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THEME

**Synthesis and Characterization of Forsterite (Mg_2SiO_4) Ceramics from
Magnesium Oxide (MgO) and Silicon Dioxide (SiO_2) Nanopowder**

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Dedication



بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

In the name of Allah, the Most Gracious, the Most Merciful

This work is dedicated to:

First, to my family, whose belief in me has been a constant source of strength. I am forever grateful to my parents for their endless sacrifices and for teaching me the value of hard work and perseverance. Your love and support have been my foundation, and without you, this accomplishment would not have been possible.

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To all those who believe in the power of education and the pursuit of knowledge, this thesis is a tribute to the collective effort of everyone who has supported me along the way.

Finally, to Myself.

-Laziri Khadidja-



Gratitude



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Contents

Contents

General Introduction	1
Chapter One: Bibliographic Overview	3
I. Overview of ceramics.....	4
I.1. Ceramics history and definition.....	4
I.2. Types of ceramics	4
I.3. Ceramic properties.....	7
II. Overview of refractories	9
II.1. Definition of refractories	9
II.2. Classification of refractories	9
II.3. Properties of refractories	10
II.4. Applications of refractories	11
III. Overview on biomaterials.....	11
III.1. The development of Biomaterials	11
III.2. Definition of Biomaterials.....	12
III.4. Properties of Biomaterials.....	13
IV. Overview of bioceramics.....	15
IV.1. History of Bioceramics	15
IV.2. Definition	15
IV.3. Classification and applications of bioceramics.....	16
V. Overview of forsterite	19
V.1. History and definition of forsterite.....	19
V.2. Forsterite properties	20
V.3. Forsterite applications	21
V.4. Forsterite preparation methods.....	23
V.5. Effect of some additives on forsterite	28
V.6. Forsterite and Traditional Bioceramics	29
VI. Overview of kinetic analysis	30

VI.1. Thermal analysis techniques	30
VI.2. Calculation of crystallization kinetics and mechanism.....	30
VI.3. Thermodynamic parameters of crystallization	36
References	37
Chapter Two: Materials & Method.....	46
I.1. Forsterite-Silica composites (FS _x) raw materials and methods.....	47
I.1.1. Raw materials	47
I.1.2. Magnesium oxide (MgO)	48
I.1.3. Silicon dioxide (SiO ₂).....	48
I.1.4. Forsterite (Mg ₂ SiO ₄)	48
I.1.5. Powders preparation	49
I.1.6. Preparing sintered samples	50
II.2. Hydroxyapatite-Forsterite composites (HAF _x) raw materials and methods	51
II.2.1. Raw materials	51
II.2.2. Hydroxyapatite (HA).....	51
II.2.3. Powders preparation	52
II.2.4. Preparing sintered samples	53
III.3. Characterization techniques and equipment	53
III.3.1. Thermal Analysis and Calorimetry (TGA/DSC/DTA)	53
III.3.2. Dilatometry (DL)	55
III.3.3. X-ray Diffraction (XRD).....	57
III.3.4. Scanning Electron Microscopy (SEM)	59
III.3.5. Energy Dispersive Spectroscopy (EDS)	60
III.3.6. Fourier Transformation Infrared Spectroscopy (FT-IR)	61
III.3.7. Measurement of density	63
III.3.8. Vickers Micro-hardness (HV) test	64
III.3.9. Antibacterial activity analyses	65
Reference.....	70
Chapter Three: Results & Discussion	72
Part One: An analytical study of the raw materials used	73
I.1. Physicochemical and morphological analyses of the initial materials	74

I.1.1. Magnesium oxide (MgO)	74
I.1.2. Silicone dioxide (SiO ₂).....	76
I.1.3. Natural Hydroxyapatite (N-HA).....	78
I.1.4. Forsterite	80
Part Two: Forsterite composites with excess SiO₂: A comprehensive study of thermal, mechanical, microstructural and biological properties	83
II.1. Thermogravimetry (TG/DTG), Differential thermal analysis (DTA) and X-ray diffraction (XRD) analyses of FS ₀ powder	84
II.2. Dilatometry (DL) and X-ray diffraction analyses of FS _x powder.....	86
II.3. Analysis of shaped and sintered forsterite-silica composites (FS _x) samples.....	88
II.3.1. X-ray analysis of forsterite-silica composites (FS _x) samples after sintering.....	88
II.3.2. Measurement of bulk density and open porosity of FS _x samples.....	90
II.3.3. Micro-hardness measurement of FS _x samples.....	92
II.3.4. Coefficient of thermal expansion (CTE) measurement of FS _x samples.....	92
II.3.5. Morphological analyses of FS _x samples.....	95
II.4. Antibacterial activity of FS _x composition.....	100
Part Three: Kinetics of enstatite and forsterite phase crystallization	85
III.1. Kinetic analyses	106
III.1.1. Activation energy determination of enstatite and forsterite crystallization	106
III.1.2. Reaction model determination of forsterite and enstatite crystallization.....	117
III.1.3. Kinetic parameters determination of enstatite and forsterite crystallization.....	121
III.1.4. Simulation and experimental data.....	124
III.2. Thermodynamic properties of forsterite and enstatite crystallization	126
Part Four: Hydroxyapatite-forsterite composites: A study of thermal, mechanical, microstructural and biological properties	107
IV.1. Thermogravimetry (TG/DTG), Differential thermal analysis (DTA) and X-ray diffraction (XRD) analyses of bovine bone powder.....	129
IV.2. Analysis of shaped and sintered Hydroxyapatite-forsterite composites (HAF _x)samples	132
IV.2.1. X-ray analysis of Hydroxyapatite-forsterite composites (HAF _x) samples after sintering.....	132
IV.2.2. Measurement of density and open porosity of Hydroxyapatite-forsterite composites (HAF _x) sintered samples	134

IV.2.3. Micro-hardness measurement of HAF _x sintered samples.....	136
IV.2.4. Morphological analyses of HAF _x samples.....	136
IV.3. Antibacterial activity of HAF _x composition.....	141
Reference	144
Conclusion	153
Future Work	154

General Introduction

General Introduction

Forsterite (Mg_2SiO_4) is a magnesium silicate mineral with a wide range of applications in fields such as biomaterials, refractories, and ceramics. Its unique combination of thermal stability, mechanical strength, and biocompatibility makes it an attractive material for advanced technological and biomedical uses. However, synthesizing forsterite in a pure phase remains challenging due to several inherent factors. The primary difficulties include the slow reaction of the initial oxides and the tendency to form secondary phases, such as enstatite (MgSiO_3) and periclase (MgO), instead of forsterite. These challenges are often attributed to limited diffusion at the temperatures typically employed during forsterite synthesis, inhibiting the precursor materials' complete reaction.

Numerous methods have been explored to address these challenges, including sol-gel techniques, co-precipitation, and hydrothermal synthesis. While these approaches have achieved varying levels of success, each comes with limitations, such as high processing costs and complex procedures. Despite the extensive research on alternative synthesis methods, the solid-state reaction of MgO and SiO_2 , particularly using nanopowders, remains not fully explored. Nanopowders offer increased surface area and enhanced reactivity, which could potentially overcome the diffusion limitations that hinder the formation of pure forsterite. However, to the author's knowledge, no comprehensive studies have been conducted to evaluate the feasibility of synthesizing forsterite through this approach and investigate the associated formation kinetics, microstructure, and material properties.

The primary goal of this thesis is to synthesize and characterize a pure phase of forsterite using the solid-state reaction of MgO and SiO_2 nanopowders. This study seeks to examine the thermal, mechanical, kinetic, and biological properties of the synthesized material in detail. By focusing on the effect of SiO_2 content on phase crystallization and mechanical properties, this research aims to shed light on the critical parameters influencing forsterite synthesis. Additionally, the biological aspect of this study investigates the potential of forsterite as an additive to enhance the mechanical, biological, and microstructural properties of synthesized natural hydroxyapatite. Hydroxyapatite (HA) is a well-established biomaterial used in orthopedic and dental applications, and the incorporation of forsterite may provide synergistic benefits, such as improved bioactivity and mechanical performance.

The motivation behind this research lies not only in addressing the technical challenges associated with forsterite synthesis but also in exploring its potential applications as a functional material. For example, the biocompatibility and bioactivity of forsterite make it a promising candidate for bone tissue engineering and implant coatings. Understanding the interplay between its microstructure and properties could pave the way for innovations in biomaterials science. Furthermore, the development of a reliable and cost-effective synthesis method could expand the industrial applicability of forsterite in areas such as high-temperature ceramics and refractories.

This study advances our understanding of the synthesis and characteristics of forsterite, contributing valuable insights into its potential applications in fields such as biomaterials and advanced ceramics. Therefore, our dissertation was outlined in three chapters.

Outline of Dissertation

This study contains three (3) chapters, the structure of which is organized as follows.

Chapter 1 is divided into six sections, including overviews of Ceramics, Refractories, Biomaterials, Bioceramics, and Forsterite, respectively, and an introduction to solid-state thermal analysis kinetics, the development of a general kinetic equation, also activation energy and kinetic models.

Chapter 2 has three sections: the first covers the main raw materials and the experimental method used in preparing Forsterite-silica composites (FS_x), the second covers the raw materials and experimental method used in preparing Hydroxyapatite-Forsterite composites (HAF_x), and the third covers Characterization techniques and equipment.

Chapter 3 is the main focus of this study and consists of four parts. The first part is an analyses of raw materials. The second part studies the preparation of monolithic forsterite and the effect of the SiO_2 excess on the thermal, mechanical, morphological, and biological properties of forsterite. The third part focuses on kinetic analyses of the crystallized forsterite and enstatite phases, including determining the activation energy, kinetic model, kinetic parameters, and thermodynamic parameters. The fourth part study the preparation of natural hydroxyapatite and the effect of forsterite on the thermal, mechanical, morphological, and biological properties. Finally, the conclusion of this study contains a summary of the most important experimental results.

Chapter One: Bibliographic Overview

This chapter focuses on a bibliographic overview of the physicochemical properties, including the structure, preparation methods, and applications of ceramics, refractories, biomaterials, bioceramics, and forsterite. Also the kinetic theory.

I. Overview of ceramics

I.1. Ceramics history and definition

Three classes of materials are distinguished by their chemical bounding, which is what engineering technology and, nowadays, materials science focus on: metal, polymers, and ceramics. Ceramics is the oldest made material. Figure I.1 presents the lifetime of materials. The earlier ceramic technology discovered was some Japanese vessels that dated back to Jomon culture. Yet, in 2009 in China, new remnants of ceramic technology were discovered and dated to 15430 cal B.P. Such report can only suggest an approximate time since humans started producing such material, Karmas in Greek refers to ceramic as “the burned stuff”, a material at high temperature gain its properties, typically defined as non-metallic, inorganic and predominantly polycrystalline materials and contains at minimum 30 % crystalline compounds, normally ceramics grains are in the range of 1 to 50 μm and visible under a microscope, ceramic obtain wide range of thermal, optical, mechanical, electronic and biological properties. Ceramics are inorganic compounds consisting of silicates, simple and complex oxides, nitrides, and, in some cases, monoxides. From a physics of materials perspective, the atomic structure and bonding nature in ceramics give rise to their brittleness and high melting points. Their unique phonon transport behavior also contributes to their exceptional thermal insulation properties [1-4].

I.2. Types of ceramics

Ceramics were distinguished into two types: traditional and advanced, which were also classified as the first (traditional) and second (advanced) ceramics age in the scientific society.

I.2.1. Traditional ceramics

Clay, micas, feldspars, and quartz are considered the most used siliceous minerals. In some cases, non-silicate minerals such as magnesite or simple oxides are used as natural raw materials to prepare traditional ceramics. Common types of ceramics can be seen as general pottery, Chinese pottery, porcelain products, sanitary ware, bricks, and tiles [2].

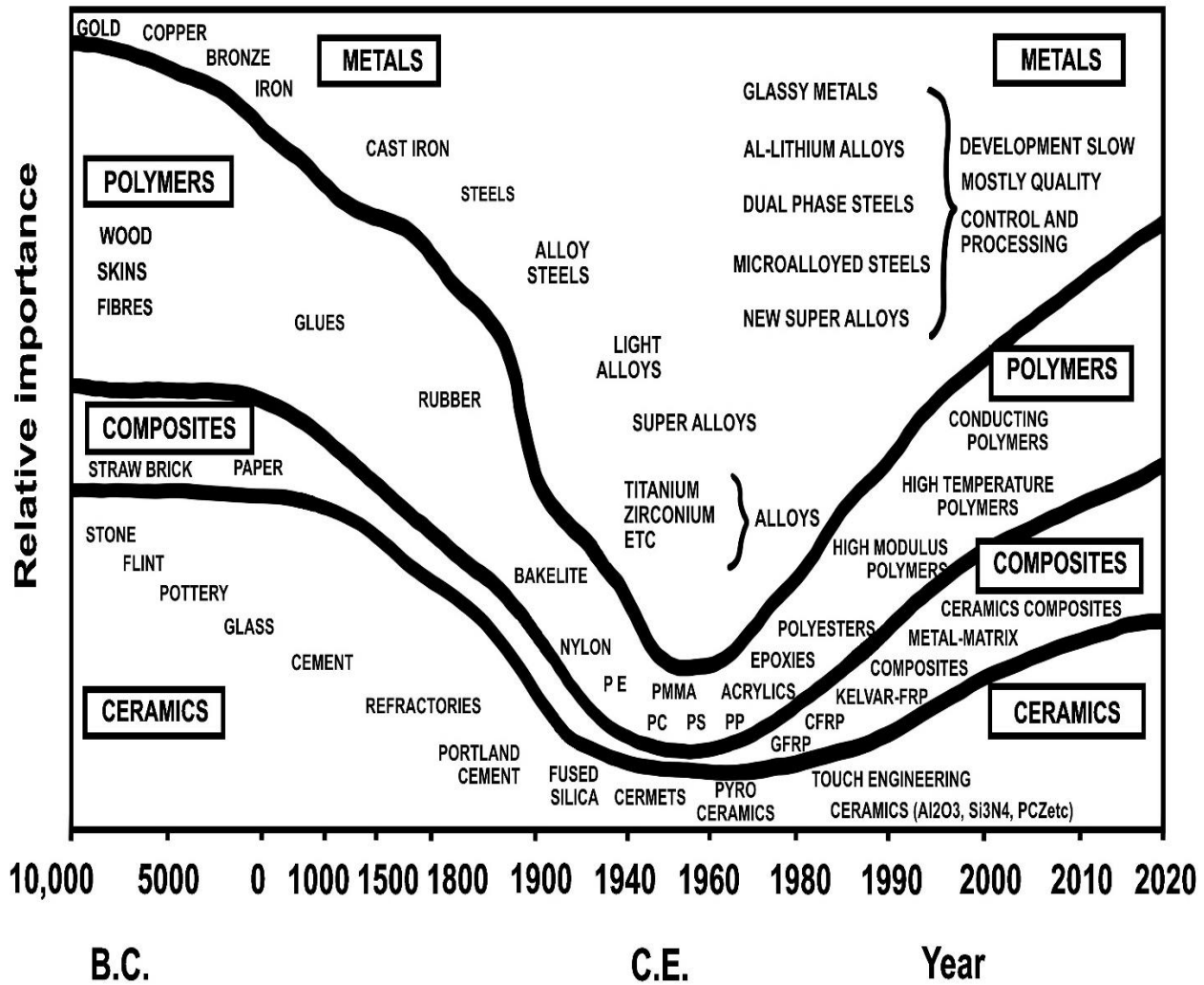


Figure I.1: Timeline of materials development [2].

I.2.2. Advanced ceramics

The desperate need for a ceramic that surpasses the properties of traditional ceramics shifted the interest to develop an advanced ceramic (functional and structural ceramics) to suit various fields of applications (electrical, optical, medical and thermal) as shown in Figures I.2, I.3. Chemically synthesized magnesia, alumina, silicate in their pure nano or microscale form and other simple and complex oxides are commonly used to prepare such advanced ceramics, as carbides, and nitrides of silicon [2, 3]. Usually, in ceramics development for specific applications, a combination of properties is favorable over others. Ceramics is competing with polymers and metals in various industrial fields, as Table I.1 presents the applications for advanced ceramics nowadays.

Table I.1 Advanced ceramic application by function [3, 5].

Function	Ceramic	Applications
Chemical	ZnO, Fe ₂ O ₃ , SnO ₂	Gas sensor, gas leakage.
	MgCr ₂ O ₄ -TiO ₂	Cooking control element in a microwave oven.
Thermal	ZrO ₂ , TiO ₂	Infrared radiator.
Mechanical	Al ₂ O ₃ , TiC	Cutting tools, sintered CBN.
	Al ₂ O ₃ , ZrO ₂	Wear-resistant applications (mechanical seal, pressure sensors).
	SiC, Al ₂ O ₃ , Si ₃ N ₄	Heat-resistant applications (ceramic engine, turbine blade).
Biological	Alumina	Medical applications (Artificial tooth, bone, and joint).
	Hydroxyapatite, bioglass	
Optical	UO ₂ , UO ₂ -PuO ₂	Nuclear fuels.
	SiC, B ₄ C	Cladding materials.
	SiC, Al ₂ O ₃ , B ₄ C	Shielding materials.
Electric	BaTiO ₃ , SiC, V ₂ O ₅	Semiconductors
	PZT	Piezoelectric (vibrator, oscillator, transducer)
	Al ₂ O ₃ , BeC, MgO	Insulators (package, wiring substrate)

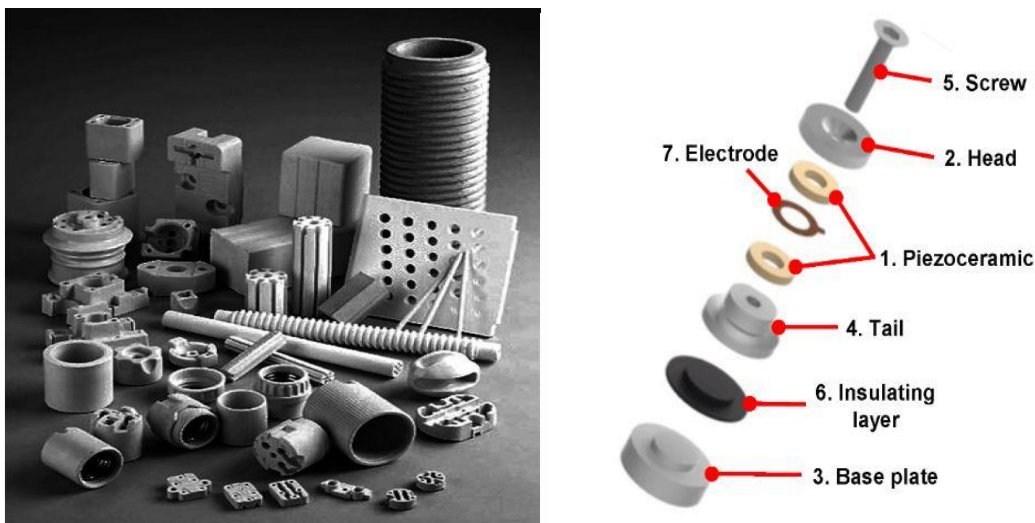


Figure I.2 Ceramic piezoelectric parts, assemblies, and accelerometer [5, 6].

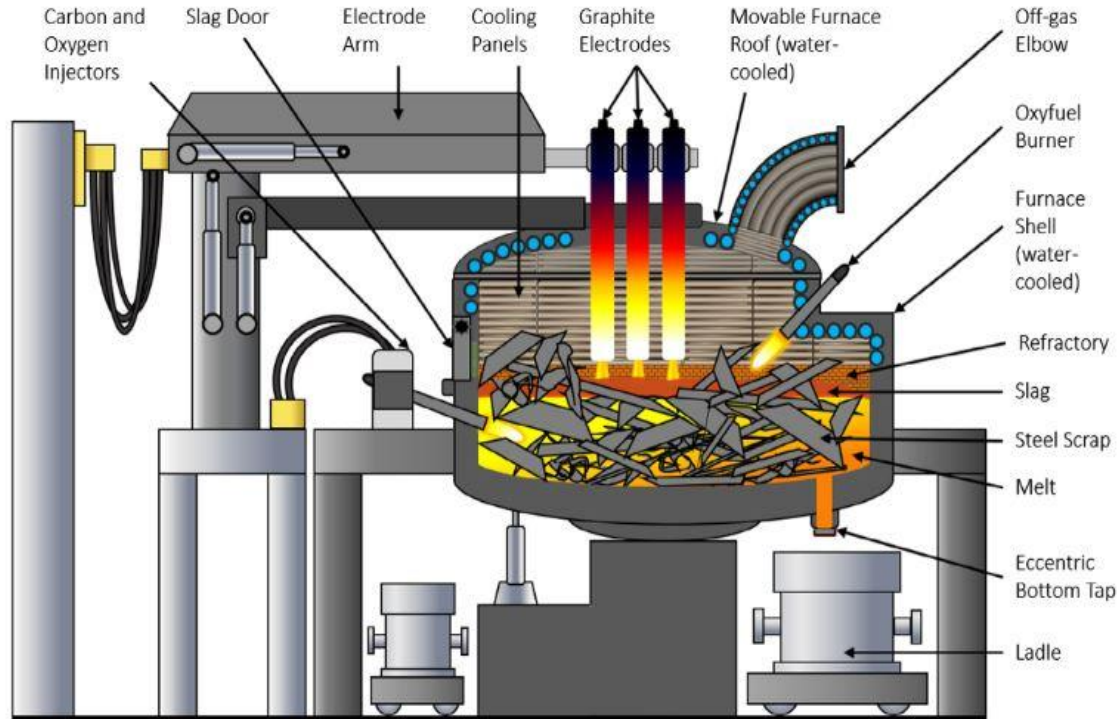


Figure I.3 Electric arc furnace [7].

I.3. Ceramic properties

Ceramic materials are distinguished from other classes of materials by their physical and chemical properties, some of which are shown in Table I.2. The nature and directionality of the interatomic bonds holding the solid determine the atoms' arrangement and properties.

I.3.1. Structural and bonding

The crystalline structure is linked to the type of primary bonding between atoms in the materials, which generally determines the mechanical, optical, electric, and other properties. At the atomic level, the predominant bond in ceramics materials are ionic, covalent bonds, which is considered stronger than metals. The predominant ionic bonds crystalline structure of ceramic is compact with the highest density possible, where each ion is surrounded by the largest number of opposite charge ions possible. As for the covalent being the dominant bond in a ceramic, the arrangement and position of atoms in the crystalline structure are determined by the free bond number, and in nearly most cases, the structure is similar to the diamond structure. The binding energy depends on each compound, like Si-Si, C-Si, C-C, and Si-O are 2.3, 3.38 and 3.6 eV, respectively [8, 9].

I.3.2. Thermal and electrical properties

The stable and strong bonding (ionic and covalent) of ceramics makes such material obtain a high melting point, which is usually above 2000 °C, low expansion coefficient, low thermal conductivity and low electric conductivity and high dielectric constant (dielectric permittivity) compared to other classes of materials. It is worth mentioning that some ceramics can take the behavior of conductor, semiconductor, and superconductor in certain conditions. For instance, perovskite-type ceramics exhibit high dielectric responses, while YBCO ceramics display superconductivity below critical temperatures [5, 9].

I.3.3. Mechanical properties

A small range of elasticity characterizes ceramic materials compared to metals, this is due to the atoms bonds nature and its compact crystalline structure disabling crystal planes movement [10]. Table I.2 presents some ceramics properties.

Table I.2 Properties of some ceramics [6, 9, 11-14].

Ceramics	Thermal expansion coefficient ($10^{-6} \text{ }^{\circ}\text{C}^{-1}$)	Thermal conductivity ($\text{Wm}^{-1}\cdot\text{C}^{-1}$)	Melting point ($^{\circ}\text{C}$)	Density ($\text{g}\cdot\text{cm}^{-3}$)	Hardness (GPa)	Young's modulus (GPa)
Al_2O_3	7.2- 8.6	27	2054	3.9	18- 20	300- 330
ZrO_2 (cub)	8- 10	1.7- 2.2	2677	5.83	10- 15	100- 200
SiC	4.5- 4.8	60- 150	2837	3.20	18- 25	410- 450
TiC	7.4- 7.7	33- 35	3070	4.95	25- 30	450- 470
Diamond	0.8- 1.5	1000- 2000	3550	3.52	80- 100	910- 1050
B_4C	4.2- 4.5	40- 45	2470	2.52	25- 45	420- 450
TiB_2	6.5- 8.5	65- 120	2897	4.50	22- 30	550- 470
Si_3N_4	3.2- 3.5	32- 35	1890	3.20	15	280- 310
SiO_2	0.55	1.4	1713	2.648	~ 5.5	75
MgO	9- 12	45- 60	2852	3.56	5- 7	~ 300
Forsterite	10	2.8- 4.5	1890	3.27	7.5	12.1- 29.3
Enstatite	8	4.5- 5	1557	3,2	5- 5.5	/

II. Overview of refractories

II.1. Definition of refractories

Refractory materials are a specialized class of inorganic, non-metallic ceramics designed to withstand extremely high temperatures, typically above 2000°C, without losing their shape, strength, or chemical identity in contact with corrosive solid, liquid, and gas, such as oxides, silicon, nitrides, and alkaline earth metals. These materials are crucial for applications in furnaces, kilns, incinerators, reactors, and other industrial equipment that operate under extreme thermal conditions. Characterized by their high melting points, resistance to thermal shock, chemical inertness, and mechanical strength under compression, refractory materials retain their physical structure and properties even in corrosive environments, protecting the underlying structures from heat and chemical damage. Various elements melting points are shared in Table I.2 [5, 15].

II.2. Classification of refractories

Refractories are classified into three main categories: acidic, basic, and neutral, based on their behavior when interacting with slags. This classification depends on how refractories react with slags of varying chemical compositions. However, there is no strict standard for classifying refractories, and they can be categorized in several ways. These methods of classification include the basicity of oxides and their physical form.

II.2.1. Classification by basicity

II.2.1.1. Basic refractories

These refractories are designed for use in environments where basic (alkaline) conditions exist (steelmaking furnaces). They resist basic slags but are easily attacked by acidic slags. Basic refractories are essential for industries like steel production, such refractories contain materials like magnesia (MgO) and dolomite.

II.2.1.2. Acidic refractories

These refractories are ideal for environments where acidic conditions prevail, such as in glass-making furnaces. Acidic refractories resist attack by acidic slags but are vulnerable to basic slags. They have high melting points and are primarily used in processes that involve acidic materials or

by-products. Acidic refractories include silica refractories (SiO_2), zirconia refractories, sillimanite, and fireclay.

II.2.1.3. Neutral refractories

These refractories do not react chemically with either acidic or basic slags; therefore, they are chemically stable, making them versatile for various environments and industrial applications. Carbon, chromite (FeCr_2O_4), and forsterite (Mg_2SiO_4) are examples of neutral refractories.

II.2.2. Classification by physical form

The refractories are also classified according to their physical form: shaped and unshaped.

II.2.2.1. Shaped refractories

These include standard and non-standard brick and block shapes used for furnace linings. The bricks are typically rectangular but may be customized for specific industrial needs.

II.2.2.2. Unshaped refractories

known as monolithic refractories, which include castables, ramming mixes, and plastic refractories that can be molded or applied in situ to repair or form refractory linings without pre-shaping; such refractories are usually supplied as powder [5, 15, 16].

II.3. Properties of refractories

Refractories are distinguished from other materials by a set of properties summarized as follows [17, 18]:

- Resistance to deformation and ability to maintain physical form at high temperatures.
- High melting point.
- Physical and chemical stability at elevated temperatures.
- Excellent corrosion resistance.
- Chemical inertness at high temperatures towards metal slag, pollutants, and gases.
- Low coefficient of thermal expansion at high temperatures.
- Good resistance to thermal shock.

II.4. Applications of refractories

The previously mentioned physical and chemical properties make refractories suitable for a variety of industrial applications [19], including:

- Use as firebricks and lining materials in high-temperature furnaces.
- Manufacturing molds for melting metals and glass, as well as for the cement industry, where refractories contribute more than 70 % of the materials used in the fabrication of iron and steel.
- Serving as filters for purifying metals from slag.
- Acting as pipes for transporting molten metals and as tanks for storage.
- Applications in rocket nozzles, thermal collectors, and as tiling materials and lenses in space shuttles and satellites.

Figure I.4 shows a few applications of shaped and unshaped refractories.



Figure I.4 (a) shaped and (b) unshaped refractory materials [19].

III. Overview on biomaterials

III.1. The development of Biomaterials

The development of biomaterials has been ongoing for over a century and can be categorized into four distinct generations based on their evolution and interaction with biological systems:

III.1.1. First Generation

Early biomaterials used common materials like polyethylene and steel. These materials were not developed with biological interaction in mind, and the body had to adapt to the materials. This approach often failed due to a lack of biocompatibility.

III.1.2. Second Generation

With technological advancements, materials such as titanium and its alloys were synthesized for specific biological applications. These materials are still in use today, particularly for implants. However, they were inert but did not necessarily foster interaction with biological tissues.

III.1.3. Third Generation

This generation focused on bioactive materials that could interact positively with the body, promoting integration with biological tissues. These include materials like bioactive glasses and calcium phosphates, which can bond with bone and other tissues.

III.1.4. Fourth Generation

The current generation of biomaterials involves "smart" biomaterials, which can respond dynamically to environmental changes within the body. These include biodegradable, stimuli-responsive materials that can release therapeutic agents over time [4, 20, 21].

III.2. Definition of Biomaterials

Biomaterials are any natural or synthetic materials unique in their ability to function in biological environments without causing or sustaining damage, unlike other materials, primarily in medical devices, for therapeutic purposes. These interactions can range from treating, augmenting, repairing, or replacing damaged tissues and organs. In modern applications, biomaterials are also used in diagnostics, drug delivery systems, and tissue engineering [4, 21].

III.3. Classification of Biomaterials

Biomaterials are classified into the following categories based on their composition and application.

III.3.1. Metals

Used in orthopedic implants, dental implants, and cardiovascular devices. Common metals include titanium, stainless steel, and cobalt-chromium alloys.

III.3.2. Ceramics

These include bioactive and bioinert ceramics, such as alumina, zirconia, and calcium phosphates, which are widely used in bone implants due to their hardness and biocompatibility.

III.3.3. Polymers

Thermosetting polymers are utilized in medical applications requiring high structural integrity, while thermoplastics, known for their flexibility, are commonly used in soft tissue applications. Elastomers are also recognized for their flexibility and are employed in areas like catheters and soft tissue engineering. Hydrogels, valued for their water-retention properties, are applied in drug delivery systems and wound care. Biodegradable polymers are designed to degrade within the body over time, making them ideal for temporary implants.

III.3.4. Composites

A combination of two or more materials to achieve better mechanical and biological properties. Common examples include fiber-reinforced polymers and bioceramics.

III.3.5. Natural Biomaterials

These are often derived from biological sources, such as collagen, chitosan, and silk, and are often used in tissue engineering [21].

III.4. Properties of Biomaterials

III.4.1. Chemical Properties

Focus on bonding present within the material. There are three types of bonds that influence the biomaterial properties: ionic bonds, which are common in ceramics and result in their high melting point and good electrical insulation; covalent bonds in polymers, which lead to flexibility

and wear resistance and low mechanical strength compared to metals; and metallic bonds in metals, which provide excellent electrical conductivity.

III.4.2. Physical Properties

Physical properties are primarily associated with the microstructure and surface characteristics of materials. Crystalline structure significantly affects mechanical strength, especially in metals and ceramics. Surface energy determines the interactions of the material with biological fluids, influencing properties such as adhesion and protein adsorption. Porosity is a crucial parameter in ceramics and composite materials, particularly in tissue engineering scaffolds, where it enhances cellular infiltration and nutrient transport.

III.4.3. Mechanical Properties

Mechanical properties are essential in applications such as load-bearing implants, including hip and knee replacements, where attributes like strength, elastic modulus, toughness, ductility, and hardness are critical. These properties ensure that the material can withstand mechanical loads while maintaining structural integrity and resilience, making them highly relevant to medical implant performance.

III.4.4. Biological Properties

A biomaterial's most important biological property is its biocompatibility, defined as a biomaterial's ability to perform its intended function without eliciting any adverse reactions in the host. It is crucial that the biomaterial does not induce any negative immune response, toxicity, or chronic inflammation. Other primarily biological properties include:

III.4.4.1. Bioactivity

A material's ability to bond with surrounding tissues (hydroxyapatite used in bone grafts).

III.4.4.2. Biodegradability

Some materials are designed to degrade over time and be replaced by natural tissue, such as in the case of bioresorbable polymers used in temporary implants [4, 21].

IV. Overview of bioceramics

IV.1. History of Bioceramics

IV.1.1. Alumina

Alumina was first synthetically produced in the 1700s and has since become widely used in dental and orthopaedic applications due to its biocompatibility and wear resistance. It gained popularity in the 1970s when it was used to manufacture femoral heads for hip implants [22].

IV.1.2. Bioglass

Bioglass, developed by Professor Larry Hench in 1969, was one of the first bioactive glasses to bond with hard and soft tissue. It was initially applied to ossicles in the middle ear to restore hearing [23].

IV.1.3. Hydroxyapatite and Tricalcium Phosphate

These calcium phosphate ceramics mimic natural bone minerals and were developed for bone tissue engineering. Hydroxyapatite is known for its exceptional biocompatibility, osteoconductivity, and ability to integrate with bone tissue, making it ideal for promoting bone growth and healing. HAp can be synthesized through various methods, including precipitation, sol-gel, hydrothermal techniques, biomimetic deposition, and electrodeposition. Each method allows control over particle size, shape, and crystallinity, which is crucial for tailoring HAp's properties for specific applications. Its porous structure also makes HAp useful for drug delivery systems, offering sustained release of therapeutic agents for conditions like osteoporosis, osteomyelitis, and cancer. The material's ion substitution capability further enhances its functionality, enabling it to be customized for improved mechanical strength and biological activity. Overall, HAp's versatile properties continue to drive advancements in its use for bone regeneration, implants, and targeted drug delivery systems [24, 25]. While TCP is a biodegradable ceramic used for bone repair [26].

IV.2. Definition

The term “bioceramics” first appeared in papers in 1971[27]. Bioceramics are ceramic materials that are used to replace or repair musculoskeletal systems. They are characterized by their high

hardness, brittleness, and resistance to wear and temperature. Despite these advantages, bioceramics often face challenges related to fabrication and reshaping due to their low tensile strength and fracture toughness [20, 26].

IV.3. Classification and applications of bioceramics

Bioceramics can be classified into three main categories (bioinert, bioactive, and biodegradable):

IV.3.1. Bioinert Ceramics

These materials remain stable in the body without reacting with the surrounding tissues, including alumina and zirconia. Applications include load-bearing implants like hip joints and dental crowns, as shown in Figures I.5 and I.6.

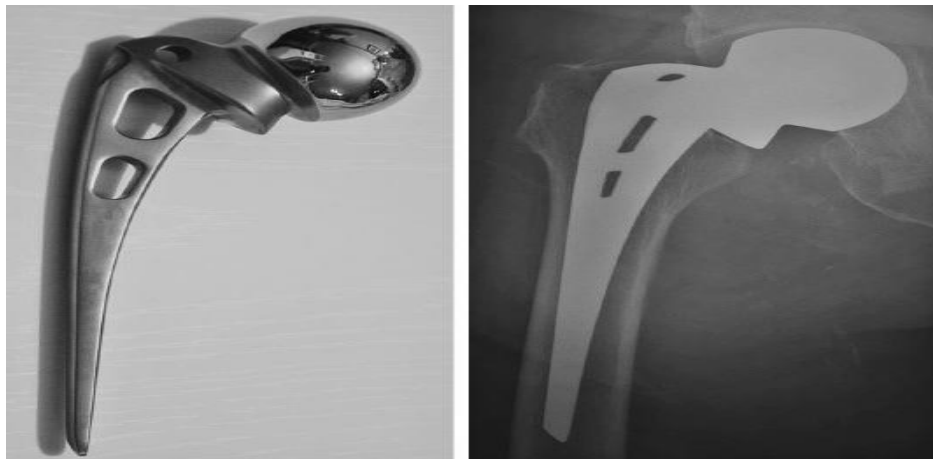


Figure I.5 Load-bearing implants (hip joint) [21, 28].

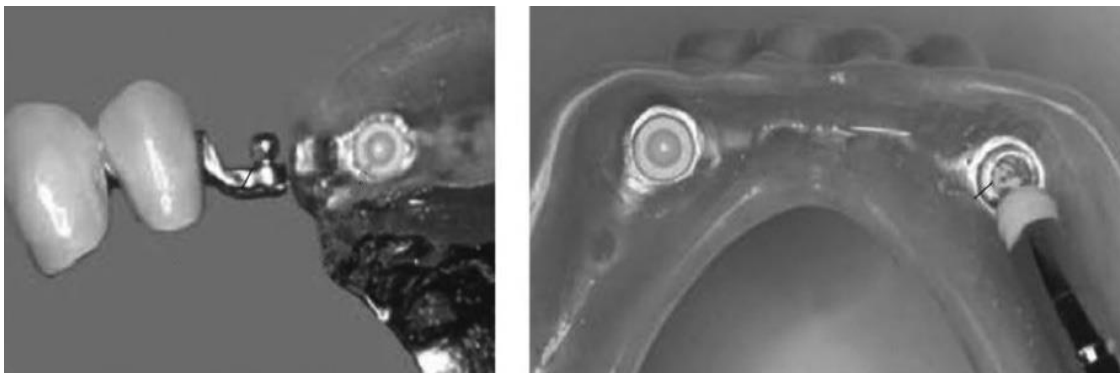


Figure I.6 Composites in dentistry (dental crown) [21, 29].

