
JOURNAL OF THE ASIA RESEARCH CENTRE

YANGON UNIVERSITY

Vol.5, No. 1 & 2

Published by

The Asia Research Centre, Yangon University

Yangon, MYANMAR

JOURNAL OF THE ASIA RESEARCH CENTRE

YANGON UNIVERSITY

Vol.5, No. 1 & 2

Published by

The Asia Research Centre, Yangon University

Yangon, MYANMAR

First Edition: January 2016

200 copies

**The publication of this journal was funded by the Asia Research Centre,
Yangon University**

Published by

The Asia Research Centre, Yangon University

MYANMAR

Tel: 095-1-536503, Fax: 95-1-527067

Email: contact@uy.edu.mm

Foreword

University of Yangon (UY) makes an all-out effort to be a leading higher educational institution in Myanmar as a Flagship university on par with regional counterparts and in line with international trends. UY therefore expands the frontiers of knowledge by developing research culture.

UY created a research-teaching nexus namely Universities' Research Centre (URC-UY) where research informs and enhances teaching agenda. University education is fundamentally about how to solve problems based on data and/or logical thought. Those involved in research are better at imparting these skills to students with inquiring minds. The Korea Foundation for Advanced Studies (KFAS) has been supporting research activities in UY through the Asia Research Centre (ARC-UY). To a researcher in UY, ARC-UY and URC-UY should be seen as two sides of the same coin in much the same way as financial support and research activity should be regarded.

Research is only meaningful if it is communicated, so the research outcomes must be published and contribute to the body of knowledge; even better if research outcomes can be impactful through commercialization or implementation. This journal proudly presents 17 research papers resulted from the outstanding research projects carried out by the academic departments of UY.

I would like to express my appreciation and congratulations on the concerted effort of the researchers who have made a great deal of excellent contribution to this issue. I also would like to express my heartfelt thanks to Mr. Park In-Kook, President of the KFAS for his continued support to the ARC-UY.

Prof. Dr Pho Kaung
Rector, University of Yangon

Unification of Nano-Hydroxyapatite for Bone Replacement

Pho Kaung¹, Myat Shwe Wah², Naw Mary Mya Tint² and Aye Aye Thant*

¹Universities' Research Centre, University of Yangon

²Department of Physics, University of Yangon

Abstract

Hydroxyapatite (HAP) is effectively used as a bio-implant material because it closely resembles bone apatite and exhibits good biocompatibility. Pure HAP has been synthesized in the first stage and SiO₂ doped HAP has been prepared by using a sol-gel method in the second stage by the formula Ca_{10-x}Si_x(PO₄)₆(OH)₂. The as-prepared HAP powder and Si substituted HAP powder has been calcined at 800°C. The calcined powder have been pressed into pellet and then sintered at 1000°C and 1100°C. Structural characterization of samples has been performed by using X-ray diffraction (XRD) technique. The molecular vibration of HAP has been observed by Fourier Transform Infrared Spectroscopy (FTIR).

Keywords: molecular vibration; structural characterization; Si doped Hydroxyapatite; XRD; bone replacement

1. Introduction

Hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂, HAP), an important inorganic biomaterial, has attracted the attention of researchers related to biomaterial field. Due to its chemical and structural similarity with the mineral phase of bone and teeth, HAP is widely used for hard tissues repair. As a result, this inorganic phosphate has been studied extensively for medical applications in the formation of powders, composites or even coating. Furthermore, HAP has been studied for other non-medical application. HAP can also be used as biological chromatography supports in protein purification and Deoxyribonucleic acid (DNA) isolation. The chemical structural and morphological properties of synthesized HAP can be modulated by varying method and the conditions of synthesis. Classical methods for HAP powder synthesis include direct precipitation, hydrothermal techniques, hydrolysis as well as solid state reactions and mechano-chemical method. Among these methods, sol-gel technique has attracted much attention recently due to its well-known inherent advantages to generate glass, glass ceramic and ceramics powder. These include homogeneous molecular mixing, low processing temperature, the ability to generate sized particles, thin film and bulk amorphous monolithic solids and thin films. The sol gel process is easily applicable to surface coating and it allows the preparation of high quality HAP thin films on metal substances. Thus, the sol-gel process can be usefully utilized to synthesize both HAP powder and HAP thin film under significantly mild condition. Moreover, doping with (biocompatible or even better bioactive) oxides has been resulted in strong HAP composites. In this study, SiO₂ has been doped in HAP because SiO₂ has been related to bioactivity. Si is related to body's metabolism, clinically proven in studies on bone and collagen weakening, the level of arteriosclerosis, osteoarthritis, aging process etc. Ca_{10-x}(Si)_x(PO₄)₆(OH)₂ with x= 0.0, 0.5, 1.0, 1.5 have been synthesized by sol-gel method in this work. The substitution of silicon into the hydroxyapatite bioceramics is excellent biocompatible with living organism.

* Aye Aye Thant, Universities' Research Centre, University of Yangon.

2. Materials and Method

The required amount of phosphoric pentoxide, calcium nitrate tetrahydrate and silicon dioxide powders have been used as the starting materials. Firstly phosphoric pentoxide (P_2O_5) has been dissolved in absolute ethanol and secondly calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$) and silicon dioxide (SiO_2) have been dissolved in ethanol. Then, both solutions have been mixed rapidly. The mixture has been continuously stirred about 10 minutes at room temperature. Furthermore, the mixture has been heated in a water bath at $60^\circ C$ for 1 h to get the formation of gel. The gel has been aged for 4h at the ambient temperature, and then dried at $90^\circ C$ for 24 hours in an air oven to get the formation of powder, followed by heat treatment at $800^\circ C$ for 4 hours. Finally, the as-prepared HAP powders have been calcined at $1000^\circ C$ and $1100^\circ C$ with a heating rate of $10^\circ C/min$. Obtained dried powders have been ground using an A-gate mortar and pestle. The calcined powder have been pressed into pellet by uniaxial hydraulics press at a pressure of 150 MPa and then sintered at $1000^\circ C$ and $1100^\circ C$. The phase formations of calcined powder sample and pellets have been identified by XRD. The structural analysis has also been analyzed by FTIR.

3. Results and Discussion

Phase formation

The pure HAP powder and SiO_2 doped HAP powder have been prepared by using a sol-gel method using phosphoric pentoxide (P_2O_5), calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$) and silicon dioxide (SiO_2) with the calcination and sintering temperature at $800^\circ C$, $1000^\circ C$, $1100^\circ C$ for 4hr. XRD analysis has been conducted to check the phase formation of powders of pure HAP and SiO_2 doped HAP.

