



Ain Shams University
Faculty Collage of Women
For Arts, Science and Education
Physics Department

Preparation and Spectral Characterization of Some Bio-Phosphate Glasses for Bio-Medical Applications

A Thesis

**Submitted to Faculty of Girls
for Arts, Science and Education- Ain Shams University**

For the Ph. D. Degree in Biophysics

By

**Rasha Abdel-Hakam Youness Abdel-Aziz
M. Sc. Biophysics**

Supervision Committee

Prof. Dr.

Hamdia Abd El-Hamid Zayed

Prof. of Solid State Physics
Physics Department
University Collage of Women for Arts,
Science, and Education
Ain Shams University

Prof. Dr.

El-Sayed Mahmoud El-Sayed

Prof. of Biophysics
Physics Department
Ain Shams University

Prof. Dr.

El-Sayed Mostafa Khalil

Prof. of Spectroscopy
Spectroscopy Department
Physics Division
National Research Centre

Prof. Dr.

Sherief Mohammed Abo-Naf

Prof. of Materials Science & Technology
Glass Research Department
Chemical Industries & Mineral Resources
Division
National Research Centre

2015



Ain Shams University
Faculty Collage of Women
For Arts, Science and Education
Physics Department

Preparation and Spectral Characterization of Some Bio-Phosphate Glasses for Bio-Medical Applications

**Thesis Submitted
for the Ph. D. Degree in Bio-Physics**

**By
Rasha Abdel-Hakam Youness Abdel-Aziz**

Supervision Committee

**Prof. Dr.
Hamdia Abd El-Hamid Zayed**

Prof. of Solid State Physics
Physics Department
University Collage of Girls for Arts, Science,
and Education
Ain Shams University

**Prof. Dr.
El-Sayed Mahmoud El-Sayed**

Prof. of Biophysics
Physics Department
Ain Shams University

**Prof. Dr.
El-Sayed Mostafa Khalil**

Prof. of Spectroscopy
Spectroscopy Department
Physics Division
National Research Center

**Prof. Dr.
Sherief Mohammed Abo-Naf**
Prof. of Materials Science & Technology
Glass Research Department
Chemical Industries & Mineral Resources
Division
National Research Center

Date of Research: / / 2015

Approval Stamp:

Approval of Faculty Council.

Date of Approval: / / 2015

Approval of University Council.

Name of Student:

Rasha Abdel-Hakam Youness Abdel-Aziz

Title of Thesis:

**Preparation and Spectral
Characterization of Some Bio-
Phosphate Glasses for Bio-Medical
Applications**

Scientific Degree:

**Doctor of Philosophy in Physics (Bio-
Physics).**

Department:

Physics

Name of Faculty:

**Faculty Collage of Women for Arts,
Science and Education.**

University:

Ain-Shams.

B. SC. Graduation Date :

2005

M. SC. Graduation Date :

2010

Ph. D. Graduation Date :

2015



جامعة عين شمس
كلية البنات للأداب والعلوم والتربية
قسم الطبيعة

تحضير وتوصيف طيفى لبعض انواع من زجاج الفوسفات الحيوى لاستخدامها فى التطبيقات الحيوية الطبية

رسالة مقدمة إلي
كلية البنات للأداب والعلوم والتربية
جامعة عين شمس

للحصول علي درجة دكتوراة الفلسفة فى العلوم- فيزياء تخصص فيزياء حيوية
مقدمة من

رشا عبد الحكم يونس عبد العزيز
ماجستير في الفيزياء الحيوية

تحت إشراف

أ.د. السيد محمود السيد
أستاذ الفيزياء الحيوية-كلية العلوم
جامعة عين شمس

أ.د. حمدية عبد الحميد إبراهيم زايد
أستاذ فيزياء الجوامد
قسم الطبيعة-كلية البنات
جامعة عين شمس

أ.د. شريف محمد أبو ناف
أستاذ كيمياء علوم المواد والتكنولوجيا
قسم بحوث الزجاج
المركز القومي للبحوث

أ.د. السيد مصطفى خليل
أستاذ الاطيفاف
قسم الطيف
المركز القومي للبحوث



جامعة عين شمس
كلية البنات للآداب والعلوم والتربية
قسم الطبيعة

رسالة دكتوراة

اسم الطالب:

