BALL, KEVIN NICHOLAS. Synthesis, Fabrication and Characterization of Doped and Undoped Hydroxyapatite Targets. A Foundation For Controlled Thin-Film IBAD Deposition. (Under the direction of Jerome J. Cuomo.)

This study investigates the development of bulk hydroxyapatite compositions and their resultant structures. A simple precipitation reaction was implemented to synthesize and dope the basic apatite composition. Stoichiometric, calcium deficient, and barium stabilized calcium deficient composition were investigated using x-ray diffraction and Fourier transform infrared spectroscopy. This knowledge was subsequently applied to ion beam assisted thin film deposition using the synthesized hydroxyapatite.

The bulk studies revealed a necessity for washing the precipitates after the reaction was complete to remove excess calcium from the powders. Concurrently, only 5 atom percent barium can be incorporated into the apatite composition before the apatite phase begins to deteriorate. Significant amounts of carbonate contaminant is removed when the samples are sintered; however, those composition containing barium do not readily evolve the said carbonate groups.

Bulk hydroxyapatite was lastly used as the target material for development of thin films. Those films deposited on substrates heated at 420° C and those exposed to a pre-sputter etch provided the bonding environments necessary to develop the apatite phase when an optimum annealing temperature of 850° C was used. The ability to fabricate the targets and implement them in the IBAD system allows the researcher to tailor the bulk material for specific properties in the thin film.
Synthesis, Fabrication and Characterization of Doped and Undoped Hydroxyapatite Targets

A Foundation For Controlled Thin-Film IBAD Deposition

by

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Biography

Hailing from “The Valley” in northern West Virginia, where he was born and breed, Kevin Ball left for the wilds of western New York and Alfred University where he received his bachelor of science degree in Ceramic Engineering in the twelfth month in the year of our Lord 2003. Kevin was the eldest of three children by Cathy and James Ball. In the fall of 2004 Kevin relocated to the tobacco road region of North Carolina to pursue an advanced degree in Materials Science and Engineering where his research was titled *Synthesis, Fabrication and Characterization of Doped and Undoped Hydroxyapatite Targets and Thin Films.*
Acknowledgments

First, the work discussed herein would not have been possible without God. I would also like to thank my family, and my wife Heather for the unending support. I am also grateful for the second chance, and opportunities provided by Dr. Cuomo. Lastly, without Dr. Guarnieri’s persistence and insightfulness, I would still be in the lab.
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1. Introduction

1.1 Background

“Dust thou art, and unto dust shalt thou return”, were the words God spoke to Adam in the book of Genesis as he and Eve were being expelled from the Garden of Eden. From a scientific standpoint, these words could not have been spoken more accurately. Biologists have known for sometime that human bone, enamel and dentin (the substance between the enamel and tooth pulp) is composed of apatitic calcium phosphates minerals similar to those that are also found abundantly throughout the soils across the earth.

The complexity of the human body is epitomized when its structural components, specifically bone and teeth, are scrutinized. For example, the carbon dioxide content of dentin and bone are similar but significantly higher than that of enamel. At the same time, the magnesium content of bone is half that of dentin, yet significantly greater than that found in enamel. Finally, the calcium to phosphorous molar ratios in enamel is much lower than the stoichiometric, 1.67 molar ratio found in dentin and bone. [1] Although compositionally similar, the differences that do arise have profound biological implications.

Such diversity is complicated by the fact that the apatitic calcium phosphates are extremely flexible with respect to their ability to accept an array of substitutional ions, whilst maintaining the apatite crystal structure. Early literature[2] reveals an understanding of this flexibility when different anions (F\(^-\), OH\(^-\)) and cations (Ca\(^+\)) are considered with respect to the material’s structure, and the need to maintain a level of
stability in this structure. This knowledge gave way to the foundation of fluorinated water technology as a means to reduce dental caries. With time, the body loses fluorine within the apatite structure of teeth.[3] As a result, the structure is de-stabilized and the tooth becomes susceptible to the bacteria responsible for dental caries.

In medicine, there are two types of regeneration, physiological and reparative.[4] An example of natural physiological regeneration was given in the prior paragraph. Reparative regeneration, on the other hand, is needed when the body is incapable of restoration of a damaged body part. Such cases arise because of traumas, disease and aging. In these situations, medicinal intercession is necessary to accommodate the natural responses of the body working to ameliorate the damaged area.

Relationships similar to those observed in teeth, where the body naturally compensates for fluorine deficiencies, to stabilize the tooth’s apatite structure, has helped drive the research for synthetic biocompatible materials such as hydroxyapatite, and other calcium phosphate compositions that might acts as osteogenesis (bone growth) precursors. These materials will allay with the body’s physiological reparative responses in cases where reparative regeneration is deemed necessary to prevent further damage from occurring. Furthermore, due to the ability of hydroxyapatite to acclimatize to different elements and environments, the material has recently incorporated different antibiotics to prevent inflammation and subsequent infection upon implantation.
Hydroxyapatite was initially synthesized to correct restoration problems that the body itself could not solve with its natural physiological responses. While the majority of applications utilizing hydroxyapatite relate to its compatibility with the body’s osteochemistry, other research has taken advantage of the structural and compositional information realized by Beevers and McIntyre [2]. Specifically, ‘lacunary’ apatites are used as phosphors in fluorescent light bulbs and electrolytes for fuel cells.[5] Many lead apatites have exhibited characteristic properties that would allow them to be used as photocatalysts, and as a nuclear waste management material.[1] Hydroxyapatite is also a potential candidate as a gas sensing material. Wet precipitation synthesis techniques yield particles that have a very high surface area, which allows the material to react readily with changes in its environment. Such reactions allow the material to be used as a sensor to environmental changes.

Nagai et. al. [6] took advantage of some of these properties to investigate changes in the HAp’s electrical response at different concentrations of carbon dioxide at elevated temperatures. Nagai’s work spawned the research of Mahabole et. al. [7] who studied the material’s ability to accept carbon monoxide for gas sensing purposes. Mahabole found that at Ca/P molar ratios between 1.6 and 1.7, (the same ratio important for biological applications), hydroxyapatite was able to detect minute CO concentrations at an optimum temperature of 125º C.
Other researchers [8][9] have taken advantage of the materials ability to accept different anions and cations to develop sensors and other electrical devices. Groups including Kimihiro et. al. [10] have been able to conflate the material’s science of hydroxyapatite, specifically its electrical properties, with the material’s biocompatibility. Specifically, Kimihiro demonstrated accelerated bone-like crystal growth on the surfaces of polarized hydroxyapatite. Other research conducted by Fukada et. al. [11] and published in Nature [12], demonstrates a connection between the electrical properties of hydroxyapatite and bone growth when damaged bone is subject to ultrasound. The ultrasound provides the impetus necessary to observe a piezoelectric response in the material. This response causes the hydroxyl groups to reorient such that surface charges develop and preferential growth of bone-like material occurs at these sites.

While the research described in the previous paragraphs was conducted using bulk materials, significant biomedical research is also being performed on the thin film deposition of hydroxyapatite. This research is the consequence of the materials brittle nature when in the bulk form. Due to its fragility, the material cannot be used as implants in locations where significant loads are experienced, i.e. hip, knee and shoulder implants. Coating the implant with a thin layer of hydroxyapatite helps to solve this problem by allowing the metallic implant to maintain the necessary mechanical properties while exhibiting a significant measure of biocompatibility. [13]
For many years, the preferred deposition technique for coating implants has been plasma spraying because of its ability to generate significant amounts of material in a short period. Unfortunately, this process yields non-uniform films that have poor adherence to the substrate and poor structural and compositional integrity. Even though plasma processes are utilized extensively, some disconnect remains between simply depositing a material such as hydroxyapatite and understanding the mechanisms by which the plasma is able to modify the film. [14] Difficulty in understanding the mechanisms behind plasma deposition is the direct result of the inability to independently vary particle energy and flux, gas pressure and substrate temperature. Moreover, a lack of appreciation of the mechanisms controlling deposition greatly prevents control over the properties of the deposited materials. With such control lacking, the technological applications for the processing technique are limited.

To combat the disadvantages posed by plasma spraying hydroxyapatite on implant materials, some groups are now using techniques such as magnetron sputtering and Ion Beam Assisted Deposition (IBAD). [13][15][16][17][18][19]. While these techniques are unable to yield the thicknesses and deposition rates of plasma spraying, they both provide films having excellent adhesion and uniformity. Specifically, IBAD has the ability to control many deposition parameters including beam energy, beam current, substrate temperature and system pressures. This control in turn leads the ability to tailor film microstructure and composition. Chapter 5 describes how IBAD was
implemented in this research to deposit thin films of synthesized hydroxyapatite on (100) silicon substrates.

Beginning with a need for biocompatible materials that complement the human body’s natural response to reparation of failing body parts, this introduction has elucidated many of the applications that utilize hydroxyapatite and other materials having similar structural properties. Analogous technological applications such as fuel cells, sensors and the use of electrical stimulation for the promotion of bone growth, has helped integrate what was at one point a dedicated biological material with technologies having more electrically active applications. Concurrently, the advances made by hydroxyapatite have brought with it innovative processing techniques that allow the material to diversify and integrate with emerging technologies that are helpless without those properties inherent to hydroxyapatite.

1.2 Motivation for the Present Work

The major impetus for the current work being conducted comes from a long-lived desire to help other people. The following personal event has also provided significant motivation. Approximately 7 years ago, my mother was slowly succumbing to the debilitating pains resulting from a tumor located in her shoulder. The pathological testing of the biopsy revealed that the tumor was benign, yet was located near an ensemble of tendons, ligaments, muscles and nerves. As a result, the tumor was interfering with the natural movements of her arm and causing a significant amount of pain. To ameliorate the situation, doctors decided it was best to remove the tumor. However, because the
tumor was quite large and embedded in the bone, its abstraction would leave a large gap that would have to be patched. Thus, physicians decided to fill the void with a biocompatible ceramic known as hydroxyapatite. X-ray images of the tumor and the hydroxyapatite filling can be seen in Figure 1.

![Figure 1](image_url)

**Figure 1** The left hand image shows where the tumor is located in the shoulder. The right hand image details the hydroxyapatite filling used to repair the damaged area and promote bone growth.

Upon hearing the word ‘ceramic’ my mother instinctively called me at Alfred University, where I was a freshman studying for my B.S. in ceramic engineering. Not knowing how a ceramic could make her life easier she proceeded to inquire about the implant’s benefits, and any complications that could arise. At the other end of the line was born another skeptic as to how the ceramic might help. How do you sinter a material inside the body? Why won’t the body immediately reject the material? After reading a few articles about hydroxyapatite, and its similarities to the structural properties and
composition of bone, the decision to employ it became apparent. Subsequent classes were able to clarify my doubt surrounding the material’s ability to densify without heat treatment, while maintaining a level of homeostasis within the body.

My mother’s procedure was a success, and the hydroxyapatite has maintained the desired biocompatibility in conjunction with superior mechanical properties in lieu of the tumor. From this event, hydroxyapatite and similar biocompatible materials have persisted to mediate themselves into my life. The most significant intercession came with the opportunity to research hydroxyapatite at North Carolina State University. With this opportunity came the chance to help, and make a difference in the lives of others and begin fulfillment of a long time dream.

1.3 Present Work

The work described herein was totally supported by the Institute of Maintenance Science and Technology (IMST) at NCSU. Prior to this work, Dr. Rabiei of the Mechanical Engineering Department utilized the IBAD system in IMST facility for hydroxyapatite thin film deposition on titanium substrates. The funding for this work was provided by the National Science Foundation.[20] The deposition technique and subsequent film properties, specifically crystallinity and mechanical strength were investigated and modified for better osseointegration such that implants become viable to extended periods of time. Other work examines the antimicrobial benefits that arise when the hydroxyapatite is doped with varying concentrations of silver and/or gold.
The earlier work performed for Dr. Rabiei work utilized one six-inch hydroxyapatite target purchased for approximately $1000.00 from CERAC™ incorporated. At such an outstanding cost, the consumer is limited to using only deposition technique, and its encompassing facilities, as a means for modifying the properties of the deposited film. Thus, the decision was made investigate affordable fabrication techniques of hydroxyapatite target. In doing so, wet precipitation was discovered as an inexpensive and simple means for developing targets, which exhibit the same composition as those purchased from CERAC™. These targets were developed at 90% of the cost one would pay for the CERAC™ target.

Moreover, the ease in fabrication, in conjunction with the compliant structure of hydroxyapatite, allows significant compositional modifications to be made. The ability to modify the material’s composition and structure has provided the crux of this research. Significant structural and bonding studies were performed on three types of hydroxyapatite. These include stoichiometric Hydroxyapatite (HA), Calcium Deficient Hydroxyapatite (CDHA) and Barium stabilized Calcium Deficient Hydroxyapatite (Ba-CDHA). CDHA was synthesized for two purposes; the first was to investigate the structural changes that take place upon removal of calcium from the composition, and to study the stabilization of the structure using different cations having the same valency as the deficient calcium. [21] [22] The capability of compositional modification provides another dimension of flexibility that can be implemented to tailor either the bulk material properties or subsequent thin films properties.
Targets of stoichiometric hydroxyapatite were also fabricated and used in conjunction with the dual ion beam processing technique to deposit films on (100) silicon wafers. The structure and composition of the deposited films in this study were analyzed and compared to those of the bulk target material to gain a better understand of the deposition process. From these findings, adjustments to the process parameters were made to develop an experimental window to be used as a guideline for the deposition of films that emulate their parent target’s composition and structure. Post deposition thin film processing was also investigated to help develop the film crystallinity and enhance the overall structure of the material.

The ability to easily synthesize and modify target compositions that can be used in tandem with ion beam assisted deposition, establishes an all-encompassing process for developing inexpensive thin films. Furthermore, IBAD provides many parameters that can be manipulated to tailor the composition and structure of thin properties for specific applications. Thus, new applications and improvements upon existing ones can occur without having to incur significant monetary losses.
2. Hydroxyapatite Composition, Structure and Properties

This chapter will consider the basic apatite structure germane to hydroxyapatite and other synthetic apatites. A general understanding of the atomic constituents of hydroxyapatite will provide a staging area from which the bonding and subsequent structure can be understood. With this information, compositional alterations will be considered to help realize the resultant structural affects observed within other apatite structures and the studies of this thesis. Table I [22] below provides a detailed catalog of the related calcium-phosphate apatites. An understanding of the structural affects incurred by compositional changes can assist the researcher tailor the apatites for different applications. Lastly, the non-calcium phosphate based apatites will be considered and compared to the calcium phosphate apatites.

2.1 Apatitic Atomic Constituencies

The word apatite is derived from the Greek word for deceit, απατω, because naturally occurring apatites are often confused with other minerals such as crystalite, amethyst, fluorite and schorl. Such deceit becomes apparent when considering the multitude of atomic constituents that the apatite structure is able to accommodate. This section illustrates this deceit through various examples. A full appreciation of these accommodations will be achieved in section 2.2 wherein the structure of the material is
emphasized and in 2.3 where the atomic constituents and structure are integrated to reinforce the material’s legitimacy for certain applications.

Calcium phosphate (Ca-P) apatites, such as those outline in Table I [1] are derived from the basic chemical formula, Ca_{10}(PO_4)_xX_2. This formula represents a nonspecific stoichiometric Ca-P apatite, whose Ca/P molar ratio is 1.67. The nomenclature used to further define the type of Ca-P apatite is indicated by the X component of the chemical formula. It is from this X component that hydroxyapatite (X=OH), fluorapatite (X=F) and chloroapatite (X=Cl) acquire their names. Again, Table I [1] below helps identify and describe some of the different Ca-P apatites.

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Explanation</th>
</tr>
</thead>
<tbody>
<tr>
<td>OHAp</td>
<td>Hydroxyapatite, Ca_{10}(PO_4)_4(OH)_2</td>
</tr>
<tr>
<td>s-OHAp*</td>
<td>Stoichiometric OHAp. Used when emphasis is required that the compounds has a chemical composition corresponding to the ideal, Ca_{10}(PO_4)_4(OH)_2</td>
</tr>
<tr>
<td>ns-OHAP</td>
<td>Non-stoichiometric hydroxyapatite (CO_3-free). Indicates that the chemical analysis shows (or would show) a departure from that of s-OHAp. This may involve lattice H_2O, HPO_4^{2-}, Ca^{2+} ions and/or 2OH^- replaced by O_2^-</td>
</tr>
<tr>
<td>Ca-Def OHAp*</td>
<td>A precipitated apatitic calcium phosphate (CO_3-free) with a Ca/P molar ratio in the range 1.66 to 1.5 or less. Compounds that might contain interlayers of OCP are included</td>
</tr>
<tr>
<td>CaCl_2-def ClAp</td>
<td>An apatite that departs from the ideal for ClAp, Ca_{10}(PO_4)_4Cl_2, in its calcium and chlorine contents in the molar ratio 1:2. Likewise for FAp</td>
</tr>
<tr>
<td>BCaP</td>
<td>Precipitated basic apatitic calcium phosphate with an uncertain composition which may include CO_3^{2-}, or HCO_3^- ions</td>
</tr>
<tr>
<td>A-CO_3Ap</td>
<td>A-type carbonate apatite, ideally Ca_{10}(PO_4)_4CO_3.</td>
</tr>
<tr>
<td>B-CO_3Ap</td>
<td>B-type carbonate apatite, i.e. a carbonate-containing apatite in which PO_4^{3-} ions are replaced by CO_3^{2-} ions</td>
</tr>
<tr>
<td>AB-CO_3Ap*</td>
<td>Carbonate-containing apatite in which both the above substitutions take place.</td>
</tr>
<tr>
<td>CO_3Ap</td>
<td>Any carbonate-containing apatite</td>
</tr>
</tbody>
</table>

* denotes compositions investigated in this study
The stoichiometry of the chemical formula, $\text{Ca}_{10}(\text{PO}_4)_6X_2$, noted in the previous paragraph is important when considering the ability of the apatite structure to accept other atomic elements. Compromising the stoichiometry presents an opportunity for promoting a greater appreciation of the structural complexity of the apatite family. At the same time, these substitutions ultimately provide a better understanding of the materials structure, which is discussed in section 2.2.

Many groups have taken advantage of Calcium Deficient (non-stoichiometric) Hydroxyapatite Apatites (CDHA) to investigate the effects of incorporating zinc, barium, magnesium, and strontium into the material. [23]. Their subsequent findings demonstrate that elemental doping of the structure is highly dependent upon the synthesis technique. Different techniques allow for varying concentrations of the same element to be incorporated into the structure. For example, T. Narasaraju et. al.[24] utilized a hydrothermal technique to substitute the calcium atoms for barium atoms up to $\frac{\text{Ba}}{\text{Ba} + \text{Ca}} = 1$. On the other hand, Bigi et. al. [25] employed a precipitation technique that allowed for only 0-25 atom % barium incorporation. Above this percentage, amorphous precipitates and tri-barium phosphate were obtained. The same group, in the same paper [25] also showed that solid state reactions between $\text{Ca}_5(\text{OH})(\text{PO}_4)_3$ and $\text{Ba}_5(\text{OH})(\text{PO}_4)_3$ at 1200 C, would only form solid solutions of barium-calcium hydroxyapatite when the atomic % of barium was between 60-100%.

Stoichiometry can also be maintained through substitutions with the phosphate groups in the material. For example, when the material becomes phosphate deficient, the
structure is able to take-up carbon dioxide. This behavior is often exhibited by bone. At the same time, other anionic groups such as $\text{AsO}_4^{3-}$, $\text{NO}_3^-$, $\text{NO}_2^-$, and $\text{VO}_4^{3-}$ may find residence in the structure depending upon the materials environment. Again, processing techniques can also be used to determine what groups can be substituted, and in what amounts. Section 2.2 will delineate the compositional and structural changes observed when the phosphates are both partially and fully substituted with other anionic components.

### 2.2 The Hydroxypatite Structure

#### 2.2.1 Introduction

Having identified the atomic constituents of hydroxyapatite, the blueprints must now be established to determine the location of the individual atoms. The high degree of substitutional tolerance suggested by simply studying the chemical formula, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, is fully appreciated when a full appreciation of the structure is attained. Understanding the arrangements of the atomic species will allow for the evolution of the material such that the structure will provide an outline from which the properties of the material can be tailored. The ability to tailor the material to exhibit certain properties presents an opportunity to establish new applications including carbon monoxide, phosphor and tissue growth sensors [7] [26] [27], fuel cells [28], and implants that help promote bone growth via the piezoelectric response of hydroxyapatite [29]. The synopsis detailing the relationship between structure and application is discussed in section 2.3
To understand the structure of hydroxyapatite, the fundamental fluoroapatite structure, $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$, is initially considered. This material provides a simple description of the numerous apatitic compositions[1]. From this knowledge, hydroxyl substitutions will then be considered to help reveal how they define the hydroxyapatite structure. Lastly, ionic substitutions are considered to understand how they affect the apatite structure. In later chapters the information concerning the bulk structure of hydroxyapatite will be utilized to understand the thin film structures created through ion beam assisted deposition.