The XRD spectra of HAP powder for $Ca_{10-x}Si_x(PO_4)_6(OH)_2$ with $x = 0.0, 0.5, 1.0, 1.5$ sintered at $800^\circ C$, $1000^\circ C$, $1100^\circ C$ are shown in Figure 1, Figure 2 and Figure 3 respectively. As seen in the XRD spectra in Figure 1, the hydroxyapatite phase has been formed after sintering with $800^\circ C$ for all compositions. There is no trace of SiO_2 in the hydroxyapatite structure. Therefore, it has been identified that single phase structure has been formed via sol gel method.

According to the appearance of diffraction peaks in XRD spectra sintered at $1000^\circ C$ and $1100^\circ C$, it is interesting to note that the HAP hexagonal structure ($Ca(NO_3)_2 \cdot 4H_2O$) has changed into Calcium phosphate Rhombohedral structure ($Ca_3(PO_4)_2$) with Si doping for $x=1.0$ and $x = 1.5$.

The crystallite size for (1 2 1) intense reflection peak for $Ca_{10-x}(Si)_x(PO_4)_6(OH)_2$ with SiO_2 of $x = 0.0, 0.5, 1.0, 1.5$ sintered at $800^\circ C$ estimated by the Scherrer equation are presented in the Table 1. It is worth to note that the crystallite size is in nano-range and almost the same for SiO_2 concentration of $x = 0.0, 0.5, 1.0$. However, sample with SiO_2 concentration of $x = 1.5$ shows bigger crystallite size.

Furthermore, the crystallite size for $Ca_{3-x}Si_x(PO_4)_2$, $x = 1.0, x = 1.5$ with (1 7 0) intense reflection peak sintered at $1000^\circ C$ and $1100^\circ C$ are presented in the Table 2 and Table 3.

It is worth to note that the crystallite size was decreased with increasing Si concentration upon the formation of Rhombohedral with $x = 1.0$ and $x = 1.5$.