رشا عبد الحكم يونس عبد العزيز

عنوان الرسالة:

تحضير وتوصيف طيفى لبعض انواع من زجاج
الفوسفات الحيوى لاستخدامها فى التطبيقات
الحيوية الطبية

اسم الدرجة:

دكتوراة الفلسفة فى العلوم- فيزياء تخصص فيزياء
حيوية

تحت إشراف

ا.د. السيد محمود السيد

قسم الطبيعة- كلية العلوم-جامعة عين شمس

ا.د. حمدية عبد الحميد إبراهيم زايد

قسم الطبيعة - كلية البنات - جامعة عين شمس

ا.د. السيد مصطفى خليل

قسم الطيف - المركز القومي للبحوث

ا.د. شريف محمد أبو ناف

قسم بحوث الزجاج - المركز القومي للبحوث

الدراسات العليا

تاريخ البحث / /

ختم الإجازة

اجيزت الرسالة بتاريخ: / /

موافقة مجلس الكلية: / /

موافقة مجلس الجامعة: / /



جامعة عين شمس
كلية البنات للأداب والعلوم والتربية
قسم الطبيعة

الطالبة: رشا عبد الحكم يونس عبد العزيز

القسم التابع له: فيزياء

سنة التخرج: ٢٠٠٥

سنة منح الماجستير: ٢٠١٠

سنة منح الدكتوراة: ٢٠١٥ كلية البنات – جامعة عين شمس

CONTENT

LIST OF FIGURES	<i>I</i>
LIST OF TABLES	<i>IV</i>
ACKNOWLEDGEMENTS	<i>VII</i>
ABSTRACT	<i>VIII</i>
1. Introduction	<i>1</i>
1.1. Biomaterials	<i>1</i>
1.1.1. Requirements of Biomaterials	<i>2</i>
1.1.2. Types of Compatibility	<i>3</i>
1.1.3. Classification of Biomaterials According to Material Tissue Interactions.....	<i>4</i>
1.2. Bone	<i>5</i>
1.2.1. Bone Functions	<i>5</i>
1.2.2. Bone Structure	<i>7</i>
1.2.3. Mechanical Properties of Bones	<i>9</i>
1.2.4. Methods of Bone Replacement	<i>9</i>
1.3. Bioactive Glass	<i>11</i>
1.3.1. Antibacterial Properties of Bioglasses	<i>16</i>
1.3.2. Clinical Applications of Bioactive Glasses	<i>17</i>
1.4. Literature Review.....	<i>19</i>
1.4.1. Borophosphate Glasses.....	<i>19</i>
1.4.2. Zn- or Cu-Containing Glasses.....	<i>21</i>
1.4.3. Antibacterial Behaviors of Zn or Cu	<i>26</i>
2. Theoretical background.....	<i>30</i>

2.1. Structural Concepts of Glass Formation	30
2.2. Infrared (IR) Spectroscopy	32
2.3. X-Ray Diffraction (XRD)	33
2.4. Mechanical Properties.....	35
2.4.1. Vickers Microhardness	35
2.4.2. Fracture Toughness	36
3. Material and Experimental Processes	39
3.1. Preparation of Glasses	39
3.2. Measurement of Density	42
3.3. Measurement of Microhardness and Fracture Toughness	43
3.4. In-Vitro Bioactivity Evaluation	44
3.5. Characterization of Glasses after Soaking	46
3.5.1. FTIR Analysis of Glasses	46
3.5.2. X-Ray Diffraction (XRD) Analyses	47
3.5.3. Transmission Electron Microscope (TEM)	47
3.5.4. Inductive Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) Analyses	47
3.5.5. Weight Loss Measurements	47
3.5.6. Scanning Electron Microscope (SEM)	48
3.6. Antibacterial Activity Test.....	49
4. Results and Discussions	50
4.1. Characterization of Borophosphate Glasses	50
4.1.1. Density Measurements	50
4.1.2. Mechanical Properties Measurements	50
4.1.3. The Analysis of X-Ray Diffraction (XRD)	54