2.2.2 Fluorapatite as a Model for other Apatites

Published in 1930 were the individual works of Naray-Szabo [30] and Mehmel [31] who first reported on the basic structure of fluoroapatite. Both researchers revealed the structure of the material to be hexagonal with a space group of $\text{P}6_3/m$. This is shown with its symmetry elements in Figure 2 [1]. Two crystallographically different calcium atoms (Ca$_1$ and Ca$_2$) and three different oxygen atoms (O$_1$, O$_2$ and O$_3$) were identified. This structure was modeled by Beevers et. al. using balls and sticks, and is illustrated in Figure 3 [32] below.
Figure 2 Vertical symmetry elements of the space group P63/m. The dashed lines indicate the apatite unit cells with the c-axis out of the plane of the diagram. There are also horizontal mirror planes at z=1/4 and ¾ and numerous centers of symmetry. (After Fig. 1 of Beevers and McIntyre [32])

Figure 3 (a) Oxygen coordination of columnar Ca(1) ions in apatite. (b) linking of columns via PO4 tetrahedra. The oxygen atoms in (a) and in one tetrahedron in (b) have been numbered, and positions of the horizontal mirror planes at 1/4, 3/4 etc. marked on the c-axis. Fig. 2.2 of Elliott [1] after Fig. 3 of Beevers and McIntyre [32].
The ominous structure depicted in Figure 3 can be simplified by thinking of the phosphate ionic tetrahedra, \( \text{PO}_4^{3-} \), as hexagonally packed spheres of the ABABAB sequence. When this ordering is vertically stacked, the first and third, second and fourth sheets lie directly on top of one another. From this stacking two different sized holes/interstitial locations are formed. The first and largest interstitials are referred to as “octahedral holes” due to their six-fold coordination with the corners of the surrounding octahedral spheres. The octahedral holes reside midway between the two sheets and have dimensions that can accommodate smaller six-fold coordinated spheres/ions having radii that fulfill the equation: \( 0.41 \cdot r = 1.1 \text{ Angstroms} \) (Ca\(^{2+}\) radius 1.06 Angstroms and F\(^-\) radius 1.33 Angstroms). The smaller holes can only accommodate spheres/ions having radii that fulfill the equation: \( 0.225 \cdot r = 0.58 \text{ Angstroms} \). This dimension is too small to allow for most ions; therefore, it will not be taken into consideration.

To better understand the comparison made between the hexagonal unit cell described above and the apatite unit cell, Figure 4 [1] provides a detailed illustration of the two situations. In Figure 4A the view is directly down the c-axis of the structure. The solid lines, plus the red lines form a hexagonally packed sheet of A atoms that lie directly on top of one another at \( z = 0 \) and \( z = 1 \). At the same time, the dashed lines denote a sheet of hexagonally packed B atoms sandwiched between the A atoms, at \( z = \frac{1}{2} \). This sequencing results in interstices/octahedral holes (X) and a mirror plane at \( z = 1/4 \) and \( 3/4 \). This description is summarized by the red unit cell shown in Figures 4A and 4B, wherein there are two spheres and two octahedral holes.
While the HCP unit cell described above contains 2 spheres and 2 octahedral holes, the apatite unit cell has 6 spheres, (PO$_4^{3-}$), and six octahedral six holes. Thus, to fully define the apatite unit cell, 3 HCP unit cells are needed. Figure 4B shows the union of the three HCP units to generate the apatite unit outlined in black. The octahedral holes, circled in blue, are occupied by the X ions from the chemical formula Ca$_{10}$(PO$_4$)$_6$X$_2$. The remaining octahedral sites, outlined in green, are occupied by calcium ions (Ca$_1$) that appear every one half step along the c-axis. These Ca$_1$ ions form columns that extend along the c-axis. These are known as Ca$_1$ columns.

Above and below the Ca$_1$ ions are three oxygen atoms that link successive Ca$_1$ ions, as seen in Figure 3a. Those oxygen atoms above and below the Ca$_1$ ions are labeled O$_1$ and O$_2$, respectively. Surrounding the Ca$_1$ ions are three more O$_3$ ions at approximately the same z-parameter as the Ca$_1$. These O3 atoms increase the

Figure 4 Represented in A is the unit cell of HCP spheres and the resultant interstices that arise upon stacking of ABABAB planes of atoms. The apatite cell represented in Figure B is modeled using three HCP unit cells.
coordination number of Ca$_1$ to oxygen atoms to 9. The Ca$_1$ columns are linked to neighboring Ca$_1$ columns through phosphate tetrahedra (PO$_4$). The red oval in Figure 3b highlights one of the phosphate groups linking the Ca$_1$ columns. Two O$_3$ atoms and one O$_1$ or O$_2$ are connected through a phosphate group that is linked to a second column of Ca$_1$ ions though either the O$_2$ or O$_1$, respectively.

Thus far, only four of the ten calcium atoms (Ca$_1$ columns) constituting the chemical formula, Ca$_{10}$(PO$_4$)$_6$X$_2$, have been considered. The remaining six calcium atoms, known as Ca$_2$, are located within the caves formed by the aforementioned O$_3$ atoms of the phosphate groups that link Ca$_1$ columns. The axes of the Ca$_2$ channels coincide with the corners of the unit cell depicted in Figure 4B. Two groups of three Ca$_2$ ion triangles, rotated by 60 degree from one another, are stacked and centered on the mirror planes at z=1/4 and 3/4, as seen in Figure 5.[1] Lying on the mirror planes and centered within the Ca$_2$ triangles are the fluorine ions. Additionally, the presence of Ca$_1$ and fluorine expands the structure within the close packed sheets. This is expected as these ions are coordinated by PO$_4$ ions in the c-axis direction; thereby expanding the structure in the a-axis direction. The Ca$_2$ ions located in plane with the PO$_4$ ions will also expand the structure in the a-axis. [22][32].
To summarize the apatite structure, Beevers and McIntyre [2] identified three critically important structural elements. The first element considers the tunnels structure of the material, whose walls are composed of corner connected, (Ca$_1$), CaO$_6$ and PO$_4$ polyhedra. The second element states that by filling the tunnels with Ca and other anions such as F$^-$ will significantly change the bond length of the structure. Finally, their work revealed that the slightest changes in the ionic radii of the tunnel atoms would lead to an
expansion or contractions of the tunnel. Thus, a critical fit for the X ion emerges and dictates the stability of the apatite formed. Again, this relates back to the example that explains why water is fluorinated. The walled structure first proposed by Beevers and McIntyre and later modified is seen in Figure 6 A and B, respectively.

**Figure 6** A. Taken from Beevers et. al. [2] this figure shows the first drawing of the apatite structure as suggested by Beevers and McIntyre. B. Projection of the fluorapatite structure as proposed by Beevers and McIntyre.
2.2.3 The Structure of Hydroxyapatite

While fluorapatite provides a great working model for many other apatite compositions, it should not be accepted as all-inclusive. Considering the three critical elements identified by Beevers and McIntyre, modifications to an apatite’s composition can significantly affect its structure such that the properties of the material are also changed. To confirm the latter statement, the next few sections will investigate compositional changes made to the X ion in the chemical formula Ca$_{10}$(PO$_4$)$_6$X$_2$. Specifically, the two fluorine ions in fluorapatite will be substituted with two hydroxyl groups to create hydroxyapatite.

When considering the structural changes that occur when the fluorine ions are substituted with hydroxyl ions, the critical elements proposed by Beevers and McIntyre help develop predictions concerning the resultant structure. Of the three critical elements proposed by Beevers and McIntyre, the most significant are the two that directly relate the overall structure of the material to a dependence on the tunnel structure and its composition.

Recalling the fluorapatite structure, the fluorine ions are located within channels formed by the union of the Ca$_1$ ions through the oxygen atoms of neighboring phosphate tetrahedra. More specifically, they are located within the Ca$_2$ triangles on the mirror planes at $z = 1/4$ and $3/4$. These are the mirror planes indicated by the P6$_3$/m space group. Compared to chloroapatite (which exhibits the same low temperature monoclinic phase as hydroxyapatite) and hydroxyapatite the fluorine ion of fluorapatite is significantly smaller than both the chlorine and hydroxyl ion. Thus, when fluorine ions are substituted...
for larger hydroxyl ions, the tunnel structure of hydroxyapatite is modified to retain the apatite structure. However, the mirror plane that defines fluorapatite is removed to accommodate the larger hydroxyl ions located at 0.3 Angstroms above the mirror plane at $z = ¼$. [22] [33]. Thus, the space group of hydroxyapatite becomes decreases from $P6_3/m$ to $P6_3$. Some diffraction results reveal the presence of a mirror plane, but depends upon the ordering of hydroxyl groups within the columns.

The ordering of the hydroxyl ions also plays a significant role in defining the ultimate phase assumed by hydroxyapatite. Specifically, hydroxyapatite can assume either the hexagonal, $P6_3/m$ or $P6_3$, or the monoclinic phase, $P2_1/b$. For hexagonal mineral hydroxyapatite, a disordered hydroxyl column model was introduced. Inherent to this model are impurity fluorine ions that act as reversal points for the hydroxyl ions in the tunnels (e.g. $\text{OHOHOHOH F HOHOHOHO}$). Such reversal points exist to prevent head-to-head configurations of $\text{OH HO}$. An ordered model for hexagonal hydroxyapatite also exists where ordering may exist in one tunnel, but is independent of the orientation in neighboring tunnels.[1]

Moreover, in high purity monoclinic hydroxyapatite, whole columns of hydroxyl groups are ordered in the same direction along the c and a-axes. Concurrently, this ordering occurs such that all the hydroxyl groups have the same displacement from $z = ¼$ along the c-axis. Figure 7 helps illustrate the hydroxyl ordering within monoclinic hydroxyapatite. In one column, all hydroxyl groups are pointing in the same direction. The adjacent columns exhibit an anti-parallel behavior, wherein the hydroxyls are
pointing in the opposite direction of the former column. Thus, the mirror plane observed in the \( P6_3/m \) space groups now becomes a glide plane in the \( P2_1/b \) space group. More importantly, the consistent alternating behavior of monoclinic hydroxyapatite separates it from the disorder inherent to hexagonal hydroxyapatite.

![Figure 7](image)

**Figure 7** For synthetic hydroxyapatite, the hydroxyl groups are ordered along the c-axis. Within a plane parallel to the c and a axes, all of the hydroxyl groups are pointed in the same direction.

### 2.2.4 Calcium Deficient Hydroxyapatite

While the majority of the previous structural discussion has focused on the effects that the hydroxyl group have on the apatite structure, there remains the need to explain the changes observed when the calcium ions are removed and or substituted for different ions. To help with this explanation, Table II has been constructed from Table 1.4 of J.C. Elliott’s book [1]. This modified table outlines some of the structural changes that occur in different apatite materials when different anions or cations are introduced. It should be noted that in this table the strontium, barium and lead apatites of Table II contain no
calcium. These apatites were included to help demonstrate the extreme effects of cation substitution. Comparisons with literature, wherein fractional substitutions take place, will ultimately show how the calcium ions of hydroxyapatite are manipulated to accommodate for vacancies or substitutions will different ions.

Table 2  Lattice parameters, refractive indices (sodium light) and densities calculated from lattice parameters for various apatites.[1]

<table>
<thead>
<tr>
<th>Apatite</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>E</th>
<th>O</th>
<th>Density g·cm⁻³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydroxyapatite</td>
<td>9.4176</td>
<td>6.8814</td>
<td>1.644</td>
<td>1.650</td>
<td>3.156</td>
</tr>
<tr>
<td>Fluorapatite</td>
<td>9.367(1)</td>
<td>6.884(1)</td>
<td>1.629</td>
<td>1.633</td>
<td>3.202</td>
</tr>
<tr>
<td>Chlorapatite</td>
<td>9.628(5)</td>
<td>6.764(5)</td>
<td>1.670±0.001°</td>
<td>1.670±0.001°</td>
<td>3.185</td>
</tr>
<tr>
<td>Strontium HAp</td>
<td>9.760±0.003°</td>
<td>7.284±0.003°</td>
<td>-</td>
<td>-</td>
<td>4.090</td>
</tr>
<tr>
<td>Barium HAp</td>
<td>10.177</td>
<td>7.731</td>
<td>-</td>
<td>-</td>
<td>4.735</td>
</tr>
<tr>
<td>Lead HAp</td>
<td>9.879</td>
<td>7.434</td>
<td>-</td>
<td>-</td>
<td>7.072</td>
</tr>
</tbody>
</table>

To understand the importance and effects that the calcium ion has on the apatite structure, Calcium Deficient Hydroxyapatite (CDHA-Ca⁹(HPO₄)(PO₄)₅(OH)) will be considered first. The work performed by Gibson et. al. [34] and Yubao et. al. [35] show striking similarities in that upon precipitation of the CDHA powders, the X-ray diffraction patterns are indistinguishable from that of hydroxyapatite. This should come as no surprise due to the fact that the apatite structure is retained in non-stoichiometric/CDHA having Ca/P ratios between 1.33 and 1.67.[37] In contrast, upon subsequent heat treatments at temperatures exceeding 650 C, both Gibson and Yubao
both report the development Tricalcium Phosphate (TCP). The quantity of TCP formed depends upon the initial Ca/P ratio. Gibson precipitated non-stoichiometric HA with a Ca/P ratio of 1.50, the same Ca/P ratio as TCP. On the other hand, Yubao worked with Ca/P ratios around 1.52 to attain a biphasic composition of HAp and TCP.

Based upon these two studies, there exist specific Ca/P ratios that yield either TCP or a biphasic composition of HA and TCP. Furthermore, depending upon the heat treatment used two phases of TCP can exist. One phase is the low temperature beta phase that is stable up to 1125 C. The second is an alpha phase that is stable between 1125 and 1430 C. Respectively, the space groups of each are rhombohedral (R3c) and monoclinic P2\textsubscript{1}/a.

To justify the presence of a biphasic composition, Yubao needed to discriminate between the two different Ca/P ratios. He explained that by having an initial Ca/P ratio of 1.52, the HA phase would remain non-stoichiometric, with a Ca/P ratio between 1.67 and 1.52. This would compensate for the lower Ca/P ratio of 1.50 exhibited by TCP. In other words, regardless of the phases developed upon heat treatment, the overall Ca/P ratio must remain 1.52. The HA phase compensates for the lower Ca/P of TCP by having a Ca/P ratio grater than 1.52 such that the overall Ca/P ratio is 1.52. As the Ca/P decreases the probability of developing only TCP increases.

Although it is difficult to draw direct conclusions about the exact location of calcium ions in CDHA, there do exist many consistencies in the research reviewed by Elliott. Typically, all experimenters reported expansions of the a-axis parameter due to
the expulsion of lattice water and \( \text{HPO}_4^{2-} \) ions that form TCP upon heat treatment. Concurrently, slight contractions in the c-axis parameter were also observed. Infrared data gathered by Young et. al. [36] suggests that the observed axial displacements result from the formation of vacancy clusters of \( \text{OH}_\text{v}, \text{Ca}(2) \text{v} \) and \( \text{HPO}_4 \text{v} \), where \( \text{v} \) represents a vacancy of the indicated site, when the phosphate groups are removed from the structure.

The works referenced by Elliott [1] offer a multitude of explanations to describe the behaviors observed when a few calcium atoms are removed from the stoichiometric hydroxyapatite composition. Unfortunately, different processing techniques and variables such as pH, temperature, aging and heat treatment remain inconsistent from one experimenter to the next. This has led to an unsatisfactory description of the CDHA structure. Subsequently, accurate predictions concerning the stabilization of the CDHA structure, which is discussed in the next section, will be difficult to develop. While the structural details remain sparse, suggestions can be made utilizing the aforementioned vacancy generalizations presented by the majority of the researchers. This, in combination with an understanding of the chemistries inherent to certain elements, may lead to a better structural understanding of the stabilized version of CDHA.

### 2.2.5 Stabilized Calcium Deficient Hydroxyapatite

While the former investigations fall short in thoroughly defining the specific calcium atom of CDHA, Ca(1) or Ca(2), responsible for the structural changes observed
in when the material is heat treated, doping studies may provide important information regarding the role of the calcium site when stabilized with another atom of equivalent valency. In other words, non-calcium (X) cations incorporated into calcium deficient compositions will preferentially distribute themselves on the deficient sites to maintain a level of stability in the apatite structure. Subsequent analytical techniques allow a structural comparison to be made between the calcium deficient and X stabilized apatite structures. Inferences concerning the specific location of the X ion with respect to changes in structure can then be proposed. Most importantly, an understanding of the structural dynamics that occur in stabilization of the system provides a means for tailoring the material to yield properties for specific applications.

To help understand the structural dynamics that take place upon stabilization, apatites whose calcium atoms have been stoichiometrically substituted with other atoms will initially be considered (i.e. \( \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 \rightarrow X_{10}(\text{PO}_4)_6(\text{OH})_2 \)). This knowledge will then be applied to those apatite systems that incorporate a small percentage of substitutional cations with the intrinsic calcium atoms. For brevity and simplicity, both cases will consider only those cations having the same valance as the calcium cation, +2.

Considering Table II, a significant difference exists between the lattice parameters of hydroxyapatite and those of pure barium, lead and strontium apatite, whose cations also have a +2 charge. The axial displacements that occur are a linear function of the size of the substitutional cation radii. Figure 8 confirms this statement in a plot of the lattice parameters of the four apatites as a function of their corresponding cation radii. Thus, as
long as the apatites remain homogenous with respect to the cations that define them, the only structural effect observed will be in increase in all lattice parameters.

A more complex situation arises when the apatite structure incorporates a fraction of dopant ions, X, in conjunction with the intrinsic calcium cations of a calcium-based apatite. The site preferred by the dopant ion, either Ca(1) or Ca(2), is highly dependent on the surrounding environment. Concurrently, preparation techniques can incorporate impurity ions that can alter the overall structure of the material. Differences between the valences of the host and dopant atom also influence the location and distributions of the dopant material. For simplicity, the latter conditions will not be considered as this
dissertation is only concerned with equivalent charge substitutions. Thus, many factors dictate the manner by which the stabilization process transpires.

To understand the structural role of non-calcium atoms mixed with calcium atoms, Khudolozhkin [39] prepared solid solutions of Ca-Sr hydroxyapatite over the entire range of strontium content, 0-100%. These compositions were based upon the following exchange reaction: 

$$6 \text{Ca}(2) + 4 \text{Sr}(1) \leftrightarrow 4 \text{Ca}(1) + 6\text{Sr}(2).$$

Subsequent x-ray diffraction studies revealed a preferential distribution (ordering) of the strontium ions throughout the Ca(2) sites of the apatite structure. The diffraction results also revealed an increase in the a and c-axis lattice parameters upon substitution. This is not surprising as the strontium ion is larger than the calcium ion. Moreover, as the mol % Sr increased, a linear decrease in the order of Sr at Ca(2) sites occurred.

A second study by Kholozhkin [40] further explored the structural effects of compositional modifications by comparing the XRD patterns of Ca-Ba and Ba-Sr fluorapatites (note: this work revealed no structural difference when the fluorine ion was replace with a hydroxyl ion). Again, in both cases, an increase in the a and c-axis lattice parameters was observed. At elevated temperatures the Ca-Ba compositions exhibited an immiscibility gap between 6 and 64 mol% Ba while no gap was observed over 20 mol% intervals in the Sr-Ba systems. In contrast to Kholozhkin’s Ca-Sr apatite experiment, this research revealed an increasing preference of barium for the Ca(2) sites as the mol% barium increased. This preference was more discernible than the Sr ions preference for the Ca(2) sites in Sr-Ba apatites. Concurrently, the preference of Ba for Ca(2) sites in the
Sr-Ba systems was greater than that of Sr in the Ca-Sr system, but less than that of Ba in the Ca-Ba apatites.

These observations suggest that a predetermined size constraint intrinsic to the apatite structure determines the degree of ordering of the X cations in the Ca(2) sites. In other words, the degree of preference for the Ca(2) site by the larger cation, in the apatite being considered, is greatest when the difference between the two cationic radii is the greatest. (i.e. Ca\(^{2+}\) - Sr\(^{2+}\) = 0.16 < Sr\(^{2+}\) - Ba\(^{2+}\) = 0.20 < Ca\(^{2+}\) - Ba\(^{2+}\) = 0.36 Angstroms)[40]. The following discussion will reveal that this relationship alone cannot be used to explain the observed events. Rather, size constraints and bonding environments must be mutually considered.

To a lesser degree, the aforementioned immiscibility gap in the Ca-Ba system was also observed by Bigi et. al.[25]. Upon heat-treatment of the Ca-Ba apatite mechanical mixtures at 1200° C, solid solutions could only be attained between 60-100% barium incorporation. Conversely, when a co-precipitation technique was implemented at lower temperatures (100C), solid solutions of Ca-Ba formed in the range of 0-25% Ba. Between 25-60% barium content, an immiscibility gap was observed wherein hydroxyapatite, beta-tricalcium phosphate, and barium-substituted tricalcium phosphate were formed. Elliott[1] explains that in systems having a minimum barium content of 60%, the calcium ions will be forced to the Ca(1) sites while the barium atoms will assume the Ca(2) sites that constitute 60% of the total calcium positions.
in hydroxyapatite. Again, the larger barium atom resulted in an increase of the a-axis and c-axis.