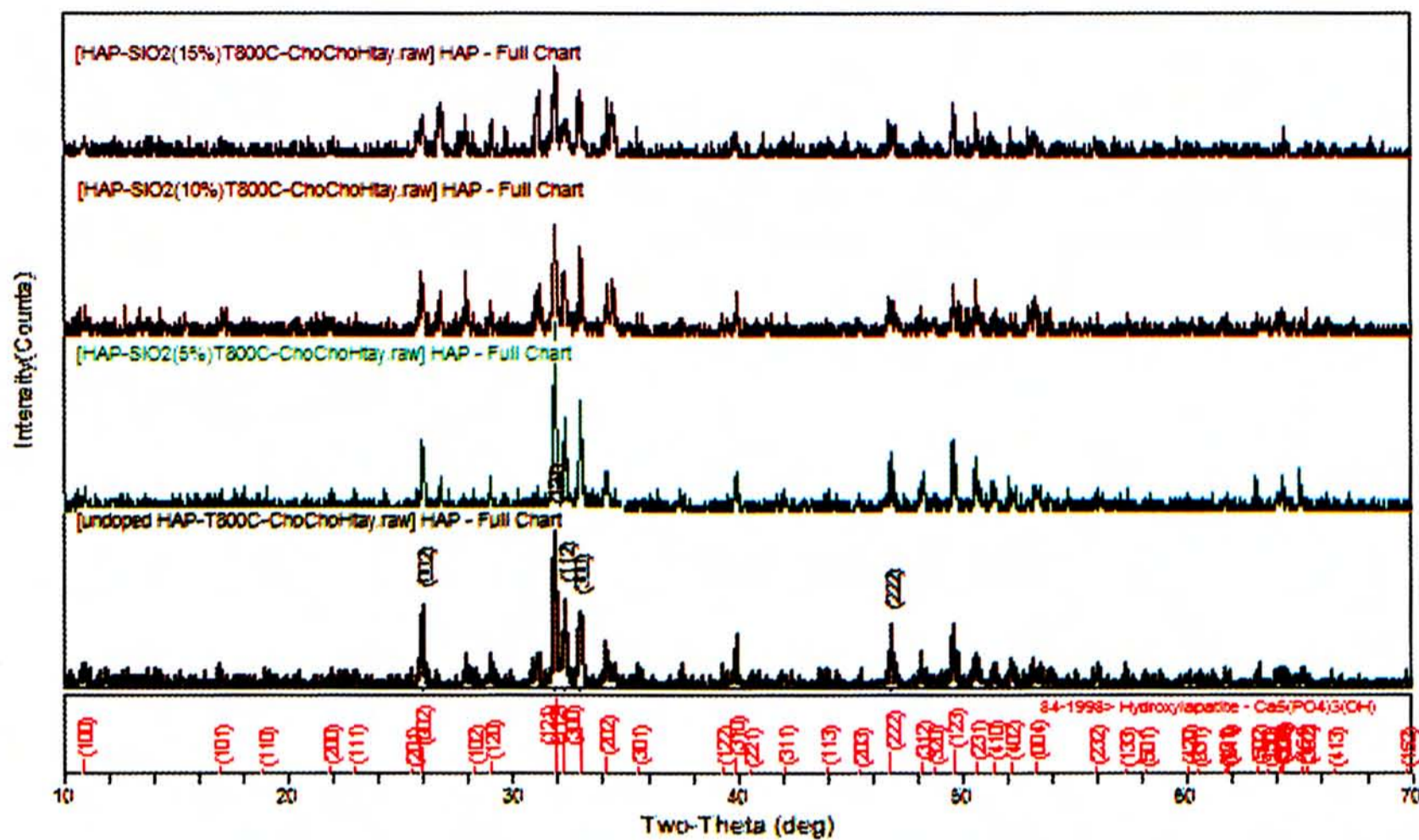


Figure 1. XRD spectra of $Ca_{10-x}Si_x(PO_4)_6(OH)_2$ heat-treated at 800°C

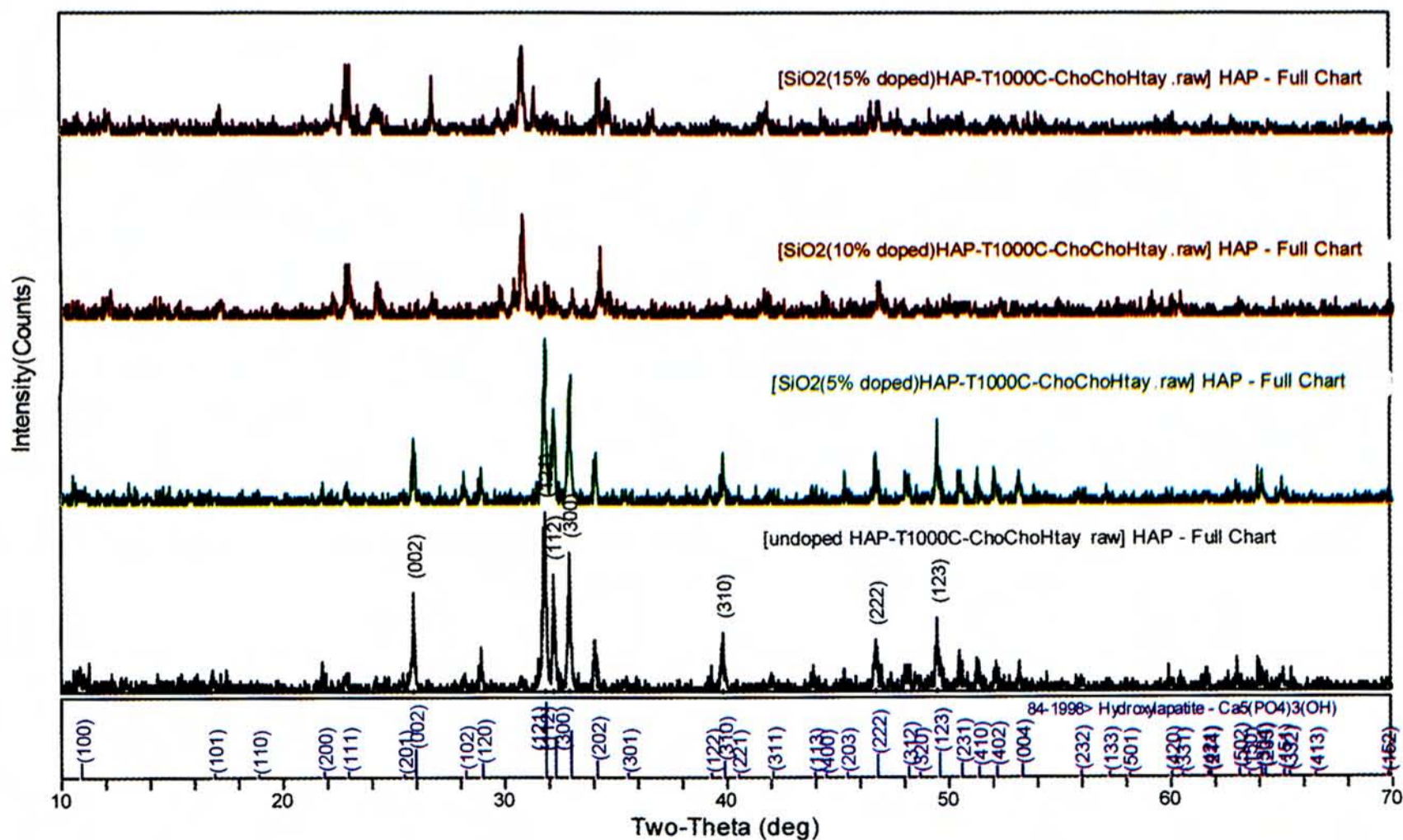


Figure 2. XRD spectra of $Ca_{10-x}Si_x(PO_4)_6(OH)_2$ heat-treated at 1000°C

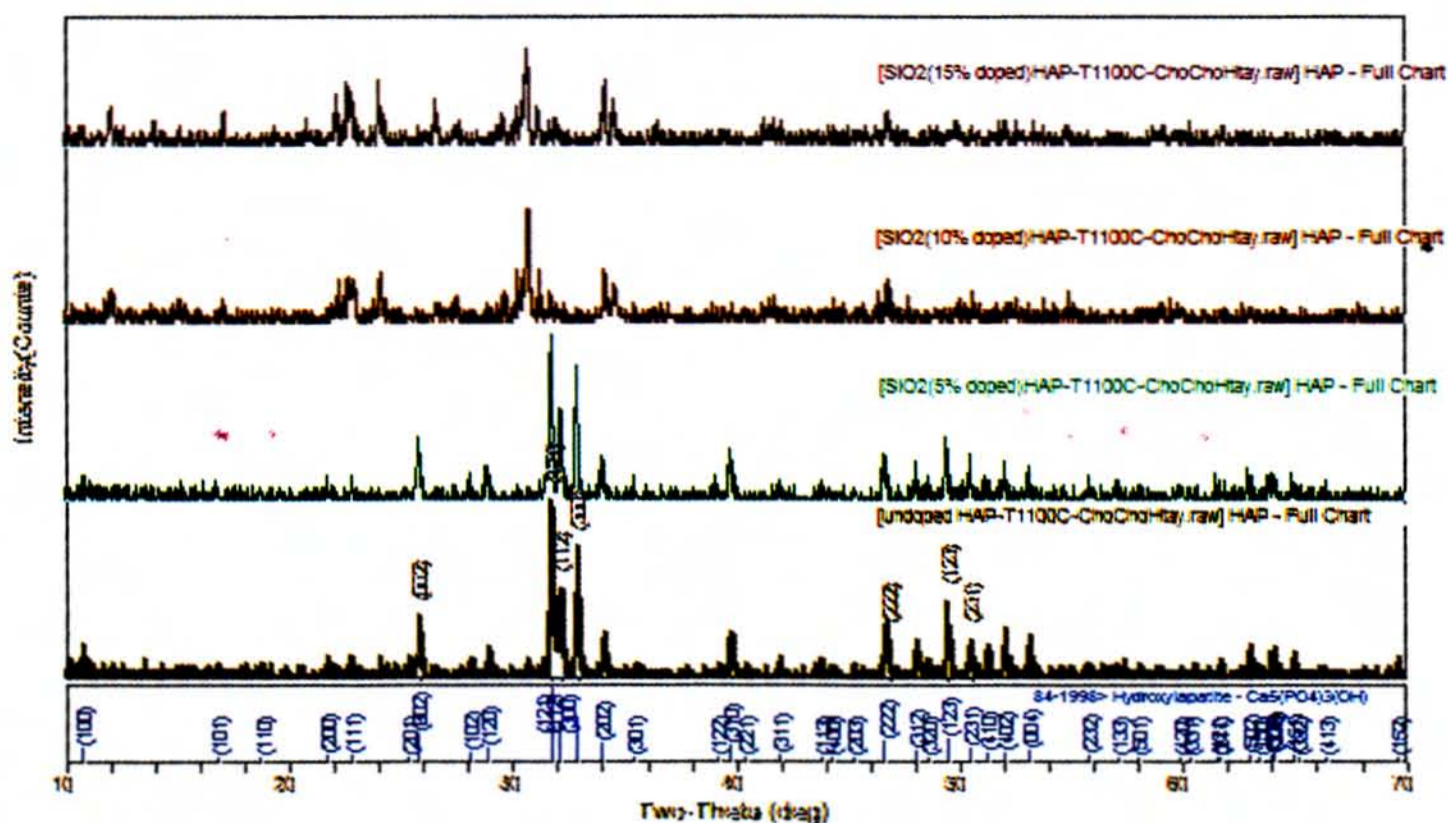


Figure 3. XRD spectra of $\text{Ca}_{10-x}\text{Si}_x(\text{PO}_4)_6(\text{OH})_2$ heat-treated at 1100°C

Table 1. The variation of crystallite size of $\text{Ca}_{10-x}\text{Si}_x(\text{PO}_4)_6(\text{OH})_2$ with $x = 0.0, 0.5, 1.0, 1.5$ at 800°C .

