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Study on immobilizing radionuclides in apatite-based host phase materials

Gunanda Weduge Chinthaka Silva

University of Nevada, Las Vegas

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STUDY ON IMMOBILIZING RADIONUCLIDES IN APATITE-BASED HOST
PHASE MATERIALS

by

Gunanda Waduge Chinthaka Silva

Bachelor of Science
University of Colombo, Sri Lanka
2000

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Gunanda Waduge Chinthaka Silva

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Examination Committee Chair

Dean of the Graduate College

Examination Committee Member

Examination Committee Member

Graduate College Faculty Representative
ABSTRACT

Study on Immobilizing Radionuclides in Apatite-Based Host Phase Materials

by

Gunanda Waduge Chinthaka Silva

Dr. Dennis W. Lindle, Examination Committee Chair
Professor of Chemistry
University of Nevada, Las Vegas

Fluorapatite is well known for its properties such as high thermal stability, chemical durability and its resistibility to radiation damage. These properties have been taken into account when it was considered as waste form material for fluoride salts like Cs, Sr and rare earths. The research as described in this thesis was carried out in order to determine the feasibility of incorporating other elements into fluorapatite as surrogate for nuclear waste without affecting any of its properties, especially the thermal stability. The aim was to accomplish incorporations in a way so that some of the calcium ions in the fluorapatite structure would be replaced with those other cations. In order to study any structural changes or the reduction of stability of fluorapatite, two different non-radioactive cations Zn$^{2+}$ and Zr$^{4+}$ were used as surrogates.

Although calcium substitution of up to 100% was tried only a certain maximum amount of calcium was replaced with either Zn or Zr. The thermal stability of Zn-containing fluorapatites decreased when the zinc amount was increased and this was identified by the lack of certain fluorapatite characteristics of these samples. The
zirconium samples were thermally stable at higher levels even with large amounts of zirconium. The presence of highly stable compounds like ZrO$_2$ and the retention of the cation to phosphorous molar ratio were the reason for this high thermal stability of the zirconium substituted samples.
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CHAPTER 1

INTRODUCTION

1.1 Hypothesis

Transmutation of plutonium and minor actinides offers an opportunity to minimize the radioactive waste load to be disposed at the Yucca mountain repository site. High temperature gas-cooled reactors (HTGR) are able to achieve high burn outs and to transmute radioactive nuclides, like Pu, Am, Cm and Np, into stable isotopes\(^1\). The HTGR design uses TRISO-coated particle fuel with a silicon-carbide and pyrocarbon composite coating\(^1\). This fuel form allows high burn-ups but it is more difficult to separate uranium, plutonium and the minor actinides from the fission products. For this purpose a fluoride extraction process (FLEX process) was developed by the Argonne National Laboratory. FLEX is a fluoride-salt-based extraction process and its primary waste stream contains zirconium fluoride (ZrF\(_4\)) salts and about 15wt% fluoride salts mainly with the fission products Cs, Sr and rare earth elements. The radiotoxic content of the fluoride salt waste stream cannot be immobilized in a borosilicate glass matrix applying traditional high-level-waste vitrification technology. Therefore the aim of this research work is to identify new waste form matrices to stabilize the radiotoxic content of the FLEX waste stream.
Fluorapatite \((\text{Ca}_5\text{(PO}_4\text{)}_3\text{F})\) was chosen as a potential candidate because its crystal chemistry allows the incorporation of monovalent, divalent, trivalent and tetravalent cations in its crystal structure and therefore the potential immobilization of a wide range of the radioactive isotopes created by the FLEX process. Single phase crystalline waste forms, like apatite, monazite, zirconolite or sodium zirconium phosphate, can incorporate nearly all of the radionuclides into their structures, especially if the radionuclide has been separated into a group such as lanthanides or actinides. Furthermore, apatites, especially fluorapatite, have high thermal stability (melting point of fluorapatite is 1650°C), excellent chemical durability (solubility product of fluorapatite is \(3.16 \times 10^{-60}\)) and a high tolerance to radiation damage. For example high energy ion irradiation using 128 MeV iodine and 70 MeV krypton with up to of \(5 \times 10^{13}\) ions/cm\(^2\) at \(10^0\)C was not sufficient to completely amorphize fluorapatite\(^8\). Irradiation studies applying 1.5 MeV Kr demonstrated that the critical amorphization dose for fluorapatite\(^9\) is slightly higher than for monazite (CePO\(_4\)), which is a naturally occurring host phase for trace amounts of thorium (Th); however it is not as high as zircon (ZrSiO\(_4\)), a natural host for uranium (U). The sensitivity of fluorapatite as a potential fission product host phase to radiolysis under expected repository conditions has not yet studied.

Rare-earth silicate phosphate with apatite structure has been proposed as an actinide host in high-level waste glass to form glass ceramics\(^10\). Actinide hosts with apatite structure have been observed as recrystallized alteration products on the leached and corroded surfaces of simulated high-level glasses, which indicate the inherent chemical and thermodynamic stability of apatite as actinide hosts compared to high-level-waste (HLW) glasses\(^11\). Apatites, containing significant amounts of \(^{235}\text{U}\) due to the decay of
plutonium ($^{239}$Pu), have been found at the Oklo natural reactor site in the Republic of Gabon in Africa. $^{239}$Pu was incorporated into the apatite crystal structure during crystallization about two billion year ago. This observation shows that natural apatites can contain U and other actinides like Th and are generally found in a crystallized state.

Due to these findings and other work done on the properties of apatites, especially on fluorapatite, the study of fluorapatite as a potential matrix for the waste stream from FLEX process was begun. The research was done in a manner such that sample preparations and characterizations of samples and their thermal behavior could be done under normal laboratory conditions. The stabilities of the samples were evaluated with respect to their thermal behavior. Different samples were prepared using zinc, and commercially available hydroxyapatite was used to study the thermal stability of zinc-containing hydroxyapatite. Then, the thermal stability of the fluorapatite samples together with different amounts of zinc and zirconium were studied. These results were further explained using Ca/P, (Ca+Zn)/P and (Ca+Zr)/P molar ratios. Finally, conclusions were made based on the thermal behavior of the samples containing different amounts of zinc and zirconium.

1.2 Properties of the Apatites

The general formula$^{12}$ of apatites is $M_{10}(XO_4)_6Y_2$ where M represents divalent cations like calcium (Ca), barium (Ba) and lead (Pb) while the $XO_4^{2-}$ can be phosphate ($PO_4^{3-}$) or vanadate ($VO_4^{3-}$). The Y represents a monovalent anion, which balances the charge of the formula; most abundant apatites in nature have anions like $F^-$, $OH^-$ and $Cl^-$. The general chemical formula of these natural apatites is $Ca_{10}(PO_4)_6(F$ or $OH$ or $Cl)_2$ and when it is
F\textsuperscript{−}, OH\textsuperscript{−} or Cl\textsuperscript{−} the apatites are named as fluorapatite, hydroxyapatite or chlorapatite respectively.

![Figure 1.1 Schematic of fluorapatite unit cell along the [0001] direction\textsuperscript{16} (not to scale).](image)

The crystallographic data of these three major apatites are similar to each other. These belong to a space group of $P6_3/m$ with similar unit cell parameters\textsuperscript{13} of $a \approx 9 \, \text{Å}$ and $c \approx 6.8 \, \text{Å}$. The unit cells are mostly hexagonal\textsuperscript{14} but some studies have shown that it is energetically possible for hydroxyapatite and chlorapatite to have a monoclinic structure\textsuperscript{13} as well. This same study showed that the stoichiometry has no relationship to the crystal structure of these apatites. But there is a relationship between the stoichiometry and the thermal stability of some of these apatites, especially of
hydroxyapatite. However, the apatite structure enables different anions and cations to be added to the structure.

The lattice symmetries of the crystal structure can only be seen when a number of adjacent unit cells are considered. The uniqueness of the structure of these apatites is the presence of different elements in different environments. Figure 1.1 shows how the different groups and elements in a unit cell of fluorapatite are oriented. For simplicity, the environments of calcium, fluorine and phosphate are shown in figure 1.2 and figure 1.3.

For calcium there are two unequal sites, \( \text{Ca}_1 \) and \( \text{Ca}_{\|} \), and for oxygen there are three, \( O_{\|}, O_{\|\|}, \) and \( O_{\|\|\|} \). Interactions between these elements are based mostly on ionic bonds. \( \text{Ca}_1 \) ions are surrounded by six oxygen atoms, three \( O_{\|} \) above and three \( O_{\|\|} \) below

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each calcium ion as shown in figure 1.2 (a). Also, three more $O_{\text{III}}$ atoms, in the same plane, are attached to the same calcium ion by ionic bonds. The $Ca_{\text{II}}$ ions are bonded to six more oxygen atoms (one $O_{\text{I}}$, one $O_{\text{II}}$ and four $O_{\text{III}}$) by ionic bonds and that same calcium ion is coordinated to a fluorine ion by a partially covalent bond (figure 1.2 (b)).

There is only one environment for fluorine and these fluorine ions are found in columns within the fluorapatite (figure 1.3 (a)). Fluorine atoms, located on the c-c' axes, are bonded to each other and each of these fluorines is also bonded to three other $Ca_{\text{II}}$ atoms forming calcium triangles\textsuperscript{13}. Phosphates in apatites have a short-range environment composed of four $Ca_{\text{I}}$ and five $Ca_{\text{II}}$ atoms (figure 1.3 (b)) \textsuperscript{18}. Oxygen atoms in these phosphate groups are also bonded with three calcium atoms.

Generally, substitutions for phosphate\textsuperscript{18} and the monovalent ion\textsuperscript{19, 20} are known to be more common than for Ca in the apatite structure. The effects of calcium substitution on the Ca/P molar ratio and structural modifications of the apatite are some of the major reasons why Ca substitution is not common. Disturbances in the crystal structure of apatite can be found when the substituent element is smaller than the calcium ion,\textsuperscript{16} or when it is not a divalent cation\textsuperscript{19} with the given conditions.

In most cases hydroxyapatite is of interest because of its existence in biological tissues. By partially substituting fluoride ions for hydroxide ions, it was shown that the mechanical properties of apatites, like decomposition temperatures, have been lowered\textsuperscript{21}. Decreases in these mechanochemical properties could be because the resulting compound is not hydroxyapatite or fluorapatite but an intermediate form of them. However, this substitution has made apatite to be more crystalline in some cases\textsuperscript{22}. A similar kind of
behavior with the apatite-wollastonite glass-ceramics was described by Calver et al.\textsuperscript{23} in 2004.

Figure 1.3 $F^-$ ion column (a) and $PO_4^{3-}$ ion environment (b)\textsuperscript{16}.

A considerable number of studies can be found in which the thermal stability of the synthesized hydroxyapatite was described as a function of the Ca/P molar ratio and the stoichiometry of hydroxyapatite. Generally, the conclusion of most of these studies is that the thermal stability and the crystallinity of the hydroxyapatite depend mostly on the Ca/P molar ratio or the stoichiometry of the mineral\textsuperscript{24, 25}. In the case of fluorapatite, high thermal stability (no phase transitions or melting) was observed\textsuperscript{26}. These studies also show that depending on the method and the conditions, such as temperature and pH,
synthesized apatites could be a mixture of some impurities, such as $\text{HPO}_4^{2-}$, due to the reagents used.