What is more, Kholozhkin [40] was able to eliminate the observed immiscibility gap within the Ca-Ba systems by synthesizing the following ternary apatite Ca-Sr-Ba (Ca$_{x_1}$Sr$_{x_2}$Ba$_{x_3}$)$_{10}$(PO$_4$)$_6$F$_2$, where ($x_1+x_2+x_3=1$). These compositions were formed in the Ba-rich region at 1100°C with the following strontium additions: $x_2 = 0.5, 1.0, 1.5$ and 2.0. The incorporation of greater than 15 mol% Sr, whose size is intermediate to Ca and Ba, eliminated the immiscibility gap intrinsic to the Ca-Ba binary apatite. The hatched region in Figure 9 [1] represents the immiscibility gap for the Ca-Ba-Sr ternary system.

**Figure 9** Ternary phase diagram for the Ca-Sr-Ba apatites. The hatched region represents the immiscibility gap in the Ca-Ba system. The dots and circles represent one and two-phase apatites, respectively. Connecting lines are apatites that exhibit the same degree of ordering.
Based on structural considerations, the occupation of Ca(2) sites by larger cations should not occur. Rather, these cations should occupy the Ca(1) sites that have larger coordination numbers and thus more space for the larger cations. To help explain this event, the nature of the bonds present in the structure must also be taken into consideration.[39] Recalling the detailed description of the basic apatite structure, the phosphate groups act as interconnects between the two calcium sites. Surrounding the Ca(1) and Ca(2) sites are 6 and 4 phosphate groups, respectively. These phosphate groups possess positively charged P-O bond ionicities, $P^{5+}$, that have a greater repulsion at the Ca(1) sites because they are surrounded by more phosphate groups than the Ca(2) sites. Therefore, those atoms such as Sr and Ba, whose electronegativities are less than calcium, will be more inclined to develop covalent bonds with the less positive Ca(2) position. In turn, these energetic relationships are responsible for relegating the immiscibility gap that develops in Ca-Ba apatites.

In works referenced by Elliott [1][41][42], the formation of covalent bonds with the surrounding phosphate groups has also been observed in Ca-Pb fluorapatite systems. Just as in the Ca-Ba and Ca-Sr apatites, the lead cation also exhibits a propensity to assume the more negative Ca(2) positions and develop covalent bonds with the surrounding oxygen atoms. In comparison to the Ca(2)-O bonds of calcium fluorapatite, the Pb(2)-O bonds of Ca-Pb are significantly shorter. This shortening in turn leads to a deviation from Vegard’s law at 60 atom% Pb. Such deviations are realized by variations in the c-axis parameter at this percentage of lead. This system is also interesting in that
lead has a greater electronegativity than the barium and strontium ions that occupy the same Ca(2) sites. One explanation for lead’s occupation of the Ca(2) sites lies in its unusual lone pair electron configuration[41], which permits the formation of covalent bonds in the Ca(2) sites. In the solid state this results in the distorted metal coordination observed in PbO and SnO.

The incorporation of smaller ions such as magnesium (Mg$^{2+}$) and iron (Fe$^{2+}$) behave quite differently. In accordance with Vegard’s law, the substitution of calcium ions with smaller ions resulted in a lowering of the a-axis and c-axis lattice parameters. Unlike the behavior observed in the Ca-Sr and Ca-Ba apatite systems, wherein the substituting atoms are larger, these smaller atoms have a predisposition for the Ca(1) sites rather than the Ca(2) sites. From an electronegativity standpoint, both magnesium and iron ions exhibit a greater electronegativity than calcium.[43] Subsequently, these ions will prefer the Ca(1) sites wherein covalent bonding is likely to occur. This is in juxtaposition to the less electronegative strontium ions that prefer the more negative Ca(2) positions.

As it turns out, describing the apatite’s structural response to compositional manipulations can be quite cumbersome. Although some behavioral consistencies emerge when one type of substitution is considered, a similar substitution may provide a completely different result. Thus, there are no definitive theories that can be used to predict the structural behavior of a doped apatite structure. For example, although the electronegativity school of thought works well in describing the anomalous behavior
evidenced by strontium and barium’s occupation of the smaller Ca(2) sites (or how Mg$^{2+}$ and Fe$^{2+}$ occupy of the more spacious Ca(1) sites), it fails to justify the same effect exhibited by lead, whose electronegativity causes a breakdown in this theory. Different arguments have also been postulated to explain the decrease in order of Sr as the Sr content increases. These same arguments are unable to explain why Mn, a much smaller ion, exists in both the Ca(2) and Ca(1) positions.[39] At the same time, the presence of the immiscibility gap can not be explained using size of electronegativity arguments.

While the counterintuitive events cannot be explained with specific rules, the dimensional consistencies that have emerged allow for the formation of some generalizations. For example, the hydroxyapatite and fluorapatite structures permit substitutions of ions that are smaller and larger than the intrinsic calcium ions. In accordance with the aforementioned substitutions, Vegard’s law was continuously obeyed. With respect to the substitutional dynamics, the smaller ions have a tendency to occupy the Ca(1) sites while the larger ions congregate at the Ca(2) sites. Unfortunately, the manganese ions complicate matters as they have shown proclivity for both sites. Finally, upon substitutions, the alkaline earth’s exhibited the greatest structural consistencies from the standpoint of ionic size differences. Evidence of these generalizations will arise again in the following applications section.
2.3 Hydroxyapatite Applications

Although the aforementioned generalizations are not applicable in every substitutional event, they do provide a basis from which structural and property predictions can be made when compositional changes occur. For example, these events provide a foundation for a better understanding of the physiological phenomena intrinsic to bone. This has already been exemplified in bone’s natural ability to reconstitute fluorine into the apatite structure when deficiencies arise. Similar behavior is observed when bone incorporates lead into its structure. Understanding such situations can help in the development of lead poisoning treatments. Furthermore, elements such as silver and gold are used in medicine as antimicrobial coatings on the instruments to prevent the occurrence of osteomyelitis and other infections incurred from unsanitary conditions. Using this knowledge, Oh et. al.\textsuperscript{[44]} incorporated silver into the hydroxyapatite structure to develop a sterile environment for osteogenesis to occur. Lastly, the latter structural discussions on calcium deficiencies should reinforce the statement, “Milk, it does the body good.”

The knowledge ascertained in studying the structure of hydroxyapatite has also yielded innovative applications beyond the realm of electrical passivity. Electrically active hydroxyapatite is the direct result of hydroxyl dipole orientations within the tunnels formed by the Ca(2) triangles discussed above. Depending upon their ordering, these dipoles can establish an intrinsic electric field whose magnitude is proportional to the degree of hydroxyl polarization. When exposed to an external stimulus such as an
AC electric field, the degree of hydroxyl polarization can increase. This dielectric behavior is analogous to that observed in ferroelectric materials. Consequently, many groups have explored the possibility of using hydroxyapatite in applications traditionally reserved for high dielectric constant materials like barium titanate and lead zirconate titanate.

Since the 1950s researchers have known that dried bone (which possesses a similar structure to hydroxyapatite) generates an electric potential when subjected to external stresses [45]. The electric potential established is the direct result of hydroxyl dipole reorientation within the tunnel structure formed by the Ca(2) atoms of hydroxyapatite. Over the same 50 years, the medical community has also known that mechanical stimulation of fractured bones accelerates the convalescence period. Thus, the two concepts were combined by Kimihiro et. al. [46] who demonstrated that polarized hydroxyapatite samples, when submerged in Simulated Body Fluid (SBF), provided an excellent surface on which bone-like crystals could grow larger and faster than those grown on non-poled hydroxyapatite samples. Furthermore, Kimihiro showed that the growth of bone-like crystal occurred primarily on the Negative (N-side) of the poled hydroxyapatite samples. Figure 10 illustrates the growth of bone-like crystals on poled and non-poled HAp samples.
The concept of dipole reorientability was investigated further by Hitmi et al. [47] who showed that larger strontium atoms, when substituted for calcium on the Ca(2) sites, of Sr$_{10}$(PO$_4$)$_6$(OH)$_2$, expand the tunnel diameters wherein the hydroxyl groups are located. As a result, the dipoles have less difficulty reorienting. Conversely, the hydroxyls intrinsic to Ca$_{10}$(PO$_4$)$_6$OH$_2$ have greater difficulty reorienting themselves due to decreased tunnel diameters formed by the smaller calcium ions at the Ca(2) sites.

Other groups [48][49] have taken advantage of hydroxyl reorientability to design CO and CO$_2$ sensors. When the hydroxyapatite samples are exposed to different gases, measured resistivity changes reflect the degree of sensitivity. Mahabole demonstrated hydroxyapatite’s ability to detect CO by applying 90V D.C. electric field across the hydroxyapatite to polarize the hydroxyl groups in the structure. At a temperature of 125°C, the material exhibited a heightened sensitivity for carbon monoxide. Based upon these findings, Mahabole suggested the following mechanism for oxidizing the carbon monoxide. $OH^- + CO \rightarrow CO_2 + H_2$ or $OH^- + CO \rightarrow CO_2 + H_2O$. This mechanism explains hydroxyapatite’s increased conductivity when exposed to CO.
The electrolytic properties intrinsic to the apatite structure have also been studied and considered for Solid Oxide Fuel Cell (SOFCs) applications. Early work suggests that the hydroxyl groups are responsible for the observed conduction in hydroxyapatite[50], while later studies [51] suggest that the conduction occurs via complex interactions between Ca(2) tunnel vacancies, the ions on the Ca(2) sites and the oxygen atoms of the phosphate tetrahedral that connect the tunnel structures to one another. Once again, the complex nature of the hydroxyapatite structure reveals itself, leaving only empirical observations and trends that stimulate an amalgamation of interesting, yet plausible explanations.

Bouhaouss et. al. [51] studied the ionic conduction mechanisms within hydroxyapatite (M_{10}(PO_4)_6(OH)_2 where M=Ca, Pb and Ba) and lanthanum vanadocalcic oxyapatites (Ca_{10-x}La_x(VO_4)_6O_{1+x/2} 1-x/2 (LaCaOAp), via complex impedance measurements. Their respective plots are seen in Figure 11a and 11b. Within the hydroxyapatites, conductivity increases as the larger cations Pb and Ba replaced the smaller calcium ions. The complex conductivity measurements suggests that the observed increases in ion mobility within Pb_{10}(PO_4)_6(OH)_2 and Ba_{10}(PO_4)_6(OH)_2 are the result of jump relaxation and mobile ion jumping, respectively. On the other hand, the ions of Ca_{10}(PO_4)_6(OH)_2 possess both modes of ion conduction. Thus, based solely upon tunnel dimensions (larger ions=larger tunnel diameters) the jumping of mobile ions is the preferred conduction mechanism, even though relaxation occurs in the lead apatites. Later studies revealed that higher temperatures reduced the relaxation.
Figure 11 Plot A illustrates the Arrhenius plots of conductivity for the MOHAp’s. Shown in plot B is the Arrhenius plot of conductivity for the oxyapatites

The lanthanum vanadocalcic oxyapatites studied by Bouhaouss display large tunnel diameters when the larger La$^{3+}$ ions replace the smaller Ca$^{2+}$ ions on the Ca(2) sites. Infrared absorption spectroscopy of this composition reveals the presence of two types of VO$_4^{3-}$, one surrounded by vacancies and the other surrounded by O$^{2-}$ ions. The oxygen ion conduction relies upon La$^{3+}$ and O$^{2-}$ to decrease the activation energy. The O$^{2-}$ ions diffuse along the c-axis when sufficient room within the tunnel is provided by the large lanthanum ions, and when enough anionic oxygen is present to decrease the activation energy.

Kharton et. al. [52] reports that the greatest ionic transport is observed in those apatite phases containing more than 26 oxygen ions per unit formula. This observation confirms Bouhaouss’s findings, in that the interstitial oxygen ion migration dictates ionic conductivity within the oxyapatites. Furthermore, Kharton was also able to show that decreasing oxygen content leads to increased vacancy concentrations which in turn
decreases the overall ionic conductivity of the material. Cation site deficiencies are also influential in controlling the volume of the unit cells. Such changes can yield oxygen displacements into the available interstices. Left in the wake of these displacements are vacant oxygen sites. Bouhaouss [51] found that these oxygen ions and their subsequent vacancies exhibit coulombic interaction that result in a linear dependence of conductivity with the applied frequency.

Provided in the former paragraphs is a brief synopsis of the many possible applications for which hydroxyapatite has been considered. An evolutionary type of behavior is observed as the material has transitioned from biological to electrical applications. Without the myriad of processing techniques that exist many of the applications assumed by hydroxyapatite would have never come to fruition and the material’s current benefits would have remained dormant. As an example, the inability of bulk hydroxyapatite to assume many of the load-bearing functions required of implant materials was overcome with the help of plasma deposition techniques. Such processing lead to load bearing implants that exhibited superior biological and mechanical properties when compared to other non-coated implants.

What is more, without a general understanding of the material’s composition and structure the observed diversifications within biology and other scientific communities would not have transpired. Thus, the structural and compositional generalizations, in conjunction with the vast available processing techniques, have been taken advantage of
in the following dissertation to explore and reveal those benefits of hydroxyapatite that remain furtive.

In conclusion, the generalizations developed from the previous discussions concerning compositional modifications, will be used to explain the results observed in the following research. Specifically, this information is first applied to the bulk hydroxyapatite to help describe the observed structural and bonding changes occurring when the material is subject to compositional and temperature changes. Once the behavior of the bulk form is understood, this information will be translated into the thin film regime. New information is also presented to help understand why the immiscibility gap exists in the Ca-Ba apatite system.
3. Apatite Synthesis

3.1 Introduction

The following discussion details the precipitation process implemented for synthesizing stoichiometric hydroxyapatite (s-HAp), calcium deficient hydroxyapatite (CDHA) and various barium stabilized hydroxyapatite (BaHAp) compositions via wet precipitation chemistry. The structures of the as-precipitated compositions are subsequently investigated to understand both the precipitation reaction and the structural changes that occur because of compositional modifications. Understanding the precipitation reaction and the consequences of composition changes allows for greater control when tailoring the apatite structure to exhibit certain properties in the bulk and thin film forms. At the same time, the structural information discovered by studying the as-precipitated bulk apatites will be implemented to assist in understanding the sintered bulk apatites and thin film apatites discussed in Chapters 4 and 5, respectively.

3.2 Experimental

The wet precipitation process was chosen over other techniques for several reasons. First, the reactants (calcium hydroxide and 85 wt% orthophosphoric acid) and labware necessary for precipitating hydroxyapatite are simple in comparison to other techniques such as hydrothermal and sol-gel synthesis. Hydrothermal synthesis is primarily used to grow single crystals via condensation from the vapor phase. Although the compositions of these crystals are highly controlled, the precipitation process is able to generate greater amounts in less time. Sol-gel synthesis, although relatively simple is
also unable to compete with the large volumes produced using precipitation. The ability to produce a large amount of fine particles via precipitation provides more liberties when fabricating the targets for the ion beam deposition process. At the same time, precipitation also offers greater microstructural control compared to other techniques.[53] Such control is essential for proper ceramic processing as outlined in section 3.3. Finally, the only by-products of the wet precipitation process is water. This is in comparison to other techniques that use ammonium based salts to yield hydroxyapatite and ammonia hydroxide that could be a source of contamination.

This is not to say the precipitation process is perfect. To generate apatites having compositions reflecting those of the reactants, significant care must be taken to avoid contamination. Specifically, the apatites have a considerable affinity for carbonate ions during precipitation. Thus, if flux condensers, CO$_2$ traps and other precautionary measures are not implemented, the carbonates will occupy the phosphate positions in the apatite structure. Although the aforementioned precautions were not taken in this research, later results will show how extreme temperatures can eliminate any unwanted carbonate. If care is taken during later ceramic processing steps, detailed in Chapter 4, the products in this dissertation cannot be distinguished from those synthesized using more controlled techniques.

The following discussion details the experimental processes implemented to generate different apatite compositions. The as-precipitated powders were subsequently analyzed using Fourier Transform Infrared spectroscopy (FTIR) and X-ray Diffraction
These techniques aid in understanding the dynamics of the precipitation reactions and the structural consequences of compositional modifications.

### 3.2.1 Experimental Procedure

Each precipitation experiment is based on the chemical formula, $10Ca(OH)_2 + 6H_3PO_4 \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 18H_2O$. The recipe invoked by Afshar et. al. [54] was used as a model for the following work, but was not strictly obeyed. In this recipe 0.3 M orthophosphoric acid and 0.5 M base solutions are needed to satisfy the above reaction. Simple modifications were made to the types of reactants used and their molar concentrations to yield the apatites produced in the subsequent paragraphs. These compositions are outlined in Table III along with the abbreviations to be used henceforth.

<table>
<thead>
<tr>
<th>Product Name</th>
<th>Chemical Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stoichiometric Calcium Hydroxyapatite (s-HAp)</td>
<td>$Ca_{10}(PO_4)_6(OH)_2$</td>
</tr>
<tr>
<td>Stoichiometric Barium Hydroxyapatite (BaHAp)</td>
<td>$Ba_{10}(PO_4)_6(OH)_2$</td>
</tr>
<tr>
<td>Calcium Deficient Hydroxyapatite (CDHA)</td>
<td>$Ca_{10-x}(HPO_4)<em>x(PO_4)</em>{6-x}(OH)_{2-x}$ where $x = 1$</td>
</tr>
<tr>
<td>Calcium Deficient Hydroxyapatite Stabilized with Barium (Ca$_{10-x}$Ba$_x$HAp)</td>
<td>$Ca_{10-x}Ba_x(PO_4)_{6}(OH)_2$ where $x = 0.5, 1.0$ and $2.0$</td>
</tr>
</tbody>
</table>

Every synthesis experiment began by vigorously stirring and heating the alkaline aqueous solutions to 40° C on a hot-stir plate. Slurries of the alkaline solutions were prepared with de-ionized water, 95.0% min. purity, Alfa Aesar Ca(OH)$_2$ and/or 95.0%
min. purity, Fisher Scientific Ba(OH)$_2$. If the apatite being synthesized is to contain both calcium and barium, the appropriate aqueous solutions of each are prepared and combined in the same beaker. This amalgamation is heated and stirred as described previously. During the heating process, each of the beakers is covered with aluminum foil to prevent concentration changes due to loss of water from evaporation.

Once the appropriate temperature is attained for the alkaline solutions, the precipitation reaction can begin. The aqueous acid solution was prepared using 85 wt%, Acros Organics orthophosphoric acid. This solution was then added to the heated alkaline solution, at a rate of $\sim$2 drops/second. As the precipitation nears the end, a noticeable change in viscosity of the reacting solution occurs. The pH of the products is slightly alkaline, $\sim$8. This ensures enough alkaline ions are present to prevent the product from being calcium deficient.

Upon completion of the reaction, the precipitated solution is allowed to stir at 40 $^\circ$C for approximately 2 hours. This step ensures that all of the reagents have an opportunity to react and precipitate apatites whose molar ratios match those anticipated by the initial calculation. The solution was then allowed to age overnight to promote Oswald ripening. Ripening, or aging, is used to describe the dissolution of smaller particles and the growth of larger ones within a medium for which they exhibit some solubility. The driving force for Oswald ripening is the reduction of interfacial energy via particle growth. This step tends to yield more equi-axed particles compared to the
rod-like particles of as-precipitated powders. The importance of this feature will become evident in the ceramic processing steps.

Three different post precipitation treatments were also investigated to determine the effect the mother solution has in developing the proposed precipitation product. The first method simply left the precipitated powder in the mother solution while drying commenced at 200-300°C (Non-Washed NW). The second technique decanted the supernatant solution from the precipitate and washed the remaining product with equivalent amount of boiling water. The precipitate was then allowed to settle, at which time the supernatant was decanted again. This process continued until a pH of ~6-7 was obtained (Water Washed WW). The precipitate was dried at 100°C. The final treatment followed the second process barring a final wash using 1mmol/L of phosphoric acid (Phosphoric Acid Washed PAW). This was used to remove any excess calcium not washed away by the boiling water. The solution was stirred overnight and subsequently decanted from the precipitate. Boiling water was used in the final step to remove the phosphoric acid solution from the precipitate before drying at 100°C. Only the s-HAp and CDHA compositions underwent the post-precipitation treatments. Those compositions incorporating barium were not washed, but allowed to dry along with the mother solution. The acronyms defined in the parentheses above are used to identify the post precipitation treatments implemented.

A mortar and pestle was used to grind the precipitated powders into fine particles. The ground material was fed through a 149-micron sieve to ensure a homogenous particle
size distribution was achieved prior to further processing. These powders were then uniaxially pressed into small pellets under 2500lbs of force. Prior to sintering the pellets were approximately 1.61 cm in diameter and 0.18 cm thick. In an effort to organize and communicate the ascertained data properly, the heat treatments will be considered in Chapter 4.

### 3.2.2 Characterization

Both x-ray diffraction and Fourier transform infrared spectroscopy were implemented for characterization of the as-precipitated powders. The former was implemented to investigate the structural development of the as-precipitated apatites with respect to composition. FTIR spectroscopy supplements the structural data by providing detailed information about the bonding responsible for the development of the observed crystalline structures and offers information regarding the purity of the compositions. At the same time, these techniques offer an insight into the dynamics of the precipitation process for the different apatites, specifically the barium-calcium apatite systems. Moreover, a general appreciation for the complexity of the apatite structure will be gained.

