Synthesis and characterization of strontium fluorapatite

Chirantha Prageeth Rodrigo
University of Nevada, Las Vegas

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SYNTHESIS AND CHARACTERIZATION OF STRONTIUM FLUORAPATITE

by

Chirantha Prageeth Rodrigo

Bachelor of Science
University of Colombo, Sri Lanka
2001

A thesis submitted in partial fulfillment
of the requirements for the

Master of Science Degree in Chemistry
Department of Chemistry
College of Sciences

Graduate College
University of Nevada, Las Vegas
August 2005
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The Graduate College
University of Nevada, Las Vegas

June 9th, 2005

The Thesis prepared by

CHIRANTHA PARGEETH RODRIGO

Entitled

SYNTHESIS AND CHARACTERIZATION OF STRONTIUM FLUORAPATITE

is approved in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Examination Committee Chair

Dean of the Graduate College

Examination Committee Member

Vernon Hodge

Examination Committee Member

Mall Fu
Proliferation of nuclear waste is a major environmental issue we all face this century. Long lived radioactive isotopes such as \(^{90}\text{Sr}\) contained in spent nuclear fuel have been causing major problems during the disposal stage of the nuclear fuel cycle. Disposal of radioactive isotopes requires a suitable confinement host material in order to dispose of them in a safe and appropriate repository. In this thesis I describe how to synthesize and characterize the mineral fluorapatite as a host material for Sr. Fluorapatite is a naturally occurring mineral with the unit cell formula of \(\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2\). This mineral possesses a stable hexagonal crystal structure and has the natural ability to accommodate foreign cations in its structure.

Pure fluorapatite and varying amounts of strontium-bearing fluorapatite were synthesized by using wet chemical synthesis methods. Products of the synthesis were confirmed by using x-ray powder diffraction analysis. Increasing lattice dimensions were observed with increasing strontium concentration. The hydroxyl stretching band in the
infrared spectra further established the formation of fluorapatite in all synthetic products. It was observed that the strontium substitutions at the Ca sites have influenced the hydroxyl stretching frequency of strontium containing fluorapatite samples. The stretching and bending modes of the phosphate groups have also been slightly affected by Sr$^{2+}$ insertion but have not changed the basic fluorapatite structure. SEM images of the annealed fluorapatite samples also verify the formation of hexagonal crystals.
TABLE OF CONTENTS

ABSTRACT .................................................................................................................................. iii

LIST OF FIGURES .................................................................................................................... vii

LIST OF TABLES ..................................................................................................................... ix

ACKNOWLEDGEMENTS ......................................................................................................... x

CHAPTER 1 INTRODUCTION ................................................................................................. 1
  1.1 Introduction to nuclear waste .................................................................................... 1
  1.2 Waste form materials .............................................................................................. 2
  1.3 Fluorapatite Mineral ................................................................................................. 3
  1.4 Review on methods of apatite synthesis .................................................................. 8
  1.5 Electronic structure of fluorapatite ......................................................................... 8
  1.6 Research goals ........................................................................................................... 11
  1.7 References ............................................................................................................... 13

CHAPTER 2 EXPERIMENTAL ............................................................................................... 15
  2.1 Introduction ............................................................................................................... 15
  2.2 Synthesis of fluorapatite ......................................................................................... 15
  2.3 Characterization of fluorapatite samples .............................................................. 20
  2.4 References ............................................................................................................... 22

CHAPTER 3 RESULTS AND DISCUSSION ....................................................................... 23
  3.1 Introduction ............................................................................................................... 23
  3.2 Synthesis of apatite and X-ray diffraction studies ............................................... 23
  3.3 FT-IR spectroscopy ................................................................................................. 30
  3.4 Raman scattering spectroscopy ............................................................................. 39
  3.5 Scanning electron microscopic studies ............................................................... 42
  3.6 References ............................................................................................................... 49

CHAPTER 4 CONCLUSIONS ................................................................................................ 50

APPENDIX I POWDER XRD DATA .................................................................................... 52

APPENDIX II FTIR SPECTRAL DATA ................................................................................ 56

APPENDIX III RAMAN SCATTERING SPECTRA .......................................................... 59

v

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LIST OF FIGURES

1.1 Computer generated unit cell of fluorapatite with PowderCell 2.4v software ..........5
1.2 Three dimensional view of the two Ca sites ..........................................................5
1.3 (a) Natural fluorapatite (b) natural rock sample from Siberia (c) synthetic fluorapatite from Russia ..........................................................6
1.4 Infrared spectra of Hydroxyl stretching region of the apatite compounds ............10
2.1 UNLV Fluorapatite synthesis apparatus .................................................................17
2.2 Synthetic fluorapatite from KRI institute, Russia ................................................19
3.1 X-ray powder diffraction patterns for (a) natural fluorapatite and (b) predicted powder pattern for fluorapatite ..............................................................24
3.2 Peak 211 shifts with increasing strontium content and 112 peak merges with 211 .................................................................26
3.3 Unit cell dimension change with increasing Sr$^{2+}$ ion content per calcium site ....27
3.4 (a) “a” and “c” increment as a product of pure fluorapatite unit cell dimensions. (b) Change of a/c ratio with increasing strontium content ..................................28
3.5 XRD pattern of RESYN001 sample ......................................................................28
3.6 FTIR spectra of (a) natural fluorapatite-Studyanka, Russia (b) KRI synthetic fluorapatite and (c) UNLV synthetic fluorapatite ......................................................31
3.7 Hydroxyl group vibration region of synthetic hydroxyapatite and UNLV fluorapatite ..............................................................................................................32
3.8 Hydroxyl stretching frequency variation with strontium content ..........................33
3.9 Hydroxyl stretching region of Ca$_5$Fap (a) before heat treatment (b) after the treatment ..................................................................................................................34
3.10 Hydroxyl group stretching region of Ca$_4$SrFap sample (a) without moisture removal treatment (b) after the moisture removal ...........................................35
3.11 (a) FTIR spectrum of RESYN001 sample (b) enlarged IR spectrum of OH stretching region .............................................................................................................36
3.12 Vibrational frequency shifts with strontium content in the fluorapatite sample...38
3.13 Raman spectra of (a) Natural fluorapatite (b) KRI fluorapatite and (c) UNLV fluorapatite ...................................................................................................................39
3.14 Phosphate group vibration frequency of fluorapatite at 965cm$^{-1}$ .....................40
3.15 Raman peak shifts observed with increasing Sr$^{2+}$ ion content ..........................41
3.16 SEM image of the surface of Ca$_5$Fap sample ......................................................42
3.17 (a) voids on Ca$_5$Fap surface (b) crystal formations inside voids ........................43
3.18 (a) $\times$ 1400 and (b) $\times$ 3500 magnification of Ca$_4$SrFap sample surface .......44
3.19 (a) $\times$ 2000 and (b) $\times$ 5000 magnification of Ca$_3$Sr$_2$Fap sample surface 45
3.20 (a) $\times$ 1600 and (b) $\times$ 7500 magnification of Ca$_4$SrFap sample surface ...........46
3.21 Two distinct positions on Ca$_4$SrFap surface with large hexagonal fluorapatite crystals ..........................................................................................................................47
3.22 (a) $\times$ 900 and (b) $\times$ 2700 magnification of Sr$_5$Fap sample surface .................48
| A-1  | XRD pattern of Ca5Fap  | 53 |
| A-2  | XRD pattern of Ca4SrFap | 53 |
| A-3  | XRD pattern of Ca3Sr2Fap | 53 |
| A-4  | XRD pattern of Ca2Sr3Fap | 54 |
| A-5  | XRD pattern of CaSr4Fap  | 54 |
| A-6  | XRD pattern of Sr5Fap   | 54 |
| A-7  | XRD pattern of geologic fluorapatite | 55 |
| A-8  | XRD pattern of KRI fluorapatite | 55 |
| B-1  | FTIR spectra of Ca5Fap  | 57 |
| B-2  | FTIR spectra of Ca4SrFap | 57 |
| B-3  | FTIR spectra of Ca3Sr2Fap | 57 |
| B-4  | FTIR spectra of Ca2Sr3Fap | 58 |
| B-5  | FTIR spectra of CaSr4Fap  | 58 |
| B-6  | FTIR spectra of Sr5Fap   | 58 |
| C-1  | Raman spectra of Ca5Fap  | 60 |
| C-2  | Raman spectra of Ca4SrFap | 60 |
| C-3  | Raman spectra of Ca3Sr2Fap | 60 |
| C-4  | Raman spectra of Ca2Sr3Fap | 61 |
| C-5  | Raman spectra of CaSr4Fap  | 61 |
| C-6  | Raman spectra of Sr5Fap   | 61 |
| C-7  | Raman spectra of KRI fluorapatite | 62 |
| C-8  | Raman spectra of natural fluorapatite | 62 |
LIST OF TABLES