1.3 Apatites as a Host Material

In recent years a considerable number of studies have been done on hydroxyapatite and fluorapatite where other elements have been substituted for the calcium ions. Incorporation of other elements into apatites can be done in different ways; substitution of Ca is one method, while incorporating elements to make a different material (e.g., $\text{ZrO}_2$) on or below the apatite phase is another. In some studies, the use of solid-state reactions to obtain solid solutions was also found. Various elements like zinc (Zn), chromium (Cr), manganese (Mn), magnesium (Mg), cadmium (Cd), lead (Pb), and even radioactive elements, like iodine (I), strontium (Sr), and cesium (Cs) were used as substitutes for calcium in apatites. There are also some studies where different groups like silicates were substituted for the phosphate group. A theoretical study, done in 2002 by Joice Terra et al., showed that the Ca$_{111}$ substitution by Zn is much more energetically favorable than the Ca$_1$ substitution in hydroxyapatite. It was also shown that in all cases zinc retains its divalent state$^{27}$. An experimental study described an inhibiting effect of Zn element on the crystallization of the hydroxyapatite$^{28}$ from which can be inferred that there must be adsorption of zinc on the hydroxyapatite surface but not necessarily incorporation into the apatite structure. However, the substitution of calcium by zinc could be done up to 25 wt% of zinc without affecting the crystallinity of hydroxyapatite.

Magnesium$^{29}$ substitution into the hydroxyapatite showed that about 18% of Ca atoms were replaced by magnesium. An increase of the magnesium amounts, however,
decreased the thermal stability of hydroxyapatite\textsuperscript{30}. Expansion of the hydroxyapatite lattice parameters with Sr\textsuperscript{2+} and Ba\textsuperscript{2+} was identified in another study\textsuperscript{31}, which was done using computational methods. In the case of Mg\textsuperscript{2+}, a decrease in the lattice parameters was identified.

When lead (Pb) was substituted for calcium in fluorapatite, there were contradictory results regarding the thermal stability and the lattice constants\textsuperscript{32}. This can be explained by the two different calcium sites in apatites; that is when the amount of lead used was higher than just enough to substitute the Ca\textsubscript{III} sites, some kind of structural disturbances were observed after Ca\textsubscript{I} sites had been substituted. This was explained using the data on distances between Ca\textsubscript{I}-Ca\textsubscript{I} and Ca\textsubscript{II}-Ca\textsubscript{II}, which has the longer distance. The adsorption mechanisms of lead substitution on fluorapatite and chlorapatite could be identified due to both heterogeneous and homogeneous\textsuperscript{33} substitutions. The only product identified was pyromorphite, Pb\textsubscript{10}(PO\textsubscript{4})\textsubscript{6}Cl\textsubscript{2} which has a similar chemical formula to apatites. However, with hydroxyapatite a definite mechanism could not be determined. The unexplained behavior of lead with hydroxyapatite could be explained by considering the ionic radii: the ionic radius of lead is larger than the calcium radius. This was explained in another publication which identified the sorption mechanism of the incorporation of cadmium into hydroxyapatite\textsuperscript{34}. The suggested mechanism for cadmium absorption into hydroxyapatite was explained via diffusion and ion exchange.

Apatite-aluminium composites have less thermal stability when they are prepared by heating in air; however, a hot isostatic pressing at 1200\textdegree{}C to obtain these composites has been seen to improve thermal and structural stabilities\textsuperscript{35}. Somewhat similar results were also obtained for silver\textsuperscript{36}. Decomposition of hydroxyapatite to tri-calcium phosphate was
limited in the silver-hydroxyapatite composites with Ag substituting for up to 20% of Ca. Improved mechanical properties of hydroxyapatite were evident after silver incorporation. The temperature necessary to obtain the full theoretical densities of the hydroxyapatite increased when silicon was added to substitute $\text{PO}_4^{3-}$. In this substitution, some of the phosphates were replaced with silicates and not the calcium. Accordingly, a retardation effect on the grain growth had been seen in these silicon-substituted hydroxyapatites. It is also mentioned that these effects toughened the material after silicon substitution.

For fluorapatite there has been a study on calcium substitution by magnesium and the resulting thermal behavior. Somewhat identical thermal stabilities of these samples, with respect to fluorapatite itself, were identified. With higher magnesium levels, another phase described as $\text{Mg}_2\text{F}(\text{PO}_4)$, was identified. However, after sintering the samples to about $1300^\circ\text{C}$ this phase disappeared giving only the magnesium-containing fluorapatite phase. For strontium, the symmetry of fluorapatite was retained as $P6_3/m$ after strontium was incorporated at up to 1.18 atoms per 10 Ca sites. For belovite, which was described as $\text{Sr}_6(\text{REE}_2\text{Na}_2)(\text{PO}_4)_6\text{F}_2$, a regeneration of the symmetry was identified. As in the case of lead-containing hydroxyapatite, this can be explained by two different sites of calcium in fluorapatite. That is, the substitution happened only with $\text{Ca}_{\parallel}$ sites in Sr-containing fluorapatite whereas in the belovite there was also substitution at $\text{Ca}_\parallel$ sites which influenced the symmetry of fluorapatite.

V. V. Silva and R. Z. Domingues have done some work on hydroxyapatite-zirconia composites, and they have found that the presence of a zirconia phase influenced the thermal stability of hydroxyapatite. This is mainly due to the well defined particle size.
distribution in compacted powders without any cracking. Moreover, the hydroxyapatite composites with yttria-doped zirconia showed a significant improvement in their mechanical properties after densification of these composites, which were accomplished by substituting fluorine\(^1\). Again this work shows some improvement in physical properties such as melting point and toughness of fluoro-hydroxyapatite. Zirconia-fluorapatite composites acted little differently from hydroxyapatite composites; that is, after zirconia and fluorapatite were isostatically pressed at 1200\(^{0}\)C to obtain zirconia-fluorapatites, some of the calcium ions were transferred to the zirconia phase\(^2\). This was due to the change of zirconia structure from tetragonal to a cubic phase with a decreasing effect on the amount of zirconia. However, the transfer of this calcium could be due to an excess of Ca\(^{2+}\), relative to the stoichiometric value, present in the synthesized fluorapatite sample as some other phase such as CaF\(_2\). Although this kind of result was obtained, the fluorapatite stability was not affected.
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3. www.ncl.ac.uk/dental/oralenv/tutorials/ksp.htm


14. www.mindat.org


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CHAPTER 2

METHODOLOGY AND INSTRUMENTATION

2.1 Introduction

Two methods were used for sample preparation; a refluxing method and a precipitation method. The refluxing methods were used first to synthesize zinc-containing hydroxyapatite while taking the ion-exchange properties of apatites into account. Commercially available zinc nitrate and hydroxyapatite were used in a number of syntheses done with the same amounts of these two reagents in order to find the optimum conditions of refluxing to prepare the samples. These conditions were used for the final sample preparations.

One of the precipitation methods was then used to synthesize fluorapatite using the reagents for $\text{Ca}^{2+}$, $\text{PO}_4^{3-}$, and $\text{F}^{-}$. After synthesizing and characterizing the fluorapatite, zinc and zirconium were separately incorporated into the fluorapatite structure using the same precipitation method. This was done with four different amounts of both zinc and zirconium. The amounts of these elements used were measured so that the total moles of calcium plus zinc or zirconium would equal the stoichiometric amount of calcium in fluorapatite. The aim was to obtain different amounts of zinc and zirconium-containing fluorapatite and thereafter to obtain fluorapatite in which the calcium was replaced partially and completely by these two elements. Once the samples were synthesized, their
characterization was done using different analytical techniques. The stability of these different samples, with different phases in some cases, was interpreted by their thermal behavior such as different weight losses at different temperatures up to 1200°C.

2.2 Reagents

The compounds used were ammonium hydrogen phosphate (ACS), ammonium fluoride (ACS), calcium nitrate tetrahydrate (ACS), zinc nitrate (Alfa Aesar), zirconium(IV) chloride (Aldrich), and hydroxyapatite (Aldrich). Aqueous ammonia solution was used to maintain pH of the reaction.

2.3 Sample Preparation Using Refluxing Method

In this method commercially available hydroxyapatite and the correct amounts of 0.2M Zn(NO₃)₂ were mixed together and the solution was refluxed using distilled water as a solvent under vigorous stirring for about 7 hours at a temperature of 100°C. A schematic of this set up is shown in Figure 2.1. The precipitate was then washed with distilled water and dried in a desiccator for almost a day. Using the same conditions, a series of three samples with initial Ca/Zn weight ratios of 1:1, 1:0.25 and 1:0.5 were synthesized. Then another series of five samples was prepared using Ca/Zn weight ratios of 1:0.25, 1:0.2, 1:0.175, 1:0.15, and 1:1.0125. The sample using Ca/Zn weight ratio of 1:0.25 was prepared twice in order to access the reproducibility of the method. The original hydroxyapatite sample was named as Hap, whereas the samples prepared using Ca/Zn weight ratios 1:0.25, 1:0.50, and 1:1 were named as Hz1025, Hz105, and Hz11, respectively.

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The expected reaction for these synthetic processes is shown in equation (2.1), assuming that the reaction is possible and the stoichiometry is retained after the reaction.

\[ x \text{Zn}^{2+} + \text{Ca}_5(\text{PO}_4)_3\text{OH} \rightarrow \text{Ca}_{(5-x)}\text{Zn}_x(\text{PO}_4)_3\text{OH} + x \text{Ca}^{2+} \quad (2.1) \]

Figure 2.1 Schematic of the refluxing method.

2.4 Sample Preparation Using Wet Method

The wet method which was published by M. Hidouri and his co-workers\(^2\) was used to synthesize fluorapatite, and Zn and Zr-containing fluorapatites. Stoichiometric amounts of Ca\(^{2+}\), PO\(_4^{3-}\), and F\(^-\) ion solutions (Ca : PO\(_4^{3-}\) : F\(^-\) = 5 : 3 : 1) were used to synthesize the fluorapatite, and, for Zn and Zr-containing fluorapatites, the stoichiometry of the Ca\(^{2+}\) ions as in the fluorapatite was maintained by using the correct amounts of Ca(NO\(_3\))\(_2\).4H\(_2\)O and Zn(NO\(_3\))\(_2\) or ZrCl\(_4\) respectively. The final cation concentration was
expected to maintain the stoichiometry of the fluorapatite by having a correct total \((\text{Ca}^{2+} + \text{Zn}^{2+} \text{ or } \text{Zr}^{4+})\) ion concentration in the reaction medium.

2.4.1 Method

A solution containing appropriate amounts of anions \((\text{NH}_4)_2\text{HPO}_4 \text{ and } \text{NH}_4\text{F})\) was prepared and boiled. A second solution with correct amounts of cations \((\text{Ca(NO}_3)_2\cdot4\text{H}_2\text{O} \text{ and } \text{Zn(NO}_3)_2 \text{ or } \text{ZrCl}_4)\) was added into this boiling solution with a roughly constant pouring speed. For fluorapatite the second solution contained only \((\text{Ca(NO}_3)_2\cdot4\text{H}_2\text{O})\), and for Zn or Zr-containing fluorapatites it was a mixture of the \((\text{Ca(NO}_3)_2\cdot4\text{H}_2\text{O} \text{ and } \text{Zn(NO}_3)_2 \text{ or } \text{ZrCl}_4)\), respectively.

