T. R.
VAN YUZUNCU YIL UNIVERSITY
INSTITUTE OF NATURAL AND APPLIED SCIENCES
DEPARTMENT OF MECHANICAL ENGINEERING

SYNTHESIS AND CHARACTERIZATION OF TRI-CALCIUM PHOSPHATE DOPED WITH STRONTIUM, CHLORIDE AND FLUORIDE IONS

MASTER THESIS

PREPARED BY: Redar Wasurahman AHMED
SUPERVISOR: Asst. Prof. Dr. Serap (GÜNGÖR) KOÇ

VAN-2018

T. R.
VAN YUZUNCU YIL UNIVERSITY
INSTITUTE OF NATURAL AND APPLIED SCIENCES
DEPARTMENT OF MECHANICAL ENGINEERING

SYNTHESIS AND CHARACTERIZATION OF TRI-CALCIUM PHOSPHATE DOPED WITH STRONTIUM, CHLORIDE AND FLUORIDE IONS

MASTER THESIS

PREPARED BY: Redar Wasurahman AHMED

VAN-2018

ACCEPTANCE and APPROVAL PAGE

This thesis entitled "SYNTHESIS AND CHARACTERIZATION OF TRI-CALCIUM PHOSPHATE DOPED WITH STRONTIUM, CHLORIDE AND FLUORIDE IONS" presented by Redar Wasurahman AHMED under the supervision of Asst. Prof. Dr. Serap (GÜNGÖR) KOÇ in the department of Mechanical engineering has been accepted as a Master Thesis according to the rules of Higher Education Instruction of Republic of Turkey on 16/01/2018 with unanimity of the member of jury.

Chair: Prof. Dr. Bekir ÖZÇELİK Signature:.........................

Member: Asst. Prof. Dr. Serap KOÇ Signature:.........................

Member: Asst. Prof. Dr. Halil İbrahim YAVUZ Signature:.........................

This thesis has been approved by the committee of institute of science on 19./01./2018 with dicision number 2018/.3.-1

Signature:
Prof. Dr. Suat SENSOY
Director of Institute

THESIS STATEMENT

All information presented in the thesis obtained in the frame of ethical behavior and academic rules. In addition, all kinds of information that does not belong to me have been cited appropriately in the thesis prepared by the thesis writing rules.

Signature
Redar Wasurahman AHMED

ABSTRACT

SYNTHESIS AND CHARACTERIZATION OF TRI-CALCIUM PHOSPHATE DOPED WITH STRONTIUM, CHLORIDE AND FLUORIDE IONS

AHMED, Redar Wasurahman
M. Sc. Thesis, Mechanical Engineering Department
Supervisor: Asst. Prof. Dr. Serap (GÜNGÖR) KOÇ
January 2018, 61 pages

In the biomechanical employment, the researches regularly explore for the design and selection of biomaterials with favorable mechanical characteristics and particular requirements. This is for the purpose of employ it for bone reform and hard tissue replacement.

Several bioceramic materials, which are a huge inorganic class of nonmetallic substances, are utilized for implantation in the human body. An example of these materials is β-tri-calcium phosphate (β-TCP). It is produced from the procedures NaH_2PO_4 and an aqueous solution of Ca $(NO_3)_2$ by wet precipitation method**.** The aim of this study was to combine tri-calcium phosphates doped with strontium, chloride and fluoride ions. A precipitation procedure was applied for synthesizing pure and doped tri-calcium phosphates. The doped samples were sintered at 1100ºC for 1 hour. To determine the measurement of the density an Archimedes method was applied. It was observed that the addition of strontium (Sr^{+2}) and chloride (Cl^-) decreased the amount of density of the samples while, the increasing of the fluoride (F^-) increasing the density of the samples due to decrease of a decomposition rate of materials that shows the highest thermal stability and improves the mechanical characteristics after sintering temperature. The strontium (Sr^{+2}), chloride (Cl^-) and fluoride (F^-) doped samples showed the variety in their density conduct after the sintering at 1100ºC for 1 hour. The XRD diffraction was employed for the characterization of the presence of phases and bonds. The outcomes of the study reached the peaks of TCP in the XRD diffraction for all samples. SEM was applied for obtaining grain sizes of the sample.

Keywords: Chloride, Fluoride, Precipitation method, Strontium, Tri-calcium phosphate.

ÖZET

STRONSİYUM, KLOR VE FLOR İYONLARI KATKILI TRİKALSİYUM FOSFAT SENTEZİ VE ÖZELLİKLERİNİN TESPİTİ

AHMED, Redar Wasurahman
Yüksek Lisans Tezi, Makine Mühendisliği Anabilim Dalı
Tez Danışmanı: Yrd. Doç. Dr. Serap (GÜNGÖR) KOÇ
Ocak 2018, 61 sayfa

Biyomekanik alanında araştırmacılar, özellikle kemik reformu ve sert doku protezleri alanlarında kullanılmak üzere, istenen mekanik özellikleri ve bazı özel gereksinimleri karşılayabilen biyomalzemeleri tasarlamaya ve seçmeye yönelik çalışmaları sıklıkla yürütmektedir.

Metalik olmayan malzemelerin oldukça büyük bir alt sınıfını teşkil etmekte olan çok sayıda biyoseramik malzeme, insan vücuduna nakledilmektedir. β-üç-kalsiyum fosfat (β-TCP)'ta işte bu malzemelere bir örnektir ve NaH_2PO_4 ve $Ca\ (NO_3)_2$ 'nin suda çözünmüş halinin ıslak çöktürülmesi ile elde edilmektedir. Bu çalışmanın amacı stronsiyum, klorür ve florür iyonları katıklı trikalsiyum fosfatlarını birleştirmektir. Saf ve katıklı trikalsiyum fosfatlarını elde etmek amacıyla uygulanmıştır. Katıklı numuneler 1100°C'de 1 saat sinterlenmiştir. Yoğunluk etkisini tespit edebilmek için Archimedes yöntemi yapılmıştır. Stronsiyum (Sr^{+2}) ve klor (Cl^-) ilavelerinin numunelerin yoğunluğunu azalttığı gözlenirken, flor katkısının hem numune. Stronsiyum, klor ve flor katıklı numuneler 1100°C'de 1 saat sinterleme sonrasında yoğunluk farklılıkları göstermiştir. Fazların ve bağların tespiti için XRD difraksiyon yöntemi kullanılmıştır. Çalışma sonucunda tüm numuneler için XRD difraksiyonunda TCP tepe noktalarına ulaşılmıştır. Numunelerin tanecik ebatlarının tespitinde SEM yöntemi kullanılmıştır.

Anahtar Kelimeler: Klor, Flor, Çöktürme yöntemi, Stronsiyum, Trikalsiyum fosfat.

ACKNOWLEDGEMENT

I would like to express my sincere gratitude to my supervisor Asst. Prof. Dr. Serap (GÜNGÖR) KOÇ for his enthusiastic guidance and patience throughout this study. I am also so grateful to my advisor for encouraging me in this interesting field, continuous encouragement and confidence in me and my work throughout the research.

I would also like to thank to Res. Asst. Mehmet TOPUZ for his help during my laboratory work and his valuable observations.

I would like to express my thanks to Mrs. Fatma BAYRAKÇEKEN from Erzurum University for XRD analysis.

I would also like to thank VAN Yuzuncu Yil University for providing the appropriate opportunity and atmosphere to study and work in laboratories to complete the research.

I would like to express my thanks to my friend Ahmed EZADIN for his help during writing the thesis.

I offer my special thanks to my parents, family and everyone who helped me to complete my thesis.

2018
Redar Wasurahman AHMED

CONTENTS

Pages

LIST OF TABLES

Tables **Pages**

LIST OF FIGURES

SYMBOLS AND ABBREVIATIONS

Some symbols and abbreviations used in this study are presented below, along with descriptions.

Symbols	**Description**
α-TCP	Alfa tri calcium phosphate
B-TCP	Beta tri calcium phosphate
TCP	Tri calcium phosphate
CaP	Calcium phosphate
HA	Hydroxyapatite
CMP	Calcium metaphosphate
HCP	Heptacalcium phosphate
DCPD	Dicalcium phosphate dehydrate
TTCP	Tetra-calcium phosphate
BCP	Biphasic calcium phosphate
SBF	Simulated Body Fluid
Ca	Calcium
O	Oxygen
P	Phosphate
Sr	Strontium
Cl	Chloride
F	Fluoride
Mg	Magnesium
XRD	X-ray diffraction
SEM	Scanning electron microscopy
D	Density
EDS	Energy dispersive X-ray spectrometry

1. INTRODUCTION

The calcium salt of phosphoric acid with the chemical composites of $Ca_3(PO_4)_2$ is called Tri-calcium phosphate (TCP). In biomaterial science, calcium phosphate is one of the most imperative products of bone. As biomaterials, the calcium phosphates CaP have been required to restructuring bone defect as well as in dental, maxillofacial orthopedic application (Guidera and Chaari, 2011). For many years clinically, calcium phosphates have been utilized for repairing bone defects. Hydroxyapatite $Ca_{10}(PO_4)_6$ $(OH)_2$, HA), tri-calcium phosphate $Ca_3(PO_4)_2$, TCP and TCP-HA composites are some examples of calcium phosphate CaP that utilized in the dental and medical utilization. Generally, when the optimal proportion relay on the specific utilization, this idea is recognized via beneficial balances of more constant (regular via HA or higher resorbable normally TCP of CaP). (Wang et al., 2004) currently, calcium phosphate based bioceramics and biomaterials are utilized in much diverse utilization thru the body, wrapping the entire space of the skeleton. Percutaneous apparatuses as well as the utilization in periodontal management, dental implants, bone defects treatment, total joint orthopedics substitution, fracture treatment, spinal surgery, cranio-maxillofacial reconstruction and otolaryngology are some application of CaP. Dissimilar calcium ortho phosphates could be utilized relying on whether a bio-resorbable or a bioactive material is wanted (Best and Porter, 2008).

Previously, several implantations have been failed owing to the infection or a shortage of information regarding the poisonousness of the nominated constituents. Consequently, the CaP utilization is logical because of their correspondence to the mineral stage of teeth and bone (Weiner and Dove, 2003). However, in accordance to accessible literature, in 1920s, the first effort for using CaP as an artificial substance for repairing surgically formed flaws in rabbits was executed (Albee, 1920). Half century later, the first calcium phosphate dental utilization in surgically formed periodontal flaws and the utilization of condensed HA cylinders for instant tooth root substitution were stated (Denissen, 1979).

Table 1.1. Different calcium phosphates with the (Ca/P) atomic ratios

Name	short form	Ca/p
Calcium metaphosphate (α, β, γ)	CMP	0.5
Heptacalcium phosphate	HCP	0.7
Dicalcium phosphate dehydrate	DCPD	1.0
Tri-calcium phosphate (α, β, γ)	TCP	1.5
Hydroxyapatite	HA	1.67
Tetra-calcium phosphate	TTCP	2.0

The calcium phosphate CaP is recognized substances to the increase of bone defects. It is accessible as allogeneic, heated substances. Regrettably, these CaP demonstrate comparatively poor shear and tensile characteristics. Practically, the CaP cements strength is lower compared to bone, teeth or heated calcium phosphate bioceramics and together with their intrinsic fragility confines, their utilization for non-loading bearing flaws or clean loading compression (Larsson and Hannink, 2011). The mechanical properties of successful enhancement could considerably prolong the calcium phosphates applicability and could be accomplished by creating compound substance (Canal and Ginebra, 2011). The calcium phosphate composites second stage additives have been either bio-inert oxides or fibrous assistances. For repairing hard tissues, tri-calcium phosphate and other calcium phosphates bioceramics are vital owing to their similarity to the substances in natural bone and their outstanding bioactivity and biocompatibility (Von and Kelly, 2000). The bone bioactive substances like tri calcium phosphate TCP and other calcium phosphate CaP implants and coatings offer an ultimate environment for colonization and cellular reaction via osteoblasts when they are implanted in an osseous site (Brown and Chow, 1986). For forming a scaffold in situ, which could be replaced and resorbed with new bone, calcium phosphate cements are injected or molded. Chemically, most calcium phosphate bioceramics is grounded upon β-TCP, HA, α-TCP and biphasic calcium phosphate BCP, which is an intimate combination of either α-TCP – HA or β-TCP – HA (Langstaff and Sayer, 2001). Under physiological conditions, HA is more constant phase in comparison to both β- and α-TCP. This is because HA has a lower solubility. Hence, the optimum balance of a more stable phase of HA and a more soluble TCP determines the BCP concept. The reactivity of BCP increases with the TCP-HA the increase in ratio because of a higher biodegradability of the β- or α-TCP component Sakka et al., (2013).

The β-TCP chemical similarity to the mineral component of mammalian bone and teeth is the key reason behind the utilization of β-TCP as bone replacement materials (LeGeros, 2002). Because tri-calcium phosphate is extraordinarily biocompatible with living bodies when substituting hard tissues and has biodegradable properties, the utilization of tri-calcium phosphate as a bone replacement has received substantial attention (Legeros, 2008). Thus, in several surgical fields like orthopedic and dental surgeries, β-TCP has been utilized as bone graft replacements (Park and Lakes, 1992). This utilization resulted in an eventual physicochemical bond in between the bone termed and osteo-integration implants (Metseger, 1999). Nonetheless, β-TCP mechanical properties which make it brittle, with poor fatigue resistance is the main restriction to the utilization of β-TCP as load bearing biomaterial. Furthermore, the mechanical properties of tri-calcium phosphate are commonly insufficient. When it utilized for making highly porous ceramics and scaffolds, its poor mechanical behavior is even highly apparent. Therefore, metal oxides ceramics, for example strontium oxide SrO as well as several oxides ZrO_2, SiO_2 have been extensively examined because of their bioinertness, excellent tribological properties, high wear resistance, fracture toughness and strength and comparatively low friction. Nonetheless, for enhancing the densification and the mechanical properties of β–TCP, bioinert ceramic oxides that have high strength are utilized. The TCP has three polymorphs, like: β-TCP is constant under 1180ºC α-TCP between 1180ºC and 1400ºC and $\bar{\alpha}$ -TCP more than 1470ºC shown in figure 1.1.

Amongst the three allotropic configurations, β -TCP is preferred as a bioceramic because of its chemical constancy, mechanical strength, and appropriate bio resumption proportion. The mechanical strength of β-TCP ceramics have to be as high as possible for using β-TCP ceramics as surgical implants. Consequently, it is imperative to intensively densify β-TCP ceramics (Kannan and Goetz, 2007).

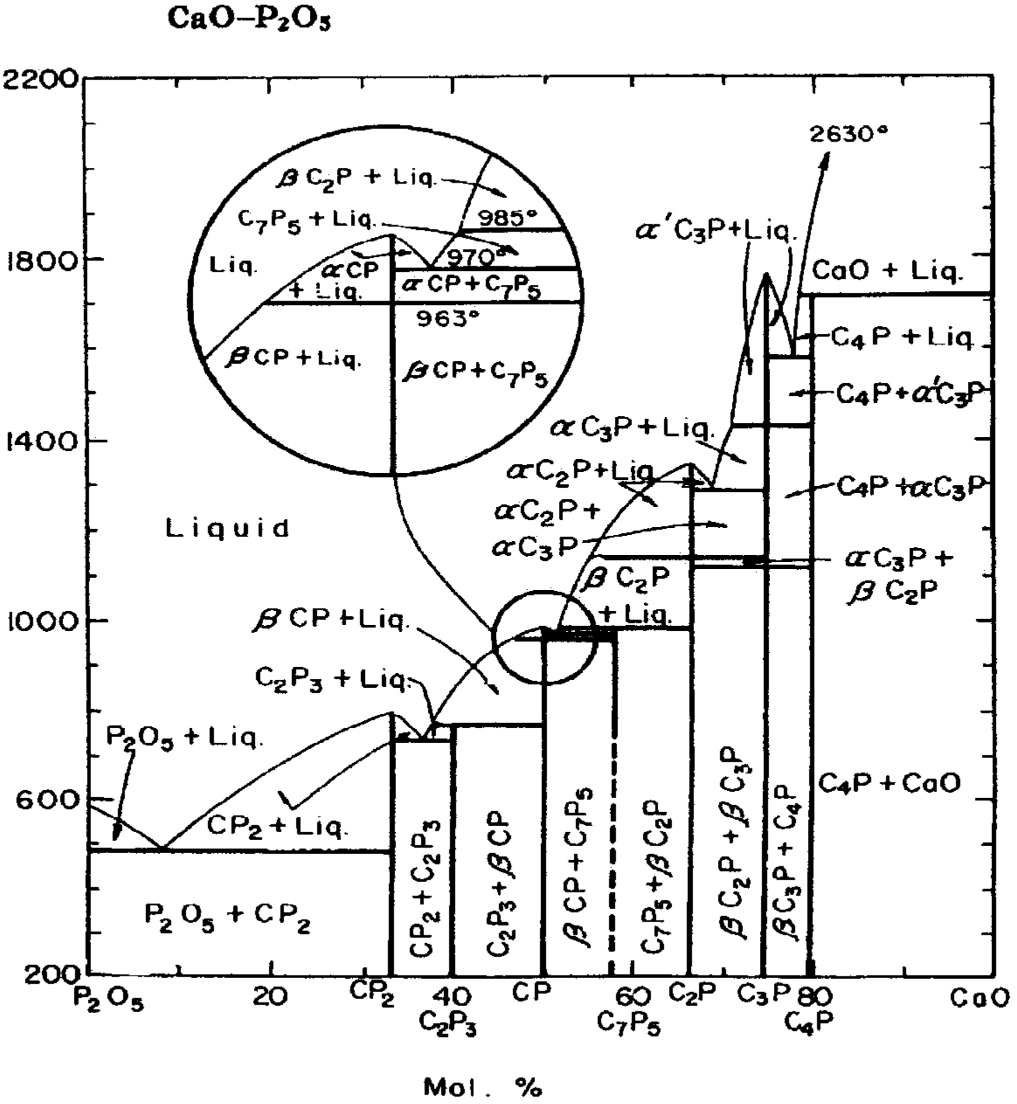

Figure 1.1. Shown the relation between temperature and percentage mole for the phase diagram of TCP (Ayers and Simske, 2013).

The higher temperature phase is the alpha phase about over 1450°C and the lower temperature phase is the beta phase about 1050°C and the translation temperature between beta and alpha phases is around 1260°C at 75% mole calcium. At this temperature, it is expected that the TCP material will contain about equal amounts of β-TCP and α-TCP. Hence, the α-TCP occurs when the TCP development is heated to a high temperature and then quickly cooled to cooling rate. Otherwise, the β-TCP phase occurs when the TCP product is heated to a high temperature and then cooled slowly, to cooling rate. When the temperature increase from 800°C to 970°C at 50% mole of CP the β-TCP with liquid is occur, in otherwise with increase the temperature to 965°C at

50% mole of CP the α-TCP with liquid is occur. With 20% mole of CaO, the α-C_3P+β-C_2P is occur at 1120°C, hence at 1700°C the CaO+ liquid is happen.

In general, as β-TCP ceramics ought to be sintered at lower temperature compared to that of phase transition to α-TCP, it is challenging to sinter β-TCP ceramics fully. The current efforts for improving β-TCP ceramics densification have been unsuccessful (Pan, 2003). Even though the sub micrometer sinter ability of sized β-TCP powder from wet chemical method is better than that of β-TCP prepared by solid-state response. Hence, the investigations of superior sinter ability of β-TCP equipped from solid-state response have been sustained. It is recommended that sintering responses of a combination of raw ingredients without calcinations might result in much bigger densification in comparison to traditional sintering of claimed β-TCP. Nonetheless, concerning contraction control and the probability of local second stage generation is not omitted, the response sintering presents difficulty (Famery, 1994).

The aim of this thesis is to combine tri-calcium phosphates doped with strontium, chloride and fluoride ions. A precipitation procedure was applied for synthesizing doped and pure tri-calcium phosphates. The combined substances were sintered at 1100ºC for 1 hour.

Table 1.2. Composition of TCP bioceramics to be produced in the project

No.	Sample Names	Ca/p rate	Sr% mole	Cl% mole	F% mole
1	1.5TCP 0Sr 0Cl 0F	1.5	0.0	0.0	0.0
2	1.5TCP 1.0Sr 1.0Cl 1.0F	1.5	1.0	1.0	1.0
3	1.5TCP 2.5Sr 1.0Cl 1.0F	1.5	2.5	1.0	1.0
4	1.5TCP 5.0Sr 1.0Cl 1.0F	1.5	5.0	1.0	1.0
5	1.5TCP 10.0Sr 1.0Cl 1.0F	1.5	10.0	1.0	1.0
6	1.5TCP 2.5Sr 2.5Cl 1.0F	1.5	2.5	2.5	1.0
7	1.5TCP 2.5Sr 5.0Cl 1.0F	1.5	2.5	5.0	1.0
8	1.5TCP 2.5Sr 10.0Cl 1.0F	1.5	2.5	10.0	1.0
9	1.5TCP 2.5Sr 2.5Cl 1.0F	1.5	2.5	2.5	1.0
10	1.5TCP 2.5Sr 2.5Cl 2.5F	1.5	2.5	2.5	2.5
11	1.5TCP 2.5Sr 2.5Cl 5.0F	1.5	2.5	2.5	5.0

1.1. Tri-calcium Phosphate Doped by Strontium TCP-Sr^{+2}

In bone, the strontium as one of bone-pursuing components is dispersed. In addition, in human bone metabolic turnover, it has significant biological role. Commonly, it is acknowledged that Sr^{+2} can substitute Ca^{+2} in the crystal lattice within a big level range because of the chemical similarity. Its replacement leads to the destabilization of crystal, mechanical property, structures and morphology, enhance its antibacterial, bioactivity properties and after that the escalating solubility. Furthermore, the low concentration of Sr^{+2} replacement has the useful effect on the reduction of bone resorption and the improvement of bone formation by hindering osteoclast resorbing function and the stimulation of osteoblast activity and diversity (Huang et al., 2014).