1.1 Unit-cell positions of fluorapatite lattice ................................................................. 4
1.2 Characteristic vibrational modes in fluorapatite and hydroxyapatite minerals ..... 9
1.3 Raman vibration modes of PO$_4^{3-}$ ion (Fluorapatite) .............................................. 11
2.1 Chemical table ........................................................................................................... 16
2.2 Concentrations of Ca$^{2+}$ and Sr$^{2+}$ used and approximated chemical compositions 18
3.1 Unit cell dimensions of fluoro and hydroxyapatite, experimental and literature values ......................................................................................................................... 25
3.2 P-O bond length of different fluorapatite samples ...................................................... 29
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CHAPTER 1

INTRODUCTION

1.1 Introduction to nuclear waste

Most activities dealing with radioactive isotopes produce wastes called nuclear waste, for example, all nuclear power plant activities, fuel cycle activities and military nuclear programs. Additional activities such as scientific research, medical and other types of industrial processes generate a wide variety of complex radioactive wastes.

There are several ways to categorize nuclear waste based upon its characteristics and content. According to the United States classification system, the major nuclear waste categories are; high-level waste (HLW), transuranic waste (TRU), uranium mill tailings and low-level waste (LLW).

High-level waste is produced as a result of reprocessing of fissile materials to produce weapons and spent fuel. More than 99% of the total radioactivity in nuclear waste is contained in HLW. This waste contains highly active radionuclides such as $^{90}\text{Sr}$, $^{137}\text{Cs}$ and long lived isotopes like $^{99}\text{Tc}$.

Transuranic waste includes all of the artificially created radioactive elements in the periodic table, which are heavier than uranium (the actinide series e.g.; Np, Pu). Formation of TRU waste is limited to nuclear reactors, or by bombardment of $^{235}\text{U}$ atoms with excess neutrons.

Uranium mill tailings are soil and other minerals, which co-existed with uranium ore at the natural deposit sites and were left behind when the pure uranium was separated.

In terms of volume, LLW makes up about 85% of the entire nuclear waste generated. LLW includes all materials contaminated with radioactive nuclides other than isotopes,
for example, the gloves and glass containers used when handling any nuclear materials fall under this category, in addition to metals, soil, building rubble and organic materials lightly contaminated with radioactive isotopes.

Disposal of nuclear waste is one of the most difficult and costly environmental problems that we face in the current era. The unsafe release of radioactive waste could lead to catastrophic consequences. One example of which is leaching of radioactive isotopes into the biosphere by ground water, which will ultimately end up contaminating living species. It is a well-known fact that nuclear radiation can cause severe damage to genes by mutation, and also to vital organs. Therefore, it is a necessity to find methods to isolate and immobilize radioactive waste for long periods of time.

Nuclear radiation primarily consists of alpha, beta and gamma particles and their interaction with matter alters the physical and chemical nature of the original form. Alpha (α) particles (\( \frac{4}{2} \text{He} \) ion) have energies of \( \sim 5 \text{MeV} \) and each α-decay can cause about 1500 atomic displacements of a material before it loses its energy. The extent of atomic displacement is considerably lower for β-particles, but they still can ionize materials causing radiolysis. Gamma (γ) radiation also causes atomic displacement through ionization processes.

The other problem associated with HLW is its ability to produce large quantities of heat, and the waste can reach temperatures above 1000°C. Long duration of radioactivity and higher temperature demand proper containment and long term isolation (10,000 to 1 million years) from the biosphere.

1.2 Waste form materials

The long duration of radioactivity and rise in temperature of nuclear waste creates serious challenges in finding suitable host materials for storage. Isolation has been exclusively based on geological and geographical factors in finding a long term storage repository. Proposed and used isolation methods include underground repositories and
under the sea-bed repositories. But factors other than the geological site such in treating nuclear waste. During transmutation most of the long-lived radioactive nuclides will be converted or mutated into less radioactive or short-lived nuclides by irradiation by neutrons. Immobilization is the use of a proper host material to contain waste, which satisfies physicochemical demands.

There have been several world wide studies conducted to find new host forms and to optimize the properties of existing waste immobilization materials. Cements, glass forms, natural ceramic, and synthetic ceramics are among the most common candidates for waste forms. To be a suitable host material, several factors must be met: including cost effectiveness, degradation resistance (cracking and powdering), accommodation of significant quantities of radioactive nuclides (~10% w/w) in their structure, and finally have the ability to sustain heavy doses of radiation. It has been shown that glass materials (e.g. boron glass) have formed air bubbles inside as a result of radiation induced reactions. Such formations in the structure lead to cracking and powdering of the waste forms. In addition, having thermal stability over 1000°C is an essential factor since most of radioactive waste will reach temperatures higher than this within the first several hundred years.

1.3 Fluorapatite Mineral

Fluorapatite is the most widespread member in the apatite family. The apatite mineral family has the common structural formula of $M_{10}(AO_4)_3X_2$ (M= alkaline earth element, A= P, S, Si and X' can be Cl', F', OH' or CO$_3^{2-}$). The most common sub-group in the apatite group is phosphate apatite. Phosphate apatite is not only a geological mineral but it is also a bio-ceramic. Some percentage of the hard body bones are comprised of apatite (carbonate apatite). The basic phosphate apatite structure has a chemical formula of $Ca_5(PO_4)_3X$ and depending on the anion F', Cl' and OH' they are categorized as fluorapatite, chloroapatite and hydroxyapatite respectively. Fluorapatite is the most
favorable out of the three due to its abundance and high strength. Fluorapatite forms the protective layer of teeth that we call enamel.\textsuperscript{14,15} Fluorapatite possesses a hexagonal crystal structure with a P6\textsubscript{3}/m space group. The Table 1.1 shows the lattice coordinates of the unit cell and Figure 1.1 shows a computer generated unit cell of fluorapatite.