After the addition of the second solution, a concentrated ammonia solution was added occasionally so that the pH was maintained at around 9.0 (pH was measured using a calibrated pH meter). Then the reaction mixture was stirred vigorously for about three hours while maintaining a pH of 9.0. After the aging process the precipitate was vacuum filtered and washed thoroughly with distilled water. The precipitate was then removed and dried overnight in an oven at 70°C. Once the drying was finished, the precipitate was weighed and crushed to powder for characterization purposes and studies on thermal behavior. Then 1.0g of each of these samples was sintered at 1200°C using a high temperature furnace for about one hour. Sintering was required in order to study thermal stability of the samples and also to increase thermodynamics so that the stable compounds will well crystallized.

Using this method, fluorapatite and four different amounts of each of Zn and Zr-containing fluorapatites were tried to synthesize separately. The amounts used of each of these two elements Zn and Zr, were consistent to 75, 50, 25 and 0% of \(\text{Ca/Zn} \text{ and } \text{Ca/Zr}\)
molar ratios. The samples synthesized using 75, 50, 25 and 0% molar ratios were named as 25ZnAp (25ZrAp), 50ZnAp (50ZrAp), 75ZnAp (75ZrAp), and ZnAp (ZrAp), respectively. The sintered samples were named as 25ZnApS (25ZrApS), 50ZnApS (50ZrApS), 75ZnApS (75ZrApS), and ZnApS (ZrApS) accordingly. And the fluorapatite samples were named as Fap before and FapS after the sintering process.

2.4.2 General Structural Formula of the Synthesized Samples

The general formula of hydroxyapatite and fluorapatite is $\text{Ca}_{10}(\text{PO}_4)_6\text{X}_2$, or $\text{Ca}_5(\text{PO}_4)_3\text{X}$, and for hydroxyapatite and fluorapatite, X is equal to OH and F, respectively. Assuming the elements Zn and Zr are incorporated into the apatite structure and that the stoichiometry of the structure of the prepared apatite samples exists the general formula can be given as $\text{Ca}_{5-y}\text{Zn}_y(\text{PO}_4)_3\text{F}$ for Zn-containing apatites and $\text{Ca}_{5-z}\text{Zr}_z(\text{PO}_4)_3\text{F}$ for Zr-containing apatites. The assumed chemical reactions in these sample preparations are as follows.

$$(5-y)\text{Ca}^{2+} + y\text{Zn}^{2+} + 3\text{PO}_4^{2-} + \text{F}^- \rightarrow \text{Ca}_{(5-y)}\text{Zn}_y(\text{PO}_4)_3\text{F}$$  \hspace{1cm} (2.2)

$$(5-2z)\text{Ca}^{2+} + z\text{Zr}^{4+} + 3\text{PO}_4^{3-} + \text{F}^- \rightarrow \text{Ca}_{(5-2z)}\text{Zr}_z(\text{PO}_4)_3\text{F}$$  \hspace{1cm} (2.3)

2.5 Instrumentation and Characterization Methods

The synthesized samples before and after sintering were characterized using different spectroscopic methods. Elemental analysis was done using atomic absorption spectroscopy (AAS) and ion chromatography. Different groups in these samples were studied using infrared spectroscopy (FTIR), and x-ray photoelectron spectroscopy (XPS) and energy-dispersive spectroscopy (EDS) were used to identify elements and their
different environments. The EDS and XPS data were used to determine the amounts of different elements. Morphologies were studied using scanning electron microscopy (SEM) with different magnifications and resolutions. The actual phase identifications were done using x-ray diffractometry (XRD), and their thermal behavior was examined by means of thermogravimetric analysis (TGA) and differential scanning calorimetric (DSC) profiles.

2.5.1 Fourier Transform Infrared Spectroscopy

DIGILAB FTS 7000 spectroscopy was used to obtain the FTIR data of the samples. The number of scans used was 64 (or 128) and the resolution used was 4 (or 8 cm\(^{-1}\)). First the photoacoustic IR data were obtained in a wave number range from 400 to 4000 cm\(^{-1}\) and transformed to obtain the transmission (%) vs wave number plots. The IR data were used to identify the different groups in the samples and to compare any differences in the structures of the synthesized samples.

2.5.2 X-ray Photoelectron Spectroscopy (XPS)

The XPS instrument at DRI (Desert Research Institute) in Las Vegas was used to get data of the samples. The original data files were used with another program called ESCA (Electron Spectroscopy for Chemical Analysis), to analyze the results. The peak positions and the chemical shifts of different peaks or elemental forms in the survey spectra were determined with respect to the carbon peak, which was identified at around 284 eV. Also the high resolution data were used to identify the different environments of the elements.
2.5.3 Scanning Electron Microscopy/ Energy Dispersive Spectroscopy (SEM/EDS)

SEM images and the supporting EDS data were obtained using the JEOL-5600 scanning electron microscope. Images up to 1μm resolution with a magnification of 10,000 X could be obtained. High-resolution images showed sample morphologies very well, as in the case of fluorapatite after it was sintered. These high-resolution images could be effectively used to study morphological changes of the apatite samples after incorporating other elements. The samples were mounted on double-sided carbon tape, which was attached to a round aluminum mount, and then the samples were coated with gold to gain conductivity. For each sample the SEM images were taken first and then the EDS data were collected using a randomly selected part of the mounted sample. The EDS data-collection software was also used to determine the elemental percentages of the samples.

2.5.4 X-ray Diffractometry (XRD)

Using Cu Kα, 1.54 Å, as an energy source we obtained powder-diffraction patterns of hydroxyapatite, Zn-containing hydroxyapatite, and Zn-containing fluorapatite with 2θ values ranging from 0° to about 60°. The Si-standard was used for more accurate comparison purposes, with fluorapatite and Zr-containing fluorapatite. The data base (ICDD : International Centre for Diffraction Data), which comes with “X’Pert HighScor Plus” software, was used in the phase identifications. The identified phases of some of the samples were quantified as a phase percentage using the same data base and the software. However, this could not be done for some samples because the RIR (Relative Intensity Ratio) values were unknown for some phases listed in the ICDD data base.
2.5.5 Thermogravimetry and Differential Scanning Calorimetry

(TGA/DSC)

We studied the thermal behavior of host samples using TGA/DSC profiles from 25°C to 500°C. For fluorapatite and Zr-containing fluorapatites a higher temperature range from 25°C to 1230°C can be used and we used a heating rate of 10°C min⁻¹ in these cases. The primary instrument used was a Netzsch STA 449 C with aluminum crucibles to heat the samples from room temperature (about 20°C) to 500°C. To heat samples to 1230°C, a high-temperature alumina crucible was used. TGA profiles were used to find any weight losses, which could be due to melting and evaporation, in the samples and these were confirmed using the DSC profiles. That is, the transitions, which were characteristic of the samples, and the temperatures at which these transitions occurred, were used to get a clear picture about the weight losses.
References


CHAPTER 3

CHARACTERIZATION OF HYDROXYAPATITE AND ZN-SUBSTITUTED HYDROXYAPATITES

3.1 Introduction

Hydroxyapatite is known for its prevalence in nature as well as its structure and stability under extreme conditions, such as high temperatures and high pressures, and its low solubility in water. Synthetic stoichiometric hydroxyapatite has a thermal stability up to 1300°C \(^1\) and other non-stoichiometric hydroxyapatites showed some different compounds or phases at lower temperatures. S. N. Vaidya et al. \(^2\) showed the existence of hydroxyapatite at higher pressure, like 10 GPa, except it is somewhat amorphous at this pressure \(^2\). The K\(_{sp}\) value of hydroxyapatite is very low \(^3\) (2.34 x 10\(^{-59}\)), but it is soluble in acidic conditions.

In most of the naturally occurring sources, hydroxyapatite is mixed with some impurities, especially in biological systems. Sr, Ba, K, Pb, Na and Mg cations are some contaminants substituting for Ca, and the phosphate group is substituted with monohydrogen phosphate and carbonate anions \(^3\). These impurities cause changes in the crystal structure and thus affect the physical and chemical properties. For instance, in biological substances, like teeth, solubility increases due to carbonate impurities \(^3\), and also these carbonate-apatites are less thermally stable than pure hydroxyapatite \(^4\). Interestingly, even
in commercially available hydroxyapatites the amount of carbonate moiety varies with brand name.

There are many uses for hydroxyapatite due to its structure and stability. W. Jie and his co-workers have shown the compatibility of synthetic hydroxyapatite/polyamide composite with natural bone. Here the polymer gives mechanical strength and toughness while hydroxyapatite is bioactive. In the process of synthesizing stable hydroxyapatite, it is important to have the correct stoichiometry, which is done by maintaining the proper initial concentrations, temperature and pH, of the solution. If these conditions are not maintained then the resulting hydroxyapatite will be calcium deficient, with more than one phase and a lower stability at higher temperatures than stoichiometric hydroxyapatite.

In this chapter, characterization of commercial hydroxyapatite and different samples of Zn-substituted hydroxyapatite are described. First the structural and elemental characterizations were done for these samples, and then their thermal behavior was studied using TGA/DSC with annealed samples. XRD was used to identify different phases of original hydroxyapatite and Zn-containing hydroxyapatite samples.

3.2 Characterization of Hydroxyapatite

As indicated, a number of characterization methods were used in this study. The morphology of the hydroxyapatite sample was studied by taking SEM images with different resolutions and magnifications. Also some effort was made to check for different environments of the hydroxyapatite particles in this sample.
Figure 3.1 SEM images of hydroxyapatite at different magnifications and locations: Hap at x700 (a), x20,000 (b), and a different shape of particle (c), (d).

Figure 3.1 shows the morphology of commercial hydroxyapatite at different sites. Basically, the sample has long thin particles with a flat needle-like shape (figure 3.1 (a)). Figure 3.1 (b) is a magnified SEM image (x20,000) of (a), where the needle shape is more evident than at x 700 magnification. Figures in figure 3.1 (c) and (d), show that this sample contains some particles which differ from the bulk. This may be a minor impurity or some other phase of hydroxyapatite. However, the other characterization data have to be considered before coming to any conclusions on this finding.
Table 3.1 Quantitative analysis of different hydroxyapatites using EDS data.

<table>
<thead>
<tr>
<th>Elemental Form</th>
<th>Atom percentages of the samples (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hap (Theoretical values)</td>
</tr>
<tr>
<td>O K</td>
<td>61.4 (59.09)</td>
</tr>
<tr>
<td>P K</td>
<td>16.9 (13.64)</td>
</tr>
<tr>
<td>Ca K</td>
<td>21.8 (22.72)</td>
</tr>
<tr>
<td>Zn K</td>
<td>-</td>
</tr>
</tbody>
</table>

The presence of different elements (Ca, P, and O) in the hydroxyapatite sample can be identified from EDS data (Appendix II Figure B-1), and table 3.1 shows quantitatively how these elements have been distributed. The theoretically calculated atom percentages of hydroxyapatite are indicated for comparison. They were calculated under the assumption that the sample contains the stoichiometric hydroxyapatite with a Ca/P molar ratio of about 1.67. There are some differences in the experimental and calculated values, and these differences could be due to the presence of some phases other than hydroxyapatite and surface might be different than bulk or the used sample size could have not correctly represented the sample. It is also worth mentioning that the Ca/P molar ratio obtained was approximately equal to 1.78, which gives a difference of 0.11 with respect to the stoichiometric value of 1.67.

The next analytical method used was FTIR, which gave information on the groups present in the sample. Mainly phosphate (PO$_4^{3-}$) and hydroxyl (OH$^-$) groups were identified at their characteristic positions in the spectrum (figure 3.4) while some bands for carbonate (CO$_3^{2-}$) and/or hypophosphate (HPO$_4^{2-}$) groups were found$^{1,5}$. Table 3.2
shows the wavenumbers of the observed peaks or bands. The presence of carbonate and HPO$_4^{2-}$ could be due to impurities in the sample.