IV.3.2. Bioactive Ceramics

These materials actively interact with the body by forming direct bonds with tissue, like hydroxyapatite and bioglass. Hydroxyapatite is often used in bone implants, while bioglass is employed in soft tissue regeneration, as shown in Figure I.7. Ceramics bioactivity is primarily attributed to the formation of a biologically active hydroxycarbonate apatite layer on their surface, which facilitates cellular attachment and tissue integration. Moreover, the ionic dissolution products of bioactive ceramics have been shown to stimulate gene expression related to osteogenesis and angiogenesis [21, 26].



Figure I.7 Soft tissue applications [21, 30].

IV.3.3. Biodegradable Ceramics

These ceramics degrade over time in the body, allowing natural tissue to replace the material, including tricalcium phosphate (TCP) and low-temperature sintered hydroxyapatite, commonly used in temporary bone [20, 26]. Various clinical uses of bioceramics in the human body are shown in Figure I.8. The degradation rate of these materials can be precisely controlled through modifications in porosity, chemical composition, and crystalline phase, enabling synchronization with the rate of host tissue regeneration. Due to their high biocompatibility and inherent osteoconductive properties, they are well-suited for applications in resorbable bone grafts and tissue engineering scaffolds.

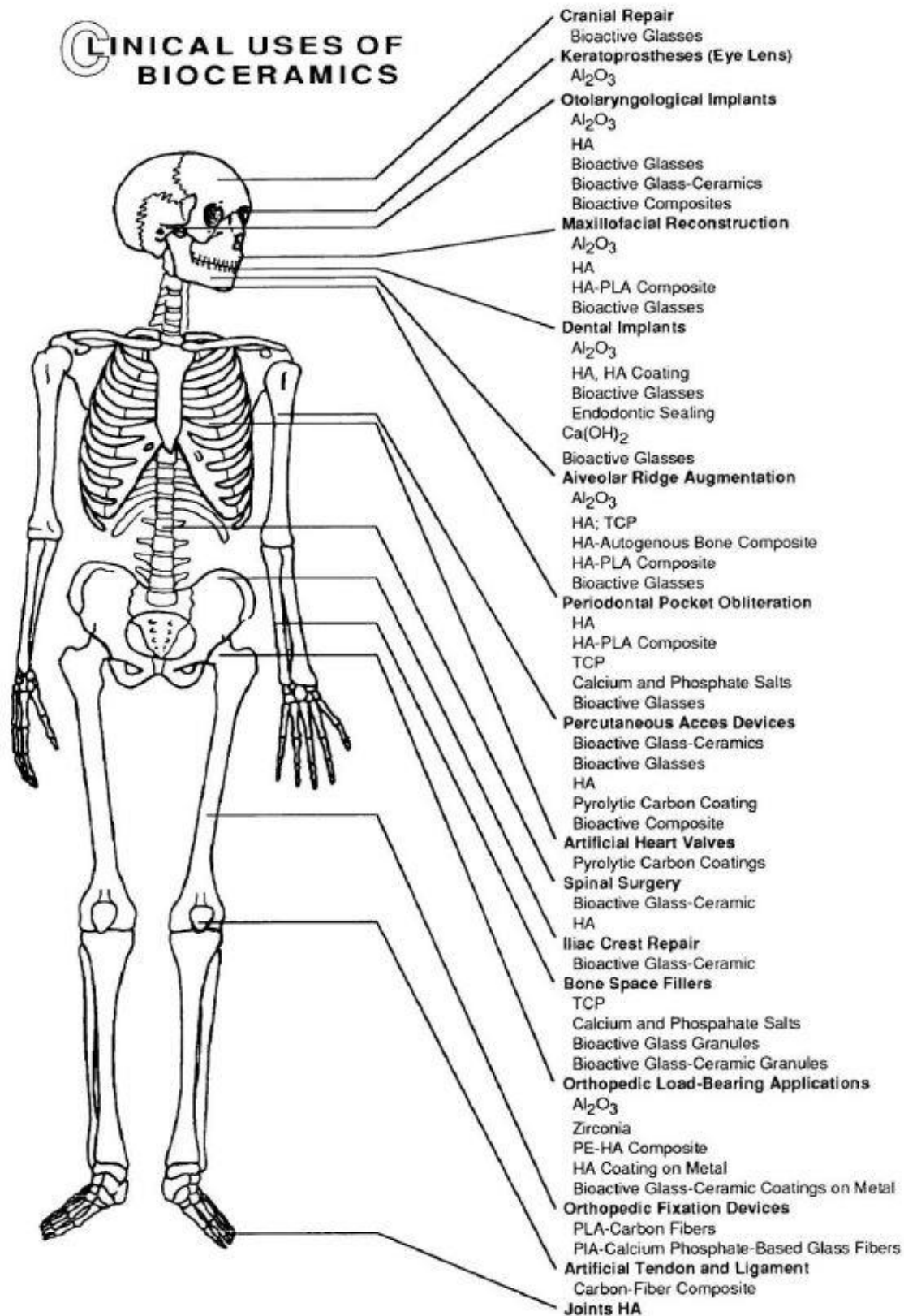


Figure I.8 Clinical uses of bioceramics throughout the human body [31].

V. Overview of forsterite

This section provides an overview of forsterite, detailing its historical significance and defining characteristics, alongside a summary of its physical and chemical properties and applications.

V.1. History and definition of forsterite

Forsterite was discovered by William Hyde Wollaston in 1824 in the mountain Somma Vesuvius, Italy, where later on was named in honor of the German mineralogist and professor of nature Johann Reinhold Forster (1729-1798). Pure forsterite Mg_2SiO_4 , also called white olivine, is part of a mineral group called Olivine; some multicolor crystals (green, yellow, and grey according to impurities ratio in forsterite) can be found as constituents in igneous, basalt, and ultramafic rocks as showcased in Figure I.9, forsterite is known to be the Mg-rich number of Olivine group characterizes outwardly by its white color crystals. Pure forsterite is rarely found in nature due to the similar ionic radius Fe^{2+} can replace Mg^{2+} , and forsterite is accompanied by Fayalite Fe_2SiO_4 in nature [32, 33].



Figure I.9 Big grain of gemmy forsterite in basalt hostrock from British Columbia and gemmy forsterite (peridot) crystals from Mogok.

V.2. Forsterite properties

V.2.1. Forsterite structure

The specific chemical formula of forsterite is (Mg_2SiO_4), with SiO_2 41.72 % and MgO 57.83 % as chemical components. Forsterite crystallizes in the orthorhombic system in the Pnma space group, with lattice parameters: $a = 10.18 \text{ \AA}$, $b = 5.97 \text{ \AA}$, and $c = 4.75 \text{ \AA}$.

The crystal structure in Figure I.10 shows the SiO_4 tetrahedral point in opposite directions, while Mg atoms are octahedrally surrounded by six O atoms. It has a density of 3.24 g.cm^{-3} and a high melting point of $1890 \text{ }^\circ\text{C}$ [33-36].

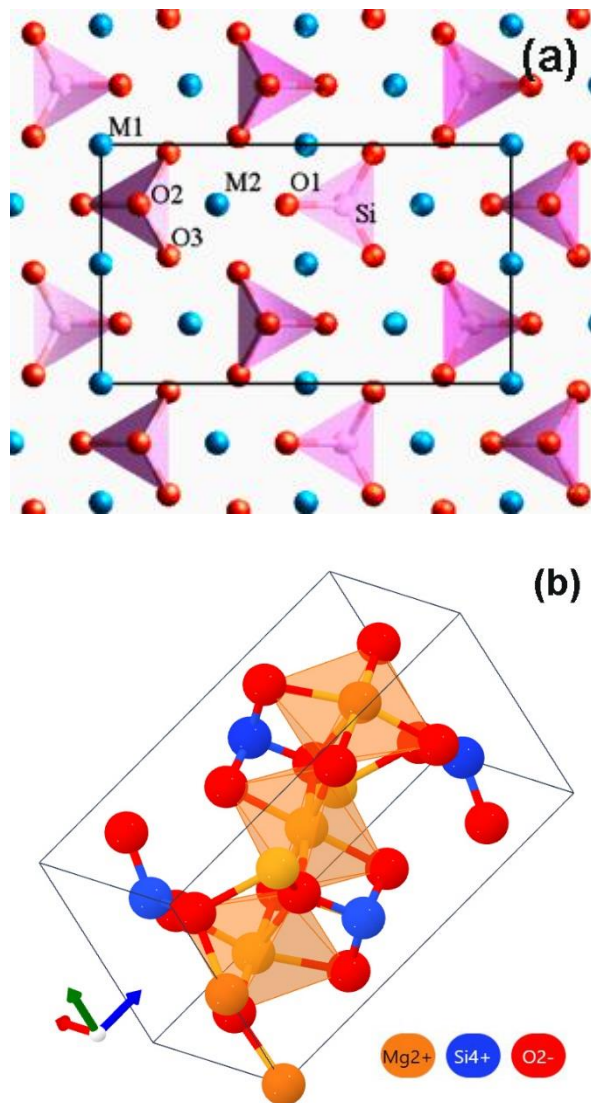


Figure I.10 The (a) 2D and (b) 3D crystal structure of forsterite (Mg_2SiO_4) [35, 36].

Other thermal and mechanical properties of forsterite are summarized in Table I.3.

Table I.3 Some properties of forsterite [33, 34].

Properties	Description
Chemical Formula	Mg ₂ SiO ₄
Mineral Group	Olivine
Crystal System	Orthorhombic
Lattice Parameters	a= 10.18 Å, b= 5.97 Å, and c= 4.75 Å
Space Group	Pnma
Melting Point	1890 °C
Density	3.24 g.cm ⁻³
Hardness (GPa)	7.5
Thermal Stability	High chemical stability at high temperatures
Electrical Conductivity	Low, suitable for electronic materials, low dielectric constant
Thermal Expansion Coefficient	Low ($10 \times 10^{-6} / \text{K}^{-1}$), which makes it ideal for high-temperature applications
Color	Yellowish green to greyish green
Main Mineral Components	Composed primarily of magnesium oxide (MgO) and silica (SiO ₂)
Calcination Temperature	Forsterite phase appears in the range of [800 °C-1400 °C] depending on the synthesis Methods

V.3. Forsterite applications

Forsterite is widely utilized in various industrial fields due to its unique thermal and chemical properties. One of its primary uses is in the production of refractory materials, where its high melting point and resistance to chemical corrosion which make it ideal for the linings of nonferrous melting furnaces, glass kiln chambers, steel-making open hearth furnaces, ladles, kilns, bricks, and other high-temperature industrial equipment [37-40] Figure I.11 shows Fireproof Forsterite Brick used in the previously mentioned industries.

Forsterite materials are proposed for lightweight heat-insulating refractories due to their desirable properties, such as low thermal conductivity and good compressive strength [40]. Forsterite contained insulating refractories have lower thermal conductivity than periclase, spinel, and aluminosilicate products, making them suitable for basic insulating applications [41].

Forsterite's low electrical conductivity and linear thermal expansion coefficient, which match well with other cell components, make it suitable for applications in solid oxide fuel cells (SOFCs) [42, 43].

Due to its favorable mechanical properties and bioactivity, forsterite has shown significant potential for application in bone tissue engineering, promoting bone regeneration, bone implantation, and integration with natural bone [44-46].

Forsterite and doped forsterite ceramics uses extend to ceramic coating, thermal coating against thermal corrosion, high potential for the use as ceramic pigments, also as thermal barrier coating (TBC) material for gas turbine applications [47, 48].

Additionally, due to forsterite's low dielectric permittivity and low thermal expansion, it is suitable for use as dielectric substrates in electronic devices and communication systems, particularly in microwave and millimeter-wave applications [43, 49].

Forsterite is used in the ceramics industry, particularly in the manufacture of magnesium-rich ceramics, which are valued for their durability and thermal stability. In metallurgy, forsterite is employed as tundish slag-stopping walls and a slag conditioner to enhance the removal of impurities during metal extraction processes.

Its role in the optical devices industry is also notable, as it is applied commercially in specialized tunable near-infrared lasers. By incorporating doped forsterite into glass or polymer waveguides, optical amplifiers with tunable amplification wavelengths can be developed, making them useful in telecommunications, optical data transmission, and recycling discarded solar PV panels [50, 51].



Figure I.11 Fireproof Forsterite Brick.

V.4. Forsterite preparation methods

Forsterite, a naturally rare mineral, has driven researchers to explore cost-effective synthesis methods that preserve its essential physical and chemical properties. Various synthesis techniques are employed, depending on the intended application of forsterite. In applications demanding high-purity material, such as in advanced technological environments, sophisticated preparation methods are utilized. However, in industrial applications, such as the production of refractory bricks for furnaces, conventional methods involving the homogenization of raw materials like silica and magnesium sources followed by sintering are preferred. Based on numerous studies, few prominent methods have been identified for the preparation of forsterite.

V.4.1. Solid-state reaction

The solid-state reaction (or solid-state synthesis) is a process used to create new materials, typically in powder form, by inducing a chemical reaction between solid reactants, and the activation of precursor powders is generally achieved by enhancing the effective surface area, thereby increasing the contact between the participating particles during the preparation process

as shown in Figure I.12. This method is commonly used in the synthesis of ceramic materials, inorganic compounds, and some types of nanomaterials [52].

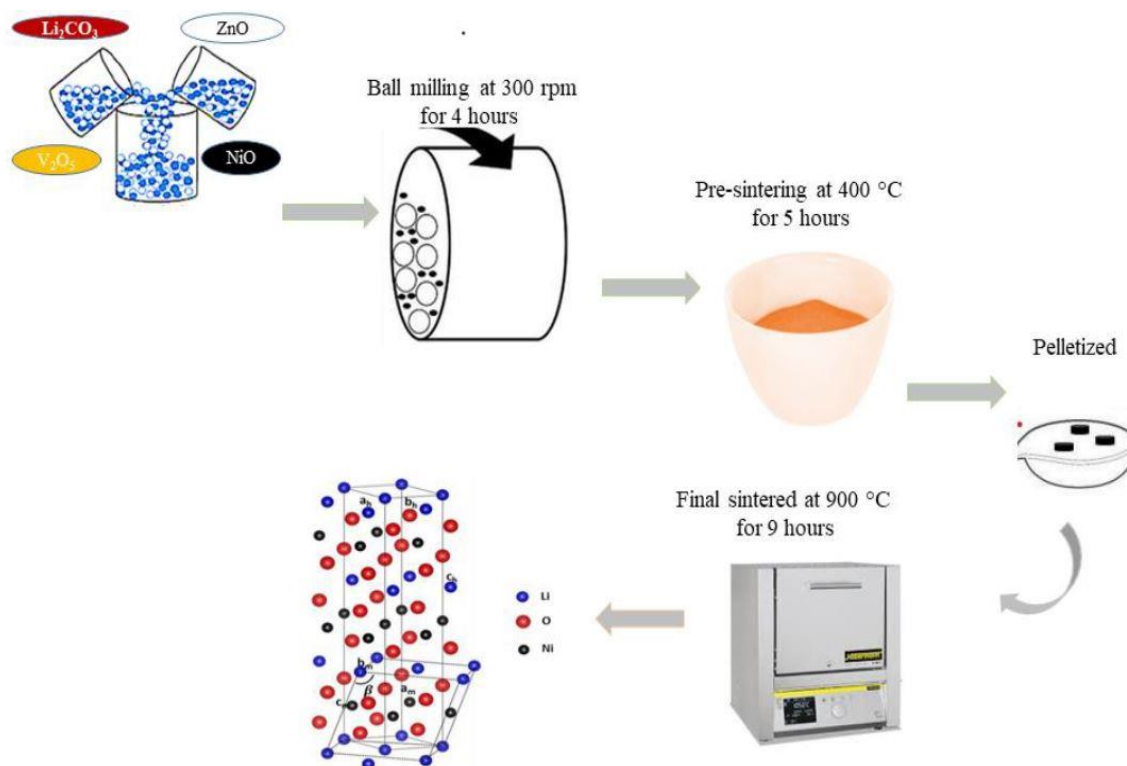


Figure I.12 Schematic representation of solid-state reaction synthesis process [53].

Mathur et al. used rice husk ash (RHA) as a source of amorphous silica (with multiple impurities such as carbon) and dead-burnt magnesia (MgO), mixed in a stoichiometric ratio and ball-milled for 12 hours. The mixture was calcined at temperatures ranging from 700 °C to 1000 °C, with forsterite formation starting at 700 °C. XRD confirmed that single-phase forsterite was achieved at 1000 °C. The crystallite size, calculated using the Scherrer equation, ranged from 80 nm at 700 °C to 85 nm at 1000 °C. Combining ball milling for a long period and calcination resulted in spherical nano-crystalline forsterite with uniform particle distribution and ideal properties for industrial applications like refractories and SOFCs [43]. To address the limited bioactivity of traditional ceramic materials used in medical applications. **Gorea** et al. prepared forsterite using a solid-state reaction between magnesium carbonate (MgCO_3) and talc ($\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$) in a 5:1 molar ratio. The mixture was ball-milled for 10 hours and then thermally treated at temperatures of 1000 °C, 1100 °C, and 1200 °C. X-ray diffraction confirmed forsterite formation, with

complete phase transformation at 1100 °C. Crystallite sizes ranged from 25-35 nm at lower temperatures, increasing to 78 nm at 1200 °C, where larger grain aggregates formed. Nano-sized forsterite particles demonstrated better bioactivity and potential use in bone tissue regeneration [54]. **Chen** et al. synthesized forsterite using two different MgO precursors: brucite ($\text{Mg}(\text{OH})_2$) and hydromagnesite ($(\text{MgCO}_3)_4 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$), both mixed with fumed silica. The mixtures were ball-milled for 20 hours, followed by calcination at temperatures ranging from 600 °C to 1000 °C. The FC mixture (hydromagnesite) formed phase-pure forsterite at 800 °C, while the FH mixture (brucite) required 1000 °C. The critical issue addressed was how different MgO precursors influence forsterite formation temperature and purity. The study found that shorter diffusion distances of Mg^{2+} and Si^{4+} in hydromagnesite resulted in lower-temperature forsterite synthesis, solving the problem of high calcination temperatures in traditional methods but still facing the problem of longer milling duration [55]. **Laziri** et al. focused on synthesizing forsterite (Mg_2SiO_4) using nano-powders of MgO and SiO_2 through a solid-state reaction. The powders were wet-milled, dried, pressed, and sintered at temperatures between 1000 °C and 1500 °C. The forsterite formation began at 860 °C, with complete formation achieved at 1200 °C after 2 hours. The problem addressed was the slow reaction and formation of unwanted phases in traditional methods. By optimizing the process with nano-powders, the study achieved faster forsterite formation with crystalline size ranging from 26-35 nm and significantly shorter milling duration for raw materials, improved mechanical properties, such as high density, hardness (7.64 GPa), low thermal expansion, and determine forsterite formation activation energy [56].

V.4.2. Sol-gel method

The sol-gel process is a novel approach for synthesizing advanced materials, primarily driven by hydrolysis and polycondensation reactions to provide greater control over the chemical processes during solid formation, as presented in Figure I.13. This technique enables the efficient production of homogeneous multi-component systems, particularly excelling in the precise preparation of uniformly mixed oxides through the combination of molecular precursor solutions.

Additionally, the sol-gel process offers advantages such as low-temperature synthesis, tunable porosity, and the ability to produce nanostructured materials, making it highly applicable in catalysis, optics, and biomedical materials. However, challenges such as shrinkage during drying and the high cost of precursors must be considered in large-scale applications [57, 58].

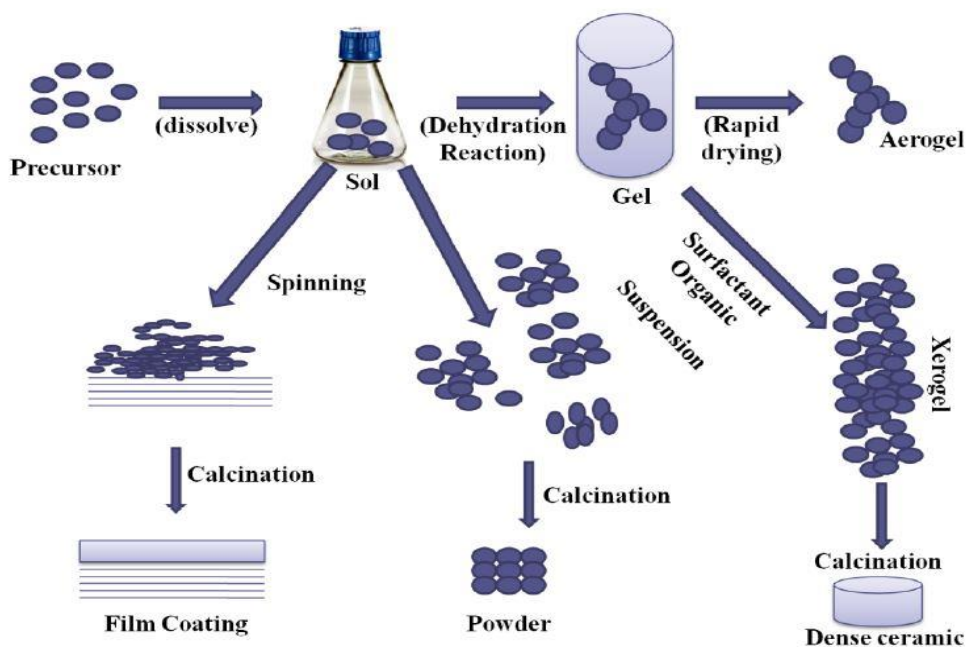


Figure I.13 Schematic representation of the sol-gel process of synthesis of nanomaterials [59].

The study, conducted by **Andrianov** et al., used the sol-gel method to synthesize forsterite (Mg_2SiO_4) by experimenting with different magnesium salts and silica sources, including magnesium chloride, nitrate, sulfate, acetate, citrate, alongside amorphous silica filler (SF) and SiO_2 sol. The precursors were dissolved, mixed, gelled at room temperature for 24 hours, and dried at 120°C to form a porous xerogel. Heat treatment between 600°C and 1200°C transformed the xerogel into forsterite. Analytical techniques like DTA, XRD, and SEM tracked phase transitions and microstructure. Forsterite formation occurred at 600°C with magnesium acetate, while other salts required higher temperatures (800°C to 1200°C). Magnesium acetate with amorphous silica yielded the best results, producing refined, homogeneous powders at lower temperatures [60]. **Afonina** et al. synthesized forsterite (Mg_2SiO_4) by mixing magnesium acetate or magnesium chloride with silica sol. Gel formation occurred through slow drying at 110 – 120°C for 24 hours, followed by heat treatment at 600 – 1250°C . Magnesium acetate produced the most stable sol and homogeneous powder, with forsterite formation beginning at 600°C and completing at 1200 – 1250°C . The process avoided issues seen in traditional methods, such as high temperatures and contamination from milling, while producing fine, uniform particles (0.1 – $0.5\ \mu\text{m}$) [61]. The same method was used by **Kharaziha** et al., where the obtained powder was calcined at 800°C for 2 hours to obtain the forsterite nanopowder, which exhibited particle sizes

ranging from 25 to 45 nm [62]. **Ghariani** et al. proposed the application of synthesized forsterite for the purification of waste frying oil; the author utilized a sol-gel synthesis method. This process involved dissolving 14.8 g of tetraethyl orthosilicate (TEOS) in 25 ml of ethanol, followed by the dropwise addition of 50 ml of magnesium nitrate solution to achieve a Mg/Si molar ratio of 2:1. A catalyst, 10 ml of 0.1 M HNO_3 , was added to promote TEOS hydrolysis. The mixture was stirred for 2 hours, aged at 65 °C for 12 hours to form a gel, then dried at 120 °C. The obtained gel was calcined from 500 to 1100 °C for 30 min, forsterite optimal crystallization occurred at 900 °C with crystalline size of 80 nm [63]. Other sol-gel variations have been introduced [64, 65].

V.4.3 Mechanochemical activation

Mechanochemical activation is a chemical reaction initiated and driven by the direct application of mechanical energy, typically from grinding or milling, to break chemical bonds and induce reactions. This energy can be applied through various devices, such as mixer mills and planetary ball mills as shown in Figure I.14. This technique stands out for its ability to promote chemical transformations without the need for solvents and multicomponent reactions (MCRs), thereby enhancing sustainability and often resulting in different reaction outcomes compared to traditional methods that rely on heat treatment or solvents, this method is particularly beneficial in pharmaceutical and agrochemical industries and used to synthesize materials such nanocrystalline materials, intermetallic compounds and composites [66, 67].

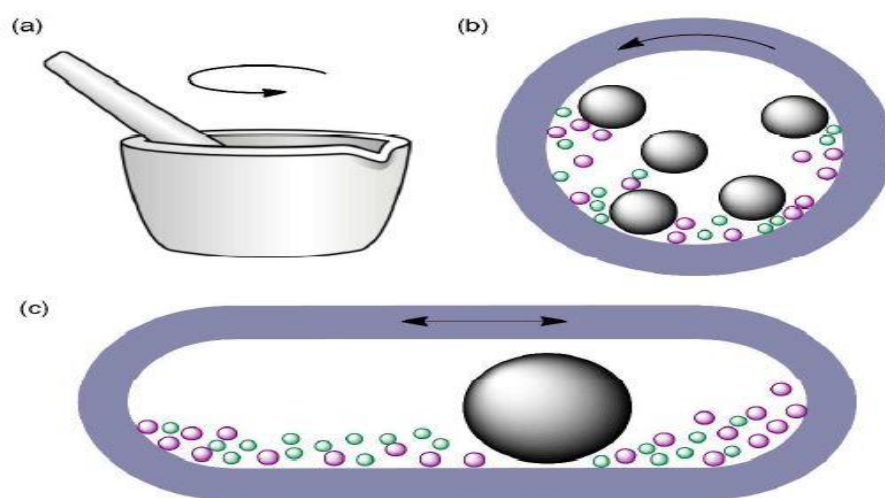


Figure I.14 Schematic representations of the three main modes of mechanical activation [67].

The preparation of forsterite (Mg_2SiO_4) powder by **Tavangarian** et al. involved a mechanical activation method utilizing a mixture of talc and magnesium carbonate in a molar ratio of 5:1. The talc and magnesium carbonate powders were milled in a planetary ball mill under ambient conditions for 10 to 100 hours, with a ball-to-powder weight ratio of 10:1 at a rotational speed of 500 rpm. Following the milling process, the powders were subjected to heat treatment at temperatures of 1000 °C and 1200 °C for 1 hour to achieve crystallization of forsterite. The results indicated that a pure nanocrystalline forsterite phase could be synthesized after annealing at 1000 °C, with a crystallite size of approximately 35 nm [68]. **Fathi** et al. involved a mechanical activation process followed by heat treatment. The starting materials, amorphous SiO_2 and magnesium carbonate (MgCO_3) were mixed in a stoichiometric ratio and mechanically activated using a planetary ball mill for 5 to 15 hours, allowing for the crystallization of forsterite to occur at a reduced temperature of approximately 820 °C with a crystallite size around 57 nm [69, 70].

Various other techniques have been developed for the synthesis of forsterite, including precipitation [71, 72], catalyst-free chemical vapor deposition [73], facile molten-salt approach [74], microwave synthesis [75, 76], hydrothermal methods [77], geopolymer technique [78].

V.5. Effect of some additives on forsterite

The applications of forsterite (Mg_2SiO_4) require the enhancement of its physical and chemical properties, particularly regarding thermal stability, electrical conductivity, and biocompatibility. This has encouraged research focused on improving these characteristics while also developing synthesis methods that allow for the stable production of forsterite at lower temperatures. Achieving this is economically significant, as it can lead to reduced manufacturing costs.

Several studies, including those by **Fathi** et al. and those by **Kan** et al., have explored the addition of LiF and CaTiO_3 to optimize the dielectric properties and formation of forsterite. The study found that forsterite formation began at temperatures above 800 °C, with complete crystallization observed at 900 °C. The addition of lithium fluoride (LiF) significantly enhanced the nucleation process of forsterite synthesis, reducing the activation energy from 1382.4 to 474.0 kJ.mol^{-1} as the crystallization fraction increased, enabling formation at lower temperatures. Moreover, the incorporation of calcium titanate (CaTiO_3) allowed for tuning of the temperature

coefficient (TCf) values, achieving near-zero TCf for enhanced temperature stability in microwave applications. These modifications led to improved dielectric properties, with the quality factor (Q_f) increasing significantly. The dielectric constant (ϵ_r) remained stable, which is advantageous for maintaining performance in high-frequency applications [70, 79].

Lui et al. attempted to address the challenge of improving the bioactivity of forsterite by depositing HA coatings onto the forsterite scaffolds. HA significantly enhances the bioactivity of forsterite scaffolds, promoting better cell responses and osteogenic differentiation of bone mesenchymal stem cells (BMSCs), making them more suitable for bone repair applications, particularly in cases of infections [80]. Another study by Choudhary et al. has concluded that forsterite-diopside composites exhibit promising features for biomedical applications, balancing mechanical stability, bioactivity, and antibacterial properties while using diopside as an additive improves biomineralization [81].

V.6. Forsterite and Traditional Bioceramics

Traditional bioceramics like hydroxyapatite and tricalcium phosphate (TCP) are bioactive and biodegradable, widely used for bone regeneration. Forsterite ceramic can be seen as complementary to these materials. While hydroxyapatite is more bioactive, it lacks the mechanical strength needed for specific applications. Forsterite, with its superior mechanical properties, could be used in composite scaffolds with hydroxyapatite, where the mechanical strength of forsterite enhances the bioactivity of HAp. Forsterite ceramic can also be used as a coating material on implants made from metals like titanium. Its bioinert nature can protect the underlying material while providing a surface that can bond with bone tissue, similar to how hydroxyapatite is used for coatings.

VI. Overview of kinetic analysis

This section highlights the main equations utilized in thermal analysis and provides a quick overview of kinetic theory, model-free methods, and reaction models.

VI.1. Thermal analysis techniques

Thermal analysis techniques are essential for explaining the mechanisms of phase transformations in solids, particularly in response to variations or stability in processing temperature. By measuring changes in physical properties as a function of temperature, thermal analysis provides insight into kinetic parameters such as activation energy and Avrami parameters, which characterize the nucleation and growth mechanisms of these transformations. Since the early twentieth century, specialized thermal analysis instruments have emerged as invaluable tools in this field. Key devices include thermogravimetric analysis (TG), differential thermal analysis (DTA), scanning calorimetry (DSC), dilatometry (DL), infrared spectroscopy with heating capabilities (FTIR), and X-ray diffraction (XRD) systems equipped with furnace. Among these, TG, DTA, DSC, and DL are particularly significant due to their ability to control heating and cooling rates precisely, analyze minimal sample quantities (typically less than a gram), and determine phase transformations during heat treatment. The primary objective of thermal analysis is to derive kinetic and thermodynamic parameters, enabling a comprehensive understanding of phase transformation kinetics through the interpretation of experimental curves and derived values from thermal treatment data [82, 83].

VI.2. Calculation of crystallization kinetics and mechanism

Model-fitting (e.g., identifying a reaction model) and isoconversional (e.g., model-free) techniques are kinetic analysis methods. Modern thermal analysis appears to prefer the latter methods for two main reasons: first, model-free kinetics are sufficiently flexible to allow for a change of mechanism during the reaction, and second, mass transfer limitations are reduced by using multiple heating rates. On the other hand, model-fitting kinetic methods usually contain a single heating rate, and the disadvantage is that activation energy varies with the heating rate due to mass and energy transfer effects. Thermal analysis can be performed using two distinct methods: either with a constant temperature (Isothermal) or a change in temperature (non-

isothermal). In the case of an isothermal method, the sample is heated until the required study temperature is reached and then fixed for a sufficient period to end the crystallization process [82]. Eq. I.1 defines the general equation of solid-state reaction rate under isothermal conditions.

$$\frac{d\alpha}{dt} = K(T)f(\alpha) \quad (\text{I. 1})$$

Where:

- α is crystallization fraction; its name varies depending on the technique and type of thermal analysis used [84]. The crystallization fraction is the change in energy relative to the total energy and is defined as Eq. I.2.

$$\alpha = \frac{\int_0^t Q dt}{\int_0^{t_f} Q dt} \quad (\text{I. 2})$$

- Q is the heat flow

$k(T)$ is the rate constant at temperature T , defined according to the Arrhenius equation as Eq. I.3 [82, 85-87].

$$K(T) = A \exp\left(-\frac{E_a}{RT}\right) \quad (\text{I. 3})$$

Where:

- E_a represents the crystallization activation energy, R is the gas constant, T is the absolute temperature, and A is the pre-exponential factor or the frequency factor.
- $f(\alpha)$ is the kinetic model, also called the reaction model, which represents the reaction mechanism.

Eq. I.1 is modified to explicitly depend on temperature by replacing $K(T)$ with the Arrhenius equation (Eq. I.3). Eq. I.4 describes the relationship between the rate of reaction and temperature.

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E_a}{RT}\right) f(\alpha) \quad (\text{I. 4})$$

Eq. I.4 integration leads to Eq. I.5:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = A \int_0^t \exp\left(\frac{-E_\alpha}{RT}\right) dt \quad (I.5)$$

Where $g(\alpha)$ represents the integral equation of the reaction model. Under constant heating rate conditions, the integral with time is replaced with the integral concerning temperature:

$$g(\alpha) = \frac{A}{\phi} \int_0^T \exp\left(\frac{-E_\alpha}{RT}\right) dT \quad (I.6)$$

Where ϕ represents the heating rate, which is defined as $\phi = \frac{dT}{dt}$.

The Approximate solutions were used in the previous integral. Different solutions of Eq. I.4 are used to calculate the kinetic parameters. One of the most popular approaches to studying thermokinetics is the model-free method [88].

VI.2.1. Model-free methods

Model-free approaches are the most reliable methods to calculate the activation energy of solid-state reactions without prior knowledge regarding the reaction model or the mechanism. These methods are categorized into three classes: differential methods like Kissinger and Ozawa methods, integral methods like Kissinger–Akahira–Sunose (KAS) and Flynn- Wall- Ozawa (FWO), and modulated thermogravimetry methods. The model-free methods involve measuring the temperature T corresponding to fixed values of crystallization fraction for three or more heating rates. The kinetic parameters, including activation energy E_α , are estimated through the linear fitting of the crystallization fraction α (extent of conversion) as a function of temperature [89, 90].

VI.2.1.1. Kissinger method

Kissinger method (model-free non-isothermal method) is considered as a special case of the isoconversional method [85, 91]. Kissinger analysis is a peak position analysis in terms of T_m and doesn't require determining the activation energy of each crystallization fraction α (conversion value). Eq. I.7 describes this method [92, 93].

$$\ln\left(\frac{\phi}{T_m^2}\right) = -\frac{E_\alpha}{RT_m} + C_1 \quad (\text{I. 7})$$

Where C_1 is a constant, ϕ is the heating rate in the DTA analysis, and T_m is the absolute peak temperature observed in the DTA curve

VI.2.1.2. Ozawa method

Ozawa's equation is shown in Eq. I.8 [94].

$$\ln(\phi) = -1.052\left(\frac{E_\alpha}{RT_m}\right) + C_2 \quad (\text{I. 8})$$

Where C_2 a constant. The activation energy values of Ozawa's method defined by Eq. I.8 were calculated by plotting $\ln(\phi)$ as a function of $1/T_m$.

VI.2.1.3. Boswell method

Boswell method is described by Eq. I.9 [95].

$$\ln\left(\frac{\phi}{T_m}\right) = -\frac{E_\alpha}{RT_m} + C_3 \quad (\text{I. 9})$$

Where C_3 a constant. Boswell's method (Eq. I.9) activation energy was calculated by plotting $\ln\left(\frac{\phi}{T_m}\right)$ as a function of $1/T_m$.

VI.2.1.4. Kissinger–Akahira–Sunose (KAS) method

Several integral isoconversional methods exist, each famous for their unique approximations of the temperature integral in Eq. I.6. Various approximations result in linear equations. Coats and Redfern [93] proposed an approximation for the temperature integral to solve Eq. I.6 and yield the Kissinger-Akahira-Sunose (KAS) method equation (Eq. I.10) [96, 97].

$$\ln\left(\frac{\phi_i}{T_{\alpha,i}^2}\right) = -\frac{E_\alpha}{RT_{\alpha,i}} + C_4 \quad (\text{I. 10})$$

Where C_4 is a constant, i and α are the heating rate and crystallization fraction values, respectively. The dependence of $\ln\left(\frac{\phi_i}{T_{\alpha,i}^2}\right) = f\left(\frac{1}{T_{\alpha,i}}\right)$ is a straight line with a slope equal to $\left(-\frac{E_{\alpha}}{RT_{\alpha,i}}\right)$. Therefore, the kinetic parameters A_{α} and E_{α} can be determined.

VI.2.1.5. Flynn- Wall- Ozawa (FWO) method

Doyle [98] introduced the simple temperature integral approximations, known as the equation of Flynn-Wall-Ozawa (Eq. I.11) [94, 99, 100].

$$\ln(\phi_i) = -1.052 \left(\frac{E_{\alpha}}{RT_{\alpha,i}} \right) + C_5 \quad (\text{I. 11})$$

Where C_5 is a constant, i and α represent the values given for the heating rate and crystallization fraction, respectively. The dependence of $\ln(\phi_i) = f\left(\frac{1}{T_{\alpha,i}}\right)$ is a straight line with a slope equal to $\left(-1.052 \left(\frac{E_{\alpha}}{RT_{\alpha,i}} \right)\right)$. Thus, the kinetic parameters A_{α} and E_{α} can be determined from the interception and the slope, respectively.