1.2. Tri-calcium Phosphate Doped by Fluoride TCP-F^-

Fluoride (F^-) ion in its crystal lattice is one of the impurities natural HA in bone. This has resulted in the concept of the addition different ion into tri calcium phosphate TCP for enhancing its mechanical, biological and chemical characteristics. Lately, ion replacement tri calcium phosphate with various impurities in ionic has collected escalated interest for utilization in novel production featured implant biomaterials. Whereas the biocompatibility and bioactivity sustained are equivalent for clean TCP, Fluoride (F^-) doping into TCP the solubility extends time in the body environment. Fluoride doping also improves the mechanical characteristics and the thermal stability of TCP. Abnormal tissue development and humble mechanical characteristics happened when elevated level of fluoride (F^-) added into TCP. However, lower fluoride concentration enhanced the mechanical properties of TCP, for example toughness of fracture, hardness, elastic modulus and brittleness. Indeed, human hard tissues growth required fluoride F^- element (Yilmaz and Evis 2014).

1.3. Tri-calcium Phosphate Doped by Chloride TCP-Cl^-

Calcium phosphate doped by chloride (Cl^-) is a biocompatible substance, which dynamically influence the orthogenesis bone, bone consolidation and dental tissues comprising through the skin. In the calcium phosphate chloride structure the ion, Cl^- is contained of the bone tissue in addition to Ca^{+2} and $3PO^{-3}_4$. Because of emptiness in the structure of the crystal of both cation nature and anion, the chemical bonds structure in addition to crystal structure, the calcium phosphate is considerably more complex. The trace elements' Bivalent cations received via a live organism and with anion, chloride (Cl^-) can fill the vacancies. The chloride gets the good thermal constancy and no damage to biological tissues when doping it with tri calcium phosphate. The density escalated to some extent and the hexagonal unit cell volume as chloride (Cl^-) doping with calcium phosphate types. With chloride (Cl^-) addition, the grain sizes of the samples reduced and the micro hardness of pure tri-calcium phosphate TCP is enhanced (Koroleva et al., 2012).

1.4. Aim of the Thesis

The objective of this study is synthesizing tri-calcium phosphates doped with strontium (Sr^{+2}), chloride (Cl^-) and fluoride (F^-) ions for developing novel nanocomposite bioceramics for biomedical utilization as well as investigating their microstructures, mechanical and properties of biocompatibility. Up to date, there are no researches in the literature about co-doping of strontium (Sr^{+2}), chloride (Cl^-) and fluoride (F^-) ions into the tri-calcium phosphate (TCP). Via a precipitation approach and sintering at 1100ºC for 1 hour, tri-calcium phosphate (TCP) doped with strontium (Sr^{+2}), chloride (Cl^-) and fluoride (F^-) ions were synthesized. The measurement of the density is determined by use an Archimedes method. By X-ray diffraction (XRD), the presence of the phases of the samples was applied. The grain sizes and microstructure of the samples were examined via scanning electron microscopy (SEM).

2. LITERATURE REVIEW

The synthesized of tri-calcium phosphate powders was applied by wet precipitation approach. The crystalline of the β-TCP was found a main phase with increasing the temperature of the sample up to 800°C. In addition, the narrow and homogeneous grain size particles seen from the synthesized of the β-TCP powders. In evaluation with chemical synthesis of the precipitation approach produces the β-TCP phase of highest purity. Furthermore, the purity of phases of the synthesizes procedure is not dependent greatly on the changed of the synthesis parameters (Grigoraviciute, 2017).

The tri-calcium phosphate or the hydroxyapatite when doped with the involvement of two or more than two biologically vital cations like magnesium (Mg^{+2}) and strontium (Sr^{+2}). Via an aqueous precipitation method, the substituted samples were combined. This tangled the supplementation of Sr^{+2} and Mg^{+2} comprising precursors in order to substitute Ca^{+2} ions partially in the structure of apatite. It is revealed that the replacement causes the creation of β-TCP and hydroxyapatite (HA) construction kinds, with a disparity of their cell factors and the amount of crystalline of hydroxyapatite HA with differing replacement levels. The amount of the Ca^{+2} ions was reduced with addition of an equimolar amount of each of the magnesium (Mg^{+2}) and strontium (Sr^{+2}) in the form of strontium nitrate $Sr\ (NO_3)_2$ (Landi et al., 2000), described that the use of ($MgCl_2$) as a reactant in the synthesis by precipitation method of biomimetic Mg-substituted hydroxyapatite, and designate any annoying co-substitution of the invention Mg^{+2}-HA structure by chloride ions (Aina et al., 2012). Researchers are mostly concerned in the structure, surface roughness, chemistry, and the mechanical properties of biomaterials (Dorozhkin, 2009). Nano-HA and nano-TCP particles exhibit improved biological and mechanical properties compared with conservative HA (Zhang et al., 2012). Sr^{+2}-HA is frequently used as a drug in osteoporosis therapy (Schumacher et al., 2013).The huge interest is existed in examining different ionic replacements on characteristics and crystallographic structure to utilize in osteoporosis averts and decrease bone restoration and escalation bone creation. The calcium phosphate CaP samples were synthesized with magnesium (Mg^{+2}) and strontium (Sr^{+2}) ionic replacements. The crystalline and crystal size differed from 84% to 99.6% and from 22 nm to 130 nm, correspondingly, relying on the ionic replacement. The impact of magnesium (Mg^{+2}) and strontium (Sr^{+2}) presences in calcium phosphate on significant parameters used in several bioceramic employment shown that the minor substitutions have substantial effects on the thermal stability, solubility and osteoclastic (Neto, et al 2015). The effect of magnesium (Mg^{+2}) and strontium (Sr^{+2}) presences on the mechanical properties of the CaP like HA and TCP bioceramics this samples that doped with strontium (Sr^{+2}), the XRD analysis shown that the entire phase was Sr^{+2}-HA. For phases with minor incorporation of strontium (Sr^{+2}), the Sr^{+2}-HA (PDF 09-0432) phase was observed, and with increased incorporation, the Sr^{+2}-HA (PDF 34-0484) phase was observed shown in figure 2.1.

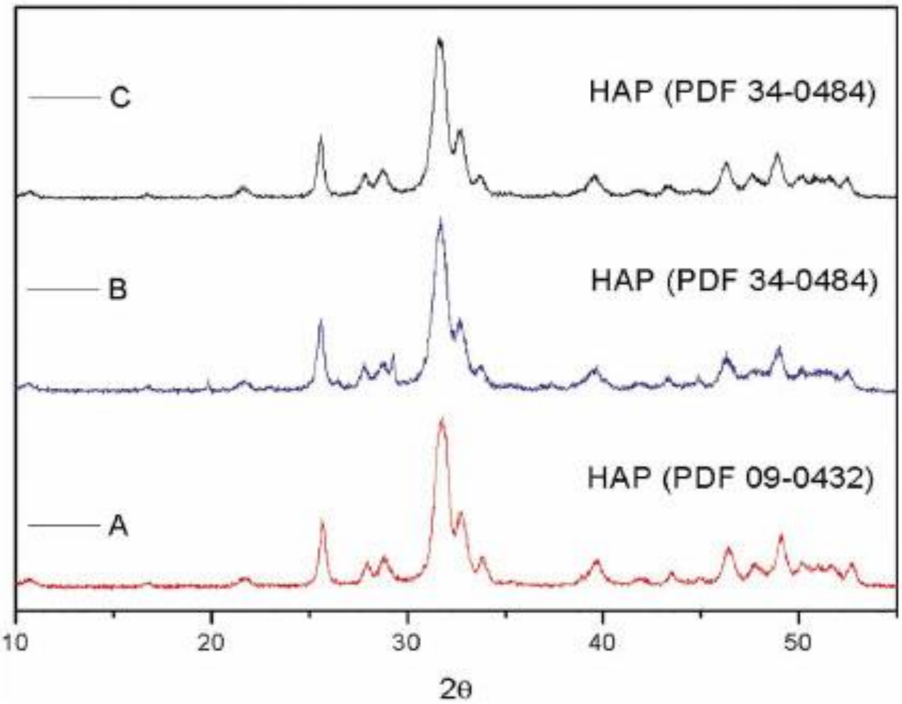

Figure 2.1. XRD patterns of samples (A), (B), and (C) revealing HA crystallographic phases after Sr+2-HA substitutions (Neto et al., 2015).

In the XRD analysis shown that the TCP and HA doped with strontium (Sr^{+2}) ions, the strontium (Sr^{+2}) principals due to an increase in crystallinity and crystal growth. Furthermore, the low in crystalline due to the mechanical properties similar to bone. Moreover, the increase in the crystalline due to the mechanical properties similar to dental surface. Then, depending on the application of the material according to crystallinity (Li et al., 2007).

To combine the HA with ions like magnesium (Mg^{+2}) and strontium (Sr^{+2}) to form Mg^{+2}-HA and Sr^{+2}-HA the solubility due to increased and the thermal stability due to reduced which displays good biocompatibility (Landi et al., 2000).

The strontium ions doped with the HA or TCP with the amount of 5% mole and 10% mole of the total amount of the calcium content on the phase assemblage and Weibull statistic of the HA are studied and compared with the pure HA at temperature range 900°C - 1200°C. The strontium doped with the HA and TCP showed the decomposition of the hydroxyapatite phase happened with strontium combination, so the strontium contented had a little effect on the main grain size subdivisions, however the addition of the strontium with 10% mole the β-TCP stabilization was obtained. The strontium doped with HA with amount of 5% mole the samples presented the highest reduction in porosity with increasing temperature whereas the strontium doped HA with 5% mole the samples stay constant from the all sintering temperature range. The strontium doped with HA by 5% mole the samples involvement the small increase in Weibull modulus with porosity specifying the potential relationship between the parameters. The samples with 10% mole of the strontium doped with HA showed the higher Weibull modulus from all sintering temperature range. It is suggested that this is due to the increased amount of the surface and lattice diffusion and because of the saturation of strontium substances happening in grain boundary movement (Yatongchai, 2013).

The strontium (Sr^{+2}) doped with pure tri-calcium phosphate with 0.5, 2 and 5% mole at 1120°C by precipitation approach, to investigate the influence of the strontium oxide (SrO) on the mechanical properties of the tri-calcium phosphate. The (SrO) doped with pure TCP showed the stability phase of the β-TCP not changed. In addition, the (SrO) doped TCP with the addition 5% mole into pure TCP the density measurement and the compressive strength of the TCP was increased. The doped strontium doped with TCP with 0.5 and 2% mole the strontium oxide had the statistically insignificant influence on the compressive strength of the samples. The strontium oxide doped with pure TCP with 2% mole had the best cell differentiation. It resulted that the strontium oxide (SrO) simultaneously improved the mechanical properties of the TCP (DeVoe, 2012).

The synthesis of the strontium doped with HA to use in biomedical applications, that strontium helps bone formation and bone reduces. The strontium doped with HA with 2 and 4% mole by wet precipitation approach with increasing the amount of the ions the Ca^{+2} partially changed to Sr^{+2}. With adding the strontium nitrate doped with HA to the reduction solution. After the filtration of the sample the precipitated of the HA was separated. Furthermore, the increase in amount of the strontium into the sample the decomposition of the HA to TCP was increased if the range of the temperature is 900°C and the thermal stability of the strontium doped with the HA powders have higher mass than the pure HA. The decreasing amount of TCP decomposition and the possibility of high thermal stability of strontium doped HA with the use of strontium chloride instead of strontium nitrate. The Sr doped with HA, showed the strontium did not have any influence on structure of the HA phase after precipitation. However, the decomposition of the TCP increased with increasing the amount of the strontium at 1200°C (Özbek, 2016).

The employed pure and magnesium (Mg^{+2}) and fluoride (F^{-}) doped nano calcium phosphates CaP that were combined via a precipitation approach for investigating their mechanical and microstructural characteristics. Subsequent the calcinations and drying processes, the samples were heated at 1100°C for 1 hour. High concentrations were achieved excluding for the samples of 7.5% mole magnesium Mg^{+2} doped. The β-TCP phase was detected besides hydroxyapatite (HA), because of the magnesium (Mg^{+2}) substitutions, leading to the creation of hydroxyapatite HA/β-TCP biphasic compounds with various structures. The ions replacements have been confirmed via the reduction in the hexagonal volumes of unit cell of the doped calcium phosphate CaP. Generally, while replacement of the fluoride (F^{-}) ions had positive impacts on their mechanical characteristics, the diametric and micro hardness tensile strength sample exposed that magnesium (Mg^{+2}) ions in big quantities 7.5% mole had adverse impact upon the micro hardness of the samples. Calcium phosphate CaP with proportion varying between 1.17 and 2.00 were generated via a precipitation approach. To examine the impact upon microstructural and mechanical properties, magnesium (Mg^{+2}) and fluoride (F^{-}) ions were doped into this material with differing quantities. The entire samples were heated at 1100°C for 1 hour. Through the Archimedes approach, the measured densities were greater in comparison to the ones measured via the geometrical approach because of the variation in the preparation approach. For the doped and pure hydroxyapatite (HA), high densities were accomplished excluding for the ones doped with 7.5% mole magnesium (Mg^{+2}). The patterns of XRD unveiled that the escalation in the β-TCP phase and the escalation in the Magnesium (Mg^{+2}) content was proportional and inversely proportional to the decline in the calcium to phosphate Ca/P proportional and the content of fluoride (F^{-}). The replacement of the ions into the apatite structure unveiled by the hexagonal lattice parameter measurements. Images of SEM exposed that the generally grain sizes enlarged with an escalation in the content of magnesium (Mg^{+2}) and reduction with an increase in the fluoride (F^{-}) content. Additionally, Strontium (Sr^{2+}) and fluoride (F^{-}) ions were doped biphasic calcium phosphate (BCP) bioceramics. The materials were successfully synthesized using a wet precipitation approach, followed by sintering at 1100°C for 1 hour. In XRD, analysis revealed that, the BCP bioceramics were composed of hydroxyapatite (HA) and β-tri-calcium phosphate (β-TCP), along with calcium oxide (CaO) as impurity. Furthermore, the increase in the strontium ions absorption inclined to increase the percentage of β-TCP. The lattice parameters of HA phase extended along with incorporation of strontium and fluoride ions. The SEM analysis when used to determine the grain sizes of the samples showed that the grain sizes decreased with strontium and fluoride ions doped with biphasic calcium phosphate (BCP) due to the morphology of the yielding materials shown in figure 2.2 (Yilmaz and Evis, 2014).

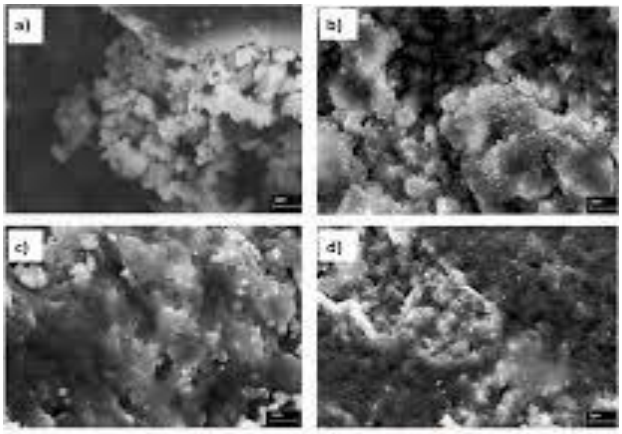

Figure 2.2. SEM image, strontium and fluoride doped BCP (Yilmaz, 2014).

The microstructures of fluoride (F^-) doped CaP at different structures, the samples; a substantial quantity of hydroxyapatite (HA) was discovered. The scanning electron microscopy (SEM) demonstrated that the doping ions addition caused in a like smaller grains. The fluoride F^- ion replacement was affirmed. Increasing the amount of fluoride (F^-), the magnetism between Ca^{+2} and F^- ions increased. For this reason, the reduction of the enemy for the distance between these ions caused a decrease in the 'a' axis. The height of the OH^- peak intensity is reduced by the amount of the F^- ion content. For this reason, the F^- ions can be said to have taken the OH^- Group. (Tahmasebifar et al., 2015).

The calcium phosphate group like HA and TCP when doped with the ions was shown that the addition of CaF_2 into composites improved the density with the reducing the porosity of the composites. Hence, the addition of the calcium fluoride (CaF_2) into the combinations let to the shrinkage of the lattice unit cell volume of the calcium phosphate types because of the fluoride (F^-) into calcium phosphate types like HA and TCP. In addition, to increase or to improvement the microhardness of the combinations the addition of the calcium fluoride (CaF_2) was applied. When the calcium fluoride (CaF_2) was added with 2.5% mole into the calcium phosphates with other composites the unit cell volume of the calcium phosphate types (HA / TCP) decreased because of the shrinkage of the a-axis parameter in pure (HA / TCP). It is means that the ionic radius of the fluoride (F^-) ions are smaller than the OH^- ions, so that the replacement of the fluoride (F^-) ions for OH^- ions in calcium phosphate (HA / TCP) due to the reduction of the unit cell volume of CaP. Therefore, the unit cell volume of the pure (HA / TCP) is bigger than the composites due to the cations are combined into CaP types at Ca sites. Furthermore, the XRD analysis showed that the addition of the ions affects the thermal stability of the calcium phosphate types (HA / TCP) composites. So that, when the amount of the ionic in the composites was increased the HA dissolution into TCP was preferred (Kutbay, 2014).

The fluoride ions doped with the HA compared with the pure hydroxyapatite had a low solubility, improved thermal stability and highest biocompatibility. The fluoride ions when doped with pure HA the amount should be attuned to an optimal value because of it will cause some disadvantage in terms of cell activities when it is absorption is above critical level. The highest amount of fluoride doped with pure HA due to decrease in mechanical properties such as elastic modules, hardness and strength because of low values of density occur with high amount of fluoride doped with pure HA (Turkoz, 2013).

The fluoride ions when doped with the hydroxyapatite show an important role in influencing the biological and physical properties of hydroxyapatite, also the fluoride doped with the HA show less solubility than the hydroxyapatite. The fluoride sometimes used as coated materials, the fluoride can produced these coatings through different methods such as plasma spraying, pulsed laser and chemical vapour deposition. The mechanical stability of the coatings failure when the above stated approaches are approved. The fluoride used, as coated materials obtained coatings possess the salient features of highest degree of crystalline when compared with the unsubstituted calcium phosphate coatings. Furthermore, from the XRD analysis showed that the obtained fluoride coatings are uniform and homogenous (Balamurugan, 2008).

The calcium chloride ($CaCl_2$) with the K-feldspar was applied to removal of the potassium. The time, calcification temperature and mass ratio of the calcium chloride ($CaCl_2$) to K-feldspar were effected. The hydrolysis reaction of the $CaCl_2$ with the moisture in the damp atmosphere occurred at high temperature. The calcification temperature reduced by the addition of the chloride salts due to the separating potassium chloride from sodium chloride is difficult; the calcium chloride may be a better alternative (Yuan, 2015).

The cations like Mg^{+2} and Sr^{+2} doped with the calcium carbonate phosphate changes the phase equilibrium in the $CaCO_3$-NH_4Cl-H_3PO_4 organization and leads to the formation of calcium phosphate chloride hydroxide. The calcium phosphate chloride structure the ion, Cl^- is contained of the bone tissue in addition to Ca^{+2} and $3PO^{-3}_4$. Because of emptiness in the structure of the crystal of both cation nature and anion, the chemical bonds structure in addition to crystal structure, the calcium phosphate is considerably more complex (Koroleva, 2012).

The chloride (Cl^-) ions doped with the calcium phosphates type synthesized by precipitation method and sintered at 1100°C for 1 h. The addition of the chloride into the calcium phosphates types shown the increasing the density slightly. For this reason, the XRD analysis detected the small amount of the CaO phase from the combination of the chloride doped with the CaP types and the increasing the amount of the chloride to

2.5% mole into the samples the hexagonal unit cell volume of the CaP was increased. The pure HA and TCP average grain sizes compared with the ionic doped samples decreased, it was establish that the pure HA and TCP doped with divalent ionic like Sr^{+2}, Mg^{+2} and Zn^{+2} had higher average grain sizes than that pure HA and TCP. In addition. The chloride (Cl^{-}) doped with the pure TCP and HA decreased the grain size of the doped samples. Additionally, the attendance of the calcium oxide (CaO) phase may affect the decreasing the grain sizes of chloride (Cl^{-}) doped samples. The divalent ionic like Sr^{+2}, Mg^{+2} and Zn^{+2} with the Cl^{-} doped samples had higher grain sizes due to the positive effect of Sr^{+2}, Mg^{+2} and Zn^{+2} on grain sizes. With the 2.5% mole amount of the chloride (Cl^{-}) doped with the calcium phosphate types, it is good for improved the mechanical properties due to it is high density, highest fraction, highest microhardness and lower grain sizes (Uysal, 2013).

3. MATERIALS AND METHODS

For synthesizing calcium phosphates, di-ammonium hydrogen phosphate ($(NH_4)_2HPO_4$) (Merck, Germany) and calcium nitrate tetra hydrate (Ca $(NO_3)_2.4H_2O$) were the major precursors of ammonium (NH_4OH).Calcium chloride ($CaCl_2$), ammonium fluoride (NH_4F) and strontium nitrate (Sr $(NO_3)_2$), were utilized in the combination of the fluoride, chloride and strontium doped calcium phosphates Aldrich, USA. In order to regulate the values of pH of the solution, the ammonia solution (Merck, Germany) was employed.

