UNIVERSITI PUTRA MALAYSIA

EFFECTS OF P_2O_5 AND SINTERING TEMPERATURE ON MORPHOLOGICAL, PHYSICAL, AND MECHANICAL PROPERTIES OF SiO_2-Na_2O-CaO-P_2O_5 GLASS-CERAMIC

NUR FADILAH BINTI BAHARUDDIN PALLAN

ITMA 2018 9

EFFECTS OF P_2O_5 AND SINTERING TEMPERATURE ON MORPHOLOGICAL, PHYSICAL, AND MECHANICAL PROPERTIES OF SiO_2-Na_2O-CaO-P_2O_5 GLASS-CERAMIC

By

NUR FADILAH BINTI BAHARUDDIN PALLAN

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Doctor of Philosophy

January 2018

DEDICATION

I dedicate this thesis to my family especially my beloved parents (Baharuddin Pallan Bin Abdullah and Kathijah Abdul Kader), my beloved siblings (Faizal, Fairuz, Faizah), sister in-law (Farizah, Allahyarhamah Imani, Aini), nieces and nephew (Farisya, Fatin, Filza, Faiq), lecturers, and also to my entire friends.

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Doctor of Philosophy

EFFECTS OF P_2O_5 AND SINTERING TEMPERATURE ON MORPHOLOGICAL, PHYSICAL, AND MECHANICAL PROPERTIES OF SiO_2-Na_2O-CaO-P_2O_5 GLASS-CERAMIC

By

NUR FADILAH BINTI BAHARUDDIN PALLAN

January 2018

Chairman: Assoc. Prof. Khamirul Amin Matori, PhD
Institute: Institute of Advanced Technology

The great varieties of compositions and microstructures with specific technological properties have allowed glass-ceramics to be used in a wide range of applications. Materials fabricate from vitreous and ceramic wastes nowadays have been widely used in order to minimize the cost of production, eco-friendly materials, and reduce the landfill disposal matters. SiO_2-Na_2O-CaO-P_2O_5 (SNCP) composition was selected since lack of study has been discussed on SNCP glass-ceramic from waste material. This approach and opportunity have been taken to investigate further about the materials properties and compare with previous study. The main waste raw materials used are clam shells (CS) and soda-lime-silica (SLS) glass bottle. There are four types batch formulation of SNCP glass-ceramic that have been fabricated via conventional melt-quenching technique and solid state sintering. Each type of SNCP series were varied with different $NaCO_3$ to P_2O_5 weight percentage and samples were sintered at temperature 550−950 °C. Samples were sintered to discover effect sintering temperature evolving on morphological, physical, and mechanical properties of SNCP are highlighted in this study. The XRD results before sintering have been confirmed the existence of amorphous-crystalline phases on SNCP 1 and SNCP 4 samples while amorphous phase formation corresponding to SNCP 2 and SNCP 3 samples. The full crystallization for SNCP 1 and SNCP 4 started to occur at 650 °C while for SNCP 2 and SNCP 3 at sintering temperature 750 °C. Overall, the glass transition temperature (T_g) started at the range of 550−580 °C and the glass crystallization temperature (T_c) started from 600 °C to 743 °C. The existence of P_2O_5 in SNCP glass-ceramic is attributed to glass crystallization correlated with high intensity of crystallization peak and enhanced volume nucleation. The microstructural study observation showed SNCP 1 sample at 550−950 °C have agglomerated grain and porosity decreased which produce fine and uniform grain as the sintering temperature increases while the SNCP 2 until SNCP 4 showed less porosity, fine and uniform grain at 550−750 °C produced high densification microstructural. The density values (2.097−2.726 g/cm^3) for SNCP 1−SNCP 4

obtained below the glass crystallization temperature at 550−750 °C contribute to excellent mechanical properties. SNCP 3 obtained the highest hardness (631 HV) at 650 °C than SNCP 1 (332 HV). The highest compressive strength in SNCP 1 (free-P_2O_5) is 49.66 MPa with Young's modulus value 0.678 GPa at sintering temperature 650 °C while SNCP 3 obtained the highest compressive strength (33.44 MPa) with Young's modulus value 0.882 GPa. Both samples have higher Young's modulus values when comparing from previous study (0.05−0.5 GPa) for the cancellous bone implantation. The influence of morphological and physical properties on SNCP 3 sample at sintering temperature 650 °C contribute to excellent mechanical strength properties.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Doktor Falsafah

KESAN P_2O_5 DAN SUHU PERSINTERAN KE ATAS SIFAT-SIFAT MORFOLOGIKAL, FIZIKAL, DAN MEKANIKAL SERAMIK-KACA SiO_2-Na_2O-CaO-P_2O_5

Oleh

NUR FADILAH BINTI BAHARUDDIN PALLAN

Januari 2018

Pengerusi: Prof. Madya Khamirul Amin Matori, PhD
Institut: Institut Teknologi Maju

Kepelbagaian komposisi dan mikrostruktur yang bagus dengan ciri-ciri teknologi yang membolehkan seramik-kaca digunakan dengan meluas dalam pelbagai aplikasi. Pada masa kini, bahan yang dihasilkan berasaskan sisa kaca dan seramik telah digunakan secara meluas untuk mengurangkan kos pembuatan, bahan mesra alam, dan mengurangkan masalah pelupusan sampah. Komposisi SiO_2-Na_2O-CaO-P_2O_5 (SNCP) telah dipilih berdasarkan kekurangan perbincangan yang dilakukan sebelum ini terhadap seramik-kaca SNCP daripada bahan buangan. Peluang dan galakan telah diambil untuk mengkaji dengan mendalam tentang sifat bahan ini dan membandingkan dengan kajian yang lepas. Bahan buangan utama yang digunakan adalah kulit kerang (CS) dan botol kaca soda-kapur-silika (SLS). Ada empat jenis formulasi siri seramik-kaca SNCP yang dibuat menggunakan teknik sepuh lindap konvensional dan pensinteran keadaan pepejal. Setiap jenis siri berlainan dengan perbezaan peratus berat $NaCO_3$ kepada P_2O_5 pada suhu pensinteran 550−950 °C. Sampel telah disinter untuk mengkaji kesan perubahan SNCP pada sifat-sifat morfologikal, fizikal, dan mekanikal ditumpukan dalam kajian ini. Data analisis XRD sebelum pensinteran telah mengesahkan kewujudan fasa kristal-amorfus pada sampel SNCP 1dan SNCP 4 sementara pembentukan fasa amorfus merujuk kepada sampel SNCP 2 dan SNCP 3. Penghabluran lengkap untuk SNCP 1 dan SNCP 4 mula berlaku pada suhu 650 °C sementara bagi SNCP 2 dan SNCP 3 pada suhu pensinteran 750 °C. Suhu perubahan kaca (T_g) berlaku pada julat suhu 550−580 °C dan suhu penghabluran kaca (T_c) bermula dari 600 °C hingga 743 °C. Pemerhatian kajian struktur mikro menunjukkan sampel SNCP 1 (tiada-P_2O_5) pada 550−950 °C mempunyai butiran bergumpal dan keliangan berkurangan menghasilkan butiran yang sekata dan teratur apabila suhu pensinteran bertambah manakala SNCP 2 hingga SNCP 4 menunjukkan kekurangan keliangan, halus, dan butiran yang sekata pada suhu 550−750 °C menghasilkan kepadatan struktur mikro yang tinggi. Nilai ketumpatan (2.097−2.726 g/cm^3) bagi SNCP 1−SNCP 4 diperolehi di bawah suhu penghabluran kaca pada 550−750 °C yang menyumbang kepada sifat-sifat mekanikal

