Graduate Student Research Day 2012
Florida Atlantic University

CHARLES E. SCHMIDT COLLEGE OF SCIENCE

Effect of Preparation Temperature on Crystal Structure Properties on Nanophase Fe-Substituted Hydroxyapatite

Vindu Kathriarachchi and A. Kyriacou, Suraj P. Khanal , Th. Leventouri

Department of Physics, Charles E. Schmidt College of Science, Florida Atlantic University, Boca Raton, FL

Purpose: To study the structural properties of iron substituted nanophase Hydroxyapatite prepared at physiological and elevated temperatures. Background: Hydroxyapatite (HAp), $Ca_5(PO_4)_3OH$, which is the main mineral phase in physiological apatite (~70 wt% in bones and dentin, and ~96 wt% in enamel) is used in orthopedic and dentistry. Physical properties of HAp can be improved by introducing ionic substitutions in its structure. Fe is one of the minor substitution elements (0.01-0.1 wt% in bone, 0.003 wt% in enamel) replacing Ca in the HAp structure. It reduces the solubility of HAp therefore it functions as a cavities preventive agent. However, Fe overload may lead to a decreased mechanical strength and osteoporosis. Method: Three sets of $Ca_{5-x}Fe_x(PO_4)_3OH$ samples were synthesized by a chemical precipitation method at RT(~23^0C), physiological temperature(37^0C) and 80^0C. The samples were characterized by powder x-ray diffraction (XRD) and transmission electron microscopy (TEM). The Rietveld refinement method was used to study the crystallographic properties of the samples.Findings: HAp was identified as the main phase in all samples while hematite (α-Fe_2O_3) or maghemite (γ-Fe_2O_3) was identified as secondary phase. Samples prepared at RT were not magnetic while the ones prepared at 37^0C and 80^0C were magnetic. Crystal structure parameters vary with the Fe content as well as with the preparation temperature. TEM images showed agglomerated spherical and elongated nanoparticles ranging from 20-80nm.Discussion: Preparation conditions considerably affect the crystal structure properties of iron substituted HAp. Samples prepared at 37^0C and 80^0C showed magnetic properties which could lead to medical applications such as drug delivery and hyperthermia treatment.

EFFECT OF PROCESSING TEMPERATURE ON CRYSTAL STRUCTURE PROPERTIES OF NANOPHASE Fe-HYDROXYAPATITE

Vindu Kathriarachchi, Suraj P. Khanal, A. Kyriacou, Th. Leventouri

Department of Physics, Center for Biological and Materials Physics
Charles E. Schmidt College of Science

Introduction 1

- Hydroxyapatite (HAp), $Ca_5(PO_4)_3OH$, is the main mineral phase in physiological apatite (~70 wt% in bones and dentin, and ~96 wt% in enamel).
- Fe is one of the minor substitution elements (0.01-0.1 wt % in bone, 0.003 wt % in enamel) replacing Ca in the HAp structure. It functions as a cavities preventive agent. However, Fe overload might lead to decreased mechanical strength and osteoporosis.

Purpose 2

- To study the crystal structural properties of Fe substituted nanophase HAp as a function of the Fe concentration and processing temperature.

Synthesis 3

- Chemical precipitation method[1]
- First, HAp was synthesized at RT(~23^{0}C), then at physiological temperature (37^{0}C) and at 80^{0}C.

$$5Ca(NO_3)_2 + 3(NH_4)_2HPO_4 \xrightarrow{NH_4OH} Ca_5(PO_4)_3OH + 3H_2O + 10NH_4NO_3$$

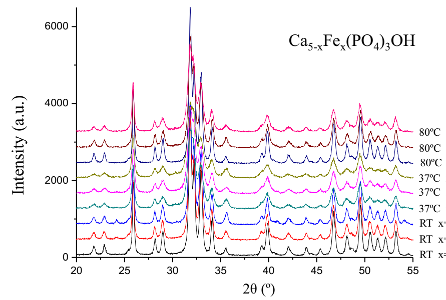
- Then Fe was pumped into HAp solution.