3.1. Synthesis of Calcium Phosphates CaP

The precipitation approach was applied for combining Nano-calcium phosphate powders. For preparing Ca $(NO_3)_2.4H_2O$ and $(NH_4)_2HPO_4$ solutions with a particular molar proportion, Precursors of ammonium (NH_4OH), calcium nitrate tetra hydrate (Ca $(NO_3)_2.4H_2O$), di-ammonium hydrogen phosphate ($(NH_4)_2HPO_4$), strontium nitrate (Sr $(NO_3)_2$), ammonium fluoride (NH_4F) and calcium chloride ($CaCl_2$) were supplemented into distilled water shown in figure 3.1.

Figure 3.1. Magnetic stirring, to mixture each of the calcium nitrate tetra hydrate and di-ammonium hydrogen phosphate with pure water.

For the doped samples, the proportion of Ca/P was maintained at 1.50 and the (Ca/P + Sr) molar proportion was kept at 1.50:1. The solution of di-ammonium hydrogen phosphate with the calcium chloride ($CaCl_2$) and ammonium fluoride (NH_4F) and the solution of calcium nitrate tetra hydrate with the strontium nitrate ($Sr(NO_3)_2$) were stirred for around 1 h Shown in figure 3.2.

Figure 3.2. Shown the stirring and combine the TCP with ions.

To bring the level of pH to 11-12, ammonia was supplemented. Furthermore, fluoride diisopropoxide, calcium nitrate solutions and Ammonia solution were simultaneously supplied to the mixture of di-ammonium hydrogen phosphate-ammonia in drops. After that the calcium chloride ($CaCl_2$), ammonium fluoride (NH_4F) and strontium nitrate ($Sr(NO_3)_2$) were added to this mixture and stirred for 10 minutes. For increasing the reaction, the final mixture was stirred for 1 h and boiled about (130ºC – 310ºC) as seen in figure 3.3.

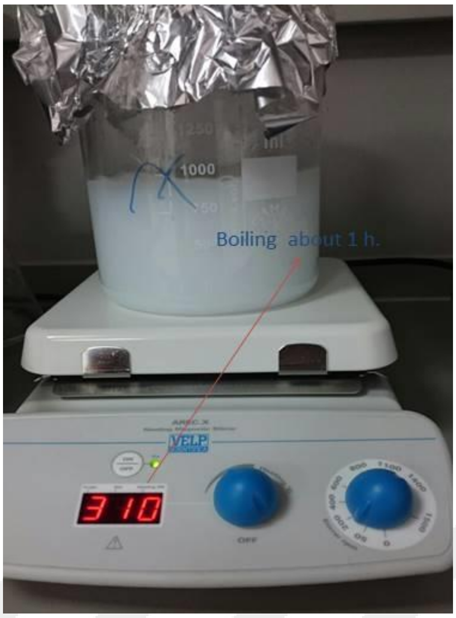

Figure 3.3. Shown the boiling the mixture from (130℃-310℃).

The mixture was stirred for 24 h, subsequent the boiling. Then, a fine filter paper was utilized for filtering the mixture to gain a wet cake as seen in figure 3.4.

Figure 3.4. Shown the filtration of the mixture (TCP doped with ions).

For eliminating the surplus water, this cake was dried in an oven at 200ºC for 10-12 h shown in figure 3.5.

Finally, it was sintered at 1100ºC for 1 h as seen in figure 3.6. The pure Caps combination process is demonstrated in the figure 3.7.

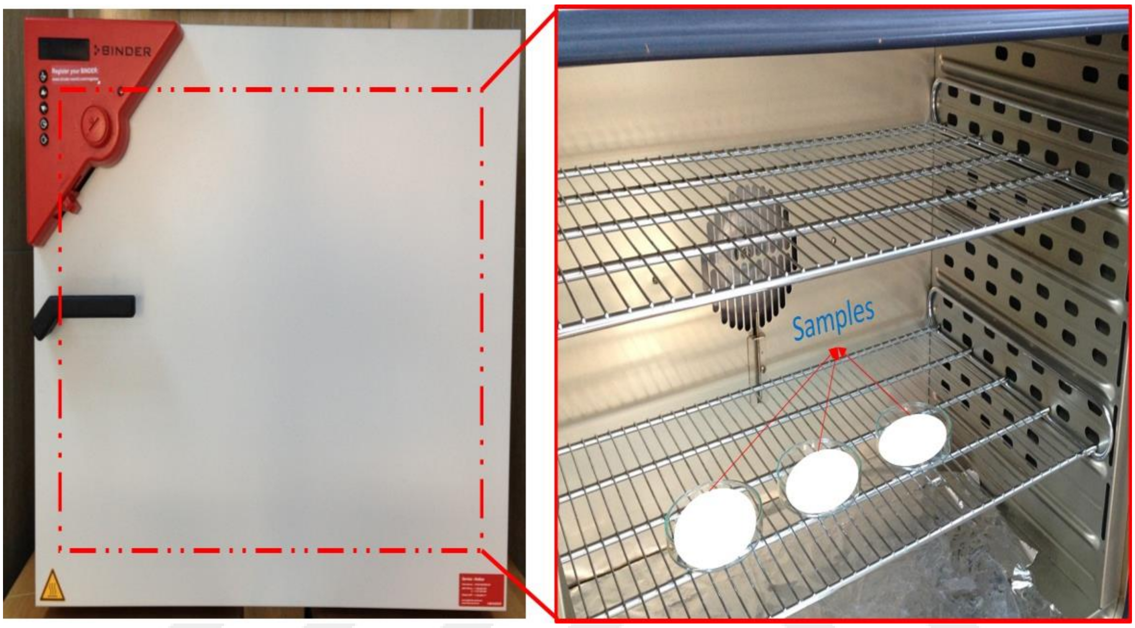

Figure 3.5. Shown the Oven used to dry the mixture.

Figure 3.6. Shown the oven machine to sintering the mixture at 1100ºC for 1 h.

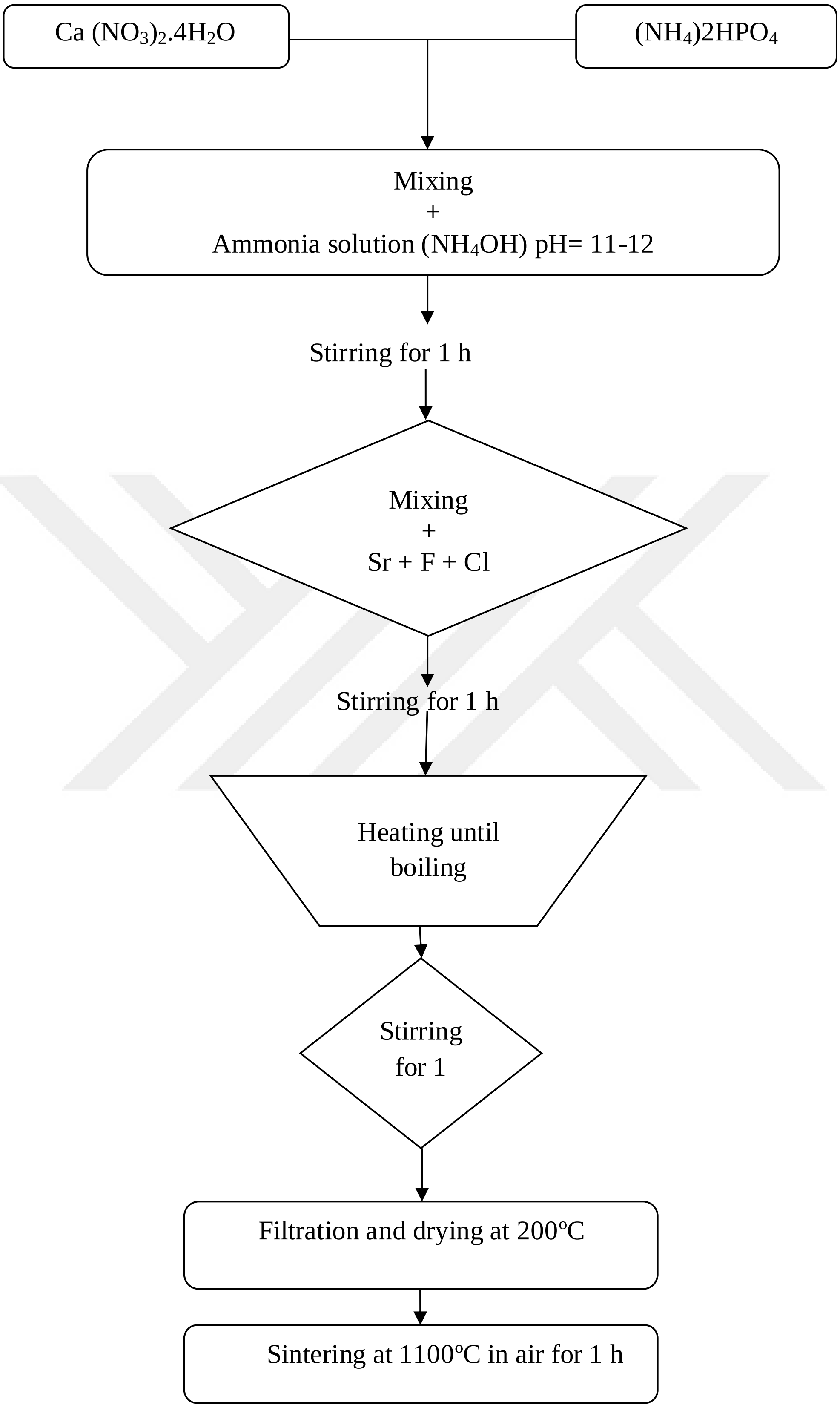

Figure 3.7. Synthesis process of pure CaP.

3.2. Synthesis of Doped Calcium Phosphates CaP

For obtaining strontium, fluoride and chloride doped calcium phosphates, strontium nitrate (Sr $(NO_3)_2$), fluoride diisopropoxide and ammonium hydroxide (NH_4OH) were utilized in addition to the main precursors pure calcium phosphates. Similar synthesizing approach was utilized to produce of the samples. Moreover, strontium nitrate (Sr $(NO_3)_2$), calcium chloride ($CaCl_2$) and ammonium fluoride (NH_4F) were presented as Cl^-, Sr^{+2} and F^-. The % mole of the dopants with Ca/p molar ratio of 1.50. The composition 100%, 99%, 97.5%, 95% and 90% of the ammonium hydroxide (NH_4OH) was added into di-ammonium phosphate solution. Then, the equivalent quantities of (Sr $(NO_3)_2$) doping were supplied to this solution. Eventually, for facilitating the precipitation of the calcium phosphate granules the calcium chloride solution was added drop by drop to the hydrogen phosphate solution at equivalent with the constant (NH_4OH) addition. In this investigation, for identification of the composition of the CaP the xxCaP, yySr, zzF and wwCl the following formula was employed. In this formula, the xx demonstrates the Ca to P proportion of the sample 1.50, and yy symbolizes the mole quantity 1.0, 2.5 and 5 of F^- ions available in the system regarding 100 moles of OH ions present in the system. Zz is the character for the mole quantity 1, 2.5, 5 and 10 of Sr^{+2} ions per 100 moles of OH ions in the system. The mole quantity 1, 2.5, 5 and 10 of Cl^- ions per 100 moles of OH ions in the system was represented by Ww. In accordance with atomic proportion of the precursors, the ratio of element insertion was accustomed. Subsequent solution was mixed the products were filtered, dried, and sintered at temperature of 1100ºC for 1 h.

3.3. Chemical Reaction Formula

From the TCP crystal structure, the ions can be replaced with others with a minimal effect. The Ca^{+2} ions were replaced with the F^- and Sr^{+2} ions replaced with the Cl^- as shown in equation (3.1).

$$2Ca\,(NO_3)_2.4H_2O+2(NH_4)_2HPO_4+2NH_4OH+2CaCl_2+2NH_4F+2Sr\,(NO_3)_2 \longrightarrow Ca_3\,(PO_4)_2+2SrCl_2+CaF_2+CaO+8NH_4NO_3+10H_2O \qquad (3.1)$$

3.4. Characterization Process

3.4.1. Measurement of density

Via Archimedes approach, the densities of the sintered constituents were derived (Grover, 2011). For every single sample, three different densities were attained for determining its mean density (average density) from the equation below:

D (g/cm$^{3)}$ = Wt (air) / (Wt (air) – Wt (water)) (3.2)

Where, D: density, Wt (air): dry weight in air and Wt (water): wet weight in water.

3.4.2. X-ray diffraction analysis

Thruogh x-ray diffraction XRD approach, phases present in the samples were examined utilizing a Rigaku DMAX 2200 machine (Zoppi, 2009). The samples were scanned from 10º to 80ºin 2θ with a scan speed of 2 min. To compare with the positions of diffracted planes taken from XRD outcome, joint committee on powder diffraction standards JCPDS data files were utilized. By utilizing relative intensity measurements of diffracted planes, the quantity of phases present in pure and doped tri-calcium phosphate with ions Sr^{+2}, Cl^{-}, and F^{-} was calculated.

3.4.3. Scanning electron microscopy SEM analysis

For determining the average grain sizes of the sintered samples, SEM Zeiss sigma 300 VP analysis was carried out. The samples were coated with gold prior to the SEM analysis. This report investigated the impacts of the dopants on the microstructure of the TCP sintered compacts.

4. RESULTS AND DISCUSSION

4.1. Density of the Samples

The density of the tri calcium phosphate TCP doped with three different ions strontium (Sr^{+2}), fluoride (F^{-}) and chloride (Cl^{-}) with Ca/P ratio 1.50, sintered at 1100ºC for 1 hour are shown in table 4.1.

Table 4.1. The densities of the tri calcium phosphate sintered at 1100ºC for 1 hour with Ca to P rate 1.50

No.	Sample Names	Density g/cm^3
1	1.5TCP	3.0433
2	1.5TCP 1.0Sr 1.0Cl 1.0F	2.9511
3	1.5TCP 2.5Sr 1.0Cl 1.0F	3.0450
4	1.5TCP 5.0Sr 1.0Cl 1.0F	2.8047
5	1.5TCP 10.0Sr 1.0Cl 1.0F	3.6444
6	1.5TCP 2.5Sr 2.5Cl 1.0F	2.5838
7	1.5TCP 2.5Sr 5.0Cl 1.0F	2.4979
8	1.5TCP 2.5Sr 10.0Cl 1.0F	2.7894
9	1.5TCP 2.5Sr 2.5Cl 1.0F	3.9766
10	1.5TCP 2.5Sr 2.5Cl 2.5F	4.0632
11	1.5TCP 2.5Sr 2.5Cl 5.0F	2.7955

The densities of the tri calcium phosphate sintered at 1100ºC for 1 hour with Ca to P rate 1.50 has shown in table 4.1 a theoretical density of pure and doped tri- calcium phosphate Ca to P 1.5 with ions strontium, chloride and fluoride was determine between 2.4979 g/cm^3 to 4.0632 g/cm^3. The strontium (Sr^{+2}) doped with pure TCP with 1% mole seen the density of the sample 1.50TCP1.0Sr1.0Cl1.0F was decreased compared with pure TCP the because the density escalated to some extent and the hexagonal unit cell volume when doping it with tri calcium phosphate TCP and because of this biocompatible substance, which dynamically influences the orthogenesis bone and dental tissues comprising through the skin. The increasing the strontium (Sr^{+2}) amount about 2.50% mole with constant amount 1.0% mole to each of the chloride (Cl^-) and fluoride (F^-) seen the density of the sample 1.5TCP 2.5Sr 1.0Cl 1.0F is increasing to near the density of the pure TCP is about (3.0450 g/cm^3). Additionally, with increasing the amount of the strontium (Sr^{+2}) to 5.0% mole the density of the sample 1.50TCP5.0Sr1.0Cl1.0F linearly decreased compared with the density of the 1.50 TCP, with 10.0% mole amount of the strontium (Sr^{+2}) doped with the pure TCP the density of the sample 1.50TCP10.0Sr1.0Cl1.0F was increased with constant 1% mole amount of the chloride (Cl^-) and fluoride (F^-). Moreover, with increase, the amount of the chloride (Cl^-) to 2.5% mole with constant amount of the strontium (Sr^{+2}) to 2.5% mole and 1% mole of fluoride (F^-) the density of the chloride (Cl^-) doped with pure TCP is decreased, with addition 5% mole of the chloride (Cl^-) into sample 1.50TCP2.5Sr5.0Cl1.0F the density of this sample decreased to minimum range is about (2.4979 g/cm^3) shown in table 4.1. In addition 10% mole of the chloride (Cl^-) doped with pure TCP with constant amount of the strontium (Sr^{+2}) and fluoride (F^-) to 2.5% and 1% mole respectively, the density of this sample is increasing due to improves the mechanical characteristics after sintering temperature. Hence, the amount of the chloride gets the good thermal constancy and no damage to biological tissues. Furthermore, with constant amount to each of the strontium (Sr^{+2}) and chloride (Cl^-) to 2.5% mole and with increasing the amount of the fluoride (F^-) to 2.5% mole doped with pure TCP in this time the density of this sample have the highest density is equal to (4.0632 g/cm^3) seen table 4.1. In addition, with increasing the amount of the fluoride (F^-) to 5% mole and 2.5% mole of each of the strontium (Sr^{+2}) and chloride (Cl^-) doped with 1.50 TCP the density of this sample decreased to lower than the density of the pure TCP shown in table 4.1, because of the decrease of a decomposition rate of materials that shows the highest thermal stability.

4.2. X-ray Diffraction Analysis

For investigating the existence of the phases, an XRD pattern of the samples was sintered at 1100°C. The samples' XRD patterns are compared because of the nature of precipitation approach applied for synthesizing calcium phosphate in this study, stoichiometric ratio was 1.50. Synthesizing pure TCP Ca to P ratio was accustomed to

1.50 at the commencement of the synthetization by precipitation method. Furthermore, Ca deficient apatite to decompose to β-TCP was occurred by heating treatments higher 750℃. The results revealed that heating temperature less than 1125℃ resulted in β-TCP phase when Ca to P ratio was 1.48 to 1.55.

By adding 2.5% mole of Sr^{+2} ion, the samples' narrow peaks appeared to be highly crystalline. The peak intensities of β-TCP increased and the peak of the α-TCP in the samples of 1.5TCP5.0Sr1.0Cl1.0F decreased when the amounts of the Sr^{+2} increased from 2.5 to 5.0% mole some of the α-TCP peaks nearly disappeared by the existence of high amount of Sr^{+2} ions. The presence of both phases of α-TCP and β-TCP resulted from escalating the quantity of the Cl^- from 2.5% to 5.0% mole When Cl^- quantity altered from 2.5% to 5.0% mole, the existence of α-TCP escalated in comparison to β-TCP phase. This indicated that the structural stability improved by the supplementation of Cl^- ion to calcium phosphates. Furthermore, the presence of 1.0% F^- in the Sr^{+2} doped TCP altered the Sr^{+2} quantity from 5.0% to 10.0% mole. In addition to the decline in the existence of the β-TCP phase with continuous existence of the α-TCP phase, correspondingly, in 1.5TCP5.0Sr1.0Cl1.0F and 1.5TCP10.0Sr1.0Cl1.0F samples. The peak intensities of β-TCP increased and the peak of the α-TCP in the samples of 1.5TCP1.0Sr1.0Cl2.5F and 1.5TCP1.0Sr1.0Cl5.0F decreased by escalating the F^- quantity from 2.5% to 5.0% mole.

From figure 4.1 seen the peaks of each of the β-TCP and α-TCP, at angles (11.11°, 13.63°, 17.02°, 21.93°, 2780°, 31.01°, 32.46°, 34.33°, 35.42°, 37.03°, 41.33° and 51.91°) presented eleven peaks for β-TCP and at angles of (29.89°, 32.008°, 54.98° and 64.15°) four peaks presented for α-TCP compared with each of β-TCP JCPDS card numbers 09-0169 and α-TCP of JCPDS numbers 09-0348.