Table 1.1 Unit-cell positions of fluorapatite lattice\textsuperscript{14}

<table>
<thead>
<tr>
<th>Atom</th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca(I)</td>
<td>0.6667</td>
<td>0.3333</td>
<td>0.0010</td>
</tr>
<tr>
<td>Ca(II)</td>
<td>-0.0071</td>
<td>0.2423</td>
<td>0.2500</td>
</tr>
<tr>
<td>P</td>
<td>0.3690</td>
<td>0.3985</td>
<td>0.2500</td>
</tr>
<tr>
<td>O(I)</td>
<td>0.4849</td>
<td>0.3237</td>
<td>0.2500</td>
</tr>
<tr>
<td>O(II)</td>
<td>0.4667</td>
<td>0.5875</td>
<td>0.2500</td>
</tr>
<tr>
<td>O(III)</td>
<td>0.2575</td>
<td>0.1342</td>
<td>0.0705</td>
</tr>
<tr>
<td>F</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.2500</td>
</tr>
</tbody>
</table>

$\alpha = 90^\circ, \beta = 90^\circ, \gamma = 120^\circ$

There are two non-equivalent, symmetrically and crystallographically different Ca\textsuperscript{2+} ions in the apatite structure. Out of the ten Ca ions in a unit cell, four Ca ions occupy four-fold (4f) sites and the other six Ca ions occupy the six-fold (6h) sites. These two types of Ca ion positions have been defined in previous studies as Ca\textsubscript{I} and Ca\textsubscript{II} respectively.\textsuperscript{14} The Ca\textsubscript{I} site is the larger of the two sites, and has a trigonal symmetry surrounded by nine polyhedra of oxygen atoms. The six Ca\textsubscript{II} sites are smaller in size and lower in symmetry because they are surrounded by six oxygen atoms and one fluorine atom, illustrated in Figure 1.2.

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Figure 1.1 Computer generated unit cell of fluorapatite with PowderCell 2.4v software

Figure 1.2 Three dimensional view of the two Ca sites

Ca$_{I}$

Ca$_{II}$

Figure 1.2 Three dimensional view of the two Ca sites
There are six phosphorus atoms in one unit cell of fluorapatite, each of which has six-fold site (6h) symmetry. The end ion fluoride (in fluorapatite) is centered on hexagonal faces and surrounded by a triangle of Ca^{II} ions.¹⁴

Fluorapatites with different colors (green, blue, white, etc.) can be found in nature. The difference in color depends on the trace cations present in the structure.¹⁶ Apatite is considered as a semi-precious gem because of its appearance and clarity, but it has a moderate hardness (fluorapatite=5, diamond=10) and is susceptible to cracking.¹⁷ Pure fluorapatite crystals have a melting point of 1923 K (1650°C) and a density of 3.2 g/cm³.¹⁸ All the phosphateapatites have very low solubility in water and fluorapatite has the lowest solubility compared to hydroxy and chloroapatite, which is confirmed by the lower solubility product of fluorapatite (logK_{sp} for chloroapatite, hydroxyapatite and fluorapatite are -112, -116 and -119, respectively).¹⁹

\[
\text{Ca}_5(\text{PO}_4)_3\text{F} \rightarrow 5 \text{Ca}^{2+} + 3 \text{PO}_4^{2-} + \text{F}^- \quad \text{pK}_{sp} = 119
\]
The solubility of fluorapatite increases with increasing temperature and decreases as the pH of the medium increases, and given enough time it will completely dissolve in mineral acids.

The thermal stability of apatites has attracted lot of attention from research scientists because of its structural ability to withstand to higher temperatures.\textsuperscript{20,21} Its high melting point is one of the many important properties required to be a host material for nuclear materials. The chemical and radiation stability of fluorapatite can be illustrated by an example found in nature, the natural reactor of Oklo (Gabon). This is a uranium deposit containing apatite that has remained intact for over two billion years.\textsuperscript{22} Some scientific research has been done to evaluate its ability to retain its crystallinity against ion beam irradiation experiments compared to other waste forms such as Zircon.\textsuperscript{2}

One exceptional characteristic of fluorapatite is its ability to accommodate different cations and anions in its structure. For example, replacement of Ca ions and, in some cases, P atoms by different cations, such as Sr, Mn, Cu, Na, Cs, Pb, Fe and Ni, has been observed in geologic fluorapatite deposits.\textsuperscript{20,23,24} The accommodation of these other ions is based on their size and oxidation state.\textsuperscript{14} A number of studies have been conducted to try and understand cation substitution in this mineral,\textsuperscript{16,18,23,24} and has shown that the substitution preference of different cations in the fluorapatite structure depends on several factors. The ionic size, the oxidation states and coordination preferences of the substituting cation are a few of them.\textsuperscript{16} As an example, Hughes \textit{et al} reported Mn and Sr distribution in fluorapatite crystal. The study shows that the large Sr\textsuperscript{2+} ion prefers to occupy the smaller Ca\textsubscript{II} sites and the smaller Mn\textsuperscript{2+} occupies the larger Ca\textsubscript{I} sites. The manganese ions prefer higher coordination and occupy nine oxygen-coordinated sites preferentially the Ca\textsubscript{II} site. Elements which form highly coordinated compounds, such as Mn also replace the P atoms with +5 oxidation state cations.\textsuperscript{16,25}

The substitutions of monovalent or trivalent cations in the apatite structure have also been observed in natural and synthetic fluorapatite. Replacement of a divalent cation with
a trivalent cation introduces an extra positive charge into the structure and an opposite effect can be observed with monovalent cations. These types of charge variations must be compensated within the existing structure and ions. As an example, it has been reported by Nelson et al with Yb$^{3+}$ doped strontium fluorapatite. Trivalent Yb has show the tendency to occupy the lower symmetry Ca$_{II}$ site, and charge compensation has been achieved by substitution of F$^{-}$ with O$^{2-}$.

1.4 Review on methods of apatite synthesis

A major advantage of fluorapatite as a waste form is the possibility of uncomplicated and low-cost synthesis under ambient conditions. There have been several popular methods used in synthesizing fluorapatite and hydroxyapatite, two effective examples being solid-state synthesis and wet chemical synthesis:

1. Solid state synthesis: Calcium Fluoride and tri-calcium phosphate mixed by an agate miller at Ca/P ratio of 1.67. The mixed chemicals were heated to 1200$^\circ$C for two hours in an alumina crucible.

2. Wet chemical synthesis: a solutions of Ca(NO$_3$)$_2$ (750mL, 0.392 molL$^{-1}$) was introduced into a boiling solution (750mL) containing 0.330molL$^{-1}$ (NH$_4$)$_2$HPO$_4$ and NH$_4$F 0.160 molL$^{-1}$, in a drop-wise manner. The pH of the mixture was adjusted to 9 by adding aqueous ammonia solution. The resulting fluorapatite was then collected by vacuum filtration.

1.5 Electronic structure of fluorapatite

The electronic and molecular structure of fluorapatite can be investigated by several different analytical tools. Fourier transformed infrared spectroscopy, Raman scattering spectroscopy and XPS (X-ray photoelectron spectroscopy) are just a few of them. Comparison and understanding of spectroscopic characteristics of fluorapatite provides essential information for the process of fabricating a stable waste form.
1.5.1 Infrared Spectroscopy studies on Fluorapatite

The most essential and the only polyatomic ion in fluorapatite is the phosphate group. A unit cell contains six phosphorous atoms and each phosphorous atom is surrounded by a tetrahedron of oxygen atoms. The covalent P-O bond distance is approximately $1.54\text{Å}$ in the ideal model. The vibrational modes of the phosphate group are the most prominent IR bands of fluorapatite. Table 1.2 summarizes most of the IR bands of fluorapatite and hydroxyapatite. It has been reported that the substitution of different ions into the apatite structure reduces the symmetry and hence gives rise to a number of new absorbance bands in the IR spectra. The most basic differences between hydroxyapatite and fluorapatite IR spectra can be observed in 3500-3650 cm$^{-1}$ region.