Table 3.2 FTIR band positions of used hydroxyapatite sample.

<table>
<thead>
<tr>
<th>Peak assignments</th>
<th>Peak positions (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH- stretching</td>
<td>3572</td>
</tr>
<tr>
<td>Carbonate v3 and/or residual water</td>
<td>1680–1300</td>
</tr>
<tr>
<td>Phosphate v3</td>
<td>1190–976</td>
</tr>
<tr>
<td>Phosphate v1</td>
<td>962</td>
</tr>
<tr>
<td>HPO$_4^{2-}$ or Carbonate v2</td>
<td>875</td>
</tr>
<tr>
<td>Phosphate v4</td>
<td>660–520</td>
</tr>
<tr>
<td>Phosphate v2</td>
<td>474</td>
</tr>
</tbody>
</table>

Again the presence of Ca, O, and P in this sample can be confirmed from XPS data (Appendix IV Figure D-1). Table 3.3 summarizes the binding energies obtained from XPS survey spectra which were corrected with respect to the carbon peak at 284.59 eV. These values will be discussed in section 3.3.

Table 3.4 gives the atom percentages obtained from the XPS analysis. To obtain these, an elemental form for each element was selected based on the cross-sectional values from the Scofield data for that particular element. For example, the highest cross section for Ca is found in Ca 2p. Therefore, the Ca 2p peak was used to calculate the atom percentage. For oxygen and phosphorous, O 1s and P 2p peaks were selected, respectively. Again these atom percentages and the Ca/P molar ratio, which equals about...
1.30, are different from the theoretical values calculated for stoichiometric hydroxyapatite (table 3.1). This may verify the presence of more than one phase or the presence of non-stoichiometric hydroxyapatite.

Table 3.3 Adjacent XPS binding energies of elements in different samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Adjacent binding energies (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ca 2p</td>
</tr>
<tr>
<td>Hap</td>
<td>346.36</td>
</tr>
<tr>
<td>Hz1025</td>
<td>347.04</td>
</tr>
<tr>
<td>Hz105</td>
<td>346.67</td>
</tr>
<tr>
<td>Hz11</td>
<td>346.79</td>
</tr>
</tbody>
</table>

From the XRD pattern of the original sample, brushite \((\text{CaHPO}_4\cdot\text{2H}_2\text{O})\) was identified as the major phase other than hydroxyapatite itself. In order to understand this result, the original hydroxyapatite sample was annealed at four different temperatures \((100^\circ\text{C}, 500^\circ\text{C}, 750^\circ\text{C}, \text{and} 1000^\circ\text{C})\) for about half an hour. The original sample and the Hap_100 sample had almost the same phase distributions, and from the Hap_500 to Hap_1000, the peak intensities of two phases, hydroxyapatite and brushite, start to decrease. Some other phases like tri-calcium phosphate \((\text{Ca}_3(\text{PO}_4)_2)\), calcium pyrophosphate \((\text{Ca}_2\text{P}_2\text{O}_7)\), and calcium phosphate oxide \((\text{Ca}_4\text{P}_2\text{O}_9)\) were the other compounds identified in the Hap_1000 sample. The presence of these new phases after heating the original sample to \(1000^\circ\text{C}\) suggests that the original hydroxyapatite sample was non-stoichiometric. Also the disappearance of the brushite phase after annealing the
sample at higher temperatures and the presence of calcium pyrophosphate affirms the conclusion about the presence of brushite in the original sample.

![TGA/DSC profiles of commercial synthetic hydroxyapatite.](image)

Figure 3.2 TGA/DSC profiles of commercial synthetic hydroxyapatite.

Results supporting the above statement were obtained from the TGA/DSC profiles of the original hydroxyapatite sample. In TGA there were two main weight losses in the sample while the temperature ranged from 25°C to 500°C (figure 3.2). These weight losses were coincident with two endothermic peaks in the DSC profile. The two endothermic effects start at around 200°C and 450°C temperatures, respectively. These temperatures were consistent with the decomposition temperatures of brushite according to a study carried out by Joshi et al. They characterized the two decompositions as due to the conversion of brushite to calcium hypophosphate (CaHPO₄) and then to calcium pyrophosphate.
3.3 Characterization of Zn-Substituted Hydroxyapatites

The SEM images of the synthesized samples using zinc are shown in figure 3.3. Basically, the particle shapes have been changed with the increase of Zn levels in these samples. Hydroxyapatite has a kind of flat and needle-shaped particles (figure 3.1 (a)) and in Hz11 it has started to change to a round shape (figure 3.2 (c)). This morphology difference could be due to the incorporation of zinc into the hydroxyapatite.

Figure 3.3 SEM micrographs of Hz102 (a), Hz105 (b), and Hz11 (c).

The EDS data (Appendix B-2) on these samples confirmed the presence of four different elements. The quantitative data obtained from EDS are shown in table 3.1. These data do not show any particular pattern, except in the case of Zn, where increasing atom percentages can be seen from Hz1025 to Hz11. This shows the direct proportionality between the amount of zinc used and the amount of the zinc incorporated in the sample.

From the FTIR data the absorption bands for $\text{PO}_4^{3-}$ (474, 520-660, 968, 980 cm$^{-1}$) and $\text{OH}^-$ (3600 cm$^{-1}$) groups were identified in the Zn-containing hydroxyapatite samples (figure 3.4). Some other peaks which may be due to $\text{CO}_3^{2-}$, $\text{HPO}_4^{2-}$, and residual $\text{H}_2\text{O}$...
could also be seen in the hydroxyapatite sample. An additional broad peak at around 2002 cm$^{-1}$ was identified for the Hz11 sample and is probably due to PO$_4^{3-}$ overtones$^{11}$.

Figure 3.4 FTIR spectra of hydroxyapatite and Zn-containing hydroxyapatites.

The presence of Zn together with other elements was also confirmed by XPS survey spectra. By referring to the binding energies in table 3.3 it can be observed that binding energies of Zn-containing samples are different from those of the original hydroxyapatite sample. This may be due to Zn incorporation. In the case of Zn 3p, the binding energies increased with the increase in Zn amounts in these samples. Table 3.4 also shows that the highest zinc atom percentage is seen in the Hz11 sample.
Table 3.4 Quantitative measurement using XPS data.

<table>
<thead>
<tr>
<th>XPS Line</th>
<th>Atom percentages of different samples (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hap</td>
</tr>
<tr>
<td>Zn 3p</td>
<td></td>
</tr>
<tr>
<td>P 2p</td>
<td>16.88</td>
</tr>
<tr>
<td>Ca 2p</td>
<td>21.84</td>
</tr>
<tr>
<td>O 1s</td>
<td>61.28</td>
</tr>
</tbody>
</table>

* = Paraschoizite
# = Brushite

Figure 3.5 XRD patterns of the Hap and Zn-containing Hap samples.

Other than hydroxyapatite, the main phase observed in these Zn-containing samples was paraschoizite (CaZn$_2$(PO$_4$)$_2$.2H$_2$O). Some of the identified XRD peak patterns are shown in figure 3.5. Some peaks shifted with respect to the original hydroxyapatite and
their splittings in these patterns verified the incorporation of zinc into the hydroxyapatite. Especially the (200) peak has shifted in the prepared samples using zinc and hydroxyapatite while the peak splittings are prominent in (002) and (300).

The TGA and DSC profiles of these samples showed some weight losses in the temperature range from 25°C to 500°C (Appendix F-1 and F-2). The weight loss in the original hydroxyapatite sample at around 200°C could not be found in the Zn-substituted samples. Instead, a weight loss before 200°C was seen for all the Zn-substituted samples; this could be due to some phase transition because this temperature shifted to higher values from Hz1025 to Hz11 samples, or due to the removal of interstitial water. Two other small weight losses were found at around 300°C and 375°C temperatures, respectively. The significance of the last weight loss decreases as the amount of zinc in the samples decreases which might be linked to the phases that include zinc or in other words a removal of a volatile species of zinc. The XRD patterns of the samples after annealing at 1000°C for half an hour show that the phases were identical to those in the Hap_1000 sample. Tri-calcium phosphate was identified in all sintered samples but calcium pyrophosphate could only be found in the Hz1025 and Hz105 samples. This can be explained by the presence of parascholzite in the Hz11 sample after heating it to 1000°C. Since the greatest amount of zinc was used in this Hz11 sample the largest amount of parascholzite may be formed in this sample, and somehow this phase was protected even after the sample was sintered. This may be because the source, CaHPO₄, which decomposed to give calcium pyrophosphate, has been used almost completely to form parascholzite. The quantitative measurements obtained from the XRD data show that the lowest hydroxyapatite character found among the sintered samples was in Hz11.
This was confirmed using five more samples synthesized with different Ca/Zn weight ratios lower than Hz105. These five samples had only hydroxyapatite and parascholzite phases in their synthesized forms. After sintering at 1000°C they possessed hydroxyapatite, tri-calcium phosphate and calcium pyrophosphate as in the case of sintered Hap, Hz1025 and Hz105. Also the TGA and DSC profiles of these five samples showed similar weight losses and transition peaks as for Hz105 and Hz1025 samples.

3.4 Discussion

There are different ways to synthesize hydroxyapatite. The wet method, also called precipitation method, is one of them. Depending on the preparation conditions such as pH and temperature, the purity of the sample varies\(^1\). The possibility that the commercial hydroxyapatite sample used is non-stoichiometric is higher due to these reasons. Thus the presence of more than one phase in the hydroxyapatite sample is probable. This was first suggested by the SEM micrographs and the presence of monetite (CaHPO\(_4\)) and brushite (CaHPO\(_4\).2H\(_2\)O), hydrated CaHPO\(_4\) found in the XRD patterns. This result was confirmed from TGA/DSC profiles and the data obtained for the same sample after it was annealed at different temperatures up to 1000°C. The presence of CaHPO\(_4\) in non-stoichiometric hydroxyapatite was described by Raynaud et al., and the presence of brushite may be due to absorption of water in this phase during its preparation.

Incorporation of zinc into the hydroxyapatite sample was verified by comparing spectroscopic data of the synthesized samples and the original hydroxyapatite sample. Among them the XPS and XRD data gave some prominent results to confirm the incorporation of zinc. The binding energies obtained from XPS data of different
elemental forms were higher in the samples prepared using zinc than that of the original sample. Also some peak splittings and shifts of XRD patterns were observed for the prepared samples with respect to the original hydroxyapatite sample. The SEM micrographs showed some differences after zinc was used. The TGA/DSC profiles of these samples showed a number of weight losses that could not be found for the original sample. These data were used to confirm the substitution of calcium in hydroxyapatite by zinc. Absence of calcium pyrophosphate in a sample after it was annealed at 1000°C for about half an hour showed that not only the calcium in hydroxyapatite has been substituted by zinc but also almost all the calcium in brushite. According to the spectroscopic data obtained, the hydroxyapatite characteristics were lower in this sample than in the samples prepared with zinc and hydroxyapatite. It could be shown that the thermal stability of the hydroxyapatite sample was not affected by incorporation of zinc because most of the final products were the same after heating to 1000°C.
References


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CHAPTER 4

PROPERTIES OF FLUORAPATITE AND SURROGATE-LOADED FLUORAPATITE

4.1 Introduction

Fluorapatite is the mineral name given to calcium phosphate fluoride which is the ICSD (Inorganic Crystal Structure Database) name. It contains hexagonal unit cells of the P6_3/m space group with cell parameters of $a = b = 9.367 \, \text Å$ and $c = 6.884 \, \text Å$. Its calculated density is 3.16 g/cm$^3$ with a cell volume of $523.09 \times 10^6 \, \text{pm}^3$. Naturally occurring fluorapatite can be found in different colors like green and blue, with a vitreous nature. However the color of a fine powdered fluorapatite sample is white. The chemical formula is $\text{Ca}_5(\text{PO}_4)_3\text{F}$ with a 1.67 Ca/P molar ratio. It’s physical and chemical properties have allowed fluorapatite to be considered for a huge number of applications.

