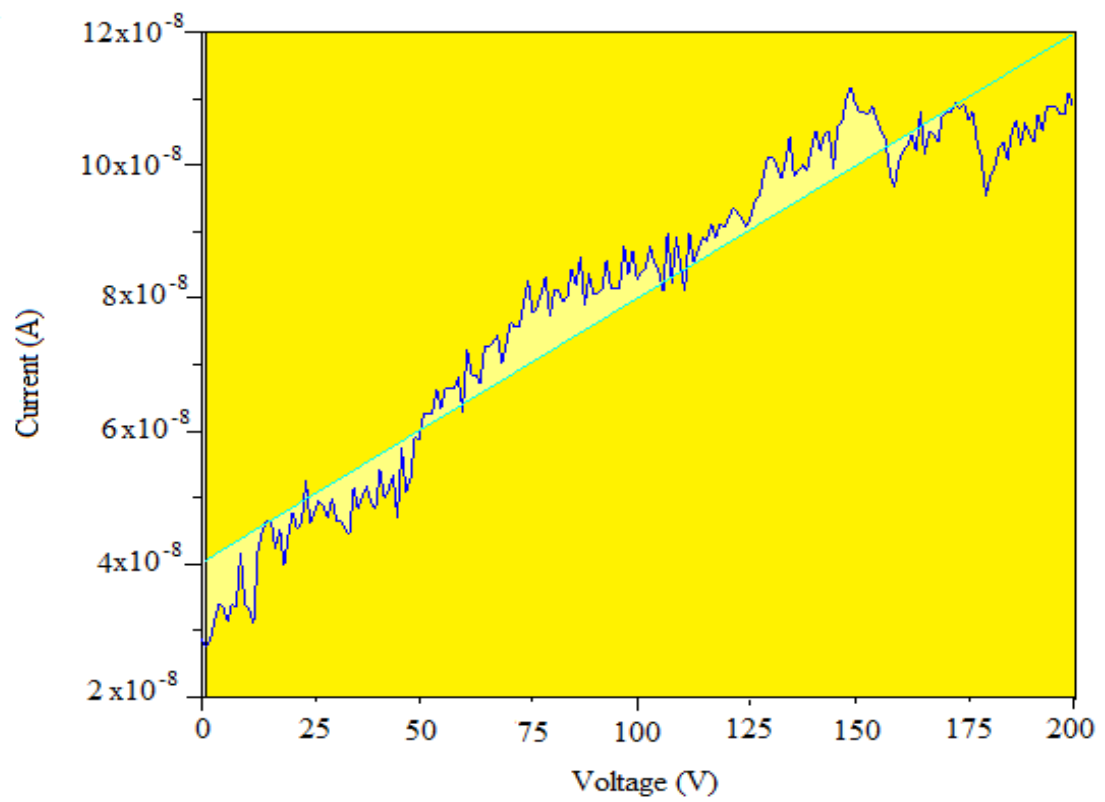


Figure 5.8. I-V characterization curve of the sample.

6. CONCLUSION

In this work, hydroxyapatite was prepared via the hydrothermal method. Also characterised of sample determine by XRD, FTIR, I-V, TG-DTA, EDS, SEM, chemical and thermal analyses were used to investigate the structure, morphology, and composition of the obtained product. XRD is used to analyse the structural properties of material, the crystallite size obtained from XRD was found to be 12.2 nm. In I-V characterization of the sample, the electrical conductivity of the sample was obtained as 1.2×10^{-10} S/cm; the electrical conductivity value calculated for sample is really good for HAP as compared in literature. TG-DTA analysis was done to determine the thermal stability, the thermal analysis demonstration the confirm construction of stability compound of the material. Also by used the TGA (thermogravimetric analysis) demonstrates the total weight loss 8.583% in the temperature range from room temperature to 925°C. FTIR is a way used for chemical identification, based on the fact that the selective absorption of material occurs in the infrared region. The most intense peak among the phosphate group was observed in the region of $\sim 720\text{cm}^{-1}$. Scanning electron microscopy instrument have been invoked to know the morphology of the obtained HAP. The morphology HAP sample exhibit shape plate-like structure with a smooth surface. The elemental analysis of the sample was performed by X-ray Energy Dispersive spectroscopy (EDS). The phosphorus, calcium, and oxygen were observed only in obtained EDS spectra of the HAP sample. The best Ca/P ratio for synthesised sample was found to be 1.65.

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