Powder x-ray diffraction was performed using a Bruker AXS diffractometer equipped with a general area detector to observe changes in the crystal structure, crystallinity and phases occurring when the apatite composition is modified. Monochromatic Cu Kα (λ=1.5406 nm) x-rays are produced using a tube voltage and
current of 30kV and 20mA, respectively. For each sample, a 20-40° 2θ range was used at 0.005° steps. The resolution for the diffractometer, when using a 0.8mm collimator, is approximately ± 0.2° 2θ, when the sample is 15 cm from the detector. The entire scan took 15 minutes; therefore, the dwell time at each step was approximately 0.11s. The sample’s height was adjusted until the surface came into focus when viewed through a monocle at a set geometry with respect to the detector. The phases present within each of the synthesized compositions were identified using standard patterns amassed by the Joint Committee on Powder Diffraction Standards (JCPDS).[55]

Fourier transform infrared spectroscopy was performed using a Perkin-Elmer xxx model. Infrared transmission spectra were obtained in the 650-4000 wavenumber (cm⁻¹) range using the KBr method. Potassium bromide, in contrast to the apatites, is 100% IR transparent within the aforementioned range. Therefore, incorporation of 1.0 wt% apatite powder with a given amount of KBr, prevents the apatite from absorbing all of the IR radiation. This technique is highly sensitive to contamination, and great care must be taken when mixing the two materials.

3.3 Results and Discussion

Provided in Table IV are the names and compositions of the as-precipitated apatite powders. Also indicated are the colors used to identify the compositions within the XRD and FTIR spectra. The compositions having only calcium cations are considered first. To understand the structural evolution that occurs when the
compositions are modified and heat-treated, the spectra of the synthesized samples are compared to those of a stoichiometric hydroxyapatite standard synthesized by NIST. Later discussions will consider those apatites having mixed cationic elements, Ca$^{2+}$ and Ba$^{2+}$. Rounding out the as-precipitated apatites will be the fully substituted apatite whose calcium atoms have been replaced with barium atoms.

**Table 4** Nomenclature of the as-precipitated apatites

<table>
<thead>
<tr>
<th>Name</th>
<th>Composition</th>
<th>Color Code</th>
</tr>
</thead>
<tbody>
<tr>
<td>s-HAp_0*</td>
<td>Ca$_{10}$(PO$_4$)$_6$(OH)$_2$</td>
<td>Light Blue</td>
</tr>
<tr>
<td>CDHA_0*</td>
<td>Ca$_9$(HPO$_4$)(PO$_4$)$_5$(OH)</td>
<td>Red</td>
</tr>
<tr>
<td>s-BaHAp_0</td>
<td>Ba$_{10}$(PO$_4$)$_6$(OH)$_2$</td>
<td>Dark Blue</td>
</tr>
<tr>
<td>Ca$<em>{0.5}$Ba$</em>{0.5}$HAp_0</td>
<td>Ca$<em>{0.5}$Ba$</em>{0.5}$(PO$_4$)$_6$(OH)$_2$</td>
<td>Orange</td>
</tr>
<tr>
<td>Ca$_9$Ba$_1$HAp_0</td>
<td>Ca$_9$Ba$_1$(PO$_4$)$_6$(OH)$_2$</td>
<td>Green</td>
</tr>
<tr>
<td>Ca$_8$Ba$_2$HAp_0</td>
<td>Ca$_8$Ba$_2$(PO$_4$)$_6$(OH)$_2$</td>
<td>Black</td>
</tr>
<tr>
<td>NIST and JCPDS standards</td>
<td>As labeled</td>
<td>Pink</td>
</tr>
</tbody>
</table>

* These samples have undergone an ancillary study that investigated the effects of washing the as-precipitated apatite powders. Non-washed, water washed and a 1mmol H$_3$PO$_4$ washed samples were prepared and are labeled accordingly.

### 3.3.1 s-HAp and CDHA XRD

The x-ray diffraction patterns of the Non-Washed (NW), Water Washed (WW) and 1 mmol Phosphoric Acid Washed (PAW), as precipitated hydroxyapatites are shown in blue and red in Figure 12a. Each pattern is labeled according to the post precipitation wash that was implemented for that composition. The patterns were indexed to the hexagonal pattern produced by NIST, JCPDS (No. 9-432 [56]) and other experiments[54][57]. The NIST pattern has been included in Figure 13. The diffracting
planes in conjunction with their diffraction angles are listed in Table V. In comparing the standard pattern to the experimental pattern, the rarely detected monoclinic phase does not appear. Elliott [1] reports that the monoclinic phase will be observed only in those samples that do not deviate from stoichiometry of posses any impurities that might disrupt the ordered OH\(^-\) columns that defines the monoclinic phase.

**Figure 12** Shown here are the diffraction patterns for the as-precipitated calcium apatites. The post chemical treatment used on each composition is labeled accordingly.
Table 5 This table identifies the peaks of a stoichiometric hydroxyapatite. The seven most intense peaks are highlighted in yellow and labeled #’s 1-7.

<table>
<thead>
<tr>
<th>$2\theta$</th>
<th>Hkl</th>
<th>$2\theta$</th>
<th>hkl</th>
</tr>
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<tbody>
<tr>
<td>25.35</td>
<td>201</td>
<td>42.3</td>
<td>302</td>
</tr>
<tr>
<td>#1 25.86</td>
<td>002</td>
<td>43.84</td>
<td>113</td>
</tr>
<tr>
<td>28.11</td>
<td>102</td>
<td>44.36</td>
<td>400</td>
</tr>
<tr>
<td>28.92</td>
<td>210</td>
<td>45.29</td>
<td>203</td>
</tr>
<tr>
<td>#2 31.77</td>
<td>211</td>
<td>#6 46.683</td>
<td>222</td>
</tr>
<tr>
<td>32.18</td>
<td>112</td>
<td>48.068</td>
<td>312</td>
</tr>
<tr>
<td>#3 32.9</td>
<td>300</td>
<td>48.58</td>
<td>320</td>
</tr>
<tr>
<td>#4 34.04</td>
<td>202</td>
<td>#7 49.458</td>
<td>213</td>
</tr>
<tr>
<td>35.44</td>
<td>301</td>
<td>50.474</td>
<td>321</td>
</tr>
<tr>
<td>39.18</td>
<td>212</td>
<td>51.254</td>
<td>410</td>
</tr>
<tr>
<td>#5 39.793</td>
<td>310</td>
<td>52.061</td>
<td>402</td>
</tr>
<tr>
<td>40.43</td>
<td>221</td>
<td>53.167</td>
<td>004</td>
</tr>
<tr>
<td>41.98</td>
<td>311</td>
<td>54.43</td>
<td>104</td>
</tr>
</tbody>
</table>

At first glance, the diffraction patterns of the as precipitated s-HAp and CDHA cannot be distinguished from one another. Other researchers have also noted this unanticipated behavior [34][35]. However, they fail to provide a definitive explanation.
as to why the CDHA diffraction pattern does not differ from that of its stoichiometric counterpart. The best that can be said for these compositions is that all of the peaks present in the diffraction profiles are representative of a structurally immature, apatitic material. Chapter 4 offers more insight into the differences between the two materials upon heat treatments at temperatures greater than 650° C.

When comparing the as-precipitated calcium apatite diffraction patterns with that of the s-HAp pattern generated by NIST, two distinct differences emerge. First, the peaks of the as-precipitated powders are much broader than those in the pattern produced by NIST. This broadening occurs because of crystalline lattice strain and/or small crystallite sizes. The second difference between the two patterns is a manifestation of the first, wherein some of the peaks representative of s-HAp coincide with the more intense apatite peaks. Such coincidence prevents the peaks of the tiny crystallites from being distinguished from their more intense neighboring peaks. An example of this occurs between the (211) and (112) peaks. Within the as-precipitated patterns shown in figure 12, only the (211) plane can be discerned. On the other hand, the 112 peak is observed in the structurally mature apatite shown in figure 13. Another reason for the observed overlap is discussed below.

Peak broadening, B, similar to that observed in Figure 12 [58], is often attributed to very small unstrained crystallites. The sizes of which are often determined using the Scherrer formula: 

$$t = \frac{0.9\lambda}{B \cos \theta_B}.$$ [58] Yet, if the crystallites being analyzed are not strain free, then the resultant broadening, as observed in figure 14c, cannot be differentiated
from broadening due to small crystallites. Therefore, the use of Scherrer’s formula to
determine crystallite size is jeopardized.

\[
\frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2} \quad \text{where } h, k \text{ and } l \text{ define the diffracting plane}
\]

The changes in d-spacing are revealed as shifted diffraction peaks, as defined by Braggs law. Some shifting is observed in Figure 15, which compares the as-precipitated calcium apatite diffraction peaks with the fully mature NIST peaks. The observed shifting to
larger diffraction angles is indicative of an apatite structure whose d-spacings are smaller than those of the well crystallized apatite standard shown by the sharp green lines in Figure 15.

Figure 15 The diffraction peaks of the synthesized calcium apatites shift with respect to equivalent peaks of the NIST standard

X-ray data reported Legeros [58] in a study that investigated the effects of carbonate content on crystallite morphology supports some of the shifts observed in Figure 15. [59] Figure 16 presents five XRD patterns whose carbonate content increase from 0.5-20 wt% in going from A to F. According to their results, as the amount of carbonate content increases three events take place that ultimately effect the morphology of the precipitated crystals. The first event is the superimposition of the 211 and 112 reflections. This behavior has also been observed for the apatites synthesized herein. The next two events involve the 002 and 300 atomic planes within the apatite unit cell. As the percentage of
carbonate increases within the structure, the 002 and 300 reflections exhibit greater shifts to smaller and larger diffraction angles, respectively. Such shifting corresponds to an increased $c$-axis and a smaller $a$-axis. This relationship was not observed in the apatites synthesized for this thesis.

![Figure 16](image.png)

**Figure 16** Plots A through E examine the effects of increasing carbonate content within the apatite structure. Percentage of CO2 by weight (A) 0.5 (B) 5.0 (C) 10.0 (D) 15.0 (E) (F) 20.0

Other reasons for observing the shift to larger diffraction angles include excess calcium in s-HAp and calcium deficiencies in CDHA compositions. Excess calcium content, as shown by Bonel et. al. [59][58] decreases the $a$-axis parameter while keeping the $c$-axis constant. As a result the 300 reflection should shift to a larger diffraction angle as it does in Figure 15. However, with respect to the calcium deficient apatites, Rowles [59] observed a 0.23% volumetric increase in the apatite unit cell after removing 6% of the calcium atoms from the structure to yield an apatite whose $Ca/P=1.56$. The observed
expansion is the direct result of an increase in the a-lattice parameter from 9.418 to 9.433 Å, and a subsequent decrease in the c-lattice parameter from 6.881 to 6.875 Å. The lattice parameter changes are not in agreement with the observed shifts occurring in Figure 15.

Although some shifting occurs within the diffraction peaks of the as precipitated apatites, the source of this shifting cannot be confidently attributed to any of the events described by Legeros, Bonel and Rowles. To confirm their shifting observations, a more precise x-ray diffractometer is needed. However, later FTIR results in conjunction with XRD results obtained for the sintered apatites can be used to provide a better understanding of the apatite compositions in the as precipitated state.

To summarize, when compared to a NIST standard the as precipitated compositions produced herein exhibit similar apatite structure. However, the broadening of the diffraction peaks in conjunction with their low intensities, suggest that they are poorly crystallized. Some peak shifting is also observed, but this observation can not be attributed to one specific event. More information will be revealed when the compositions are characterized using FTIR, and after the compositions have been further processes. The following section, which details the effect of barium on as precipitated apatites also provides some insight into the role of the cations during the precipitation reaction.

### 3.3.2 Barium Stabilized Apatites XRD

The apatites discussed herein incorporate barium atoms in place of the calcium atoms. Compositions having 5, 10 and 20-atom% (Ca$_{0.5}$Ba$_{0.5}$HAp, Ca$_9$Ba$_1$HAp and
Ca₈Ba₂HAp, respectively) barium in the place of equivalently removed calcium atoms, have been analyzed via XRD. Another apatite whose calcium atoms have been completely replaced with barium atoms will also be considered. The chemical formulae for these compositions are indicated in Table IV along with their respective color-coding. Once again, only the as-precipitated compositions are initially considered along with their respective XRD data. Infrared absorption data is presented later in chapter 3.

The diffraction patterns for the three barium-stabilized apatites are shown below in Figure 17a. This pattern has been expanded in Figures 17 b and c to show how the peak intensities and positions vary over two different ranges, 30-35 and 45-55° 2θ. As the barium content increases, the peaks diminish in intensity and increase in breadth. At the same time, over the entire scan range (25-55° 2θ), a general shift of the barium peaks to values of 2θ that are less than the NIST peaks are also observed. The degree of this shifting increases with increasing diffraction angle. Lastly, the diffraction peaks of the individual compositions shift with respect to one another as the diffraction angle increases.
Each of the diffraction patterns of the as-precipitated barium doped hydroxyapatite compositions indicates the formation of hydroxyapatite. However, the crystallinity of this material decreases as the percentage of barium increases. This decrease in crystallinity is recognized by the decreased peak intensity and increased peak
breadth. These findings suggest that beyond a certain barium concentration, the apatite phase will be destroyed.

In fact, groups that have synthesized apatites with greater barium concentrations discovered that between 25-60 atom % Ba, an immiscibility gap exists and prevents the apatite phase from existing.[23] Moreover, depending upon the type of synthesis technique implemented, the amount of barium that can be incorporated differs considerably. For example, the precipitation technique is only able to incorporate 0-25 atom % barium into the structure, while mechanical mixing is able to extend over 60-100 atomic % Ba.[1] Thus, an immiscibility gap develops between 25-60 atomic %

The threshold of the aforementioned immiscibility gap is observed in the diffraction patterns for the precipitated Ca₈Ba₂HAp composition whose peak intensities have diminished considerably in comparison to the other barium apatites. Previous works [23][60] have reported similar observations when strontium, barium and magnesium are substituted for calcium. Furthermore, analytical work performed by Bigi [23] suggests that the actual amount of barium incorporated into the structure is significantly less than that present in the aqueous solution used for precipitation. Figure 18 presents their analytical results with respect to the actual and expected atomic percentage of barium. The phase diagram in Figure 9, as obtained by Khudolozhkin[39][40], also supports the findings presented in this research. The hatched region represents the immiscibility gap, which begins at 6 atom % Ba and extends to 60 atom %. This also correlates well with Bigi’s results wherein less than 3 atom percent
was found in those compositions whose barium content was expected to be between 5 and 20%.

<table>
<thead>
<tr>
<th>Atom % Ba in solution</th>
<th>Atom % Ba in the solid phase</th>
<th>(a) axis (nm)</th>
<th>(c) axis (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0.9427(2)</td>
<td>0.6875(3)</td>
</tr>
<tr>
<td>5</td>
<td>1.9(1)</td>
<td>0.9432(3)</td>
<td>0.6886(3)</td>
</tr>
<tr>
<td>10</td>
<td>2.8(1)</td>
<td>0.9461(4)</td>
<td>0.6901(4)</td>
</tr>
</tbody>
</table>

*Figure 18* Presented here are the percentages of barium in solution compared with that incorporated into the apatite structure. Also given are the lattice parameters for the different compositions.

The same association between the actual and expected amount of \(X\) cation has also been observed for the calcium apatites. Precautions such as water and phosphoric acid washings are taken to eliminate the excess calcium that might lead to the development of tricalcium phosphate and calcium oxide upon subsequent heat treatments. These phases in conjunction with those that develop because of excess barium will be revealed and discussed in chapter 4.

To understand the influence that the barium ion has on the apatite structure, the diffraction peak locations must be studied with respect to a standard and one another. As stated earlier, the diffraction peaks of the barium substituted apatites shift to lower diffraction angles in comparison to equivalent peak positions for the stoichiometric calcium hydroxyapatite NIST standard. This trend is to be expected, as the barium cationic radii are greater than the calcium cationic radii, which they are replacing. Considering Bragg’s law, diffraction peaks at lower diffraction angles indicate an enlarged d-spacing, which in turn implies an increase in the structure’s overall volume.
This expansion, though not confirmed with lattice parameter data herein, has been reported by Bigi et al. [23] Their results, seen in figure 17, reveal an increase in the lattice parameters as the atomic percent barium increases.

Relative to the same s-HAp NIST pattern presented in Figure 13, the barium-doped apatites exhibit a continuously increasing shift to smaller $2\theta$ values as the diffraction angle increases. This behavior is illustrated in Figures 19, which emphasizes the diffraction peaks for the (321), (410), (402) and (004) atomic planes. The increased shift to smaller diffraction angles for these atomic planes suggests that they are more sensitive to modifications made to their proximate environment.

![As-Precipitated Barium Stabilized Apatites](image)

**Figure 19** Expanded view of those peaks existing at larger $2\theta$. The increased shift to smaller $2\theta$ indicates greater sensitivity in their respective atomic planes.

Recalling the description of the apatite structure provided in chapter 2, in
conjunction with figure 5, the Ca(2) cations lie approximately at \( z = \frac{1}{4} \) and \( \frac{3}{4} \). These same Ca(2) sites are considered to be those occupied by cations such as barium, when introduced to the apatite structure [1][25][40]. Thus, upon substitution of the barium ions for the calcium ions, a significant increase in the d-spacing between the Ca(2) planes should be observed, as the larger barium atoms begin to infiltrate these sites. Any changes that occur at these sites will be reflected by shifts of the 004 peak, which represents the inverse of the fractional intercept of the 0,0,1/4 plane. This fractional intercept lies parallel with the Ca(2) sites located at \( z = \frac{1}{4} \) and \( \frac{3}{4} \) as defined earlier. Therefore, when modifications are made to the Ca(2) sites, significant shifts will be observed in the 004 peak as shown in Figure 19.

Considering the individual barium diffraction patterns, a variable degree in shifting is observed over the entire range of diffraction angles. Starting at 25° and ending at 35° 2θ, the diffraction peaks for each barium doped apatite composition are aligned with one another. This observation suggests that within this range, the interplanar spacings of the diffracting planes are independent of changes in barium concentration. On the other hand, beyond 35°, the diffraction pattern for Ca₉Ba₁HAp and Ca₈Ba₂HAp shifts to smaller diffraction angles away from the Ca₉.₅Ba₅.₅HAp composition, but do not shift with respect to one another.

These results help to support the existence of the immiscibility gap in the Ca-Ba family of apatites. Specifically, as the barium concentration increases from 0-5 and 5-10
atom % the peaks shift to smaller diffraction angles. After 10 atom % Ba, the peaks remain at the same diffraction angle; thus suggesting no more barium can be incorporated into the structure. The excess barium in the as-precipitated compositions does not affect the peaks representative of the apatite structure. Later heat treatments reveal the role of the excess barium within the structure.

The last composition investigated was an apatite whose calcium’s were completely replaced with larger barium cations. The diffraction pattern for this composition shown in Figure 20 differs significantly from the calcium apatite patterns. Specifically, many new peaks have emerged while the more intense peaks have shifted to smaller diffraction angles as the overall structure has increased in volume. Lastly, the as-precipitated structure is poorly crystallized, and many of the peaks expected to occur have yet to develop. Sintering studies in chapter 4 reveal the evolution of this structure.

**Figure 20** Shown here is the diffraction pattern for barium apatite where all of the calcium atoms have been replaced with barium atoms.
In conclusion, regardless of the percentage of barium incorporated into apatite composition, the as precipitated structure resembles that of a pure calcium apatite. Just as before, the as precipitated compositions exhibit poor crystallinity. However, in this case the crystallinity is further jeopardized as the percentage of barium increases. The observed peak shiftings to smaller diffraction angles also suggests that the structure is expanding to accommodate the larger barium cations. This shift is more pronounced at larger diffraction angles, and in those compositions containing more barium. Thus, as the barium concentration increases, a more pronounced effect will be observed in those planes of atoms having smaller d-spacings. Specifically, the (004) plane exhibits a large increase in d-spacing. This event is thought to be the result of the barium atoms replacing the Ca(2) atoms at 0,0,1/4 along the c-axis. In other words within the (004) plane.

3.3.3 s-HAp and CDHA FTIR Results and Discussion

FTIR spectroscopy was implemented to provide bonding information necessary to support the observed structural changes that discussed in sections 3.3.1 and 3.3.2. This section, and section 3.3.4, will investigate the FTIR results of the same as precipitated compositions investigated using XRD. These results will be discussed in combination with the XRD findings to provide a well-developed understanding of the as precipitated apatite structure, and how it responds to compositional changes.
The regions to be discussed include those absorption band frequencies unique to the phosphate, hydroxyl and carbonate groups. Their different modes of vibration found in s-HAp in conjunction with their respective mode frequencies are found in Table VI. Some of these bands, though IR active, do not appear in the spectra for two different reasons. First, some bands are very weak, and might be masked by larger more intense bands. Such is the case when trying to locate the weak carbonate ν₁ band around 1060 cm⁻¹ whose characteristic frequency is dominated by the more intense ν₃ phosphate band located at 1088 and 1029 cm⁻¹. Secondly, other bands may not appear because they are not within the 650-7000 cm⁻¹ detection range of this instrument. For example, the characteristic absorption frequencies for the calcium atoms are not observed as they occur between 200cm⁻¹-400cm⁻¹, which is well outside the detector's limits. Although the absorption bands for ions such as calcium are not observed in these spectra, inferences can be made about their bonding by observing the changes that occur within the absorption bands of the ions associated with the cations.
The FTIR plots of the calcium apatites presented in this section, have been scaled to better project those regions of interest that are otherwise concealed by the full-scale spectra. These regions will be compared to understand the difference between the bonding environments of s-HAp and CDHA. At the same time, the effects of post precipitation treatments on the bonding will also be discussed. Table VII has also been constructed to facilitate interpretation of the scaled spectra, and provide quick reference to those band frequencies and band assignments for the as precipitated calcium apatites.