yang bagus. SNCP 3 memperolehi mikrokekuatan paling tinggi (631 HV) pada 650 °C berbanding SNCP 1 (322 HV). Kekuatan tekanan yang paling tinggi dalam SNCP 1 (tiada-P_2O_5) adalah 49.66 MPa dengan nilai modulus Young 0.678 GPa pada suhu pensinteran 650 °C sementara sampel SNCP 3 memperolehi kekuatan tekanan paling tinggi (33.44 MPa) dengan nilai modulus Young 0.882 GPa. Kedua-dua sampel telah memperbaiki dan mencapai nilai tinggi modulus Young apabila dibandingkan dengan kajian yang lepas (0.05−0.5 GPa) untuk implan jenis tulang kancelus. Pengaruh sifat-sifat morfologikal dan fizikal terhadap sampel SNCP 3 pada suhu 650 °C menyumbang kepada sifat-sifat kekuatan mekanikal yang bagus.

ACKNOWLEDGEMENTS

First praise and foremost is to Allah (S.W.T), on whom ultimately we depend for sustenance and guidance with his blessing, help, and will, we were able made this work a success. I would like to express my sincere appreciation and utmost gratitude to Assoc. Prof. Dr. Khamirul Amin Matori, Allahyarham Dr. Mansor Hashim, Dr. Norhazlin Zainuddin, and Dr. Raba'ah Syahidah Aziz for their constant monitoring, supporting, encouragement and sponsoring during the period of research. Working with them has provided me with a vast understanding on the materials science and theoretical experiences from which I will continue to draw benefit in the future. The most appreciation I would like to express is to my family, especially to my beloved father; Baharuddin Pallan Bin Abdullah, my beloved mother; Kathijah Binti Abdul Kader, and my beloved family; Mohd. Faizal, Muhammad Fairuz, Nor Faizah, Fariza, Allahyarhamah Imani, Aini, nieces and nephew for their endless support, encouragement and prayer. Thank you to my childhood best friend; Nor Ain Shahajar Ahmad Sohdi and Ikha Fadzila Md Idris for the support, help, and prayer.

I would like to thank to ITMA staff (Mr. Ali Rani, Mr. Kadri, Mrs. Sarinawani, Mrs. Roslina, Dr. Ismayadi, Miss Ija, and Mrs. Linda), XRD lab officer (Pn. Haslinda and Pn. Khamsiah), and mechanical lab; Mr. Wildan. To my colleagues in the GCCM Laboratory and MSCL Laboratory; Siti Nor Ain Rusly, Fadzidah Mohd Idris, Nurzilla Mohamed, Idza Riati Ibrahim, Zarifah Alassan, Nor Hapishah Abdullah, Noorfauzana Adnin, Rodziah Nadzlan, Wan Norailiana, Zamratul Maisarah, Farah Nabilah, Zaiti, Yusnita, Nuraine Mariana, Rosnah Nawang, Shamsul, Ghazal, Loy Chee Wah, Mohammad Zulhasif, Mohd Hafiz, Muhammad Syazwan, and Low Zhi Huang for their tremendous assistance and support throughout this research, idea, memorable interactions, support and encouragement. To my fellow friends during my postgraduate study; Dian Najihah, Nor Amalina Hafiza, Noraziah Ahmad, Maria Nuid, Aima Ramli, Arlina Ali, Noorhanim, Fiqa, Amy, Nazyha, Mahir, Maya, Nad, Yana, and many others for their great help and contributions. Thank you for everything.

I certify that a Thesis Examination Committee has met on 4 January 2018 to conduct the final examination of Nur Fadilah binti Baharuddin Pallan on her thesis entitled "Effects of P_2O_5 and Sintering Temperature on Morphological, Physical, and Mechanical Properties of SiO_2-Na_2O-CaO-P_2O_5 Glass-Ceramic" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy.

Members of the Thesis Examination Committee were as follows:

Mohd Nizar bin Hamidon, PhD
Associate Professor
Faculty of Engineering
Universiti Putra Malaysia
(Chairman)

Irmawati binti Ramli, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Abdul Halim bin Abdullah, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Yasser Bakr Saddeek Muhammed, PhD
Professor
Al Azhar University
Egypt
(External Examiner)

NOR AINI AB. SHUKOR, PhD
Professor and Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 26 April 2018

This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfillment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

Khamirul Amin Bin Matori, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Raba'ah Syahidah Binti Aziz, PhD
Senior Lecturer
Faculty of Science
Universiti Putra Malaysia
(Member)

Norhazlin Binti Zainuddin, PhD
Senior Lecturer
Faculty of Science,
Universiti Putra Malaysia
(Member)

____
ROBIAH BINTI YUNUS, PhD
Professor and Dean
School of Graduates Studies
Universiti Putra Malaysia

Date:

Declaration by Graduate Student

I hereby confirm that:

- this thesis is my original work;
- quotations, illustrations and citations have been duly referenced;
- this thesis has not been submitted previously or concurrently for any other degree at any other institutions;
- intellectual property from the thesis and copyright of thesis are fully-owned by Universiti Putra Malaysia, as according to the Universiti Putra Malaysia (Research) Rules 2012;
- written permission must be obtained from supervisor and the office of Deputy Vice-Chancellor (Research and Innovation) before thesis is published (in the form of written, printed or in electronic form) including books, journals, modules, proceedings, popular writings, seminar papers, manuscripts, posters, reports, lecture notes, learning modules or any other materials as stated in the Universiti Putra Malaysia (Research) Rules 2012;
- there is no plagiarism or data falsification/fabrication in the thesis, and scholarly integrity is upheld as according to the Universiti Putra Malaysia (Graduate Studies) Rules 2003 (Revision 2012-2013) and the Universiti Putra Malaysia (Research) Rules 2012. The thesis has undergone plagiarism detection software.