Structure	SiO_2 composition (x)	Plane (h k l)	2θ (degree)	FWHM (rad)	Crystallize size (nm)
Hexagonal	0.0	(1 2 1)	31.823	0.144	57.36
Hexagonal	0.5	(1 2 1)	31.873	0.155	53.30
Hexagonal	1.0	(1 2 1)	31.843	0.159	51.95
Hexagonal	1.5	(1 2 1)	31.829	0.141	58.58

Table 2. The variation of crystallite size of $\text{Ca}_{10-x}\text{Si}_x(\text{PO}_4)_6(\text{OH})_2$ with $x = 0.0, 0.5$ and $\text{Ca}_{3-x}\text{Si}_x(\text{PO}_4)_2$, $x = 1.0, 1.5$ at 1000°C .

Structure	SiO_2 Composition (x)	Plane (h k l)	2θ (degree)	FWHM (rad)	Crystallize size (nm)
Hexagonal	0.0	(1 2 1)	31.835	0.145	56.97
Hexagonal	0.5	(1 2 1)	31.744	0.125	66.07
Rhombohedral	1.0	(1 7 0)	30.799	0.191	43.14
Rhombohedral	1.5	(1 7 0)	30.781	0.226	35.82

Table 3. The variation of crystallite size of $\text{Ca}_{10-x}\text{Si}_x(\text{PO}_4)_6(\text{OH})_2$ with $x = 0.0, 0.5$ and $\text{Ca}_{3-x}\text{Si}_x(\text{PO}_4)_2$, $x = 1.0, 1.5$ at 1100°C .

Structure	SiO ₂ composition (x)	Plane (h k l)	2θ (degree)	FWHM (rad)	Crystallize size (nm)
Hexagonal	0.0	(1 2 1)	31.784	0.098	84.28
Hexagonal	0.5	(1 2 1)	31.802	0.146	56.57
Rhombohedral	1.0	(1 7 0)	30.781	0.198	41.61
Rhombohedral	1.5	(1 7 0)	30.760	0.183	45.02

4. Study by Fourier Transform Infrared Spectroscopy (FTIR)

FT-IR spectroscopy has been performed in order to investigate the functional groups presented in hydroxyapatite synthesized by sol gel method. The functional groups present in hydroxyapatite clearly revealed the presence of various vibrational modes corresponding to phosphate and hydroxyl groups. Chemical groups with vibration bands are confirmed by the FTIR transmission bands of synthesized pure HAP and Si doped HAP.

The functional groups present in hydroxyapatite clearly revealed the presence of various vibrational modes corresponding to phosphate and hydroxyl groups. Chemical groups with vibration bands are confirmed by the FTIR transmission bands of synthesized pure HAP and Si doped HAP.

FT-IR spectra obtained for the samples with formula $\text{Ca}_{10-x}\text{Si}_x(\text{PO}_4)_6(\text{OH})_2$, $x=0.0$, 0.5 is shown in Figure 4 and Figure 5 for 1000 °C and Figure 6 and Figure 7 for 1100 °C. The FT-IR spectra obtained for the samples with formula $\text{Ca}_{3-x}\text{Si}_x(\text{PO}_4)_2$, $x = 1.0$, 1.5 is shown in Figure 8 and Figure 9 for 1000 °C and Figure 10 and 11 for 1100 °C.

FTIR was evaluated to confirm the effect of the silicon substitution on the different functional groups, such as hydroxyl and phosphate groups of hydroxyapatite. Firstly the bands at $3570\text{-}3627\text{ cm}^{-1}$ and 631 cm^{-1} corresponded to the hydroxyl group stretching and vibrational modes, respectively. The intense bands at $960\text{-}964\text{ cm}^{-1}$ corresponded to P-O stretching vibration modes, whereas the doublet at $605\text{-}569\text{ cm}^{-1}$ corresponds to the O-P-O bending mode.

The functional groups presented in hydroxyapatite clearly revealed the presence of various vibrational modes corresponding to phosphate and hydroxyl groups. Chemical groups with vibration bands are confirmed by the FTIR transmission bands of synthesized pure HAP and Si doped HAP. No additional absorption peaks were observed with Si addition, indicating its homogeneous dispersion in the support material.