<table>
<thead>
<tr>
<th>Band Frequency (cm⁻¹)</th>
<th>Mode</th>
<th>Band Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3572</td>
<td>Stretching</td>
<td>OH⁻</td>
</tr>
<tr>
<td>631</td>
<td>Librational</td>
<td>OH⁻</td>
</tr>
<tr>
<td>342</td>
<td>Translational</td>
<td>OH⁻</td>
</tr>
<tr>
<td>1090 &amp; 1040</td>
<td>v₃</td>
<td>PO₄²⁻</td>
</tr>
<tr>
<td>962</td>
<td>v₁</td>
<td>PO₄²⁻</td>
</tr>
<tr>
<td>2200 to 1950</td>
<td>Overtones and combinations of the v₃ and v₁ modes</td>
<td>PO₄²⁻</td>
</tr>
<tr>
<td>601 and 574</td>
<td>v₄</td>
<td>PO₄²⁻</td>
</tr>
<tr>
<td>472</td>
<td>v₂</td>
<td>PO₄²⁻</td>
</tr>
</tbody>
</table>

1410 & 1450 "B" type carbonates that replace the PO₄³⁻ ions in HA

<table>
<thead>
<tr>
<th>Band</th>
<th>Mode</th>
<th>Band Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>v₃</td>
<td>CO₃²⁻</td>
<td></td>
</tr>
<tr>
<td>not detected v₁ Carbonate is obstructed by the v₃ phosphate</td>
<td>v₄ and v₁</td>
<td>CO₃²⁻</td>
</tr>
<tr>
<td>v₂</td>
<td>CO₃²⁻</td>
<td></td>
</tr>
</tbody>
</table>

872 Obstructed by HPO₄ Band at 875

1455 and 1540 "A" type carbonate that replaces the OH⁻ in HA

<table>
<thead>
<tr>
<th>Band</th>
<th>Mode</th>
<th>Band Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>875</td>
<td>12 possible bands others obscured by PO₄⁻</td>
<td>*HPO₄²⁻</td>
</tr>
<tr>
<td>3700-2500</td>
<td>v₃ and v₁ stretching of hydrogen bonds</td>
<td>**H₂O</td>
</tr>
<tr>
<td>1630</td>
<td>v₂ bending of water molecule</td>
<td>**H₂O</td>
</tr>
</tbody>
</table>

* This band is missing at temperatures greater than 550 C because these ions condense to form P₂O₇⁴⁻ ions and water
The FTIR spectra from 850-1250 cm\(^{-1}\), for the as-precipitated non-washed calcium apatite compositions, are shown in Figure 21. An expanded view of those absorption bands between 850 and 1000 cm\(^{-1}\) is also provided. Similar to the XRD patterns, the IR spectra for the s-HAp and CDHA look very similar to one another. According to the findings of B.O. Fowler \cite{57,61}, the bands that appear are related to the phosphate groups in the apatite structure.

The first peak, in going from smallest to largest wavenumbers, appears at 875-880 cm\(^{-1}\) for CHDA, and 880 cm\(^{-1}\) for s-HAp. Regardless of the post precipitation treatment implemented, this band is much broader in the calcium deficient compositions than in their stoichiometric counterparts. The breadth of this peak is attributed to the presence of both the carbonate and hydrogen phosphate ions in the apatite structure. The propinquity of their respective band frequencies manifests an overlap in the two peaks such that at low concentrations, their intensities cannot be distinguished from one another. According to the chemical equation for CDHA, \(Ca_{10-x}(HPO_4)_x(PO_4)_{6-x}(OH)_{2-x}\),

<table>
<thead>
<tr>
<th>Band Frequency (cm(^{-1}))</th>
<th>Band Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>878</td>
<td>HPO(_4)^-</td>
</tr>
<tr>
<td>963</td>
<td>(v_1) PO(_4)</td>
</tr>
<tr>
<td>1042</td>
<td>(v_2) PO(_4)</td>
</tr>
<tr>
<td>1093</td>
<td>(v_3) CO(_3)^2- bands</td>
</tr>
<tr>
<td>1066</td>
<td>(v_1) CO(_3)^2-</td>
</tr>
<tr>
<td>1419</td>
<td>H(_2)O Bands</td>
</tr>
<tr>
<td>1454</td>
<td>OH(^-) Stretching</td>
</tr>
</tbody>
</table>

**Table 7 Band Frequencies and band assignments for the as-precipitated calcium apatite compositions**

<table>
<thead>
<tr>
<th>Bands</th>
<th>HAp.0_nw</th>
<th>HAp.0_ww</th>
<th>HAp.0_paw</th>
<th>CDHA.0_nw</th>
<th>CDHA.0_ww</th>
<th>CDHA.0_paw</th>
</tr>
</thead>
<tbody>
<tr>
<td>878</td>
<td>879</td>
<td>878</td>
<td>878</td>
<td>876</td>
<td>877</td>
<td></td>
</tr>
<tr>
<td>963</td>
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<td>963</td>
<td>963</td>
<td>962</td>
<td>962</td>
<td></td>
</tr>
<tr>
<td>1042</td>
<td>1034</td>
<td>1034</td>
<td>1034</td>
<td>1033</td>
<td>1033</td>
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</tr>
<tr>
<td>1093</td>
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<td>1094</td>
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<td></td>
</tr>
<tr>
<td>1066</td>
<td>1063(^m)</td>
<td>1067(^m)</td>
<td>1066(^m)</td>
<td>1064(^m)</td>
<td>1066(^m)</td>
<td></td>
</tr>
<tr>
<td>1419</td>
<td>1418</td>
<td>1420</td>
<td>1419</td>
<td>1420</td>
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</tr>
<tr>
<td>1454</td>
<td>1458</td>
<td>1460</td>
<td>1454</td>
<td>1457</td>
<td>1457</td>
<td></td>
</tr>
<tr>
<td>1485(^m)</td>
<td>1490(^m)</td>
<td>1493(^m)</td>
<td>-</td>
<td>1490(^m)</td>
<td>1494(^m)</td>
<td></td>
</tr>
<tr>
<td>1536</td>
<td>1626</td>
<td>-</td>
<td>1644</td>
<td>1626</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>1655</td>
<td></td>
<td>-</td>
<td>1653</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>3572</td>
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<td>3573</td>
<td>3573</td>
<td>3573</td>
<td>3573</td>
<td></td>
</tr>
</tbody>
</table>

**Combinations and Overtones of \(v_1\) and \(v_3\)**
hydrogen phosphate bands are expected to appear in the FTIR spectra. On the other hand, because the s-HAp has no hydrogen phosphate in its structure, the lone carbonate band is sharper and better defined than when both species are present.

The appearance of the carbonate ion decreases the order within the apatite structure. This is thought to yield disordered arrangement of phosphate ions that do not assemble in the expected hexagonal structure that defines hydroxyapatite. One idea suggests that HCO$_3^-$ ions will exchange with HPO$_4^{2-}$ plus a calcium ion.[62] At the same
time, the carbonate has been shown to reduce the amount of pyrophosphate phase, which is responsible for the formation of tricalcium phosphate phases upon subsequent heat treatments.[63] Further discussion about these ions and their role within the apatite structure upon exposure to elevated temperatures is provided in Chapter 4.

When these compositions are washed with water or phosphoric acid, the intensity of the aforementioned absorption band for CDHA, with respect to the same band in the non-washed apatite, increases more so than that of s-HAp. Joris et. al. [64] related the change in the HPO$_4^{2-}$ peak intensity, for CDHA, to increased calcium deficiencies. Considering the non-washed apatites, this research suspects that the excess calcium remaining in solution after precipitation acts to diminish calcium deficiencies in the precipitated apatite. The following equation was taken from E.E. Berry[65] to support the previous argument:

$$Ca_{10}(PO_4)_6(OH)_2 + xH^+ \leftrightarrow Ca_{10-x}(HPO_4)_x(PO_4)_{6-x}(OH)_{2-x} + xCa^{2+} + xOH^-$$

If the precipitate is not washed, excess calcium in solution, after precipitation, will drive the previous reaction towards the left to precipitate stoichiometric hydroxyapatite. Moreover, the absorption band intensity for the HPO$_4^{2-}$ ion in those non-washed CDHA compositions is expected to be, and is much less intense than in the washed apatites.

Unfortunately, due to many variables such as pH, temperature, and time in conjunction with the fact that the conditions governing precipitation change as more solid separates, assigning a reaction equation to summarize the entire precipitation is extremely
difficult. For example, in an article written Bjerrum[66], and referenced by Arnold [67] the calcium ion assumed an entirely different form than the one suggested in the above equation. Bjerrum supposed that the Ca(HPO$_4$)$_2$ ion might develop to account for 10% of the dissolved calcium.

On the other hand, the carbonate band at 880 cm$^{-1}$ is one of six normal modes of vibration intrinsic to the carbonate ion whose undistorted structure consists of a planar arrangement of C-O bonds that yield a point-group symmetry of D$_{3h}$. Of the six normal modes of vibration, four form two doubly degenerate pairs because of high symmetry. The modes are: $\nu_1 = 1063$ cm$^{-1}$, $\nu_2 = 879$ cm$^{-1}$, the doubly degenerate $\nu_3 = 1415$ and 680 cm$^{-1}$, and $\nu_4 = 680$ cm$^{-1}$. If the symmetry of this ion is lowered to say C$_{2v}$ then the $\nu_1$ mode, normally only Raman active, becomes IR active at 1060 cm$^{-1}$. Continuing along the abscissa, this band shows up as a weak shoulder around 1064 cm$^{-1}$.

The neighboring bands at 960, 1040 and 1090 cm$^{-1}$ belong to the $\nu_1$ and $\nu_3$ phosphate absorption bands, respectively. Upon closer examination, several shoulders appear around the $\nu_3$ PO$_4^{3-}$ band 1040 cm$^{-1}$. These shoulders, in conjunction with the well-defined band at 1090 cm$^{-1}$, are attributed to the triply degenerate asymmetric stretching mode of the P-O bond of the phosphate group. In those samples that were not washed after precipitation, the bands around 1040 cm$^{-1}$ are broader than equivalent bands of the washed precipitates. This broadening effect is evidence of the excessive calcium within the system after precipitation has occurred. The excess calcium saturates the
stoichiometric hydroxyapatite such that the ν₃ PO₄³⁻ band at 1040 cm⁻¹ broadens as the phosphate ions accommodate the calcium surplus. The broadening behavior is also observed at elevated temperatures as the phosphate groups become more organized within the different apatite structures, and as new phases develop to accommodate the calcium deficiencies. This will be discussed in detail in Chapter 4.

The phosphate absorption band intensity for stoichiometric hydroxyapatite is much greater than that of calcium deficient hydroxyapatite. Concurrently, these peaks are sharper and better defined in those samples that experienced a post precipitation wash to remove excess calcium. The decrease in peak intensity is attributed to increased disorder within the apatite structure, resulting from the additional hydrogen phosphate and carbonate ions. These ions act to mitigate the vibrational response of the phosphate ions intrinsic to the apatite structure. On the other hand, the phosphate groups intrinsic to stoichiometric hydroxyapatite only have the carbonate ions to contend with when responding to the infrared stimulus. Consequently, these peaks are more intense than those for CDHA. Lastly, the well-defined peaks of the washed precipitated suggest that the excess calcium within non-washed apatites work to decrease the order in the as-precipitated apatites.

The next set of bands between 1400-1550 cm⁻¹, as seen in Figure 22, belong to the carbonate groups within the apatite lattice. These carbonate ions are able to substitute for the hydroxyl and phosphate groups in the apatite lattice. An A-type substitution is said to
occur when the carbonates replace the hydroxyl groups while the B-type refers to phosphate group substitutions. A third substitution type is a combination of the A and B combinations. These carbonates are referred to as AB-type. The latter substitution is most likely responsible for the bands observed in the as precipitated, washed and non-washed compositions of this thesis.

Considering the planar arrangement of the carbonate ion, there exist two possible orientations for the C-O bond with respect to the c-axis. If these orientations exist a decrease in site symmetry will result and a subsequent loss of the degeneracy of the $\nu_3$ band will occur. The lost degeneracy causes $\nu_3$ band to split into the $\nu_a$ and $\nu_b$ bands,
which are located at 1460 cm\(^{-1}\) (for s-HAp and CDHA) and 1550 cm\(^{-1}\) (only for s-HAp), respectively. This splitting is only observed in the washed s-HAp compositions and indicates an A type substitution is occurring. In one set of results\cite{1}, the \(\nu_{3b}\) decreased non-linearly from 1565 to 1527 cm\(^{-1}\) as the degree of substitution of OH\(^-\) by CO\(_3^{2-}\) increases, while the \(\nu_{3a}\) band remained independent of the substitution. The variability of \(\nu_{3b}\) and consistency of \(\nu_{3a}\) have been linked to the fact that their transition moments are parallel and perpendicular, respectively to the c-axis.

The appearance and disappearance of the \(\nu_{3b}\) band in the different compositions suggests that the calcium ions and their respective vacancies play a major role in determining the type of carbonate bonding that will occur in the apatite structure. Another type of carbonate bonding has been associated with the \(\nu_{3a}\) carbonate band at 1460 cm\(^{-1}\) and the band located at 1420 cm\(^{-1}\). Together, these two bands have been ascribed to a special B-type substitution that occurs when the carbonate ions are accompanied with a hydroxyl group to replace the phosphate groups in the apatite structure. Although these two peaks are found in every composition for every post precipitation treatment, they are the only carbonate peaks that appear for the CDHA compositions.

The appearance of the 1550 cm\(^{-1}\) band in conjunction with the 1460 cm\(^{-1}\) band suggests that the carbonate ions are replacing the hydroxyl groups within the apatite structure. Hypothetically, the hydroxyl groups that were substituted for in s-HAp might unite with other carbonates to replace the phosphates in the apatite structure. Such
behavior could be used to explain the appearance of the 1420 cm$^{-1}$ band that has been associated with the 1460 cm$^{-1}$ band. On the other hand, the disappearance of the 1550 cm$^{-1}$ band might suggest that only the phosphate groups are being substituted for in CDHA and non-washed s-HAp. More research on the effects of carbonate in CDHA is needed before these theories can be fully accepted. Therefore, the most that can be said is that the presence of calcium plays a significant role in determining the types of substitutions that will occur when carbonate ions are present.

The final segment of the FTIR spectra for the calcium-based apatite’s extends from 3000 cm$^{-1}$ to 3750 cm$^{-1}$. This section is seen below in Figure 23. The large hump occurring between 3000 and 3500 is attributed to adsorbed water on the surfaces of the apatite particles, while the spike at 3573 cm$^{-1}$ is attributed to the hydroxyl groups within apatite structure. Regardless of the post precipitation procedure implemented, these peaks look the same. Chapter 4 will reveal how this peak’s presence, after exposure to elevated temperatures, confirms that the hydroxyls are in integral part of the apatite structure.
Several significant features are revealed within the FTIR spectra of the as-precipitated calcium apatites. Specifically, the CDHA compositions contain both carbonates and hydrogen phosphate species, while s-HAp only contains carbonates. The FTIR spectra of the phosphate bands have been used as an indicator to determine monitor the effects of post precipitation washings. For those non-washed apatites, broadened phosphate bands were observed. Concurrently, the same bands of non-washed CDHA were more intense than those same bands for washed precipitates. In each case, regardless of the post precipitation process implemented, the phosphate band intensities for the s-HAp composition were more intense than CDHA’s phosphate bands.
The appearance of the $\nu_1$ carbonate band appearing at 1060 cm$^{-1}$ is a result of the ions decreased symmetry. Concurrently, the $\nu_3$ carbonate band for s-HAp has split in the $\nu_{3a}$ and $\nu_{3b}$ bands at 1460 and 1550 cm$^{-1}$, respectively. Such splitting suggests an A-type carbonates are replacing the hydroxyl groups. However, in each composition, carbonate bands at 1460 and 1420 cm$^{-1}$ are present. These bands suggest that the carbonates, in conjunction with a hydroxyl group, are replacing the phosphates. Thus, it appears that the as precipitated s-HAp are AB-type carbonate apatites, while the CDHA compositions are B-type carbonate apatites. The presence of the hydroxyl group supports the XRD evidence that suggests hydroxyapatite has been synthesized.

### 3.3.4 Barium Doped Apatite FTIR Results and Discussion

The current section is concerned with the changes that take place between the vibrational modes observed in the calcium apatites and those modes that appear in the as-precipitated barium doped apatites. Previous work [25] has examined the effects of barium-doped apatites synthesized via solid state mixing, in the range of 60-100 atom% barium. These samples unlike those studied herein were heat treated at 1200 C. The same work also synthesized barium-doped apatites having 0-25 atom% Ba, via precipitation. No attempt was made to correlate these band frequencies with changes in barium concentrations because of significant band broadening and shifting.

Based upon the calculations found in Appendix A, the compositions investigated below should contain 5, 10 and 20 atom% barium. These samples were not exposed to
high temperatures as they were in the aforementioned work. As a result, the bands that appeared could be easily characterized. Later studies in Chapter 4 will attempt to characterize the same samples after heat treatment. A final composition containing 100 atom% barium has also been investigated.

The FTIR spectra for the barium-doped apatites have been cropped to elucidate the most important regions. At the same time, Table IX provides a summary of absorption band frequencies observed in Ca-Ba apatite systems. The FTIR results of similar compositions obtained by Bigi et. al.[25] are presented in Figure 24 for comparison purposes. This plot illustrates absorption band response relative to the characteristic bands of hydroxyapatite as the atomic percentage of barium increases from 60-100 atom%. The following discussion will only be concerned with absorption bands greater than 800 cm\(^{-1}\). Below this value, the detector does not reveal any significant information.

According to Bigi’s[23] results illustrated in Figure 24, as the percentage of barium increases, the absorption band frequencies shift away from the characteristic bands of hydroxyapatite. Barring the hydroxyl stretching mode, all species exhibit a linear decrease in absorption band frequency as the barium concentrations increase. The peculiar hydroxyl response supports the idea that the barium atoms will exhibit a propensity towards occupation of those Ca(2) sites that surround the hydroxyl groups. This behavior is expected as the ionic radii and electronegativity differences between the calcium and barium atoms disrupt the bonding environment of the apatite structure.
The absorption band frequencies for the as-precipitated barium apatites, presented in Table IX, are in close agreement similar bands found for s-HAp in Table VII. However, small shifts occur, specifically between the phosphate and carbonates, suggesting that the barium does have a minor effect on the as-precipitated apatite structure. More ubiquitous changes occur in the barium apatite peak shape as the barium concentration increases.
Presented in Figure 25 is the FTIR spectrum for the calcium-barium apatites, from 800-1000 cm\(^{-1}\). Within this range, the barium apatites exhibit the same peaks as s-HAp with the exception of the barium apatite containing 20 atom% barium. For this composition a new peak at 857 cm\(^{-1}\) appears. According to the NIST WebBook[68] the new peak is indicative of a phosphate-oxygen bonding environment. Moreover, this band suggests that before the material is ever heat-treated the apatite structure is unable to accommodate the additional barium atoms within its structure. Thus, the material compensates for the excess barium with new bonding environments such as the one occurring at 857 cm\(^{-1}\). Apatite phase diminution is also revealed by the decreasing absorption band intensity of the Ca\(_8\)Ba\(_2\)HAp composition. Intensity differences also occur between the other two compositions; but are thought to be the result of errors in background subtraction.

### Table 8 Absorption band assignments and frequencies for the as precipitated barium stabilized CDHA compositions

<table>
<thead>
<tr>
<th></th>
<th>Ca(_9)Ba(_0.5)HAp</th>
<th>Ca(_9)Ba(_1)HAp</th>
<th>Ca(_8)Ba(_2)HAp</th>
<th>Band Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Band</td>
<td>Frequency (cm(^{-1}))</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>857</td>
<td></td>
<td>POH or P(_2)O(_3)</td>
</tr>
<tr>
<td>878</td>
<td>879</td>
<td>877</td>
<td></td>
<td>HPO(_4)^-</td>
</tr>
<tr>
<td>960</td>
<td>960</td>
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<td></td>
<td>(\nu_1)PO(_4)</td>
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<td>1092</td>
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<td>(\nu_3) CO(_3)^{2-}) bands</td>
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<td>Combinations and Overtones of (\nu_1) and (\nu_3)</td>
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<td>(\nu_3) CO(_3)^{2-}) bands</td>
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<td>(\nu_3) CO(_3)^{2-}) bands</td>
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<td>3572</td>
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<td>(\nu_3) CO(_3)^{2-}) bands</td>
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\(\nu_1\)PO\(_4\) is the asymmetric stretching mode and \(\nu_3\)PO\(_4\) is the symmetric stretching mode of the phosphate group. \(\nu_3\)CO\(_3\)^{2-}\) is the antisymmetric stretching mode of the carbonate group.
Continuing with the reasoning developed in section 3.3.3, the absorption band occurring at $\sim 879 \text{ cm}^{-1}$ is indicative of the $\nu_2$ carbonate band. Chapter 4 will show the disappearance of this band on subsequent heat treatments. The hydrogen phosphate band that also occurs within this region does not appear. Concurrently, the chemical reactions do not predict the presence of the hydrogen phosphate band even though calcium deficient hydroxyapatite was the composition for which barium was to be incorporated, see Appendix A.