Signature: ________________________ Date: ___________________

Name and Matric No.: ____

Declaration by Members of Supervisory Committee

This is to confirm that:

- the research conducted and the writing of this thesis was under our supervision;
- supervision responsibilities as stated in the Universiti Putra Malaysia (Graduate Studies) Rules 2003 (Revision 2012-2013) are adhered to.

Signature: ______________________
Name of Chairman of Supervisory Committee: ______________________

Signature: ______________________
Name of Member of Supervisory Committee: ______________________

Signature: ______________________
Name of Member of Supervisory Committee: ______________________

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS AND SYMBOLS

SNCP	SiO_2-Na_2O-CaO-P_2O_5
$CaSiO_3$	Wollastonite
Na_3PO_4	Trisodium phosphate
W/A	Wollastonite apatite
SLS	Soda-lime-silica
CS	Clam shell
Wt	Weight
μm	Micrometre
T_g	Glass transition temperature
T_c	Glass crystallization temperature
T_m	Glass melting temperature
TEM	Transmission Electron Microscopy
XRD	X-ray Diffraction
FESEM	Field Emission Electron Microscopy
DSC	Differential Scanning Calorimetry
EDX	Energy Dispersive X-ray Spectroscopy
P	Density
HV	Vickers hardness
V	Volume
kgf	Kilogram force
F	Force
Å	Angstrom unit
MPa	Megapascal
GPa	Gigapascal
N	Newton

CHAPTER 1

INTRODUCTION

1.1 Background of the study

New glass-ceramic fabrication with special properties is an interesting study in the modern glass science and technology. Production of glass-ceramic has being a broad diversity and well-known materials in variety of applications. Glass-ceramics are a series of composite materials in which residual amorphous phase and crystalline phase coexist. Since the glass-ceramic is used in a large scale application, the materials technology is evolving rapidly. Glass-ceramic have been developed as essential clinical applications that associated to repair and reconstruction of skeletal system (bone, joints, and teeth) due to their biocompatibility with living tissue.

The bioactive materials incorporate of bioglasses, bioglass-ceramics, and calcium phosphate ceramics (Hench, 1991). The SNCP glass-ceramic is a suitable material to design and possible to produce high mechanical strength properties to be applied for bone implantation. The development of biomedical glass-ceramic generally is fabricated based on SNCP composition has been designed by Hench and the 45S5 bioglass were first found by Hench in 1969 which these types of glasses were able to bond to tissues (Hench, 2006). The bioglass fabricated by Hench were added with P_2O_5 compound as the ordinary starting powder substances. The Hench's glass composition is composed of SiO_2 (45%), Na_2O (24.5%), CaO (24.5%), and P_2O_5 (6%) in weight percentage (Hench et al., 1971). The same raw chemical materials according to Hench's glass composition were developed by Peitl et al. (1996) by thermal treatments. Peitl et al. (2001) developed SNCP glass-ceramics having chemical composition $1Na_2O\text{-}2CaO\text{-}3SiO_2$ and $1.5Na_2O\text{-}1.5CaO\text{-}3SiO_2$, containing 0−6 wt% of P_2O_5. Mostly the applications of bioactive materials have been used in the medical field to repair and reconstruct diseased or damaged bones or tissues (Hench, 1991).

Nowadays, materials science researchers have found out the correlation between structure and properties of a novelty and improved materials with low cost production by using waste materials. The interesting part in this study, the SNCP glass-ceramic composition is fabricated from mixed powders of chemical and waste raw materials. The waste raw materials used are SLS glass bottle and clam shells. SNCP glass-ceramic composition from waste materials used in this study is the same as Hench's glass composition, but have been modified in different weight percentage. Abbasi and Hashemi (2014) was the first group using SLS waste glass to synthesize SNCP glass-ceramic via solid-state reaction method.

1.2 Mechanical properties of SNCP glass-ceramic

The sintering technique is used to obtain SNCP glass-ceramic final product which have better physical and mechanical properties for medical implantation. The mechanical interaction between implant and surrounding tissues need to be focus for the development of SNCP glass-ceramic from vitreous waste at different sintering temperature that affect to the changes in micostructural and physical properties. Low density glass-ceramic in the Na-Ca-Si-P-O system obtained low value of Young's modulus that closer to the cortical bone (Peitl, 1995). The Na_2O in SNCP glass-ceramic system have influenced the T_g value to obtain a linear relationship. There is a linear relation with Young's modulus values after the measurement of hardness, fracture toughness and fracture surface energy. The decrement in elastic moduli value as a function of temperature revealed the existence of structural softening in the glass network (Rajendran et al., 2002). When the T_g value decreased, the hardness value of a SNCP glass-ceramic is decreased (O'Donnell, 2011). The mechanical properties of SNCP glass-ceramic materials are greater than the amorphous glass and calcium phosphate ceramics (Rezwan et al., 2006). The value of Young's modulus for 45S5 bioglass is 30−35 GPa which is near to the cortical bone value (Kokubo, 1999). Sample sintered at 800−880 °C were compared with bulk sample before sintering (Sola et al., 2011). The effect after sintering on sample BG_Ca with high content of CaO showed vickers hardness is increased (Sola et al., 2011). The intention in this study is to evaluate influence of microstructural and physical properties to produce excellent mechanical strength properties at different sintering temperature with different batch formulation of SNCP glass-ceramic from vitreous waste. The mechanical properties will be compared with available literature and detect the suitable type of bone that possible for bone implantation.

1.3 Problem statement

The SNCP glass-ceramic materials have been developed widely with lots of changes occur due to the modification of composition by addition, doping or difference in ratio weight percentages for substances used in SNCP composition. Mostly, the SNCP compositions have been prepared using chemical raw materials but lack of previous research used SLS waste glass and CS waste to fabricate SNCP glass-ceramic system and reported about the mechanical strength properties specifically on microvickers hardness and compressive strength. The fabrication and characterization of SNCP glass-ceramic from SLS waste glass have been reported but the mechanical properties still absent (Abbasi and Hashemi, 2014). Hence, this effort have been taken to be the first research using the combination of SLS waste glass and clam shells waste to fabricate SNCP compositions subsequently to find optimal mechanical properties that can use for potential bone implantation application. This study is focused to evaluate morphology and physical properties that will influence the changes on mechanical properties of SNCP glass-ceramic from vitreous waste with low cost production and to save the environment from pollution matters (air and water pollution) which correlated with excess usage of chemical materials.