4.1.4. Structural Analysis Using Fourier Transform Infrared (FTIR) Spectroscopy	58
4.1.5. Transmission Electron Microscopy (TEM) Observations	67
4.1.6. Inductive Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) Results	73
4.1.7. Weight Loss Measurements	77
4.1.8. Evaluation of Microstructures by Scanning Electron Microscopy (SEM) in Case of Testing Bulk Samples	79
4.2. Characterization of Zn- and Cu-Containing Glasses.....	88
4.2.1. Density Measurements	88
4.2.2. Mechanical Properties Measurements	88
4.2.3. The Analysis of XRD	92
4.2.4. Structural Analysis Using FTIR	98
4.2.5. TEM Observations	110
4.2.6. ICP-AES Results	111
4.2.7. Weight Loss Measurements	118
4.2.8. Study SEM Micrographs	120
4.2.9. Antibacterial Activity	123
5. CONCLUSION	129
REFERENCES	132
المخلص العربى	

LIST OF FIGURES

Figure 1.1. Microscopic representation of bone	8
Figure 1.2. Compositional dependence of bone bonding and soft tissue bonding of bioactive glasses and glass-ceramics. All compositions in the region A have a constant 6 wt% of P_2O_5 . Region E (soft tissue bonding) is inside the dashed line where $I_b > 8$ (45S5Bioglass [®] , Ceravital [®]).	13
Figure 1.3. Sequence of interfacial reactions involved in forming a bond between tissue and bioactive glasses	14
Figure.2.1 XRD basic principle schematic diagram.....	34
Figure 2.2. Vickers hardness indenters	36
Figure 2.3. Palmqvist cracking system.....	37
Figure 4.1. The measured density values of the as-prepared glasses versus boron content.....	52
Figure 4.2. Vickers microhardness and fracture toughness of the as-prepared glasses versus B_2O_3 content.....	53
Figure 4.3. XRD patterns of a) parent glasses and the products obtained after reacting the glass samples in SBF for b) 3 days, c) 7 days, d) 14 days and e) 30 days; together with the standard diffractogram pattern of HA.....	55-57
Figure 4.4. Deconvoluted FTIR spectra of the studied glasses a) before and after soaking in SBF for b) 3 days, c) 7 days, d) 14 days and e) 30 days.....	60-62
Figure 4.5. TEM images of a) B15 parent glass and the glasses b) B5, c) B15 and d) B30 after soaking in SBF for 14 days...	68,69

- Figure 4.6.** TEM images of the formed nano-HA after immersion of the glasses a) B 5, b) B 15 and c) B 30 in SBF for 30 days.....70,71
- Figure 4.7.** SAED patterns of the formed nano-HA after immersion of the glasses a) B 5, b) B 15 and c) B 30 in SBF for 30 days.....71,72
- Figure 4.8.** Variation of B-, P- and Ca-ions concentrations in the SBF solution before and after immersion of B 5, B 15 and B 30 glass samples for 3, 14 and 30 days..... 75,76
- Figure 4.9.** Weight loss percentage of the studied glasses after soaking in SBF for 7, 14 and 30 days as a function of the B_2O_3 content.....79
- Figure 4.10.** SEM micrographs of a) as-prepared B15 glass sample and HA-like layer formed on the surface of b) B 5, c) B 15 and d) B 30 bioactive glass samples after immersion in the SBF for 30 days.....80,81
- Figure 4.11.** The EDS spectra of a) as-prepared B 15 glass sample and HA-like surface layer formed on the surface of b) B 5, c) B 15 and d) B 30 bioactive glass samples after immersion in the SBF for 30 days.....82,83
- Figure 4.12.** XRD patterns for a) Zn 5 and Zn 10 base samples and the products obtained by reacting glass samples in SBF for b) 3 days, c) 7 days, d) 14 days and e) 30 days.....93-95
- Figure 4.13.** XRD patterns for a) Cu 0.01, Cu 2 and Cu 5 base samples and the products obtained by reacting glass samples in SBF for b) 3 days, c) 7 days, d) 14 days and e) 30 days.....96-98
- Figure 4.14.** The deconvoluted FTIR spectra of a) Zn 5 and Zn 10 as-prepared samples and after immersion in SBF for b) 3 days, c) 7 days, d) 14 days and e) 30 days.....102-104