The next set of absorption bands occur between 1000-1100 cm$^{-1}$. Unlike the purely calcium hydroxyapatites, the calcium-barium apatites do not exhibit the $\nu_1$ carbonate shoulder at 1060 cm$^{-1}$. The loss of this band is attributed to the ability of the carbonate ion to retain its symmetry in the presence of the larger barium, thus preventing this band from becoming IR active. Although the $\nu_1$ carbonate band is not visible, the $\nu_3$ phosphate bands observed for the calcium apatites are observed in the barium apatites.
These bands have been shifted to larger absorption band frequencies away from the as precipitated s-HAp. Such behavior is in contrast to that observed for the heat-treated apatites whose barium concentrations ranged from 60-100 atom%.[25] The same behavior will be observed in chapter 4 once the samples have been heat-treated. Broad phosphate absorption bands support the x-ray evidence of a poorly crystallized structure, and suggest that the much larger barium is interacting with the phosphate groups in the apatite structure.

![As precipitated Barium Apatites](image)

**Figure 26** As precipitated Ca-Ba apatites 850-1250cm\(^{-1}\)

The \(\nu_3\) phosphate bands also differ in shape with respect to one another and the calcium apatites. As the barium concentration increases, a subsequent increase in band breadth is observed in conjunction with a decrease in the resolution between the phosphate bands at 1050 and 1090 cm\(^{-1}\). This trend suggests the presence of a poorly crystallized apatite whose structure is further influenced by the presence of the larger barium cation. The differences in peak intensity are thought to be the result of poor
background subtraction.

Progressing along the abscissa, the \( \nu_3 \) carbonate absorption bands appear between 1300-1600 cm\(^{-1}\) as shown in Figure 27. Like the \( \nu_3 \) phosphate bands, the carbonate band at 1450 cm\(^{-1}\) exhibits a slight shift. However, this shift, unlike the phosphate band shift, occurs towards smaller wavenumbers when compared to equivalent band frequencies of the calciumapatites. At the same time, based upon increasing absorption band intensity and area, there seems to exist a carbonate concentration dependence upon the percentage of barium within the composition. Thus, as the barium concentration increases, an increase in carbonate content is also observed. The difference in the carbonate peak intensities and shape for Ca8Ba2HAp suggest that there is an entirely different type of interaction taking place between the bariums and remaining apatite molecular species.

The carbonate peaks that appear at 1450 and 1420 cm\(^{-1}\) look very similar to those peaks indicative of a B-type carbonate apatite. There is no indication of the 1550 carbonate band to suggest that the carbonates are substituting for the hydroxyls. This is in contrast to the earlier stoichiometric hydroxyapatite compound, which did exhibit some hydroxyl substitution. Thus, this type of substitution does not appear to be dependent upon stoichiometry, but rather the size of the dopant ion. Increased intensity of these bands for the composition containing more barium also suggests that the carbonates are replacing more phosphate groups. The XRD results after sintering support a break down in the structure that might be the result of significant amounts of carbonate removing the phosphates necessary to define the apatite structure.
Figure 27 As precipitated Ca-Ba apatites showing the carbonates bands within the compositions

The peak occurring at 3573 cm\(^{-1}\) provides an indication that the hydroxyl groups are ordered in a manner similar to that of s-HAp. Slight peak shifting to larger wavenumbers is observed, but does not support the same shifts observed by Bigi et. al.\cite{25} In comparison to the hydroxyl groups in pure calcium apatites, the hydroxyl groups in the calcium barium system are significantly less intense. The drop in intensity suggests that the larger barium atoms surrounding the hydroxyls inhibit their vibrational response to IR light.
In conclusion, increasing barium concentrations tend to increase the disorder of the bonding within the apatite structure. This is first suggested by the new P-O band occurring around 857 cm\(^{-1}\). Concurrently as the barium concentration increases, the resolution between the \(\nu_3\) phosphate bands decreases while the band breadth increases. Increasing barium concentration also increases the amount of carbonate that substitutes for phosphates within the structure. Lastly, the larger barium ions tend to inhibit the vibrational response of the hydroxyl groups because they are surrounded by cations larger than the calcium cations of s-HAp and CDHA.

Although the absorption band response to increasing barium content within the as-precipitated apatites are not as ubiquitous as they are for those synthesized by Bigi et al., the compositions produced herein allow for a better understanding of the bonding that occurs at lower concentrations of barium prior to heat treated. The earlier research performed on these doped apatites has been concerned only with the final heat-treated compositions. To understand how a composition realizes its final state, studies concerning the initial processing conditions, and its variables, are necessary for...
developing processing methods that can be easily modified to render the desired properties.

Figure 29 FTIR spectra for the apatite compositions containing only Ba
The FTIR spectra of s-HAp and BaHAp are presented above in Figure 29. Barring an overall shift of the BaHAp absorption bands to smaller wavenumbers, this spectrum does not differ significantly from that of the s-HAp. However, no absorption band is present to indicate the existence of hydroxyl groups within this structure. One explanation for the bands absence accounts for the massive barium atom interfering with the hydroxyl groups response to IR stimulation. Later XRD results will reveal patterns that are in accordance with a standard pattern provided by JCPDS.

### 3.4 Conclusions

The x-ray diffraction results for the as precipitated calcium apatites were able to reveal that in fact an apatite-like structure had been precipitated. However, the poor crystallinity of these powders prevented the compositions from being fully characterized. FTIR results provided more information and revealed that each composition, regardless of the post precipitation washing, contained a significant amount of carbonate ions. For s-Hap, the carbonates substituted for both the hydroxyl groups and the phosphate groups. In contrast, only the phosphate groups were substituted for in CDHA. These different situations suggest that calcium deficiencies prefer substitution via phosphate groups rather than hydroxyl groups. This makes sense considering the fact that the calcium atoms are directly bonded to the phosphate groups in the structure. If this bond is missing, then the carbonates will exhibit a propensity towards satiating this missing bond.

The absorption band intensities of the phosphate groups for CDHA were
noticeably larger in those compositions not washed after precipitation. This behavior suggests that significant amounts of calcium exist within the system after precipitation has occurred. In each case, regardless of the post precipitation process implemented, the phosphate band intensities for the s-HAp composition were more intense than CDHA’s phosphate bands.

When the CDHA compositions are stabilized with a larger barium atom, many significant structural changes can be detected using XRD and FTIR. Once again, x-ray results suggest that a poorly crystallized apatite precipitated from solution. However, closer examination of the diffraction pattern reveals that the (004) peak has shifted significantly. This peak represented the plane located at \( \frac{1}{4} \) steps along the c-axis of the apatite unit cell. Recalling the apatite unit cell, the Ca(2) atoms are located at these positions. Thus, the observed shift to smaller diffraction angles suggests that the barium atoms are occupying the Ca(2) sites.

The barium atoms also have a tendency to destroy the apatite structure as their concentration is increased within the apatite unit cell. This was first noticed by the appearance of a new peak at 857 cm\(^{-1}\). This peak is not normally observed in compositions having an apatite structure. At the same time, as the barium concentration increases, the resolution between the \( \nu_3 \) phosphate bands decreases while the band breadth increases. Increasing barium concentration also increases the amount of carbonate that substitutes for phosphates within the structure. Lastly, the larger barium
ions tend to inhibit the vibrational response of the hydroxyl groups because they are surrounded by cations larger than the calcium cations of s-HAp and CDHA.

This information, specifically that concerning the carbonate ions is important when considering the development of new phases upon exposure to elevated temperatures. The as precipitated information is also important when considering the precipitation reaction itself. Based upon these results, significant carbonate concentration exists within the solution during precipitation. After precipitation, excess calcium exists. This excess calcium will also play a significant role in defining how the compositions behave at elevated temperatures.
4. Sintering and Densification

The x-ray diffraction and FTIR results of the apatites studied in chapter 3 revealed a material whose microstructure and chemistry is poorly developed. Furthermore, the mechanical strength of the as precipitated, “green”, uniaxially pressed compositions is unsatisfactory. In an effort to develop the chemistry microstructure and mechanical properties, the apatite compositions needed to experience several post precipitation processing steps. This chapter is concerned with describing those post precipitation-processing steps, and the subsequent x-ray diffraction and FTIR results concerning the structure and bonding that develop. The information acquired from this study will be used in conjunction with the as-precipitated results to provide an understanding of how the precipitation processing conditions affect the overall properties of the final fired body.

4.1 Driving Force for Sintering

As pointed out above, there are many reasons why the sintering process is necessary. However, an understanding of the actual sintering process is necessary for interpreting the resultant properties of a sintered body. This small introduction provides an overall description of the sintering driving forces in conjunction with mechanisms that allow for sintering to occur. Densification and coarsening are also briefly discussed.

The driving force for sintering as described by Rahaman [69] is the lowering of the systems free energy. Several driving forces including surface curvature, applied
pressure and chemical reactions all promote a reduction in free energy of the system. Generally, when present, a chemical reaction provides the greatest driving force for sintering. This is followed by the driving force provided by pressure during the heat treatment. Lastly, but most significant in this research is the reduction in surface free energy of the green material during the sintering process.

The reduction in free energy of the system resulting from surface curvature is related directly to the surface energy of the particles. Thus, those particles having the greatest free energy will provide a greater driving force for sintering. In order to increase the free energy of the particles, they are generally ground to increase their surface area. The relationship between surface area and surface energy is described by the following equations:

\[
S_A = 4\pi a^2 N = 3V_m/a
\]
\[
E_s = 3\gamma_{ss}V_m/a
\]

Although no pressure was applied during the sintering process, the green samples were pressed to attain the disc shapes used for characterization. Concurrently, the degree of chemical reactions taking place during the sintering process is thought to be minimal due to the stoichiometric nature of the chemical reactions implemented. However, in order for sintering to occur in polycrystalline materials, matter must be transported via diffusion between adjacent particles.

During the sintering process, matter is transported from regions of higher chemical potential to region of lower chemical potential. Six mechanisms contribute to this type of transport, each of which is depicted in Figure 30. The material transported
via the diffusion mechanisms ultimately results in necking between adjacent particles. As this necking is translated throughout the entire consortium of particles, the overall strength of the system increases.

Accompanied with the strengthening and transport of material is densification of the material. Only mechanisms 4-6 contribute to the densification of the material. Mechanisms 1-3 are also known as nondensifying mechanisms. These mechanisms work to reduce the curvature (high surface area, free energy) of the neck and the rate of densification. Consequently, the overall size of the article decreases. Competing with
the densification process is the coarsening of the microstructure, where the grains and pores grow in size. The coarsening occurs during the entire sintering process, but is predominately observed in the final sintering stages.

Many other factors can be considered when determining an optimum sintering profile for a specific material. However, this thesis does not explore those factors as they are outside of the realm of this research. Although a full sintering study was not performed in this thesis, the results obtained from smaller sintering studies were able to provide some insight into how the apatite structure behaves over a range of temperatures.

4.2 Experimental

Prior to sintering, the mass and dimensions of the individual pellets were measured. This data was used to determine the total shrinkage and density changes sustain as a result of sintering. After the pre-sinter measurements, the pellets were sintered in a basic electrical resistance furnace. To prevent contamination from volatilized components within the refractory brick, the pellets were placed on a washed refractories and covered with virgin crucibles.

The sintering schedule used for each of the pellets consisted of a heating and cooling rate of 25°C per minute. The sintering temperature ranged from 650-1250°C, for the non-washed calcium apatites, and 850-1250°C for the barium apatites. The compositions that experienced a post precipitation washing were only subjected to 1250°C sintering temperature. For each composition 7 hour dwell times were used. The lower
650 C temperature for the non washed apatites was chosen because at this temperature all organics and absorbed water are lost. Concurrently, 850° C was chosen for the barium apatites because at this temperature all phases of hydroxyapatite were fully developed. The optimum temperature, however, was chosen based upon several papers.[54][70][71]

After the pellets were sintered, their mass and dimensions were measured once again. This information was used to determine final density and the overall shrinkage of some of the material. Some of the s-HAp was used to produce larger diameter discs to be used as targets in the IBAD deposition system. This information will be presented in Chapter 5. Finally, the pellets underwent the same XRD and FTIR characterization performed in chapter 3 on the as-precipitated compositions.

4.3 Results and Discussion

4.3.1 Density and Dimensional Changes

Provided in the following figures are plots of density and % shrinkage versus sintering temperature for Non-Washed (NW) s-HAp, NW CDHA, Ca_{0.5}Ba_{0.5}HAp, Ca_{8}Ba_{2}HAp and BaHAp. The densities and % shrinkage of three NW s-HAP and three NW CDHA pellets were averaged together to generate their respective plots shown in Figures 31A and B. The density and % shrinkage for the remaining compositions are shown in Figure 32A and B, respectively. Only two pellets were used to determine the average density and % shrinkage for these compositions. All of the sintering density data is in agreement with the results obtained by Murray et. al.[72].
The average green densities of non-washed s-HAp and CDHA are 1.33 and 1.26 g/cm³, respectively. Upon heat treatment, the s-HAp density immediately begins to increase, while the CDHA densification onset temperature occurs at a larger temperature, 950° C. This is as expected based upon later XRD results which show that around 800-900° C the CDHA composition becomes a biphasic mixture of hydroxyapatite and...
tricalcium phosphate. Thus until this temperature is reached, significant compositional changes are occurring, which prevent immediate densification of the CDHA.

According to Murray [72], the theoretical density of hydroxyapatite is 3.156 g/cm$^3$. The NW s-HAp reached a maximum density of 2.9 g/cm$^3$ at approximately 1125$^\circ$ C. This density is 91% that of the theoretical density. At the same time, the density for the NW CDHA remained less than that of its stoichiometric counterpart for every sintering temperature except 1250$^\circ$ C. Reasons for not attaining theoretical density include the development of agglomerates within the green bodies, which promotes differential sintering. This type of sintering is predisposed for the development of inter-agglomerate voids upon sintering.

The maximum shrinkage was approximately 55% for both non-washed calcium apatite materials. This shrinkage is significant, and is though to be the result of poor initial pressing. While most pressing occurs at approximately 11,000 psi, the pressing performed herein was limited to one-quarter of this amount. If the initial pressure can be increased, and the number of agglomerates decreased then the sintering temperature can be reduced such that the final density might be closer to that of the theoretical.

Although no theoretical density is available for barium-doped apatites, some trends exist that are worth noting. First, the average green densities for Ca$_{9.5}$Ba$_{0.5}$HAp, Ca$_8$Ba$_2$HAp and BaHAp are 1.29, 1.43 and 2.34 g/cm$^3$, respectively. The same trend of increasing density with increasing barium content is also observed upon sintering. This trend is thought to be the result of the heavier barium atom. The densification onset
temperature for Ca$_{9.5}$Ba$_{0.5}$HAp appears to occur at 1000° C, whereas the other compositions have already started to densification at 850° C.

Based upon these findings, increased calcium deficiencies necessitate higher temperatures to initiate densification. At the same time, due to pressure limitation in the compaction stage, a much greater sintering temperature is needed to attain a fully dense material. If the compaction pressure can be increased, less input energy (temperature) will be needed to promote densification. This in turn promotes greater densities via preclusion of pores, which often encountered at high temperatures.

By increasing the barium concentration in the apatite, the green and sintered densities increase. Again, this increase is attributed to the larger mass of the barium atom. Figure 32B also suggests that the onset temperature for shrinkage is comparable to that of the non-washed CDHA. Again, due to non-stoichiometry the shrinkage onset is attributed to the development and growth of phases not within the apatite family. These changes in conjunction with their onset temperature are revealed in section 4.3.2

4.3.2 Sintered Calcium Apatite XRD

Once again, for organizational purposes, the calcium apatites will be considered prior to the barium apatites. The color-coding implemented to distinguish between the compositions in chapter 3 will be followed in this chapter as well. However, for each composition there are a number of different spectra representing the different heat
treatments employed. These heat treatments are labeled on their respective spectra. In an effort to better illustrate the effects of increasing temperature, only a small diffraction angle window will be considered, 30-40° 2θ. Within this window, significant spectral changes occur. The washing experiment has also been included to show how the removal of excess calcium affects the overall XRD patterns.

Shown below in Figure 33 and 34 are the spectra obtained after heat-treating the non-washed s-HAp and CDHA compositions at temperatures ranging from 650-1250 C°. Each pattern is labeled according to the heat treatment implemented. In going from the as-precipitated spectra to between 850 and 950°C, the patterns do not change appreciably. As indicated by the poor intensity and broadening of the diffraction peaks, the crystallites have yet to fully develop. Although no significant structural changes have occurred, many organics and other volatiles are lost within this temperature regime. At the same time, any adsorbed water is also removed.
Figure 33  XRD spectra of non-washed s-HAp sintered at different temperatures
Within the temperature range of 750-950° C the diffraction patterns for the non-washed s-HAp and CDHA, reveal the previously obscured (112) peak at approximately 32.1° 2θ. At the same time, the other peaks indicative of hydroxyapatite becomes sharper and better defined than the as-precipitated patterns. The development of these peaks suggests that their respective crystallites have grown in size and are large enough to be detected using x-ray diffraction techniques.

This temperature range also marks the onset of calcination, where at the solids begin to decompose or react chemically with one other. As seen in Figure 32, the onset of s-HAp calcination is indicated by the development of a small peak at 37.3° 2θ. According to Afshar, [73] this peak is indicative of a biphasic mixture of hydroxyapatite and calcium oxide. The calcium oxide develops via thermal decomposition of the
excessive Ca(OH)$_2$ within non-washed s-HAp composition. To support this supposition, Figure 35 shows the diffraction patterns for non-washed s-HAp sintered at 1050° C, and water washed, and phosphoric acid washed sintered at 1250°C. The 1050° C pattern had to be used because at higher temperatures the CaO phase decreases in intensity such that its presence can not be positively identified. Those washed precipitates do not show any CaO within the system and thus suggest that any excess calcium has been removed upon post-precipitation washings. The presence of excessive calcium in the form of calcium hydroxide is further supported by the systems slightly basic pH just before decantation.

In this same temperature range, the calcium deficient apatites shown in figure 36 give rise to an additional set of peaks at 31.05 and 34.4° 2θ. These peaks are indicative of a biphasic mixture of HAp and β-TCP, which results when Ca$_{10-x}$(HPO$_4$)$_x$(PO$_4$)$_6-x$(OH)$_2-x$ decomposes. The thermal decomposition of CDHA begins with the transformation of the hydrogen phosphate ion into P$_2$O$_7^{4-}$ [74] via:

\[
2\text{HPO}_4^{2-} \rightarrow \text{P}_2\text{O}_7^{4-} + \text{H}_2\text{O}
\]

Within the 750-950°C temperature range, the P$_2$O$_7^{4-}$ transforms into the phosphate ion which in turn yields the TCP phase via:

\[
P_2\text{O}_7^{4-} + 2\text{OH}^- \rightarrow 2\text{PO}_4^{3-} + \text{H}_2\text{O}
\]

\[
\text{Ca}_{10-x}(\text{HPO}_4)_x(\text{PO}_4)_x(\text{OH})_{2-x} \rightarrow (1-x)\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 + 3x\text{Ca}_3(\text{PO}_4)_2 + x\text{H}_2\text{O}
\]

FTIR results will reveal the disappearance of the hydrogen phosphate peak upon heat treatment.
Figure 35  Effects of washing the precipitate

The development of the tricalcium phosphate phase is observed in CDHA regardless of the post precipitation process implemented. Unlike other research, the amount developed herein is significantly less.[35] This might be due to increased carbonate content in these precipitated apatites that do not have as much hydrogen phosphate ion necessary for this reaction to occur.[1] Concurrently, the peaks for the non-washed CDHA composition are much more defined than the other washed compositions. This finding suggests that the excess calcium atoms will occupy the calcium deficient sites such that the crystallinity of material is comparable to that of s-HAp. At the same time, the likelihood of developing TCP decreases as calcium deficient apatite structure is stabilized with the excess calcium that remains in after precipitation. If the excess calcium atoms occupy the deficient sites, the lattice parameters should be similar to those of is stoichiometric counterpart. In fact, the non-washed CDHA peaks
appear to be shifted closer to equivalent peaks of the washed s-HAp. However, more work is needed to verify the legitimacy of the observed shifts.

**Figure 36** XRD diffraction patterns showing the effects of washing CDHA apatites.

The amount of non-reacted excess calcium can be back calculated to provide a better understanding of the precipitation reaction such that this problem can be eliminated and or used advantageously. If the amount of calcium rejected by the system can be determined consistently, under the same precipitation parameters, a better understanding of the apatites ability to maintain stoichiometry might be achieved. This would also provide a better understanding of the apatites propensity towards accepting dopant ions. Further studies are warranted to investigate the presence of excess calcium within the non-washed precipitates.
As the temperature increases from 650-1250° C, both compositions exhibit an increased crystallinity as noted by the increase in peak intensity and decrease in peak breadth. However, these effects are much more outstanding for s-HAp than CDHA; thus suggesting calcium deficiencies result in decreased crystallinity. The increase in crystallinity is also accompanied by an increase in the materials thermal expansion. This behavior is indicated by peaks shifts towards smaller diffraction angles. For s-HAp, the peaks shift to smaller diffraction angles, until approximately 1150° C. Coincidentally, a significant decrease in the peak intensity for calcium oxide occurs at this temperature. After 1150° C, the peaks shift to larger diffraction angles, and the peak intensity decreases. This decrease in peak intensity has been attributed to hydroxyl losses.[75][76]

This aforementioned shift might be the result of the apatite structure compensating for the loss of calcium oxide. More work is needed to correlate the presence of calcium oxide with changes in the apatite structure. One proposed experiment would investigate calcium hydroxide’s ability to react with carbon dioxide and form calcium carbonate. If this occurs, and the excess calcium is in the form of Ca(OH)$_2$, the apatite may contain less carbonate as it reacts with the calcium hydroxide. The resultant calcium carbonate, when heated will transform into Calcium oxide. At greater temperatures, this calcium oxide might be incorporated back into the apatite structure, and cause the apatite peaks to shift.