Table 1.2 Characteristic vibrational modes in fluorapatite and hydroxyapatite minerals$^{19,24}$

<table>
<thead>
<tr>
<th>Vibration mode</th>
<th>Vibration frequency (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fluorapatite</td>
</tr>
<tr>
<td>$\text{PO}_4 v_1$</td>
<td>965</td>
</tr>
<tr>
<td>$\text{PO}_4 v_2$</td>
<td>432</td>
</tr>
<tr>
<td></td>
<td>449</td>
</tr>
<tr>
<td>$\text{PO}_4 v_3$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1034</td>
</tr>
<tr>
<td></td>
<td>1042</td>
</tr>
<tr>
<td></td>
<td>1053</td>
</tr>
<tr>
<td></td>
<td>1061</td>
</tr>
<tr>
<td></td>
<td>1081</td>
</tr>
<tr>
<td>$\text{PO}_4 v_4$</td>
<td>581</td>
</tr>
<tr>
<td></td>
<td>592</td>
</tr>
<tr>
<td></td>
<td>608</td>
</tr>
<tr>
<td></td>
<td>615</td>
</tr>
<tr>
<td>$\text{OH} v_1$</td>
<td>3540</td>
</tr>
</tbody>
</table>
The stretching mode of the OH group in hydroxyapatite is found to be at 3575 cm\(^{-1}\) and has shown significant shifting depending on the nearest neighboring X ion (X=Cl, F). Most synthetic and natural chloroapatite and fluorapatite have a tendency to accommodate small percentages of hydroxyl groups in the apatite structure, in these instances, the hydroxyl group forms hydrogen bonding with the adjacent X ion. This type of interaction shifts the OH stretching band towards lower frequency by 35 cm\(^{-1}\) to 80 cm\(^{-1}\) for F and Cl, respectively, as can be seen in Figure 1.4. The vibrational frequency of the OH group also varies with the cation substitution on the Ca\(_{II}\) site. Partial replacements at the Ca\(_{II}\) site could also result in peak broadening of the OH stretching band.

1.5.2 Raman spectroscopy

Just like the infrared spectroscopy studies, Raman spectra of fluorapatite also shows four internal vibrational modes for the PO\(_4^{3-}\) group. Table 1.3 lists the vibrational frequencies for each symmetry element.
Table 1.3 Raman vibration modes of PO$_4^{3-}$ ion (Fluorapatite)$^{15,19}$

<table>
<thead>
<tr>
<th>Vibration mode</th>
<th>Symmetry element</th>
<th>Wavenumber (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_1$</td>
<td>$A_gE_{2g}$</td>
<td>963</td>
</tr>
<tr>
<td>$v_2$</td>
<td>$E_{1g}A_g$</td>
<td>430</td>
</tr>
<tr>
<td></td>
<td>$E_{2g}$</td>
<td>446</td>
</tr>
<tr>
<td></td>
<td>$A_g$</td>
<td>451</td>
</tr>
<tr>
<td>$v_3$</td>
<td>$E_{2g}$</td>
<td>1034</td>
</tr>
<tr>
<td></td>
<td>$E_{1g}$</td>
<td>1042</td>
</tr>
<tr>
<td></td>
<td>$A_g$</td>
<td>1052</td>
</tr>
<tr>
<td></td>
<td>$E_{2g}$</td>
<td>1060</td>
</tr>
<tr>
<td></td>
<td>$A_g$</td>
<td>1080</td>
</tr>
<tr>
<td>$v_4$</td>
<td>$E_{2g}$</td>
<td>580</td>
</tr>
<tr>
<td></td>
<td>$A_g$</td>
<td>592</td>
</tr>
<tr>
<td></td>
<td>$E_{1g}$</td>
<td>592</td>
</tr>
<tr>
<td></td>
<td>$A_g$</td>
<td>608</td>
</tr>
<tr>
<td></td>
<td>$E_{2g}$</td>
<td>617</td>
</tr>
</tbody>
</table>

A cage of cations surrounds all the phosphate groups in the fluorapatite crystal. It has been reported that the substitution of different cations in Ca sites at varying degree influences the Raman bands by peak broadening and shifting.$^{15}$

1.5.3 XPS and XANES studies on fluorapatite

The XPS and X-ray absorption studies for fluorapatite have not been extensively documented. Since both techniques deal with inner electrons of atomic systems, they provide methods of probing the electronic configuration, coordination and oxidation states of substituted atoms in the apatite structure.$^{26,29}$

1.6 Research goals

The initial goal of this thesis was the synthesis of fluorapatite and Sr-bearing fluorapatite, the results of which were confirmed by X-ray powder diffraction analysis. Furthermore, the characterization of pure fluorapatite and strontium-apatite was done using spectroscopic methods such as FTIR, Raman and scanning electron micro imaging.
techniques. The influence of strontium on the fluorapatite crystal structure was closely investigated by Raman and IR band shifts. In addition, a novel fluorapatite synthesis procedure was also tested using a natural fluorapatite sample. Products of this synthesis were also analyzed with FTIR and crystallographic methods.
1.7 References

1. Yim M. S., Murty K. L., JOM, 2000, 52(9), 26-29
5. Rodriguze C., Baxter A.; 8th International conference on nuclear engineering, ICONE 8, April, 2000, Baltimore, MD, USA
17. http://webmineral.com/data/Fluorapatite.shtml

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   V.G. Khlopin Radium Institute, Saint-Petersburg, Russia
CHAPTER 2

EXPERIMENTAL

2.1 Introduction

The experimental section of this research study will be discussed in two sections: (1), synthesizing fluorapatite and waste loaded fluorapatite, and (2) the characterization of natural apatite and synthesized fluorapatite. The synthesis was done using a wet chemical method under laboratory conditions, and the initial characterization was done using x-ray diffraction (XRD) technique. Spectroscopic methods such as Fourier transformed infrared spectroscopy (FTIR), Raman scattering spectroscopy, X-ray photoelectron spectroscopy (XPS) and x-ray absorption spectroscopy (XANES) were also employed to investigate the physical and electronic structural alterations of the ceramic. Scanning electron microscopy (SEM) images were obtained for topological studies. We also characterized natural apatite samples from the Russian Federation and Pakistan for comparison to our synthesized ceramics. Finally, synthetically formed fluorapatite from our project collaborators in V.G. Khlopin Radium Institute, Saint Petersburg, Russia were also characterized and compared to our results.

2.2 Synthesis of fluorapatite

There are only a few published methods on the synthesis of fluorapatite and other apatites, and these types can be further categorized into wet chemical methods and solid state synthesis. The method of synthesis merely depends on the application of the material and the target form of the apatite.
2.2.1 Fluorapatite synthesis at UNLV

We adopted the wet chemical method to synthesize fluorapatite which was published by Hidouri et al in 2003. The chemicals used for this synthesis are shown in Table 2.1.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Formulae</th>
<th>CAS Number</th>
<th>Product of</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium nitrate tetrahydrate</td>
<td>Ca(NO₃)₂·4H₂O</td>
<td>13477-34-4</td>
<td>Merck, Germany</td>
</tr>
<tr>
<td>Strontium nitrate</td>
<td>Sr(NO₃)₂</td>
<td>10042-76-9</td>
<td>Alfa-Aesar, MA</td>
</tr>
<tr>
<td>Ammonium fluoride</td>
<td>NH₄F</td>
<td>12125-01-8</td>
<td>Alfa-Aesar, MA</td>
</tr>
<tr>
<td>Ammonium hydrogenphosphate</td>
<td>(NH₄)₂HPO₄</td>
<td>7783-28-0</td>
<td>Alfa-Aesar, MA</td>
</tr>
</tbody>
</table>