VI.2.2. Reaction model $f(\alpha)$ determination

A reaction model is a mathematical function of the crystallization fraction made up of one or more intermediates, numerous reaction modeling methodologies are available in thermal analysis field. One of the methodologies used is the J. Malek method [80], which is relatively systematic, more accurate, and easier than the other mentioned methodologies used in many studies [101-103]. J. Malek method depends mainly on the establishment of the functions $y(\alpha)$ and $z(\alpha)$ using experimental data as described in Eqns. I.12 and I.13, which is done after evaluating or calculating the average value of the activation energy calculated by the Kissinger method and, from there, accessing to the interaction model and thus its kinetic parameters n and m .

$$y(\alpha) = \frac{d\alpha}{dt} \exp(x) \quad (\text{I. 12})$$

$$z(\alpha) = \frac{d\alpha}{dt} \frac{T}{\phi} \pi(x) \quad (\text{I. 13})$$

In Eqs. I.12 and I.13, $\pi(x)$ is the integral function of the temperature, where $x=E_a/RT$.

Senum and Yang [104] proposed a numerical approximation of $\pi(x)$, which Flynn [105] later modified as described in Eq. I.14.

$$\pi(x) = \frac{x^3 + 18x^2 + 88x + 96}{x^4 + 20x^3 + 120x^2 + 240x + 120} \quad (\text{I. 14})$$

The functions $y(\alpha)$, $z(\alpha)$, and da/dt are constructed in terms of crystallization fraction α at different heating rates for the crystallized phase. The maximum α_p , α_m , and α_p^∞ of the functions $y(\alpha)$ and $z(\alpha)$ and (da/dt) , respectively, at different heating rates. Based on the comparison between α_p , α_p^∞ , and α_m experimental values and the theoretical conditions defined by J . Malek, as shown in Table I.4 [101], the appropriate reaction model $f(\alpha)$ is selected. After the determination of reaction model Eq. I.1 can be rewritten as the logarithm of Eq. I.1 and the reaction model equation combination to determine n and m value.

Table I.4 Reaction models and α_p^∞ and α_m according to Malek's method [101].

Reaction model	Notation	$f(\alpha)$	α_p^∞	α_m
Reaction order	RO (n)	$(1 - \alpha)^n$	1 - $n^{1/(1-n)}$	0
Jhonson Mehl Avrami general equation	JMA (m>1)	$m(1 - \alpha) \{-\ln(1n\alpha)\}^{1-\frac{1}{m}}$	0.633	$1 - \exp(\frac{1}{m} - 1)$
2D diffusion	D2	$-1/(\ln(1 - \alpha))$	0.834	0
3D diffusion (jander's equation)	D3	$\frac{3(1 - \alpha)^{2/3}}{2\{1 - (1 - \alpha)^{\frac{1}{3}}\}}$	0.704	0
3D diffusion (jander's equation)	D4	$\frac{3}{2\{(1 - \alpha)^{-\frac{1}{3}} - 1\}}$	0.776	0
<i>Šesták Berggren</i>	SB (m,n)	$\alpha^m(1 - \alpha)^n$	$(0, \alpha_p)$	$m/(m + n)$

VI.3. Thermodynamic parameters of crystallization

Once the kinetic parameters, including the activation energy (E_a), are determined, the thermodynamic parameters (Gibbs free energy (ΔG), entropy (ΔS), enthalpy (ΔH)) were calculated using Eqns. I.15, I.16, and I.17 [106, 107].

$$A \exp\left(-\frac{E_a}{RT}\right) = v \exp\left(-\frac{\Delta G}{RT}\right) \quad (\text{I. 15})$$

$$\Delta H = E_a - RT \quad (\text{I. 16})$$

$$\Delta G = \Delta H - T\Delta S \quad (\text{I. 17})$$

Where, $v = \frac{K_B T}{h}$, K_B is Boltzmann, h is the Plank constant.

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Chapter Two: Materials & Method

This chapter comprehensively describes the methodologies employed for synthesis and analyses within this thesis. Detailed information on the raw materials used for powder synthesis, preparation of sintered samples, and the techniques applied are presented. Furthermore, an overview of the equipment utilized for physicochemical characterization is included and the biological test explained. Our thesis aims to synthesize forsterite and study SiO_2 as an additive to forsterite and its effect on the thermal, mechanical, microstructural, and biological properties of prepared samples. It also examines the effect of forsterite as an additive on the thermal, mechanical, microstructural, and biological properties of hydroxyapatite.

I.1. Forsterite-Silica composites (FS_x) raw materials and methods

I.1.1. Raw materials

Materials with exceptional purity were selected. Two types of commercial nanopowders shown in Figure II.1 (a, b) were used as raw materials obtained from US Research Nanomaterials, Inc.: magnesium oxide (MgO) crystallized as periclase with a purity rate of 99 % and an average grain size of 40 nm, and amorphous silicate oxide (SiO_2) powders with a purity rate of 98 % and an average grain size of about 60 nm.

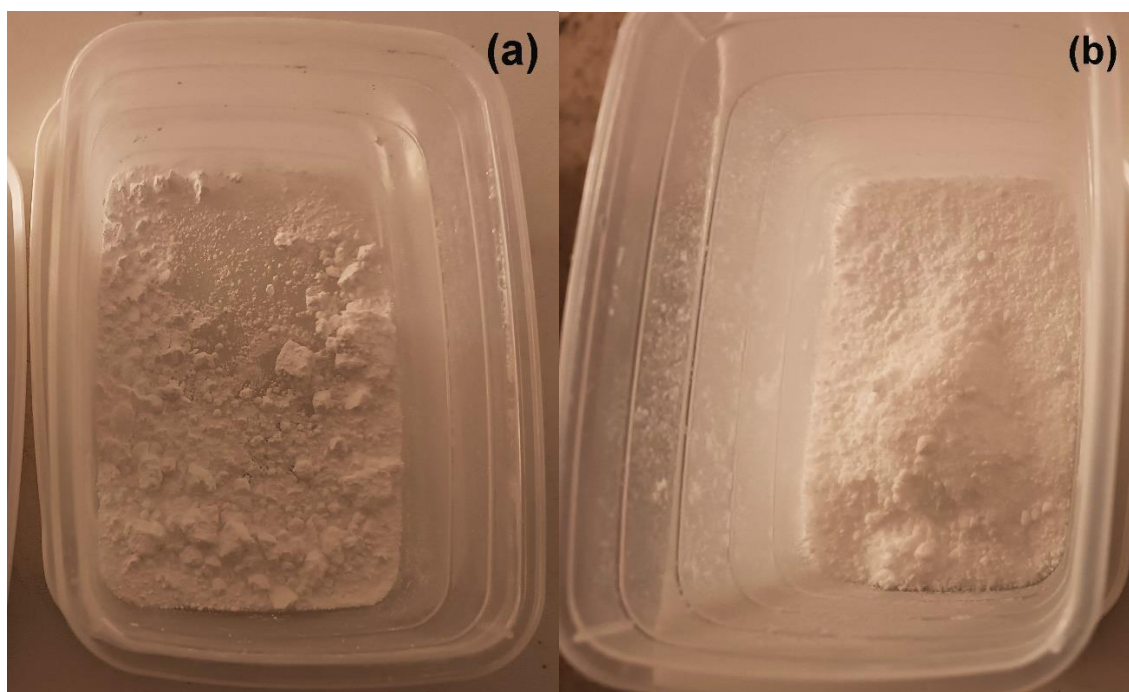


Figure II.1 (a) MgO and (b) SiO_2 nano-oxides powder used as raw material.

I.1.2. Magnesium oxide (MgO)

Magnesium oxide (MgO) is an inorganic compound of magnesium and oxygen. Known for its high melting point and thermal stability, MgO is widely utilized in applications that demand heat resistance, such as refractory materials, insulation, and ceramics production. It primarily occurs in the mineral form of periclase, which is found naturally in marble and other magnesium-rich metamorphic rocks. Historically, magnesium oxide has been valued for its refractory qualities, making it essential in industries requiring high-temperature insulation, including steel and glass manufacturing. MgO also plays a role in the medical and environmental sectors; it is commonly used as an antacid and laxative in medicine and as a neutralizing agent in environmental applications due to its basicity, which helps counteract acidic pollutants. Synthetic production of MgO has grown to meet the demands of these diverse fields, taking advantage of its chemical stability, thermal resistance, and insulation properties, which enhance durability and efficiency across various industrial applications [1].

I.1.3. Silicon dioxide (SiO₂)

Silicon dioxide (SiO₂), or silica, is a compound of silicon and oxygen with significant geological, structural, and technological relevance. It primarily occurs in crystalline forms like quartz, tridymite, and cristobalite. Quartz, the most abundant form, is a primary component of Earth's crust and is widely used in industrial applications, including glass, ceramics, and semiconductor manufacturing. Historically, silica has been utilized for centuries in glass and ceramics; ancient civilizations used quartz in pottery and tools, and the Romans developed techniques for producing transparent glass around the first century AD. Today, both natural and synthetic silicon dioxide are produced to meet demands in industries from microelectronics to pharmaceuticals, with its unique properties enhancing product durability and efficiency. Its abundance and physical attributes make it essential across disciplines, including geology, materials science, electronics, and optics [2].

I.1.4. Forsterite (Mg₂SiO₄)

Forsterite (Mg₂SiO₄) is a magnesium-rich silicate mineral belonging to the olivine group, important in geology and industrial applications. It commonly occurs in igneous and metamorphic rocks and is a major component of the Earth's upper mantle. Forsterite is valued for

its high melting point, hardness, and resistance to chemical weathering. Historically, it has been studied for its role in understanding mantle composition and geologic processes. Today, synthetic forsterite is used in refractory materials, ceramics, bioceramics, as a component in specialty glass and electronic devices. Its physical and chemical properties make it significant in sciences, materials engineering, and advanced manufacturing.

I.1.5. Powders preparation

A series of forsterite-silica composites (FS_x) (where F is forsterite, S is silica, and x: 0, 1.5, 3, 4.5, and 6 wt.% is SiO_2 excess) were prepared to examine the influence of excess silica SiO_2 on thermal, mechanical and microstructural properties and to study the kinetic parameters of forsterite crystallization. Table II.1 shows the chemical composition of forsterite-silica (FS_x) powders with varying excess SiO_2 content. Forsterite-silica composites (FS_x) are synthesized following the solid-state reaction method. A planetary ball mill was used to ensure the reduction and homogeneity of powder particles. The SiO_2 and MgO mixtures, distilled water (80 ml), and Polyvinyl alcohol (PVA) at 1 wt.%, and ZrO_2 balls (diameter of 10 mm) were charged in ZrO_2 bowl (250 ml capacity). The ratio of powder mass to ball mass was 1 to 10. The mixture was milled using a Fritsch P6 planetary ball mill at 180 rpm for 4 hours, as shown in Figure II.2. The obtained slurry mixture was placed in a beaker and then dried at 120 °C for 24 hours (the beaker must be covered with aluminium foil in this process). All the steps are summarized in Figure II.23, which shows the followed protocol for preparing and characterizing the powders and samples.

Table II.1 Chemical composition of Forsterite-Silica (FS_x) powders with varying excess SiO_2 content.

samples	SiO_2 (g)	MgO (g)	Excess SiO_2 (wt.%)
FS_0	42.71	57.29	0
$FS_{1.5}$	43.56	56.44	1.5
FS_3	44.42	55.58	3
$FS_{4.5}$	45.29	54.72	4.5
FS_6	46.14	53.86	6



Figure II.2 Planetary ball mill (Fritch P6) and grinding bowl with zirconia balls.

I.1.6. Preparing sintered samples

FS_x powders were manually ground and sieved through a 100 μm sieve. Then, using a uniaxial press type, they were uniaxially pressed at 100 MPa for 5 min. The samples were compacted in a 13 mm cylinder mold and then heated to a chosen temperature. The process of molding and sintering is shown in Figure II.3.

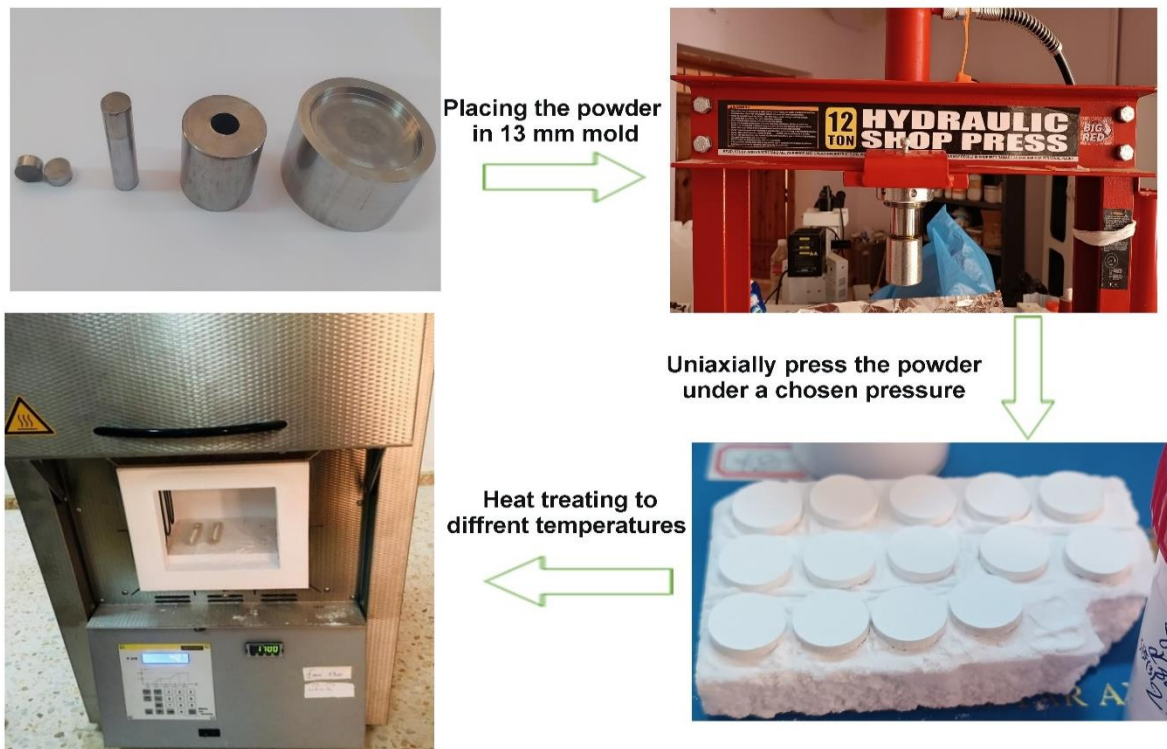


Figure II.3 The process of molding and sintering samples.

II.2. Hydroxyapatite-Forsterite composites (HAF_x) raw materials and methods

II.2.1. Raw materials

Two synthesized powders were used to investigate the effect of forsterite (Mg_2SiO_4) as an additive on hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ properties from natural origin. Hydroxyapatite was synthesized from a natural source (bovine bones) and the previously synthesized forsterite in part one. The prepared hydroxyapatite powder is shown in Figure II.4 as raw materials.



Figure II.4 Prepared natural hydroxyapatite N-HA.

II.2.2. Hydroxyapatite (HA)

Hydroxyapatite (HA), expressed chemically as $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, is a stable and minimally soluble calcium phosphate compound, surpassed in stability only by fluorapatite. It crystallizes in a monoclinic structure at room temperature, transitioning to a hexagonal form above approximately 250°C . The structural understanding of HA gained prominence in 1964 through the work of Kay, Young, and Posner, whose findings included "Posner's clusters," describing energetically favorable $\text{Ca}_9(\text{PO}_4)_6$ groupings. This foundational insight has facilitated HA's application in biomaterials, particularly in orthopedic and dental implants, due to its compositional similarity to human bone and teeth. The historical examination of HA dates back to the 18th century, with Johan Gottlieb Gahn's identification of calcium phosphate in bones in 1769, followed by Carl Wilhelm Scheele's research in 1771. Abraham Gottlob Werner introduced the term "apatite" in 1786 to classify minerals sharing a crystallographic structure, derived from the Greek word "apatao" meaning "to deceive". By the 19th century, Gustav Rose

and his contemporaries identified hydroxyapatite as a distinct form of apatite, advancing its characterization. The early 20th century saw significant progress in HA's crystallography and synthetic production, cementing its role in medical applications like bone grafts and implants [3-5].

II.2.3. Powders preparation

The FS0 equivalent powder used was prepared following the previous method in part one. It was then heat treated at 1400 °C for 2 hours with a heating rate of 5 °C/ min in a furnace (Nabertherm 30- 3000 °C) to ensure the formation of a pure forsterite phase, which was confirmed by XRD analysis of the powder in chapter 3, part 1. The powder was manually ground and sieved through a 100 µm sieve.

A natural-origin hydroxyapatite powder was prepared using bovine bones (stripped of bone marrow). The bones were crushed into small pieces and heated up to 800 °C for 2 hours with a heating rate of 5 °C/ min to ensure the removal of organic materials and fats, then manually ground and sieved through a 100 µm sieve. The accomplished powder was pure hydroxyapatite, confirmed by XRD and FT-IR analyses in Chapter 3, part 1. Figure II.5 shows the flowchart for a similar natural hydroxyapatite preparation process.

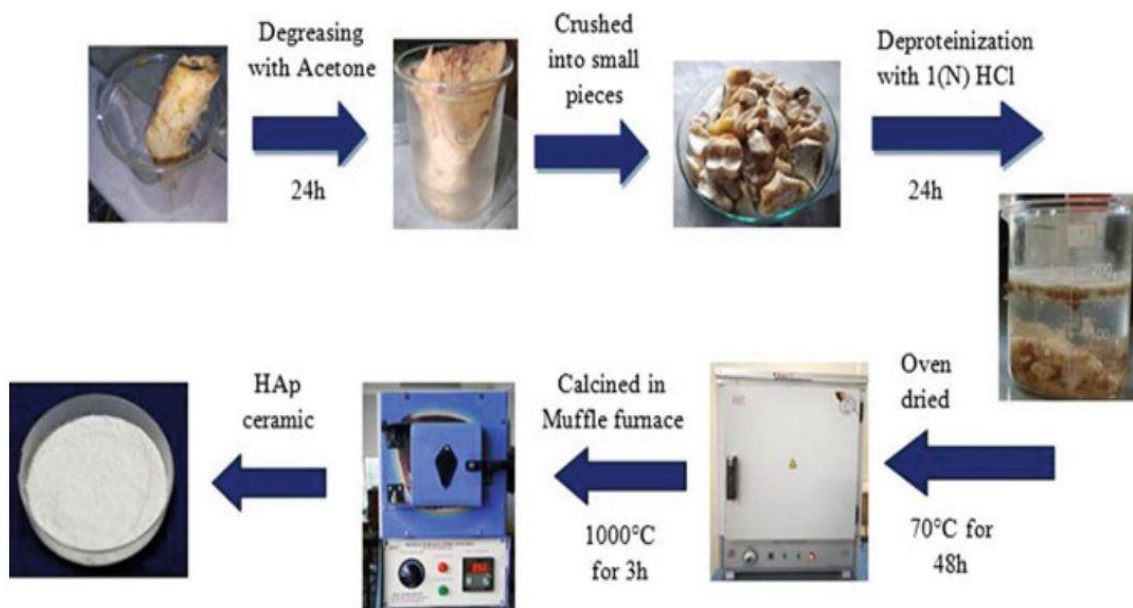


Figure II.5 Flowcharts to prepare natural hydroxyapatite N-HA [6].

Hydroxyapatite-Forsterite composites powders HAF_x , where $x = 0, 10, 20$ (x : the weight percentage (wt.%) of initially used forsterite, HA and F as hydroxyapatite and forsterite powders, respectively.). Forsterite and hydroxyapatite powders were milled according to Table 2 weights with 17 ml of distilled water using a planetary ball mill (Fritsch P6) for 4 hours at a rotation speed of 250 rpm with 10 min rest every 30 min round; the slurry mixture was poured to a beaker (covered with aluminum foil) and dried at 120 °C for 24 hours in furnace, then manually ground and sieved in 100 μm sieve.

Table II.2 The chemical composition of the HAF_x prepared powders.

HAF_x	HA (g)	F (g)	Total mass (g)
HAF_0	10	0	10
HAF_{10}	9	1	
HAF_{20}	8	2	

II.2.4. Preparing sintered samples

HAF_x powder was manually ground and sieved through a 100 μm sieve. Two drops of water were mixed with the powder, then uniaxially pressed at 100 MPa for 5 min. The samples were compacted in a 13 mm cylinder mold and then heated up to the chosen temperatures.

III.3. Characterization techniques and equipment

III.3.1. Thermal Analysis and Calorimetry (TGA/DSC/DTA)

TG/DSC/DTA are the most commonly used techniques in thermal analysis (TA) to provide information about a material (properties such as thermal capacity, mass changes, enthalpy, and the coefficient of heat expansion). Thermogravimetry TGA measures the weight change of materials (ceramics, metal, and polymers) as a function of temperature or as a function of time isothermally under a few conditions, including environment (using various gases like nitrogen, helium, and air), powder weight over 25 mg and heating rate about 1- 50 °C/ min, such technique can also measure evaporation rate and decomposition reactions weight. DTG the derivative

weight loss curve as function of temperature or time can provide us with qualitative and quantitative information about the powder like the most apparent weight loss. Differential Scanning calorimetry (DSC) measures the required heat input to change the sample temperature (heating, cooling or isothermally), the word differential is used referring to the measurement with respect to a standard reference as illustrated in Figure II.6, DSC mainly measures heat flow as a function of temperature and time which allow researchers to identify different phase transitions, in heat flow curve the endotherms transitions (negative temperature differential) are pointing downward while the exothermal transitions point upward. DTA works in the same principle as DSC analysis, while DTA maintains Δt as a microvolt signal [7-10].

To identify and determine the phase transformation for FS_x and HAF_0 powders synthesized in our work, thermal analysis using LABSYS Evo DTA/DSC-TG SETARAM 1600 °C equipment (TG/DTG and DSC) shown in Figure II.7 was used.

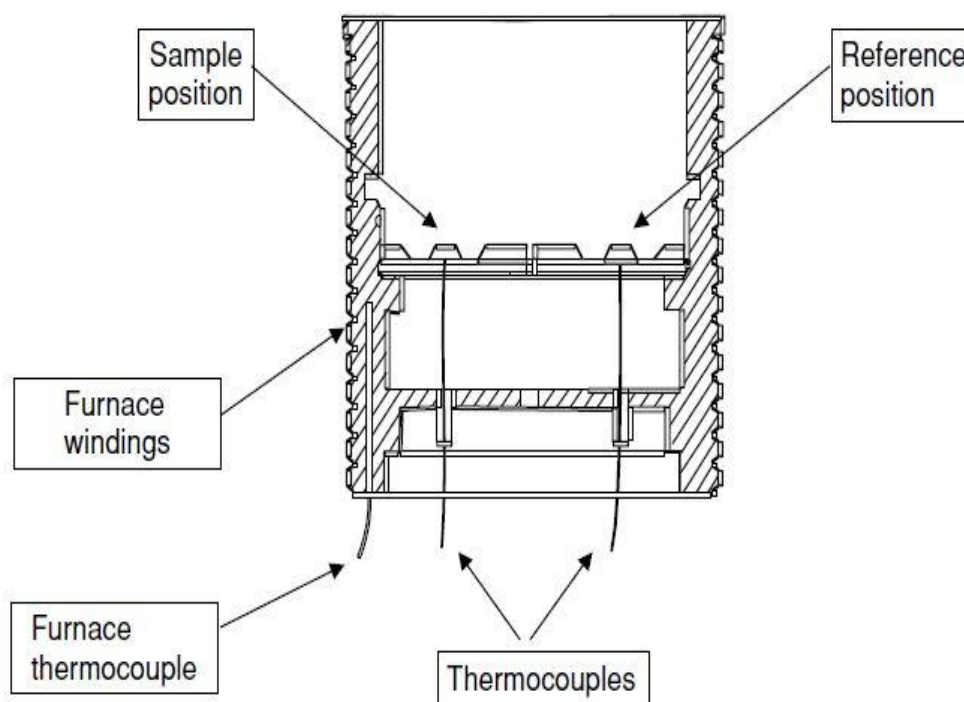


Figure II.6 Diagram of a heat flux DSC system [7].

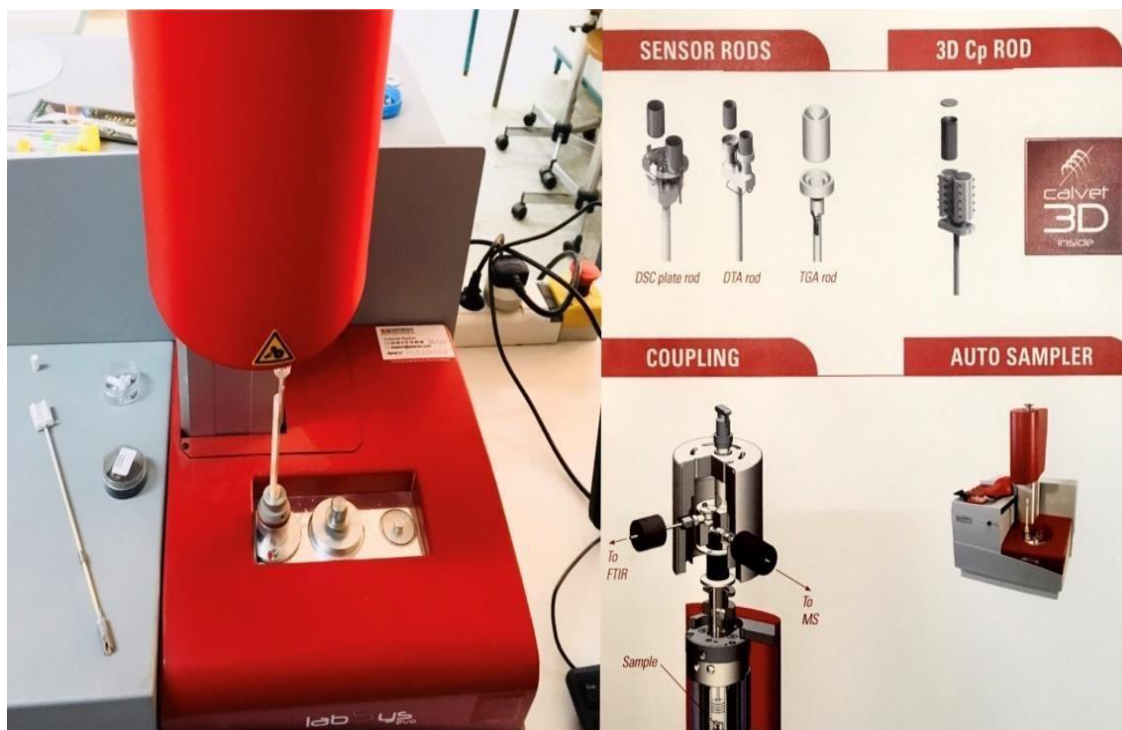


Figure II.7 LABSYS Evo DTA/DSC-TG SETARAM 1600 °C equipment (univ of M'sila).

III.3.2. Dilatometry (DL)

Dilatometry is a technique used to measure the thermal expansion of materials by observing the length change of a sample as it is subjected to controlled temperature variations, the dilatometry equipment used is shown in Figure II.8. The method involves using a pushrod to transmit the displacement of the expanding sample to a Linear Differential Variable Transformer (LVDT), which converts the mechanical movement into a voltage signal that is recorded and processed by specialized software. This allows precise monitoring of the sample's elongation as a function of temperature. The equipment used in dilatometry includes a dilatometer apparatus equipped with an LVDT, a sample holder, and a furnace for heating the sample, as shown in Figure II.9. Netzsch DIL 402 ES dilatometer system also incorporates a Thermal Analysis System Controller (TASC) to connect the dilatometer to the measurement software, a coolant system to maintain the LVDT at a constant temperature (25°C), and a vacuum pump for removing oxidizing gases. The entire system is managed through a CPU that logs and processes the collected data [11, 12]. FS_x powders and samples were analyzed using a Netzsch DIL 402 ES dilatometer. CTE of FS_x was also determined in the range of [200- 1300 °C].

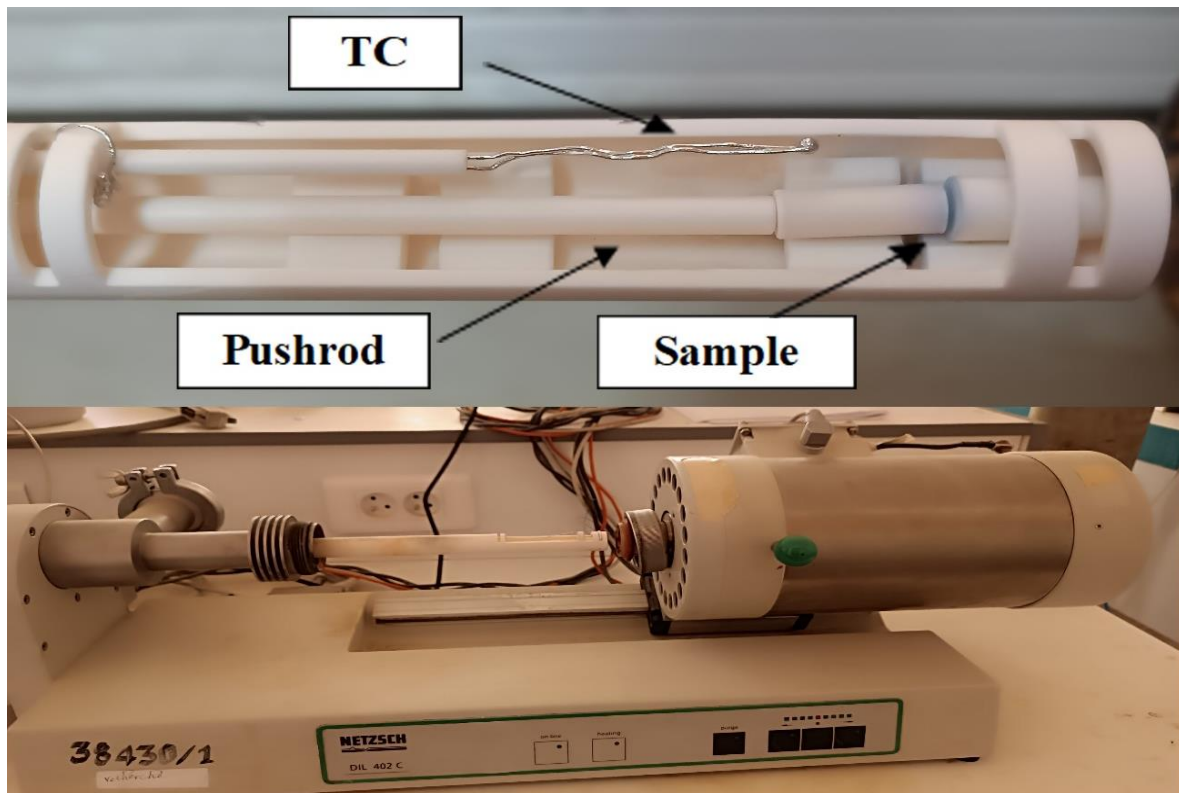


Figure II.8 Netzsch DIL 402 C dilatometry (DL) equipment and close-up view of the sample holder (univ of M'sila).

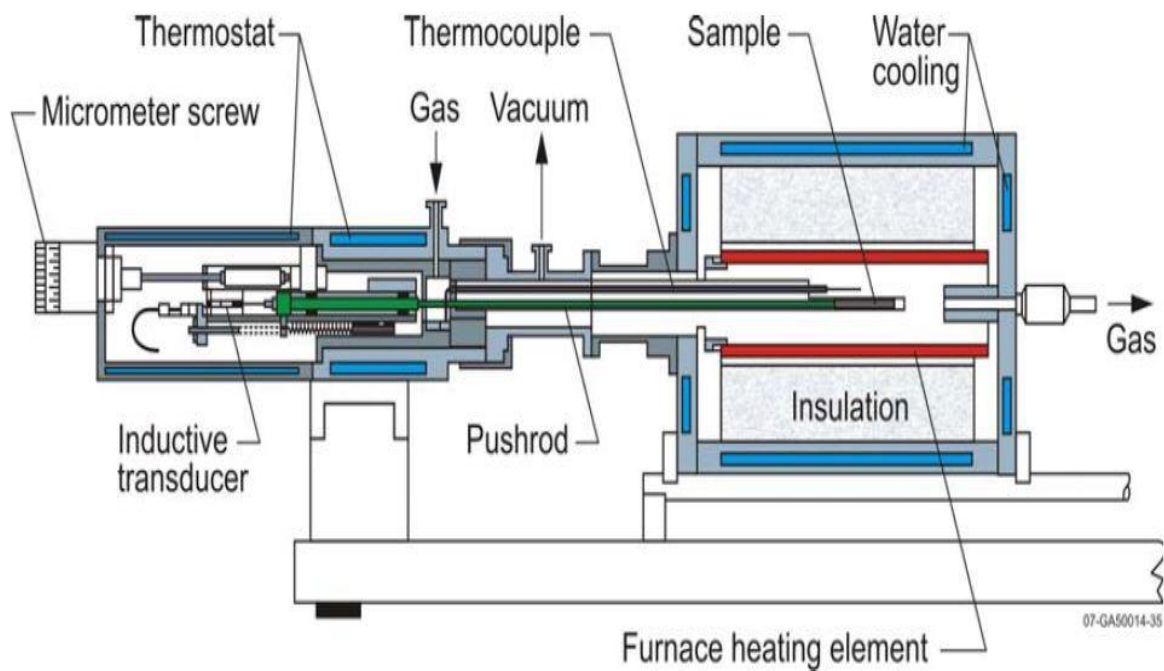


Figure II.9 Schematic of dilatometer in horizontal configuration [12].

III.3.3. X-ray Diffraction (XRD)

X-ray diffraction is a non-destructive means of determining crystalline structure, studying phase equilibria, determining the orientation of crystals, and measuring particle size. The technique of x-ray diffractions at the beginning was linked to the German physicist Von Laue's (1879-1960) discovery in 1912, which stated that x-rays diffract by means in crystals if the interatomic distance in crystals were equal to the wavelength of x-rays electromagnetic waves, later on, an English physicist W. L. Bragg expressed necessary conditions for diffraction to occur and formulated what is known today as the Bragg's law (Eq. II.1):

$$2. d \sin \theta = n\lambda \quad (\text{II.1})$$

Where d is the spacing between the planes in the atomic lattice, θ is the angle between the incident ray and the scattering planes, n is an integer determined by the diffraction order, and λ is the x-ray wavelength, as demonstrated in Figure II.10 [13-15].

X-rays diffraction were used to analyze the raw materials and FS_x and HAF_x composites samples and powders, which are presented as spectra (diffracted intensity I as a function of scattering angle 2θ), provided by an X'Pert Pro x-ray diffractometer with $\text{CuK}\alpha$ radiation at 40 kV, 30 mA, and 2θ ranging from 10°C to 80°C , Figure II.11 and II.12 shows the used X'Pert Pro x-rays diffractometer and its parts. Phases identification of XRD patterns was accomplished by comparing them with reference cards within a COD (Crystallographic Open Database) containing the diffraction patterns of known crystals [16].

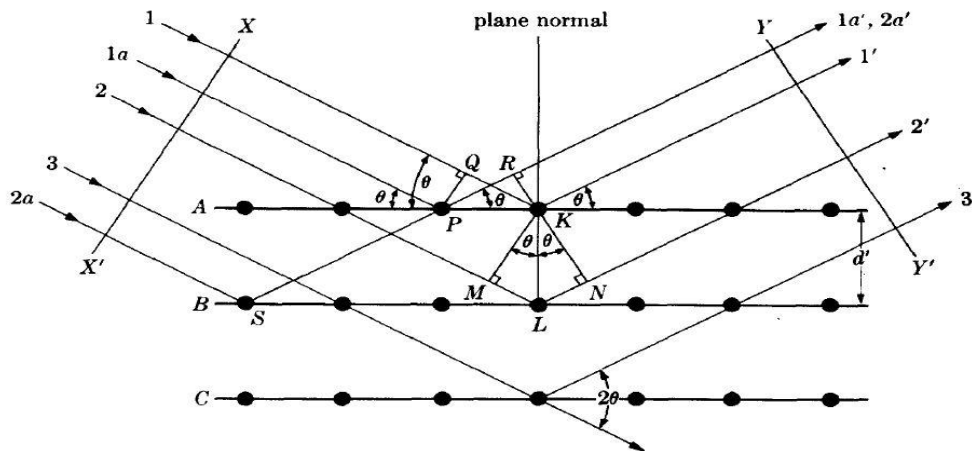


Figure II.10 Diffraction of X-rays by a crystal [13].

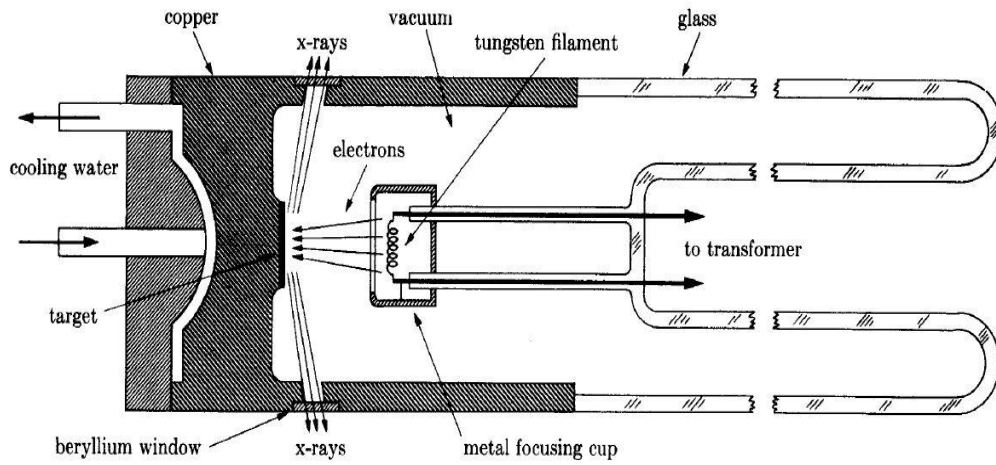


Figure II.11 Cross section of X-rays tube [13].