The peaks of CDHA also shift to smaller diffraction angles, but reverse direction at a lower temperature than s-HAp. This reversal occurs between 850 and 950° C,
temperature range at which the TCP phase becomes more noticeable. Between 1150 and 1250° C the shifting reverses as the peaks shift to smaller diffraction angles. This was also observed in the s-HAp composition. However, unlike s-HAp, the CDHA contains TCP, which has two polymorphs. The first is the beta TCP observed herein, while the second is the alpha TCP phase generally observed at temperatures greater than 1200° C. Thus, the CDHA peak shifts observed at elevated temperatures might be the result of the beta TCP transforming into alpha TCP. Another proposed transformation considers the decomposition of hydroxyapatite into the alpha phase via:

\[ \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 \rightarrow (\alpha)2\text{Ca}_3(\text{PO}_4)_2 + \text{Ca}_4\text{P}_2\text{O}_9 + \text{H}_2\text{O} \]

This is unlikely to have occurred in these experiments, as the \( \text{Ca}_4\text{P}_2\text{O}_9 \) phase did not show up in any of the XRD patterns.

These results suggest that when the calcium apatite compositions are sintered, they exhibit a slight thermal expansion as indicated by the peak shifting to smaller diffraction angles. At the same time, increased temperatures increase the crystallinity of the compositions. This increase in crystallinity was more pronounced for the s-HAp than CDHA. The presence of excess calcium was also evidenced in small experiment that investigated the effects of sintering washed and non-washed apatite compositions. This same experiment also showed that less TCP forms when non-washed CDHA is sintered. Again, this is a direct result of excess calcium within the system. More studies are needed to determine how the presence and evolution of carbonate ions within the system effects end compositions.
4.3.3 Barium Apatites

The heat treatments employed in this study are a manifestation of the results obtained from the calcium apatites. Specifically, the onset sintering temperature of 850°C for the calcium apatites was used as the initial temperature for studying the barium apatites. Four additional heat treatments at 950, 1050, 1150 and 1250°C were also implemented. However, diffraction patterns of the Ca$_9$Ba$_1$HAp samples fired at 1150 and 1250°C were not investigated. Each diffraction pattern is labeled according to the temperature at which the respective sample was fired. The same color-coding used in the discussion of the as precipitated barium apatites is also used here to prevent confusion. Discussions will proceed from smallest to largest atomic percentage of barium substituted into the apatite structure. These patterns will be compared to the diffraction pattern generated for s-HAp composition sintered at 1050°C.

The diffraction patterns generated for the Ca$_{9.5}$Ba$_{0.5}$HAp composition fired at different temperatures are seen below in Figure 37. As the sintering temperature increases the diffraction pattern does not differ significantly from that of a purely calcium stoichiometric hydroxyapatite. In fact, all of the peaks that allude to the presence of hydroxyapatite appear in the composition containing 5 atom% barium. However, new peaks emerge at the following 2θ locations: 28-29° and 40-45°. Such developments are indicative of a biphasic composition of hydroxyapatite and some barium-phosphate or barium-calcium-phosphate amalgamation. At the same time, the intensities of the peaks occurring between 50-55° have also changed. This same region, in the patterns generated
for the as precipitated barium compositions, also demonstrates noteworthy behavior. Specifically, the considerable shifts of the 004 peak to smaller 2θ values suggested that the bariums were substituting for the Ca(2) atoms along the c-axis. Thus, the changes in the intensity of the peaks within this region suggest that the barium atoms exhibit a propensity for the Ca(2) sites as suggested by others.[1][25][40]

The presence of new peaks and diminishment of expected apatite peaks also supports the work of Bigi who found that the actual amount of barium accepted by the apatite structure is far less than the amount predicted by the chemical equations. This is further supported by considering Figures 38 and 39 wherein the diffraction patterns for the Ca₉Ba₁HAp and Ca₈Ba₂HAp compositions, fired at different temperatures, are presented. The pattern generated for Ca₉Ba₁HAp fired at 850° retains some semblance to that of stoichiometric hydroxyapatite. Significant changes have also taken place in those peaks at larger 2θ values, 50-55° 2θ, wherein the 004 peak is located. Barring a couple of new peaks between 30 and 35° 2θ, the remaining peaks do not differ significantly from those observed for hydroxyapatite. This behavior suggests that the bariums have a more pronounced effect on those planes of atoms at large 2θ values, whose d-spacings are much smaller. The 004 peak is within this region, and such behavior makes sense from a geometric standpoint.
At temperatures between 850 and 950° C the 211 peak, found in hydroxyapatite and in the Ca\textsubscript{9}Ba\textsubscript{1}HAp composition, begins to divide into two new peaks. As seen in Figure 38, the same degradation is observed for the Ca\textsubscript{8}Ba\textsubscript{2}HAp composition fired at the same temperature. However, the peaks at larger 2θ values exhibit a greater degree of degradation than the equivalent peaks for compositions containing less barium, and fired at the same temperature. As the sintering temperature increase from 950 to 1250° C, the apatite structure can no longer be distinguished from the new peaks that emerge as the barium deteriorates the apatite structure.
The diffraction patterns for the barium apatite composition fired at 850, 950, 1050, 1150 and 1250° C is presented in Figure 40. Unlike the previous diffraction patterns of the compositions that contained both barium and calcium, these patterns are
much more uniform with increasing sintering temperature. The only change observed occurs in the peak located around 47° 2θ. This peak begins to split at a temperature below 850° C, while definitive separation occurs between 950 and 1050° C.

The diffraction pattern for BaHAp sintered at 1250° C has also been compared with the standard pattern generated by NIST. This comparison is seen in Figure 41. The previously observed peak splitting should yield three new peaks when the structure is fully developed. However, only two peaks are observed. The JCPDS pattern also shows several other peaks that should be present, but are not. Such observations suggest that the 1250° C sintering temperature is not high enough to yield the fully developed structure.
obtained by JCPDS. This hypothesis could not be tested because the furnace was unable to achieve higher temperature.

![Heat Treated BaHAp](image)

**Figure 41** Heat treated barium apatite indexed with respect the JCPDS standard [55]

Based upon these results, the most that can be said for sintered the calcium-bariumsapatites is that only small quantities barium can be incorporated in the structure via precipitation. In fact, the results suggests that even at 5 atom % Barium, the apatite structure is compromised. However, this same composition retained the (004) peak discussed earlier. The same peak shifting was also retained and suggests that the bariums are locked in the Ca(2) positions of the apatite structure.
4.3.4 Sintered Calcium Apatite FTIR

All non-washed, water washed and phosphoric acid washed calcium apatites sintered at 1250° C were studied using FTIR. The spectra of each composition have been analyzed to understand the effects that post precipitation washings and deviations from stoichiometry, resulting from intentional calcium deficiencies, have on the final structure of the fully sintered apatite compositions. For simplicity, the three spectra generated for both s-HAp and CDHA are presented together the following figures. Once again, each spectrum is divided into several other spectra to help view the details of the absorption bands. A new color-coding has been implemented to distinguish between the spectra generated for each post precipitation process.

The FTIR spectra ranging from 800-1250 cm\(^{-1}\), for sintered s-HAp and CDHA, are shown in Figures 42 and 43, respectively. Although these spectra reveal many similar absorption bands, those of s-HAp are much more intense than those of CDHA. Specifically, the removal of 10 atom% calcium from the structure, in conjunction with sintering at elevated temperatures, reduces the absorption band intensities by one-half and significantly increases their bandwidth. Specific bands are investigated in the following paragraphs to help explain the bonding changes that occur within the sintered apatite structure.

The bands between 875 and 880 cm\(^{-1}\) in the as precipitated calcium apatites are no longer present in the sintered spectra. For s-HAp, the absence of these bands indicates that all of the carbonate has been removed from the structure. At the same time, for
CDHA, the absence of this band indicates that both carbonate and hydrogen phosphate ions are no longer present.

The absorption band for the P-O symmetric stretching mode of the phosphates, previously observed at 960 cm\(^{-1}\), is still present within these spectra. However, the intensity of this band is lower for CDHA than s-HAp. This behavior is also mimicked by triply degenerate asymmetric stretching mode of the P-O band occurring at 1049 and 1093 cm\(^{-1}\). Moreover, unlike the spectra for the as-precipitated compositions, the triply degenerate phosphate bands that were observed between 1035 and 1045 have transformed into one obvious band at 1049 cm\(^{-1}\) after sintering. The 1049 and 1093 absorption bands are those expected to be observed after sintering.[1]

![Figure 42 FTIR spectra for the washed and non washed s-HAp compositions showing the phosphate bands indicative of the apatite structure](image-url)
The aforementioned changes are indicative of two phosphate-bonding events. The first event, which results in the observed decreased peak intensity and broadening, is a direct result of the biphasic mixture of TCP and s-HAp that develops when CDHA is sintered. Secondly, the transformation of the as precipitated phosphate bands between 1035 and 1045 into one lone band at 1049 cm$^{-1}$ is evidence of the phosphate bonding environment expected for sintered hydroxyapatite.[57] This change in bonding environment might be attributed to the loss of carbonate ions within the structure. Upon their evolution, the normal vibrational modes expected of phosphate groups in an apatite structure will appear.

**Figure 43** FTIR spectra for the washed and non washed CDHA composition showing the phosphate bands indicative of the apatite structure
Accompanying the manifestation of the singular phosphate band at 1049 cm\(^{-1}\) is the disappearance of the \(\nu_1\) carbonate band previously observed 1060 cm\(^{-1}\) in the as-precipitated apatites. Recalling the as-precipitated FTIR results, the presence of this band suggests that the carbonate ion is located in a crystal lattice position having a point-group symmetry lower than \(D_{3h}\). This relationship suggests that the carbonate ions do not affect the hydroxyl groups in the apatite structure, only the phosphate groups. The carbonate loss is further supported by the absence of their respective absorption bands that normally appear between 1400-1550 cm\(^{-1}\).

The last segment of the calcium apatite spectra comprises the absorption band for the hydroxyl group at 3573 cm\(^{-1}\). Within the non-washed s-HAp spectra, a broadened hump extends from 3200-3500 cm\(^{-1}\). This is likely the result of water inclusion during the pressing of the KBr pellets. All of the other samples no longer have this hump because the water has evaporated. The decreased intensity hydroxyl absorption band within the sintered CDHA samples substantiates the claim that a biphasic mixture of s-HAp and TCP develops at elevated temperatures. A decrease in hydroxyl intensity is expected as the concentration of hydroxyapatite decreases to accommodate the development of TCP. What is more, the presence of this peak after exposure to such high temperatures, regardless of the composition, confirms that the hydroxyl group is in fact an integral part of the apatite structure. Otherwise, the peak would have disappeared along with the water.
Figure 44 FTIR spectra for the washed and non washed s-HAp compositions showing the hydroxyl groups in the apatite structure

Figure 45 FTIR spectra for the washed and non washed CDHA compositions showing the hydroxyl groups in the apatite structure

The FTIR spectra of calcium apatites reveal a significant change in the bonding environments when the material is sintered. Specifically, all of the carbonate has been driven off at the elevated temperatures. This event might be responsible for the
development of the phosphate vibrational modes expected for a purely s-HAp. The broadening observed for the CDHA samples is a result of the biphasic mixture providing combinations and of the phosphate groups for TCP and HAp. Peak intensities for the hydroxyl groups of s-HAp are greater than CDHA. This is a direct result of less HAp within the biphasic mixture.

4.3.5 Sintered Barium Apatite FTIR

To better understand the effects of sintering has on an apatite whose structure is doped with a cation larger than calcium; the FTIR results obtained for the barium-sintered apatites are presented in conjunction with the FTIR spectra of the non-washed sintered s-HAp. The sintered s-HAp data will act as a standard from which conclusions concerning the bonding environments within the sintered barium apatite may be made. This information will supplement comparisons made between the individual compositions to understand how the bonding environments are effected by increasing barium concentration. Lastly, the pure barium hydroxyapatite will be compared and contrasted to its non-washed s-HAp counterpart. The hydroxyl group will be emphasized to determine why its absorption band is not present in the as-precipitated apatites, but is evident after sintering. Once again, the FTIR spectra have been divided into sections to better visualize all of the absorption bands.
The FTIR spectra presented in Figure 46 highlights the region containing the phosphate absorption bands. For each composition, regardless of the cation substitution, the same phosphate absorption bands appear. However, their location, with respect to the non-washed s-HAp spectra, is consistently shifted to smaller vibrational frequencies. At the same time, the intensity and breadth of these absorption bands decreases as the mass and concentration of the dopant cation increases.

The $\nu_3$ and $\nu_1$ vibrational modes of the phosphate ion in s-HAp that occur at 1094, 1050 and 962 cm$^{-1}$, shift to smaller vibrational frequencies as the percentage of barium substituting for calcium cations increases. However, at 5 atom% barium
(Ca$_{0.5}$Ba$_{0.5}$HAp), there appears to be two $\nu_1$ modes. The first appears at 962 cm$^{-1}$, while the second is located at 939 cm$^{-1}$. As the percentage of barium increases the peak at 962 cm$^{-1}$ disappears, leaving only the absorption band at 939 cm$^{-1}$. This is a fair indication that the expected apatite phase has been destroyed.

According to B.O. Fowler [77], the FTIR spectra for apatites having mixed cation compositions will exhibit vibrational frequencies intermediate to the two extreme apatites. For example, according to the plot provided by Fowler in Figure 47, if the apatite structure contains both barium and calcium cations, such that the a-axis lattice dimension is 10 Angstroms, then the $\nu_1$ phosphate mode will be shifted to approximately 940 cm$^{-1}$. However, the FTIR spectra for Ca$_{0.5}$Ba$_{0.5}$HAp exhibits both the absorption band at 962 cm$^{-1}$, normally associated with s-HAp, and the absorption band at 940 cm$^{-1}$.
The appearance of both peaks suggests that a biphasic mixture of Ca-Ba apatite and some other barium component seems to have developed. This supposition is supported by the XRD data for Ca$_{0.5}$Ba$_{0.5}$HAp, which shows the basic apatite structure of a pure s-HAp in conjunction with minor additional peaks that are in close proximity of peak positions observed for BaHAp. One reason for observing the biphasic mixture relates to the synthesis techniques implemented. Fowler implemented solid state reactions at elevated temperatures to obtain mixed cationic apatites, while this work was performed via wet precipitation.

As the barium concentration increases, the band at 962 cm$^{-1}$ disappears, leaving only the band at ~940 cm$^{-1}$. This development is more in accordance with the mixed
cationic state observed by B.O. Fowler. However, the x-ray diffraction results for these compositions do not suggest that an apatite structure exists. More work is needed to determine the phases that develop upon when these compositions are sintered.

As these changes occur, the $\nu_3$ vibrational modes shift from the s-HAp frequencies at 1094 and 1050 cm$^{-1}$ to 1087 and 1045 cm$^{-1}$, respectively. Accompanying these shifts are decreased peak intensities and increased peak breadth. According to Fowler, these events are attributed to the decreased anion-anion repulsion and increased anion-anion separation, which is caused by the increasing concentration of the larger barium cation. Although the absorption band positions observed by Fowler are slightly greater than those presented here, the trend of decreasing phosphate vibrational frequency is observed upon increasing barium content.

In each of the compositions, no carbonate ions could be identified. At the same time, as the barium concentration increased from 5 to 20 atoms % barium, no hydroxyl groups could be observed. However, the FTIR spectrum of Ca9.5Ba0.5HAp, shown in Figure 49, reveals the presence of hydroxyls at 3573 cm$^{-1}$. Had the barium been incorporated into the structure, or if a biphasic mixture developed, this band would have shifted to a larger frequency closer to 3606 cm$^{-1}$.
The spectrum for pure barium apatite has been divided into three separate spectra shown in Figures 49, 50 and 51. The s-HAp spectrum has also been provided for comparison. The first figure shows the $\nu_1$ and $\nu_3$ phosphate bands of BaHAp at 933 cm$^{-1}$, 1017 and 1052, respectively. Fowler reported the same absorption frequencies for the pure barium apatite. The small region before the $\nu_1$ mode at 933 cm$^{-1}$ is likely the result of poor background subtraction.
Figure 49 FTIR spectra showing the phosphate absorption bands in sintered BaHAp

Figure 50 reveals significant carbonate incorporation within the apatite structure. These absorption bands have also been shifted to smaller frequencies. Moreover, they suggest that the carbonates substitute for the phosphate ions within the apatite. Thus, this composition can be considered to be an A-type carbonated apatite.

Lastly, Figure 51 shows the hydroxyl region of the FTIR spectra. At 3610 cm\(^{-1}\) a very faint disturbance is observed. Until more work is be performed, this band is assumed to be related to the hydroxyl group. Fowler suggests that smaller electronegativity of barium, and thus less electron-withdrawing power, will contribute to the diminishment of the hydroxyl band. At the same time, Fowler also observed an increase in band position for the hydroxyl group. This is in contrast to the rest of the ionic species that move to smaller frequencies upon barium substitution.
Results similar to Bigi[25] and Fowler[61] suggest that to some degree the apatite structure remains for the Ca$_{9.3}$Ba$_{0.5}$HAp composition. However, this structure is
compromised as the percentage of barium increases beyond 5 atom%. As the Ba concentration increases the absorption bands intensities decrease and increase in breadth. Concurrently, small shifts in peak positions are also observed. The absence of hydroxyl groups in those compositions having greater than 5 atom% barium suggests that in fact the structure is unable to accommodate that much doping via wet precipitation.

4.4 Conclusions

Sintering of the apatite compositions evoked increases in crystallinity and density of the fired wares. X-ray results of the sintered calcium apatite compositions were able to confirm the presence of excess calcium atoms within those apatites that did not experience a post precipitation washing. This was evidenced by the appearance of CaO in the spectra for s-HAp. At the same time, each sintered CDHA composition revealed the development of TCP around 800° C. The presence of this phase was less when the precipitate was not washed after precipitation. This suggests that the excess calcium assumes the available Ca(2) sites to prevent the formation of TCP.

Development of the TCP phase is also inhibited in those washed samples. This has been attributed to the increased amount of carbonate, seen in Figure 22, in those precipitates washed after the reaction has occurred. The substitution of the carbonate ion for the phosphate groups might prevent the development of the hydrogen phosphate ion required for the development of the TCP. Thus, both excess calcium and carbonate, work to diminish the development of TCP phase at elevated temperature. This behavior
suggests that the apatite structure exhibits a strong propensity towards remaining stoichiometric.

The development of the biphasic mixture of TCP and HAp is evidenced in both the XRD pattern and FTIR patterns. More specifically, the FTIR results show a decreased in absorption band intensity for the hydroxyl groups of sintered CDHA. This is related to the presence of less HAp and more TCP, which contains no hydroxyl groups.

Sintering of the barium apatites reveals a complex situation. Above 5 atom%, the normally observed apatite pattern is completely destroyed. At 5 atom% XRD and FTIR results suggest that the apatite phase is still present, but is beginning to lose its identity. The presence of the (004) diffraction peak and its shift from the equivalent peak for s-HAp suggests that the bariums are in fact interacting and occupying the Ca(2) sites. Finally, the FTIR results reveal that there are not hydroxyl groups in the compositions have more than 5 atoms % barium. Thus, the upper limit of barium that can be incorporated into the apatite structure is around 5 atom%. This is a little less than what other groups report [1], and might be attributed once again to the carbonate ions within the as-precipitated compositions. Future studies are needed to confirm that the carbonate ions are preventing barium incorporations into the structure.
5. Ion Beam Assisted Deposition

The preceding compositional investigation is concluded with a brief study that utilizes the previously synthesized stoichiometric hydroxyapatite composition as target material for deposition of thin film hydroxyapatite on silicon substrates. Although succinct, the following study yields results that provide a significant foundation from which further studies may be born. Concurrently the previous compositional studies provide a knowledge base that can be applied to help understand the effects seen when the material is deposited as a thin film.

A similar study performed by B. Thomas [78] utilized a non-sintered hydroxyapatite target purchased from Cerac, Inc. Many of the same parameters including substrate temperature, beam voltages and deposition times remained the same. However, the films in this study were annealed in the presences of water vapor after the deposition occurred. Some images and compositional data acquired by Thomas will be referenced to supplement the research in this thesis. Specifically, data relating to the Ca/P ratio with respect to deposition time will be used to provide an approximation of this ratio for the thin films deposited herein.