The main objective of this research work is based on fluorapatite, its structural stability and ability to accommodate other elements. In this chapter, the characterization of a synthesized sample of pure fluorapatite and samples containing zinc and zirconium be described. The samples were analyzed after preparation and also after sintering at a temperature of $1200^\circ\text{C}$ for one hour. In the first part of this chapter the characterization of the synthesized fluorapatite and sintered fluorapatite is described. Next the results obtained for Zn-containing and Zr-containing samples are presented. In most cases these results were compared with that of the fluorapatite sample. In the final section of the
chapter XPS data are used to describe the electronic binding energies of different elemental forms in the samples containing zinc and zirconium.

4.2 Characterization of Synthesized Fluorapatite

As mentioned in chapter 2, a precipitation method was used to synthesize fluorapatite. To confirm the formation of fluorapatite during the synthesis a number of studies were performed. First the as-prepared sample was characterized using different techniques, and then we did the same studies on part of the sample after sintering it at 1200°C for one hour. The weight of the as-prepared sample was 8.22g after drying at 70°C overnight and this weight was higher than the expected theoretical sample weight of about 8.07g. The difference between these two weights should be due to insufficient drying. However, since the difference (about 0.15g) is very low it can be considered that the reaction in the sample preparation chamber has been almost complete according to equation (4.1). A 1.00 g sample was used in the sintering process and about 0.90g of it remained. The sample’s ability to withstand the high temperature of 1200°C suggests that fluorapatite sample preparation has been successful. This thermal stability was further observed from TGA (Appendix F-3) and DSC (Appendix F-4) profiles and these will be discussed later in this chapter.

\[
5 \text{Ca}^{2+} + 3 \text{PO}_4^{3-} + \text{F}^- \rightarrow \text{Ca}_5(\text{PO}_4)_3\text{F} \quad (4.1)
\]

The SEM images of these two samples, before and after sintering, are shown in figure 4.1. As is evident, the micrograph of the prepared sample was not clear but after
annealing it has become a well-crystallized sample with an organized particle pattern. The particles have a flat, round shape.

![Micrographs](image)

Figure 4.1 Micrographs of fluorapatite before (a) and after sintering at 1200°C (b).

The XRD patterns obtained (Appendix V Figure E-2) for these two samples showed that the peak intensities of the sintered sample were higher than that of the freshly synthesized sample. Also, the only phase identified in the XRD data of both samples was fluorapatite. The elements, Ca, O, P, and F in the samples were identified using EDS (Appendix II Figure B-3) and XPS (Appendix IV Figure D-2) data. In both methods the sintered Fap sample had higher peak intensities which show that the sintered sample has been well-crystallized.

The FTIR spectra of fluorapatite before and after sintering are shown in figure 4.2. Mainly the PO$_4^{3-}$ bands around 474, 520-660, 968, 980 cm$^{-1}$ were identified. The peak at 875 cm$^{-1}$ could be due to CO$_3^{2-}$ and (or) HPO$_4^{2-}$ bands$^{4,5}$. Another series of peaks around 1300-1750 cm$^{-1}$ were found that may be due to CO$_3^{2-}$ or perhaps to residual water, because this series of peaks could not be seen in the sample after it was sintered. Also,
the peak at around 875 cm\(^{-1}\) could not be found in the sintered sample, therefore these peaks, at 875 cm\(^{-1}\) and from 1300-1750 cm\(^{-1}\), probably are due to the residual water and volatile products\(^6\) like HPO\(_4^{2-}\) and CO\(_2^{2-}\). The broad peak at around 2002 cm\(^{-1}\), which is more prominent in the sintered sample, is probably due to PO\(_4^{3-}\) overtones\(^7\). Because the sintering of the sample increased its crystallinity this band might be more significant. A band for OH\(^-\) stretching could be found in the sintered sample at around 3537 cm\(^{-1}\), which was acceptable since the sample was sintered in air.

![FTIR spectra of fluorapatite sample before and after sintering at 1200\(^{0}\)C.](image)

Figure 4.2 FTIR spectra of fluorapatite sample before and after sintering at 1200\(^{0}\)C.

4.3 Characterization of Zn-containing Fluorapatites

Samples synthesized using Ca/Zn molar ratios of 75, 50, 25, and 0% were named 25ZnAp, 50ZnAp, 75ZnAp, and ZnAp, respectively. After they were sintered at 1200\(^{0}\)C...
for one hour the names were 25ZnApS, 50ZnApS, 75ZnApS and ZnApS, while FapS was the name given to the sintered Fap sample.

Table 4.1 Comparison of the sample weights.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Experimental Weight (g)</th>
<th>Theoretically Calculated Weights (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>With (Ca + Zn)</td>
</tr>
<tr>
<td>Fap</td>
<td>8.22</td>
<td>-</td>
</tr>
<tr>
<td>25ZnAp</td>
<td>8.04</td>
<td>8.57</td>
</tr>
<tr>
<td>50ZnAp</td>
<td>8.22</td>
<td>9.08</td>
</tr>
<tr>
<td>75ZnAp</td>
<td>9.26</td>
<td>9.59</td>
</tr>
<tr>
<td>ZnAp</td>
<td>8.15</td>
<td>10.09</td>
</tr>
</tbody>
</table>

Table 4.1 shows the weights of different samples that were obtained experimentally and theoretically. The theoretical weights are tabulated in two ways; with Ca and with (Ca + Zn). The first set of theoretical weights was calculated assuming the expected reaction (equation (4.2)) happened during sample preparation; the second set was calculated with only the number of moles of calcium used to synthesize the samples and assuming there was no zinc in the sample. This second set of weights was used to check the possibility that none of the zinc used could be in these samples. Since the sample (other than Fap) weights obtained experimentally were higher than the values calculated using only the used calcium, the Zn has to be incorporated in to these samples either partially or completely. In 25ZnAp, 50ZnAp and 75ZnAp the weight differences between the experimental and theoretical data sets are lower than in the case of ZnAp where only
Zn was used. Of course as mentioned earlier the lowest weight difference could be seen in Fap and it is about 0.15g.

The above statement shows good agreement with XRD studies (Appendix V Figure E-3) because the fluorapatite phase could be found in all four samples (Fap, 25ZnAp, 50ZnAp and 75ZnAp) where calcium was used (table 4.2). In Fap and 25ZnAp the only phase which could be identified was fluorapatite. Some significant percentage of the fluorapatite phase was found in the 50ZnAp sample as well. Among the phases that were identified in the 50ZnAp, 75ZnAp and ZnAp samples, hopeite (Zn$_3$(PO$_4$)$_2$(H$_2$O)$_4$) was the most prominent, and this was the most probable phase in 75ZnAp and ZnAp samples. Thus, the probability of finding fluorapatite phase in these samples decreased with the increase in the amounts of zinc used.

$$5\text{Ca}^{2+} + x\text{Zn} + 3\text{PO}_4^{3-} + \text{F}^- \rightarrow \text{Ca}_{5-x}\text{Zn}_x\text{(PO}_4)_3\text{F} \quad (4.2)$$

These results obtained by XRD can also be used to explain the results obtained for morphologies of the same samples. The SEM images showed that the particle shapes were quite similar in 25ZnAp and 50ZnAp compared to the shape in the Fap sample (figure 4.3), but the particle size of 25ZnAp was greater than the particle size in Fap. This could be an indication of incorporation of zinc into the fluorapatite structure. For the 75ZnAp and ZnAp samples the particle sizes and the shapes (Appendix I Figure A-1) were very different from the particles of the Fap sample.
Table 4.2 Different compounds identified in XRD patterns of Zn-substituted samples.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Phases Identified</th>
</tr>
</thead>
<tbody>
<tr>
<td>25ZnAp</td>
<td>Fluorapatite [Ca₅(PO₄)₃F]</td>
</tr>
<tr>
<td>50ZnAp</td>
<td>Fluorapatite [Ca₅(PO₄)₃F], Hopeite [Zn₃(PO₄)₂(H₂O)₄]</td>
</tr>
<tr>
<td>75ZnAp</td>
<td>Hopeite [Zn₃(PO₄)₂(H₂O)₄], Zinc Phosphate [Zn₃(PO₄)₂]</td>
</tr>
<tr>
<td>ZnAp</td>
<td>Hopeite [Zn₃(PO₄)₂(H₂O)₄], Zinc Phosphate [Zn₃(PO₄)₂]</td>
</tr>
</tbody>
</table>

Figure 4.3 SEM micrographs of Fap (a), 25ZnAp (b) and 50ZnAp (c).

Considering the FTIR spectra, it can be noted that there were no significant differences in the FTIR spectra (Appendix III Figure C-1) of the Zn-substituted samples from the Fap sample. The bands due to the phosphate group with similar spectral shapes could be found for each of the samples. The EDS (Appendix II Figure B-4) and XPS (Appendix IV Figure D-3 to D-6) data showed the presence of Ca, F, O, P, and Zn in the samples from 25ZnAp to 75ZnAp, and in ZnAp the elements F, O, P, and Zn were identified.
Table 4.3 Quantitative analysis of Fap and Zn-containing Fap using XPS.

<table>
<thead>
<tr>
<th>XPS Line</th>
<th>Atom percentages of different samples (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P 2p</td>
<td>13.32</td>
</tr>
<tr>
<td>Ca 2p</td>
<td>19.74</td>
</tr>
<tr>
<td>O 1s</td>
<td>61.10</td>
</tr>
<tr>
<td>F 1s</td>
<td>5.84</td>
</tr>
<tr>
<td>Zn 2p3</td>
<td>-</td>
</tr>
</tbody>
</table>

The atom percentages obtained from XPS and EDS showed some differences (table 4.3 and table 4.4). However, based on these two quantitative measurements, an increasing trend was observed in the Ca and Zn atom percentages. In Fap and 25ZnAp the Ca atom percentages are almost the same. Also the P atom percentages obtained from XPS data (table 4.3) for these same two samples are very close to each other. However, in the 75ZnAp and ZnAp samples the P atom percentages obtained from XPS data were unexpectedly large. This could be due to peak overlaps of P 2p (BE ~ 136 eV) and Zn 3s (BE ~ 139.8 eV) that were identified in the survey spectra of 75ZnAp and ZnAp samples, but in the EDS data these P amounts are reasonable and therefore the Ca/P and (Ca+Zn)/P molar ratios were calculated as average values of these two measurements. They are tabulated in table 4.5.
Table 4.4 Quantitative analysis of Fap and Zn-containing samples using EDS.