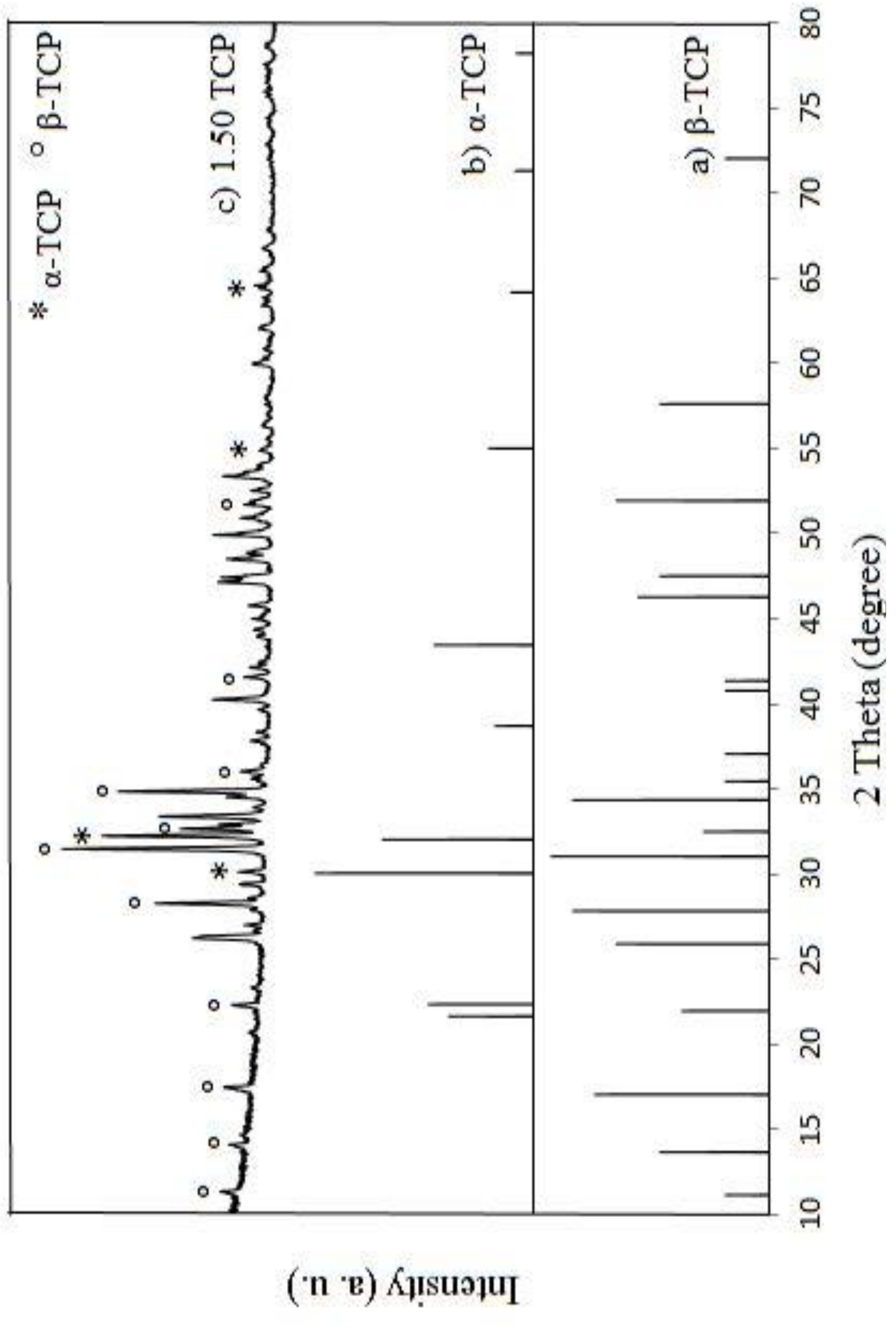

Figure 4.1. XRD patterns of 1.50 TCP sintered at 1100°C for 1 hour. (a) β-TCP of JCPDS # 09-0169 (b) α-TCP of JCPDS # 09-0348. (c) 1.50 TCP.

In addition the weight of ions strontium, chloride and fluoride about 1% mole for the pure TCP the decomposition of β-TCP, α-TCP and formation of CaO, $SrCl_2$ and CaF_2 occurred. The formation of each of the CaO, $SrCl_2$ and CaF_2 presented peaks at angles of 26.63°, 34.03°, 38.035°, 44.25°, 53.14°, 20.99°, 29.89°, 32.36°, 43.93°, 55.57°

and 46.97° respectively. However, the peaks intensities decreased with addition the weight of 1% mole of ions due to the crystallinity of TCP decreased shown in figure 4.2.

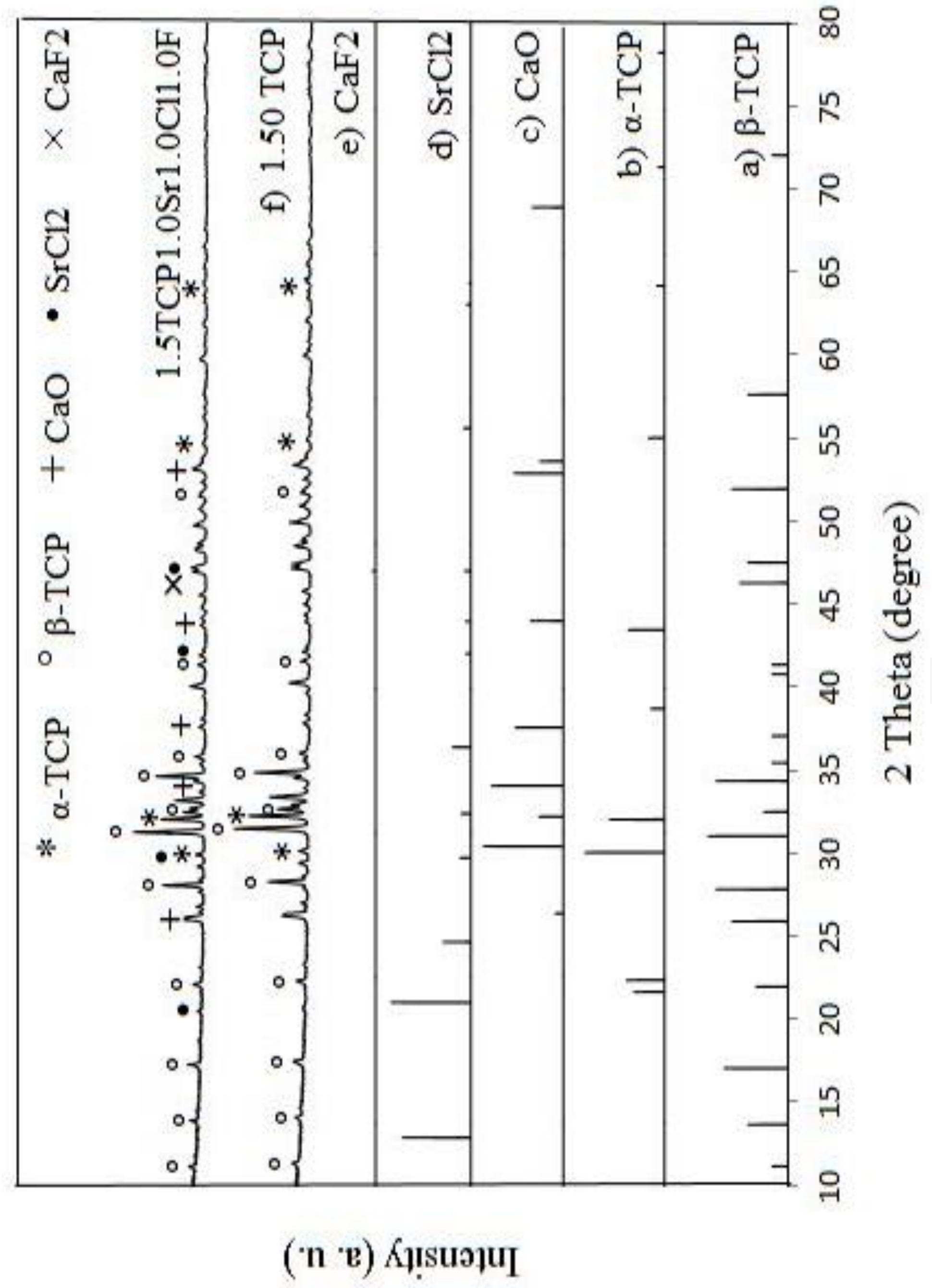

Figure 4.2. XRD patterns of doped 1.50TCP1.0Sr1.0Cl1.0F sintered at 1100°C for 1 hour. (a) β-TCP of JCPDS # 09-0169. (b) α-TCP of JCPDS # 09-0348. (c) CaO of JCPDS # 01-076-8925. (d) SrCl2 of JCPDS # 01-074-0523. (e) CaF2 of JCPDS # 01-0702739. (f) 1.50 TCP.

According to figure 4.3 the increase in addition of weight percentage of strontium the peak intensıty of β-TCP linearly decreased because of main crystalline lattice parameters will be changed and it is good for mechanical properties, so that the β-TCP may be more stability than pure TCP phase in this case.

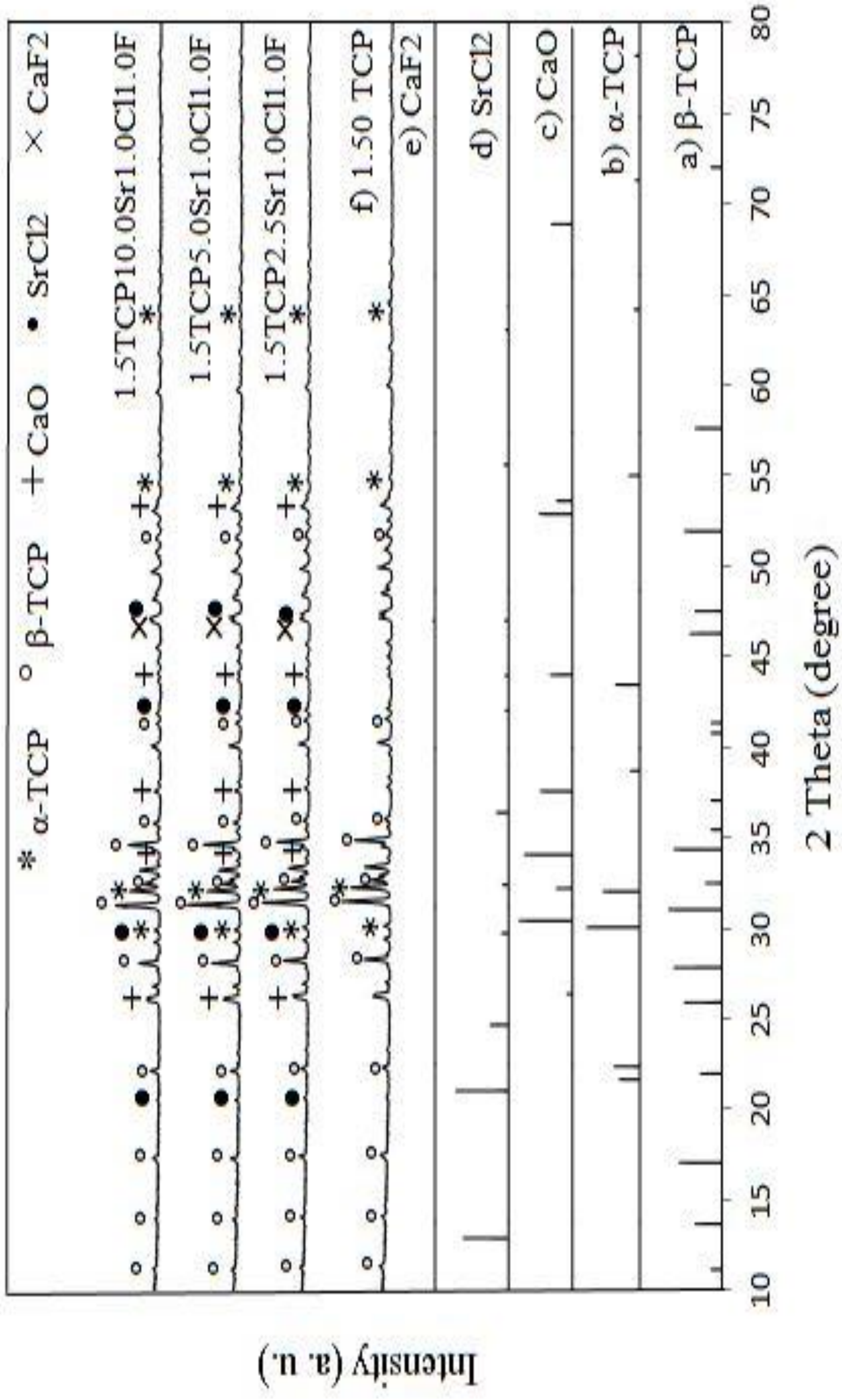

Figure 4.3. XRD patterns of doped 1.50TCP2.5Sr1.0Cl1.0F, 1.50TCP5.0Sr1.0Cl1.0F and 1.50TCP10.0Sr0Cl1.0F sintered at 1100°C for 1 hour. (a) β-TCP of JCPDS # 09-0169. (b) α-TCP of JCPDS # 09-0348. (c) CaO of JCPDS # 01-076-8925. (d) $SrCl_2$ of JCPDS # 01-074-0523. (e) CaF_2 of JCPDS # 01-070-2739. (f) 1.50 TCP.

From figure 4.4 the change the amount of strontium to 2.5% mole and increase the amount of the chloride to 2.5% mole with 1% mole of fluoride the intensity peaks of each of the β-TCP and α-TCP peaks quickly decreased and that is good for high strength of materials and other mechanical properties like modulus elasticity and shrinkage of materials that depended on the crystalline of the materials (Kutbay, 2014). However, the increase in amount of the chloride higher than 2.5% mole the intensity of the peaks increased due to the loss of strength and not homogeneous shape of crystalline.

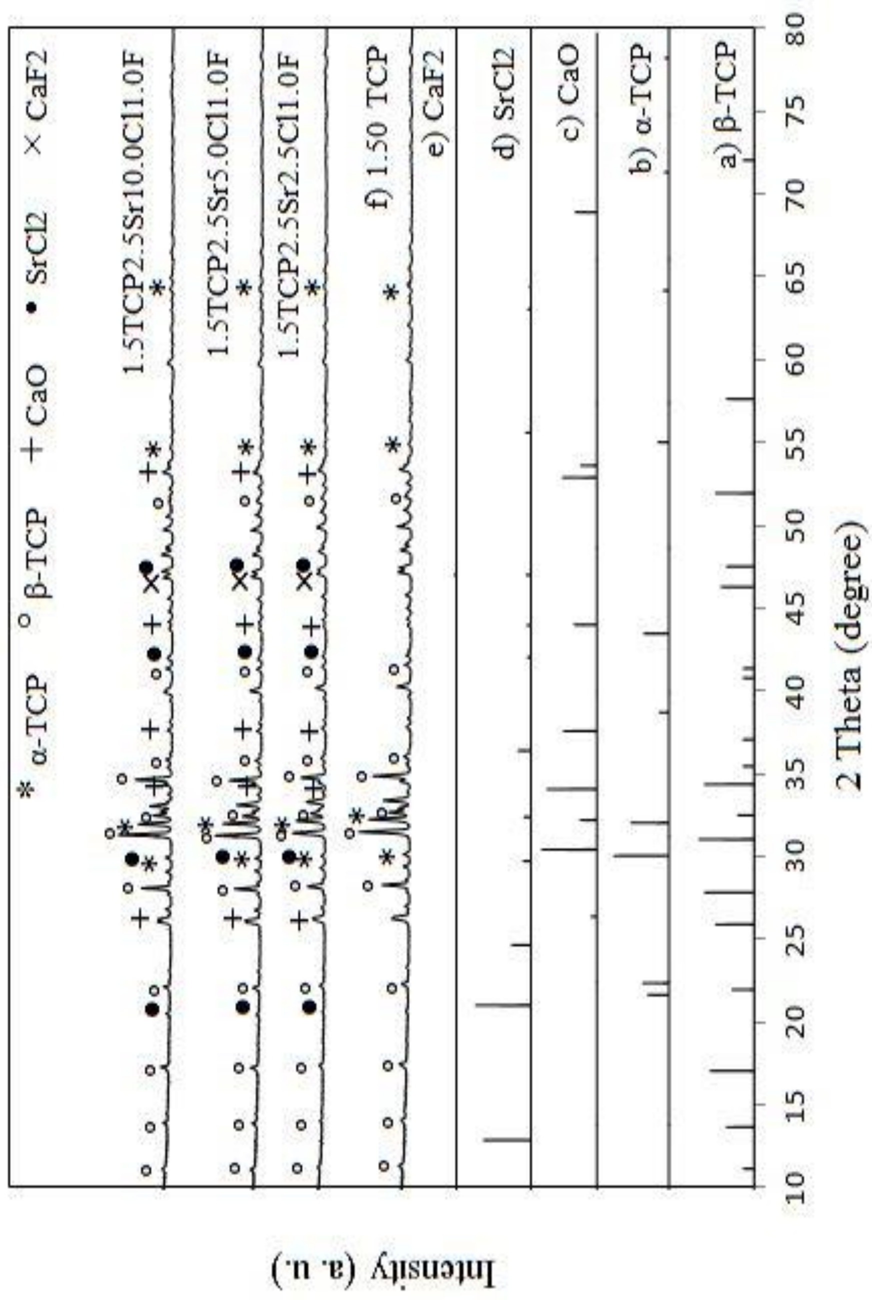

Figure 4.4. XRD patterns of doped 1.50TCP 2.5Sr 2.5C l1.0F, 1.50TCP 2.5Sr 5.0Cl1.0F and 1.50TCP2.5Sr10.0Cl1.0F sintered at 1100°C for 1 hour. (a) β-TCP of JCPDS # 09-0169. (b) α-TCP of JCPDS # 09-0348. (c) CaO of JCPDS # 01-076-8925. (d) $SrCl_2$ of JCPDS # 01-074-0523. (e) CaF_2 of JCPDS # 01-070-2739. (f) 1.50 TCP.

With reduce the amount of fluoride to 5% mole with constant amount of each of strontium and chloride with 2.5% mole the intensity of β-TCP and α-TCP linearly increased the materials might more brittle and loss fatigue strength shown in figure 4.5.

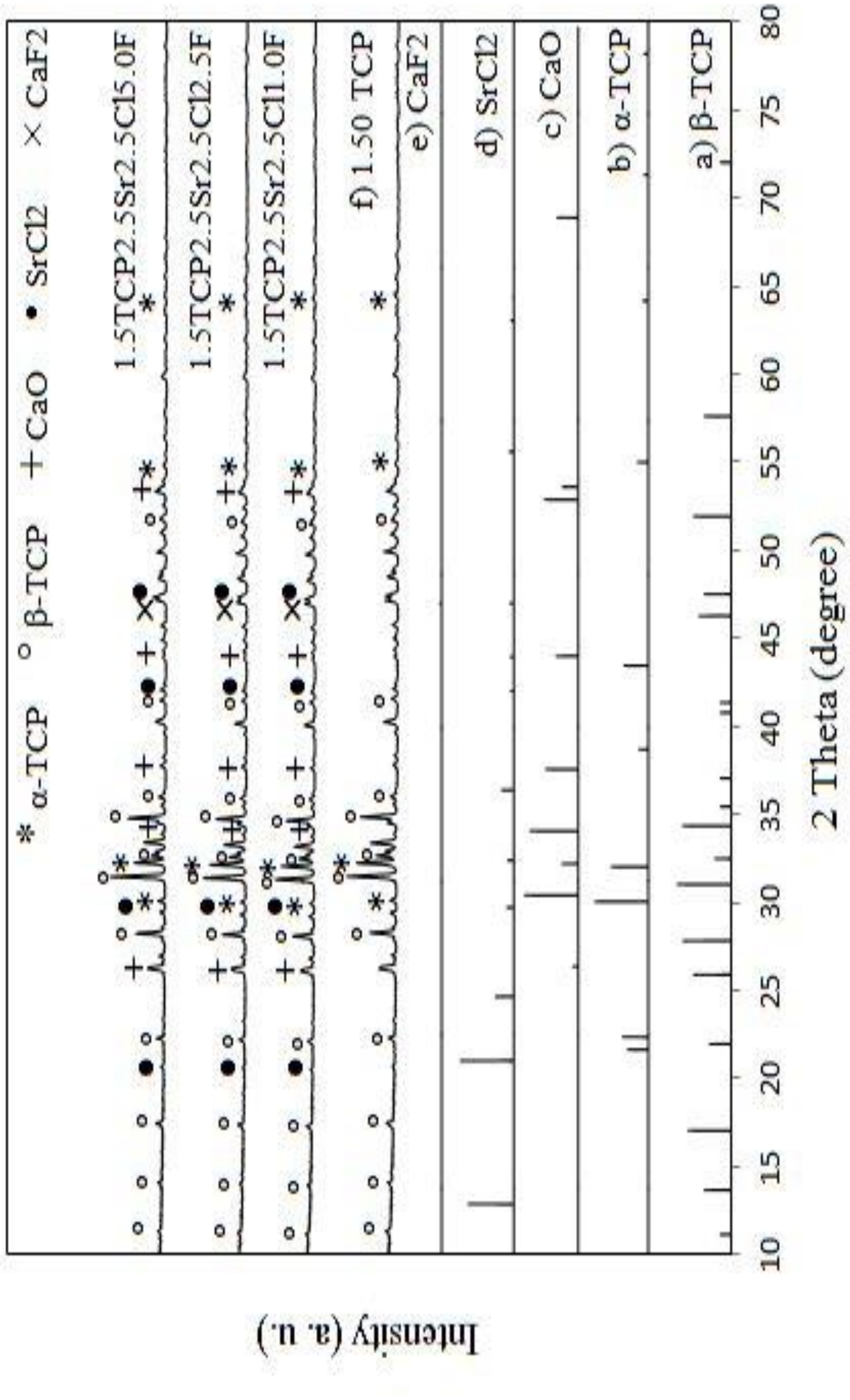

Figure 4.5. XRD patterns of doped 1.50TCP 2.5Sr 2.5C l1.0F, 1.50TCP 2.5Sr 2.5C l2.5F and 1.50TCP2.5Sr2.5Cl5.0F sintered at 1100°C for 1 hour. (a) β-TCP of JCPDS # 09-0169. (b) α-TCP of JCPDS # 09-0348. (c) CaO of JCPDS # 01-076-8925. (d) $SrCl_2$ of JCPDS # 01-074-0523. (e) CaF_2 of JCPDS # 01-070-2739. (f) 1.50 TCP.

4.3. Scanning Electron Microscopy SEM Analysis

The tri-calcium phosphate doped with the ions strontium (Sr^{+2}), chloride (Cl^-) and fluoride (F^-) sintered at 1100°C for 1 hour, to determine the effect and the microstructure of the samples the SEM analysis was applied. From the EDS images presented the Ca^{+2}, P, O, N, Sr^{+2} and Cl^- elements.

SEM micrographs for the top surfaces of the heated samples are displayed in the figures. Comparatively elevated amount of porosity was demonstrated in both pure TCP and ions doped samples. This clarifies the minor bulk densities for those compositions. This result recommended that throughout the heating process, substantial grain growth in TCP compact because by the presence of $SrCl_2$. This might be because of the phosphorous atoms replacing Ca^{+2} ions. The oxygen vacancies are attracted by some substitutional ions that results in elevated balance concentration of vacancies. This process generates faster grain development throughout heating process.