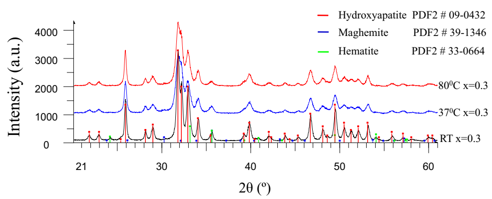
$$xFeCl_2 + Ca_5(PO_4)_3OH \longrightarrow Ca_{5-x}Fe_x(PO_4)_3OH$$

x=0, 0.20, 0.30

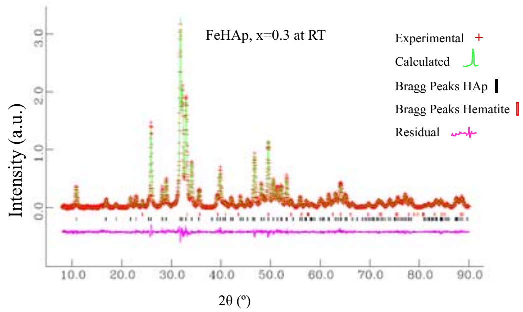
1. Hsi-Chin Wu et al. Nanotechnology **18** (2007)

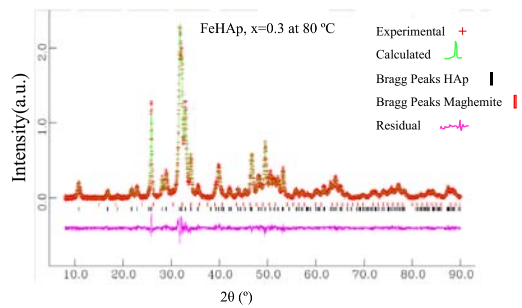
XRD phase identification 4



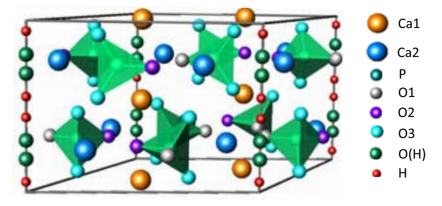


Rietveld refinement 5



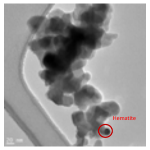


Hydroxyapatite unit cell 6



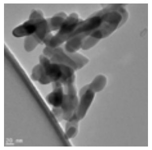
$Ca_5(PO_4)_3OH$ Space Group: $P6_3/m$

Transmission Electron Microscopy 7



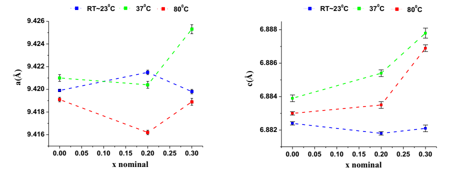
TEM image of FeHAp02 prepared at RT. Particle Shape: Spherical with diameter 15-60 nm.

Fe EELS spectrum of FeHAp02 prepared at RT. Brighter area corresponds to Fe concentration. It confirms the presence of Fe in both HAp and Hematite phase.

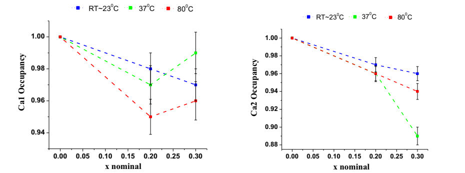


TEM image of FeHAp02 prepared at 80^{0}C. Particle Shape: Rod like and Size: long axis 60-80nm, short axis 20nm.

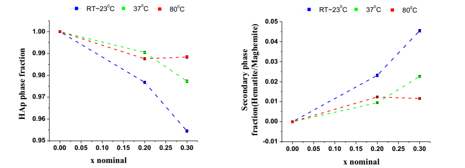
Crystal Structure Results 8



- a and c lattice parameters as a function of Fe concentration and preparation temperature.



- Ca1 and Ca2 occupancies as a function of Fe concentration and preparation temperature.



- HAp phase fraction and secondary phase fraction (Hematite/Maghemite) as a function of Fe concentration and preparation temperature.

Results 9

- Hematite is identified as a secondary phase in samples prepared at RT for x=0.2 and 0.3.
- Maghemite is identified as a secondary phase in samples prepared at physiological (37ºC) and 80ºC for x=0.2 and 0.3.
- Overall increase in a and c lattice parameters with increasing Fe concentration at 37ºC and 80ºC.
- Spherical crystallites are formed in all samples prepared at RT ranging from 15-60nm. Rod like crystallites are formed in all samples prepared at 80ºC with dimensions of 20nm in the short axis and 60 nm to 80 nm in long axis.

Preliminary Conclusion 10

- Processing temperature considerably affects the crystal structure properties and morphology of iron substituted HAp.

Future Work 11

- Prepare x=0.1 and 0.4 at 37ºC and 80ºC.
- Neutron powder diffraction(NPD) studies.
- Magnetic measurements.
- Simultaneous Rietveld refinement of XRD and NPD.

Acknowledgement 12

- A. J. Rondinone, Center for Nanophase Materials Sciences (CNMS), Oak Ridge National Laboratory , TN.