Figure II.12 X-ray diffractometer (X'Pert Pro, Analytical) (univ of M'sila).

The crystallite size was calculated from the X-ray diffractograms using the Scherrer equation (Eq. II.2) [17]:

$$D = \frac{K\lambda}{\beta_{1/2} \cos(\theta)} \quad (\text{II. 2})$$

Where D represents the crystallite size, K is the dimensionless shape factor set to 0.9, λ denotes the X-ray wavelength, θ is the diffraction angle in radians, and $\beta_{1/2}$ is determined using Eq. II.3 [18]:

$$\beta_{1/2} = \sqrt{B^2 - b^2} \quad (\text{II. 3})$$

Where B represents the diffraction peak width at half maximum, and $b = 0.065$ denotes the instrument's intrinsic width. Using the Scherrer equation, SiO₂, MgO nano oxide, forsterite, and hydroxyapatite crystalline size was determined.

III.3.4. Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) is a versatile technique used to obtain high-resolution and detailed imagery for selected sample surfaces compared to optical microscopy. Such type of analysis uses a focused accelerated electron (1 KeV- 30 KeV) beam (1- 20 nm diameter) to scan and then create an image of the specimen surface, as shown in Figure II.13. The produced signals collected using specialized detectors (detectors such as backscattered electron detector (BSD) and secondary electron detector (SED)) are used to provide high-resolution imagery. The signals detected with the aid of an external computer help in forming images and collecting various information like the surface's elements composition and topography [8, 19-21]. This thesis used the SEM (QUANTA 250 FEG-FEI) shown in Figure II.14 to study the microstructure of samples.

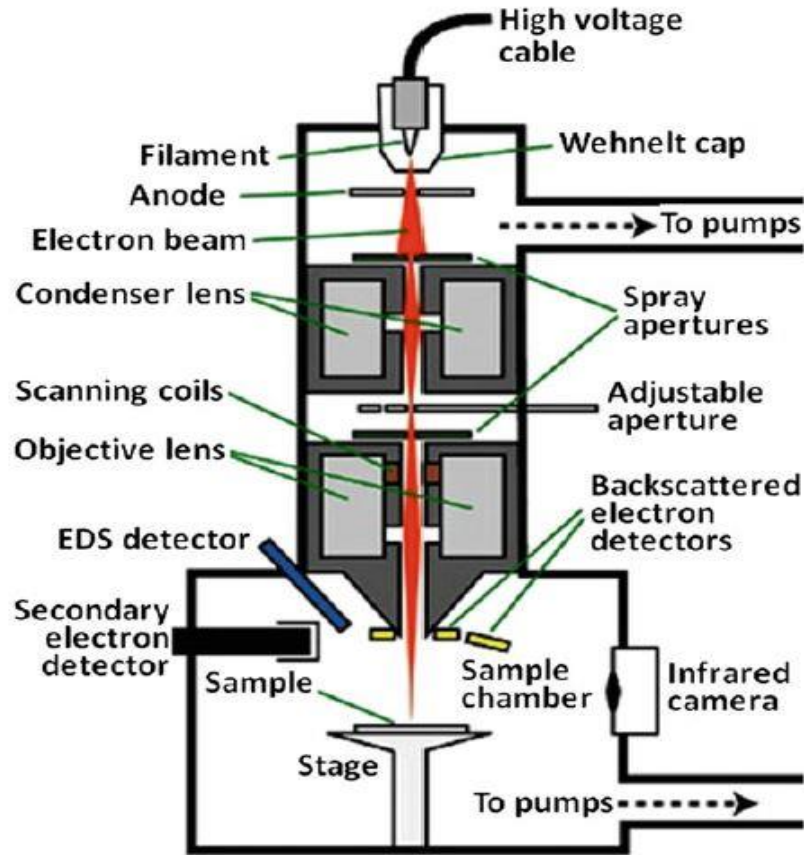


Figure II.13 Scanning electron microscopy (SEM) schematic with other detectors [20].

III.3.5. Energy Dispersive Spectroscopy (EDS)

Understanding that the unique electrons transition between different energy levels inside different element atoms can be used to characterize materials. EDS or EDX can be coupled with scanning electron microscopy. EDS measures the energy of the characteristic x-ray spectrum emitted by the material; these X-rays are produced when a primarily focused electron beam (sufficient to knock electrons off from the inner layer in atoms) bombards the sample. To convert the x-ray energy to voltage signals, a detector is used; by displaying selected x-ray line intensity, the chemical composition and elements distribution of the sample can be determined [8, 22].



Figure II.14 Scanning electron microscopy (SEM) combined with Energy Dispersive Spectroscopy (EDS) (univ of Bejaia).

III.3.6. Fourier Transformation Infrared Spectroscopy (FT-IR)

Fourier transform infrared spectroscopy or FT-IR analysis is the most common technique in infrared spectroscopies, used to obtain an infrared spectrum of absorption or emission of a solid, liquid, and gas, identify various materials (organic, polymeric, and inorganic), and observe chemical properties. FT-IR equipment is usually composed of a few components, including an IR

radiation source, interferometer, sample holder, detector, analog-to-digital converter, and a separate computer. FT-IR instruments use infrared (IR) light beams about 10000 to 100 cm^{-1} through the sample; the absorbed infrared radiation induces vibrations like stretching or bending in the sample molecules that produce unique signals (depending on bonds and group functions), then reach the detector. The amplified signal is converted and transferred to the computer for Fourier transformation. A spectrum representing the molecular fingerprint of the sample, usually about 4000 to 400 cm^{-1} , is accomplished, making chemical identification possible [9, 23, 24]. Figure II.15 demonstrates the light path through the DialPath accessory.

The chemical identification and functional groups for SiO_2 , MgO nano oxide, forsterite, and hydroxyapatite powder were determined from the spectrum (wavelength range of 2000- 400 cm^{-1}) using Agilent Cary 630 Fourier transformation infrared spectroscopy (FTIR) equipment shown in Figure II.16.

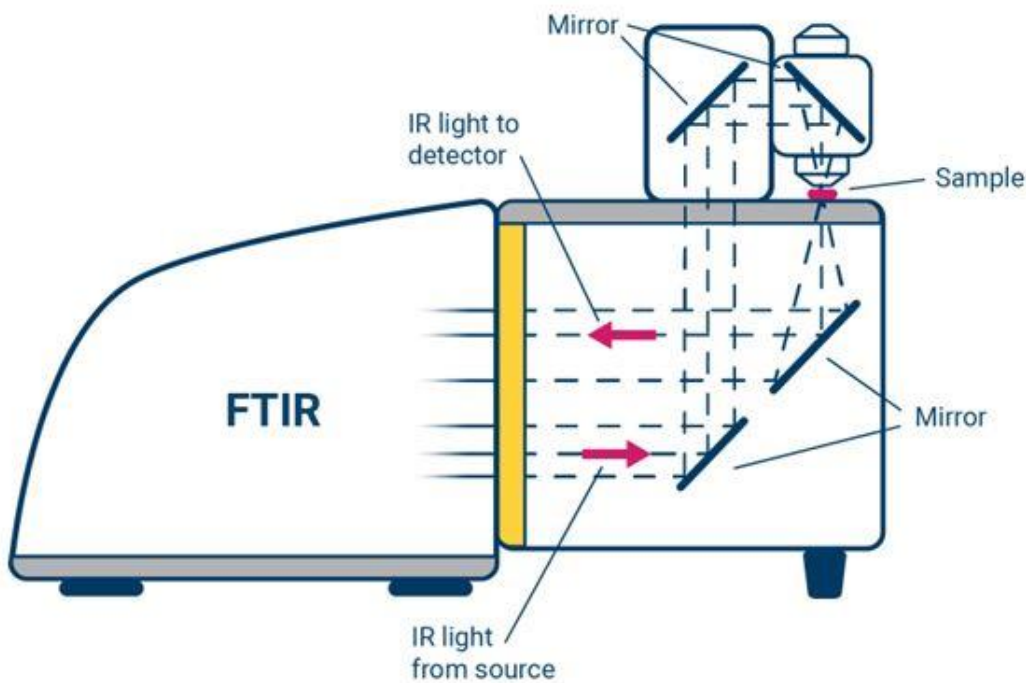


Figure II.15 An optical diagram of the light path through the DialPath accessory and the Cary 630 instrument.



Figure II.16 Agilent Cary 630 FTIR equipment (univ of M'sila).

III.3.7. Measurement of density

In Archimedes' method, the sample volume is estimated when submerged in liquid, usually distilled water, and by applying Archimedes' principle for materials with pores, it is possible to determine the density and the open porosity of the sample by following this protocol and Eqs. II.4, II.5 and II.6:

1. Weighting the sintered samples in air (m_1).
2. weighting the samples in distilled water (m_2) after submerging the samples in distilled water inside a flask while removing the air from the flask using air pump resulting in filling the open pores in the sample with distilled water
3. weighting the samples filled with water in the air (m_3)

$$\rho_{app} = \frac{m}{V_T} = \frac{m_1}{m_2 - m_3} \times \rho_{H_2O} \quad (II.4)$$

$$\rho_{bulk} = \frac{m_1}{m_1 - m_3} \times \rho_{H_2O} \quad (II.5)$$

$$X_{V_{po}} \% = \frac{V_{po}}{V_T} \times 100 = \frac{m_2 - m_1}{m_2 - m_3} \times 100 \quad (\text{II. 6})$$

Where ρ_{app} is the apparent density, ρ_{bulk} is the bulk density, ρ_{H_2O} is water density (1 g/cm³), V_T is the total volume, and $X_{V_{po}}$ is the open porosity percentage [25]. FS_x and HAF_x samples density and open porosity were measured using the tools in Figure II.17.



Figure II.17 The tools used in determining the density and open porosity (Univ of M'sila).

III.3.8. Vickers Micro-hardness (HV) test

Vickers microhardness test is one of the mechanical properties developed by **L. Smith** and **G. E. Sandland** that is presented as the resistance to permanent deformation (plastic deformation) by making an indentation on the polished flat surface of the sample. Certain conditions should be considered during the test to guarantee reliable results, including no cracking caused by the indenting load around the indentation; in the case of testing new ceramic composition, the test by various loads is necessary to estimate the true hardness. Vickers hardness test requires the calculation of the indentation size following Eq. II.7:

$$H_V(\text{GPa}) = 1.8544 \times \frac{P}{d^2} \quad (\text{II. 7})$$

H_v is Vickers microhardness, P is the applied load, and d is the average length of two diagonals [26-28]. To determine Vickers microhardness for polished sintered samples, Zwick Roell Indentec equipment was used, as shown in Figure II.18, applying 300 g of indentation load held for 10 s. To ensure accuracy, various measurements were taken for FS_x and HAF_x samples.

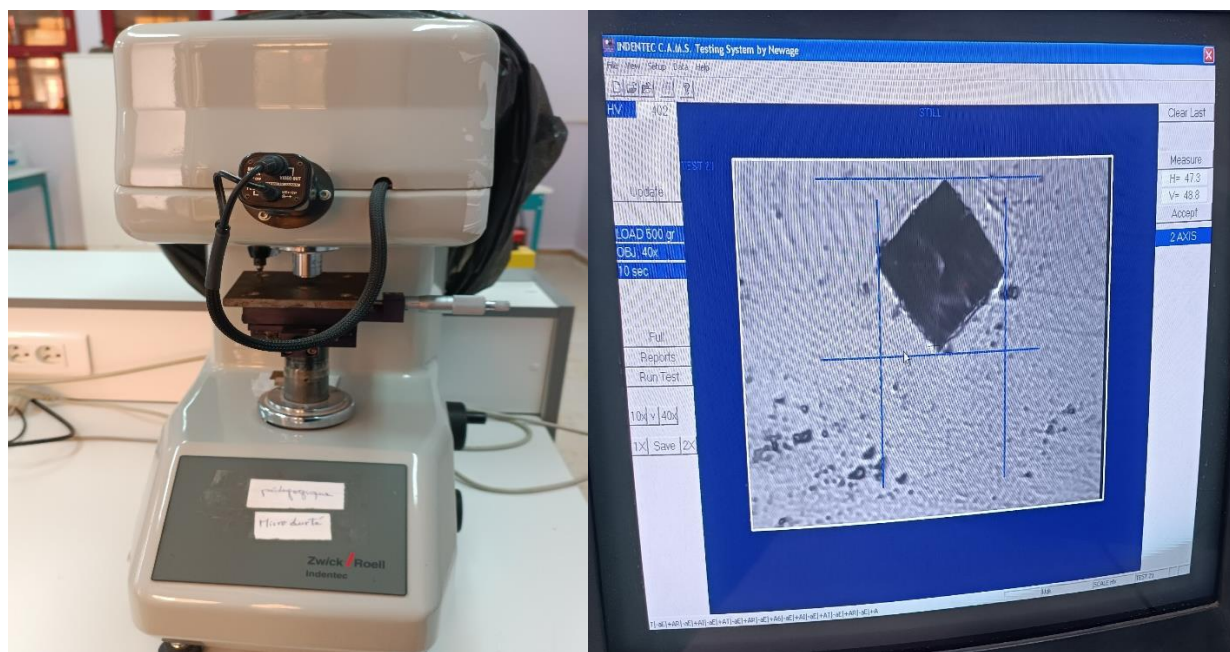


Figure II.18 Zwick Roell Indentec equipment and its indentation mark (univ of M'sila).

III.3.9. Antibacterial activity analyses

III.3.9.1. Materials

FS_x and HAF_x powders were used as the primary test materials, prepared at concentrations of 4 mg/mL and 8 mg/mL for some tests. Disk-shaped samples of these powders were also fabricated for specific tests. Ciprofloxacin (CIP) and Pefloxacin (PEF) were included as positive controls. Dimethyl sulfoxide (DMSO) was used as a solvent for certain applications.

III.3.9.2. Bacterial Strains

The antibacterial activity was tested against four bacterial strains: *Staphylococcus aureus* (S.C.), *Escherichia coli* (E.C.), *Pseudomonas aeruginosa* (*Pseudomonas*), and *Bacillus subtilis* (*Bacillus*). These strains were selected to represent both Gram-positive and Gram-negative bacteria.

Pathogenic bacteria of different Gram bacteria were prepared by diluting a broth culture to match a 0.5 McFarland turbidity standard. The bacterial solution was placed on Mueller-Hinton agar plates using a sterile cotton swab.

III.3.9.3. Pre-Test Preparation

The FS_x and HAF_x were sterilized using a Biological Safety Cabinet (BSC) under ultraviolet (UV) light for 30 min to eliminate potential bacterial contamination. Figure II.19 shows the UV sterilization setup.

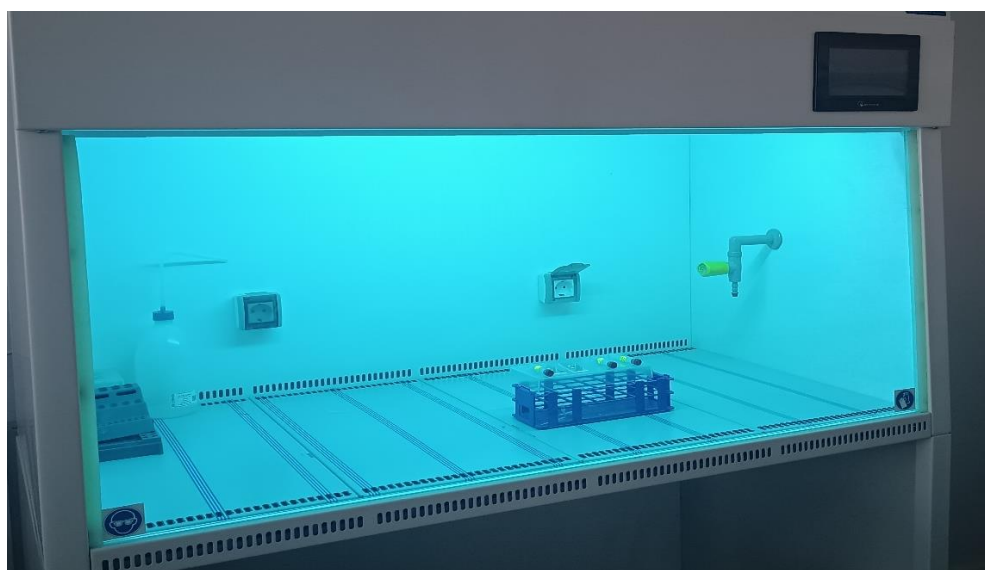


Figure II.19 BIO II PML 0150 Biological Safety Cabinet (BSC) (University of Msila).

III.3.9.4. Antibacterial Testing Methods

The following methods were employed:

III.3.9.4.1. Disk Diffusion Method

Disk-shaped samples of FS_x and HAF_x were placed directly on agar plates inoculated with the bacterial strains. The plates were incubated in a Memmert incubator at 37°C for 24 hours. The disk diffusion process is described schematically in Figure II.20.

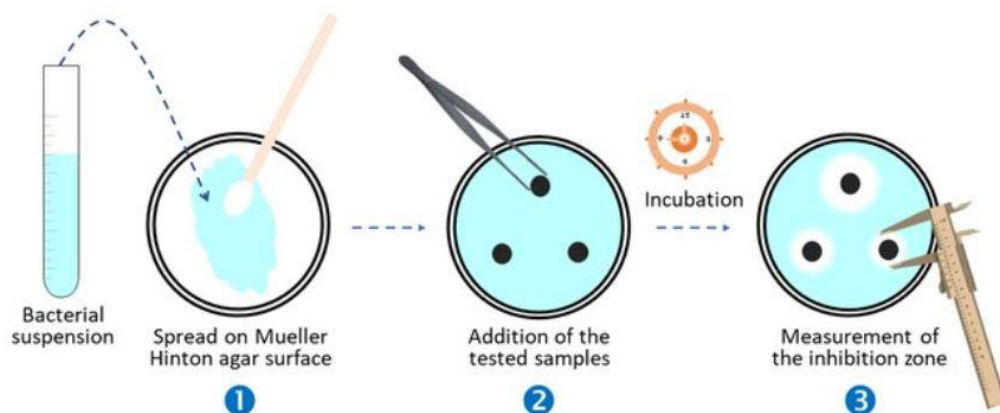


Figure II.20 Schematic representation of the disk diffusion method of Kirby and Bauer [29].

III.3.9.4.2. Well Diffusion Method

The sterilized powders were dissolved in 1mL of DMSO at respective concentrations and placed in wells on agar plates pre-inoculated with the bacterial strains. The antibacterial study of the composites was conducted twice ($n = 2$) to ensure accurate reading. Ciprofloxacin and Pefloxacin served as positive controls. The plates were incubated at 37°C for 24 hours. Figure II.21 shows a schematic of the well diffusion process.

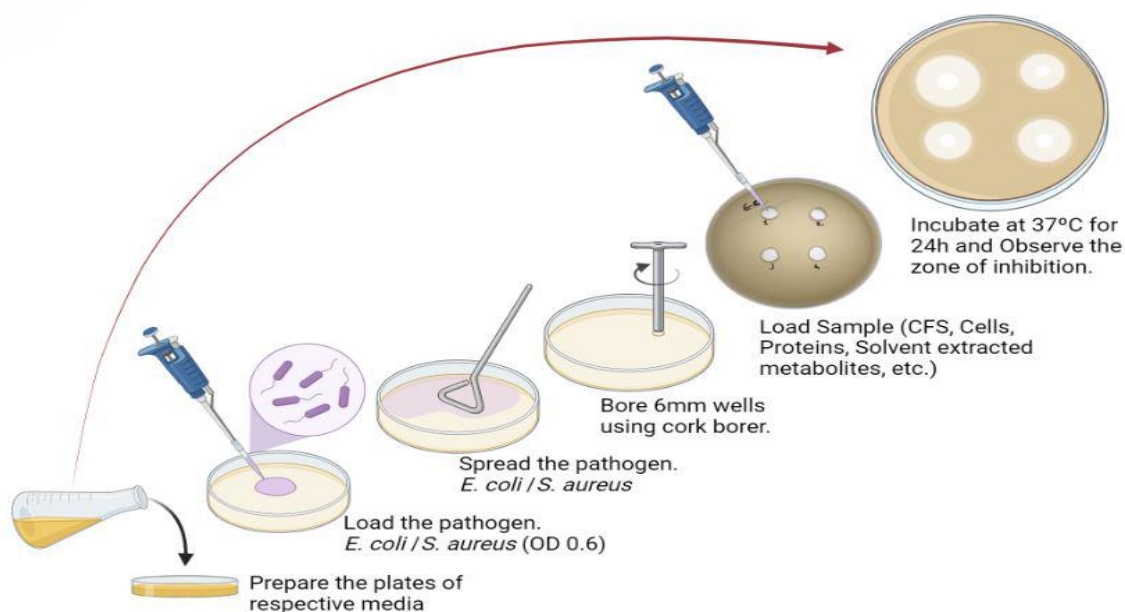


Figure II.21 Schematic of Well diffusion assay for antimicrobial test [30].

III.3.9.4.3. Dilution Method

The Minimum Inhibitory Concentration (MIC) is the lowest antimicrobial concentration that stops visible microbial growth. The Minimum Bactericidal Concentration (MBC) is the lowest concentration that kills 99.9% of bacteria, preventing growth on antibiotic free media. The MIC and MBC were determined using a serial dilution technique. The powders and antibiotics were prepared at four concentrations: 0.5 mg/mL, 1 mg/mL, 2 mg/mL, and 4 mg/mL.

III.3.9.5. Determination of MIC and MBC

The MIC was defined as the lowest concentration, showing no visible bacterial growth. The MBC was confirmed by subculturing samples from MIC wells onto fresh agar plates and incubating them at 37 °C for 24 hours. The MBC was identified as the lowest concentration at which no bacterial colonies were observed. Figure II.22 shows the process of dilution technique and determining MIC and MBC.

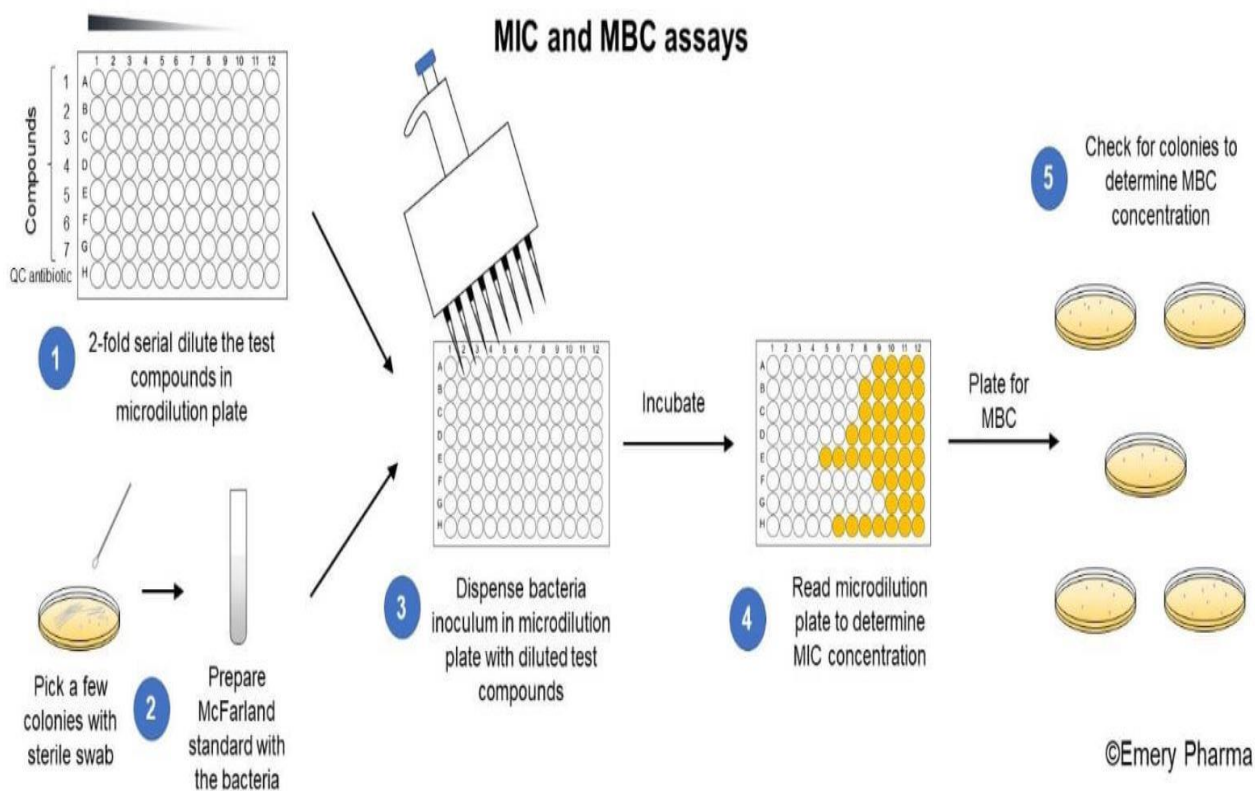


Figure II.22 Schematic of dilution technique, MIC, and MBC assay [31].

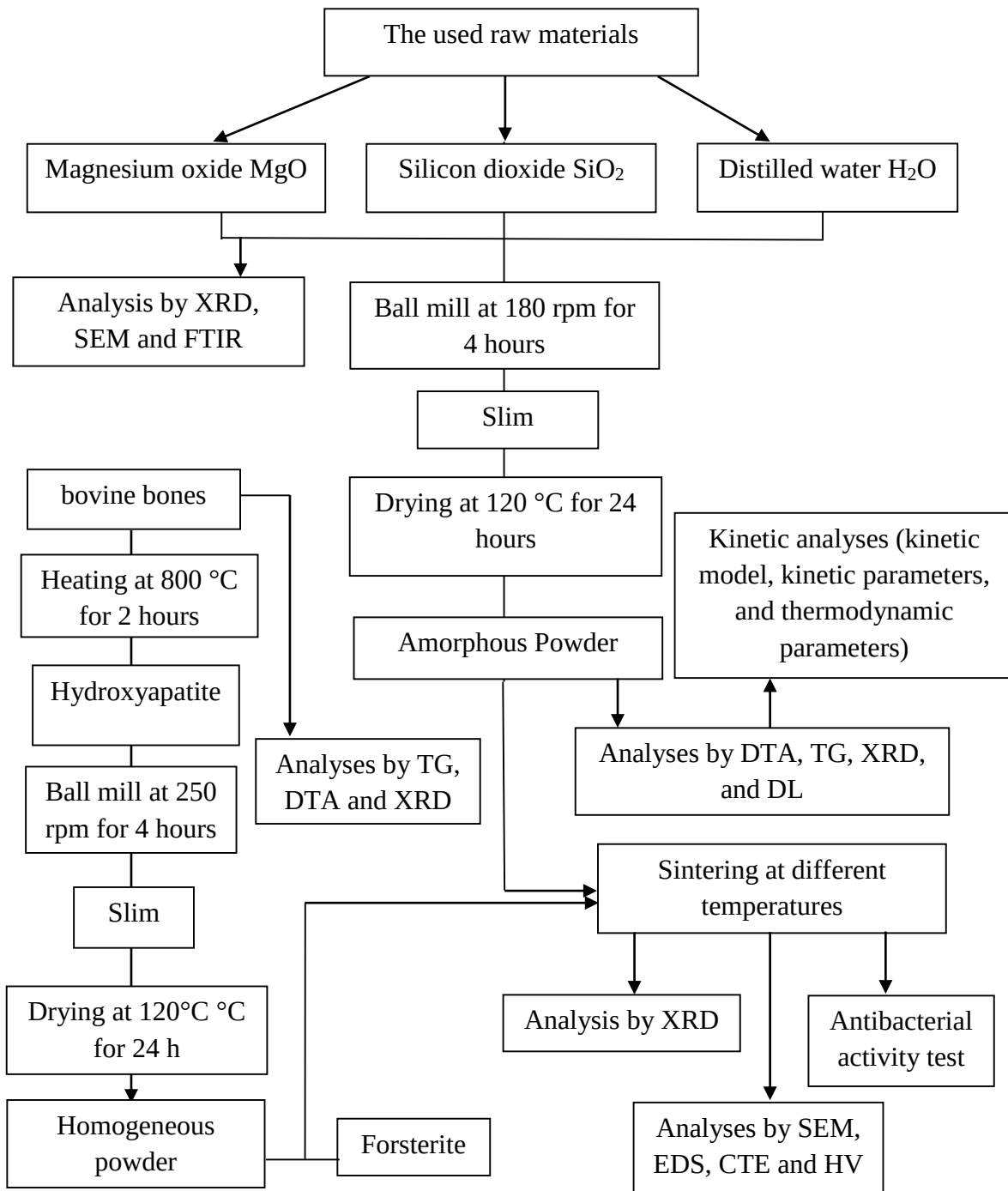


Figure II.23 The followed protocol for preparing and analyzing powders and samples.

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Chapter Three: Results & Discussion

Part One: *An analytical study* of the raw materials used

This part of the thesis describes the analyses of raw materials utilized to prepare Forsterite-Silica composites (FS_x) in different ratios ($x = 0, 1.5, 3, 4.5$, and 6 wt.%) and also to prepare hydroxyapatite- forsterite composites (HAF_x) in different ratios ($x = 0, 10$, and 20 wt.%). The raw materials were comprehensively characterized using the following:

Scanning electron microscopy (SEM) was employed to examine the microstructural features, while X-ray Diffraction (XRD) analysis was used to identify the crystalline phases. Fourier Transformation Infrared Spectroscopy (FT-IR) was performed to evaluate the vibrational modes of functional groups and identify bonding characteristics in the material. Additionally, the particle size distribution of the raw materials was analyzed to ensure consistency in the composite preparation process.

I.1. Physicochemical and morphological analyses of the initial materials

To identify the raw materials (SiO_2 , MgO nano-oxides used in part two forsterite–silica composites (FS_x) and Natural hydroxyapatite and forsterite used in part four hydroxyapatite-forsterite composites HAF_x) used in this study and its morphology. An X-ray diffractometer (operating at 40 KV, 30 mA, with $CuK\alpha$ radiation and wavelength of 0.15418 nm) was used for phase analysis with High-Score plus software (COD database 2023). Fourier transform infrared spectroscopy or FT-IR equipment (operating in the range of 400 cm^{-1} to 4000 cm^{-1}) is used to detect function groups in both crystallized and amorphous phases. A FEG-FEI field emission scanning electron microscope (FESEM) equipped with energy dispersive spectroscopy (EDS) was used to examine the microstructure of the powder and determine the grain size distribution with ImageJ software.

I.1.1. Magnesium oxide (MgO)

I.1.1.1. XRD and FT-IR analyses

Figures III.1 (a) and (b) present the MgO nano-oxide powder's XRD and FT-IR spectra. In Figure III.1 (a), the XRD spectra reveal that the magnesia exhibits clear and high-intensity diffraction peaks corresponding to the periclase phase only with XRD data file no. [900-6786]. To confirm the purity of MgO oxide from any amorphous impurity by the manufacturer. Figure III.1 (b) shows the FT-IR spectrum. The band observed at 850.27 cm^{-1} is associated with $Mg-O$ bending

vibrations, similar to those reported in the literature [1]. While the distinct peaks at 1417.55 cm^{-1} and 1479.78 cm^{-1} are correspond to the hydroxyl groups (Mg-OH) vibrations. The band at 3698.83 cm^{-1} is attributed to OH stretching vibrations of the water molecules. These findings confirm the presence of highly pure MgO oxide particles, which aligns with previous studies by **A. Behnami** et al. and **M. Kandiban** et al. [2, 3].

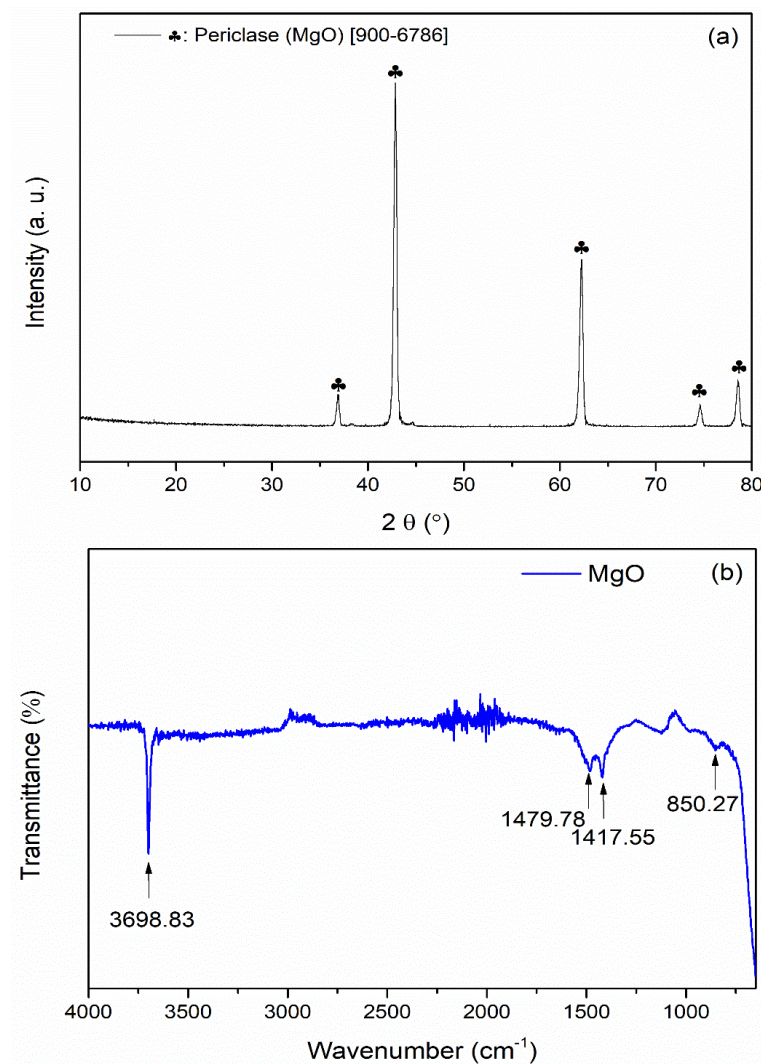


Figure III.1 (a) XRD and (b) FT-IR spectra of MgO nano-oxide powder.

I.1.1.2. Morphological observation

Figures III.2 (a) and (b) present FE-SEM images of MgO nano-oxide powder and its grain size distribution. As shown in Figure III.2 (a), the MgO nanoparticles exhibit a nearly spherical morphology and a relatively uniform size distribution. The particle sizes range from 50 to 80 nm,

with a peak frequency observed at 65 nm, as depicted in Figure III.2 (b). The SEM images indicate that the MgO nanoparticles possess a large active surface area, with most particles measuring below 70 nm.

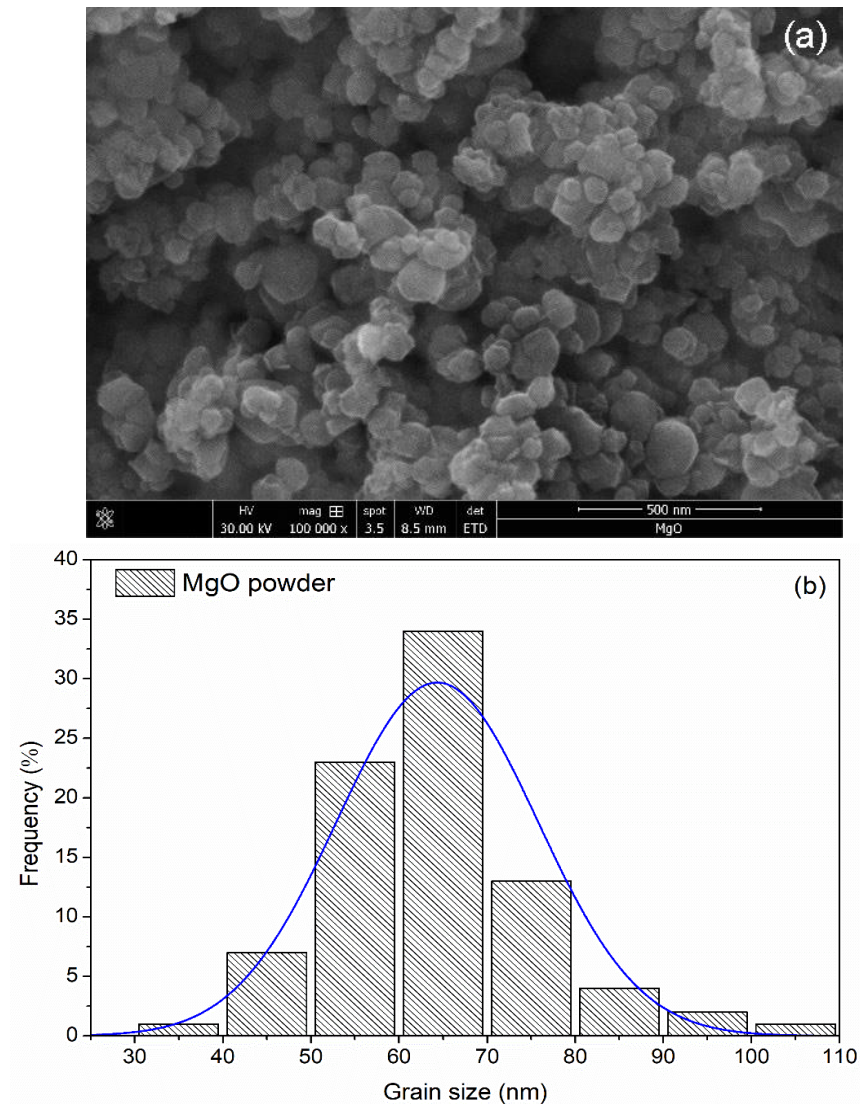


Figure III.2 (a) SEM image and (b) gain size distribution of MgO nano-oxide powder.