1.4 Objectives of the study

The primary goal of this research was to find out possibilities for improving the mechanical properties of SNCP glass-ceramic from vitreous waste and trace the potential type of bone for implantation.

The following objectives have been set in order to accomplish the primary goal of the research:

i) To prepare SNCP glass-ceramic from mixed of chemical and waste materials at different batch formulation.
ii) To determine the effect of different sintering temperatures on morphology-related properties, physical properties, and mechanical properties at different batch formulation of SNCP system.
iii) To investigate the relationship and influence of morphology-related properties and physical properties on the mechanical properties of SNCP system.

1.5 Scope of study

The scope of study has been carried out as following**:**

i) To prepare the SNCP 1−SNCP 4 glass-ceramic by using the chemical materials (Na_2CO_3 and P_2O_5) mixed with vitreous waste (SLS waste glass and CS waste) by using conventional melt-quenching and solid-state sintering technique at 550−950 °C.
ii) The chemical elements analysis of SNCP samples were detected by utilizing EDX while the microstructural properties were observed through FESEM. The phase crystallization and crystal system of samples were confirmed via XRD analysis.
iii) The chemical functional group and thermal properties (T_g and T_c) of SNCP have been analyzed by using FTIR and DSC respectively.
iv) The physical properties were measured by means of Archimedes method to obtain density and volume of sample. The mechanical properties were measured via microvickers hardness tester while Universal Testing Machine (UTM) for measuring compressive strength and Young's modulus of SNCP.

1.6 Hypotheses of the study

The hypotheses of the study are correlated with the objective and the problem statement of the research. In this study, the sintering temperatures of SNCP samples are 550−950 °C with step temperature 50 °C for each sample. SNCP glass-ceramic sintering temperature increases would lead to high intensity, phase's transformation, new phases crystallization, and crystal system transformation. SNCP glass-ceramic sintering temperature increases would enhance grain size and increase porosity of SNCP glass-ceramic. The enhancement of grain size and porosity would lead to lower density value. At high sintering temperature, the elemental weight percentage of phosphorus would increases as the percentage of P_2O_5 increases. Excellent morphology and physical properties would develop superior mechanical properties of SNCP glass-ceramic. Hardness value would decrease as the glass transition temperature (T_g) decrease when sample is heated at high sintering temperature. Compressive strength of sample would increases as density and Young's modulus increases.

1.7 Organization of the dissertation

The dissertation is arranged as stated to clarify the structure of the dissertation and to present the different parts relate to each other. The current chapter (Chapter 1) provides a brief introduction background of the study, objectives and hypotheses of the research. The previous research area on glass-ceramic which focused on morphology, physical, thermal, structural bonding, and mechanical-related properties were discussed in Chapter 2. The details on research design and characterizations employed in this study can be found in Chapter 3. The results and discussion in Chapter 4 is divided into four different batch formulations of SNCP glass-ceramic which consist of SNCP 1, SNCP 2, SNCP 3, and SNCP 4 at different sintering temperature and evaluated on morphology, physical, thermal, structural bonding, and mechanical-related properties. Chapter 5 are conclusions effect of sintering temperature on morphology, physical, and mechanical-related properties separately at different SNCP compositions and subsequently recommendations for future work. The references, biodata of student, and list of publication were attached at the end of dissertation.

REFERENCES

Abbasi, M., and Hashemi, B. (2014). Fabrication and characterization of bioactive glass-ceramic using soda–lime–silica waste glass. *Materials Science and Engineering C*, *37*, 399–404.

Adams, L. A., Essien, E. R., Shaibu, R. O., and Oki, A. (2013). Sol-gel synthesis of SiO_2-CaO-Na_2O-P_2O_5 bioactive glass ceramic from sodium metasilicate. *New Journal of Glass and Ceramics*, *3*, 11-15.

Arakcheeva, A., and Chapuis, G. (2005). A reinterpretation of the phase transitions in Na_2CO_3. *Acta Crystallographica Section B Structural Science*, *61*, 601–607.

Arstila, H., Vedel, E., Hupa, L., and Hupa, M. (2007). Factors affecting crystallization of bioactive-glasses. *Journal of the European Ceramic Society*, *27*, 1543–1546.

Baesso, M. L., Bento, A. C., Duarte, A. R., Neto, A. M., Miranda, L. C. M., Sampaio, J. A., Catunda, T., Gama, S., and Gandra, F. C. G. (1999). NdO doped low silica calcium aluminisilicate glasses; Thermomechanical properties. *Journal of Applied Physics*, *85*, 8112-8118.

Baharuddin Pallan, N. F., Matori, K. A., Hashim, M., Lim, W. F., Hock, J. Q., Fauzana, A. N., Rosnah, N., Khiri, M. Z. A., Farhana, S., Norhazlin, Z., Zarifah, N. A., Nurzilla, M., Hafiz, M. Z. M., Loy, C. W., and Zamratul, M. I. M. (2016). Preparation of SiO_2-Na_2O-CaO-P_2O_5 glass-ceramic from waste materials and heat treatment effects on its morphology. *Materials Science Forum*, 846, 189-192.

Baino, F., Novajra, G., Miguez-Pacheco, V., Boccaccini, A. R., and Vitale-Brovarone, C. (2016). Bioactive glasses: Special applications outside the skeletal system. *Journal Non-Crystalline Solids*, *432*, 15–30.

Brentrup, G. J., Moawad, H. M. M., Santos, L. F., Almeida, R. M., and Jain, H. (2009). Structure of Na_2O–CaO–P_2O_5–SiO_2 glass–ceramics with multimodal porosity. *Journal of the American Ceramic Society*, *92* (1), 249–252.

Bromer, H., Deutscher, B., Blenke, B., Pfeil, E., and Strunz, V. (1977). Properties of the bioactive implant material Ceravital®. In *Science of Ceramics*, *9*, 1977, 219–223.

Best, S. M., Porter, A. E., Thian, E. S., and Huang, J. (2008). Bioceramics: Past, present and for the future. *Journal of the European Ceramic Society*, *28*, 1319–1327.

Calata, J. N. (2005). *Densification Behavior of Ceramic and Crystallizable Glass Materials Constrained on a Rigid Substrate*. PhD Thesis, Virginia Polytechnic Institute and State University.

Chatzistavrou, X., Zorbal, T. T., Kontonasaki, E., Chrissafis, K., Koidis, P., and Paraskevopoulos, K. M. (2004). Following bioactive glass behaviour beyond melting temperature by thermal and optical methods. *Physic state solid(a)*, *201* (5), 944–951.