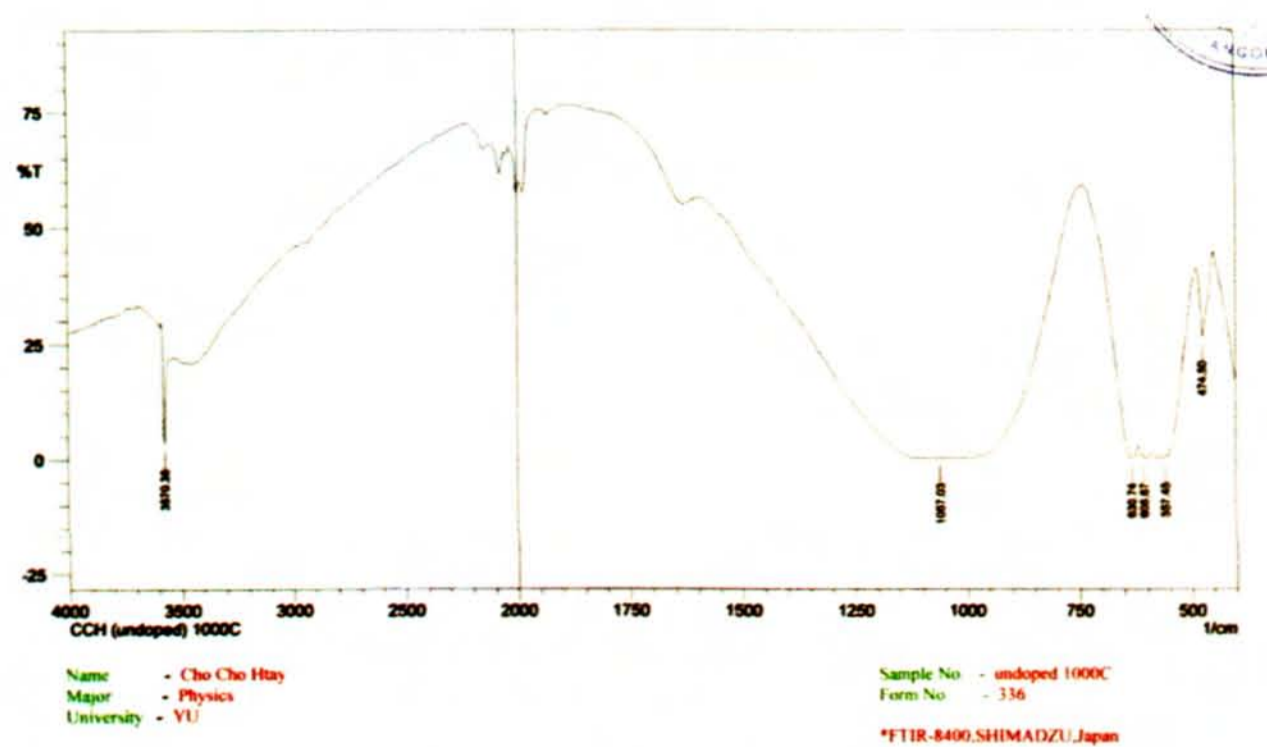


Figure 4. FTIR spectrum of $\text{Ca}_{10-x}\text{Si}_x(\text{PO}_4)_6(\text{OH})_2$ with $x=0.0$ sintered at 1000°C

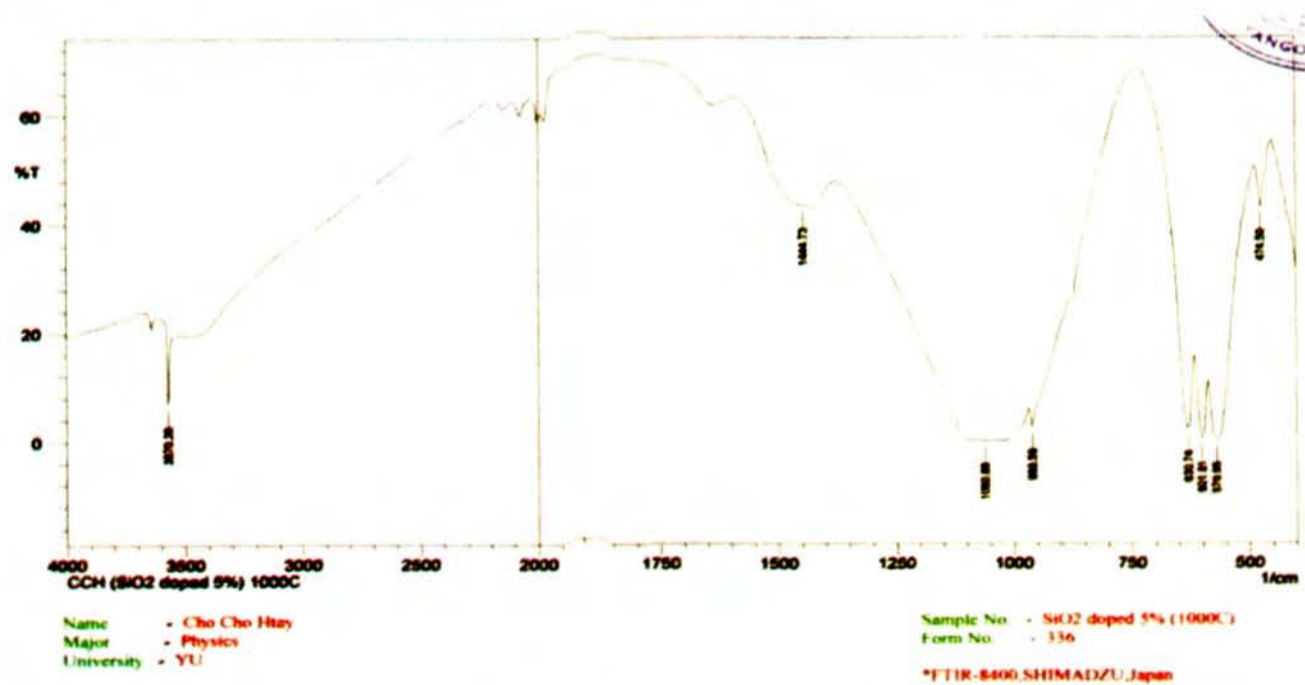


Figure 5. FTIR spectrum of $\text{Ca}_{10-x}\text{Si}_x(\text{PO}_4)_6(\text{OH})_2$ with $x=0.5$ sintered at 1000°C

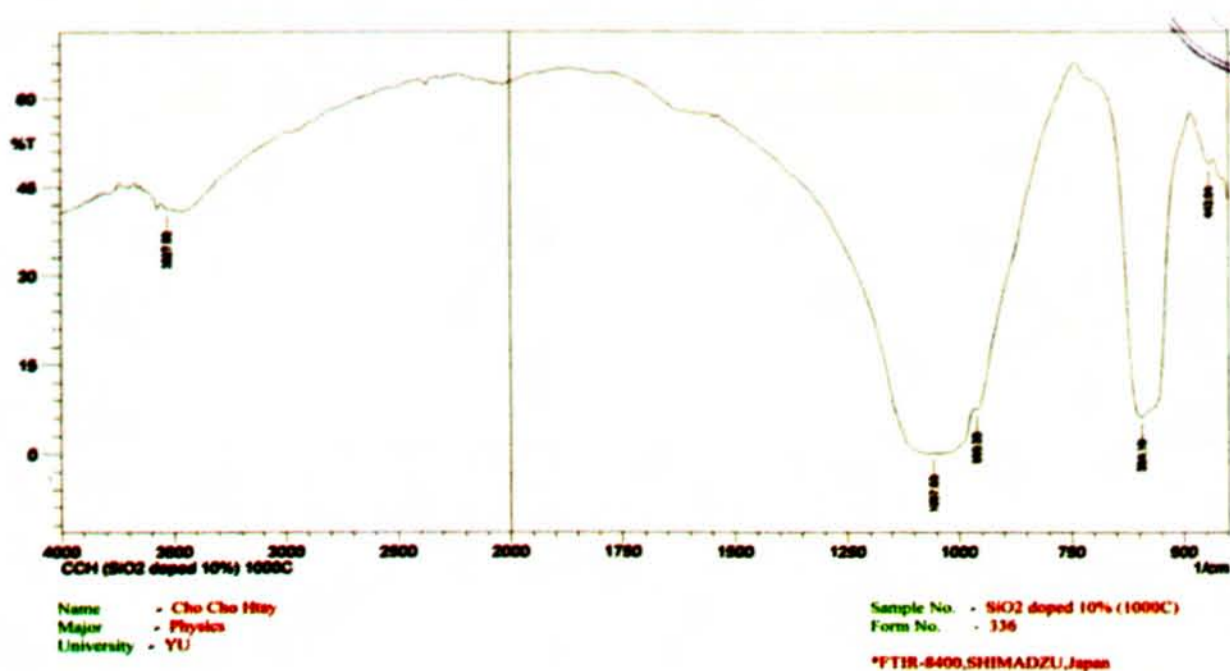


Figure 6. FTIR spectrum of $\text{Ca}_{3-x}\text{Si}_x(\text{PO}_4)_2$ with $x=1.0$ after sintered at 1000°C