I.1.2. Silicone dioxide (SiO₂)

I.1.2.1. XRD and FT-IR analyses

Figures III.3 (a) and (b) display the XRD and FT-IR spectra of the SiO₂ oxide nanopowder. Figure III.3 (a) shows that XRD spectra exhibit a broad diffraction peak of amorphous silica, visible in the 2θ range between 15 and 30 degrees. Figure III.3 (b) provides detailed information

on the functional groups present. As we notice, the 447.9 cm^{-1} and 1063.5 cm^{-1} bands were attributed to Si-O-Si bending vibrations. 802 cm^{-1} and 1636.6 cm^{-1} bonds are Si-O-Si symmetric vibration, and 979 cm^{-1} bond is assigned to Si-OH stretching vibrations. These results for the existence of bonds confirmed the pure SiO_2 oxide particles, as reported by **R. Dong** et al. and **T. Tran** et al. [4, 5].

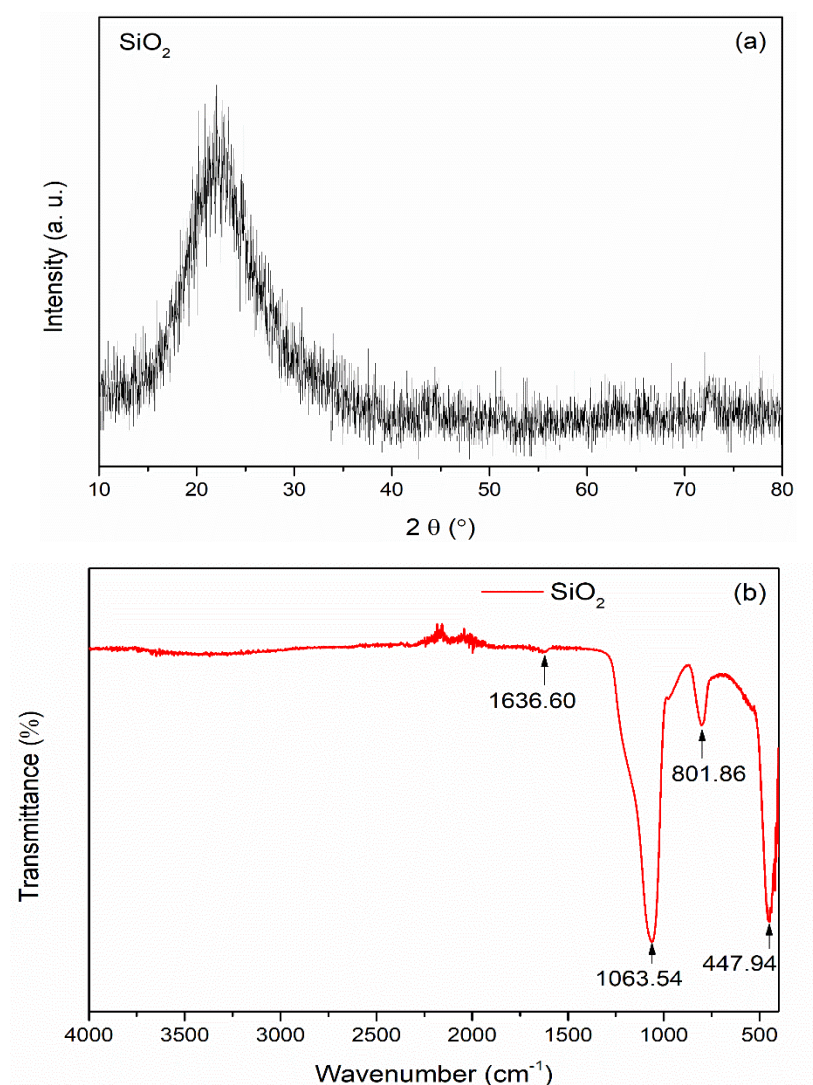


Figure III.3 (a) XRD and (b) FT-IR spectra of SiO_2 nano-oxide powder.

I.1.2.1. Morphological observation

FE-SEM images of SiO_2 nano-oxide powder are shown in Figure III.4 (a) and (b), respectively. Figure III.4 (a) shows a spherical morphology and homogenous size distribution of SiO_2

nanoparticles. The spherical particles have a size distribution ranging between 20 and 40 nm with a higher frequency at 27 nm, as seen in Figure III.4 (b). The SiO_2 nanoparticles, as observed in the SEM images, provide a large active surface area and enhance chemical reaction, diffusion, and homogeneity [6].

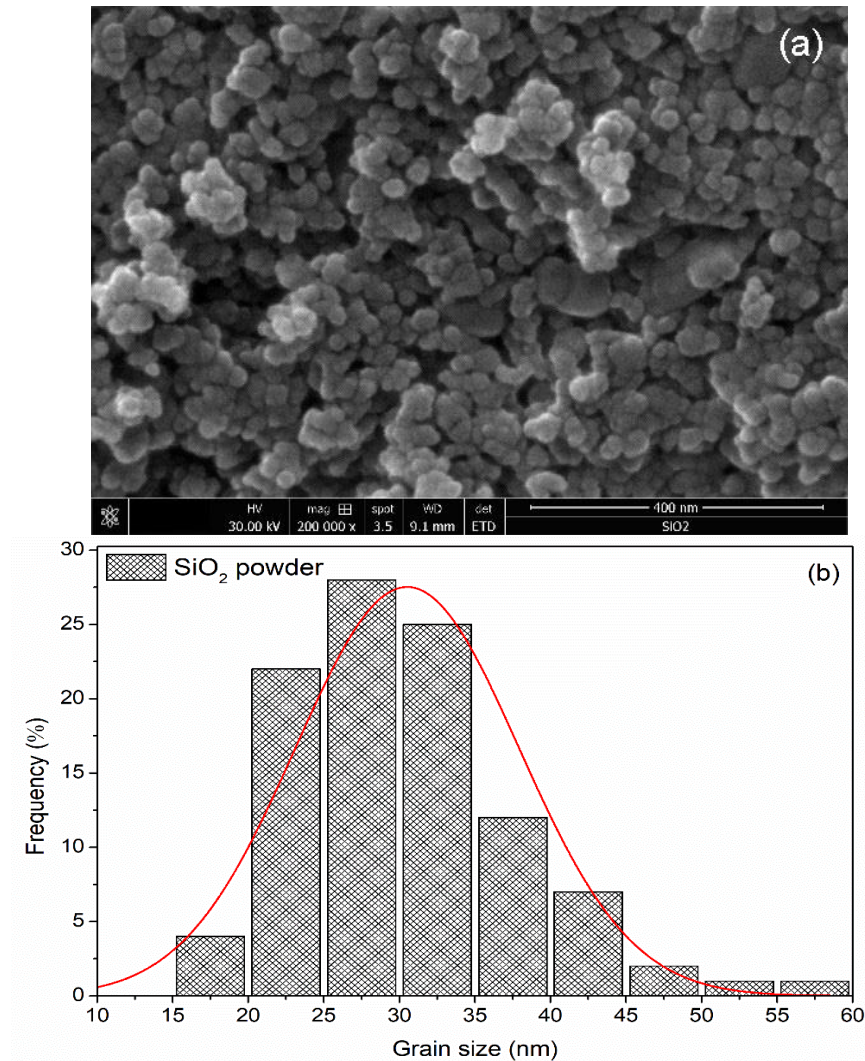


Figure III.4 (a) SEM image and (b) grain size distribution analyses of SiO_2 nano-oxide powder.

I.1.3. Natural Hydroxyapatite (N-HA)

I.1.3.1. XRD and FTIR analyses

The natural hydroxyapatite (HAF_0) powder was synthesized and subjected to heat treatment up to 800 °C, followed by XRD and FT-IR spectroscopy analyses. Figures III.5 (a) and (b) present

XRD and FT-IR spectra of the prepared natural hydroxyapatite powder. In Figure III.5 (a), the XRD spectra show clear intensity diffraction peaks of the crystallized hydroxyapatite phase with XRD data file no. [009-0432]. The FT-IR spectra of hydroxyapatite are shown in Figure III.5 (b). The bands at 3570, 871, and 630 cm^{-1} are associated with the stretching and vibration modes of the OH group. The bands at 475, 560.6, 598, 954, 1020, 1069, and 1099 cm^{-1} are associated with the tetrahedral PO_4^{3-} bending vibration. The band at 1407 cm^{-1} is assigned to CO_3^{2-} , which represents the natural hydroxyapatite. **M. Manoj** et al., **O. Kesmez** et al., and **H. Sahana** et al. reported preparing natural hydroxyapatite in which their results of XRD and FT-IR analyses aligned with the prepared hydroxyapatite in this study [7-9].

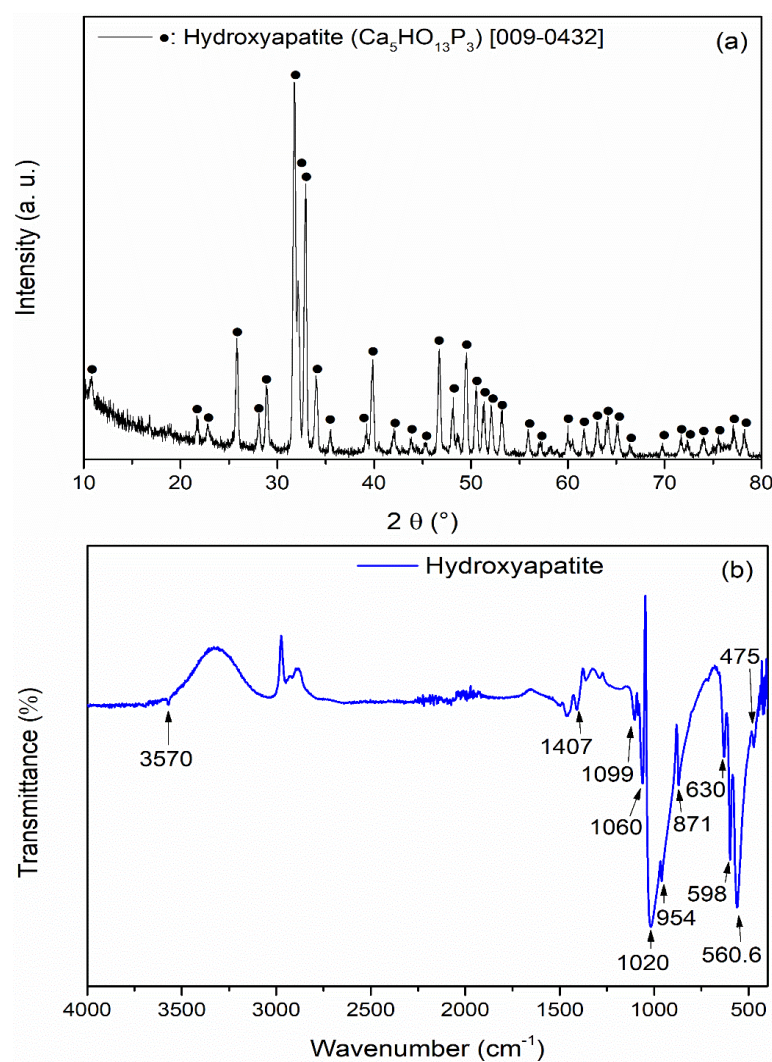


Figure III.5 (a) XRD and (b) FT-IR spectra of the natural hydroxyapatite N-HA powder.

I.1.3.2. Morphological observation

Figure III.6 (a) presents an FE-SEM image of the hydroxyapatite powder and (b) its corresponded grain size distribution. As illustrated in Figure III.6 (a), the hydroxyapatite particles exhibit a nearly spherical morphology with a relatively uniform size distribution. The particle sizes are observed to range from 200 to 400 nm, with a peak frequency in 345 nm. The grain size distribution, shown in Figure III.6 (b), further confirms that the particles are below 500 nm in size.

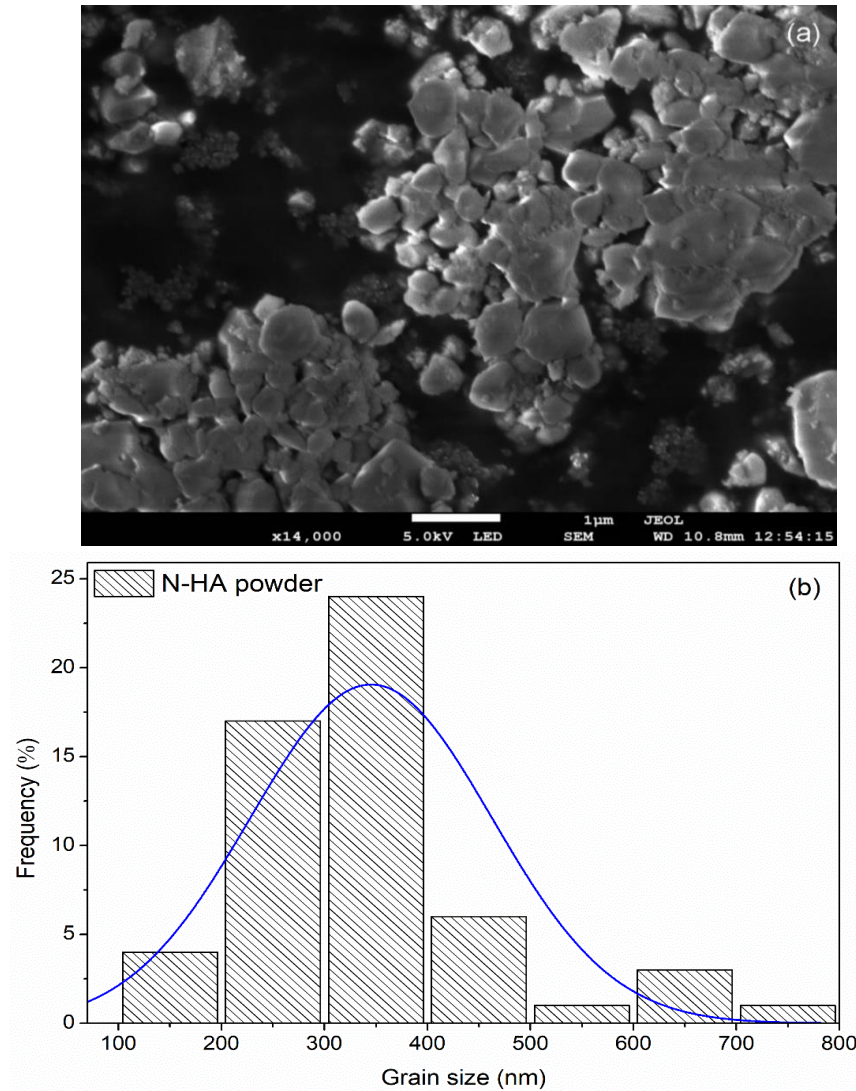


Figure III.6 (a) SEM image and (b) gain size distribution analysis of hydroxyapatite powder.

I.1.4. Forsterite

I.1.4.1. XRD and FT-IR analyses

The repared forsterite powder was treated up to 1400 °C and analyzed using XRD and FT-IR spectroscopy. Figures III.7 (a) and (b) present the XRD and FT-IR spectra of the synthesized forsterite (FS₀) powder, respectively. In Figure III.7 (a), the XRD spectra exhibit distinct diffraction peaks, confirming the crystallization of forsterite, with XRD data file no. [96-901-3095]. The FT-IR spectrum, shown in Figure 7 (b), reveals a characteristic absorbance band. Specifically, the band at 437.44 cm⁻¹ is attributed to the stretching vibrations of Mg-O. The band at 468.42 cm⁻¹ corresponds to the O-Mg-O group bending vibrations. The band at 604 cm⁻¹ is assigned to the O-Si-O group. The 556.5 cm⁻¹ and 960.75 cm⁻¹ bands correspond to Mg-O octahedral vibration and Si-O-Si group symmetric stretching, respectively. The XRD and FT-IR results obtained in this study agree with those reported by **S. Venkatraman** et al., **S. Tamin** et al., and **M. Naghiu** et al.[10-12], confirming the successful synthesis of pure forsterite phase.

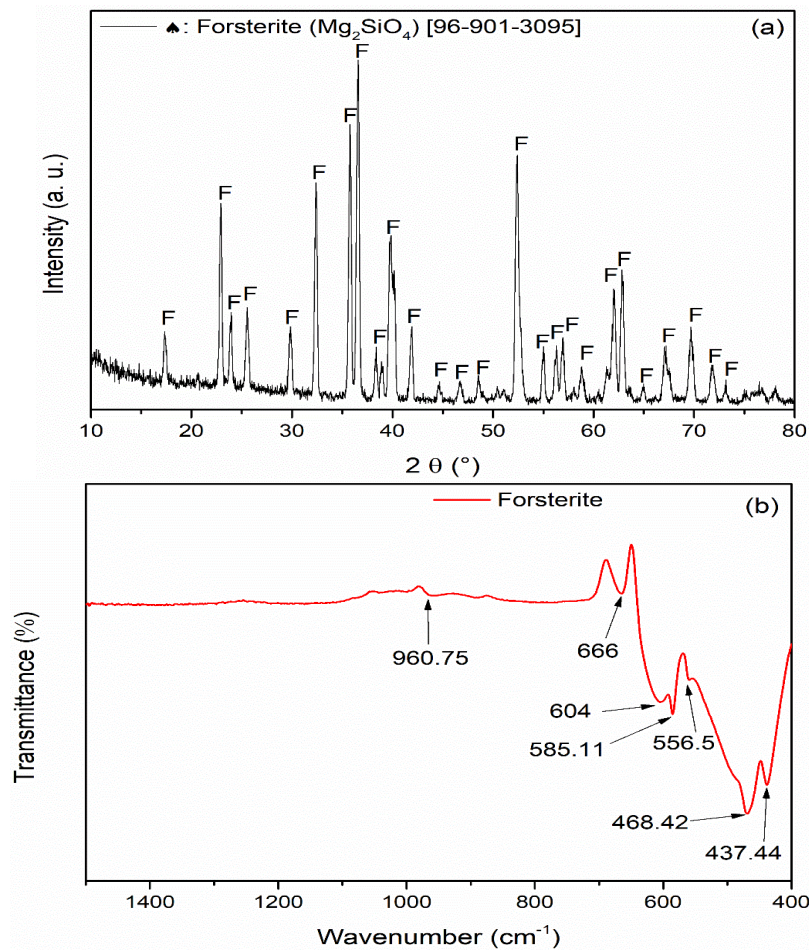


Figure III.7 (a) XRD and (b) FT-IR analyses of forsterite equivalent powder (FS₀) treated at 1400 °C.

I.1.4.2. Morphological observation

Figure III.8 presents FE-SEM images of forsterite equivalent powder treated up to 1400 °C. As shown in Figure III.8, forsterite particles exhibit a random morphology and a relatively heterogeneous size distribution. The particle sizes range from 300 nm to 3 μm .

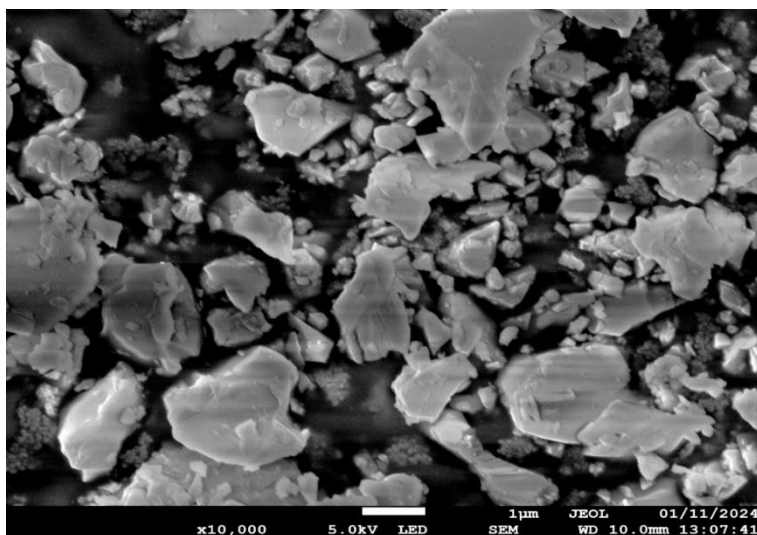


Figure III.8 SEM image of forsterite equivalent powder treated at 1400 °C.

**Part Two: Forsterite
composites with excess SiO₂:
A comprehensive study of
thermal, mechanical,
microstructural and biological
properties**

In this section, forsterite- silica composites (FS_x) were synthesized using a combination of SiO_2 and MgO nano oxides. The primary objective of this study was to prepare forsterite and evaluate the influence of SiO_2 excess, up to a maximum of 6 wt%, on the phase composition and densification behavior of forsterite-silica (FS_x) under sintering conditions.

II.1. Thermogravimetry (TG/DTG), Differential thermal analysis (DTA) and X-ray diffraction (XRD) analyses of FS_0 powder

To determine the mass loss and the phase transformations accruing in forsterite equivalent (FS_0) powder under heat treatment process, a quantity of forsterite equivalent powder was thermally treated at 20 °C/min rate under 40 ml/min flow of argon gas using thermogravimetry and differential thermal analysis equipment.

Figure III.9 (a) illustrates the TG, DTG, and DTA curves for the sample heated at 20 °C/min up to 1300 °C. The DTA curve reveals the presence of two endothermic peaks and one exothermic peak. Between room temperature and 700°C, two endothermic peaks are observed. The first peak at 165°C corresponds to the evaporation of water, and the second peak at 433°C is due to the decomposition of magnesium hydroxide ($Mg(OH)_2$) to MgO [13] and water. The $Mg(OH)_2$ forms during preparation by wet milling. The two peaks are associated with two mass losses estimated to be 29.04 % and 4.94 %, as shown on the TG curve. The exothermic peak at 830-860 °C is believed to be related to forsterite, possibly forming through two reactions. The first reaction involves the reaction of MgO and SiO_2 to form enstatite, and the second one leads to the formation of forsterite due to enstatite reacting further with MgO . The possibility that forsterite could form through a one-step formation mechanism was ruled out. However, the reaction is thermodynamically feasible [14], and the DTA curve recorded at a high heating rate only showed one peak. This is because this single peak is believed to result from two overlapping peaks, which can be distinguished at lower heating rates as demonstrated by experiments and further discussed below. The mass of the sample remains constant above 700 °C. Other researchers reported similar results [14, 15].

To identify the change in the phase associated with the exothermal peak observed at 830-860 °C on the DTA curve, XRD spectra were obtained for three specimens heated to 800, 860, and 1300 °C and are shown in Figure III.9 (b). At 800 °C, periclase (MgO) peaks are apparent, while silica (SiO_2) peaks are not detected due to its amorphous state. Peaks characteristic of the forsterite

phase (Mg_2SiO_4) were observed on the spectra of the specimen heated to 860 °C. The intensity of the peaks of the periclase phase decreased, indicating the crystallization of forsterite from the reaction of SiO_2 and MgO . This confirms that the exothermic peak observed at 830-860 °C on the DTA curve is due to the formation of forsterite. At 1300 °C, only peaks of the forsterite phase were visible. These results indicate that the reaction between MgO and SiO_2 in the sample heated at a rate of 20°C/min begins at a temperature as low as 860°C and results in the production of monolithic forsterite.

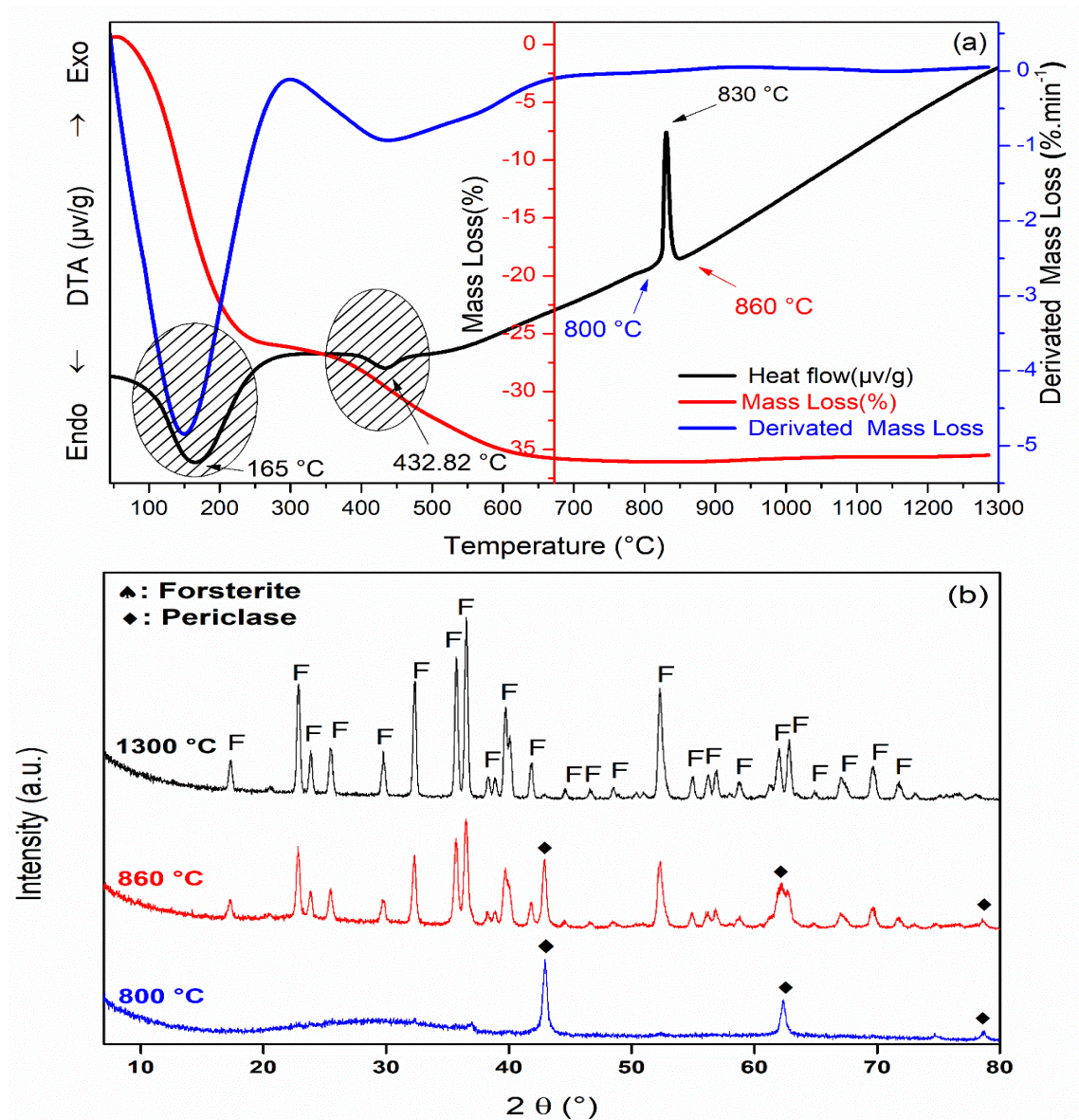


Figure III.9 (a) TG, DTG, and DTA curves for FS0 sample heated at 20 °C/min up to 1300 °C. (b) XRD spectra of heated specimens up to 800, 860, and 1300 °C.

II.2. Dilatometry (DL) and X-ray diffraction analyses of FS_x powder

A dilatometry study was conducted on the FS₀ sample, carried from room temperature to 1500 °C at a 5 °C/min heating rate. Dilatometry curves of FS₀ during heating and cooling are illustrated in Figure III.10 (a).

During heating, we can note two phase transformations from room temperature to 200 °C, related to the water removal that is associated with minor elongation, and other from 300 °C to 600 °C with 3 % linear shrinkage related to OH bound breakage in MgO(OH)₂ compound formed during collecting the powder after calcination to 500 °C, other two significant transformations were apparent with 17.43 % linear shrinkage from 623 °C to 823°C, and 28.69 % linear shrinkage from 1105 °C to 1500 °C. As for the cooling curve, there was no phase transformation linked to any shrinkage or elongation, ensuring the formation of a stable phase during heating. The derivative curve of dilatometry indicates the shrinkage rate is the greatest at 763 °C

To identify the last two linear shrinkage transformations, a dilatometry analysis was performed on the FS₀ sample prior and after phases transformation temperatures, as shown in Figure III.10 (a), then subsequently investigated using X-ray diffraction; the XRD spectra obtained are shown in Figure III.10 (b). Periclase (MgO) phase peaks are apparent up to 623 °C, indicating the presence of raw materials only.

At 823 °C and 1105 °C, forsterite phase peaks appear along with weak intensity peaks of periclase, which confirms that the linear shrinkage accruing between 623 °C and 823 °C is forsterite phase crystallization. At 1500 °C, no additional phase was detected. Higher intensity forsterite phase peaks were apparent, right after heat-treatment around 823 °C, the amorphous silica reacted with periclase, and forsterite appeared as a single phase, suggesting the reaction was given enough time to form a pure forsterite phase [16], and that the last linear shrinkage shown in Figure III.10 (a) was due to an accrued sintering process.

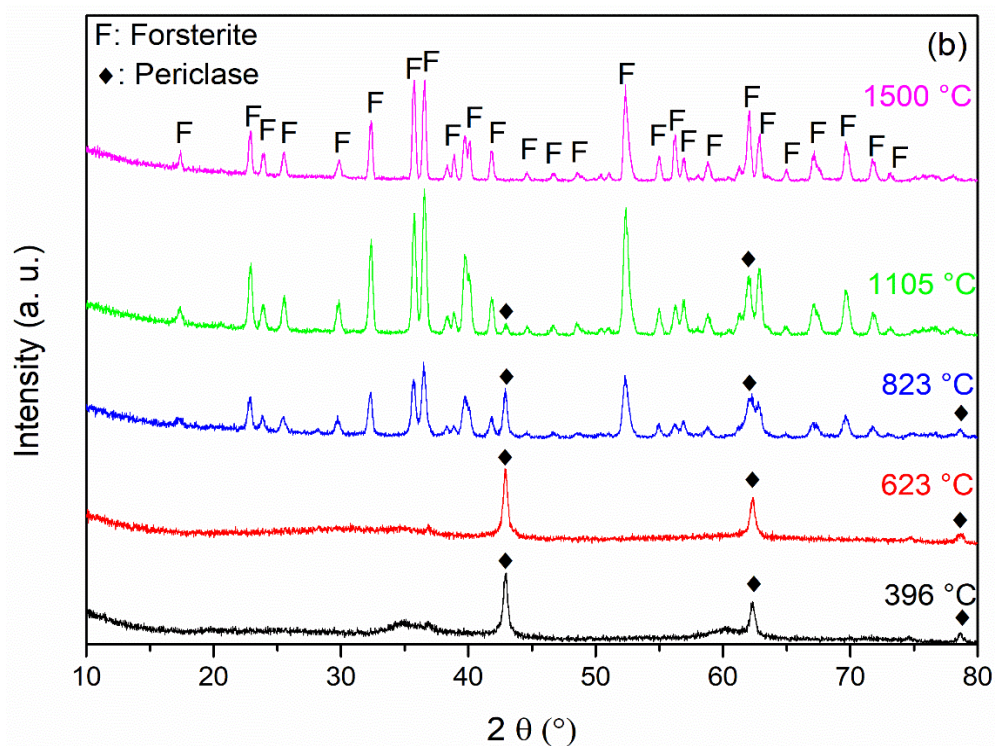
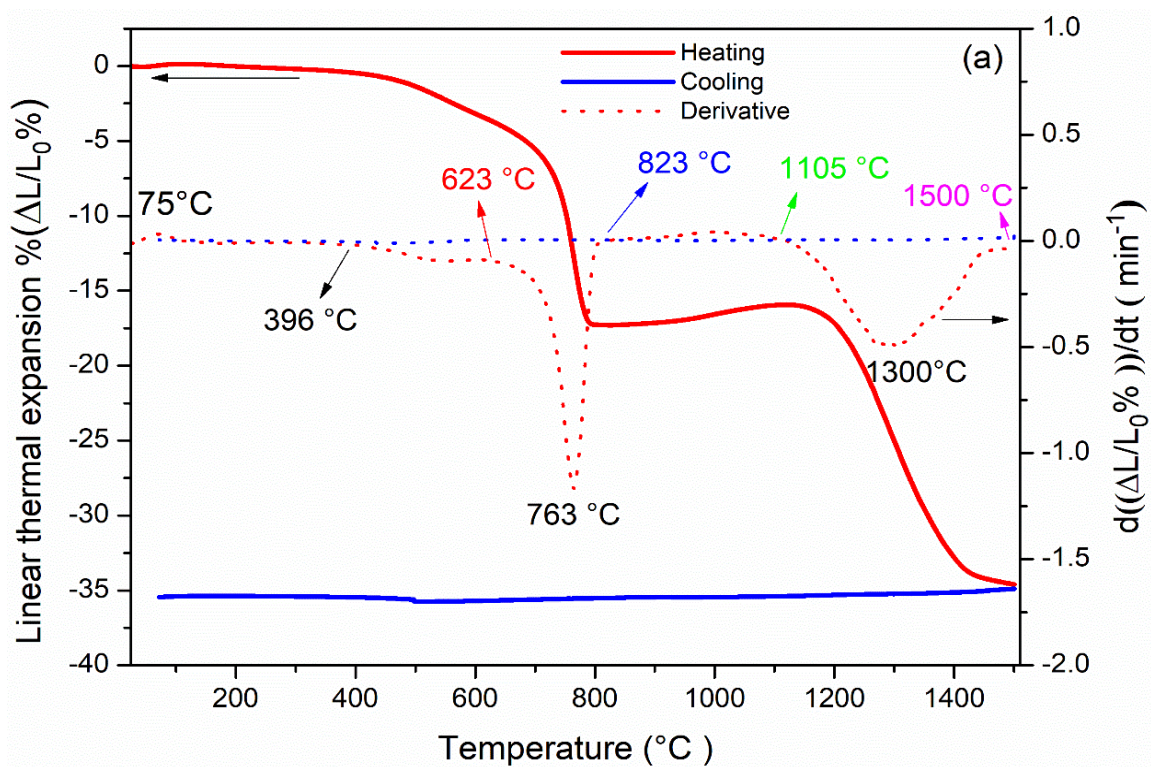


Figure III.10 (a) Dilatometry curves of FS_0 (compacted precursor powders) heated at 5 °C/min up to 1500 °C (b) XRD spectra of heated specimens up to 396, 623, 823, 1105, 1500 °C.

II.3. Analysis of shaped and sintered forsterite-silica composites (FS_x) samples

II.3.1. X-ray analysis of forsterite-silica composites (FS_x) samples after sintering

The FS_x samples were sintered in a furnace for 2 hours to 1000, 1100, 1200, 1300, 1400, and 1500 °C by heating at a 5 °C/min rate. Figure III.11 (a, b, c, d, e) shows XRD spectra of FS₀, FS_{1.5}, FS₃, FS_{4.5}, and FS₆ samples. The results were summarized as follows:

In all samples sintered at 1000 °C, only peaks corresponding to periclase (MgO) and forsterite are present. Furthermore, new peaks of enstatite crystallization were observed while all periclase peaks disappeared on FS_{1.5}, FS₃, FS_{4.5}, and FS₆ samples spectra sintered at 1100 °C. Meanwhile, no additional change was observed in FS₀ sample spectra at 1100 °C. The same peaks were observed in FS_{1.5}, FS₃, FS_{4.5}, and FS₆ samples, but with an increased intensity of the enstatite phase at 1200 °C, 1300 °C, 1400 °C and 1500 °C. Only peaks of forsterite were observed on the spectra of FS₀ sample at 1200 °C 1300 °C, 1400 °C and 1500 °C. The XRD results indicate that 1200 °C is sufficient sintering temperature for the formation of monolithic forsterite in the stoichiometric composition for a relatively short time of 2 hours. As for FS_{1.5}, FS₃, FS_{4.5}, and FS₆ samples (samples with excess of SiO₂), forsterite along with enstatite was formed. It is important to mention that the different methods for producing forsterite have been reported to achieve formation temperatures within specific ranges. For example, researchers have observed temperatures of approximately 800 °C using co-precipitation [17], the polymer precursor method [18], and the sol–gel technique [19]. The heterogeneous sol–gel approach and mechanochemical activation have shown temperatures of 1000 °C [20] and 1000–1200 °C [21–23], respectively, while the solid-state reaction method typically requires higher temperatures of 1100–1400 °C [24, 25] to overcome kinetic constraints [25]. In this study, XRD analysis of FS₀ sample heated using DTA equipment (Figure III.9 (b)) demonstrated that the reaction between MgO and SiO₂ to form forsterite begins near 860 °C, with pure forsterite forming at 1300 °C. For FS₀ sample sintered in a furnace, XRD results indicated the initial formation of forsterite at 1000 °C, with complete conversion to pure forsterite at 1200 °C. These temperature differences can be attributed to experimental factors, as thermal analysis is sensitive to variables like sample size, weight, and heating or cooling rates [26]. The formation temperatures observed in this study align with previously reported values. The use of nanopowders, known for their high reactivity, superior

diffusion properties, and enhanced sinterability [27], likely contributed to the observed results. Additionally, ball milling the raw powder mixture for four hours to achieve homogeneity may have further activated the initial powders. These factors appear to have played a role in lowering the forsterite formation temperature compared to traditional methods such as co-precipitation, polymer precursor techniques, and the sol-gel method.