Chen, Q. Z., and Boccaccini, A. R. (2006). Poly(D,L-lactic acid) coated 45S5 Bioglass-based scaffolds for bone engineering. *Journal of Biomedical Material Research A*, 77(3), 445-457.

Clupper, D. C., and Hench, L. L. (2003). Crystallization kinetics of tape cast bioactive glass 45S5. *Biomaterials*, *318*, 43-48.

Combes, C., Miao, B., Bareille, R., and Rey, C. (2006). Preparation, physical-chemical characterisation and cytocompatibility of calcium carbonate cements. *Biomaterials*, *27*, 1945-1945.

Cramer von Clausbruch, S., Schweiger, M., Holand, W., and Rheinberger, V. (2000). The effect of P_2O_5 on the crystallization and microstructure of glass-ceramics in the SiO_2-Li_2O-K_2O-ZnO-P_2O_5 system. *Journal of Non-Crystalline Solids*, *263&264*, 388-394.

Di marzio, E. A., and Gibbs, J. H. (1959). Glass temperature of copolymers. *Polymer Science*, *40*, 121.

Ducheyne, P., El-Ghannam, A., and Shapiro, I. (1997), us patent no. 5 676 720.

ElBatal, H. A., Azooz, M. A., Khalil, E. M. A., Soltan Monem, A., and Hamdy, Y. M. (2003). Characterization of some bioglass-ceramics. *Materials Chemistry and Physic*s, *80*, 599–609.

ElBatal, F. H., and El-Bassyouni, G. T. (2011). Bioactivity of Hench bioglass and corresponding glass-ceramic and the effect of transition metal oxide. *Silicon*, *3*, 185-197.

El-Ghannam, A., Hamazawy, E., and Yehia, A. (2001). Effect of thermal treatment on bioactive glass microstructure, corrosion behavior, Zeta potential, and protein adsorption. *Journal of Biomedical Materials Research*, *55*, 387–98.

El-Ghannam, A. (2004). Advanced bioceramic composite for bone tissue engineering: Design principles and structure–bioactivity relationship. *Journal of Biomedical Materials Research A*, *69*, 490-501.

Farmer, V. C. (1974). *The Infrared Spectra of Minerals*. Mineralogical Society Monograph 4, London, 484–490.

Filgueiras, M. R. T., La Torre, G. P., and Hench, L. L., Solution effects on the surface reactions of three bioactive glass compositions. *Journal of Biomedical Materials Research*, *27* (1993) 1485–1493.

Filho, O. P., La Torre, G. P., and Hench, L. L. (1996). Effect of crystallization on apatite-layer formation of bioactive glass 45S5. *Journal of Biomedical Materials Research*., *30* (4), 509-514.

Francis, A. A., AbdelRahman, M. K., and Daoud, A. (2013). Processing, structures and compressive properties of porous glass-ceramic composites prepared from secondary by-product materials. *Ceramics International*, *39*, 7089–7095.

German, R. M. (1991). Fundamentals of Sintering in Engineered Materials and Book ASM International. Materials Park, Ohio, Volume 4.

German, R. M., Suri, P., and Park, S. J. (2009). Review: liquid phase sintering. *Journal of Materials Science*, *44*, 1–39.

Gervais, F., Blin, A., Massiot, D., Coutures, J. P., Chopinet, M. H., and Naudin, F. (1987). Infrared reflectivity spectroscopy of silicate glasses. *Journal Non-Crystalline Solids*, *89*, 384.

Giesen, E. B. W, Ding, M., Dalstra, M., and van Eijden, T. M. G. J. (2001). Mechanical properties of cancellous bone in the human mandibular condyle are anisotropic. *Journal of Biomechanical*, *34*, 799–803.

Gong, W., Abdelouas, A., and Lutze, W. (2001). Porous bioactive glass and glass–ceramics made by reaction sintering under pressure. *Journal of Biomedical Materials Research*, *54*, 320-327.

Hanna, R., and Su, G. J. (1964). Infrared absorption spectra of sodium silicate glasses from 4 to 30µm. *Journal of the American Ceramic Society*, *47*, 597.

Hariharan, M., Varghese, N., Cherian, A. B., Sreenivasan, P. V., Paul, J., and Asmy Antony, K. A. (2014). Synthesis and characterization of $CaCO_3$ (Calcite) nano particles from cockle shells using chitosan as precursor. International *Journal of Scientific and Research Publications*, *4* (10), ISSN 2250-3153.

Hasan, S. A., Salman, S. M., Darwish, H., and Mahdy, E. A. (2009). Effect of Na_2O on the crystallization characteristics and microstructure of glass-ceramics based on the $CaO–MgO–P_2O_5–CaF_2–SiO_2$ System. *Ceramics – Silikáty*, *53* (3), 165-170.

Hench, L. L., Splinter, R. J., Allen, W. C., and Greenlee, T. K. (1971). Bonding mechanisms at the interface of ceramic prosthetic materials. *Journal of Biomedical Materials Research Symposium 2*, Part 1, 117.

Hench, L. L., and Wilson, J. (1984). Surface active biomaterials. *Science*., *266*, 630.

Hench, L. L. (1991). Bioceramics: From concept to clinic. *Journal of the American Ceramic Society*. *74*, 1487–1510.

Hench, L. L., and Wilson, J. (1993). *Introduction to Bioceramics*, Chapter 1 (World Scientific).

Hench, L. L, and Wilson, J. (1999). *An introduction to bioceramics*. Second edition, London: Word Scientific.

Hench, L. L. (2006). The story of bioglass. *Journal of Materials Science: Materials in Medicine*, *17*, 967–978.

Hench, L. L. (2015). The future of bioactive ceramics. *Journal of Materials Science: Materials in Medicine*, *26*, 1–4.

Hench, L. L. (2013). *An Introduction to Bioceramics*. Second edition, London, UK: Imperial College Press.

Henry, J., and Hill, R. G. (2003). The influence of lithia content on the properties of fluorphlogopite glass-ceramics. I. Microstructure hardness and machineability, *Journal Non-Crystalline Solids*, *319*, 13–30.

Higazy, A. A., and Bridge, B. (1985). Infrared spectra of the vitreous system Co_3O_4–P_2O_5 and their interpretation. *Journal of Materials Science*, *20*, 2345–2358.

Holland, W., and Beall, G. H. (2002). *Glass-ceramic Technology*, The American Ceramic Society, Ohio.

Holand, M., Dommann, A., Holand, W., Apel, E., and Rheinberger, V. (2005). *Glass Science Technology*, *78*(4), 153–158.