<table>
<thead>
<tr>
<th>Element</th>
<th>Atom percentages of different samples (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P K</td>
<td>7.37</td>
</tr>
<tr>
<td>Ca K</td>
<td>17.47</td>
</tr>
<tr>
<td>O K</td>
<td>63.40</td>
</tr>
<tr>
<td>F K</td>
<td>11.76</td>
</tr>
<tr>
<td>Zn K</td>
<td>-</td>
</tr>
</tbody>
</table>

The average Ca/P molar ratio of Fap is about 1.80, which is a reasonable value in comparison to the stoichiometric value of 1.67. In the 25ZnAp sample this Ca/P molar ratio is 1.58, which is lower than the value of Fap, but the (Ca+Zn)/P molar ratio is very close to the Ca/P molar ratio of Fap. This indicates some of the calcium was replaced with zinc, and the substituted calcium amount was almost equal to the incorporated amount of zinc. This is another confirmation of the results obtained from the XRD data and morphological data of these two samples. From the 50ZnAp to the 75ZnAp sample the Ca/P and (Ca+Zn)/P molar ratios have decreased. The amount of fluorapatite formed being lower and the presence of other phases would be a reason for the lower molar ratios in these two samples. The Zn/P molar ratio in the ZnAp sample, which was prepared without calcium, is 1.76. Although this value is close to the Ca/P molar ratio of the Fap sample, XRD patterns were not similar to fluorapatite.
Table 4.5 Average Ca/P and (Ca+Zn)/P molar ratios calculated using XPS and EDS data.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average molar ratios</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ca/P</td>
</tr>
<tr>
<td>Fap</td>
<td>1.80</td>
</tr>
<tr>
<td>25ZnAp</td>
<td>1.58</td>
</tr>
<tr>
<td>50ZnAp</td>
<td>1.18</td>
</tr>
<tr>
<td>75ZnAp</td>
<td>0.44</td>
</tr>
<tr>
<td>ZnAp</td>
<td>-</td>
</tr>
</tbody>
</table>

In the TGA (Appendix F-3) and DSC (Appendix F-4) profiles there were no significant weight losses or transitions in the Fap and 25ZnAp samples over a temperature range of 25°-500°C. However the presence of residual water and volatile products from CO$_3^{2-}$ or HPO$_4^{2-}$ (identified from FTIR spectra) may have caused about 2% and 4% weight loss in this temperature range for the Fap and 25ZnAp sample, respectively. Three other samples showed some significant weight losses based on TGA data. This was confirmed by the endothermic peaks at around the same temperatures in the DSC plots of the same samples. The determined total weight losses of 50ZnAp, 75ZnAp and ZnAp samples were about 8%, 13% and 17%, respectively.
As shown in figure 4.4 the weight losses increase with the increase in the amounts of zinc in the sample preparations. This further confirms the substitution of Zn into the fluorapatite and could be used to assess an effect of decreasing thermal stability of these samples with the incorporation of zinc. The lack of fluorapatite characteristics in the samples where larger amounts of zinc were incorporated would also be another explanation for their thermal instabilities.

In the FTIR spectrum of the 25ZnApS sample the peak at around 3530 cm\(^{-1}\), which should be due to hydroxyl stretching, could be found as it was in the sintered Fap sample. The SEM image of the sintered 25ZnAp sample was somewhat different from the sintered Fap sample (Appendix I Figure A-2).
4.4 Characterization of Zr-containing Fluorapatites

The weights obtained for the synthesized samples are tabulated in table 4.6. Again the theoretical values were calculated assuming the reaction in the sample preparation followed equation (4.3). In all samples the experimentally obtained sample weights were higher than the calculated weights, especially in the 75ZrAp and ZrAp samples. The weight differences imply that the reactions in the sample preparation may not be according to equation (4.3) but may also involve reactions that form other compounds. Furthermore, XRD of the sintered samples (table 4.8) support this idea.

\[(5-2z)\text{Ca}^{2+} + z\text{Zr}^{4+} + 3\text{PO}_4^{3-} + \text{F}^- \rightarrow \text{Ca}_{(5-2z)}\text{Zr}_z\text{(PO}_4)_3\text{F} \quad (4.3)\]

Table 4.6 Weights of Zr-containing samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Weight (g)</th>
<th>Weight difference (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Experimental ($W_{Exp}$)</td>
<td>Theoretical ($W_{Calc}$)</td>
</tr>
<tr>
<td>25ZrAp</td>
<td>10.43</td>
<td>9.09</td>
</tr>
<tr>
<td>50ZrAp</td>
<td>14.04</td>
<td>10.12</td>
</tr>
<tr>
<td>75ZrAp</td>
<td>27.01</td>
<td>11.14</td>
</tr>
<tr>
<td>ZrAp</td>
<td>21.40</td>
<td>12.16</td>
</tr>
</tbody>
</table>

SEM micrographs (figure A-3) showed that the Zr-containing samples have some agglomerates of compounds with round, broad particle shapes. Although there were some
differences in their particle sizes, 25ZrAp and 50ZrAp show some similarities in their morphology (particle size and shape) to the Fap sample.

Even after sintering, part of the morphology that could be seen in the 25ZrAp and 50ZrAp samples (figure 4.5 (b) and (c) respectively) was comparable to the Fap sample (figure 4.5 (a)) in the SEM micrographs. The flat shape of the particles in the FapS sample can be seen in 25ZrApS and 50ZrApS, but they are thinner than in the FapS sample. The particles in the FapS sample are packed whereas in the 25ZrApS and ZrApS (e).

Figure 4.5 SEM images of FapS (a), 25ZrApS (b), 50ZrApS (c), 75ZrApS (d), and ZrApS (e).
50ZrApS samples the particles do not have such packing pattern, and the particles are more resolved than in the FapS.

![Average particle sizes of different sintered samples.](image)

Figure 4.6 Average particle sizes of different sintered samples.

For the 75ZrApS sample it first looks as if the morphology is completely different from the 25ZrApS or 50ZrApS samples, but it is not. The particle shapes have some similarities with that of the 25ZrApS and 50ZrApS samples but the composite density of 75ZrApS sample has been increased more than in the other two samples. However, this has to be verified by TGA/DSC and XRD. In the case of the ZrApS sample, the SEM image showed an almost completely different morphology from that of the FapS sample. Instead of a well-packed pattern, the particles are arranged randomly. This could be due
to the presence of a number of indistinct compounds such as zirconium oxide and zirconium phosphates in the sample. Indeed this would also give some explanation as to why these two samples, especially 75ZrAp, have higher thermal stability than 25ZrAp and 50ZrAp as in the case of Fap (Appendix VI Figure F-5).

The SEM images show that the particle sizes decrease from FapS to 50ZrApS shown in figure 4.6. The average particle sizes shown in this figure were obtained by averaging the sizes of three randomly selected particles in SEM images with the magnification of 7500 of each sintered sample. Two significant variations could be identified in the particle size distribution, first a decrease from Fap to 50ZrAp and then an increase from 50ZrAp to ZrAp samples. These two particle size distribution patterns and the different particle shapes of the samples indicate that not only has the zirconium been incorporated into fluorapatite but it also formed some other compounds, especially in the samples where large amounts of zirconium were used.

The XRD peak intensities of Zr-containing samples before the sintering process were very weak with respect to the peak intensities of the Si-standard in the XRD studies. However, some intense peaks were obtained for these samples after they were sintered. Figure 4.7 shows that the peak intensities for the 25ZrAp sample are lower than in the Fap sample. A further decrease in peak intensities can be seen for 50ZrAp, 75ZrAp and ZrAp. The peak pattern near 33° was identified as zirconium phosphate (Zr2P2O9) in the ZrAp sample. The appearance of this phase could be due to the use of larger amounts of zirconium in this sample than in the other samples because this sample was synthesized without calcium. However, the appearance of this new peak near 33° indicates the other
Zr-containing samples are more amorphous compared to the Fap sample. Thus the incorporation of zirconium into the fluorapatite decreases the crystallinity of fluorapatite.

![XRD patterns of Fap and Zr-substituted apatite samples before sintering.](image)

Figure 4.7 XRD patterns of Fap and Zr-substituted apatite samples before sintering.

Table 4.7 compares the (200), (111), (002), and (300) peak positions of Zr-substituted samples with the peak positions of the Fap sample. The peak positions were obtained by correcting the values with respect to the (111) peak of the Si-standard at $28.44^\circ\theta$. The peaks for the 75ZrAp and the ZrAp samples cannot be identified because the intensities are too weak. The peak shifts of all samples from the peaks of the Fap sample have been presented in brackets. The highest peak position differences could be found for the 25ZrAp sample and they correspond to the planes of (111) and (300). These peak shifts suggest the substitution for calcium by zirconium in the samples.
Table 4.7 Corrected XRD peak positions with respect to (111) Si-Std peak at 28.44°.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Position (°2θ)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(200)</td>
</tr>
<tr>
<td>Fap</td>
<td>21.86</td>
</tr>
<tr>
<td>25ZrAp</td>
<td>21.85 (0.01)</td>
</tr>
<tr>
<td>50ZrAp</td>
<td>-</td>
</tr>
</tbody>
</table>

Among the sintered Zr-substituted samples, the highest fluorapatite percentage was identified in the 25ZrAp sample from XRD patterns (table 4.8). In 50ZrApS and 75ZrApS, mainly baddeleyite (ZrO$_2$) and calcium zirconium phosphate were identified. Presence of these zirconium minerals, especially zirconium oxide (melting point 2700°C), might be the reason for thermal stability of these samples even with higher zirconium amounts. For ZrApS, mainly two types of zirconium phosphates were identified.

Table 4.8 Most probable phases identified for sintered Zr-substituted samples.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Identified Phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>25ZrApS</td>
<td>Fluorapatite [Ca$_5$(PO$_4$)$_3$F], Baddeleyite [ZrO$_2$]</td>
</tr>
<tr>
<td>50ZrApS</td>
<td>Baddeleyite [ZrO$_2$], calcium zirconium phosphate [CaZr(PO$_4$)$_2$]</td>
</tr>
<tr>
<td>75ZrApS</td>
<td>Baddeleyite [ZrO$_2$], calcium zirconium phosphate [CaZr(PO$_4$)$_2$ and CaZr$_4$(PO$_4$)$_6$]</td>
</tr>
<tr>
<td>ZrApS</td>
<td>Zirconium Phosphate [Zr$_2$P$_2$O$_7$ and ZrP$_2$O$_7$]</td>
</tr>
</tbody>
</table>

The FTIR spectrum of the 25ZrAp sample was identified as the closest to that of Fap. As can be seen from figure 4.8, the PO$_4$\(^{3-}\) bands identified in the Fap sample at around 55
474, 520-660, 968, and 980 cm\(^{-1}\) were broader in the zirconium samples. Also, from 25ZrAp to ZrAp, the resolution of these absorption bands has decreased. A similar kind of pattern could be seen for the sintered samples (Appendix C-2) as well. But the peaks identified in the 1300-1750 cm\(^{-1}\) region for the synthesized samples could not be identified in the sintered samples. As for fluorapatite these bands are most likely due to the presence of residual species like H\(_2\)O, CO\(_3\)\(^{2-}\) and HPO\(_4\)\(^{2-}\).

![FTIR spectra of Fap and Zr-containing samples](image)

Figure 4.8 The FTIR spectra of Fap and Zr-containing samples.

The OH\(^-\) band at around 3537 cm\(^{-1}\) could only be identified for 25ZrApS among the Zr-substituted samples and might be due to sintering the samples in air. This proves that 25ZrAp has the highest amount of fluorapatite phase of the zirconium-containing
samples. Furthermore, the absorption bands of $\text{PO}_4^{3-}$ overtones could be prominently seen near 2002 cm$^{-1}$ in all sintered samples. Higher peak resolutions have been observed in these samples after sintering.

Table 4.9 Quantitative analysis of Fap and Zr-containing samples using EDS.