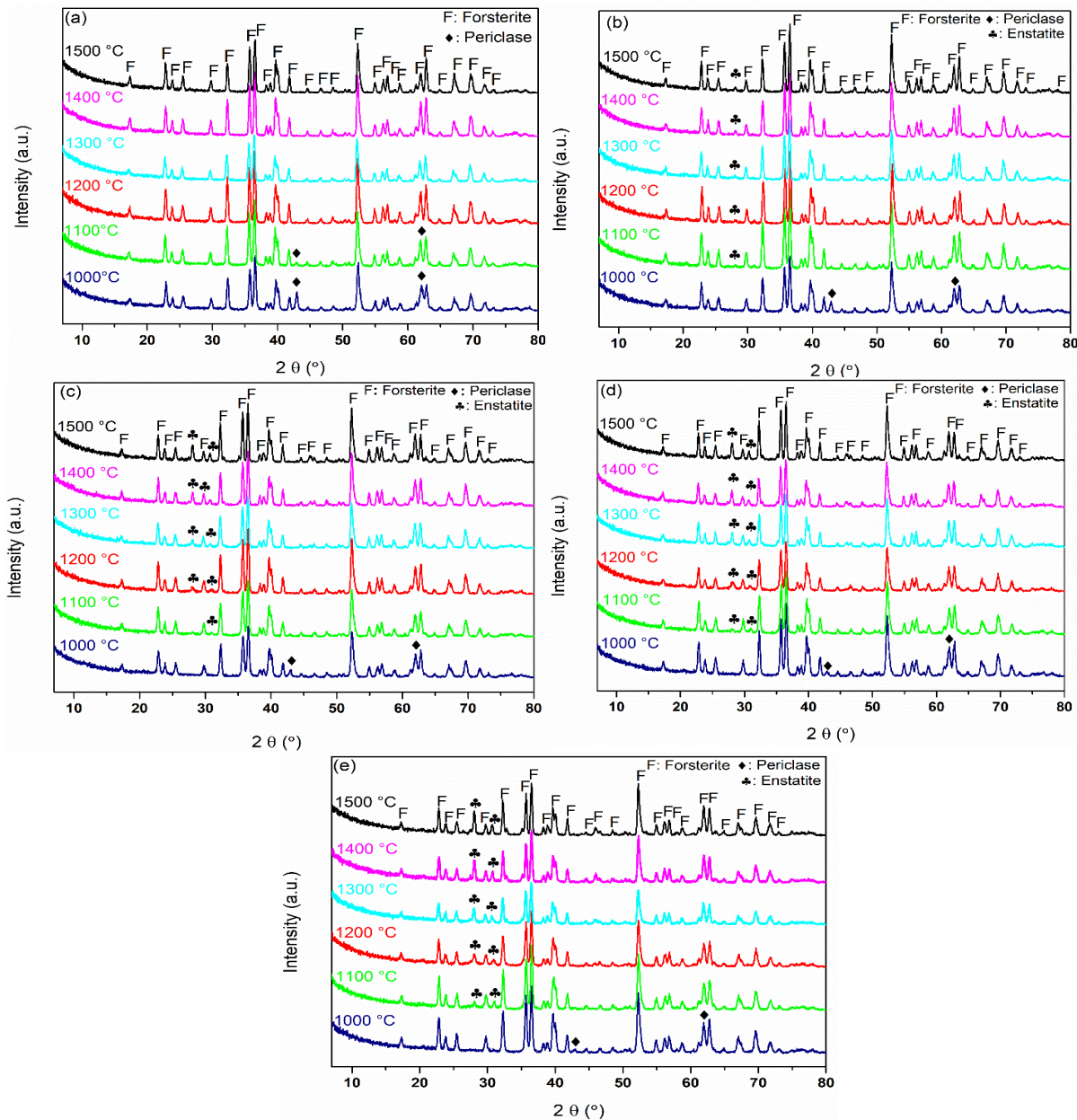


Figure III.11 XRD spectra of (a) FS₀, (b) FS_{1.5}, (c) FS₃, (d) FS_{4.5}, and (e) FS₆ sample sintered at different temperatures.

II.3.2. Measurement of bulk density and open porosity of FS_x samples

Figure III.12 shows (a) density (b) and open porosity (b) of FS_x samples at different sintering temperatures.

The monolithic forsterite (FS₀) sample shows that increasing in temperature from 1200 °C to 1500 °C increased density from 2.043 g.cm⁻³ to 3.089 g.cm⁻³ with decrease in open porosity from 35.5 % to 0.31 %. Which is achieved in shorter sintering time compared to **Ni** et al. [28] where forsterite samples reached 82.6-92.5 densification in 3-8 hours between 1350 °C to 1550 °C. while **Brindley** et al.[29] formed forsterite from fine particles of MgO and SiO₂ between 1100 °C and 1400 °C but in 144 hours of sintering time. Similar results of density were reported [15, 30].

The FS_{1.5}, FS₃, FS_{4.5}, and FS₆ samples show an increase in density were 2.76, 2.94, 2.95, and 2.97 g.cm⁻³, respectively, and a decrease in open porosity up to 1300 °C. We note an increase in open porosity by 0.97, 2.69, 2.32, and 3.90 %, and a decrease in density for FS_{1.5}, FS₃, FS_{4.5}, and FS₆ samples, respectively at 1400 °C, reaching an open porosity of 12.13 % for FS₆ sample at 1500 °C. The results suggest that the increase in open porosity and the decrease in bulk density in the samples sintered after 1300 °C can be attributed to the grain size of enstatite increases. Since enstatite crystallization is controlled by linear nuclei growth, the linear growth of enstatite grains led to the formation of open porosity, which contributed to an overall increase in FS_{1.5}, FS₃, FS_{4.5}, and FS₆ sample's volume, such notion was clearly observed in the upcoming microstructure analysis of FS₆ sample (Figure III.16 (a)).

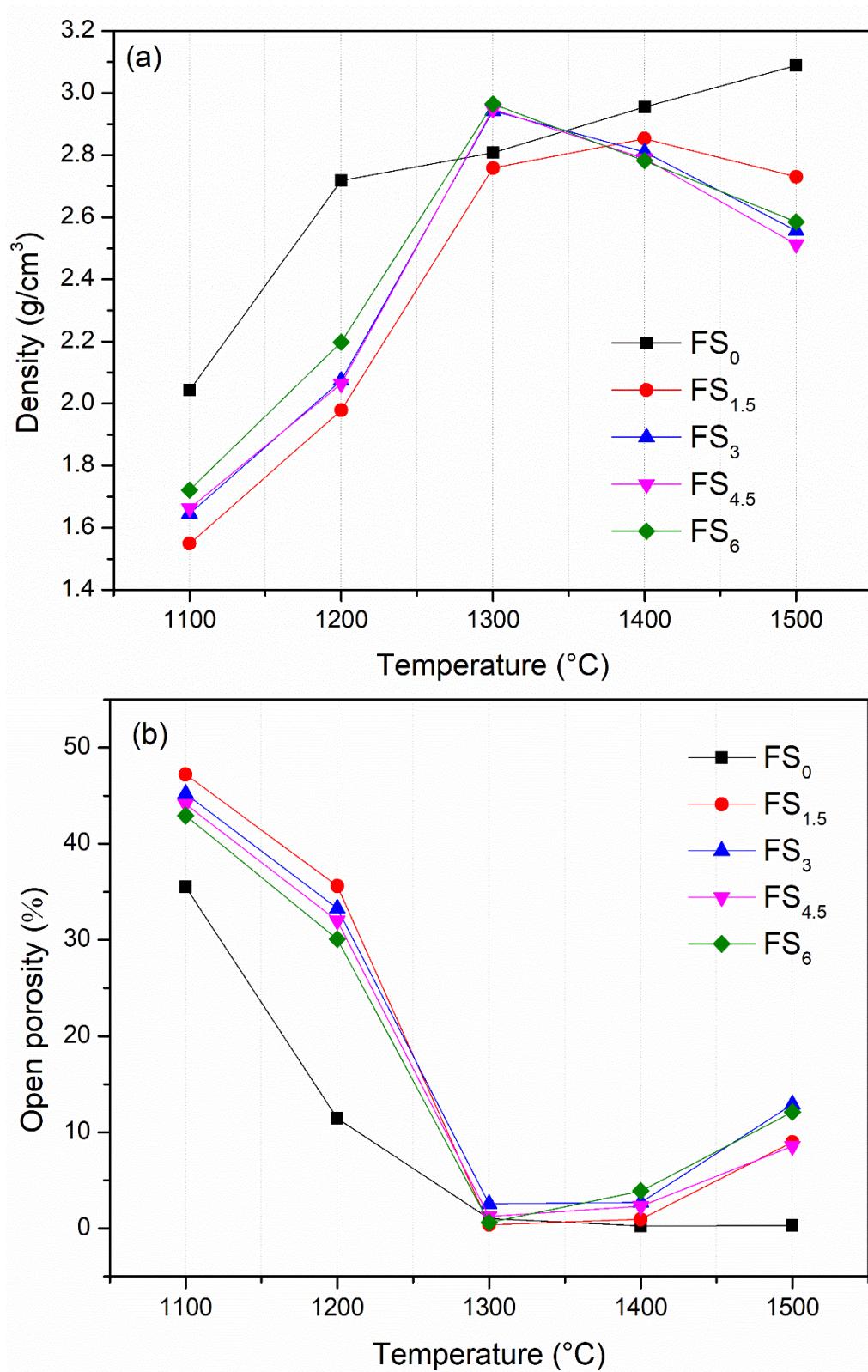


Figure III.12 (a) Density and (b) open porosity of FS_x at different sintering temperatures.

II.3.3. Micro-hardness measurement of FS_x samples

Vickers microhardness (Hv) of FS_x sintered samples with the lowest and highest SiO₂ content sintered at 1400 °C are shown in Table 1.

The Vickers microhardness of the FS₀, FS_{1.5}, FS₃, FS_{4.5}, and FS₆ samples was measured at 7.64 GPa, 5.786 GPa, 5.457 GPa, 5.166 GPa, and 5.145 GPa, respectively.

The observed trend in Vickers microhardness closely corresponded to the density and open porosity of FS_x samples sintered at 1400 °C, as shown in Table III.1. This demonstrates that the hardness of the samples containing increasing enstatite due to the excess SiO₂, as shown in Figure III.11 (b, c, d, e), decreases accordingly.

Similarly, the results for the FS₀ sample revealed a higher Vickers microhardness value compared to prior studies, which reported the hardness of forsterite obtained by sintering MgO and talk of to be 7.68 GPa at 1500 °C for 2 hours. A few other studies reported 5.5- 7.1 GPa at 1400 °C and 2.28 GPa at 1300 °C for the forsterite sample [31-34], and 5- 5.5 GPa for the enstatite [35, 36].

The weaker microhardness of samples containing Enstatite, compared to the FS₀ sample containing pure Forsterite, may be attributed to the inherently weaker mechanical strength of Enstatite aggregates [37].

This relation is supported by the observation that samples with higher Enstatite content exhibit higher open porosity and lower density at 1400 °C, which are known to contribute to reduced strength and hardness.

Table III.1 Microhardness of sintered sample at 1400 °C for 2 hours.

Samples	FS ₀	FS _{1.5}	FS ₃	FS _{4.5}	FS ₆
HV (GPa)	7.64	5.786	5.457	5.166	5.145

II.3.4. Coefficient of thermal expansion (CTE) measurement of FS_x samples

Thermal treatment was carried out for FS_x samples in the furnace at 1400 °C with a heating rate of 5 °C/min for 2 hours to obtain a stable crystallized phase by the end of the reaction between the primary materials. Then, a thermal analysis was performed using dilatometry equipment for 15 min at a heating rate of 5 °C/min after polishing the samples using mechanical polishing equipment.

The sample's thermal expansion coefficients CTE were calculated from 200 °C to 1300 °C and summarized in Table III.2 as demonstrated in Figure III.13 (a, b). The CTE of our synthesized

monolithic forsterite was $10.24 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$, the result is close to $9.3 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ of a sol-gel synthesized powder that contains 90 wt% of forsterite sintered $1300 \text{ }^{\circ}\text{C}$ for 4 hours [38], similar to that of **Yu** et al. report [14, 39]. Forsterite exhibits a low coefficient of thermal expansion (CTE), enabling it to maintain stability and structural integrity under temperature fluctuations. This characteristic ensures its suitability for applications in fields such as medicine. In contrast, phosphates lack thermal stability at elevated temperatures, limiting their applicability in such conditions [40].

The increase in SiO_2 content in the samples results in a decrease in the thermal expansion coefficient from $10.24 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ to $7.929 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ for FS_0 and FS_6 samples, respectively. Suggesting that our forsterite-silica ceramics thermal expansion coefficient is in the suitable range for high-temperature applications like furnace linings.

Figure III.11 (a, b, c, d, e) shows the XRD spectra of FS_x samples sintered at different temperatures. It's clear that the enstatite phase increased in the FS_x samples treated to 1300°C . Enstatite thermal expansion coefficient was reported to be 7.6 to $8 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ [41]. The decrease of the thermal expansion coefficient in FS_x samples is due to enstatite phase formation. In high-temperature environments, the reduction in the thermal expansion coefficient of FS_x ceramics indicates improved thermal stability, reduced thermal stress, and enhanced durability [42].

Table III.2 Coefficient of thermal expansion ($200\text{-}1300 \text{ }^{\circ}\text{C}$) samples sintered at $1400 \text{ }^{\circ}\text{C}$ for 2 hours.

Samples	FS_0	$\text{FS}_{1.5}$	FS_3	$\text{FS}_{4.5}$	FS_6
$\text{CTE} \times 10^{-6} (\text{K}^{-1})$	10.24	9.927	9.688	9.047	7.929

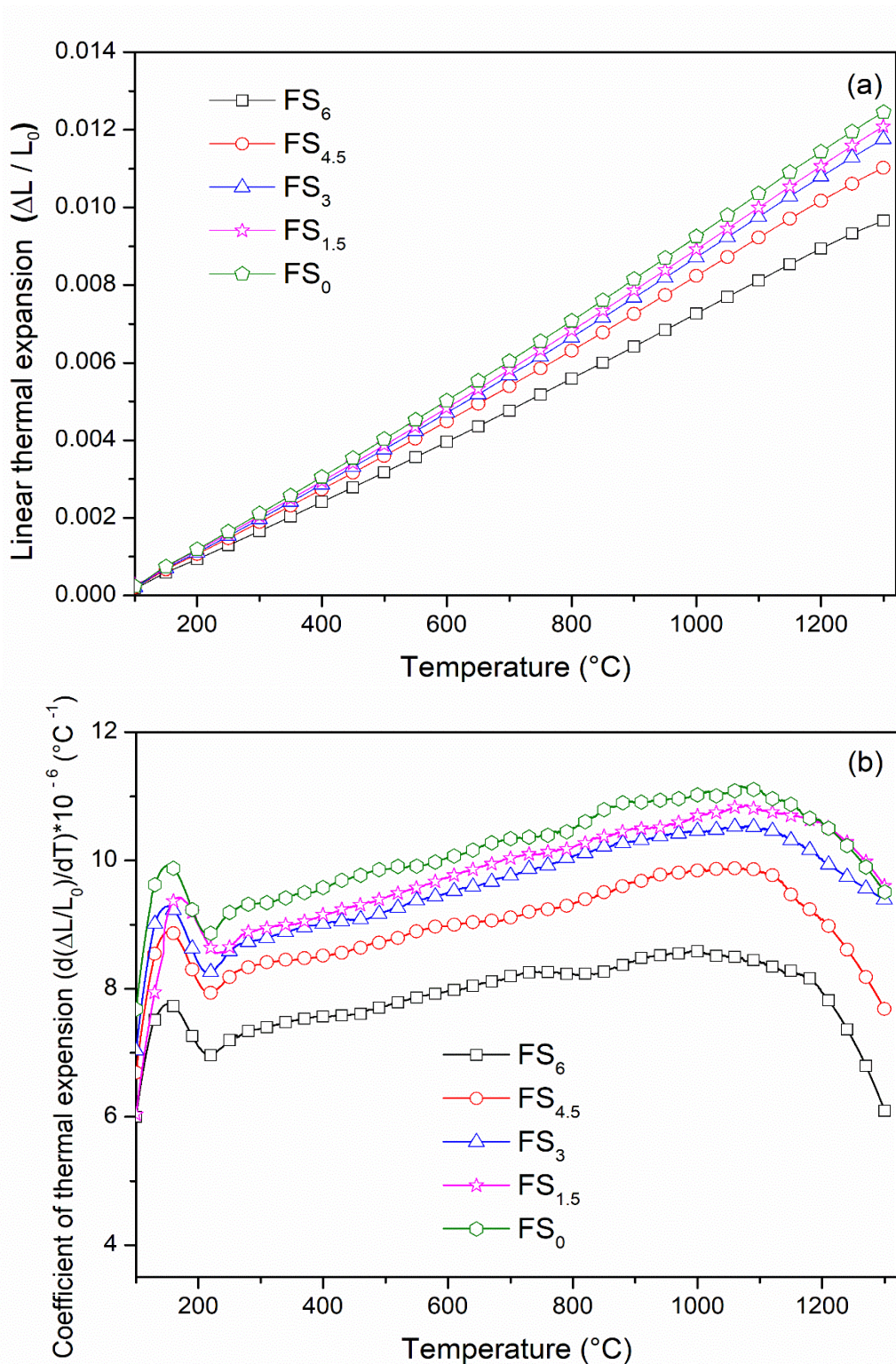


Figure III.13 (a) Linear thermal expansion and (b) the coefficient of thermal expansion of FS_x samples treated from 200 °C to 1300 °C.

II.3.5. Morphological analyses of FS_x samples

The microstructure, morphologies, elemental distribution, and grain size distribution of the ground and polished FS₀ and FS₆ samples sintered at 1400 °C for 2 hours were analyzed using a SEM equipped with an EDS facility. The results of these analyses are presented in Figures III.14 (a, b), III.15 (a, b), III.16 (a, b), and III.17 (a, b).

High sintering temperature of 1400 °C in FS₀ sample led to the formation of single-phase with homogenous grains, dense microstructure and lack of large pores. This observation confirms the low porosity of 0.26 % and the high density previously noted in Figure III.12 (a, b) for the FS₀ sample. The average grain size was statistically analyzed and determined using ImageJ software to be 5-10 μm, as shown in Figure III.14 (b).

The EDS image of three selected areas of FS₀ sample are shown in Figure III.15 (a). The mass percentage of Mg, Si, and O of the three different areas are closely matches, proving the homogeneity in elements distribution across the sample, and also indicates identical stoichiometric composition to forsterite phase. Other reports have attempted to synthesize forsterite yet found much difference in the stoichiometric composition by EDS analysis due to the formation of a secondary enstatite phase or the residual MgO [43-45].

Figure III.15 (b) shows spots maps of elements (Mg, Si, and O) and it suggest a homogeneous distribution, confirming the previous results in Figure III.15 (a).

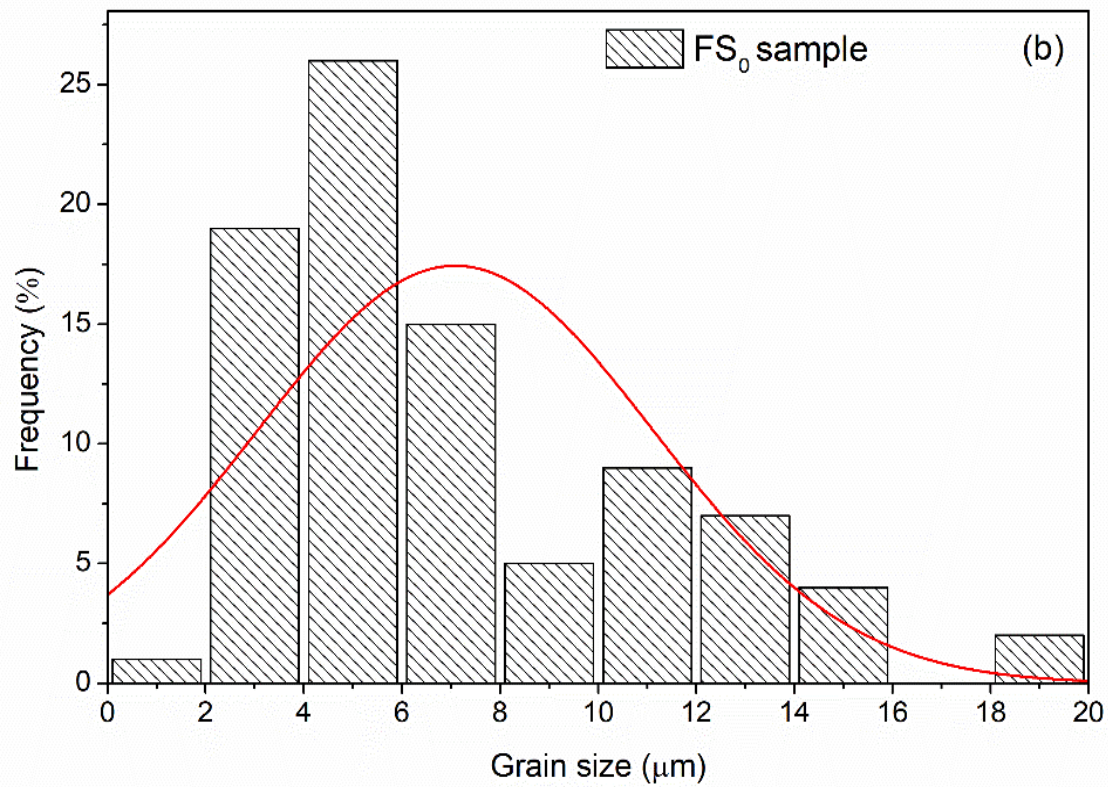
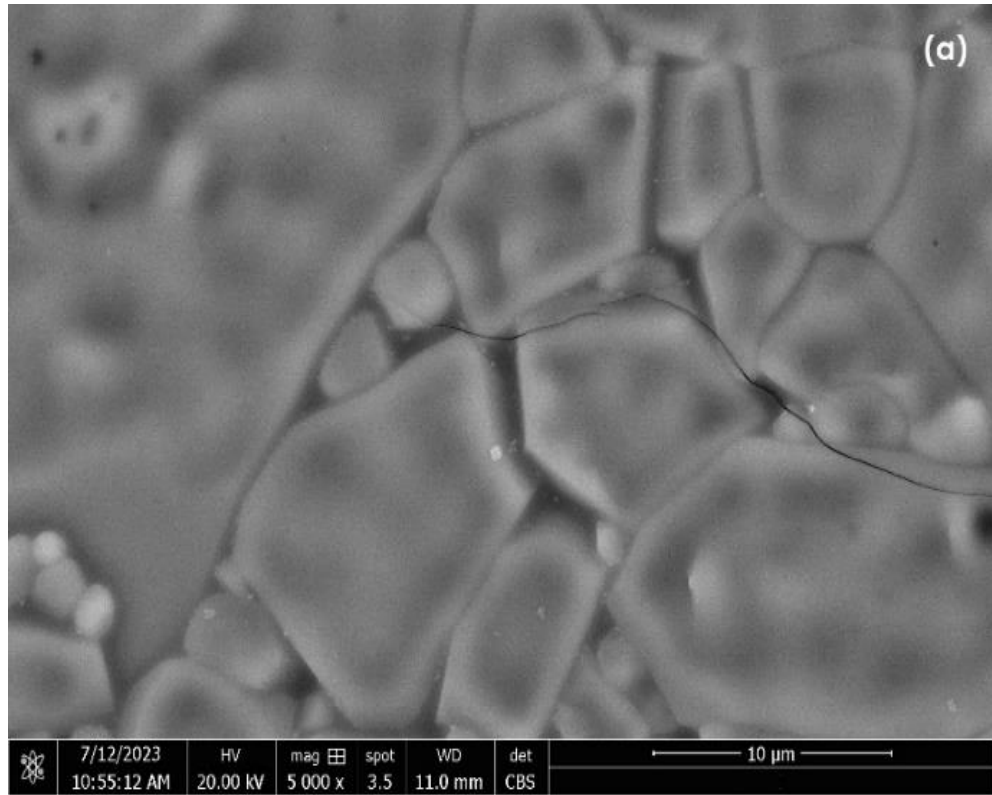


Figure III.14 (a) A typical SEM image of FS_6 sample after being sintered at 1400 °C for 2 hours;
(b) the grain size distribution.

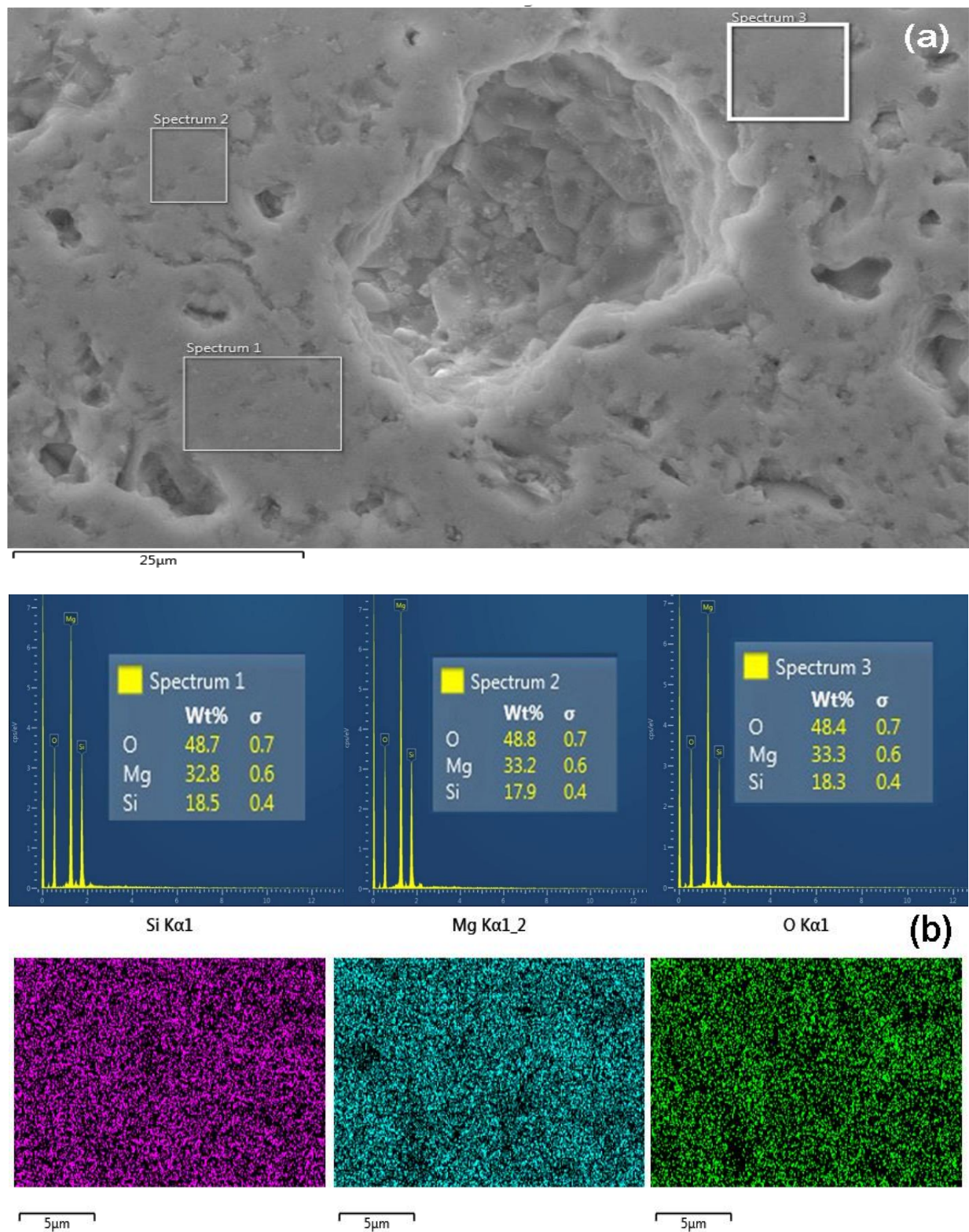


Figure III.15 (a) SEM image and (b) corresponding elemental mapping of magnesium, silicon, and oxygen of FS₀ sample.

Figure III.16 (a, b, c) shows a typical FE-SEM micrograph of ground and polished FS₆ specimen sintered at 1400°C for 2 hours. Upon careful examination of the micrograph, it is evident that there is a heterogeneous structure with two phases present, a lack of large pores, and a dense microstructure with a rod-like shape microstructure. Enstatite phase grain size was determined to be 0.7 μm as indicated in Figure III.16 (c). EDS analysis was conducted in various areas, as depicted in Figure III.17 (a, b), confirming the presence of forsterite as the main formed phase and secondary phase of enstatite. The mass percentage of Mg, Si, and O obtained from two different areas, as presented in Figure III.17 (b), closely matches that of stoichiometric forsterite and enstatite. The SEM/EDS analysis of FS₆ sample aligns with the XRD spectra in Figure III.11 (e).

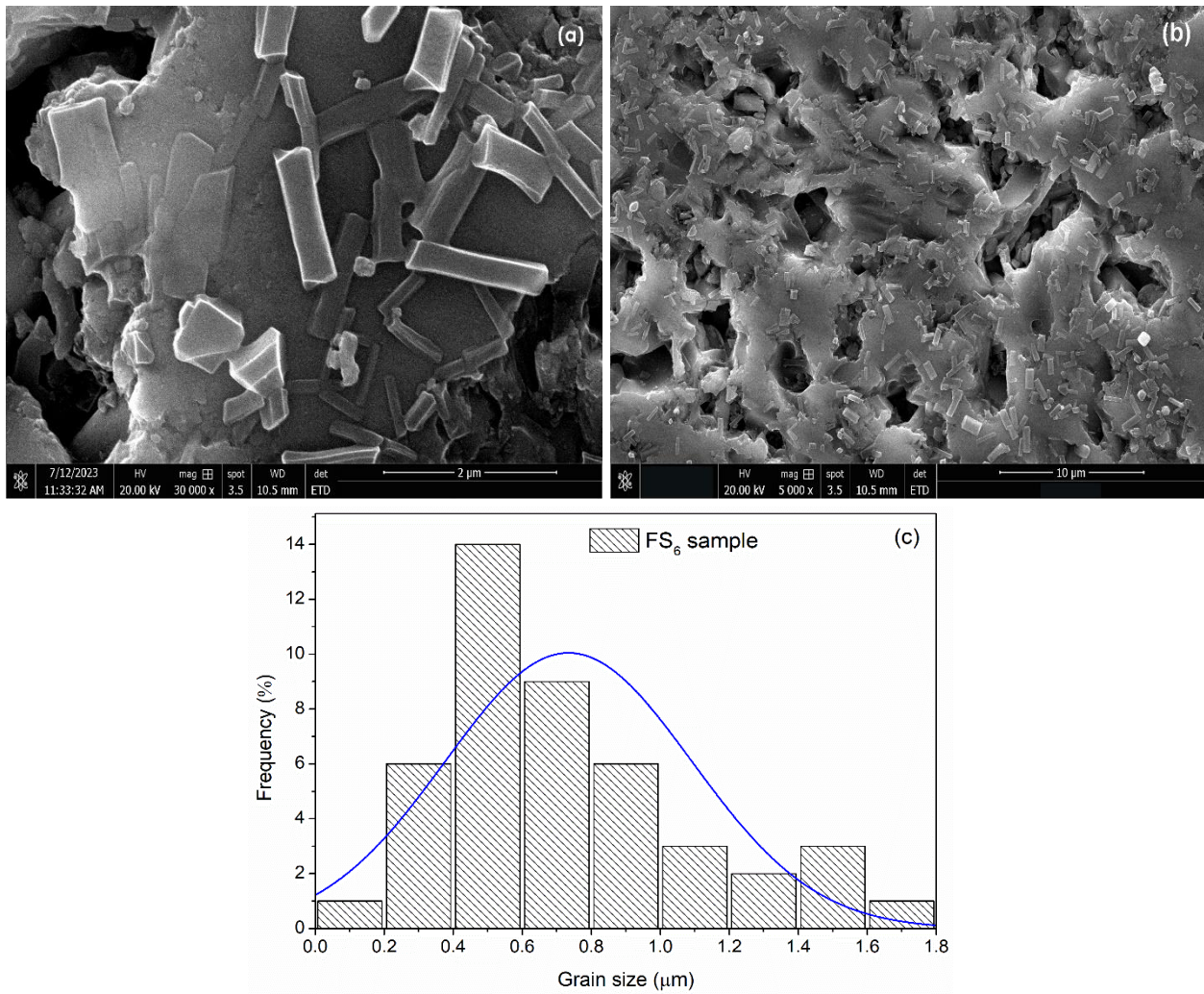


Figure III.16 (a, b) A typical SEM image and (c) grain distribution of FS₆ sample after being sintered at 1400 °C for 2 hours

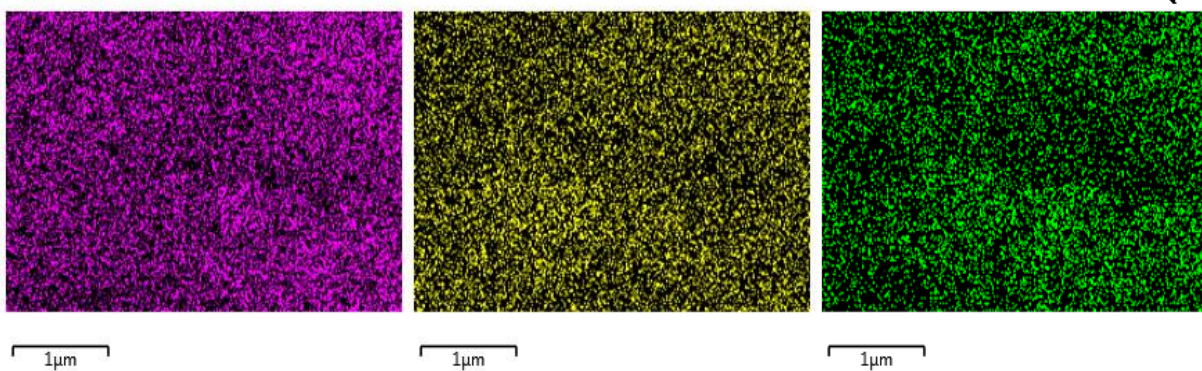
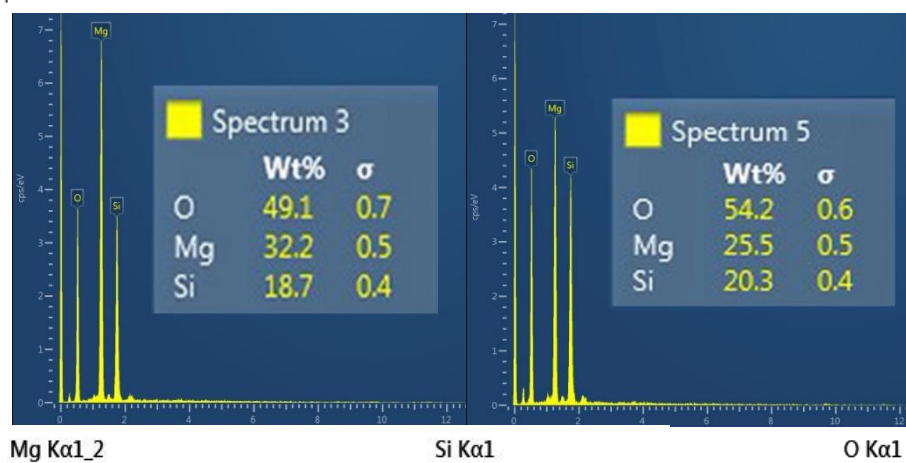
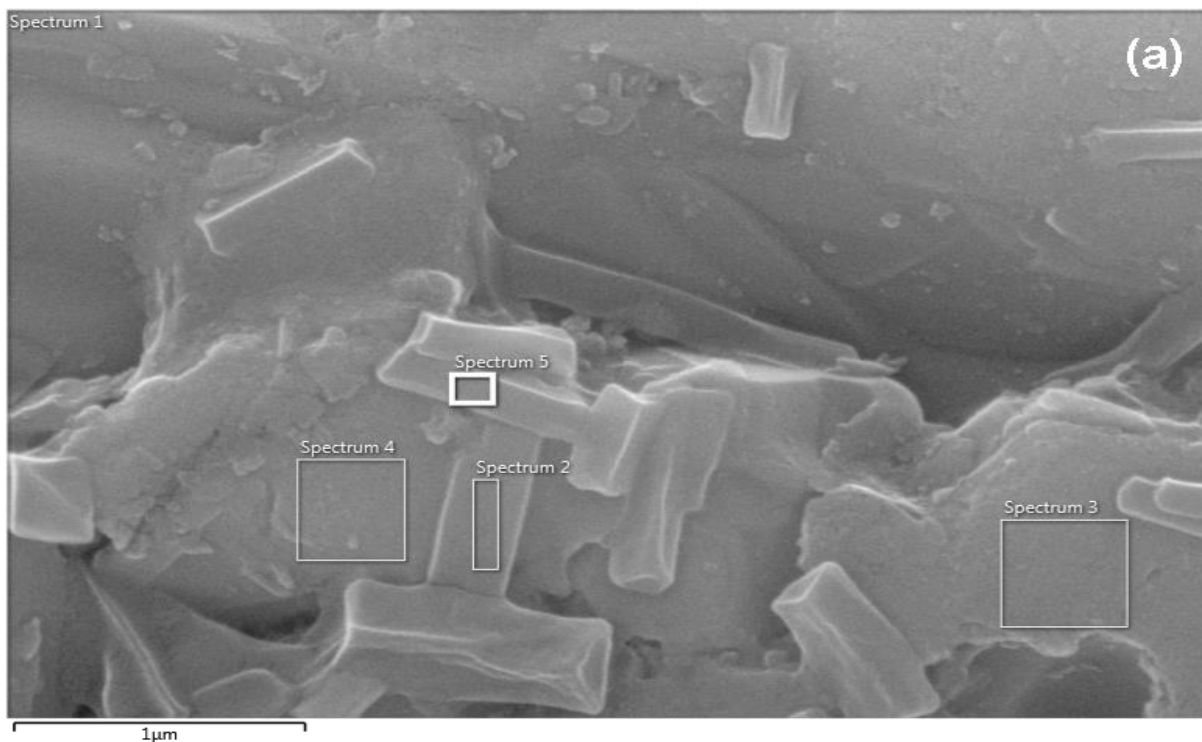


Figure III.17 (a) SEM image and (b) corresponding elemental mapping of magnesium, silicon, and oxygen of FS₆ sample.