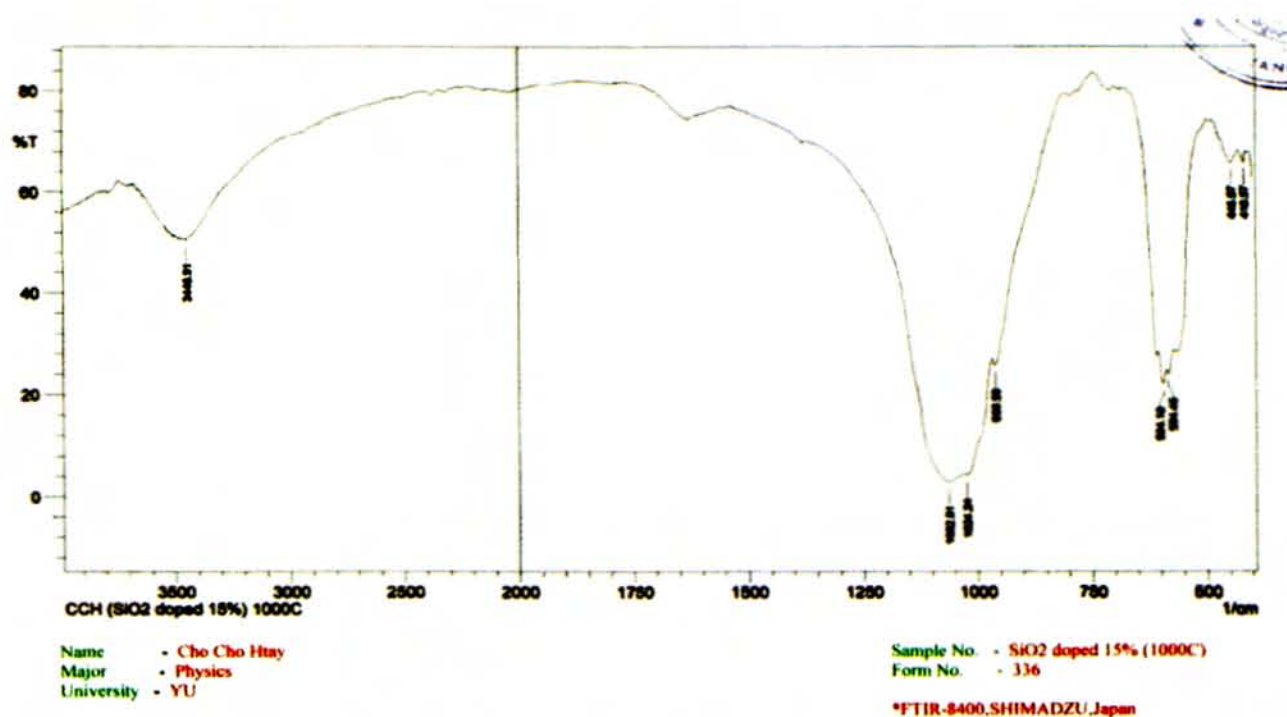


Figure 7. FTIR spectrum of $Ca_{3-x}Si_x(PO_4)_2$ with $x = 1.5$ after sintered at $1000^\circ C$

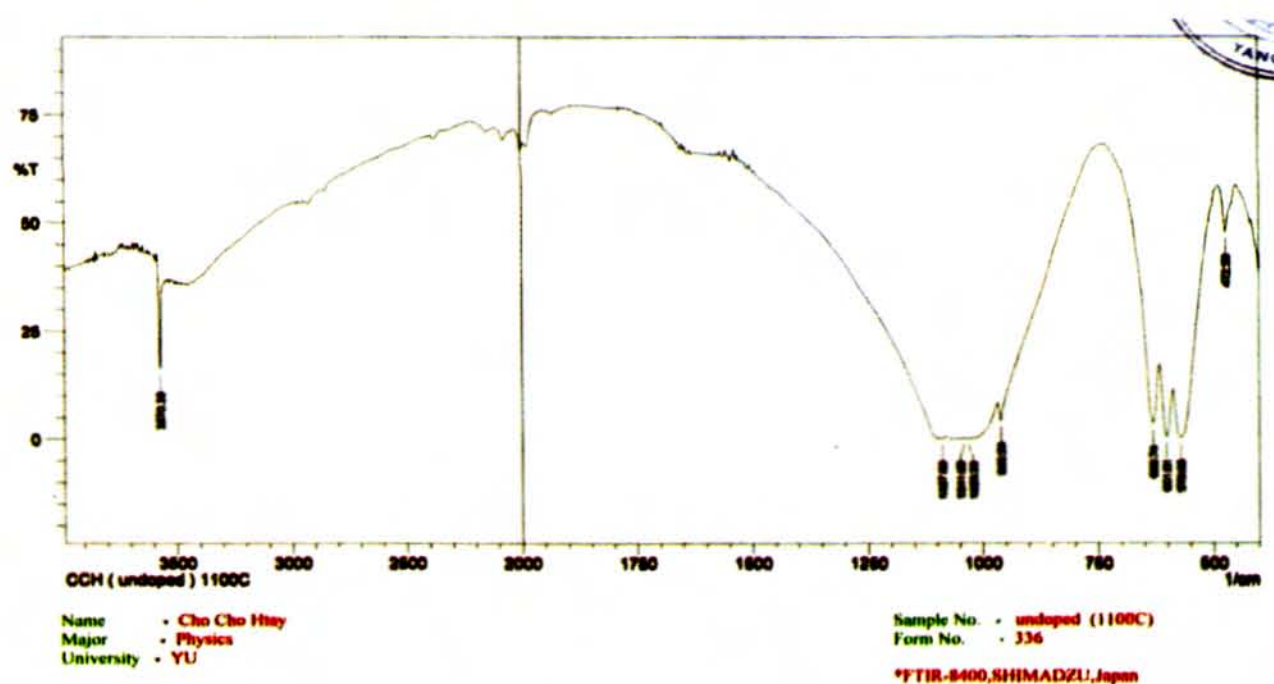


Figure 8. FTIR spectrum of $Ca_{10-x}Si_x(PO_4)_6(OH)_2$ with $x=0.0$ sintered at $1100^\circ C$