<table>
<thead>
<tr>
<th>Element</th>
<th>Atom percentages of different samples (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P K</td>
<td>7.37</td>
</tr>
<tr>
<td>Ca K</td>
<td>17.47</td>
</tr>
<tr>
<td>O K</td>
<td>63.40</td>
</tr>
<tr>
<td>F K</td>
<td>11.76</td>
</tr>
<tr>
<td>Zr L</td>
<td>-</td>
</tr>
</tbody>
</table>

The EDS data show the presence of different elements in the zirconium-containing samples (Appendix B-5), and table 4.9 shows how the atom percentages are distributed among these samples. Data for the Fap sample are also included. The calcium level in the samples decreases from Fap to 75ZrAp sample, and the zirconium level increases from 25ZrAp to ZrAp. Therefore, it can be concluded that there is a direct proportionality between the amounts of zirconium used and the amounts of zirconium in the samples.

Somewhat similar atom percentages of oxygen could be seen in the samples except for 50ZrAp. The same pattern can be found in the phosphorous percentages as well. In the case of fluorine the nearest atom percentage for the Fap is found in the 25ZrAp. This
observation verifies that the 25ZrAp sample has some characteristics similar to those of the Fap sample which were identified through other techniques as well.

Table 4.10 Quantitative analysis of Fap and Zr-containing samples using XPS.

<table>
<thead>
<tr>
<th>XPS Line</th>
<th>Atom percentages of different samples (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fap</td>
</tr>
<tr>
<td>P 2p</td>
<td>13.32</td>
</tr>
<tr>
<td>Ca 2p</td>
<td>19.74</td>
</tr>
<tr>
<td>O 1s</td>
<td>61.10</td>
</tr>
<tr>
<td>F 1s</td>
<td>5.84</td>
</tr>
<tr>
<td>Zr 3p3/2</td>
<td>-</td>
</tr>
</tbody>
</table>

Additionally, XPS spectra were used to identify different elemental forms in the zirconium-substituted samples. Table 4.10 shows the atom percentages of different samples obtained from the XPS survey spectra. Here the increase in Zr amounts from 25ZrAp to ZrAp samples was not found as in the data obtained from EDS, but a decrease in Ca atom percentages from Fap to SOZrAp could be identified. For 50ZrAp the obtained atom percentage for Zr is unexpectedly higher than all other samples. This could be due to an inaccuracy of the measurement since the quantification is done by calculating the specific peak area. For 75ZrAp this value is very high and is due to the overlap of Ca 2p (BE ~ 346.2 eV) peak with Zr 3p3/2 (BE ~ 343.5 eV) peak. Therefore average Zr/P and (Ca+Zr)/P molar ratios of this sample are lower than that of the 50ZrAp sample (table 4.11). The average values of different molar ratios shown in this table were calculated to
overcome the inaccuracies of the results obtained from these two techniques, especially the XPS data. The values inside the brackets were calculated using EDS data only. Obviously, these values are more reasonable than the averaged values for Zr-containing samples. Therefore the molar ratios calculated using EDS data are used for comparison with averaged Ca/P molar ratio of Fap.

Table 4.11 Average Ca/P and (Ca+Zr)/P molar ratios calculated using XPS and EDS data.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average molar ratios (from EDS data)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ca/P</td>
</tr>
<tr>
<td>Fap</td>
<td>1.80 (2.37)</td>
</tr>
<tr>
<td>25ZrAp</td>
<td>1.31 (1.69)</td>
</tr>
<tr>
<td>50ZrAp</td>
<td>0.72 (0.68)</td>
</tr>
<tr>
<td>75ZrAp</td>
<td>1.17 (0.53)</td>
</tr>
<tr>
<td>ZrAp</td>
<td>-</td>
</tr>
</tbody>
</table>

The Ca/P molar ratios decrease from 25ZrAp to 75ZrAp samples. But the (Ca+Zr)/P molar ratios of these samples do not match with the Ca/P molar ratio of Fap sample. This suggests that more than one phase is present in these samples. The observation of only one phase in the 25ZrAp sample from the XRD patterns could be due to insufficient crystallinity of the sample.
The total weight loss percentages obtained for Fap and Zr-containing apatites are shown in Figure 4.9. The weight loss increases from Fap to 50ZrAp and for 75ZrAp it decreases to about 1.4%. Then it increases again up to 7.4% for ZrAp. The increase in weight loss from Fap to 50ZrAp is due to the increase in zirconium amounts in the fluorapatite phase. The lowest total weight loss as observed in 75ZrAp could be due to the large amount of ZrO₂ present in the sample that is stabilizing the sample by increasing its composite density. This also supports the different morphology observed in the SEM micrograph of the sintered sample.
Figure 4.10 TGA/DSC profiles of the 25ZrAp (a), 50ZrAp (b), 75ZrAp (c), and ZrAp (d) samples in a temperature range from 500°C to 1230°C.

Figures in Appendix F-5 and F-6 describe the respective high temperature (up to 1230°C) TGA and DSC profiles for Fap and Zr-containing samples. Almost all samples had some weight loss in the temperature range between 26°C and 500°C. The weight losses in this temperature range could be due to the removal of residual water and the evaporation of volatile products resulting from species like CO$_3^{2-}$ or HPO$_4^{2-}$ that were identified in the FTIR spectra.

A comparative study of the thermal behavior of the Zr-containing samples is shown for the temperature range 500°C-1230°C in figure 4.10. In this temperature range,
phase changes for some samples were identified (from exothermic behavior from 900° to 1000°C). Two small endothermic peaks in the DSC profiles were found near 792° and 771°C for 25ZrAp and 50ZrAp, respectively. These peaks correspond to about a 0.1% weight loss in the TGA curves for both the samples. Thus it is reasonable to assume that a small decomposition happened for these two samples at those temperatures. An endothermic peak near 801°C in the DSC plot could also be found for 75ZrAp but it was not supported with a sudden weight loss in the corresponding TGA plot. There are also some exothermic regions for most of these samples. These exothermic peaks can be identified near 957°C, 986°C and 902°C temperatures in 25ZrAp, 50ZrAp and ZrAp respectively. For the 75ZrAp sample the exothermic behavior is somewhat different from the other samples. There are two regions of exothermic behaviors starting near 600°C and 850°C, corresponding to some re-crystallizations.

4.5 High Resolution XPS Data

Table 4.12 summarizes the binding energies of different elemental forms for Ca, O, P, F, Zn, and Zr found in the synthesized samples. XPS data obtained for all the fluorapatite samples are tabulated in this table for comparison. The Zn 2p3/2 binding energies of the 25ZnAp and 50ZnAp samples were found to be similar. This could be due to similar zinc environments for those two samples. However, the higher binding energy for Zn 2p1/2 in 50ZnAp compared to 25ZnAp is an indication of different zinc environments. This supports the presence of different zinc phosphates in the 50ZnAp sample. For the 75ZnAp and ZnAp samples, the binding energies of Zn 2p3/2 are very close to each other and these values are different from the 25ZnAp or the 50ZnAp samples. This is because
these two samples (75ZnAp and ZnAp) have lower fluorapatite characteristics than 25ZnAp and 50ZnAp.

Table 4.12 Adjacent binding energies of different elemental forms obtained from the survey spectra of Fap, Zn and Zr-containing samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Adjacent BE (eV)</th>
<th>O 1s</th>
<th>Ca 2p</th>
<th>P 2p</th>
<th>F 1s</th>
<th>Zn 2p(^{3/2})</th>
<th>Zn 2p(^{1/2})</th>
<th>Zr 3p(^{3/2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fap</td>
<td></td>
<td>531.9</td>
<td>347.9</td>
<td>133.9</td>
<td>685.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>25ZnAp</td>
<td></td>
<td>532.3</td>
<td>347.4</td>
<td>133.4</td>
<td>685.2</td>
<td>1023.3</td>
<td>1042.4</td>
<td>-</td>
</tr>
<tr>
<td>50ZnAp</td>
<td></td>
<td>532.3</td>
<td>348.7</td>
<td>134.9</td>
<td>685.9</td>
<td>1023.4</td>
<td>1042.5</td>
<td>-</td>
</tr>
<tr>
<td>75ZnAp</td>
<td></td>
<td>531.4</td>
<td>347.8</td>
<td>135.2</td>
<td>686.0</td>
<td>1022.6</td>
<td>1045.3</td>
<td>-</td>
</tr>
<tr>
<td>ZnAp</td>
<td></td>
<td>531.2</td>
<td>-</td>
<td>133.5</td>
<td>665.8</td>
<td>1022.4</td>
<td>1044.9</td>
<td>-</td>
</tr>
<tr>
<td>25ZrAp</td>
<td></td>
<td>531.4</td>
<td>346.4</td>
<td>134.6</td>
<td>687.0</td>
<td>-</td>
<td>-</td>
<td>333.0</td>
</tr>
<tr>
<td>50ZrAp</td>
<td></td>
<td>531.6</td>
<td>347.4</td>
<td>133.6</td>
<td>684.5</td>
<td>-</td>
<td>-</td>
<td>333.7</td>
</tr>
<tr>
<td>75ZrAp</td>
<td></td>
<td>530.7</td>
<td>347.7</td>
<td>133.5</td>
<td>685.0</td>
<td>-</td>
<td>-</td>
<td>332.9</td>
</tr>
<tr>
<td>ZrAp</td>
<td></td>
<td>530.4</td>
<td>345.8</td>
<td>132.3</td>
<td>685.0</td>
<td>-</td>
<td>-</td>
<td>332.2</td>
</tr>
</tbody>
</table>

Fap and 25ZnAp have almost the same binding energies for the Ca 2p peaks. This suggests that these two samples have quite similar calcium environments, which is not surprising because both samples mainly consist of the fluorapatite phase. However, the binding energy for the 25ZnAp sample is lower than that of the Fap sample by about 0.5 eV; this is due to zinc substitution for some of the calcium in fluorapatite, which varies the spatial properties of calcium atoms inside fluorapatite. The 50ZnAp sample shows...
differences for the Ca 2p binding energies compared to Fap and 25ZnAp of about 0.8 and 1.3 eV respectively.

The high-resolution data shows that the Ca 2p peak can be resolved into two peaks with about 3.0 eV binding energy difference for the 50ZnAp sample. This is due to spin-orbit coupling which separates the calcium peak into Ca 2p\textsubscript{1/2} and Ca 2p\textsubscript{3/2}. However, this separation cannot be seen in other samples. This may be due to the low crystallinity of the samples. In the 75ZnAp sample, the Ca 2p binding energy has been decreased to about 347.8 eV, which is close to that of Fap. This could be because only a small amount of the zinc actually replaced the calcium in fluorapatite and the rest of the zinc made other phases like zinc phosphates.

The high-resolution spectrum of O 1s (figure 4.11) for the 25ZnAp sample was broader than the one for the Fap sample. Since fluorapatite has three types of states for oxygen (figure 1.2), and its high-resolution peak is not as broad as the peak for the 25ZnAp sample, there should be more oxygen environments in this zinc-substituted sample. These new oxygen sites should be due to incorporation of zinc into the fluorapatite structure. A similar broadness for the P 2p peak was found for the same 25ZnAp sample. A much broader O 1s peak was measured for the ZnAp sample and this is probably due to the presence of different phases in the sample as seen in the XRD patterns.
The O 1s binding energies of the 25ZnAp and 50ZnAp samples are higher than that of the Fap sample and their binding energy difference is 0.4 eV. This behavior is likely a consequence of the change in the oxygen environment after zinc was incorporated into the fluorapatite. In the 75ZnAp and ZnAp samples, the O 1s binding energies are lower than that for the Fap sample. This tells us the oxygen in fluorapatite is more strongly bound, perhaps through ionic bonding, than it is in 75ZnAp and ZnAp samples.