II.4. Antibacterial activity of FS_x composition

The antibacterial activity of FS_x composite samples treated at 1400 °C was studied against both Gram-positive and Gram-negative bacteria, as illustrated in Figure III.18 (a, b). Two bacterial strains were selected: *Pseudomonas* (Gram-negative) and *Staphylococcus aureus* (Gram-positive). The FS₀ sample, which consisted of a pure forsterite phase as confirmed in Figure III.9 (b), demonstrated significant antibacterial activity against Gram-negative *Pseudomonas*, exhibiting a 10 mm zone of inhibition as shown in Table III.3. This result suggests that the presence of free Mg atoms, inherently alkaline in nature, created an alkaline environment that inhibited bacterial activity around the sample. However, the FS₀ sample showed no antibacterial activity against Gram-positive *Staphylococcus aureus*. This discrepancy in antibacterial efficacy is likely due to differences in the cellular structure between Gram-positive and Gram-negative bacteria.

In contrast, the FS₃ and FS₆ samples exhibited no antibacterial activity against either type of bacteria. This indicates that increasing the SiO₂ content in the composite may reduce the antibacterial effectiveness of the material.

Table III.3 inhibition zone in mm of FS_x samples sintered at 1400 °C.

Type	FS ₀	FS ₃	FS ₆
<i>Pseudomonas</i> (-)	10	0	0
<i>Bacillus</i> (+)	0	0	0

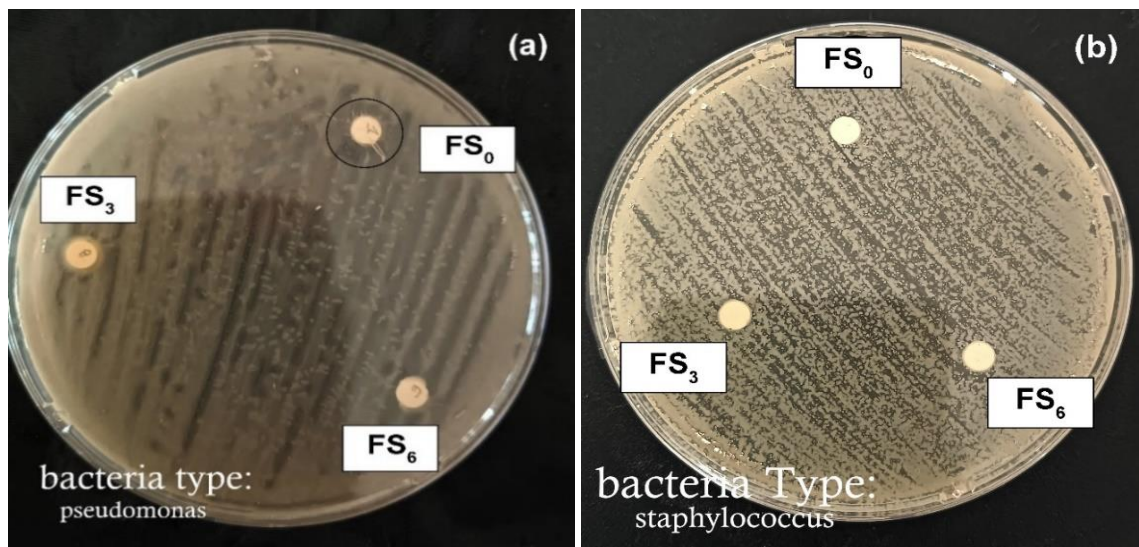


Figure III.18 Antibacterial agar test of FS_x against two types of bacteria.

No proper recognizable zone of inhibition on the agar plates was visible in the previous test, suggesting that under such test conditions, the diffusion of antibacterial agents from the solid disk into the agar medium was limited. The lack of solubility or poor diffusion rate of active compounds could contribute to this result, as antibacterial efficacy depends on the release and migration of active agents from the sample into the surrounding medium. **R. Choudhary** et al. have reported that the disk diffusion method is not suitable for obtaining an accurate assessment of the antibacterial activity of ceramic samples [46]. To verify the accuracy of the previous results, a wall diffusion test was done, where sterilized FS₀ and FS₆ powders were dissolved in 1mL of DMSO at respective concentrations of (8 mg/ml and 4 mg/ml) and placed the agar wall, against *Pseudomonas aeruginosa* bacteria which has been identified as a contributor to infections following orthopedic surgeries and *Bacillus* bacteria that relates to the foodborne illness [47, 48]. In this study, the antibacterial activity of FS_x powder was compared to Ciprofloxacin (CLOP 30 µg) and Pefloxacin (PEF 5 µg) discs, two well-established fluoroquinolone antibiotics commonly used in treating bacterial infections. Both antibiotics were selected as controls to evaluate the efficacy of the tested compound against *Pseudomonas* bacterial strains, as shown in Figure III.19 (e).

Antibacterial wall tests of FS_x solution of powder sintered at 1400 °C are shown in Figure III.19 (a, b, c, d) and summarized in Table III.4. Figure III.19 (a, b) shows a clear inhibition zone around FS₀ solution that increases in diameter from 20 mm to 23 mm while increasing the concentration from 4mg/ml to 8 mg/ml against *Pseudomonas* bacteria and from 10 mm to 14 mm against *Bacillus* bacteria, as shown in Table III.4. Figure III.19 (a) and (e) confirm the forsterite's efficacy as an antibiotic agent against *Pseudomonas*, where the inhibition zone of CLOP and PEF antibiotic was 23 mm and 22 mm, respectively, similar to that of FS₀ solution as shown in Table III.5. Observations suggest that forsterite could be a promising biomaterial for treating bacterial infections, including osteomyelitis and septic arthritis. Figure III.19 (c, d) indicates that the FS₆ solution concentration of 8 mg/ml also shows an inhibition zone of 12 mm and 11 mm against *Pseudomonas* and *Bacillus* bacteria, respectively. No evident antibacterial activity is observed for 4mg/ml concentration. Figure III.19 shows a decrease in the diameter of the inhibition zone for the FS₆ solution, which suggests that the formation of the enstatite phase in FS₆ composition has affected the antibacterial activity negatively. The negative influence of enstatite on forsterite antibacterial activity has not been researched before, but **J. Zerhouni** et al.

have reported the significant effect of the enstatite phase on decreasing the antibacterial activity [49].

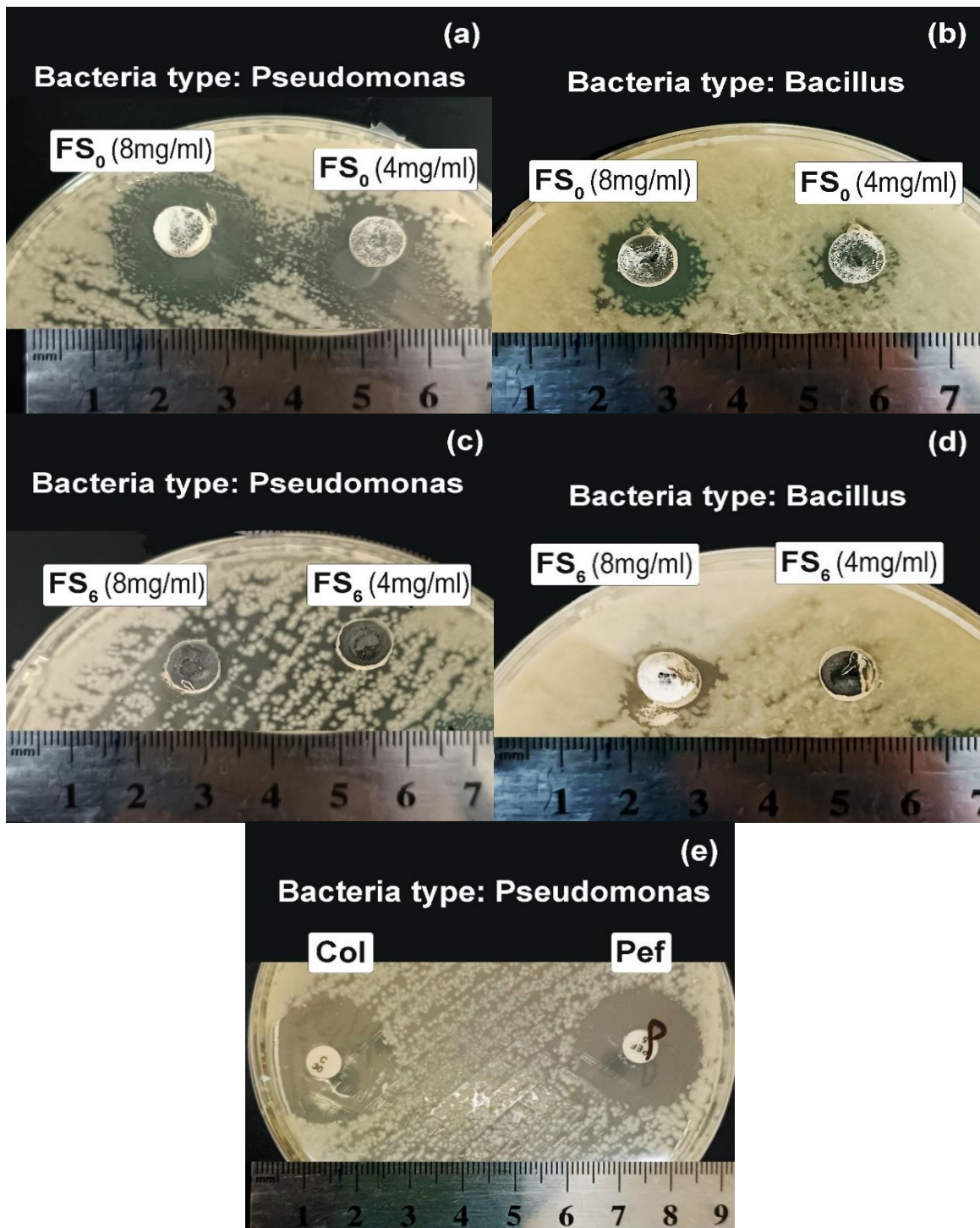


Figure III.19 (a, b, c, d) Antibacterial wall test of FS_x powder sintered at 1400 °C and e the disk agar test of CLOP and FEF antibiotics.

Table III.4 Inhibition zone in mm of different clinical pathogens by FS_x composites using the wall dilution technique.

Samples	Type			
	Pseudomonas (-)		Bacillus (+)	
Concentration	8 mg/ml	4 mg/ml	8 mg/ml	4 mg/ml
FS ₀	23	20	14	10
FS ₆	12	0	11	0

Table III.5 Inhibition zone in mm of CLOP and PEF antibiotic using disk diffusion method

sample	Pseudomonas (-)	
COL	23	/
PEF	/	22

To quantitatively evaluate the results of FS_x in the previous wall diffusion method, we conducted a broth dilution technique to determine the Minimum Inhibitory Concentration (MIC) and Minimum Bactericidal Concentration (MBC) of FS₀ and FS₆ solution. Where 4 dilutions of FS₀ and FS₆ powder were prepared (0.5 mg/ml, 1 mg/ml, 2 mg/ml, and 4 mg/ml) and tested against Pseudomonas and Bacillus bacteria using a 96-well plate, then incubated for 24 h at 37 °C, a sterilized swap was used to wipe the solutions of each concentration on clear agar then incubate it for 24 h. The results are summarized in Table III.6.

The Minimum Inhibitory Concentration (MIC) and Minimum Bactericidal Concentration (MBC) of FS₀ and FS₆ solutions were determined to be 4 mg/mL and 2 mg/mL, respectively, against Pseudomonas and Bacillus bacteria. These results indicate that both solutions exhibit bacteriostatic and bactericidal activity at the same concentrations. Specifically, FS₀ and FS₆ were bacteriostatic and bactericidal against Pseudomonas at 4 mg/mL and against Bacillus at 2 mg/mL.

The observed differences in activity can be attributed to the structural variations in bacterial cell walls. Gram-positive bacteria like Bacillus possess a thick, peptidoglycan-rich cell wall, which includes teichoic and lipoteichoic acids, whereas Gram-negative bacteria, such as Pseudomonas, have a thinner peptidoglycan layer but a more complex cell wall with an outer membrane. This outer membrane in Gram-negative bacteria enhances their defense by regulating molecule

passage and impeding external agents, contributing to their increased resistance to antimicrobial agents compared to Gram-positive bacteria. Consequently, the structural complexity of Gram-negative bacteria likely explains their higher MIC and MBC values in this study [50, 51].

Table III.6 MIC and MBC test values of FS_x powders.

Samples	Type			
	Pseudomonas (-)		Bacillus (-)	
	MIC	MBC	MIC	MBC
FS ₀	4	4	2	2
FS ₆	4	4	2	2

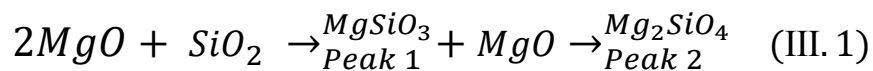
Part Three: Kinetics of enstatite and forsterite phase crystallization

In this section, the activation energy of enstatite and forsterite crystallization was determined, including their kinetic parameters (n, m), kinetic model, and thermodynamic parameters. The primary objective of this study was to evaluate the influence of crystallization on the kinetic behavior of these phases, focusing on understanding the mechanism involved in their formation under controlled heating conditions.

III.1. Kinetic analyses

III.1.1. Activation energy determination of enstatite and forsterite crystallization

To determine the activation energy for the previously formed forsterite phase, specimens were heated in the DTA equipment to 1300 °C at 5, 10, and 20 °C/min heating rates. The obtained curves are shown in Figure III.20 (a, b). Figure III.20 (a) shows that in addition to the peak of the forsterite phase observed at 20 °C/min heating rate, a new phase transformation appeared when the specimens were heated at relatively low heating rates of 5 and 10 °C/min. This peak is not detected at a relatively high 20 °C/min heating rate. Therefore, other specimens were heated up to 1300 °C at low heating rates of 2, 3, and 4 °C/min, and the obtained curves are presented in Figure III.20 (b). Enlarged portions of DTA curves obtained at low heating rates show two peaks in the temperature ranges of 770 to 840 °C and 810 to 850 °C, as shown in Figures III.21 (a, b). The first peak is believed to be due to the formation of enstatite, while the second one is associated with the formation of forsterite. These consecutive peaks observed at low heating rates could be due to a two-step phase transformation. In the first step, enstatite is formed, followed by the formation of forsterite in the second step as a result of enstatite reacting further with MgO. This can be described by the following equation:



Researchers who synthesized forsterite found that a layer of Mg₂SiO₄/MgSiO₃ forms between the MgO and SiO₂ particles during the solid-state reaction process. Forsterite then forms as a result of the diffusion of Mg²⁺ and Si⁴⁺ ions through this layer [29, 52, 53].

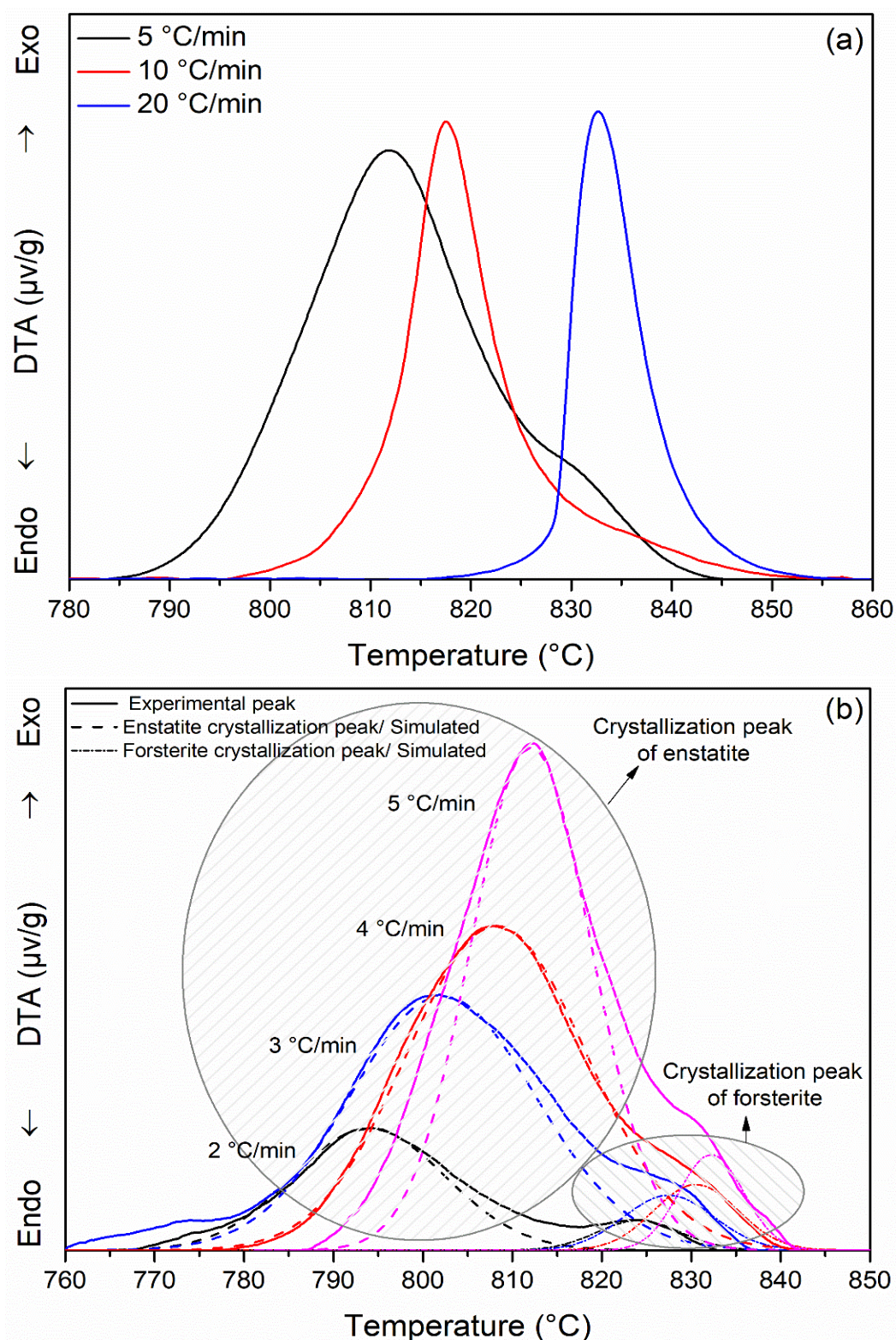


Figure III.20 DTA curves for FS_0 sample heated at (a) high heating rates (overlapping peaks) and (b) low heating rates (separated peaks).

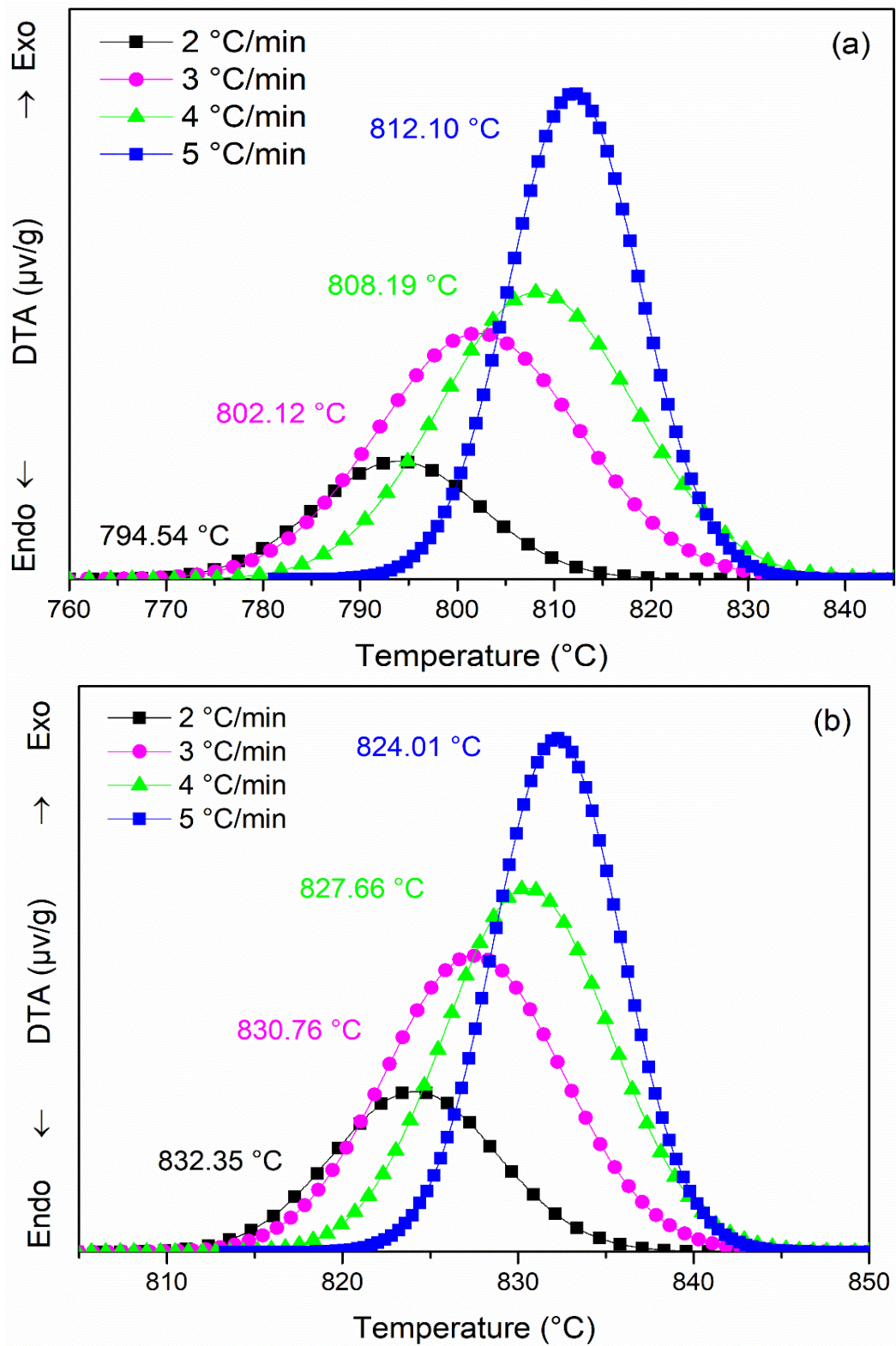


Figure III.21 DTA curves of (a) enstatite and (b) forsterite phase crystallization in FS_0 powder treated at different heating rates.

To determine the exothermal absolute peak temperature T_m of enstatite and forsterite phase crystallization at different heating rates (2 °C, 3 °C, 4 °C, and 5 °C), the DTA curves of enstatite and forsterite crystallization are shown in Figure III.21 (a, b). The activation energy values of Kissinger's, Ozawa's, and Boswell's methods are indicated by Eqs. III.2, III.3, and III.4 were obtained by plotting $\ln(\phi)$, $\ln\left(\frac{\phi}{T_m^2}\right)$, and $\ln\left(\frac{\phi}{T_m}\right)$ as a function of $1/T_m$.

$$\ln\left(\frac{\phi}{T_m^2}\right) = -\frac{E_\alpha}{RT_m} + C_1 \quad (\text{III. 2})$$

$$\ln(\phi) = -1.052\left(\frac{E_\alpha}{RT_m}\right) + C_2 \quad (\text{III. 3})$$

$$\ln\left(\frac{\phi}{T_m}\right) = -\frac{E_\alpha}{RT_m} + C_3 \quad (\text{III. 4})$$

The curves are illustrated in Figure III.22 (a, b), and E_α and R^2 (the coefficient of determination) values were compiled in Table III.7. The activation energy values obtained for enstatite phase formation were 472.46 kJ/mol (Ozawa), 479.14 kJ/mol (Kissinger), and 488.08 kJ/mol (Boswell). The results of activation energy were compared with those available in previous reports. **I. Naoya** et al. also reported similar results, finding enstatite activation energy to be 505 ± 188 kJ/mol prepared by the double-capsule technique [54]. As for forsterite formation phase activation energy values were 1028.89 kJ/mol (Ozawa), 1064.08 kJ/mol (Kissinger), and 1073.24 kJ/mol (Boswell), Our findings suggest that the activation energies for the enstatite and forsterite phases within the forsterite equivalent powder (FS₀) closely align with the results of available reported. The crystallization fraction α and its crystallization rate da/dt curves of enstatite and forsterite phase in forsterite equivalent powder (FS₀) are plotted at different heating rates (2 °C, 3 °C, 4 °C, and 5 °C) in Figure III.23 (a, b), and were calculated based on the DTA curves shown in Figure III.21 (a, b) by applying Eq. III.5.

$$\alpha = \frac{\int_0^t Q dt}{\int_0^{t_f} Q dt} \quad (\text{III. 5})$$

It was noted that the temperature T_m and the crystallization rate da/dt for both exothermal peaks of enstatite and forsterite increase while the heating rate increases.

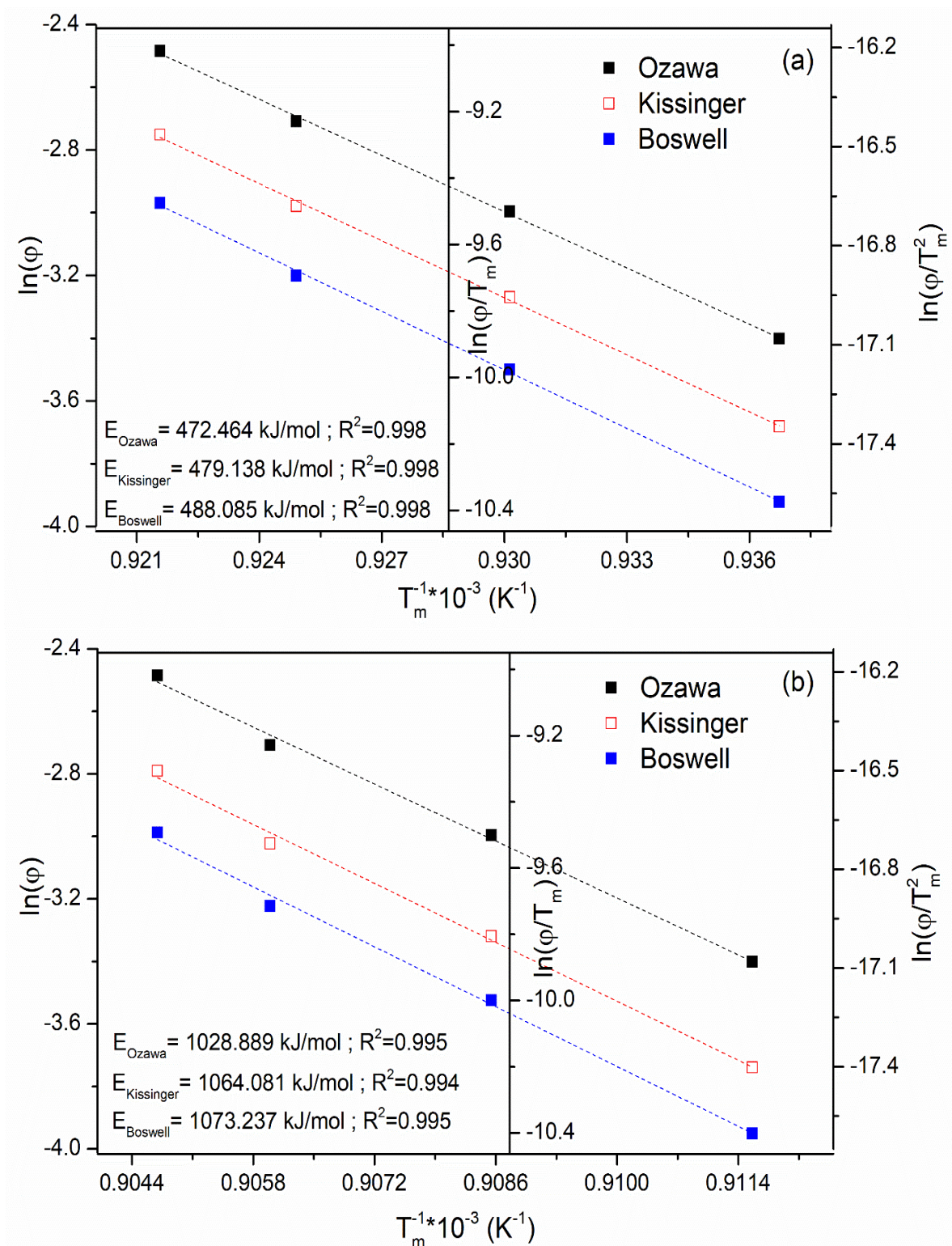


Figure III.22 Plots of $\ln(\phi)$, $\ln\left(\frac{\phi}{T_m^2}\right)$, and $\ln\left(\frac{\phi}{T_m}\right)$ as a function of $1/T_m$ for the formation of (a) enstatite and (b) forsterite.

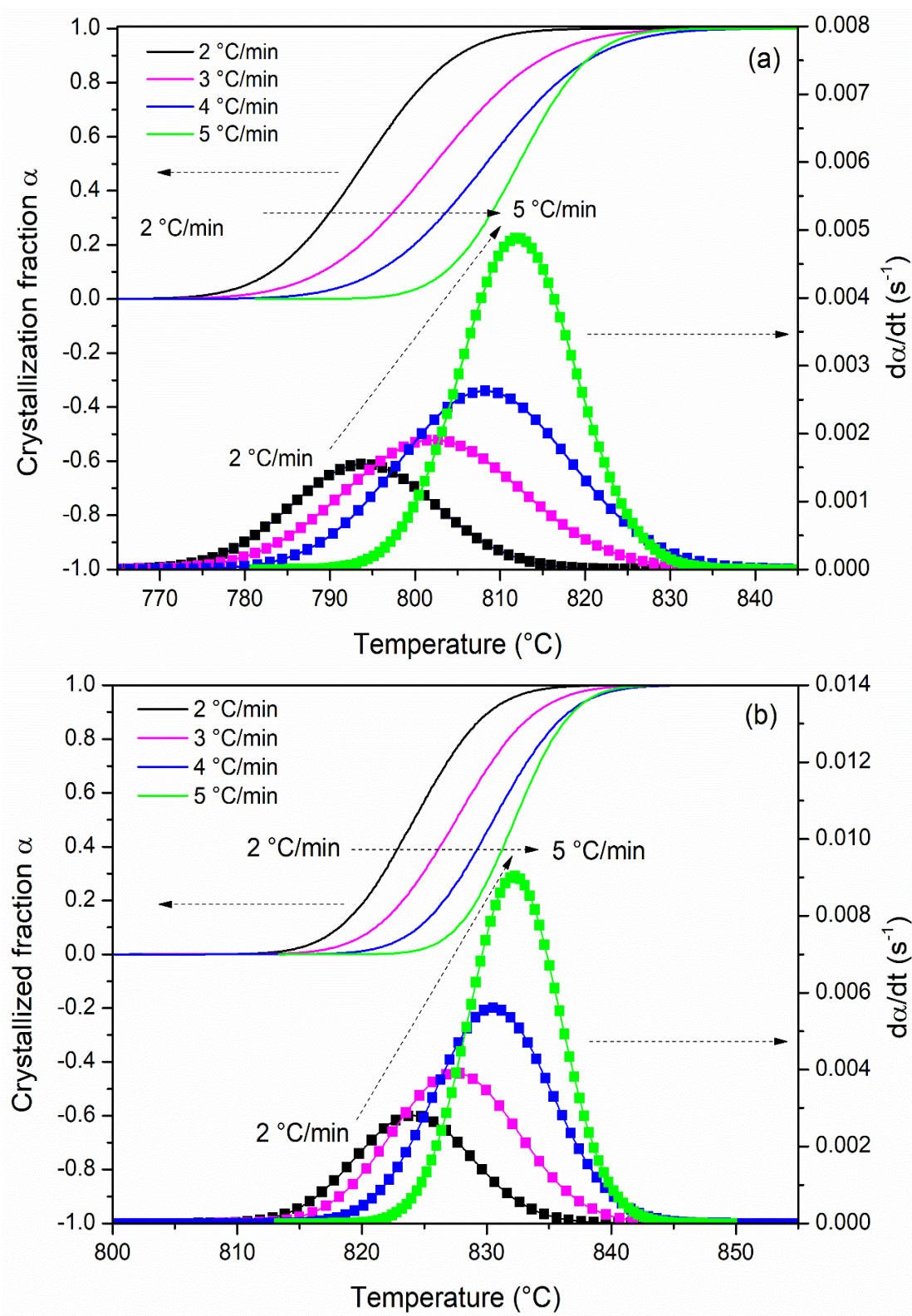


Figure III.23 Changes in the crystallized fraction and rate of crystallization during the formation of (a) enstatite and (b) forsterite at various heating rates.

Table III.7 The E_a and R^2 values of enstatite and forsterite crystallization using Kissinger, Ozawa, and Boswell methods.

Phase formation	R^2	E_a (Kj/mol)	Method
Enstatite	0.998	479.138	Kissinger
	0.998	472.464	Ozawa
	0.998	488.085	Boswell
Forsterite	0.994	1064.082	Kissinger
	0.995	1028.889	Ozawa
	0.995	1073.237	Boswell

To evaluate the activation energy throughout the crystallization process. The activation energy E_a of enstatite and forsterite crystallization in our work was calculated using Flynn–Wall–Ozawa (FWO) and Kissinger-Akahira-Sunose (KSA) methods according to Eqs. III.6 and III.7, respectively.

$$\ln(\phi_i) = -1.052 \left(\frac{E_a}{RT_{\alpha,i}} \right) + C_4 \quad (\text{III. 6})$$

$$\ln \left(\frac{\phi_i}{T_{\alpha,i}^2} \right) = - \frac{E_a}{RT_{\alpha,i}} + C_5 \quad (\text{III. 7})$$

$\ln(\phi_i)$ and $\ln \left(\frac{\phi_i}{T_{\alpha,i}^2} \right)$ are plotted as a function of $1/T_{\alpha,i}$, illustrated in Figure III.24 (a, b). and Figure III.25 (a, b), where $T_{\alpha,i}$ is the temperature at various conversion values within the range of $\alpha \in [0.3, 0.75]$. The values obtained from the slope of activation energies E_a and R^2 are listed in Table III.8. The average enstatite phase activation energy E_a values for the FOW and KAS methods were 456.32 kJ/mol and 462.20 kJ/mol, respectively. The average value of forsterite activation energy E_a for FWO and KAS were 1068.40 kJ/mol and 1105.66 kJ/mol, respectively.

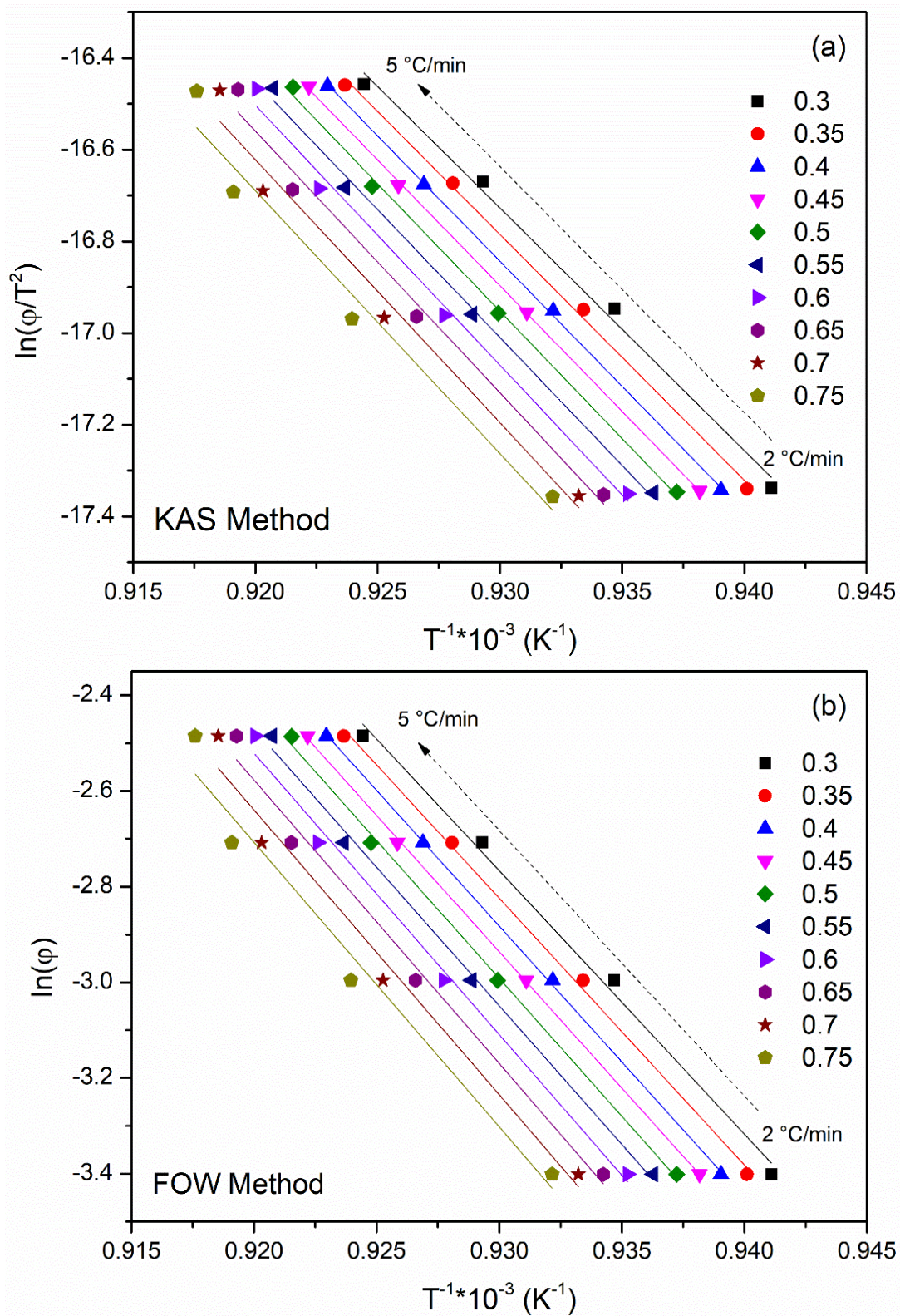


Figure III.24 Plot of (a, b) $\ln(\phi)$ and $\ln\left(\frac{\phi}{T_m^2}\right)$ versus $(1/T_m)$ following the (a) KAS and (b) FWO methods for the formation of the enstatite phase.