Fluorapatite and strontium substituted fluorapatite were synthesized by aqueous precipitation from calcium nitrate and strontium nitrate reacting with an aqueous mixture of ammonium hydrogen phosphate and ammonium fluoride. The experimental setup is shown in the Fig 2.1. A solution of 100 mL, containing 0.33 mol/L (NH₄)₂HPO₄ and 0.16 mol/L NH₄F was heated to its boiling temperature and the pH of the solution was maintained at 9 with occasional addition of aqueous ammonia solution during the reaction time. The cation mixture, containing Ca²⁺ and Sr²⁺ at appropriate concentrations as shown in Table 2.2, was added by slowly dropping it in while stirring the product vigorously. The mixture was aged under stirring for three hours. The precipitate was collected by vacuum filtration and washed with distilled water. All samples were dried overnight at room temperature in a dessicator before grinding to powder form. The powdered samples were heated to 150°C for two hours to remove any residual moisture and then annealed at 1200°C for two hours.
Figure 2.1 UNLV Fluorapatite synthesis apparatus
Table 2.2 Concentrations of Ca\(^{2+}\) and Sr\(^{2+}\) used and approximated chemical compositions.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Sr(NO(_3))(_2) molL(^{-1})</th>
<th>Ca(NO(_3))(_2) molL(^{-1})</th>
<th>Approx. Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca5Fap</td>
<td>-</td>
<td>0.3920</td>
<td>Ca(_5)(PO(_4))(_3)F</td>
</tr>
<tr>
<td>Ca4Sr1Fap</td>
<td>0.0784</td>
<td>0.3136</td>
<td>Ca(_4)Sr(PO(_4))(_3)F</td>
</tr>
<tr>
<td>Ca3Sr2Fap</td>
<td>0.1568</td>
<td>0.2352</td>
<td>Ca(_3)Sr(_2)(PO(_4))(_3)F</td>
</tr>
<tr>
<td>Ca2Sr3Fap</td>
<td>0.2352</td>
<td>0.1568</td>
<td>Ca(_2)Sr(_3)(PO(_4))(_3)F</td>
</tr>
<tr>
<td>Ca1Sr4Fap</td>
<td>0.3136</td>
<td>0.0784</td>
<td>CaSr(_4)(PO(_4))(_3)F</td>
</tr>
<tr>
<td>Sr5Fap</td>
<td>0.3920</td>
<td>-</td>
<td>Sr(_5)(PO(_4))(_3)F</td>
</tr>
</tbody>
</table>

2.2.2 Fluorapatite synthesis at KRI, Russia

The following procedures were used by the KRI institute for the preparation of their starting precursor materials for the synthesis of un-doped fluorapatite [Ca\(_5\)(PO\(_4\))\(_3\)F] and Sr-apatite [Sr\(_5\)(PO\(_4\))\(_3\)F]. An aqueous solution of Ca(NO\(_3\))\(_2\) was mixed with an excess of phosphoric acid [H\(_3\)PO\(_4\)]. In the Sr-apatite synthesis, dried Sr(OH)\(_2\) was reacted with the excess phosphoric acid. These aqueous mixtures were then mixed with excess (NH\(_4\))F:HF, while maintaining the pH of the solution at 7 by adding NH\(_4\)OH. The increase of pH caused precipitation of “raw” apatite material. The powder obtained was then rinsed in distilled water and air dried at 150°C for 1 hour. The “raw” apatite powder was ground in a ball mill (with Al\(_2\)O\(_3\) balls) in a water medium for 3 hours. This wet powder was filtered and air dried at 25°C for 24 hours. The precursors obtained were then mixed with an aqueous solution of 5% polyvinyl-alcohol (weight ratio of powder to solution was 10:1) and then dried in air at 25°C for 24 hours. The starting materials were finally cold pressed into pellets of 10 mm in diameter. Figure 2.2 shows the synthetic fluorapatite samples from the KRI institute.\(^2\)
2.2.3 Apatite synthesis using natural apatite as the starting chemical

We also experimented with a new synthesis procedure to re-synthesize apatite using naturally occurring fluorapatite as the starting material. Natural fluorapatite has a very low solubility in water but we can increase the solubility by increasing the liquid acidity. A rock sample of natural apatite (1.0g) was crushed and ground to a fine powder. It was then suspended in 100 mL of water and the pH value was reduced to 3 by the addition of nitric acid [HNO₃]. The mixture was boiled until the precipitate dissolved completely. The resulting solution was then treated with a concentrated solution of ammonia by adding drop-wise till the pH reached a value above 8. A white precipitate was formed and it was washed with distilled water before separation under vacuum filtration. The product was dried overnight at room temperature in a desiccator before it was ground to powder form. The powdered sample was heated to 150°C for two hours to remove residual moisture, and labeled as RESYN001.
2.3 Characterization of fluorapatite samples

2.3.1 X-ray powder diffraction analysis

X-ray powder diffraction patterns were obtained for all synthetic samples and natural apatite samples as a first step of characterization. Fluorapatite samples were analyzed using a Philips PANalytical® X-ray diffractometer with Cu-Kα wavelength (1.54060Å). Each scan was done within the 2θ range from 6° to 75° with a step size of 0.0170° and a scanning step time of 22 seconds. The finely powdered samples were mixed with ethanol in order to get a slurry of the powder, which allows a uniform distribution of the sample on a silicon plate. The silicon plate holds the sample during the irradiation with a X-ray beam. The ethanol was evaporated thoroughly before the start of the experiment. Diffraction patterns were refined with the Rietveld method by using Powder Cell version 2.4.

2.3.2 Fourier Transformed Infrared spectroscopy

Fourier transform infrared spectroscopy, FTIR, was employed to yield valuable evidence regarding the IR active covalent functional groups of the synthetic fluorapatite and natural fluorapatite. FTIR measurements were obtained with a BIO-RAD FTS 7000 spectrometer using a photoacoustic detector. FTIR spectra for each sample were taken in the region from 400 cm\(^{-1}\) to 4000 cm\(^{-1}\). Samples were scanned 64 times with a resolution of 3.86 cm\(^{-1}\). This instrument can measure both powder forms and solid pieces of samples.

2.3.3 Raman scattering spectroscopy

Raman scattering spectroscopy data provides information about vibrational modes of the phosphate group and changes of bands with the introduction of foreign cations into the apatite structure. Raman spectra were obtained in the range of 200 cm\(^{-1}\) to 1200 cm\(^{-1}\) with the step size of 0.22 cm\(^{-1}\). All measurements were performed using a laser beam with a radiation source at 514.5 nm wave length. The slit width was kept at 200 μm and each point was scanned for 3-5 seconds.
2.3.4 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy of fluorapatite provides atomic composition of the surface of samples. X-ray Photoelectron spectroscopic measurements were collected by employing a surface science SSX-100 system with an Al-Kα X-ray source (1486.67eV) and a hemispherical electron analyzer. The powdered fluorapatite samples were mounted on a double-sided tape on a piece of aluminum foil. During the measurements pressure in the analysis chamber was maintained at $5 \times 10^{-9}$ Torr or lower.

2.3.5 X-ray absorption near edge structure spectroscopy

X-ray absorption studies of apatite samples were done at the Advanced Light Source at Berkeley, California. The bend magnet beam-line 6.3.1 was used for measurements in the range of 300eV to 2000eV. The oxygen K-edge, Ca-L\textsubscript{2,3} edges and Sr-M\textsubscript{2,3} edges were measured with a step size of 0.1eV. All samples were measured in powder form because of the non-conducting nature of the material. Thin layers of powder samples were mounted on carbon tape for analysis. The pressure in the analysis chamber was brought down to $1\times10^{-8}$ Pa before taking the measurements.