Holand, W., Vogel, W., and Naumann, K. (1985). Interface reactions between machinable bioactive glass-ceramics and bone. *Journal of Biomedical Materials Research*, *19*, 303-312.

Holand, W., and Beall, G. (2012). *Glass-ceramic Technology*. Second edition, The American Ceramic Society and Wiley.

James, P. F. (1989). *Glasses and Glass–ceramics*, In: Lewis, M. H., editors. Chapman and Hall, London, 59.

James, P. F. (1995). Glass ceramics: New compositions and uses. *Journal Non-Crystalline Solids*, *181*, 1–15.

Kahlenberg, V., and Hösch, A. (2002). The crystal structure of $Na_2Ca_2Si_2O_7$ - a mixed anion silicate with defect perovskite characteristics. *Zeitschrift für Kristallographie*, *217*, 155–163.

Kamba, A. S., Ismail, M., Ibrahim, T. A. T., and Zakaria, Z. A. B. (2013). Synthesis and characterisation of calcium carbonate aragonite nanocrystals from cockle shell powder (*Anadara granosa*). *Journal of Nanomaterials*, *Article ID 398357*, 1-9.

Karamanova, E., Avdeev, G., and Karamanov, A. (2011). Ceramics from blast furnace slag, kaolin and quartz. *Journal of the European Ceramic Society*, *31*, 989–998.

Kaygili, O. (2014). Synthesis and characterization of Na_2O-CaO-SiO_2 glass–ceramic. *Journal of Thermal Analysis and Calorimetry*, *117*, 223–227.

Keaveny, T. M., Hayes, W. C. (1993). Mechanical properties of cortical and trabecular bone. In: Hall B. K., editor. *Bone growth*. Boca Raton, FL: CRC Press, 285–344.

Kucynski, G. C., Hooten, N. A., and Gibson, C. F. (1967). *Sintering and Related Phenomena*. Gordon and Breach, New York.

Khiri, M. Z. A., Matori, K. A., Zainuddin, N., Abdullah, C. A. C., Alassan, Z. N., Baharuddin, N. F., and Zaid, M. H. M. (2016). The usability of ark clam shell (Anadara granosa) as calcium precursor to produce hydroxyapatite nanoparticle via wet chemical precipitate method in various sintering temperature. *Springer Plus*, *(5)* 1206, 1-15.

Kiani, A., Hanna, J. V., King, S. P., Rees, G. J., Smith, M. E., Roohpour, N., Salih, V., and Knowles, J. C. Structural characterization and physical properties of P_2O_5-CaO-Na_2O-TiO_2 glasses by Fourier transform infrared, Raman and solid-state magic angle spinning nuclear magnetic resonance spectroscopies. *Acta Biomaterialia*, *8*, 333–340.

Kim, C. Y., Clark, A. E., and Hench, L. L. (1989). Early stages of calcium-phosphate layer formation in bioglasses. *Journal of Non-Crystalline Solids*, *113*, 195–202.

Kim, H. M., Miyaji, F., Kokubo, T., Ohtsuki, C., and Nakamura, T. (1995). Bioactivity of Na_2O-CaO-SiO_2 glasses. *Journal of the American Ceramic Society*, *78*(9), 2405-2411.

Kingery, W. D., Bowen, H. K., and Uhlmann., D. R. (1976). *Introduction to ceramics*. A Wiley –Interscience publication, John Wiley & Sons.

Kontonasaki, E., Zorba, T., Papadopoulou, L., Chatzistavrou, X., Paraskevopoulos, K., and Koidis, P. (2002). Hydroxy carbonate apatite formation on particulate bioglass in vitro as a function of time. *Crystal Research and Technology*, *37*, 1165–1171.

Kokubo, T. (1991). Bioactive glass-ceramics: Properties and applications. *Biomaterials*, *12*, 155–163.

Kokubo, T. (1999). A/W glass-ceramic: Processing and properties, In: Hench, L. L., and, Wilson, J., editors. *An introduction to bioceramics*. Second edition, London, World Scientific, 75–88.

Kokubo, T. (2008). *Bioceramics and their clinical applications*. USA: Woodhead publishing limited.

Kreidel, N. J. (1983). *Glass science and technology*, In: D. R. Uhlmann, editors. Volume 1, Academic Press, 193.

Kucynski, G. C., Hooten, N. A., and Gibson, C. F. (1967). *Sintering and related phenomena*, Gordon and Breach, New York.

Kwon, O. H. (1991). *Liquid Phase Sintering in Engineered Materials Handbook ASM International*. Materials Park, Ohio, 4, 285-303.

La Torre, G., and Hench, L. L. (1993). *Characterization methods for the solid-solution interface in ceramic system*, In: Adair, J. H., and Casey, J. A., editors. *American Ceramic Society*, Wester-ville, OH.

Lazarev, A. N., and Tenisheva, T. F. (1961). The vibrational spectra of silicates, III, Infrared spectra of the pyroxenoids and other chain metasilicates. *Optics Spectroscopy*, *10*, 37-40.

Lefebvre, L., Chevalier, J., Gremillard, L., Zenati, R., Thollet, G., Bernache-Assolant, D., and Govin, A. (2007). Structural transformations of bioactive glass 45S5 with thermal treatments. *Acta Materialia*, *55*, 3305–3313.

Li, H. C., Wang, D. G., Hu, J. H., and Chen, C. Z. (2013). Effect of various additives on microstructure, mechanical properties, and in vitro bioactivity of sodium oxide-calcium oxide-silica-phosphorus pentoxide glass–ceramics. *Journal of Colloid and Interface Science*, *405*, 296–304.

Lin, F. H., and Hon, M. H. (1988). A study on bioglass ceramics in the Na_2O-CaO-SiO_2-P_2O_5 system. *Journal of Materials Science*, *23*, 4295-4299.

Lin, C. C, Huang, L. C., and Shen, P. (2005). $Na_2CaSi_2O_6$–P_2O_5 based bioactive glasses. Part 1: Elasticity and structure. *Journal of Non-Crystalline Solids*, *351*, 3195–3203.

Linga Raju, C., Narasimhulu, K. V., Gopal, N. O., Rao, J. L., and Reddy, B. C. V. (2002). Electron paramagnetic resonance, optical and infrared spectral studies on the marine mussel Arca burnesi shells. *Journal of Molecular Structure*, *608* (2-3), 201–211.

Lockyer, M. W. G., Holland, D., and Dupree, R. (1995). NMR investigation of the structure of some bioactive and related glasses. *Journal of Non-Crystalline Solids*, *188*, 207-219.