Fine grains and more uniform microstructures are observed in SEM images that the TCP sintered at 1100°C. The grain sizes of apatite had a relationship between heating temperature and quantity of dopant. It was stated that subsequent the sintering at 900 °C and 1100°C, TCP had nano size grains.

As shown in Figure (9) that grain size were augmented by increasing the Sr^{+2} quantities from 1.0% mole to 5.0% mole. In comparison to the pure TCP. Furthermore, higher size of an average grain was determined in samples doped with Sr^{+2} compared to pure TCP. Thus, the samples' mechanical properties can be changed. In accordance to SEM images, comparing to pure β-TCP, samples' grain sizes increased. The grain sizes of the samples augmented because of augmenting in the content of Sr^{+2} and Cl^- ions. It was monitored that via escalating the quantity of F^- ion, grain sizes of doped samples with F^- ions escalated. Nevertheless, the surface of co-doped samples with Cl^- ions had more pores. It is demonstrated that Co-doped samples with Cl^- ions had smaller grain size.

Generally, the unit cell volume of the TCP reduced when 2.5%mole F^- was supplemented to pure TCP and it is mixtures with Sr^{+2} and Cl^-. This could be because of the reduction of the TCP parameter. It is recognized that compared to the OH^- ions, the ionic radius of the F^- ions is smaller, hence the replacement of F^- ions for OH^- ions in

TCP causes decrease of the unit cell volume of the TCP. Conversely, the unit cell volumes of the pure TCP was greater than the 1.50TCP5.0Sr and 1.50TCP10.0Sr, at Ca^{+2} sites, it is stated that cations are combined into TCP. Therefore, the replacement of Sr^{+2} ions for Ca^{+2} ions might cause the reduction of the unit cell volume of 1.50TCP5.0Sr and 1.50TCP10.0Sr composites as the Ca^{+2} ions is bigger than the ionic radius of Sr^{+2}. Mostly because of decline of the c-axis parameter in TCP, The unit cell volume of the TCP doped with ions diminished.

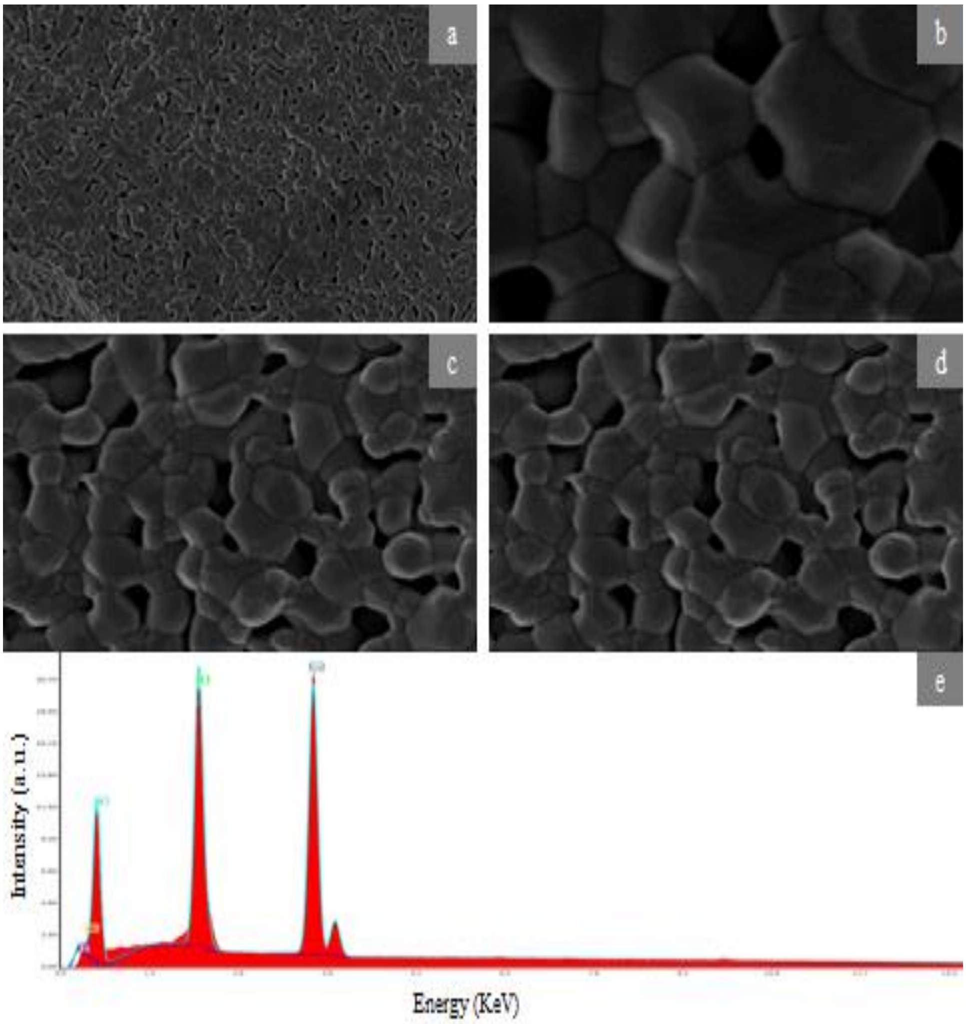

Figure 4.6. SEM images of 1.50 TCP sintered at 1100°C for 1 hour. (a) 0.5µm. (b) 1µm. (c) 200nm. (d) 100nm. (e) EDS image.

From figure 4.6 shown micro porosity with pure TCP sample seen that the microstructure of pure TCP have high purity and biocompatibility material and low solubility. The EDS images presented the Ca^{+2}, P, O and N elements a prove that the pure TCP in this combination occurred. In addition, the strontium, chloride and fluoride amount into the pure TCP by percentage of 1% mole the microstructure of the materials might to change to lower porosity volume and increase in bulk densification with homogenous shape due to decrease in grain sizes. The EDS image presented the intensity of each of Ca^{+2}, P, O, N, Sr^{+2} and Cl^{-} with fusibility the amount of F^{-}, the intensity of the oxygen (O) is increased with decreasing the intensity of each of the calcium (Ca^{+2}) and phosphate (P) due to addition 1% mole of the ionic in this sample shown in figure 4.7.

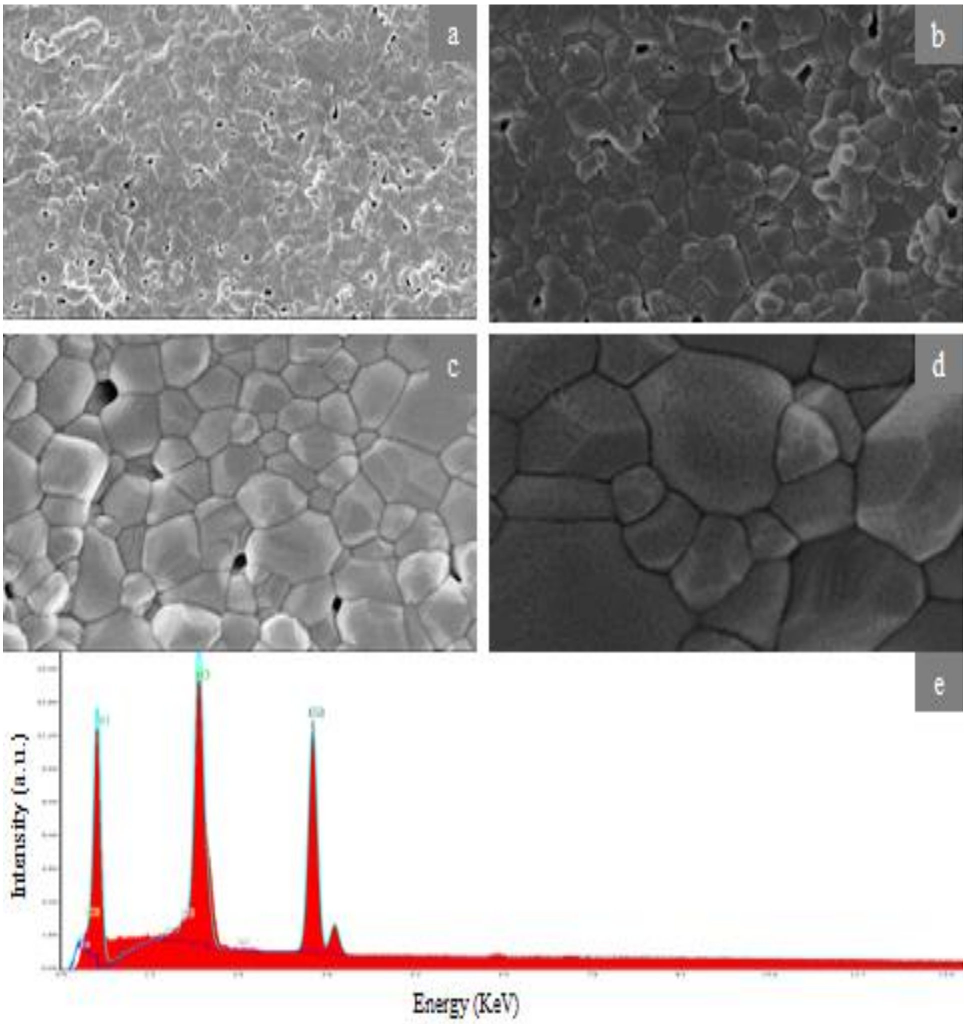

Figure 4.7. SEM images of doped 1.5TCP1.0Sr1.0Cl1.0F and 1.50 TCP sintered at 1100°C for 1 hour. (a) 0.5µm. (b) 1µm. (c) 200nm. (d) 100nm. (e) EDS image.

According to figure 4.8 the increase in amount of strontium to 2.5% mole into pure TCP, it is seen that the microstructure of the materials might to change to decrease in porosity and increase in bulk densification with homogenous shape due to decrease in grain sizes. However, the intensity of the oxygen decreased with increase the intensity of the calcium (Ca^{+2}) and phosphate (P) it is because of the increase amount of the strontium in this sample and due to the cations of the elements. The porosity of this sample is more than the porosity of the sample 1.5TCP1.0Sr1.0Cl1.0F by sab micro than that showed in figure 4.7, it is because of the increasing the amount of the strontium ions. Hence, the increasing the amounts of the strontium affect the densification of the materials that is with increasing the amount of the strontium the density of the materials may be decrease.

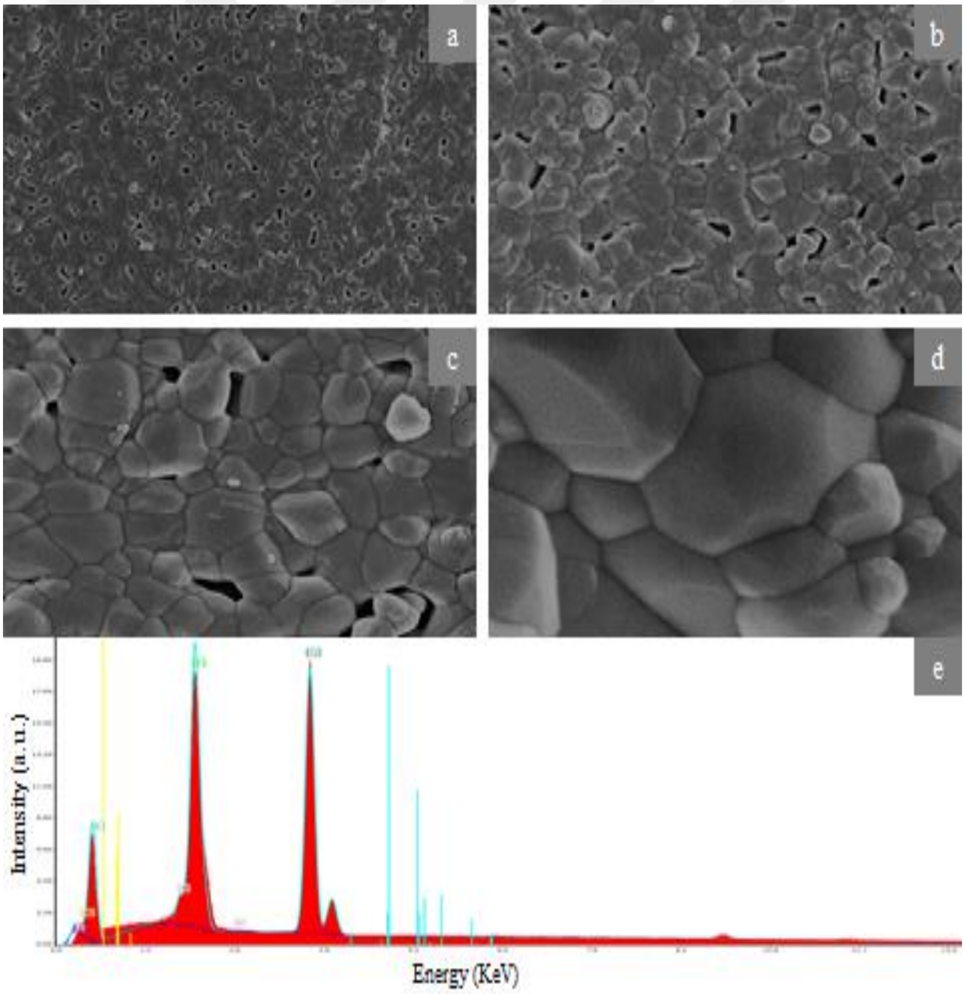

Figure 4.8. SEM images of doped 1.5TCP2.5Sr1.0Cl1.0F and 1.50 TCP sintered at 1100°C for 1 hour. (a) 0.5µm. (b) 1µm. (c) 200nm. (d) 100nm. (e) EDS image.

The increase the amount of strontium to 5% mole into pure TCP the intensity of the oxygen (O) elements linearly decreased and the calcium (Ca^{+2}) elements increased due to the strontium (Sr^{+2}) elements partially changed to the calcium (Ca^{+2}) elements. The microstructure of the materials was be changed and the grain sizes non-gained each of the others perfectly and have the micro porosity shown in figure 4.9.

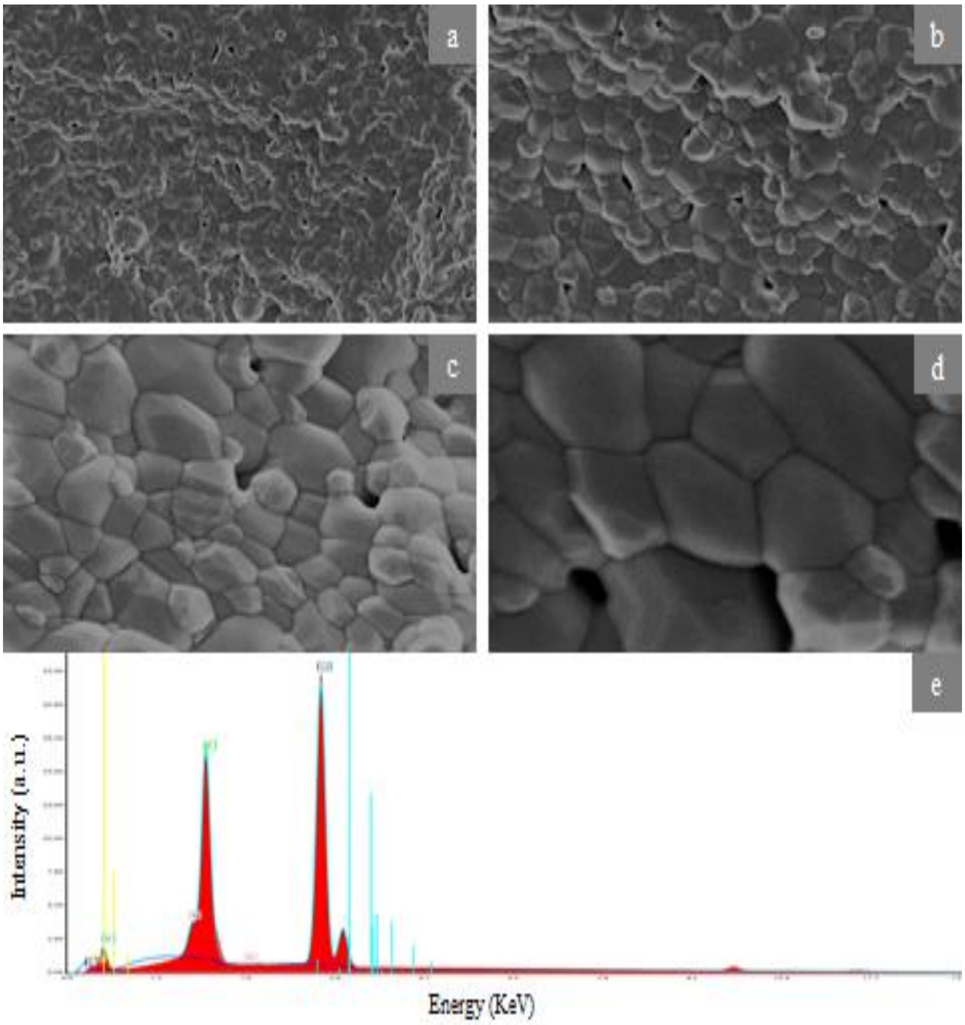

Figure 4.9. SEM images of doped 1.5TCP5.0Sr1.0Cl1.0F and 1.50 TCP sintered at 1100°C for 1 hour. (a) 0.5µm. (b) 1µm. (c) 200nm. (d) 100nm. (e) EDS image.

From figure 4.10, the increasing the amount of the strontium to 10% mole into pure TCP microstructure of the materials were be changed to non-homogenous shape and non-building the grain sizes regularly due to loss the tensile strength and make the mechanical properties very brittle and poor fatigue resistance and the materials have macro porosity. In addition, the EDS image showed the intensity of the oxygen (O) elements increased with decreasing the intensity of the calcium (Ca^{+2}) elements and increase the phosphate (P) elements due to increasing the amount of the strontium nitrate ($Sr(NO_3)_2$) to 10% mole in this sample.

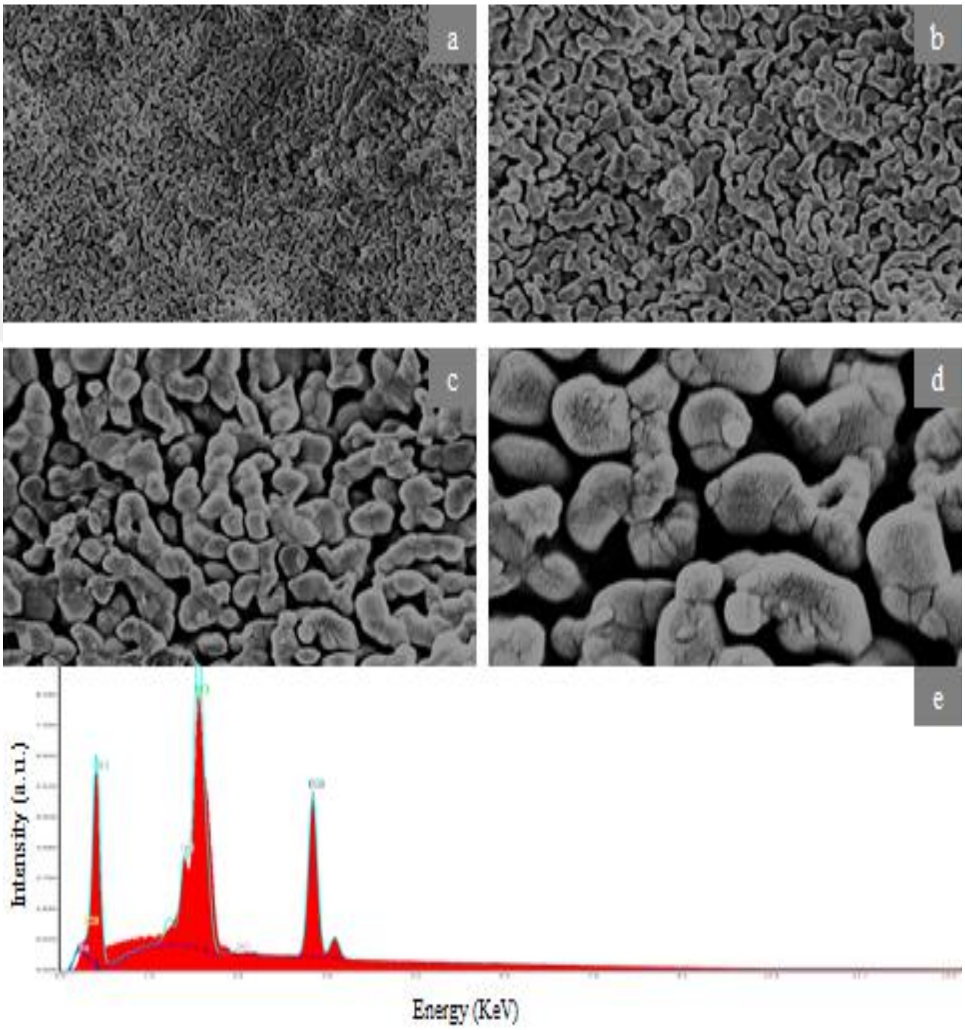

Figure 4.10. SEM images of doped 1.5TCP10.0Sr1.0Cl1.0F and 1.50 TCP sintered at 1100°C for 1 hour. (a) 0.5µm. (b) 1µm. (c) 200nm. (d) 100nm. (e) EDS image.

Figure 4.11 and figure 4.14 shown when the amount of the strontium and chloride are 2.5% mole combined into the pure TCP the microstructure of the materials might highly soluble than that 2.5% mole and 1% mole with strontium and chloride respectively, combined into pure TCP because of some small cracks between the grain sizes. In this case, the EDS images shown the increasing the amount of the strontium and chloride to 2.5% mole the intensity of each of the phosphate and oxygen decreased with increasing the intensity of the calcium due to the chemical reactions of each of the Sr $(NO_3)_2$ and $(CaCl_2)$.