2.3.6 Scanning electron microscopy

A scanning electron microscope (SEM) was employed to examine the formation and the size of the fluorapatite crystals on the ceramic surface. SEM images were obtained with a JEOL 5600 electron microscope equipped with a backscatter electron detector. The samples were mounted on carbon tape and coated with gold or carbon to sustain an electric conduction of the samples surfaces. Measurements were taken at 15kV of electron acceleration voltage.
2.4 References


2. Burakov B. E., *Development of Fluorapatite as a Waste Form* - Final Report, 2004. V.G. Khlopin Radium Institute, Saint-Petersburg, Russia
CHAPTER 3

RESULTS AND DISCUSSION

3.1 Introduction

As explained in chapter two, fluorapatite is a fairly abundant mineral deposit around the world. This fact encourages the use of geological apatite as a starting material for synthesizing waste-bearing fluorapatite. The ease of synthesizing fluorapatite under laboratory conditions also makes it an attractive choice as a waste form material. Incorporation of radioactive isotopes into a fluorapatite host material would result in many changes in the physical and chemical properties of the original material, especially, the replacement of Ca$^{2+}$ ions in fluorapatite by larger cations. This could increase the basic unit cell dimensions, causing the electronic and vibrational structure of fluorapatite to undergo changes as a consequence of heavy ion inclusion into the material. Furthermore, it has been shown that synthesis of foreign cation incorporated fluorapatite has resulted in the formation of undesired by-products.\(^2\) Therefore, the presence of crystalline or amorphous by-product phases within the fluorapatite matrix should be expected.

3.2 Synthesis of apatite and X-ray diffraction studies

X-ray powder diffraction patterns were obtained for all samples including natural apatites as the first line of analysis. The initial phase identification was performed using PANalytical® X’Pert Pro® HighScore v.2.0 software. Further structure refinements were carried out by using the Powder Cell® software version 2.4. The XRD pattern for the
natural fluorapatite(a) and the predicted powder pattern for fluorapatite(b) are presented in Figure 3.1.

![X-ray powder diffraction patterns for (a) natural fluorapatite and (b) predicted powder pattern for fluorapatite](image)

Figure 3.1 X-ray powder diffraction patterns for (a) natural fluorapatite and (b) predicted powder pattern for fluorapatite

The calculated and experimental powder patterns are in good agreement, except for slight changes in intensities of some peaks. This type of inconsistency is expected in non-ideal cases like natural minerals and because of the uneven orientation of small crystals on the sample holder. A comparison between literature and experimental values for unit cell dimensions is tabulated in Table 3.1. It is apparent that there is a slight difference in the values for “a” and “b” dimensions. Such small differences in cell dimensions can be caused by partial substitutions of hydroxyl groups and occasional substitutions at fluoride sites by carbonate (CO$_3^{2-}$) groups.$^3$
Table 3.1 Unit cell dimensions of fluoro and hydroxyapatite, experimental and literature values

<table>
<thead>
<tr>
<th>specimen</th>
<th>ICDD PDF No</th>
<th>a, b /Å</th>
<th>c /Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorapatite(lit)</td>
<td>15-0876</td>
<td>9.368</td>
<td>6.884</td>
</tr>
<tr>
<td>Hydroxyapatite(lit)</td>
<td>09-0432</td>
<td>9.418</td>
<td>6.884</td>
</tr>
<tr>
<td>Natural apatite, Russia</td>
<td>-</td>
<td>9.381</td>
<td>6.882</td>
</tr>
<tr>
<td>KRI, Fluorapatite</td>
<td>-</td>
<td>9.367</td>
<td>6.882</td>
</tr>
<tr>
<td>UNLV, Fluorapatite</td>
<td>-</td>
<td>9.364</td>
<td>6.880</td>
</tr>
<tr>
<td>Ca4srFap</td>
<td></td>
<td>9.441</td>
<td>6.965</td>
</tr>
<tr>
<td>Ca3Sr2Fap</td>
<td></td>
<td>9.513</td>
<td>7.038</td>
</tr>
<tr>
<td>Ca2Sr3Fap</td>
<td></td>
<td>9.580</td>
<td>7.118</td>
</tr>
<tr>
<td>CaSr4Fap</td>
<td></td>
<td>9.650</td>
<td>7.196</td>
</tr>
<tr>
<td>Sr5Fap</td>
<td></td>
<td>9.703</td>
<td>7.273</td>
</tr>
</tbody>
</table>

The powder diffraction pattern was obtained for the fluorapatite sample synthesized at the KRI institute. The unit cell dimensions for the KRI fluorapatite and natural and UNLV-synthesized samples are approximately the same.

With the incorporation of strontium into fluorapatite slight peak shifts can be observed in all samples. (Appendix I shows XRD powder patterns for each apatite sample). For instance, Figure 3.2 shows the peak for the 211 plane shifting to lower 20 value with increasing strontium content. In addition, it is apparent that the peak 112 merges with 211 with the incorporation of Sr\(^{2+}\). In samples CaSr4Fap and Sr5Fap, both 112 and 211 peaks have completely overlapped. Therefore the 112 peak is not observed in Sr5Fap sample.
Figure 3.2 Peak 211 shifts with increasing strontium content and 112 peak merges with 211

The unit cell lengths, c, were calculated for each sample and are also included in Table 3.1. The calculated unit cell lengths were plotted against the substituted strontium content per calcium site. The unit cell expansion shows a linear relationship with the amount of strontium incorporated and it is shown in Figure 3.3. All three unit cell parameters vary proportionately with the increasing strontium content per calcium site. This is an indication that the synthesis of strontium fluorapatite can be controlled by changing the initial concentration ratio of Ca/Sr ions. It is possible to compare the changes in cell dimension by using a normalized chart and the a/c ratio. Such a comparison is shown in Figure 3.4.
Figure 3.3 Unit cell dimension change with increasing Sr$^{2+}$ ion content per calcium site.
Figure 3.4 (a) "a" and "c" increment as a product of pure fluorapatite unit cell dimensions. (b) Change of a/c ratio with increasing strontium content

The effect of cation substitution is more prominent on the "c" axis than on the "a" or "b" axes. Figure 3.4 illustrates the increment of unit cell lengths as factors of pure fluorapatite unit cell lengths. The change in the length of the unit cell dimension influences the bond distances in strontium-incorporated fluorapatite; for example, an increase in the bond distance between P and O atoms. These P-O bond lengths are tabulated in Table 3.2. The change in the bond length may affect the vibrational spectra of fluorapatite, especially for phosphate group vibrational bands.
Table 3.2 P-O bond length of different fluorapatite samples

<table>
<thead>
<tr>
<th>Compound</th>
<th>Average P-O bond distance / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural Fap</td>
<td>1.53</td>
</tr>
<tr>
<td>KRI Fap</td>
<td>1.53</td>
</tr>
<tr>
<td>Ca5Fap</td>
<td>1.53</td>
</tr>
<tr>
<td>Ca4SrFap</td>
<td>1.54</td>
</tr>
<tr>
<td>Ca3Sr2Fap</td>
<td>1.55</td>
</tr>
<tr>
<td>Ca2Sr3Fap</td>
<td>1.57</td>
</tr>
<tr>
<td>CaSr4Fap</td>
<td>1.58</td>
</tr>
<tr>
<td>Sr5Fap</td>
<td>1.59</td>
</tr>
</tbody>
</table>

3.2.1 XRD analysis of RESYN001

The un-annealed RESYN001 sample was also analyzed with XRD for product identification (Figure 3.5). It was clear that the signal-to-noise ratio of the sample was lower than that observed for the other synthetic samples. The diffraction peaks were broad in the RESYN001 sample, indicating this sample has a low crystallinity. This may be due to the fact that this sample was not annealed, as were the other products.