In the fluorapatite structure, the phosphorous atoms are bonded by three different oxygen environments. Altogether, there are four oxygen atoms in each phosphate group, and two kinds of calcium environments respectively. Once the calcium in fluorapatite was replaced by another element, either zinc or zirconium, the phosphorous environment(s) could vary depending on the elemental suitability for the calcium.
substitution. However, since almost all the environments like oxygen and calcium were affected by zinc substitution and, in fluorapatite, all the atoms are bonded in a characteristic manner, a variation of the phosphorous binding energy could also be expected. Likewise the binding energies of P 2p for the zinc-substituted fluorapatite samples vary as for cases of other elemental forms. Similar explanations could also verify the measured binding energies for F 1s of these samples.

For the zirconium-containing samples, the lowest binding energies for O 1s, Ca 2p, P 2p, and Zr 3p\textsubscript{3/2} were found for the ZrAp sample (table 4.12). This could be because the other samples have some fluorapatite character in which the binding strengths of the elements are higher than in zirconium phosphates. For P 2p and F 1s the highest binding energies were obtained for 25ZrAp and these energies are higher than those of the original Fap as well. This confirms the incorporation of zirconium into the fluorapatite structure. This could also indicate that zirconium substituted for calcium at the Ca (II) sites in the fluorapatite structure. Here one fluorine atom is surrounded by three calcium atoms (Ca(II) sites; figure 1.3 (a)). A similar explanation could also be used for the binding energy in phosphorous. However, the highest O 1s and Ca 2p binding energies were identified for fluorapatite. Here, the increase in fluorine and phosphorous binding energies due to the incorporation of zirconium somehow weakens the other bonds in the apatite structure. For Zr 3p\textsubscript{3/2} the binding energy is lower in the 25ZrAp sample than in the 50ZrAp sample. Contributions to the zirconium bonding from some stronger environments, like ZrO\textsubscript{2}, together with Zr-containing fluorapatite could be the reason for this higher binding energy in the 50ZrAp sample. The energy difference between the
25ZrAp and 75ZrAp is about 0.1 eV which is negligible, but for ZrAp it is about 0.8 eV. This is most likely due to the different compounds in this sample.

4.6 Discussion

Using different techniques (SEM, XRD and FTIR), the presence of fluorapatite could be identified in the synthesized Fap sample. This was further confirmed by its high thermal stability, which is characteristic of fluorapatite. Although the incorporation of zinc into the samples was assessed using weight differences between experimental and theoretical values, a true calcium substitution in the fluorapatite by zinc was verified only for the 25ZnAp and 50ZnAp samples. However, high thermal stability similar to that of fluorapatite could only be found in 25ZnAp. Lower thermal stability of 50ZnAp could be due to the lower Ca/P and (Ca+Zn)/P molar ratios. Since these molar ratios are smaller, which could be due to the presence of other phases, the fluorapatite characteristics are lower in this sample which leads to a lower thermal stability. Another explanation for the lower thermal stability of these samples might be the presence of other compounds which tend to melt at higher temperatures. The following can be concluded from this research: if zinc substitution of calcium is achieved such that the (Ca+Zn)/P molar ratio is maintained close to the Ca/P molar ratio of the fluorapatite, then high thermal stability of Zn-containing fluorapatite is maintained.

For samples synthesized using zirconium for calcium substitution, we obtain different results. Zirconium incorporation into the synthesized samples was studied by comparing experimental and calculated weights. The presence of all expected elements including zirconium was confirmed from EDS and XRD. Further verification was done using atom...
percentages obtained from these two techniques, especially from EDS. The XRD patterns of the synthesized samples showed the samples start to be more amorphous after incorporation of zirconium. These results verify the substitution of zirconium for some of the calcium in fluorapatite. An increase in the crystallinity of the samples was identified from both the SEM images and intense XRD peak patterns of the sintered samples. Thermal stability similar to Fap was found for 75ZrAp, but it was also determined this high thermal stability could be due to the presence of ZrO$_2$. For the 25ZrAp and 50ZrAp samples, most of the results could be well matched with the results of Fap. But the thermal stabilities of these two samples were lower than that of Fap, and the samples were less stable when the amount of zirconium was high (in 50ZrAp). These results suggest the thermal stability of fluorapatite is lower when calcium atoms are replaced with zirconium. However, the presence of other stable zirconium compounds increases the stability of the whole sample when the amount of zirconium is higher.
References

1. ICDD database, reference pattern 01-071-0881.


CHAPTER 5

CONCLUSIONS

The refluxing method could be used to incorporate zinc into hydroxyapatite. Although calcium substitution by zinc was verified using XRD, some contradicting results were obtained due to the presence of other phases, like brushite in the original hydroxyapatite sample. Therefore, strong results on the zinc-incorporated hydroxyapatite were not observed. However the amounts of zinc used did not affect the thermal stability of the hydroxyapatite up to a temperature of 1000°C.

Other spectroscopic data (FTIR, XPS and XRD) confirmed the formation of fluorapatite in the synthesized sample (Fap). This was further verified by the sample’s thermal stability. Incorporation of zinc and zirconium into fluorapatite was identified with the samples of lower amounts of Zn and Zr. One of the main results regarding the Zn and Zr-incorporated samples was that the fluorapatite characteristics decreased with large amounts of these elements. Also, other phases could be identified when the elemental amounts were increased.

The high thermal stability of the 25ZnAp sample was maintained because its (Ca+Zn)/P molar ratio was close to the Ca/P molar ratio of the fluorapatite. This is because the correct molar ratio helps the sample to maintain the characteristics of fluorapatite. Although a significant fluorapatite character was identified in some other Zn-containing samples, especially in 50ZnAp, they did not have the same high thermal
stability as 25ZnAp. This was due to the change in the (Ca+Zn)/P molar ratio and change in fluorapatite characteristics, accordingly.

For all sample preparations, the cation concentrations (Ca, Zn and Zr) were chosen such that the final theoretical molar ratio of (Ca+Zn or Ca+Zr)/P was equal to 1.67. Therefore, although a large amount of zinc or zirconium was used, the final total cation (Ca+Zn or Ca+Zr) concentration had to be theoretically the same in all samples. In order to maintain constant (Ca+Zn) values, the zinc levels have to be increased proportionately when the calcium amounts are decreased. However, in Zn-containing samples this was not observed when the Zn/Ca molar ratio became larger than 25%. Therefore the amount of fluorapatite formed in these samples was lower than in Fap and 25ZnAp. The amounts of PO$_4^{3-}$ and F$^-$ used in these samples also had a certain weight ratio as in the Fap sample. But, since the amount of fluorapatite formed in the samples was lower (50ZnAp, 75ZnAp and ZnAp) than the expected amounts of fluorapatite the additional amounts of anions could then form other zinc-containing compounds like zinc phosphates. These anions could also have forced the Ca and Zn ions to form Ca$_{5.2}$Zn$_3$(PO$_4$)$_3$F, which places zinc not only at Ca(II) sites but also at sites where Ca(I) is found in fluorapatite. If this happened, then structural distortions are possible which could influence the bonding strengths of different elements in the sample. This would also affect the lower thermal stability in 50ZnAp compared to the 25ZnAp sample. Based on these results, zinc is not a good substitution for calcium in fluorapatite when the amount of zinc exceeds the Ca/Zn molar ratio of 75%.

For zirconium-containing samples, the thermal stability was higher when the zirconium amounts were high enough to form other compounds like ZrO$_2$. Also the
(Ca+Zr)/P molar ratios of the zirconium samples were close to the Ca/P molar ratio of fluorapatite, even when large amounts of zirconium used. This can be another reason for the retention of the high thermal stability of the zirconium-containing samples.

These results indicate it is important to maintain the cation-to-phosphorous molar ratio of the sample to equal to that of the stoichiometric fluorapatite. This is however difficult for some elements like zinc, especially when the amount of calcium in fluorapatite is replaced in larger amounts. Thus it is suggested to determine the correct amount to be used for each element in order to maintain the final cation-to-phosphorous molar ratio in fluorapatite before using fluorapatite as a waste-form material.
APPENDIX I

SEM MICROGRAPHS
Figure A-1 Micrographs of as-prepared h138 (a), h137 (b), h139 (c), and h135 (d).
Figure A-2 SEM Micrograph of sintered h138; before grinding (a) and after grinding (b).

Figure A-3 SEM images of 25ZrAp (a), 50ZrAp (b), 75ZrAp (c), and ZrAp (d).
APPENDIX II

EDS DATA
Figure B-1 EDS spectrum of used hydroxyapatite powder.

Figure B-2 EDS spectrum of the Hz11 sample.
Figure B-3 EDS spectra of the fluorapatite sample before and after sintering at 1200°C.

Figure B-4 EDS spectra of Fap and Zn-containing Fap samples.
Figure B-5 EDS spectra of Fap and Zr-containing apatite samples.
Figure C-1 FTIR spectra of fluorapatite and Zn-containing apatites.

Figure C-2 FTIR spectra of the sintered fluorapatite and Zr-containing apatites.
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XPS DATA
Figure D-1 XPS survey spectrum of the Hap sample.

Figure D-2 XPS survey spectrum of as-synthesized fluorapatite.
Figure D-3 XPS survey spectrum of the 25ZnFap sample.

Figure D-4 XPS survey spectrum of the 50ZnFap sample.
Figure D-5 XPS survey spectrum of the 75ZnFap sample.

Figure D-6 XPS survey spectrum of the ZnAp sample.
Figure D-7 XPS survey spectra of the Zr-containing samples.
APPENDIX V

XRD PATTERNS
Figure E-1 XRD pattern of used hydroxyapatite powder.

Figure E-2 XRD patterns of fluorapatite before and after sintering at 1200°C for 1 hour.
Figure E-3 XRD patterns of fluorapatite and Zn-containing apatite samples.

Figure E-4 XRD patterns of the sintered Fap and 25ZnAp samples.
APPENDIX VI

TGA/DSC PROFILES
Figure F-1 TGA profiles of Zn-containing hydroxyapatite samples.

Figure F-2 DSC profiles of Zn-containing hydroxyapatite samples.

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Figure F-3 TGA profiles of Zn-containing fluorapatite samples.

Figure F-4 DSC profiles of Zn-containing fluorapatite samples.
Figure F-5 TGA profiles of Zr-containing fluorapatite samples.

Figure F-6 DSC profiles of Zr-containing fluorapatite samples.
VITA

Graduate College
University of Nevada, Las Vegas

Gunanda Waduge Chinthaka Silva

Local Address:
3663 S. Valley View, Apt. # 611
Las Vegas, NV 89103

Home Address:
A-3, 695, Soysapura, Moratuwa
Sri Lanka

Degrees:
Bachelor of Science, Chemistry, 2000
University of Colombo, Sri Lanka

Awards:
Best Presentation in Material Science, American Nuclear Society Student Conference
2004 Wisconsin, Madison April, 2004

Thesis Title: Study on Immobilizing Radionuclides in Apatite-Based Host Phase Materials

Thesis Examination Committee:
Chairperson, Dr. Dennis W. Lindle, Ph. D.
Committee Member, Dr. Spencer M. Steinberg, Ph. D.
Committee Member, Dr. Boyd L. Earl, Ph. D.
Graduate Faculty Representative, Dr. Andrew Cornelius, Ph. D.