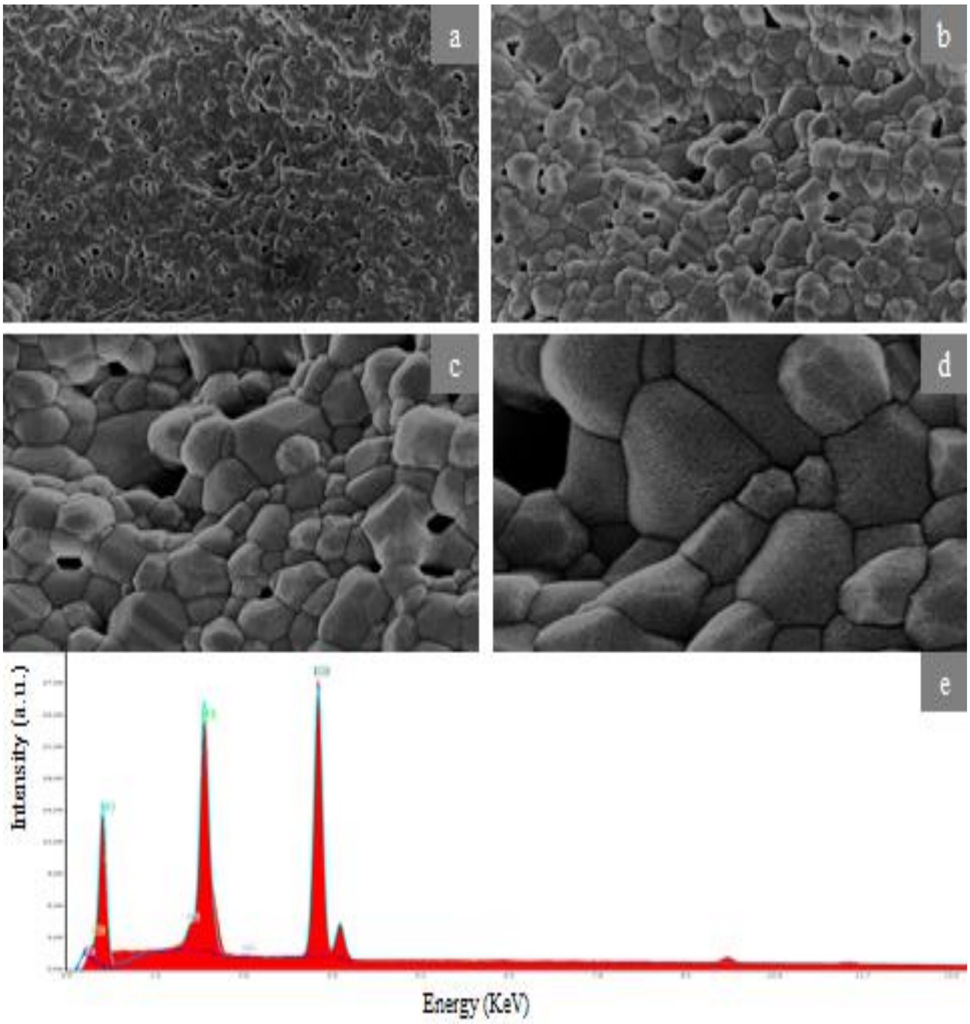

Figure 4.11. SEM images of doped 1.5TCP2.5Sr2.5Cl1.0F and 1.50 TCP sintered at 1100°C for 1 hour. (a) 0.5µm. (b) 1µm. (c) 200nm. (d) 100nm. (e) EDS image.

Figure 4.12 seen the increase in amount of the chloride (Cl^-) to 5.0% mole the materials have the non-homogenous shape, macro porosity and not make the grain sizes to building that is due to very loss in strength and quickly fracture and it is not good to applied into the biomedical applications. Furthermore, the EDS image have the highest intensity of the oxygen with lower intensity of each of the calcium and phosphate thats becase of this macro porosity and non growth the grain sizes.

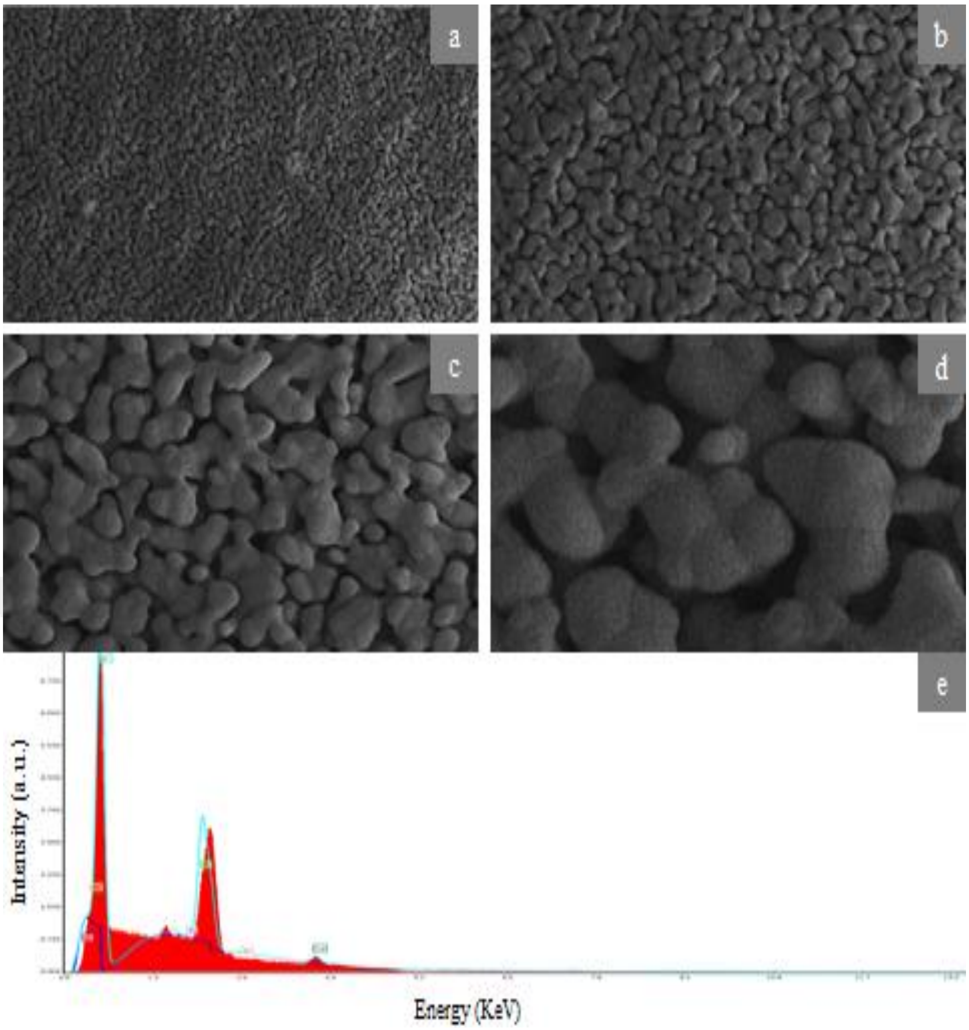

Figure 4.12. SEM images of doped and 1.50 TCP 1.5TCP2.5Sr5.0Cl1.0F sintered at 1100°C for 1 hour. (a) 0.5µm. (b) 1µm. (c) 200nm. (d) 100nm. (e) EDS image.

According to figure 4.13 the increase in the amount of the chloride to the 10% mole into the pure TCP it is better than the 5% mole putting into the pure TCP becuase of more solubility and have a growth the grain sizes and micro porosity but the grains non obtained perfectly togethr may be due to fusibility of some amount of the chloride, in this case the materials have the lower strength than the chloride doped with pure TCP with amount about 1% mole and 2.5% mole.

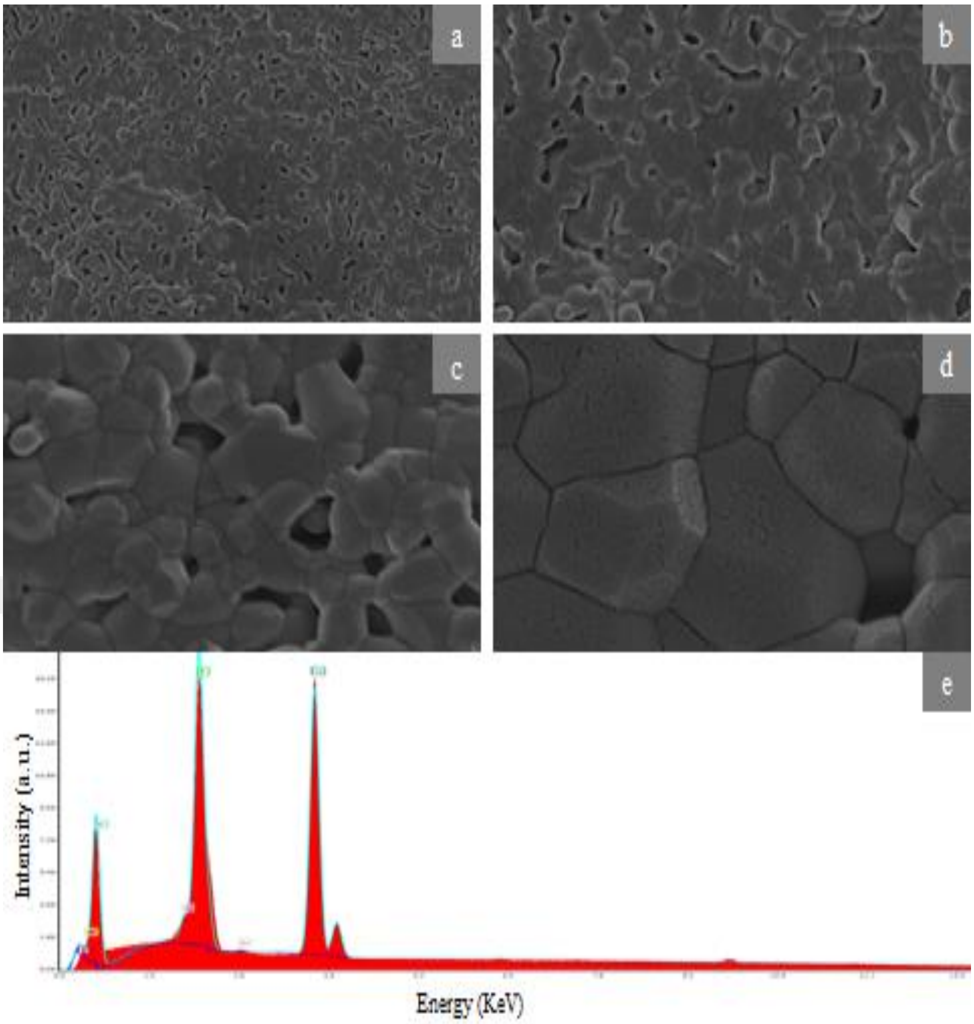

Figure 4.13. SEM images of doped 1.5TCP2.5Sr10.0Cl1.0F and 1.50 TCP sintered at 1100°C for 1 hour. (a) 0.5μm. (b) 1μm. (c) 200nm. (d) 100nm. (e) EDS image.

According to EDS image seen in figure 4.13 the intensity of the oxygen decreased compared with the 5% mole amount of the chloride doped into pure TCP but the calcium and the phosphate intensities increased it means that the chloride doped with pure TCP with 10% mole is better than the chloride doped into 1.50 TCP by 5.0% mole. Because of non-growth the grain sizes perfectly in this sample, the chloride doped with pure TCP with 10% mole also may be not good to use in biomedical applications.

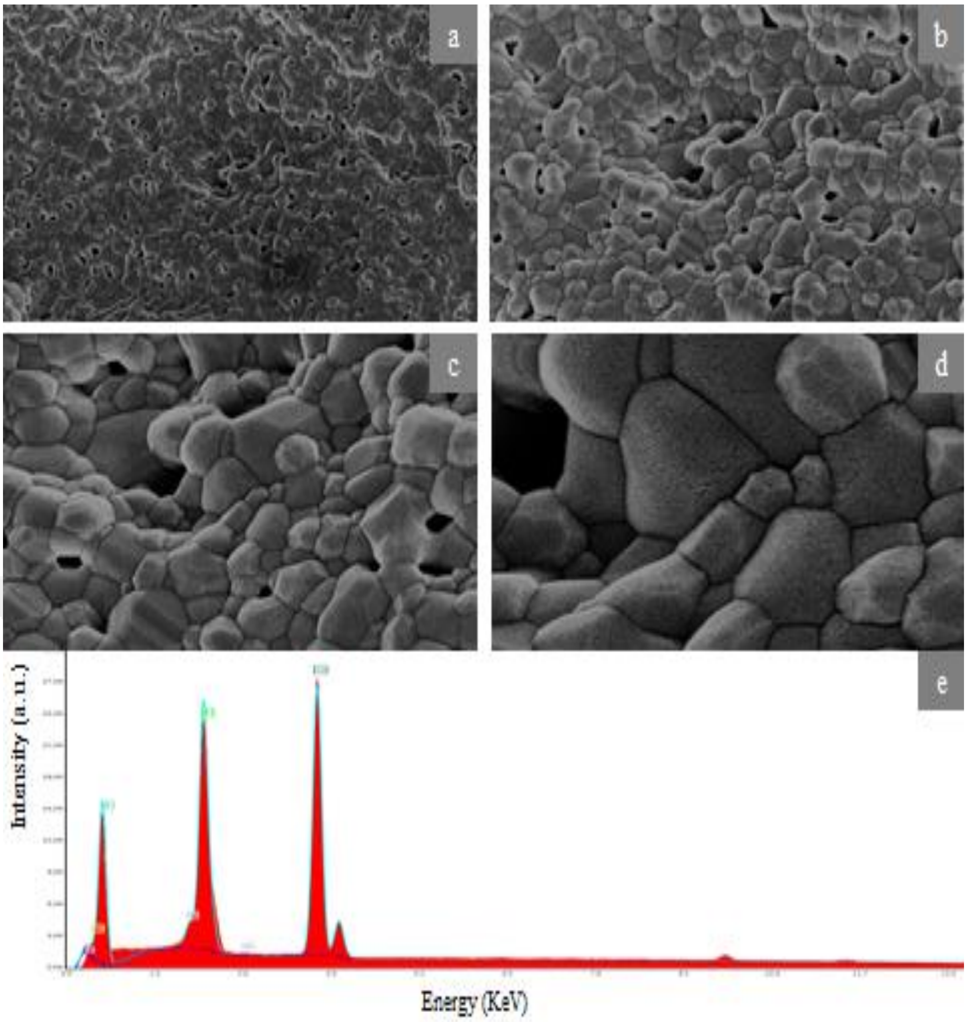

Figure 4.14. SEM images of doped 1.5TCP2.5Sr2.5Cl1.0F and 1.50 TCP sintered at 1100℃ for 1 hour. (a) 0.5µm. (b) 1µm. (c) 200nm. (d) 100nm. (e) EDS image.

In figure 4.15, the EDS image showed the intensity of the phosphate increased compared with the intensity of the calcium due to increase in amount of the fluoride to 2.5% mole that is because of the amount of the fluoride partially changed to phosphate chemical reactions that is due to the cations of each of the fluoride (F^-) and phosphate.

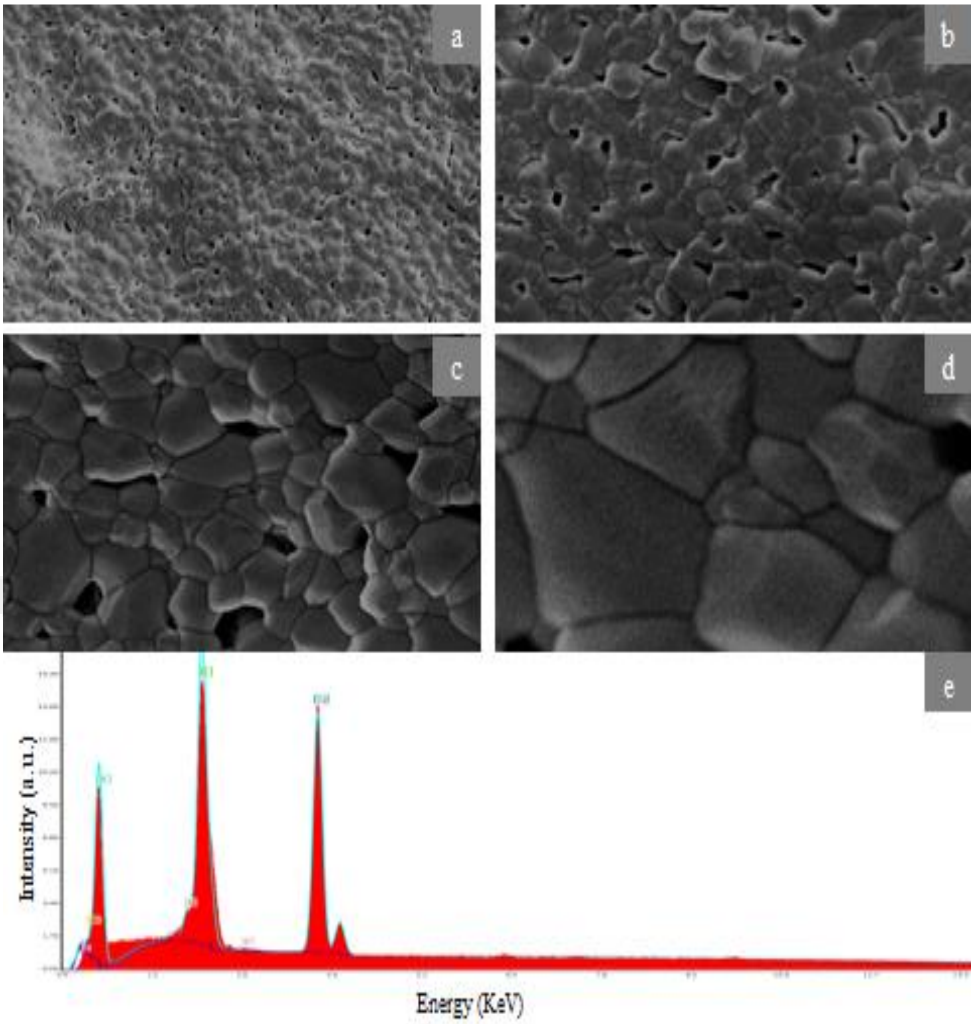

Figure 4.15. SEM images of doped 1.5TCP2.5Sr2.5Cl2.5F and 1.50 TCP sintered at 1100°C for 1 hour. (a) 0.5µm. (b) 1µm. (c) 200nm. (d) 100nm. (e) EDS image.

According to figure 4.15 and figure 4.16 the amount of fluoride when increased from to 5.0% mole the microstructure of the materials have the higher micro porosity and more cracks compare with 1% mole of the fluoride because of the fusibility an amount of the fluoride into the pure TCP when sintered at 1100°C in air for 1 hour.

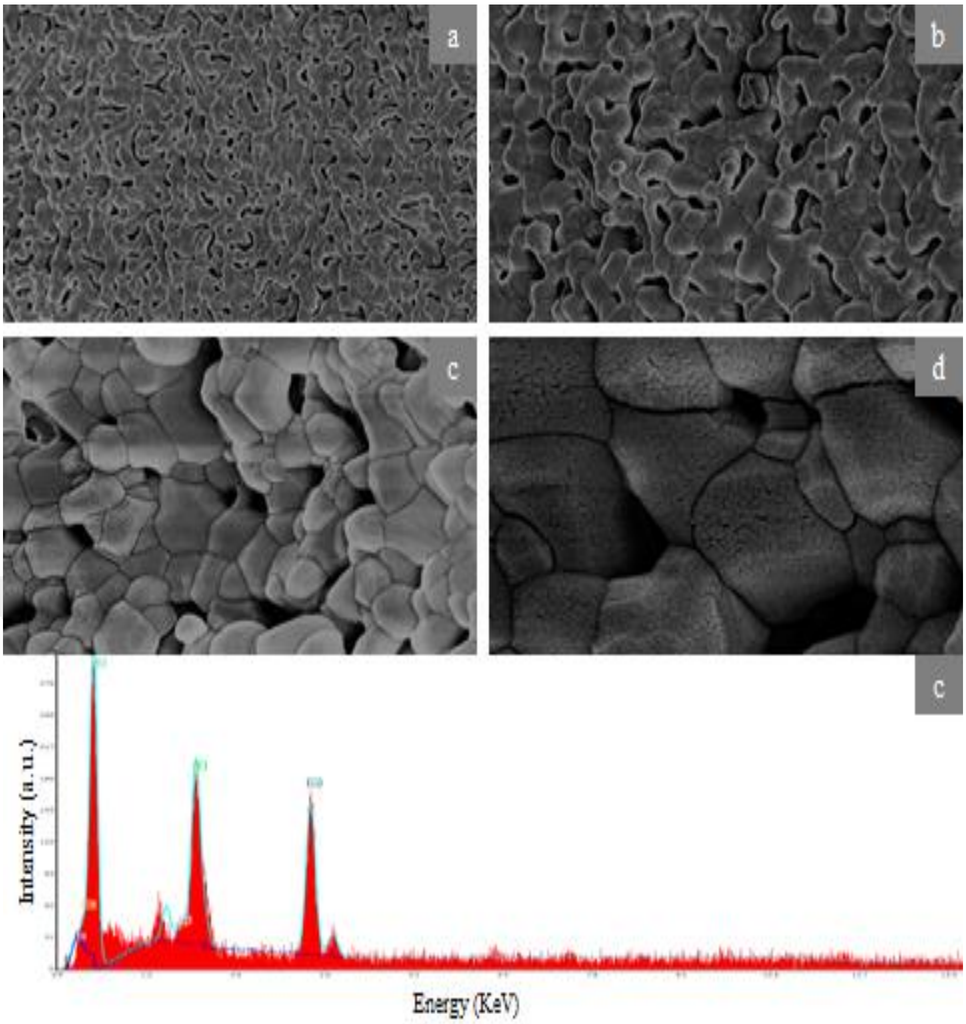

Figure 4.16. SEM images of doped 1.5TCP2.5Sr2.5Cl5.0F and 1.50 TCP sintered at 1100°C for 1 hour. (a) 0.5µm. (b) 1µm. (c) 200nm. (d) 100nm. (e) EDS image.