The XRD powder pattern of RESYN001 is also similar to the XRD patterns observed for natural fluorapatite. It is not clear by using only the XRD patterns if the RESYN001 product is hydroxyapatite or fluorapatite; both minerals have almost the same XRD pattern, and the unit cell dimension values (a=b= 9.373Å and c= 6.844Å) are also close to the values obtained for all of the other fluorapatites (Table 3.1). Thus we were required to perform other forms of measurements to clearly define this sample.
3.3 FT-IR spectroscopy

We used FTIR spectroscopy to study the incorporation of strontium and how this incorporation changes the chemical structure of fluorapatite. The infrared spectra of fluorapatite arise from the stretching and bending vibrational modes of the phosphate group ($\text{PO}_4^{3-}$), hydroxyl group, and the $\text{M-X}$ (M= Ca, Sr and X= OH, F) bonds. The photoacoustic IR spectra for all synthesized samples including KRI and natural fluorapatite were obtained to investigate any possible chemical changes occurring due to the strontium cation substitution in the crystal structure. To see these changes, it is important to be familiar with the basic FTIR spectra of natural fluorapatite and our synthetic fluorapatite bands. Figure 3.6 depicts the FTIR spectra of natural, KRI synthetic and UNLV-synthesized fluorapatite specimens.

Above 2000 cm$^{-1}$, all three of the spectra shown in Fig. 3.6 appear to be similar. The obvious difference is the KRI fluorapatite shows a prominent set of resonances near 2960 cm$^{-1}$, which were not observed in the UNLV fluorapatites, and seems to occur very
weakly in the natural fluorapatite. This set of resonances may be due to residues remaining from the polyvinyl alcohol ceramic binder.

In general, we did not expect to observe hydroxyl groups in the fluorapatite structure. Nevertheless, it has been reported that varying percentages of F ions can be replaced by OH ions in geologic fluorapatites depending on the mineral deposit. We can clearly see in Figure 3.6 a prominent resonance at 3538 cm\(^{-1}\) for all three samples, indicating the presence of hydroxyl groups, the presence of which also verifies that the hydroxyl groups have hydrogen-bond interactions with fluoride ions. The peak position (3538 cm\(^{-1}\)) confirms that the main crystal structure is fluorapatite with trace substitutions of hydroxyl groups. A pure, synthetic hydroxyapatite sample showed two distinct characteristic bands in the range of 3000-3600 cm\(^{-1}\). These bands are due to OH stretching of adsorbed moisture (~3200 cm\(^{-1}\), broad) and hydroxyl groups of hydroxyapatite (3573 cm\(^{-1}\)). As can
be seen in Figure 3.7 the hydroxyl group vibration occurring at 3573 cm\(^{-1}\) is 35 cm\(^{-1}\) higher for our sample than for the pure fluorapatite sample. The hydrogen-bond interactions between OH and F have reduced the O-H vibration frequency. The broad peak in hydroxyapatite, around 3200 cm\(^{-1}\), occurs due to adsorbed moisture with widespread hydrogen bonding.

Incorporation of strontium into the fluorapatite structure does not change the basic IR spectra, although slight peak shifts can be observed in hydroxyl and phosphate group frequencies. (Appendix II)

![Figure 3.7 Hydroxyl group vibration region of synthetic hydroxyapatite and UNLV fluorapatite](image)

Previous studies report that the X ion (F\(^-\), Cl\(^-\) or OH\(^-\)) of apatites form a weak covalent bond with the Ca\(^{II}\) ion.\(^{5,6}\) Therefore, replacement of Ca\(^{2+}\) ions by Sr\(^{2+}\) ions changes the bond strength, hence the vibrational frequency of the O-H bond. A more
prominent shift in the OH stretching peak towards higher frequency is observed as the strontium content is increased. The peak position (median) of the OH stretching mode was obtained after a linear background correction and peaks were modeled with PeakFit v.4.12 (SeaSolve Inc.). The stretching frequency linearly increases with the addition of strontium into the fluorapatite as shown in Figure 3.8.

![Graph showing OH stretching frequency variation with strontium content](image)

Figure 3.8 Hydroxyl stretching frequency variation with strontium content

From Figure 3.8 it is evident that the stretching frequency of the hydroxyl group increases with increasing strontium content. As strontium substitutions take place in the Ca sites the hydroxyl groups lose their bond with the Sr$^{2+}$ ions, causing the hydroxyl group stretching frequency to shift to a higher value. The linear dependence of the stretching frequency suggests that Sr ions occupy both Ca sites without selectivity.
3.3.1 Removal of interstitial water

The first batch of Ca-Sr fluorapatite samples was annealed at 1200 °C without moisture removal treatment, which consist of milling and heating the mineral to 150°C overnight. Three samples of fluorapatite (Ca$_5$Fap, Ca$_4$SrFap and Ca$_3$Sr$_2$Fap) showed a peak at 3640 cm$^{-1}$, which was not observed after the moisture removal process (see Figure 3.9 and Figure 3.10).

![Figure 3.9 Hydroxyl stretching region of Ca$_5$Fap (a) before heat treatment (b) after the treatment](image)

As previously reported by Tacker C., the hydroxyl group stretching above 3600 cm$^{-1}$ occurs due to interstitial water in fluorapatite.\(^5\) As seen in our measurements (see peak 3641, Figure 3.9), this resonance is relatively narrow and higher in frequency than the OH stretching peak we observed for simple moisture contamination (Figure 3.7), suggesting that these interstitial water molecules are isolated in the structure and are free of hydrogen bonding.
Figure 3.10 Hydroxyl group stretching region of Ca4SrFap sample (a) without moisture removal treatment (b) after the moisture removal

3.3.2 FTIR spectra of RESYN001 apatite

The FTIR spectrum of RESYN001 shows interesting differences in the hydroxyl-stretching region as compared to all of the other fluorapatite we ran. Figure 3.11 shows this range for the RESYN001 sample and an expanded view of hydroxyl stretching bands around 3550 cm⁻¹.
As we can see from Figure 3.11(b), there are two major and two minor resonances in the hydroxyl group stretching range. Each vibrational frequency indicates different types of hydroxyl groups existing in the RESYN001 sample. According to literature values, the most intense peak is at 3572.5 cm$^{-1}$ is due to hydroxyapatite hydroxyl groups, and the peak at 3544 cm$^{-1}$ is assigned to infrequent substitutions of hydroxyl groups in the fluorapatite structure. The two minor peaks can be assigned as being due to hydroxyl groups, 3495 cm$^{-1}$, which are hydrogen-bonded with chloride ions, and interstitial water molecules, 3653 cm$^{-1}$. These results suggest that our RESYN001 samples consist of three different types of apatites, but it is not possible to conclude the major product based on hydroxyl peak intensities. The above observations also suggest that the original natural apatite sample also contains some percentage of chloroapatite. The phosphate group
vibrational region of RESYN001 samples coincided with the natural fluorapatite IR spectra.

3.3.3 FTIR spectra of phosphate group vibrations

Apart from the hydroxyl group stretching mode, there are other prominent stretching and bending modes visible in fluorapatite samples. For example, the $v_1$ vibrational mode of the PO$_4^{3-}$ group which occurs as sharp peak at around 965 cm$^{-1}$. A set of selected peaks, such as $v_1$, was measured with varying strontium content and plotted. Figure 3.12 shows how a increase in the strontium content influences the phosphate group. It is clear from the plots that as the strontium content increases the phosphate group vibration frequency shifts to lower values. The variations show a linear dependence with the Sr$^{2+}$ content. These relationships have shown different degrees of variation or gradients for each vibrational mode, suggesting the peak shifting is not due to background or instrumental effects and is directly due to Sr incorporation into the structure. As explained in the XRD analysis section, the P-O bond elongation could have affected the phosphate group vibrations and lowered its frequency, but it is also possible that changes in the electronic structure may have affected the frequencies.
Figure 3.12 Vibrational frequency shifts with strontium content in the fluorapatite sample.
3.4 Raman scattering spectroscopy

The Raman spectral region, 200\text{cm}^{-1} to 1200\text{cm}^{-1}, contains most of the phosphate group vibrational modes and the weak M-X bond (M=Ca, Sr and X=F, OH) stretching band.