The following results provide new XRD and FTIR results that not only help to support the previous work, but also demonstrate the ability to obtain thin films whose XRD patterns look strikingly similar to those obtained for the bulk target material. Unlike other work that implemented a similar annealing process, [14][79] the films in this study do not show any cracking. As discussed earlier, with respect to implants,
mechanical integrity is crucial when used in vitro. Most importantly, because the XRD patterns and FTIR results reveal that compositions and structure of these films are more analogous to their bulk precursor, the techniques implemented herein may be used to help tailor future thin film compositions. These results subsequently provide new insight into the events that occur when hydroxyapatite is used in conjunction with ion beam assisted deposition.

5.1 Experimental

The targets used in the deposition process were fabricated following the same procedure outlined in the aforementioned sintering studies. Each target was approximately 2-inches in diameter and 1/4-inch thick. A highly viscous epoxy resin, manufactured by Varian, called Torr Seal® was used to affix the targets to a 6.5” aluminum backing plate in the approximate area where the ion beam from the 8cm source would impinge. Sputtering of the backing plate was prevented by covering the exposed aluminum surface with an amalgamation of Torr Seal and sintered hydroxyapatite powder. To prevent any chance of sputtering the Torr Seal, an additional layer of hydroxyapatite powder was forced into viscous epoxy before it hardened.

Attempts were made to enlarge the size of the targets to mask the backing plate without having to use the epoxy. Large 6” dies were machined to create larger targets, but these proved too cumbersome and resulted in a large crack that extended across the diameter of the target. However, when the remaining halves were sintered, only slight
deformations were observed. The development of a sintered target having considerable mechanical integrity demands an investigation into the pressing method and dies implemented.

The substrates, (100) silicon and (100) oxidized silicon, were then secured to a metal plate that was subsequently secured to a mounting platform within the deposition chamber. This mounting platform was recessed to accommodate three heating elements that provide substrate temperature variability. Once secured, a thermocouple was inserted into the side of the sample holder to provide an approximation of the actual temperature of the samples. The sputtering target was secured within the chamber below the 8cm ion source. The target-substrate arrangement is shown in Figure 52.

Figure 52  Cartoon illustrating the IBAD chamber used for thin film processing
To deposit thin films of the hydroxyapatite, the chamber in which the deposition occurred was first evacuated using a belt driven mechanical pump to approximately 1 mTorr. At this pressure, the mechanical pump was switched from evacuating the chamber to backing the diffusion pump. In this arrangement, the system was pumped on until a base pressure of approximately $5 \times 10^{-7}$ was attained. During evacuation, the substrate temperature is increased incrementally until the desired temperature is met. The shutter is subsequently placed in front of the substrates to prevent deposition from occurring upon activation of the ion beams. The shutter also acts as a thermal barrier and protects the target from exposure to high temperatures prior to deposition.

After the base pressure was attained, a heated water reservoir connected to a Granville-Phillips needle valve, introduced water vapor into the deposition chamber. The amount of water vapor brought into the chamber was measured via changes in the base pressure within the chamber. These changes are indicated in Table X, along with other parameters used for each run. Water is also introduced into the mounting device upon which the target material rests. This helps to cool the target material and prevent thermal shocking.
Once the appropriate chamber pressure was reached with the water vapor, flow controllers were activated to introduce argon into the ion sources and plasma bridge neutralizer. A flow rate of approximately 3 sccm was used for each source. With the gas flowing, and depending upon the amount of outgassing that occurs during the deposition, a base pressure of approximately $2.5 \times 10^{-4}$ Torr was used for each run. This value was adjusted in situ depending upon the occurrence of arcing within the chamber.

Next, the Plasma Bridge Neutralizer (PBN) was activated. Via thermionic emission, electrons are created within the chamber of the PBN. These electrons interact with some of the background argon atoms and create argon ions. However, repulsion
from the net negative cathode forces some electrons to escape through a small orifice in the PBN chamber. If the device is positioned properly within the chamber, the net positive change from the ion beams will draw electrons from the PBN into the ion beam. As a result the beam is neutralized, thus preventing arcing caused by charge build-up within the chamber.

Deposition transpired upon activation of the 8cm Kaufman ion source. The first two runs outlined in Table X did not enlist the use of the 3 cm source, which normally provides ions for substrate bombardment. For deposition to occur, each ion source relies on a tungsten filament to produce electrons via thermionic emission. This is illustrated in Figure 53 below and denoted by the number (2). These electrons subsequently ionize the argon atoms \((3)\rightarrow(9)\) within source. To supplement the ionization process a potential difference is established between the filament and anode to remove more electrons. As a result, a plasma is established within the ionization chamber. Permanent magnets work to contain the plasma within the chamber throughout the run.
Removal of the argon atoms from the source’s chamber occurs via a set of graphitic grids known as ion optics. This setup is illustrated in Figure 54, while Figure 53 shows the progression of the ions through the grids. The first grid encountered by the argon ions (6) is known as the screen grid, which aligns the ions into small beamlets. The ions within the beamlets are subsequently attracted to a negatively biased accelerator grid and extracted from the ionization chamber (7). The concavity of the grids produces a single ion beam from the many beamlets. At the same time, the grids focus the ion beam into points such that the ion beam cross section is reduced at the target. This in turn reduces sputtering of material adjacent to the target such as the backing plate and chamber walls that would otherwise pose a contamination risk.
Generally, a plasma is “sparked” first within 8cm source followed by the 3cm source. This is followed by extraction of the beam by biasing the ion optics. Having extracted a beam, the Quartz Crystal Monitor (QCM) is zeroed for measuring film thickness. Next, the shutter is moved such that the substrate is in direct line of sight with the target material being bombarded with ions. During the deposition, voltages are continuously monitored for the beam, accelerator, discharge and cathode. Chamber pressure, PBN settings and water temperature were also monitored.

Barring those samples labeled A1.1.3, A1.1.4 and A3.1.1, the procedure outlined above was followed for every run. The same procedure was used for the latter two samples, except for the fact that only the 8cm source was running. However, the substrates used to obtain the former samples were first heated to 610°C and subsequently exposed to the 3cm source. In conjunction with the 3cm source, the water source was also operated in an effort to implant hydroxyl groups within the substrate prior to

Figure 54  This illustration shows the effects of the accelerator grids on the argon ions
deposition. After approximately one half of an hour later the 8cm source was activated, and the deposition proceeded as outline above.

After each run, barring those designated A.2.1.3 and A.3.1.1, the substrate heater was turned off and the samples were allowed to cool quickly. The samples from runs A2.1.3 and A.3.1.1 were cooled slowly to allow time to anneal. However, during the cooling of samples A.3.1.1 the 3cm and water sources remained activated in an effort to prevent any hydroxyls, which might be in the film, from evaporating. Prior to performing the A.3.1.1 run, FTIR results did not indicate the presence of hydroxyls. Thus, the 3cm source pre deposition treatment was implemented to incorporate the hydroxyls back into the structure. This dilemma will be discussed further in the results section.

Each sample also underwent two annealing runs that occurred in the presence of water vapor at 800° C and 1000° C inside a tube furnace provided by Dr. Muth. The purpose for introducing water was to prevent the hydroxyls from volatilizing out of the films during the anneal. Once the annealing temperature was reached, the samples remained at this temperature for about one hour. The samples were slowly cooled to prevent thermal shocking. These samples, in conjunction with the as-precipitated samples, were then studied using FTIR and XRD techniques.
5.2 Results and Discussion

5.2.1 XRD Results and Discussion

The same x-ray diffractometer used to scan the bulk apatite compositions was also used to examine the thin films. Each sample was scanned every 0.005° over 20-40° 2θ. The entire scan took 15 minutes; therefore, the dwell time at each step was approximately 0.11s. The diffraction patterns were subsequently compared to those obtained for bulk hydroxyapatite to confirm the presence of hydroxyapatite and identify any new phases that may have developed.

Figure 55 illustrates the diffraction pattern obtained for all of the as deposited films. The signature hump of an amorphous material appears for all non-annealed films deposited between 650 and 690° C. This finding is in agreement with the findings of B. Thomas.[78] Due to limitations of the substrate heater, higher temperatures could not be attained to verify the crystalline results obtained by B. Thomas shown in Figure 56. This diffraction pattern was obtained by heating the substrate to 700° C during the deposition run.
Figure 55  Profile of the as deposited HAp films

Figure 56  Figure taken from B. Thomas [78] showing the effects of HA thin film deposition using substrate temperature in excess of 700°C
The lack of crystallinity provided the impetus for annealing the as deposited samples at 850° C. At these temperatures, the bulk samples exhibited a recognizable difference in crystallinity compared to samples sintered at lower temperatures. Thus, annealing of the thin films was chosen to take place at this temperature in hopes of evoking the crystallinity and peaks definitive of hydroxyapatite.

At elevated temperatures and in the presence of water vapor, thin films deposited on Si and oxidized Si, from runs A212, A311 and A312, yielded diffraction patterns that are in agreement with those patterns acquiesced from bulk hydroxyapatite. Figure 57 shows the six thin film XRD patterns in coincidence with the characteristic peak positions and relative intensities for stoichiometric hydroxyapatite. For the most part the patterns look similar to one another. The observed peak intensity differences are considered the result of longer deposition times. This allows more material to be deposited, which becomes easier to detect using XRD.
Although these patterns look similar, small discrepancies arise with respect to peak positions. Specifically, only those samples from the A311 run showed peak positions that align perfectly with equivalent peak positions for bulk hydroxyapatite. This is better seen in Figure 58. Before deposition, the substrates from this run were exposed to the 3 cm source for approximately one half of an hour. As a result, any pre-existing oxide layer on the surface of the substrates was removed. Concurrently, this step also created nucleation sites on the oriented silicon surface, which thus provides a more ordered surface on which the hydroxyapatite can grow. Compared to the cracked films from runs A211 and A312, the pre-sputter etch might also be responsible for the enhanced mechanical integrity of the A311 films.
The other samples, A211 and A312, were not exposed to the 3cm source prior to deposition. As a result, the surface encountered by the sputtered hydroxyapatite species was less ordered. This ordering deficiency produces the noticeable peak shift of the A212 and A312 diffraction patterns seen in Figure 57. Considering Figure 14 from chapter 3, this shift may signify strain within the film structure. Such strain is subsequently related to the non-preferential growth of the hydroxyapatite film on the amorphous oxidized silicon surface.

![Thin Film XRD (Annealed 850C)](image)

**Figure 58** XRD patterns of those films whose substrates were exposed to a pre-sputter etch. More diffraction lines are aligned with the standard
5.2.2 FTIR Results and Discussion

Characterization using FTIR is necessary to understand the bonding environments of the sputtered hydroxyapatite species within the thin films. Subsequently, the thin film bonding environments provide a basic understanding of the sputtering process, and help illustrate the erosion of the bulk hydroxyapatite species. Provided below is a brief description of the FTIR spectra obtained for the non-annealed and annealed samples from runs A212, A311 and A.312. All of the spectra were obtained in transmission mode.

The FTIR spectra for the non-annealed thin films deposited on Si, are shown in Figures 59 A and B from 800-1800 cm\(^{-1}\) and 1800-4000 cm\(^{-1}\), respectively. Also plotted is the FTIR spectrum for non-washed bulk s-HAp; which has a composition comparable to the target material. The bands that appear between 1000 and 1040 cm\(^{-1}\) are the result of phosphate groups within the thin films. However, unlike the bulk composition, the thin film phosphate bands are much broader. The broadening of these bands and their proximity to equivalent bands in the bulk suggest that the bonding environment is similar, but not exact. At the other end of the spectrum shown in Figure 59B, small disturbances around 3745 cm\(^{-1}\) indicate the presence of hydroxyl groups. However, these groups are associated with Ca(OH)\(_2\). Normally, the hydroxyls in hydroxyapatite appear at 3573 cm\(^{-1}\). No FTIR spectra were obtained for the films deposited on oxidized silicon due to its inability to transmit within the range of wavenumbers investigated.
Figure 59  FTIR spectra of the as deposited films on Si showing the absorption bands for A. phosphate and B. hydroxyl groups

Such findings suggest that the non-annealed films are not hydroxyapatite, but rather some type of calcium phosphate salt. Although the hydroxyl bands indicative of hydroxyapatite are absent, the similarities of the phosphate bands to those in the bulk suggest that a similar bonding environment in developed in thin films. The next section will show how this environment changes to accommodate hydroxyl groups when subject to elevated temperatures.

The FTIR spectra of the films annealed at 850 C in the presence of water are shown in Figures 60 A and B. Figure 60 A highlights the region between 800 and 1800 cm$^{-1}$ where the phosphate groups are normally observed. Due to the high annealing temperatures in ambient atmospheric conditions, the silicon was oxidized. As a result, the transmission of IR within this range of wavenumbers was significantly hindered.
At larger wavenumbers, the samples were able to transmit IR. Hydrocarbon bands appearing between 2000 and 3000 cm\(^{-1}\) are attributed to sputtering of the Torr Seal covering the backing plate and surrounding the target. Concurrently, the same hydroxyl band observed at 3740 cm\(^{-1}\) in the non-annealed samples also appears in the annealed samples. At the same time, a new hydroxyl peak at 3573 cm\(^{-1}\) emerges for the A212 and A311 thin films. The presence of this peak suggests that the annealed thin films possess hydroxyl groups whose bonding environment emulates that of its corresponding bulk composition. No peak was observed for the A312 groups of films.

Several factors may contribute to the absence of those hydroxyls, associated with hydroxyapatite, in the A312 films. First, these films were deposited in the presence of less water vapor than the samples of runs A211 and A311. However, this factor can be eliminated because similar hydroxyl groups were observed for all films prior to annealing. The presence of the hydroxyapatite hydroxyl in runs A211 and A311 is likely associated with the pre annealing bonding environment within the thin film species.
More specifically, the lower deposition temperature of run A211 along with the pre sputter etch of run A311 may provide two different means for achieving a bonding environment that can accommodate hydroxyl ions into positions similar to those found in the bulk.

5.3 Conclusions

The results from the XRD and FTIR characterization suggest that a calcium phosphate material has been grown on (100) silicon and oxidized silicon substrates. The XRD results revealed an amorphous film was deposited on the silicon substrates. Subsequent annealing at 850°C in the presence of water showed an increase in crystallinity of the films. This increase was more pronounced in those films deposited on silicon. Such difference rose suspicions that the oxide layer influences the growth of the film. Those peaks deposited on oxidized silicon were also observed to shift to larger diffraction angles. Intrinsic strain is suspected to be the cause of this shifting.

For those substrates that were subjected to a pre deposition etch, the diffraction peaks indicative of HAp were observed to coincide with equivalent peak position for bulk HAp. At the same time, these peaks were more intense than those films deposited on oxidized silicon. The FTIR results reveal phosphate-bonding environments that are similar to those observed in the bulk. However, only those runs deposited on etched substrates or deposited at a lower substrate temperature, exhibited the hydroxyl peak that defines the hydroxyl-bonding environment observed in bulk s-HAp.
To summarize, the discussion of the apatite structure in Chapter 2, in conjunction with the experimental observations made for bulk apatites in Chapter 3, were necessary in order to determine how the apatite composition might behave as a thin film. For example, an understanding of the hydroxyapatite’s susceptibility to carbonate ions allowed for their elimination within the thin films. The eradication of carbonates are likely to have contributed to the development of a thin film whose structure resembles the bulk. At the same time, the importance of the hydroxyl group provided an impetus for deposition and annealing in an atmosphere rich with water vapor. Without the water vapor, the formation of hydroxyapatite thin films would not have been possible.

The previous precipitation studies in Chapters 3 and 4 also provide a foundation for future thin film work using IBAD deposition. The possibility of doping the films with barium is now possible with the understanding achieved in the pervious studies. At the same time, the new processing technique may allow even more barium to be incorporated in to the films. Before this and other studies can be completed; however, larger targets need to be developed to prevent contamination from the backing plate and to eliminate the use of Torr Seal, which has also been deposited in the previous films.

**Future Work**

Once the lifetimes of the targets were reached studies using XRD were made in an effort to determine the effects that the ion beam had on the structure, and possibly the formation of new phases. It is important to note that analysis did not take place after
every run. Only after the target was used did any analysis take place. According to the results attained, proposed target compositions were made to accommodate different sputtering rates of the different compositions such that stoichiometric hydroxyapatite might be attained at the substrate.

Other non-rigorous studies investigate some of the electrical properties of the deposited thin films. Specifically, these studies examine the effects of doping the calcium deficient hydroxyapatite with a large Barium cation. In doing so the barium cation will stabilize the hydroxyapatite structure such that stoichiometry is maintained, but the electrical properties will differ from those of stoichiometric hydroxyapatite. These comparisons can only be made if the electrical properties of the HA deposited films are studied as well.
References


[55] PDF Card no. 20-141, ICDD, Newton Square, Pennsylvania, USA.

[56] PDF Card no. 9-432, ICDD, Newton Square, Pennsylvania, USA.


Appendix
Appendix A

Precipitation of Stoichiometric Hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2^*$

The Reaction: $10\text{Ca}(\text{OH})_2 + 6\text{H}_3\text{PO}_4 \rightarrow \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 + 18\text{H}_2\text{O}$

Reaction Modification to obtain 30g of s-HAp

$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ Formula Weight: 1004.62 g/mol

\[30 \text{g} \left( \frac{mol}{1004.62 \text{g}} \right) = 0.0298 \text{mol} \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2\]

\[\frac{1}{x} = 0.0298 \text{mol} \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 \Rightarrow x = 33.48\]

Where $x$ is the scaling factor by which the reaction is divided to obtain 30g of s-HAp

Thus: $0.2986\text{Ca}(\text{OH})_2 + 0.1792\text{H}_3\text{PO}_4 \rightarrow 0.02986\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 + 0.538\text{H}_2\text{O}$

From Afshar: 0.5 M $\text{Ca}(\text{OH})_2$ and 0.3 M $\text{H}_3\text{PO}_4$

For $\text{Ca}(\text{OH})_2$

\[\frac{L}{0.5\phi} (0.298\phi \text{Ca}(\text{OH})_2) = 0.596L \text{ of } \text{Ca}(\text{OH})_2 \text{ solution}\]

\[74.08 \frac{g}{\phi} (0.298\phi) = 22.08g \text{Ca}(\text{OH})_2\]

Water Needed:

\[\frac{mL}{3.25g} (22.08g) = 6.8mL \text{ of water displaced when } \text{Ca}(\text{OH})_2 \text{ is added to solution}\]

Thus: 596 mL $\text{Ca}(\text{OH})_2$ solution – 6.8 mL $\text{H}_2\text{O}$ displacement = 589 mL water needed

For $\text{H}_3\text{PO}_4$
\[
\frac{L}{0.3\phi} (0.179\phi \text{H}_3\text{PO}_4) = 0.597L \text{ of } \text{H}_3\text{PO}_4 \text{ solution}
\]

97.97 \frac{g}{\phi} (0.179\phi) = 17.54g \text{H}_3\text{PO}_4

Water Needed :
\[V_cM_c = V_DM_c\]
\[V_D = 597 \text{ mL}\]
\[M_D = 0.3M\]
\[M_C = 14.749\]

\[V_c = \frac{(597\text{mL})(0.3M)}{14.749M} = 12.13\text{mL stock H}_3\text{PO}_4 \text{ needed}\]
597 – 12.13 = 584.87mL of water needed

Precipitation of Calcium Deficient Hydroxyapatite \(\text{Ca}_{10-x}(\text{HPO}_4)_x(\text{PO}_4)_{6-x}(\text{OH})_{2-x}\)**

The Reaction: \(9\text{Ca(OH)}_2 + 6\text{H}_3\text{PO}_4 \rightarrow \text{Ca}_9(\text{HPO}_4)(\text{PO}_4)_5(\text{OH}) + 17\text{H}_2\text{O}\)

\(\text{Ca}_9(\text{HPO}_4)(\text{PO}_4)_5(\text{OH}) \) Formula Weight : 98.54 g/mol

\[30g \left(\frac{\text{mol}}{948.54g}\right) = 0.0316\text{mol} \text{Ca}_9(\text{HPO}_4)(\text{PO}_4)_5(\text{OH})\]

\[\frac{1}{x} = 0.0316\text{mol} \text{Ca}_9(\text{HPO}_4)(\text{PO}_4)_5(\text{OH}) \Rightarrow x = 31.62\]

Where \(x\) is the scaling factor by which the reaction is divided to obtain 30g of \(s-HAp\)

Thus : 0.284\text{Ca(OH)}_2 + 0.189\text{H}_3\text{PO}_4 \rightarrow 0.0316\text{Ca}_9(\text{HPO}_4)(\text{PO}_4)_5(\text{OH}) + 0.537\text{H}_2\text{O}

For \(\text{Ca(OH)}_2\)

\[\frac{L}{0.5\phi} (0.284\phi \text{Ca(OH)}_2) = 0.586L \text{ of } \text{Ca(OH)}_2 \text{ solution}\]

74.08 \frac{g}{\phi} (0.284\phi) = 21.04g \text{Ca(OH)}_2

Water Needed :
\[\frac{mL}{3.25g} (21.04g) = 6.488\text{mL of water displaced when Ca(OH)}_2 \text{ is added to solution}\]

Thus : 586mL \text{Ca(OH)}_2 \text{ solution} – 6.488\text{mL H}_2\text{O displacement} = 579\text{mL water needed}

For \(\text{H}_3\text{PO}_4\)
For Barium Stabilized CDHA

Implement the CDHA equation discussed above, and add an equivalent amount of barium in the form of barium hydroxide to stabilize the structure.