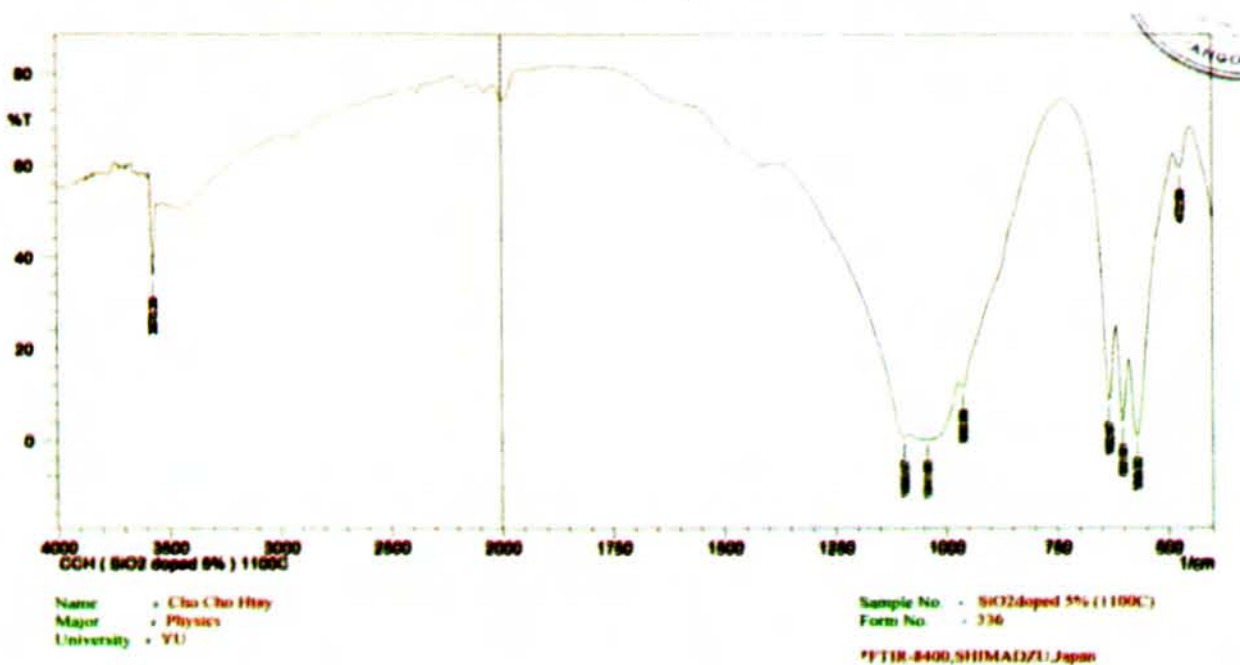


Figure 9. FTIR spectrum of $Ca_{10-x}Si_x(PO_4)_6(OH)_2$ with $x=0.5$ sintered at $1100^\circ C$

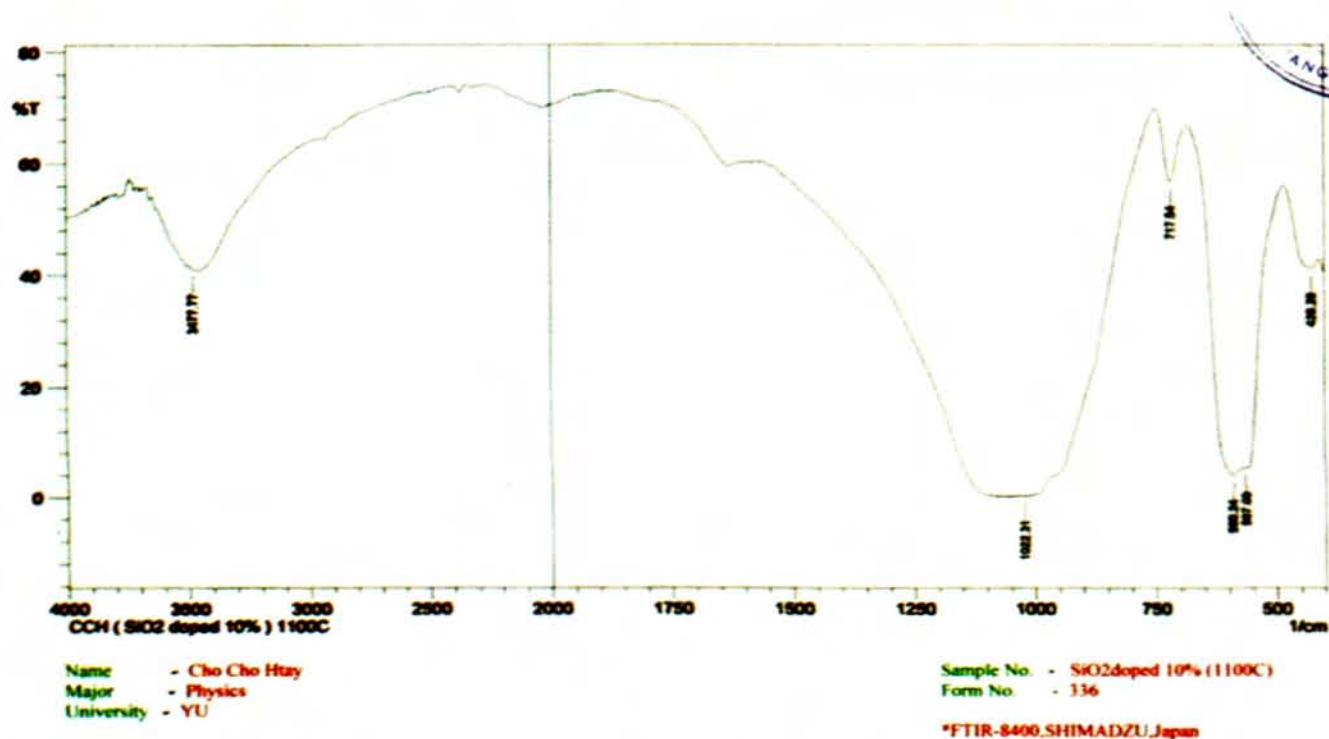


Figure 10. FTIR spectrum of $\text{Ca}_{3-x}\text{Si}_x(\text{PO}_4)_2$ with $x = 1.0$ after sintered at 1100°C