Loy, C. W., Matori, K. A., Lim, W. F., Schmid, S., Norhazlin, Z., Wahab, Z. A., Zarifah, N. A., and Hafiz, M. Z. M. (2016). Effects of calcination on the crystallography and nonbiogenic aragonite formation of ark clam shell under ambient condition. *Advances in Materials Science and Engineering*, 1-8.

Marzouk, M. A., ElBatal, F. H., and Abdelghany, A. M. (2013). Ultraviolet and infrared absorption spectra of Cr_2O_3 doped-sodium metaphosphate, lead metaphosphate and zinc metaphosphate glasses and effects of gamma irradiation: a comparative study. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, *114*, 658–667.

Mc Millan, P. W., Phillips, S. V., and Partridge, G. (1966). The structure and properties of a lithium zinc silicate glass-ceramic. *Journal of Materials Science*, *1*, 269.

McMillan, P. W. (1979). *Glass-ceramics*. Second edition, Academic Press, London.

Mear, F., Yot, P., Viennois, R., and Ribes, M. (2007). Mechanical behaviour, thermal, and electrical properties of foam glass. *Ceramics International*, *33*, 543–550.

Mehdikhani, B., and Borhani, G. H. (2013). Crystallization behaviour and microstructure of bio glass-ceramic system. *International Letters of Chemistry*, *Physics and Astronomy*, *19*, 58-68.

Metwalli, E., Brow, R. K., and Stover, F. S. (2001). Cation effects on anion distributions in aluminophosphate glasses. *Journal of the American Ceramic Society*, *84*, 1025-1032.

Miguez-Pacheco, V., Hench, L. L., and Boccaccini, A. R. (2015). Bioactive glasses beyond bone and teeth: Emerging applications in contact with soft tissues. *Acta Biomaterialia*. *13*, 1–15.

Mohamed, M., Yusup, S., and Maitra, S. (2012). Decomposition study of calcium carbonate in cockle shell. *Journal of Engineering Science and Technology*, *7* (1), 1 – 10.

Mohamad, S. F. S., Mohamad, S., and Jemaat, Z. (2016). Study of calcination condition on decomposition of calcium carbonate in waste cockle shell to calcium oxide using thermal gravimetric analysis. *Journal of Engineering and Applied Sciences*, *11*(16), 9917-9921.

Montazerian, M., Singh, S. P., and Zanotto, E. D. (2015). An analysis of glass ceramic research and commercialization. *American Ceramic Society Bulletin*, *94*, 30–35.

Mundstock, K. B., de Moraes, E. G., Hotza, D., de Oliveira, A. P. N., Siligardi, C., and Rogero, S. O. (2010). Processing and characterization of sncp (SiO_2-Na_2O-CaO-P_2O_5) glass-ceramic foams. *Quim. Nova*, *33* (3), 598-602.

Mustaffa, R., Yusof, M. R. M., and Abdullah, Y. (2015). A novelty of synthetic hydroxyapatite from cockle shell and characterization. *Advanced Materials Research*, *1087*, 429-433.

Nakamoto, K. (1970). *Infrared and Raman Spectra of Inorganic and Coordination Compounds, Part A: Theory and Applications in Inorganic Chemistry*. Wesley, New York, USA, Sixth edition.

Nelson, D. J, Rains, T. C., and Norris, J. A. (1966). High-purity calcium carbonate in freshwater clam shell. *Science*, *82*, 10-12.

Nyquist, R. A., and Kagel, R. O. (1971). Infrared spectra of inorganic compounds. Academic Press, New York, NY, USA.

Oberzan, M., Holc, J., Buh, M., Kuscer, D., Lavrac, I., and Kosec, M. (2009). High-alumina porcelain with the addition of a Li_2O-bearing fluxing agent. *Journal of the European Ceramic Society*, *29*, 2143–2152.

O'Donnell, M. D. (2011). Predicting bioactive glass properties from the molecular chemical composition: Glass transition temperature. *Acta Biomaterialia*, *7*(22), 64-69.

Pathak, T. K., Buch, J. J. U., Trivedi, U. N., Joshi, H. H., and Modi, K. B. (2008). Infrared spectroscopy and elastic properties of nanocrystalline Mg–Mn Ferrites prepared by co-precipitation technique. *Journal of Nanoscience and Nanotechnol*ogy, *8*, 4181–4187.

Pereira, M. M., Clark, A. E., and Hench, L. L. (1994). Calcium phosphate formation on sol-gel-derived bioactive glasses in vitro. *Journal of Biomedical Materials Research*, *28*, 693–698.

Peitl, O. (1995). Tese de Doutorado, Universidade Federal de São Carlos, Brazil.

Peitl, O., LaTorre, G. P., and Hench L. L. (1996). Effect of crystallization on apatite layer formation of bioactive glass 45S5. *Journal of Biomedical Materials Research*, *30*, 509–514.

Peitl, O., Zanotto, E. D., and Hench, L. L. (2001). Highly bioactive P_2O_5-Na_2O-CaO-SiO_2 glass-ceramics. *Journal of Non-Crystalline Solids*, *292*, 115–26.

Peitl, O., Zanotto, E. D., Serbena, F. C., and Hench, L. L. (2012). Compositional and microstructural design of highly bioactive P_2O_5-Na_2O-CaO-SiO_2 glass-ceramics. *Acta Biomaterialia*, *8*, 321–332.

Philips, S. V., and Mcmillan, P. W. (1965). *Glass Technology*, *6*(2), 46.

Qu, G., Luo, Z., Liu, W., and Lu. A. (2013). The preparation and properties of zirconia-doped Y–Si–Al–O–N oxynitride glasses and glass-ceramics, *Ceramics International*, *39*, 8885-8892.

Rajendran, V., Nishara Beguma, A., Azooz, M. A., and El Batal, F. H. (2002). Microstructural dependence on relevant physical–mechanical properties on SiO_2-Na_2O-CaO-P_2O_5 biological glasses. *Biomaterials*, *23*(21), 4263-4275.

Rawlings, R. D., Wu, J. P., and Boccaccini, A. R. (2006). Glass-ceramics: Their production from wastes - A Review. *Journal of Materials Science*, *41*, 733–761.

Rezwan, K., Chen, Q. Z., Blaker, J. J., and Boccaccini, A.R. (2006). Biodegradable and bioactive porous polymer/inorganic composite scaffolds for bone tissue engineering. *Biomaterials*, *27*, 3413-3431.

Ruiz, M. G., Hern´andez, J., Ba˜nos, L., Montes, J. N., and Garcia, M. E. R. (2009). Characterization of calcium carbonate, calcium oxide, and calcium hydroxide as starting point to the improvement of lime for their use in construction. *Journal of Materials in Civil Engineering*, *21* (11), 694–698.