According to figure 4.16 from the EDS image showed the increasing the amount of the fluoride (F^-) to 5% mole the intensity of the oxygen element linearly increased with decreased the calcium element for this reason the growth of the grain sizes is lower and the grains non obtained perfectly together that is show the strength of the materials in this sample is lower and highest fracture than that the samples have 1% mole of fluoride doped with pure TCP.

5. CONCLUSION

In this study, tri-calcium phosphate doped with strontium, chloride and fluoride ions were synthesized by a precipitation method. Doping amount of Sr^{+2} ions was kept at 1.0, 2.5, 5.0 and 10.0% mole whereas doping amount of each of Cl^- and F^- ions was kept at 1.0, 2.5, 5.0 and 10.0 and 1.0, 2.5, 5.0% mole respectively. Synthesized TCP had Ca/P molar ratio at 1.50. All samples were sintered at 1100°C for 1 hour in air. Microstructural of the sintered samples was investigated.

According to density measurements of doped samples. High amount of Sr^{+2} led to an increase in densities. Densities of the F^- addition revealed considerable increase except for the densities of the doped samples with molar ratio of 1.0%mol. decrease. For Sr^{+2}, Cl^- and F^- doped samples, as the Sr^{+2} raised, the density of the samples increased due to decrease in puros. These results demonstrated that optimum amount of Sr^{+2}; Cl^- and F^- ions decreased the densification. Furthermore, the results revealed that increasing the amount of strontium (Sr^{+2}) to 2.5% mole due to a decrease in porosity volume and the bulk density will be lower and it is good for medical applications.

The XRD patterns demonstrated that for Ca/P ratio 1.50 at 1100°C, β-TCP phase was observed. In XRD, small shifts in peak positions were observed, due to the incorporation of doping ions and increased crystalline. In Sr^{+2}, Cl^- and F^- doped samples of 1.50 TCP, decomposition of β-TCP, α-TCP and formation of CaO, $SrCl_2$ and CaF_2 occurred. The results demonstrated that TCP with 1.0Sr, 2.5Sr, 1.0Cl and 1.0F might have appropriate potential for biomedical applications.

SEM images confirmed that sintering temperature and amount of dopants had significant effect on grain sizes of the samples. According to the results, the average grain sizes of the doped samples decreased when Ca/P ratio is 1.50. With ions addition, average grain sizes in Ca/P ratio 1.50 raised. TCP with molar ratio of 1.50 doped with 1.0 to 2.5% mole Sr^{+2}, 1.0 to 2.5% mole Cl^- and 1.0% mole F^- sintered at 1100°C were found the most outstanding materials for future biomedical applications because of this doped samples give the lower densities and small grain sizes.

REFERENCES

Aina, V., Lusvardi, G., Annaz, B., Gibson, I. R., Imrie, F. E., Malavasi, G., Martra, G 2012. Magnesium-and strontium-co-substituted hydroxyapatite: the effects of doped-ions on the structure and chemico-physical properties. ***Journal of Materials Science***: ***Materials in Medicine***, **23**(12): 2867-2879.

Albee, F. H, 1920. Studies in bone growth: triple calcium phosphate as a stimulus to osteogenesis. ***Annals of Surgery***, **71(**1): 32.

Ayers, R. A., Simske, S. J., Moore, J. J., Castillo, M., Gottoli, G, 2013. Manufacture of Porous Net-Shaped Materials. Comprising alpha or beta tricalcium phosphate or mixtures thereof. ***U.S. Patent No***. *8,545,786*. Washington, DC: U.S. Patent and Trademark Office.

Balamurugan, A., Benhayoune, H., Dumelie, N., Laquerriere, P., and Ferreira, J. M. F. (2008). Electrodeposition of fluorine-doped calcium phosphate coatings on to Ti6Al4V alloy—chemical and structural characterization. ***Journal of the American Ceramic Society***, **91**(9): 2797-2801.

Best, S. M., Porter, A. E., Thian, E. S., Huang, J, 2008. Bioceramics: past, present and for the future. ***Journal of the European Ceramic Society***, **28**(7): 1319-1327.

Brown, W. E., Chow, L. C, 1986. Effects of neutral salts in a bench-scale caries model. ***Journal of Dental Research***, **65**(9): 1115-1120.

Canal, C., Ginebra, M. P, 2011. Fibre-reinforced calcium phosphate cements: a review. ***Journal of the Mechanical Behavior of Biomedical Materials***, **4**(8): 1658-1671.

Denissen, H. W., De Groot, K, 1979. Immediate dental root implants from synthetic dense calcium hydroxyapatite. ***The Journal of Prosthetic Dentistry***, **42**(5): 551-556.

DeVoe, K., Banerjee, S., Roy, M., Bandyopadhyay, A., Bose, S. (2012). Resorbable tricalcium phosphates for bone tissue engineering: influence of SrO doping. ***Journal of the American Ceramic Society***, **95**(10): 3095-3102.

Dorozhkin, S. V, 2009. Calcium orthophosphates in nature, biology and medicine. ***Materials***, **2**(2): 399-498.

Famery, R., Richard, N., Boch, P, 1994. Preparation of α-and β-tricalcium phosphate ceramics, with and without magnesium addition. ***The Journal of Ceramics International***, **20**(5): 327-336.

Grigoraviciute-Puroniene, I., Tsuru, K., Garskaite, E., Stankeviciute, Z., Beganskiene, A., Ishikawa, K., Kareiva, A. (2017). A novel wet polymeric precipitation synthesis method for monophasic β-TCP. **Advanced Powder Technology**, **28**(9): 2325-2331.

Grover, W. H., Bryan, A. K., Diez-Silva, M., Suresh, S., Higgins, J. M., Manalis, S. R, 2011. Measuring single-cell density. ***Proceedings of the National Academy of Sciences***, **108**(27): 10992-10996.

Guidera A, Chaari K, Bouaziz J, 2011. Elaboration and Characterization of Alumina-Fluo- rapatite Composites. ***Journal of Biomaterial Nano***. **2**(5): 103-113.

Huang, M., Li, T., Zhao, N., Yao, Y., Yang, H., Du, C., Wang, Y, 2014. Doping strontium in tricalcium phosphate microspheres using yeast-based biotemplate. ***Materials Chemistry and Physics***, **147**(3): 540-544.

Kannan, S., Goetz-Neunhoeffer, F., Neubauer, J., Ferreira, J. M. F, 2008. Ionic substitutions in biphasic hydroxyapatite and β-tricalcium phosphate mixtures: structural analysis by Rietveld refinement. ***Journal of the American Ceramic Society***, **91**(1): 1-12.

Koroleva, L. F., Larionov, L. P., Gorbunova, N. P, 2012. Biomaterial based on doped calcium carbonate-phosphate for Active Osteogenesis. ***Journal of Biomaterials and Nano biotechnology***, **3**(2): 226.

Kutbay, I., Yilmaz, B., Evis, Z., Usta, M, 2014. Effect of calcium fluoride on mechanical behavior and sinterability of nano-hydroxyapatite and titania composites. ***Ceramics International***, **40**(9): 14817-14826.

Landi, E., Tampieri, A., Celotti, G., Sprio, S, 2000. Densification behavior and mechanisms of synthetic hydroxyapatites. ***Journal of the European Ceramic Society***, **20**(14): 2377-2387.

Langstaff, S., Sayer, M., Smith, T. J. N., Pugh, S. M, 2001. Resorbable bioceramics based on stabilized calcium phosphates. Part II: evaluation of biological response. ***Biomaterials***, **22**(2): 135-150.

Larsson, S., Hannink, G, 2011. Injectable bone-graft substitutes: current products, their characteristics and indications, and new developments. ***Injury***, **42**: S30-S34.

LeGeros, R. Z, 2002. Properties of osteoconductive biomaterials: calcium phosphates. ***Clinical orthopedics and related research***, **395**:81-98.

LeGeros, R. Z, 2008. Calcium phosphate-based osteoinductive materials. ***Chemical reviews***, **108**(11): 4742-4753.

Li, Z. Y., Lam, W. M., Yang, C., Xu, B., Ni, G. X., Abbah, S. A., Lu, W. W, 2007. Chemical composition, crystal size and lattice structural changes after incorporation of strontium into biomimetic apatite. ***Biomaterials***, **28**(7): 1452-1460.

Metseger, D. Rieger, R. M, and D. W. Foreman, 1999. Mechanical properties of sintered hydroxyapatite and tricalcium phosphate ceramic. ***Journal of materials science. Materials in medicine***, **10**: 9-17.

Motisuke, M., Carrodeguas, R. G., Zavaglia, C. A. D. C, 2011. Si-tricalcium phosphate cement: preparation, characterization and bioactivity in SBF. ***Materials Research***, **14**(4): 493-498.

Neto, J. D. S. R., Knopf, T. B., Fredel, M. C., Olate, S., de Moraes, P. H., Rabelo Neto, J. S., De Moraes, P. H, 2015. Synthesis and Characterization of Calcium Phosphate Compounds with Strontium and Magnesium Ionic Substitutions. ***International of journal morphology***, **33**(3): 1189-1193.

Özbek, Y. Y., Baştan, F. E., Üstel, F. (2016). Synthesis and characterization of strontium-doped hydroxyapatite for biomedical applications. ***Journal of Thermal Analysis and Calorimetry***, **125**(2): 745-750.

Pan, Y., Huang, J. L., Shao, C. Y, 2003. Preparation of β-TCP with high thermal stability by solid reaction route. ***Journal of materials science***, **38**(5): 1049-1056.

Park, J. B., Lakes, R. S, 1992. Characterization of Materials I. ***Biomaterials***. 29-62.

Park, J. W., Kim, Y. J., Jang, J. H., Song, H, 2013. Positive modulation of osteogenesis and osteoclast genesis-related gene expression with strontium-containing micro structured Ti implants in rabbit cancellous bone. ***Journal of biomedical materials research Part A***, **101**(1): 298-306.

Sakka, S., Bouaziz, J., Ayed, F. B, 2013. Mechanical properties of biomaterials based on calcium phosphates and bioinert oxides for applications in biomedicine. ***In Advances in Biomaterials Science and Biomedical Applications***. Intech.

Schumacher, M., Henß, A., Rohnke, M., Gelinsky, M, 2013. A novel and easy-to-prepare strontium (II) modified calcium phosphate bone cement with enhanced mechanical properties. ***Acta biomaterialia***, **9**(7): 7536-7544.

Tahmasebifar, A., Güngör, S., Zafer, E. V. İ. S, 2015. Flor iyonlari ilave edilmiş nano-kalsiyum fosfatlarin mikroyapisinin araştirilmasi. ***Gazi Üniversitesi Mühendislik-Mimarlık Fakültesi Dergisi***, **30**(1).

Turkoz, M., Atilla, A. O., Evis, Z. (2013). Silver and fluoride doped hydroxyapatites: investigation by microstructure, mechanical and antibacterial properties. ***Ceramics International***, **39**(8): 8925-8931.

Uysal, I., Severcan, F., Evis, Z, 2013. Structural and mechanical characteristics of nano hydroxyapatite doped with zinc and chloride. ***Advances in Applied Ceramics***, **112**(3): 149-157.

Von Gonten, A. S., Kelly, J. R., Antonucci, J. M, 2000. Load-bearing behavior of a simulated craniofacial structure fabricated from a hydroxyapatite cement and bioresorbable fiber-mesh. ***Journal of Materials Science: Materials in Medicine***, **11**(2): 95-100.

Wang, C. X., Zhou, X., Wang, M, 2004. Influence of sintering temperatures on hardness and Young's modulus of tricalcium phosphate bioceramic by nanoindentation technique. ***Materials Characterization***, **52**(4): 301-307.

Weiner, S., Dove, P. M, 2003. An overview of biomineralization processes and the problem of the vital effect. ***Reviews in mineralogy and geochemistry***, **54**(1): 1-29.

Yatongchai, C., Wren, A. W., Curran, D. J., Hornez, J. C. (2013). Comparison of the Weibull characteristics of hydroxyapatite and strontium doped hydroxyapatite. ***Journal of the Mechanical Behavior of Biomedical Materials***, **21**: 95-108.

Yilmaz, B., Evis, Z, 2014. Raman spectroscopy investigation of nano hydroxyapatite doped with yttrium and fluoride ions. ***Spectroscopy Letters***, **47**(1): 24-29.

Yuan, B., Li, C., Liang, B., Lü, L., Yue, H., Sheng, H., Xie, H. (2015). Extraction of potassium from K-feldspar via the CaCl 2 calcination route. ***Chinese Journal of Chemical Engineering***, **23**(9): 1557-1564.

Zhang, H., Liu, M., Fan, H., Zhang, X, 2012. An efficient method to synthesize carbonated nano hydroxyapatite assisted by poly (ethylene glycol). ***Materials Letters***, **75**: 26-28.

Zoppi, G., Forbes, I., Miles, R. W., Dale, P. J., Scragg, J. J., Peter, L. M, 2009. Cu2ZnSnSe4 thin film solar cells produced by selenisation of magnetron sputtered precursors. ***Progress in Photovoltaics: Research and Applications***, **17**(5): 315-319.

APPENDIX

EXTENDED TURKISH SUMMARY (GENİŞLETİLMİŞ TÜRKÇE ÖZET)

ÖZET

STRONSİYUM, KLOR VE FLOR İYONLARI KATIKLI TRIKALSIYUM FOSFAT SENTEZİ VE ÖZELLİKLERİNİN TESPİTİ

AHMED, Redar Wasurahman
Yüksek Lisans Tezi, Makine Mühendisliği Anabilim Dalı
Tez Danışmanı: Yrd. Doç. Dr. Serap (GÜNGÖR) KOÇ
Ocak 2018, 61 sayfa

Biyomekanik alanında araştırmacılar, özellikle kemik reformu ve sert doku protezleri alanlarında kullanılmak üzere, istenen mekanik özellikleri ve bazı özel gereksinimleri karşılayabilen biyomalzemeleri tasarlamaya ve seçmeye yönelik çalışmaları sıklıkla yürütmektedir.

Metalik olmayan malzemelerin oldukça büyük bir alt sınıfını teşkil etmekte olan çok sayıda biyoseramik malzeme, insan vücuduna nakledilmektedir. β-üç-kalsiyum fosfat (β-TCP)'ta işte bu malzemelere bir örnektir ve NaH_2PO_4 ve $Ca (NO_3)_2$ 'nin suda çözünmüş halinin ıslak çöktürülmesi ile elde edilmektedir. Bu çalışmanın amacı stronsiyum, klorür ve florür iyonları katıklı trikalsiyum fosfatlarını birleştirmektir. Saf ve katıklı trikalsiyum fosfatlarını elde etmek amacıyla uygulanmıştır. Katıklı numuneler 1100^{o}C'de 1 saat sinterlenmiştir. Yoğunluk etkisini tespit edebilmek için Archimedes yöntemi yapılmıştır. Stronsiyum (Sr^{+2}) ve klor (Cl^{-}) ilavelerinin numunelerin yoğunluğunu azalttığı gözlenirken, flor katkısının hem numune. Stronsiyum, klor ve flor katıklı numuneler 1100^{o}C'de 1 saat sinterleme sonrasında yoğunluk farklılıkları göstermiştir. Fazların ve bağların tespiti için XRD difraksiyon yöntemi kullanılmıştır. Çalışma sonucunda tüm numuneler için XRD difraksiyonunda TCP tepe noktalarına ulaşılmıştır. Numunelerin tanecik ebatlarının tespitinde SEM yöntemi kullanılmıştır.

Anahtar Kelimeler: Klor, Flor, Çöktürme yöntemi, Stronsiyum, Trikalsiyum fosfat.

A. GİRİŞ

Fosforik asidin $Ca_3(PO_4)_2$ kimyasal bileşimine sahip olan tuzuna trikalsiyum fosfat (TCP) denmektedir. Kalsiyum fosfat, biyomalzeme biliminde kemik üretiminde kullanılan en önemli malzemelerden biridir. Genellikle mineral kayaları gibi inorganik kaynaklardan temin edilmektedir. Kalsiyum fosfatlar CaP dişçilikte, ortopedide ve maksillofasiyal kemiklerdeki kusurların giderilmesinde aranan biyomalzemelerdir. Kalsiyum fosfatlar kemik kusurlarının giderilmesinde yıllardır kullanılmaktadır. Hidroksiapatit ($Ca_{10}(PO_4)_6(OH)_2$, HA), trikalsiyum fosfat ($Ca_3(PO_4)_2$, TCP) ve TCP-HA alaşımları diş ve tıp alanlarında kullanılan kalsiyum fosfatlara örnektir. Alaşımlar söz konusu olduğunda ideal oran genellikle malzemenin kullanılacağı bölgeye göre değişmektedir, hangi malzemenin özellikleri daha çok isteniyorsa o malzemenin oranı artmaktadır (yoğunluk için hidroksiapatit, emilim için trikalsiyum fosfat). Günümüzde kalsiyum fosfat esaslı biyoseramikler ve biyomalzemeleri vücut çapında tüm iskeleti kapsayacak şekilde çok daha geniş ölçekte kullanılmaktadır. CaP'ler ayrıca perkutan aletlerde ve periodontal tedaviler, çatlakların tedavisi, omurga ameliyatları, kraniyo-maksillofasiyal yeniden yapılandırma ve otolaringoloji'de de kullanılmaktadır. Arzu edilen malzemenin biyo-emilebilir veya biyo-aktif olma durumuna göre farklı kalsiyum-orto-fosfatlar kullanılabilmektedir. Geçmişte çok sayıda vakada, enfeksiyonlar ya da kullanılan malzemenin toksik etkilerinin bilinmemesine bağlı nedenlerle nakiller başarısızlıkla sonuçlanmaktaydı. Nihayetinde hem diş hem de kemiklerin mineral kısımlarında bulunmalarından yola çıkarak, kalsiyum fosfatların kullanımlarının mantıklı olduğuna karar verildi. Kalsiyum fosfat'ın yapay bir malzeme olarak tavşanlarda ameliyatla meydana getirilmiş kusurların tedavisinde kullanımı 1920'lerde literatüre geçen ilk kullanım olmuştur. Bundan yarım yüzyıl sonra kalsiyum fosfat'ın ameliyatla meydana getirilmiş kusurların düzeltilmesi için diş cerrahisinde ilk kullanımı ve diş protezi olarak yoğunlaştırılmış HA silindirleri kullanımı literatüre geçmiştir.

A.1. Stronsiyum Katıklı Trikalsiyum Fosfat TCP-Sr^{+2}

Stronsiyum kemiklerin dokusunda dağılmış olarak bulunmaktadır. Ayrıca insanda kemik metabolizması döngülerinde önemli rol oynamaktadır. Sr^{+2} kimyasal özellikleri açısından Ca^{+2} ‘ya çok benzer olduğundan kristal yapısında büyük ölçüde onun yerine kullanılabileceği kabul edilmektedir. Bu şekilde değişiklik yapıldığında kristal yapının mekanik özelliklerinde, yapısında ve morfolojisinde dengeyi azaltmakta ancak antibakteriyel ve biyoaktivite özellikleri ile çözülebilirliğini artırmaktadır. Bunlara ilaveten, düşük miktarlarda Sr^{+2} değiştirilmesinin kemik emiliminde azalmayı sağlaması, osteoklast geri emilim işlevini baskılayarak kemik oluşumuna katkıda bulunması, ve osteoblast faaliyetlerin stimülasyonu ve çeşitliliklerinin artırılması gibi avantajları vardır (Huang et al., 2014).

A.2. Flor Katıklı Trikalsiyum Fosfat TCP-F^-

Kemiklerdeki HA’nın kristal yapısındaki Flor iyonu (F^-) onun saflığını bozmasına rağmen doğal olarak içinde bulunan maddelerden biridir. Bu durumdan yola çıkarak kalsiyum fosfat’a değişik iyonlar ilave ederek mekanik, biyolojik ve kimyasal özelliklerini geliştirme fikrine ulaşılmıştır. Son zamanlarda yeni implant biyomalzemeleri elde etme çalışmalarında trikalsiyum fosfat’ta iyon değişimi yapılarak farklı türden saflık bozunumları elde etme fikri giderek ilgi kazanmaktadır. Bu yöntemlerle elde edilen malzemelerin biyoaktivite ve biyo-uyumluluk seviyeleri saf TCP ile benzer olmakla beraber, TCP’ye flor katıklanması vücut ortamı içerisindeki ömrü uzatmaktadır. TCP’ye yüksek oranda flor (F^-) iyonu katıklandığı hallerde anormal doku gelişimleri ve zayıf mekanik özellikler ortaya çıkmıştır. Ancak, daha düşük yoğunluklarda flor ilavesi TCP’nin mekanik özelliklerini de geliştirmekte, örneğin çatlak direncini, sertliği, esneklik katsayısını ve gevrekliğini daha iyi hale getirmektedir. Zaten flüor insanda sert doku gelişiminin önemli bir öğesidir (Yilmaz and Evis, 2014).