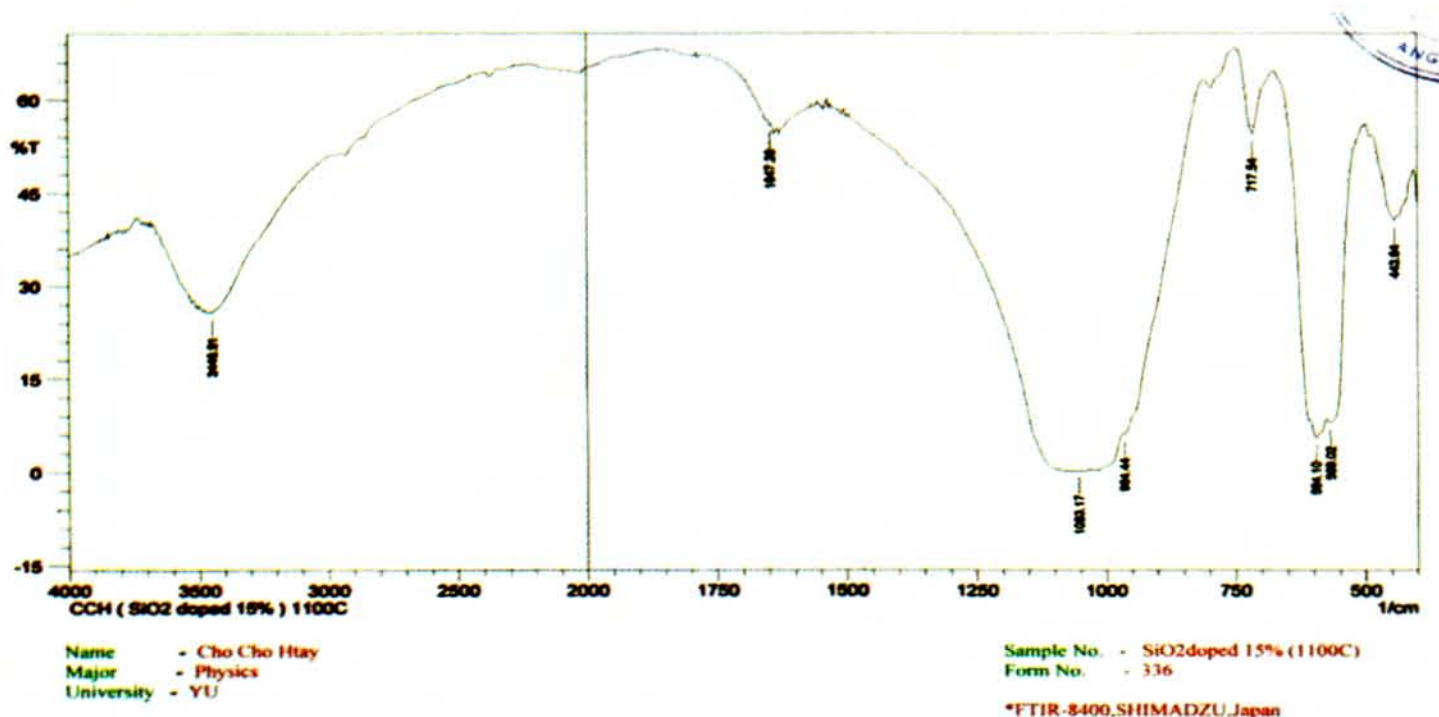


Figure 11. FTIR spectrum of $\text{Ca}_{3-x}\text{Si}_x(\text{PO}_4)_2$ with $x = 1.5$ sintered at 1100°C

5. Conclusion

The calcined powder has been prepared by Sol gel Method and phase formation has been confirmed by X-ray diffraction method. Hexagonal hydroxyapatite HA phase has been formed after heat-treatment at 800°C . It is worth to note that the crystallite size was decreased with increasing Si concentration upon the formation of Rhombohedral with $x=1.0$ and $x=1.5$. It is interesting to note that the hexagonal $\text{Ca}_{3-x}\text{Si}_x(\text{PO}_4)_2$ has changed into Calcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$) with Si doping for $x=1.0$ and $x=1.5$. The crystalline degree and morphology of the resulting nanopowders are dependent on the ratio of silicon composition. No additional absorption peaks were observed with Si addition, indicating its homogeneous dispersion in the support material. Chemical groups with vibration bands are confirmed by the FTIR transmission bands of synthesized pure HAP and Si doped HAP. The compactions of synthesized samples will be soaked in SBF solution to evaluate their bioactivity.

Acknowledgement

The authors would like to express appreciation for the support of the project with grant to Asia Research Centre, University of Yangon.

References

- Brinker, C. J. and Scherer, G. W.,**1990. Sol-gel Science. *Academic Press, Boston.*
- Jarcho M., Bolen, C. H., Thomas, M. B., Bobick, J., Kay, J. F. and Doremus, R. H.,** 1976. Hydroxylapatite Synthesis and Characterization in Dense Polycrystalline Form. *J Mater. Sci.*, 11, 2027-2035.
- Kentaro, N., Takashi, K., Chiya, N., Takamasa, O. and Atsushi, N.,** 2009. Synthesis and Characterization of Silicon-Doped Hydroxyapatite. *Materials Transactions*, 50(5), 1046-1049.
- Zhang, Q. and Saito, F.,**2000. Mechanochemical Synthesis of Hydroxyapatite from $\text{Ca}(\text{OH})_2\text{-P}_2\text{O}_5$ and $\text{CaO-Ca}(\text{OH})_2\text{-P}_2\text{O}_5$ Mixtures. *J. Mater. Sci.*, 35, 5401-5405.
- Kokubo, A. W.,** 1993. Glass-ceramic: An Introduction to Bio-ceramics. *World Scientific, London*, 75-88.
- Luo, P. and Nieh, T. G.,**1995. Synthesis of Ultrafine Hydroxyapatite Particles, *Mater Sci EngC*, 3, 75-78.
- Ramesh, S., Tan, C. Y., Sopyan, I., Hamdi M. and Teng, W. D.,** 2007. Consolidation of Nanocrystalline Hydroxyapatite Powder. *Sci.Tech. Adv. Mater.*, 8, 124-130.
- Weng, J. W. and Baptisa, A.,** 1997. A New Synthesis of Hydroxyapatite. *Journal of the European Ceramic Society*, 17, 1151-1156.
- Zhang, X. and Vecchio, K. S.,** 2007. Hydrothermal Synthesis of Hydroxyapatite Rods. *J. Cryst. Growth*, 308, 133-140.