![Raman spectra](image)

Figure 3.13 Raman spectra of (a) Natural fluorapatite (b) KRI fluorapatite and (c) UNLV fluorapatite

All three fluorapatite samples, geologic, KRI and UNLV show the basic characteristic Raman bands. The geologic sample has a low resolution due to the physical nature of the
sample. The sample is a large single crystal and most of the incident laser light passes directly through the sample unlike the synthetic fluorapatites, which are opaque. The peak positions for all three samples are similar and show small variations in frequencies. The peak variations are most apparent in the intense peak, the $v_1$ symmetric vibration band at 965 cm$^{-1}$.

![Graph](image)

Figure 3.14 Phosphate group vibration frequency of fluorapatite at 965 cm$^{-1}$

Peak positions were obtained with peak-fitting procedures and plotted against the strontium content in the fluorapatite. They show a linearly decreasing relationship with increasing strontium content. The same procedure was applied to other Raman bands to observe the shifting effect. Figure 3.15 shows a few of the selected Raman band shifts with strontium content.
Figure 3.15 Raman peak shifts observed with increasing Sr$^{2+}$ ion content

All Raman bands shift to lower frequency with the introduction of Sr$^{2+}$ ions into the fluorapatite structure. It is also clear that the gradients are different for each absorption band.
3.5 Scanning electron microscopic studies

The objective of employing SEM imaging was to investigate surface changes of fluorapatite after the annealing process. Formations of micro-scale hexagonal crystals has been observed in previous synthetic studies on both pure and foreign cation incorporated apatites. Energy Dispersive Spectroscopy (EDS) was also used to obtain the atomic compositions of selected areas on ceramic surfaces.

A magnified (x800) surface of a Ca5Fap sample is presented in Figure 3.16 which shows that the sample surface is partially covered with a CaO layer. EDS analysis of the exposed surface confirms the presence of Ca, O, P and F.

![SEM image of the surface of Ca5Fap sample](image)

Figure 3.16 SEM image of the surface of Ca5Fap sample
The exposed areas of the Ca5Fap sample have voids. Inside these voids, rod-like crystals can be observed. Even though it is not on the surface, fluorapatite crystals have formed inside the ceramic pieces.

The formation of hexagonal fluorapatite was more visible in Ca4SrFap samples. The two SEM images shown in Figure 3.18 show the rod-like crystals on the ceramic surface.
The longest crystal is about 10\(\mu\)m long and 3\(\mu\)m wide and the entire surface is covered with such crystal structure. Surfaces of Ca3Sr2Fap and Ca2Sr3Fap samples show different morphologies from the previous two samples. A SEM image of Ca3Sr2Fap surface is shown in Figure 3.19 with \(\times\) 2000 and \(\times\) 5000 magnification.
Figure 3.19 (a) x 2000 and (b) x 5000 magnification of Ca3Sr2Fap sample surface
Figure 3.20 (a) x 1600 and (b) x 7500 magnification of CaSr4Fap sample surface

It may be that the Ca3Sr2Fap sample is in a transformation stage to form rod-like crystals on its surface. A longer annealing time may be needed to get a completely crystalline surface as for the Ca4SrFap sample. On the other hand the CaSr4Fap sample showed exceptional formation of hexagonal crystals on the ceramic surface.
In the CaSr4Fap sample some of the crystals are longer than 40μm and 4μm wide. In Figure 3.20(b), we can also observe the cross-section of a crystal, which is hexagonal. Further scanning on the surface showed quite large crystals emerging from the bulk.

Figure 3.21 Two distinct positions on CaSr4Fap surface with large hexagonal fluorapatite crystals.
These large structures seem to have hexagonal shapes with sharp edges. EDS elemental analysis showed that these large crystals contains Sr, Ca, P, O and F.

The SEM images of un-annealed samples did not show any crystal formations as observed in the annealed samples. This observation concludes that the annealing procedure enables the formation of fluorapatite crystals.

The SEM images of the SrSFap sample showed a large number of voids but did not show any particular crystalline structure (see Figure 3.22).

Figure 3.22 (a) x 900 and (b) x 2700 magnification of Sr5Fap sample surface

Even though there was no indication of crystal formations, chemical composition analysis showed the presence of Sr, P, O and F on the surface.
3.6 References

1. Burakov B. E., *Development of Fluorapatite as a Waste Form - Final Report*, 2004. V.G. Khlopin Radium Institute, Saint-Petersburg, Russia


CHAPTER 4

CONCLUSIONS

The purpose of this project was to synthesize waste loaded (non-radioactive) fluorapatites and characterize the samples by using conventional spectroscopic methods, and to compare our synthetic samples with natural geologic fluorapatite and another synthetic fluorapatite (KRI) samples.

The synthesis of foreign cation-incorporated fluorapatite, in this case strontium ions, was achieved successfully using the method described in the experimental section. XRD powder patterns of fluorapatite and Sr-fluorapatite showed identical peaks except for slight peak shifts and peak merging. Increasing strontium content showed a linear relationship with unit cell dimensions, the relationship of which can allow us to measure unknown percentages of strontium in fluorapatite. It has been shown that Sr occupies only Ca sites and not P or O sites because the measured XRD spectra and calculated spectra can only be fitted successfully when Sr ions are at larger Ca sites.

The hydroxyl group stretching frequency of Sr-apatite has also confirmed the synthesis results. Sr-apatite has higher vibrational frequency for OH groups than for pure fluorapatite. The OH vibration peak shifted to higher values as the strontium concentration increases. The hydroxyl stretching frequency varies linearly with increasing strontium content, indicating Sr ion preferences for site selectivity. Most of the vibrational bands in the IR and Raman spectra arise from stretching and bending modes
of the phosphate group. It was observed that the selected bands have shifted to lower values with increasing strontium content. The gradients of variations are different for each band, indicating a possible elongation of P-O bond length or a change in the electronic structure of the mineral.

SEM images of strontium-incorporated fluorapatite showed the formation of hexagonal crystals on the surfaces of most samples. Formation of fluorapatite crystals has not been observed in the same samples before annealing at 1200 °C.

Re-synthesis of apatite using natural fluorapatite as a starting material has been achieved successfully. RESYN001 samples showed the basic XRD powder pattern and FTIR bands. The final product contained fluorapatite, chloroapatite and hydroxyapatite phases and it is inconclusive as to which was the major component.
Figure A-1 XRD pattern of Ca5Fap

Figure A-2 XRD pattern of Ca4SrFap

Figure A-3 XRD pattern of Ca3Sr2Fap
Figure A-4 XRD pattern of Ca$_2$Sr$_3$Fap

Figure A-5 XRD pattern of CaSr$_4$Fap

Figure A-6 XRD pattern of Sr$_5$Fap

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Figure A-7 XRD pattern of geologic fluorapatite

Figure A-8 XRD pattern of KRI fluorapatite
APPENDIX II

FTIR SPECTRAL DATA
Figure B-1 FTIR spectra of Ca5Fap

Figure B-2 FTIR spectra of Ca4SrFap

Figure B-3 FTIR spectra of Ca3Sr2Fap
Figure B-4 FTIR spectra of Ca$_2$Sr$_3$Fap

Figure B-5 FTIR spectra of CaSr$_4$Fap

Figure B-6 FTIR spectra of Sr$_5$Fap
APPENDIX III
Raman Scattering Spectra
Figure C-1 Raman Spectra of Ca5Fap

Figure C-2 Raman Spectra of Ca4SrFap

Figure C-3 Raman Spectra of Ca3Sr2Fap
Figure C-4 Raman Spectra of Ca$_2$Sr$_3$Fap

Figure C-5 Raman Spectra of CaSr$_4$Fap

Figure C-6 Raman Spectra of Sr$_5$Fap
Figure C-7 Raman Spectra of KRI Fluorapatite

Figure C-8 Raman Spectra of natural Fluorapatite
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