A.3. Klor Katıklı Trikalsiyum Fosfat TCP-Cl^-

Klor (Cl^-) katıklı kalsiyum fosfat, kemikler ortogenezi, kemik yoğunlaşmasını ve diş dokularını dinamik olarak etkileyen ve deriden emilebilen biyo-uyumlu bir maddedir. Kemiklerde bulunan kalsiyum fosfatta iyon olarak klor (Cl^-) iyonlarının yanı sıra Ca^{+2} ve $3PO^{-3}_4$'de bulunmaktadır. Kalsiyum fosfatın kristal yapısında hem katyon hem de anyon yapıda bu şekilde bulunan boşluklar nedeniyle kalsiyum fosfatın hem kimyasal bağları hem de kristal yapısı oldukça karmaşıktır. İz elementlerin bivalan katyonları, Cl^- ile beraber organizma tarafından alınırsa bu boşlukları doldurabilmektedir. Trikalsiyum fosfat katkılanan klor iyi bir ısıl dengeye sahiptir ve biyolojik dokulara hiç zarar vermez. Kalsiyum fosfat klorle katıklandığında yoğunluğu bir nebze artmaktadır. Klor ilavesi numunelerin tanecik ebatlarının küçülmesine ve trikalsiyum fosfat'ın mikro-sertliğinin artmasına sebep olmuştur (Koroleva et al., 2012).

A.4. Tezin Amacı

Bu tezin amacı biyomedikal amaçla kullanılabilecek yeni nano-kompozit biyoseramikler elde etmek ve mikro-yapıları ile mekanik ve biyo-uyumluluk özelliklerini incelemek amacıyla stronsiyum (Sr^{+2}), klor (Cl^-) ve flor (F^-) katıklı trikalsiyum fosfatlar sentezlenmesidir. Bu güne kadar literatürde trikalsiyum fosfat'a stronsiyum, klor ve flor iyonlarının aynı anda katıklandığı başka bir çalışma bulunmamaktadır. Çöktürme yöntemi ve 1100°C'de 1 saat sinterleme yoluyla, stronsiyum, klor ve flor iyonları ile katıklanmış trikalsiyum fosfat sentezlenmiştir. Fazların ve bağların tespiti için XRD difraksiyon yöntemi kullanılmıştır. Çalışma sonucunda tüm numuneler için XRD difraksiyonunda TCP tepe noktalarına ulaşılmıştır. Numunelerin tanecik ebatlarının tespitinde SEM yöntemi kullanılmıştır.

B. MATERYAL ve YÖNTEM

Kalsiyum fosfatların sentezi için, di-amonyum hidrojenfosfat ($(NH_4)_2HPO_4$) (Merck, Almanya) ve kalsiyumnitrat tetrahidrat (Ca $(NO_3)_{2.}4H_2O$), amonyum (NH_4OH) prekürsörleri olarak kullanılmıştır. Kalsiyum Klorür ($CaCl_2$), amonyum florür (NH_4F). Stronyum nitrat (Sr $(NO_3)_2$) flor, klor ve stronsiyum katıklı kalsiyum fosfatların birleştirilmesinde kullanılmıştır (Aldrich, ABD). Çözeltilerin pH değerlerinin tespiti için amonyum çözeltisi (Merck, Almanya) kullanılmıştır.

B.1. Kalsiyum Fosfatların (CaP) Sentezlenmesi

Nano-kalsiyum fosfat tozlarının birleştirilmesi için çöktürme yöntemi kullanılmıştır. Ca $(NO_3)_2.4H_2O$ and $(NH_4)_{2.}HPO_4$ çözeltilerini belirli bir molar oranda hazırlamak için, amonyum prekürsörleri kalsiyumnitrat tetrahidrat (Ca $(NO_3)_2.4H_2O$), di-amonyum hidrojen fosfat ($(NH_4)_2HPO_4$) ve stronsiyum nitrat distile (Sr $(NO_3)_2$) suya ilave edilmiştir. Katıklı numuneler için, Ca/P oranı olarak 1.50 sabit tutulmuş ve Ca/P+Sr molar oranı 1.50:1 şeklinde ayarlanmıştır. Kalsiyum klor ve amonyum flor içindeki di-amonyum hidrojen fosfat çözeltisi 60 dakika boyunca karıştırılmıştır. pH seviyesine 11-12 seviyesine getirmek için amonyak eklenmiştir. Ayrıca flor di-izopropoksit, kalsiyum nitrat çözeltileri ve amonyak çözeltisi aynı anda damlalar halinde di-amonyum hidrojen fosfat-amonyağa katılmıştır. Bunu takiben kalsiyum klor ($CaCl_2$), amonyum flor (NH_4F) ve stronsiyum nitrat (Sr $(NO_3)_2$) bu karışıma ilave edilerek 10 dakika karıştırılmıştır. Reaksiyonu artırmak amacıyla, nihai çözelti de 60 dakika karıştırılarak 130 – 310 ^oC'de kaynatılmıştır. Kaynatma işleminden sonra da çözelti 24 saat boyunca karıştırılmıştır. Ardından ince bir filtre kâğıdı kullanılarak çözelti filtrelenmiş ve ıslak bir hamur elde edilmiştir. Fazla suyun uzaklaştırılması için bu hamur fırında 200^oC'de 10-12 saat kadar kurutulmuştur. Son olarak, 1 saat boyunca 1100^oC'de sinterlenmiştir. Saf CaP'in katıklanma süreci aşağıdaki şekilde gösterilmiştir.

B.2. Katıklanmış Kalsiyum Fosfatlarının CaP Sentezi

Stronsiyum, flor ve klor katıklanmış kalsiyum fosfatlar elde edilebilmesi için, ana prekürsörlere (saf kalsiyum fosfatlara) ilaveten stronsiyum nitrat ($Sr\ (NO_3)_2$), flor di-izopropoksit ve amonyum hidroksit (NH_4OH) kullanılmıştır. Numunelerin elde edilmesinde de benzer bir sentez yöntemi kullanılmıştır. Ayrıca Sr^{+2}, Cl^- ve F^- kaynakları olarak sırasıyla stronyum nitrat ($Sr\ (NO_3)_2$), kalsiyum klor ($CaCl_2$) ve amonyum flor (NH_4F) kullanılmıştır. Katıkların molar yüzdesi Ca/P 1.5 olacak şekilde ayarlanmıştır. Flor di-izopropoksit, kalsiyum nitrat çözeltisi ile molar oranı olacak şekilde karıştırılmıştır. Di-amonyum fosfat çözeltisine 100%, 99%, 97.5%, 95% ve 90% oranında amonyum hidroksit (NH_4OH) ilave edilmiştir. Ardından bu çözeltiye eşit miktarlarda $Sr\ (NO_3)_2$ katkısı eklenmiştir. Nihayetinde, kalsiyum fosfat granüllerinin çökeltilmesi için, hidrojen fosfat çözeltisine eşit miktarda ve sürekli (NH_4OH) ile birlikte damla damla kalsiyum klorür çözeltisi eklenmiştir. Bu araştırmada, CaP'lerin ifadesi için, xxCaP, yySr, zzF ve wwCl şeklinde ifade edilen aşağıdaki formül kullanılmıştır. Bu formülde xx, numunedeki Ca / P oranını (1.50) gösterirken, yy sistemde mevcut her 100 mole OH^- iyonuna karşılık mevcut bulunan F^- iyonlarını (1.0, 2.5 ve 5) göstermektedir. zz sistemde mevcut her 100 mole OH^- iyonuna karşılık mevcut bulunan Sr iyonlarını (1, 2.5 ve 5 ve 10) ifade etmektedir. Sistemde bulunan her 100 mole OH^- iyonuna denk gelen Cl^- iyonları ise (1, 2.5 ve 5 ve 10) ww ile ifade edilmektedir. Prekürsörlerin atomik oranlarına denk düşecek şekilde eklenen katık oranı ayarlanmıştır. Meydana gelen karışım filtrelenmiş, kurutulmuş ve 1100°C'de 1 saat sinterlenmiştir.

C. BULGULAR ve TARTIŞMA

C.1. Numunelerin Yoğunlukları

Ca/P oranı 1.50 olacak şekilde stronsiyum (Sr^{+2}), flor (F^{-}) ve klor (Cl^{-}) olmak üzere farklı iyonlarla katkılandırılmış ve 1100°C'de 1 saat sinterlenmiş trikalsiyum fosfat'ın yoğunluğu tablo C.1'de verilmiştir.

Tablo C.1. Ca / P oranı 1.50 olan ve 1100°C'de 1 saat sinterlenmiş trikalsiyum fosfatın yoğunlukları

Numara	Numunelerin adi	Yoğunlukları g/cm^3
1	1.5TCP	3.0433
2	1.5TCP 1.0Sr 1.0Cl 1.0F	2.9511
3	1.5TCP 2.5Sr 1.0Cl 1.0F	3.0450
4	1.5TCP 5.0Sr 1.0Cl 1.0F	2.8047
5	1.5TCP 10.0Sr 1.0Cl 1.0F	3.6444
6	1.5TCP 2.5Sr 2.5Cl 1.0F	2.5838
7	1.5TCP 2.5Sr 5.0Cl 1.0F	2.4979
8	1.5TCP 2.5Sr 10.0Cl 1.0F	2.7894
9	1.5TCP 2.5Sr 2.5Cl 1.0F	3.9766
10	1.5TCP 2.5Sr 2.5Cl 2.5F	4.0632
11	1.5TCP 2.5Sr 2.5Cl 5.0F	2.7955

Tablo C.1'de Ca / P oranı 1.50 olan ve 1100°C'de 1 saat sinterlenmiş trikalsiyum fosfatın yoğunlukları saf ve stronsiyum, klor ve flor ile katıklandırılmış trikalsiyum fosfatın teorik yoğunlukları 2.4979 g/cm^3 ile 4.0632 g/cm^3 arasındadır. 1.5TCP 2.5Sr 2.5Cl 2.5F numunesi, 4.0632 g/cm^3 ile azami yoğunluğa ulaşmıştır, buna karşılık saf 1100°C'de 1 saat sinterlenmiş TCP'nin yoğunluğu 3.0433 g/cm^3'tür. %1 mol flor içeren ve yüksek miktarlarda stronsiyum ve klor iyonları katıklı numuneler genellikle aynı sürede ve sıcaklıkta sinterlenmiş %2.5 flor içeren numunelerden daha düşük yoğunluğa sahiptir. Bu şekilde iyi bir ısıl kararlılık sağlayan ve biyolojik dokulara zarar vermeyen, bununla beraber yoğunlukta bir nebze artışı sağlayan ideal klor miktarı tespit edilmiştir.

C.2. X-Işını Difraksiyon Analizi

Fazların mevcudiyetinin tespiti için 1100^{o}C'de sinterlenmiş numuneler üzerinde XRD analizi uygulanmıştır. Bu çalışmada kalsiyum fosfatın sentezi için kullanılan çöktürme yönteminin doğası gereği stokiyometrik oran 1.50 idi. Ayrıca Ca açısından eksik numunelerde 750 ^{o}C'nin üzerindeki ısılarda β-TCP'ye dönüşüm gözlenmiştir. Sonuçlar ayrıca, Ca / P oranı 1.48 ile 1.55 arasında olduğunda β-TCP oluşumunun 1125 ^{o}C'den daha düşük sıcaklıklarda oluştuğunu göstermektedir.

Numunelere 2.5% molar Sr^{+2} iyonu eklenmesiyle tepe noktalarının kırılcallığının arttığı görülmektedir. 1.5TCP5.0Sr1.0Cl1.0F numunesinde Sr^{+2} miktarı 2.5% molar'dan 5%'e çıkarıldığında β-TCP'nin tepe yoğunlukları artarken α-TCP'ninki azalmaktadır. Yüksek miktarlarda Sr^{+2} iyonları varlığında bazı α-TCP tepeleri neredeyse kaybolmuştur. Hem α-TCP hem de β-TCP varlığı Cl^{-} iyonları miktarının 2.5%'ten 5% mol'e çıkarılması ile oluşmuştur. Cl^{-} miktarı 2.5%'ten 5%'e çıkarıldığında α-TCP artışı β-TCP artışından daha yüksek olmuştur. Bu durum kalsiyum fosfatlarına Cl^{-} iyonu katkısının yapısal kararlılığı arttırdığına işaret etmektedir. Ayrıca, 1.5TCP5.0Sr1.0Cl1.0F ve 1.5TCP10.0Sr1.0Cl1.0F numunelerinde, Sr^{+2} katıklı TCP'de 1.0% F^{-} varlığı Sr^{+2} miktarını 5.0% mol'den 10% mol'e artırmış, ve α-TCP fazının varlığı devam ettiği halde β-TCP fazının azalmasına neden olmuştur. 1.5TCP1.0Sr1.0Cl2.5F ve 1.5TCP1.0Sr1.0Cl5.0F numunelerinde F^{-} miktarının 2.5%'ten 5%'e çıkarılmasıyla β-TCP tepe yoğunlukları artarken α-TCP tepeleri azalmıştır.

C.3. Tarama Elektron Mikroskobu SEM Analizi

Şekil 4.6'dan Şekil 16'ya kadar şekiller saf TCP'nin ve iyon katıklı 1100^{o}C'de sinterlenmiş numuneleri göstermektedir. Hem katıklanmış hem de katıklanmamış numuneler SEM analizine tutulmuştur.

Isıya maruz bırakılmış numunelerin SEM mikrografileri Şekilde gösterilmiştir. Hem saf hem de katıklanmış numunelerde artmış porozite gözlenmektedir. Bu gözlemler bu bileşimlerin küçük miktarlardaki yoğunluklarına ışık tutmaktadır. Bu sonuç ısıl işlem süreci boyunca $SrCl_2$ mevcudiyeti nedeniyle kayda değer miktarda tanecik büyümesi olduğuna işaret etmektedir. Bu durum fosforlu atomların Ca^{+2} iyonlarının yerini almasıyla açıklanabilir. Bu nedenle ısıl işlem süresince tanecik oluşumu hızlanmaktadır.

1100^{o}C'ye ısıtılmış TCP'lerin SEM görüntülerinde daha ince taneler ve daha bir örnek mikroyapılar gözlenmektedir. Meydana gelen tanecik ebatlarında uygulama sıcaklığının ve katkı miktarının etkisi bulunmaktadır. 900^{o}C ile 1100^{o}C arasındaki sinterlemenin ardından TCP taneciklerin nano boyutta olduğu belirtilmektedir.

Şekil (9)'de görüldüğü üzere Sr^{+2} miktarının 2.5% mol'den 5.0% mol'e artırılması ile saf TCP'ye kıyasla tanecik ebadı da artmaktadır. Ayrıca Sr^{+2} ile katıklanmış numunelerde TCP'ye oranla daha yüksek ortalama tanecik boyutu elde edilmektedir. Bu şekilde numunelerin mekanik özellikleri değiştirilebilmektedir. SEM görüntülerine göre, saf β-TCP'ye göre numunelerin tanecik boyutu artmıştır. Tanecik ebatlarının artışı Sr^{+2} ve Cl^- iyonlarının arttırılmasına bağlıdır. F^- yoğunluğunu artırmanın da F^- ile katıklanmış numunelerde tanecik ebadını arttırdığı gözlenmiştir. Her hâlükârda, Cl^- iyonları ile de katıklanmış numunelerde daha çok poroz yapı görülmüştür. Ayrıca Cl^- ile de katıklanmış numunelerde daha düşük tanecik boyutu elde edilmiştir.

Genellikle, saf TCP'ye ve Sr^{+2} ve Cl^- ile katıklanmış numunelere 2.5% mole F^- ilavesi ile birim hücre ebadı azalmaktadır. F^- iyonlarının OH^- iyonlarına kıyasla daha düşük iyonik çapı olduğu bilinmektedir, bu nedenle TCP'deki OH^- iyonlarının F^- iyonları ile değişmesinin TCP'nin birim hücre boyutunu azaltmaktadır. Tersine, saf TCP'nin hücre ebadı TCP5.0Sr ve TCP10.0Sr'e kıyasla daha yüksektir. Ca bölgelerinde katyonlar TCP'ye dahil olmaktadır. Ca^{+2} iyonik çapının Sr^{+2} iyonik çapından daha büyük olması nedeniyle Sr^{+2} iyonlarının Ca^{+2} iyonlarının yerine geçmesi TCP5.0Sr ve TCP10.0Sr bileşenlerinde küçülmeye neden olmaktadır. Genellikle TCP'nin c-ekseni parametresindeki azalmaya bağlı olarak, katıklanmış TCP birim hücre boyutu küçülmektedir.

D. SONUÇ

Bu çalışmada bir çöktürme yöntemi kullanılarak stronsiyum, klor ve flor katıklı trikalsiyum fosfat sentezlenmiştir. Sr^{+2} iyonlarının katıklama oranı olarak 1.0, 2.5, 5.0 ve 10.0% mole kullanılırken, Cl^- ve F^- iyonları için sırasıyla 1.0, 2.5, 5.0 ve 10% ile 1.0, 2.5, 5.0% değerleri kullanılmıştır. Sentezlenen TCP'lerin Ca/P oranı 1.50'dir. Tüm numuneler 1100^{o}C'de 1 saat sinterlenmiştir. Elde edilen sinterlenmiş numunelerin mikroyapısal özellikleri incelenmiştir.

Katıklı numunelerin yoğunluk ölçümlerine göre, yüksek Sr^{+2} miktarının yoğunluk artışına neden olduğu ortaya çıkmaktadır. %1 mol haricinde, F^- ilave edilmiş tüm numunelerin yoğunluklarında belirgin artış tespit edilmiştir. Sr^{+2}, Cl^- ve F^- ile katıklanmış numuneler için, Sr^{+2} arttıkça, poroz yapıdaki azalmaya bağlı olarak yoğunluk artmaktadır. Ayrıca Sr^{+2} nin 2.5% mol'e arttırılmasının poroziteyi artırarak yoğunluğu azaltacağı ortaya çıkmıştır, bu durum tıbbi uygulamalarda faydalı olabilir.

XRD sonuçları 1100^{o}C'de sinterlenmiş Ca/P oranı 1.50 numunelerde β-TCP fazının varlığını ortaya koymaktadır. XRD'de, katıklanan iyonların kırılcal yapıyı artırarak tepe noktalarında küçük kaymalara neden olduğu gözlenmiştir. Sr^{+2}, Cl^- ve F^- ile katıklanmış 1.50 Ca/P oranına sahip numunelerde β-TCP dek n ompozisyonu ve CaO, $SrCl_2$ ve CaF_2 oluşumu gözlenmiştir. Sonuçlar 1.0Sr, 2.5Sr, 1.0Cl ve 1.0F'li TCP'lerin biyomedikal uygulamalarda kullanılmaya aday olduğunu göstermektedir.

SEM görüntüleri sinterleme sıcaklığının ve katık miktarlarının numunelerin tanecik boyutlarında önemli derecede etkili olduğunu göstermiştir. Sonuçlara göre, Ca/P oranı 1.50 olduğunda ortalama tanecik boyutu azalmaktadır. İyonların ilavesi ile, Ca/P oranı 1.50 numunelerin tanecik ebatları yeniden yükselişe geçmektedir. 1.50 Ca/P oranına sahip 1.0 – 2.5% Sr^{+2} , 1.0% Cl^-, ve 1.0% F^- ile katıklanmış ve 1100^{o}C'de 1 saat sinterlenmiş numunelerin küçük tanecik boyutu ve yüksek yoğunlukları ile gelecekteki biyomedikal uygulamalar için en üstün özelliklere sahip malzemeleri meydana getirdikleri gözlenmiştir.

CURRICULUM VITAE

Name	Redar Wasurahman AHMED
Date of Birth	07. Oct. 1983
Place of Birth	IRAQ – ERBIL
Sex	Male
Marital Status	Married
Nationality	IRAQI
Permanent Address	ERBIL – Shorsh
Telephone	009647504492606 - 00905373449089
Email	rr.ahmed83@gmail.com
Education	BSc in mechanical Engineering - University of Salahaldin Erbil - College of Engineering - Iraq-Erbil From 2002 to 2007.
Employment Record	Ministry of Health Location: Erbil Duration: from 1/8/2007 to present

Date: 16/01/201

Thesis Title : "SYNTHESIS AND CHARACTERIZATION OF TRI-CALCIUM PHOSPHATE DOPED WITH STRONTIUM, CHLORIDE AND FLUORIDE IONS"

The title of the mentioned thesis, above having total 88 pages with cover page, introduction, main parts ar conclusion, has been checked for originality by Turnitin computer program on the date of 28/12/2017 and i detected similar rate was 3% according to the following specified filtering

Originality report rules:

- Excluding the Cover page,
- Excluding the Thanks,
- Excluding the Contents,
- Excluding the Symbols and Abbreviations,
- Excluding the Materials and Methods
- Excluding the Bibliography,
- Excluding the Citations,
- Excluding the publications obtained from the thesis,
- Excluding the text parts less than 7 words (Limit match size to 7 words)

I read the Thesis Originality Report Guidelines of VAN Yuzuncu Yil University for Obtaining and Using Similarity Rate for the thesis, and I declare the accuracy of the information I have given above and my thesis does not contain any plagiarism; otherwise I accept legal responsibility for any dispute arising in situations which are likely to be detected.

Sincerely yours,

16/01/2018

Name and Surname: Redar Wasurahman AHMED
Student ID: 149101234
Science: Department of Mechanical Engineering
Program:

Statute: M. Sc. ☒ Ph.D. ☐

APPROVAL OF SUPERVISOR
SUITABLE

Asst. Prof. Dr. Serap KOÇ

APPROVAL OF THE INSTITUTE
SUITABLE

Prof Dr. Suat ŞENSOY
Enstitü Müdürü