- Figure 4.15.** The deconvoluted FTIR spectra of a) Cu 0.01, Cu 2 and Cu 5 as-prepared samples and after immersion in SBF for b) 3 days, c) 7 days, d) 14 days and e) 30 days.....**104-106**
- Figure 4.16.** TEM micrographs of HA-like layer that formed on the surfaces of a) Zn 5 and b) Cu 5 after soaking in SBF for 30 days.....**110,111**
- Figure 4.17.** Ion concentrations of a) Ca-ions and b) P-ions in the SBF of Zn 5 and Zn 10 glass samples after 3, 14 and 30 days**114**
- Figure 4.18.** Ion concentrations of a) Ca-ions and b) P-ions in the SBF of Cu 0.01, Cu 2 and Cu 5 glass samples after 3, 14 and 30 days.....**116**
- Figure 4.19.** SEM micrographs of HA-like layer on the surface of a) Zn 5 and b) Cu 5 bioactive glass samples after immersion in the SBF for 30 days.....**121**
- Figure 4.20.** The EDS spectra of HA-like layer on the surface of a) Zn 5 and b) Cu 5 bioactive glass samples after immersion in the SBF for 30 days.....**122**
- Figure 4.21.** Photos of Petri dishes after conducting agar disk-diffusion assays at 37 °C for 24 h with E. coli as test micro-organisms (for tested glasses) **125**
- Figure 4.22.** Photos of Petri dishes after conducting agar disk-diffusion assays at 37 °C for 24 h with S. aureus as test micro-organisms (for tested glasses) **126**

LIST OF TABLES

Table 3.1.	Nominal compositions of the prepared borophosphate glasses (mol%).....	40
Table 3.2.	Nominal compositions of the prepared Zn-containing glasses (mol%).....	41
Table 3.3.	Nominal compositions of the prepared Cu-containing glasses (mol%).....	42
Table 3.4.	Ion concentration (mM) in the simulated body fluid (SBF) and human blood plasma.....	45
Table 4.1.	Density of the calcium borophosphate glasses.....	52
Table 4.2.	Vickers microhardness and fracture toughness of the calcium borophosphate glasses.....	53
Table 4.3.	The characteristic bands of as-prepared calcium borophosphate glasses.....	59
Table 4.4.	The characteristic bands of hydroxyapatite (HA)	59
Table 4.5.	Elemental concentrations in the SBF solution before and after immersion of B 5, B 15 and B 30 glass samples for 3, 14 and 30 days.....	74
Table 4.6.	Weight loss percentage of the studied glasses after soaking in SBF for 7, 14 and 30 days as a function of the B ₂ O ₃ content.....	78
Table 4.7.	Density values of Zn-containing glass samples.....	89
Table 4.8.	Density values of Cu-containing glass samples.....	89

Table 4.9.	The values of microhardness and fracture toughness of Zn 5 and Zn 10-containing glass samples.....	90
Table 4.10.	The values of Vickers microhardness and fracture toughness of Cu-containing glass samples.....	90
Table 4.11.	The characteristic bands of as-prepared Zn-containing glasses.....	100
Table 4.12.	The characteristic bands of as-prepared Cu-containing glasses.....	101
Table 4.13.	The elemental concentrations in SBF after immersion of Zn 5 and Zn 10 glass samples for 3, 14 and 30 days.....	113
Table 4.14.	The elemental concentrations in SBF after immersion of Cu 0.01, Cu 2 and Cu 5 glass samples for 3, 14 and 30 days.....	120
Table 4.15.	The weight loss (wt.%) of the Zn5 and Zn10 glass samples after 7, 14 and 30 days.....	113
Table 4.16.	The weight loss (wt.%) of the Cu 0.01, Cu 2 and Cu 5 glass samples after 7, 14 and 30 days immersion in the SBF.....	115
Table 4.17.	Glass composition and the measured microorganisms inhibition zone diameters (minus the diameter of the glass disc, 12 mm) were shown.....	124