Salinas, A. J., and Vallet-Regi, M. (2013). Bioactive ceramics: From bone grafts to tissue engineering. *RSC Advances*, *3*, 11116–11131.

Scherer, G. W. (1997). Sintering of sol-gel films. *Journal of Sol–gel Science and Technology*, *8*, 353-363.

Seal, B. L, Otero, T. C, and Panitch, A. (2001). Polymeric biomaterials for tissue and organ regeneration. *Materials Science and Engineering: R: Reports*, *34*, 147–230.

Segnit, E. R. (1954). The system Na_2O-CaO-SiO_2. *Journal of the American Ceramic Society*. *37*(6), 273-277.

Shackelford, J. F., and Doremus, R. H. (2008). Ceramic and glass materials: structure, properties and processing, *Springer*.

Shelby, J. E. (2005). *Introduction to glass science and technology*. Second edition, The Royal Society of Chemistry, 265.

Sigaev, V. N., Lopatina, E. V., Sarkisov, P. D., Stefanovich, S. Y., and Molev, V. I. (1997). *Materials Science and Engineering B – Solid State Materials for Advanced Technology 48*(3), 254.

Siqueira, R. L., and Zanotto, E. D. (2011). Facile route to obtain a highly bioactive SiO_2-CaO-Na_2O-P_2O_5 crystalline powder. *Materials Science and Engineering C*, *31*, 1791–1799.

Smith, B. C. (1996). Fundamentals of Fourier transform infrared spectroscopy. *CRC Press*, Boca Raton, FL.

Sola, A., Bellucci, D., Raucci, M. G., Zeppetelli, S., Ambrosio, L., and Cannillo, V. (2011). Heat treatment of Na_2O-CaO-P_2O_5-SiO_2 bioactive glasses:

Densification processes and postsintering bioactivity. *Journal of biomedical materials research A*, *100a* (2), 305-322.

Stelling, J., Behrens, H., Wilke, M., Gottlicher, J., and Aljanabi, E. C. (2011). Interaction between sulphide and H_2O in silicate melts. *Geochimica et Cosmochimica. Acta*, *75*, 3542–3557.

Tarvornpanich, T., Souza, G. P., and Lee, W. E. (2005). Microstructural evolution on firing soda–lime–silica glass fluxed whitewares. *Journal of the American Ceramic Society*, *88*, 1302–1308.

Tavangarian, F., and Emadi, R. (2011). Preparation of bioactive nanostructure scaffold with improved compressive strength. Ceramics – Silikaty, 55(1), 49-53.

Theodorou, G., Goudouri, O., Kontonasaki, E., Chatzistavrou, X., Papadopoulou, L., Kantiranis, N., and Paraskevopoulos, K. (2009). Comparative bioactivity study of 45S56 and 58S bioglasses in organic and inorganic environment, *Bioceramics*, In: Kim Sukyoung, editor. *22*, 391–394.

Thompson, I. D., and Hench, L. L. (1998). Mechanical properties of bioactive glasses, glass-ceramics and composites. *Proceedings of the Institution of Mechanical Engineers, Part H*, *212*(2), 127-36.

Toya, T., Tamura, Y., Kameshima, Y., and Okada, K. (2004). Preparation and properties of CaO-MgO-Al_2O_3-SiO_2 glass–ceramics from Kaolin Clay Refining Waste (Kira) and Dolomite. *Ceramics International*, *30*(6), 983-989.

Urist, M. R., and Johnson, R. W. (1941). Calcification and ossification. IV. The healing of fractures in man under clinical conditions. *Journal of Bone and Joint Surgery*. *25*, 375-426.

Vogel, W., and Roland, W. (1987). The development of bioglass-ceramics for medical applications. *Angewandte Chemie International Edition in English*, 26, 527-544.

Wallace, K. E., Hill, R. G., Pembroke, J. T., Brown, C. J., and Hatton, P. V. (1999). Influence of sodium oxide content on bioactive glass properties. *Journal of Materials Science: Materials in Medicine*, *12*, 697-701.

Wang, Y., Moo, Y. X., Chen, C., Gunawan, P., and Xu, R. (2010). Fast precipitation of uniform $CaCO_3$ nanospheres and their transformation to hollow hydroxyapatite nanospheres. *Journal of Colloid and Interface Science*, *352*(2), 393–400.

Wachtman, J. B., Cannon, W. R., and Matthewson, M. J. (2009). Mechanical *properties of ceramic. John Wiley & Sons, Technology & Engineering.*

Wells, A. (1950). *Structural Inorganic Chemistry*. Second edition, Oxford University Press (Clarendon), London and New York, 485.

Wu, S., Lv, X., Zhang, M., Chen, Y. J., and, Zhao, R. N. (2010). Effect of B_2O_3 and P_2O_5 on Fluorosilicic mica glass-ceramic sintering process. *Science of Sintering*, *42*, 329-335.

Yeni, Y. N, and Fyhrie, D. P. (2001). Finite element calculated uniaxial apparent stiffness is a consistent predictor of uniaxial apparent strength in human vertebral cancellous bone tested with different boundary conditions. *Journal of Biomechanical*, *34*, 1649–54.

Yoon, S. D., Lee, J. U., Lee, J. H., Yun, Y. H., and Yoon, W. J. (2013). Characterization of wollastonite glass-ceramics made from waste glass and coal fly ash. *Journal of Materials Science and Technology*, *29* (2), 149-153.

Zanotto, E. D. (2010). A bright future for glass–ceramics. *American Ceramic Society Bulletin*, *89*, 19–27.

Zarifah, N. A., Lim, W. F., Matori, K. A., Sidek, H. A. A., Wahab, Z. A., Zainuddin, N., Salleh, M. A., Fadilah, B. N., and, Fauzana, A. N. (2015). An elucidating study on physical and structural properties of 45S5 glass at different sintering temperatures. *Journal of Non-Crystalline Solids*, *412*, 24–29.

Zarifah, N. A., Matori, K. A., Sidek, H. A. A., Wahab, Z. A., Mohd Salleh, M. A., Zainuddin, N., Khiri, M. Z. A., Farhana, N. S., and Omar, N. A. S. (2016). Effect of hydroxyapatite reinforced with 45S5 glass on physical, structural and mechanical properties. *Procedia Chemistry*, 19, 30 – 37.

Zarzycki, J., and Naudin, F. (1960). *Verres Refractive*, *14*, 113-23.

Zioupos, P., and Currey, J. D. (1998). Changes in the stiffness, strength, and toughness of human cortical bone with age. *Bone*, 22, 57–66.