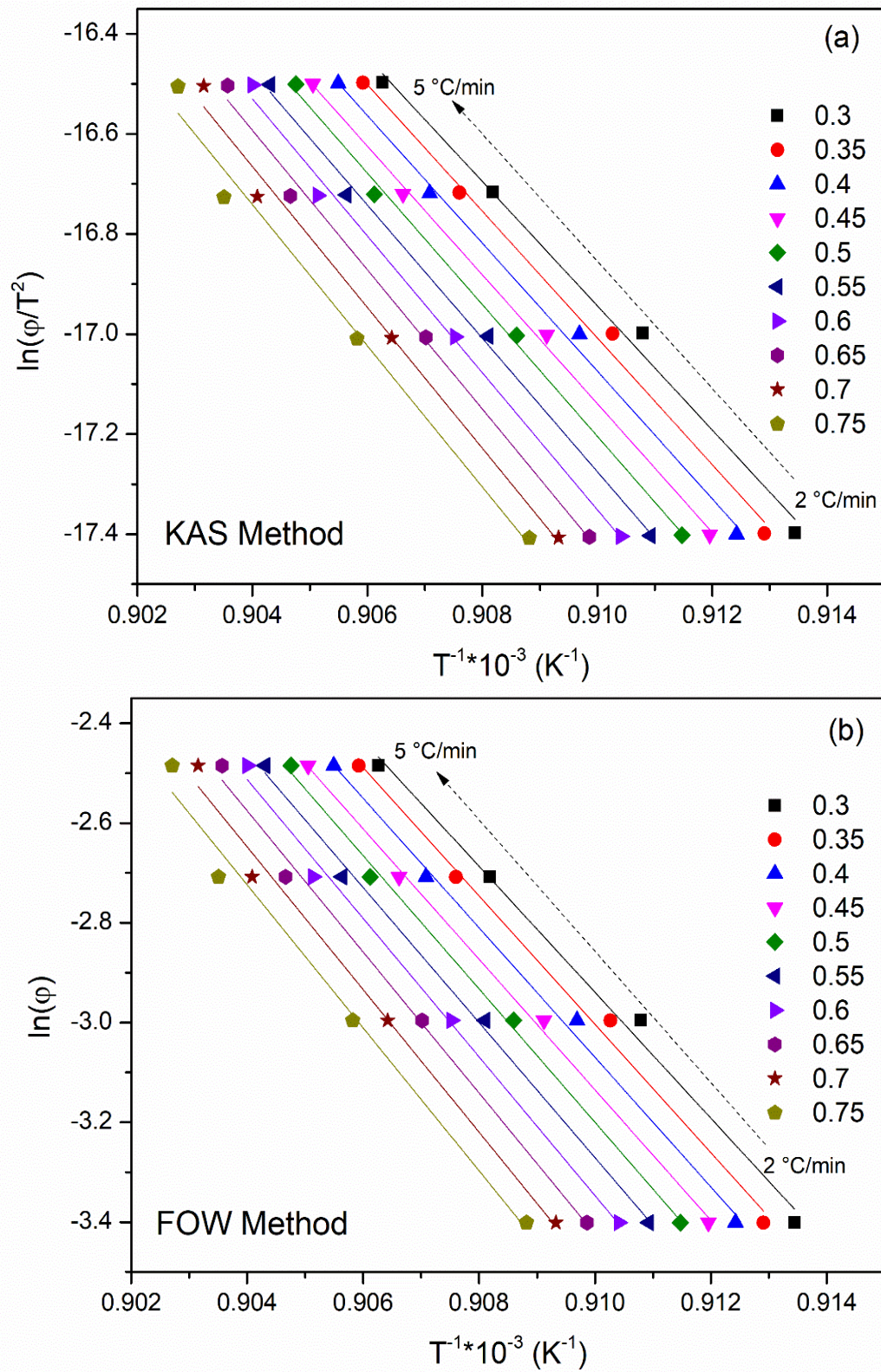


Figure III.25 Plot of (a, b) $\ln(\phi)$ and $\ln\left(\frac{\phi}{T_m^2}\right)$ versus $(1/T_m)$ following the (a) KAS and (b) FWO methods for the formation of forsterite phase.

Table III.8 The values E_α and R^2 for the formation of enstatite and forsterite using KAS and FWO methods for different crystallized fractions.

Conversion (α)	Enstatite				Forsterite			
	FWO		KAS		FWO		KAS	
	E_α (kJ/mol)	R^2	E_α (kJ/mol)	R^2	E_α (kJ/mol)	R^2	E_α (kJ/mol)	R^2
0.3	435.281	0.992	440.090	0.991	998.124	0.991	1031.752	0.99
0.35	440.81	0.997	445.890	0.997	1017.596	0.992	1052.227	0.992
0.4	448.855	0.999	454.337	0.999	1026.639	0.995	1061.731	0.994
0.45	450.480	0.999	456.031	0.999	1034.305	0.997	1069.787	0.997
0.5	455.632	0.997	461.956	0.997	1056.828	0.996	1093.656	0.996
0.55	458.004	0.994	463.914	0.994	1070.515	0.996	1107.862	0.995
0.6	465.004	0.99	471.262	0.99	1098.955	0.993	1137.773	0.992
0.65	468.358	0.982	474.774	0.981	1118.162	0.992	1157.968	0.992
0.7	470.599	0.97	477.114	0.97	1130.127	0.99	1170.54	0.99
0.75	470.139	0.96	476.61	0.96	1132.711	0.98	1173.254	0.98
Average	456.316		462.198		1068.395		1105.655	

Enstatite and forsterite calculated activation energy for the previous two methods were plotted as a function of crystallization fraction α and shown in Figure III.26 (a, b). The apparent activation energy based on the crystallization fraction (α) for both FWO and KAS methods showed similar values for all crystallization fraction α ; it remained nearly constant during enstatite and forsterite phase formation. The average energies for the enstatite phase were 456.65 kJ/mol (FWO) and 462.29 kJ/mol (KAS). For the forsterite phase were 1069.45 kJ/mol (FWO) and 1106.75 kJ/mol (KAS). This indicates the existence of a consistent mechanism that occurs in the solid-state reactions throughout the thermal reaction process [55]. **A. Kan** et al. reported an activation energy ranging from 1382.4-470 kJ/mol for forsterite crystallization, where the addition of LiF reduced the activation energy significantly due to the enhancement of nucleation and crystallization [15].

By comparing the activation energy calculated by the KAS and FWO methods with the activation energy calculated by the Kissinger method (differential and integral isoconversional method) for both phases formed, it is noted that their average activation energies are very similar which indicates that the activation energy is less dependent on the method of calculation. The slight differences in the values of kinetic parameter E_a obtained by various methods can result from the computational data treatment methods [56].

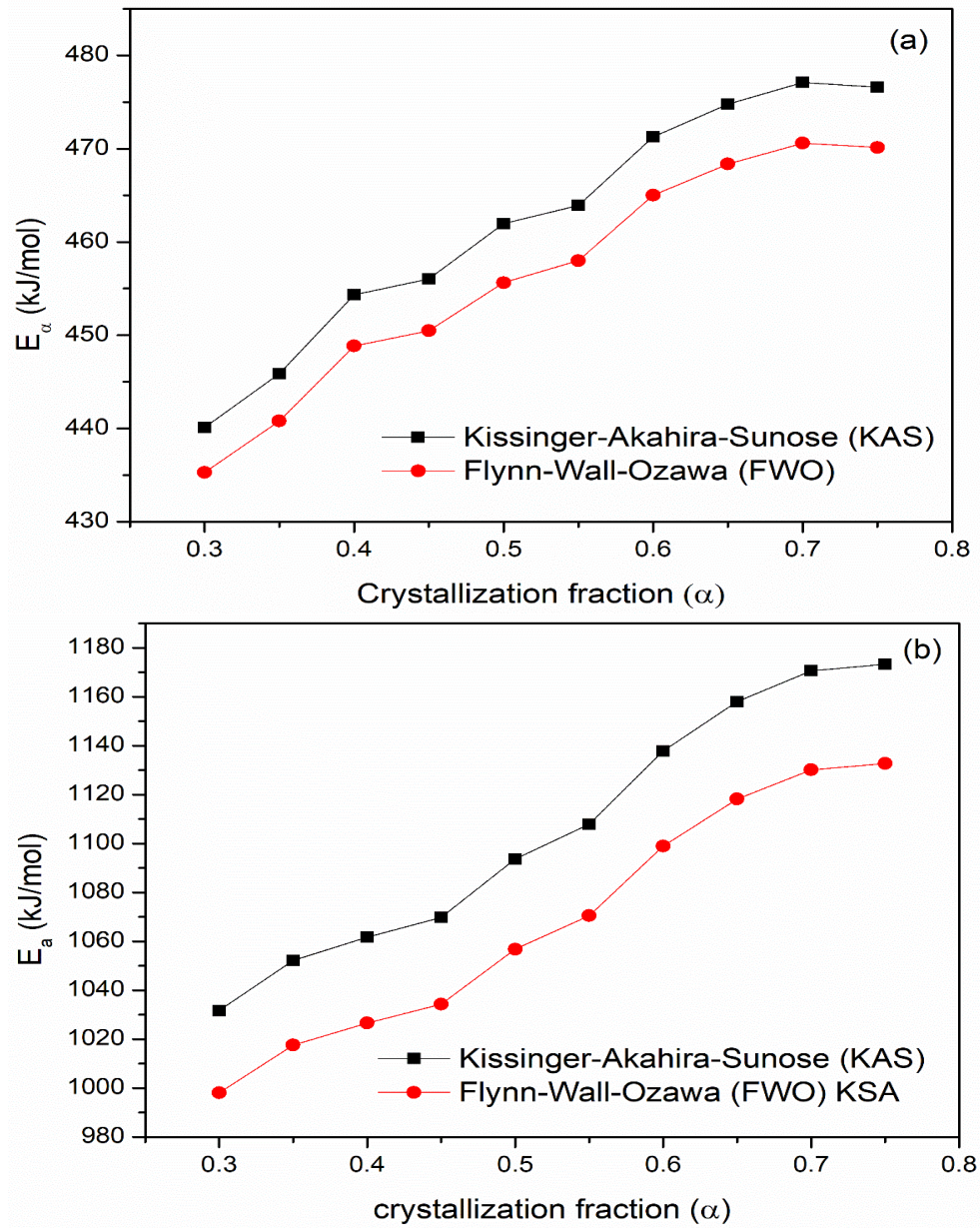


Figure III.26 Change in activation energy for forming (a) enstatite and (b) forsterite as a function of crystallization fraction following the KAS and FWO methods.

III.1.2. Reaction model determination of forsterite and enstatite crystallization

The $y(\alpha)$, $z(\alpha)$, and $d\alpha/dt$ functions are calculated using Kissinger activation energy to determine the kinetic interaction model for the crystallization of the previous phase. Figure III.23 (a, b) shows the DTA analysis of enstatite and forsterite crystallization peaks in FS_0 powder at different heating rates. The activation energy is independent of the crystallization fraction and is calculated based on the heating rate in terms of the reciprocal maximum temperature of the transformation at each heating rate, as observed in Kissinger, Ozawa, and Boswell methods [55]. The activation energy of enstatite and forsterite crystallization was calculated to be 479.138 kJ/mol and 1064.082 kJ/mol, respectively. The experimental data were used to determine the reaction model, thus its kinetic parameters, as shown in Eqs. III.8 and III.9, respectively.

$$y(\alpha) = \frac{d\alpha}{dt} \exp(x) \quad (\text{III. 8})$$

$$z(\alpha) = \frac{d\alpha}{dt} \frac{T}{\phi} \pi(x) \quad (\text{III. 9})$$

From these, the functions $y(\alpha)$, $z(\alpha)$, and $d\alpha/dt$ were constructed in terms of the conversion ratio α for different heating rates for all formed phases in FS_0 powder, as depicted in Figure III.27 (a, b) and Figure III.28 (a, b).

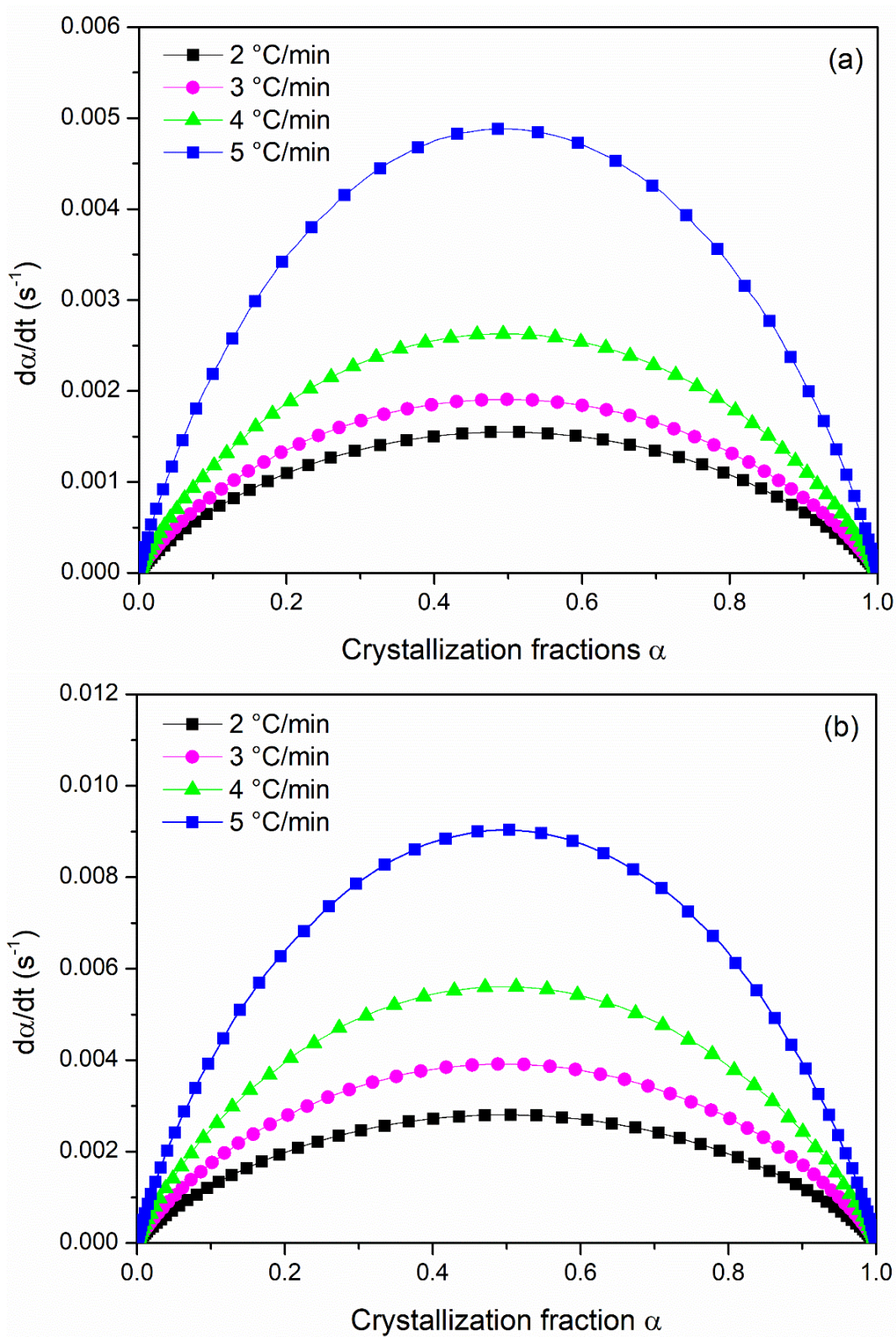


Figure III.27 Crystallization rate ($d\alpha/dt$) as a function of crystallization fraction α of the formation of enstatite and forsterite in forsterite equivalent powder treated at different heating rates.

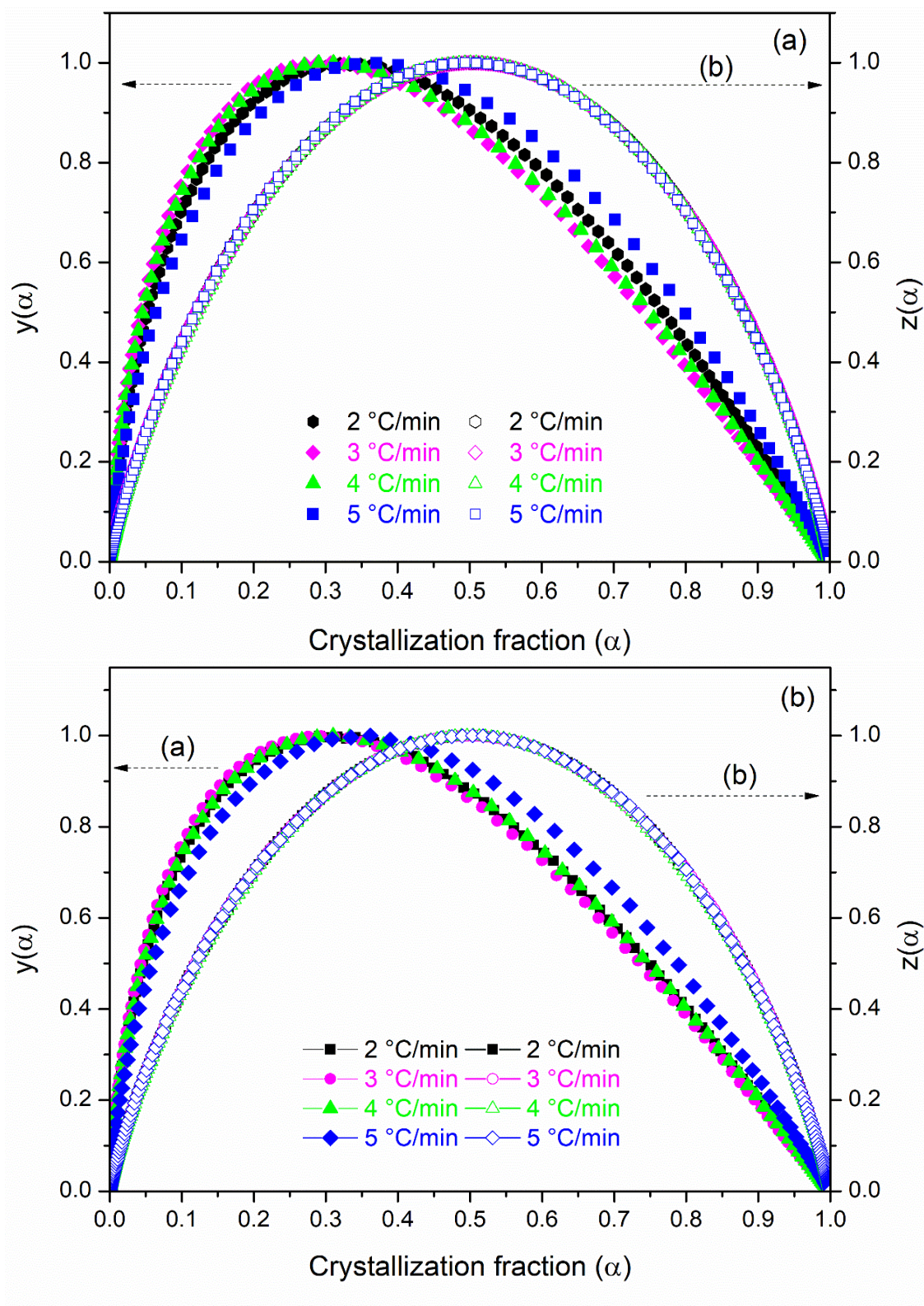


Figure III.28 Plots of normalized $y(\alpha)$ (a) and $z(\alpha)$ (b) versus α of enstatite and forsterite crystallization at different heating rates.

The maximum α_p , α_m , and α_p^∞ of the functions $y(\alpha)$ and $z(\alpha)$ and $(d\alpha/dt)$, respectively, were determined at different heating rates as shown in Table III.9, and based on these limits, the appropriate reaction model $f(\alpha)$ (Eq. III.10) is selected, under the conditions defined by J. Malek as shown in Table III.9. By comparing α_p , α_p^∞ , and α_m experimental values with the theoretical conditions shown in Table III.9 [57], it was possible to determine the enstatite and forsterite reaction model of phase crystallization $f(\alpha)$.

$$f(\alpha) = \alpha^m(1 - \alpha)^n \quad (\text{III. 10})$$

From Table III.10, our experimental results realize the Šesták Berggren (SB) model conditions, where $\alpha_m < \alpha_p < \alpha_p^\infty$ and $\alpha_p^\infty \neq 0.623$ at different heating rates. According to J. Malek [58-60], we can say that the reaction of the previous phase's formation (enstatite and forsterite phase formation) is according to the Šesták Berggren model. From the Šesták Berggren model, the reaction equation is described in Eq. III.11 as:

$$\frac{da}{dt} = A \exp\left(-\frac{E_a}{RT}\right) \alpha^m(1 - \alpha)^n \quad (\text{III. 11})$$

According to J. Malek, the SB model's kinetic parameters (n, m) follow Eq. III.12.

$$P = \frac{\alpha_m}{1 - \alpha_m} = \frac{m}{n} \quad (\text{III. 12})$$

Table III.9 The values of α_m , α_p , and α_p^∞ that define the J. Malék method.

Heating rate φ (°C/min)	Enstatite			Forsterite		
	α_p^∞	α_m	α_p	α_p^∞	α_m	α_p
2	0.5047	0.323	0.4978	0.5009	0.301	0.497
3	0.5047	0.2967	0.4957	0.4991	0.298	0.496
4	0.5047	0.307	0.4957	0.5009	0.306	0.4957
5	0.4978	0.366	0.493	0.5009	0.347	0.4991
Average	0.5029	0.3231	0.4955	0.50045	0.313	0.49695

Table III.10 Reaction models and α_p^∞ and α_m according to J. Malek's method.

Reaction model	Notation	$f(\alpha)$	α_p^∞	α_m
Reaction order	RO (n)	$(1 - \alpha)^n$	$\frac{1}{1 - n^{1/(1-n)}}$	0
Jhonson Mehl Avrami general equation	JMA (m>1)	$m(1 - \alpha) \{-\ln(1n\alpha)\}^{1-\frac{1}{m}}$	0.633	$1 - \exp(\frac{1}{m} - 1)$
2D diffusion	D2	$-1/(\ln(1 - \alpha))$	0.834	0
3D diffusion (jander's equation)	D3	$\frac{3(1 - \alpha)^{2/3}}{2\{1 - (1 - \alpha)^{\frac{1}{3}}\}}$	0.704	0
3D diffusion (jander's equation)	D4	$\frac{3}{2\{(1 - \alpha)^{-\frac{1}{3}} - 1\}}$	0.776	0
<i>Šesták Berggren</i>	SB (m,n)	$\alpha^m(1 - \alpha)^n$	$(0, \alpha_p)$	$m/(m + n)$

III.1.3. Kinetic parameters determination of enstatite and forsterite crystallization

Eq. III.13 was obtained by taking the logarithm of Eq. III.11.

$$\ln \left[\left(\frac{da}{dt} \right) \exp(x) \right] = \ln A + n \ln [\alpha^P (1 - \alpha)] \quad (\text{III. 13})$$

Eq. III.13 represents a straight line of the type $y = a + bx$, where $x = \ln [\alpha^P (1 - \alpha)]$, $a = \ln A$, and $b = n$. n is the slope, and $\ln A$ is the interception of the plotted $\ln \left[\left(\frac{da}{dt} \right) \exp(x) \right]$ as a function of $\ln [\alpha^P (1 - \alpha)]$. We chose α values in the range $\alpha \in [0.3, 0.75]$ for different heating rates, as plotted in Figure III.29 (a, b).

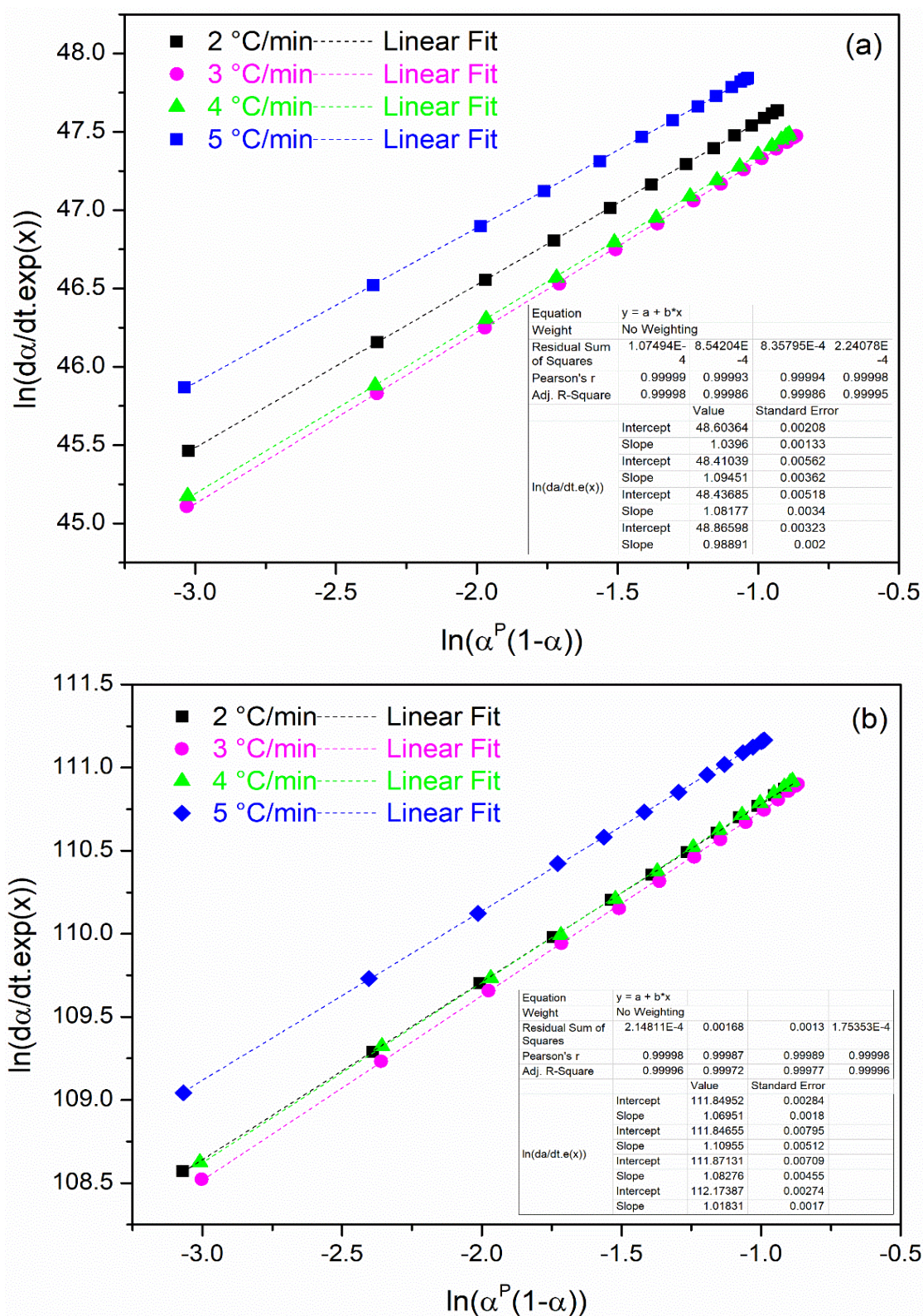


Figure III.29 Plots of $\ln(da/dt.exp(x))$ versus $\ln(\alpha^P(1-\alpha))$ of (a) enstatite and (b) forsterite crystallization at different heating rates.

The kinetic parameters (n, m) were obtained from Eqs. III.12 and III.13. Table III.11 represents the calculated kinetic parameters (n, m), p, and lnA values at different heating rate and their average value for enstatite and forsterite phases.

Table III.11 Values of Avrami parameters (n, m), frequency factor (A) of enstatite and forsterite at different heating rates.

Heat rate ϕ ($^{\circ}\text{C}/\text{min}$)					Average	
Parametres	2	3	4	5		
P	0.4771	0.4218	0.4430	0.5772	0.4568	Enstatite
n	1.0395	1.0945	1.0817	0.9890	1.0512	
m	0.4960	0.4617	0.4792	0.4843	0.5019	
ln(A)	48.6036	48.4103	48.4368	48.8660	48.5792	
A ($\times 10^{+21}$)	1.2832	1.06	1.09	1.67	1.25	
P	0.4306	0.4245	0.4409	0.5314	0.4568	Forsterite
n	1.0695	1.1095	1.0827	1.0183	1.070	
m	0.4605	0.4710	0.4774	0.5411	0.4875	
ln(A)	111.8495	111.8465	111.8713	112.1739	111.9353	
A ($\times 10^{+48}$)	3.7638	3.7527	3.8467	5.2059	4.1423	

The kinetic parameters (n, m) and lnA of enstatite were found to be 1.06, 0.529, and 48.60, respectively. We note that the heating didn't affect these parameters significantly. By calculating n, m, and A of the SB model, the reaction equation of enstatite crystallization is written as:

$$\frac{da}{dt} = 1.25 \times 10^{+21} \exp\left(-\frac{479.138 \times 10^3}{RT}\right) \alpha^{0.502} (1 - \alpha)^{1.051} \quad (\text{III. 14})$$

As for the reaction mechanism, J. Šesták and G. Berggren have published a report describing various reaction mechanisms [61]. The enstatite reaction equation suggests a reaction controlled by nucleation followed by linear nuclei growth, where $n > 1$ and $m < 1$. The kinetic parameters (n, m) and lnA of forsterite were 1.07, 0.487, and 111.93, respectively. We note that the heating didn't affect these parameters significantly.

By calculating the kinetic parameters (n, m), and A of the Šesták Berggren (SB) model, the reaction equation of forsterite can be written as follows:

$$\frac{da}{dt} = 4.1423 \times 10^{+48} \exp\left(-\frac{1064.082 \times 10^3}{RT}\right) \alpha^{0.487} (1 - \alpha)^{1.070} \quad (\text{III. 15})$$

As for the reaction mechanism, J. Šesták and G. Berggren have published a report describing various reaction mechanisms [56, 61]. The forsterite reaction equation suggests the growth of spherical particles controlled by diffusion, where the p value of the forsterite phase is below 0.5.

III.1.4. Simulation and experimental data

To observe the accuracy of the model $f(\alpha)$ used in our study, the DTA experimental data were compared with the calculated crystallization rates $\left(\frac{da}{dt}\right)$ and crystallization fraction (α) (after determining activation energy E_a , reaction model, and the kinetic parameters of the reaction).

After comparing the simulation curves of enstatite and forsterite crystallization rate $\left(\frac{da}{dt}\right)$ and crystallization fraction (α) in terms of temperature with the experimental ones. we say it is established that the used reaction model is the most compatible with studying and describing the progress of these reactions. The process in which enstatite and forsterite phases in FS_0 powder were formed is well expressed through the Šesták-Berggren model. Figure III.30 (a, b) shows that the Šesták Berggren (SB) model equation generally agrees with the experimental data.

The kinetic analyses we carried out in the study of enstatite and forsterite crystallization are the first to determine the reaction model that describes both crystallizations and mechanisms. Therefore, our data can generally be utilized as a reference study to the kinetics of the enstatite and forsterite phases.

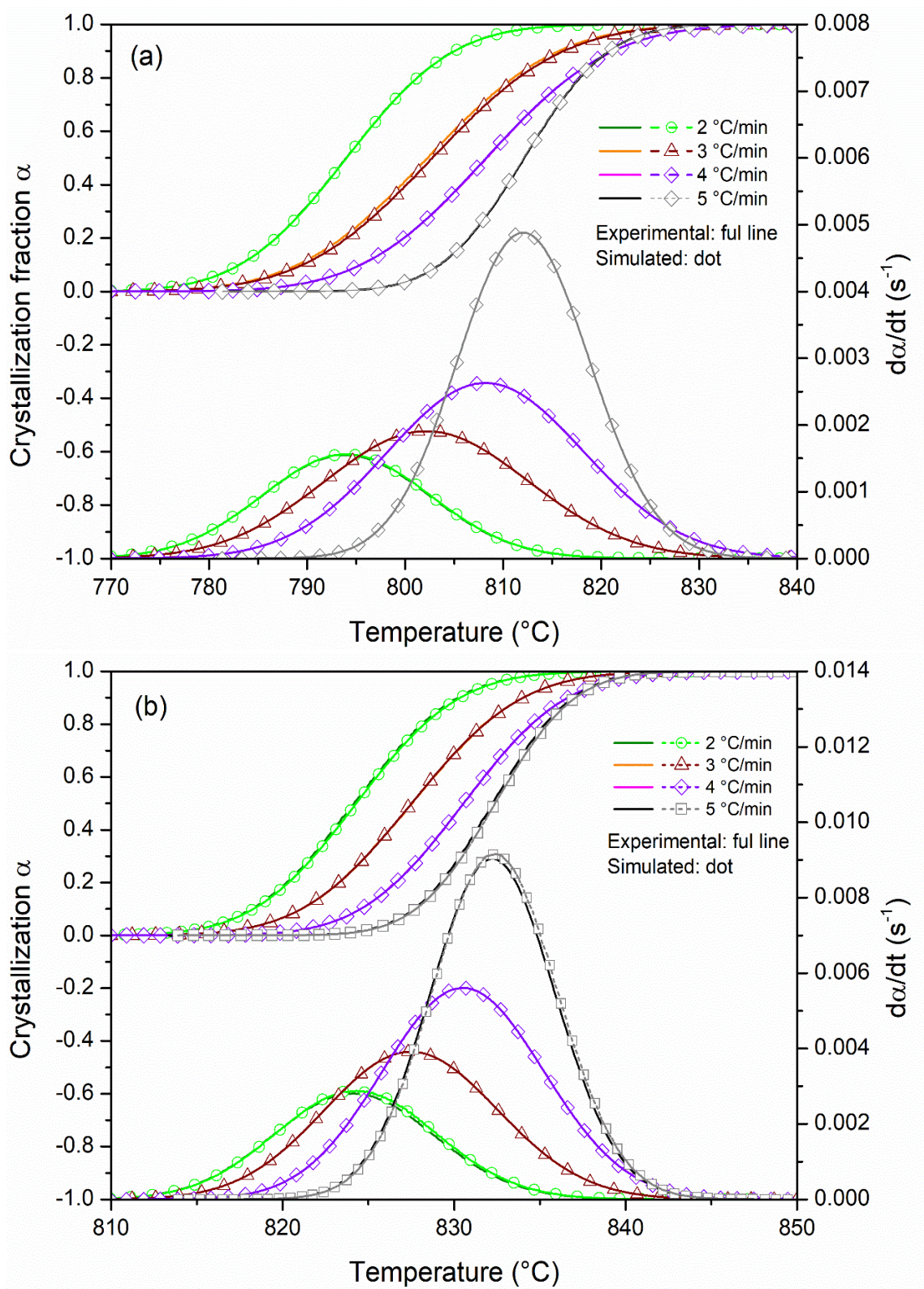


Figure III.30 Normalized experimental and simulated crystallization fractions and rate for the formation of (a) enstatite and (b) forsterite treated at different heating rates.

III.2. Thermodynamic properties of forsterite and enstatite crystallization

After determining the activation energy (E_a) and the pre-expansion coefficient (A) for both enstatite and forsterite crystallized in FS_0 powder under low heating rates of 2, 3, 4, 5 °C/min, we calculated the thermodynamic parameters of enstatite and forsterite crystallization using Eqs III.16, III.17, and III.18 in order to determine the free enthalpy (ΔG), enthalpy (ΔH), and the entropy (ΔS), the results are summarized in Table III.12.

$$A \exp\left(-\frac{E_a}{RT}\right) = v \exp\left(-\frac{\Delta G}{RT}\right) \quad (\text{III. 16})$$

$$\Delta H = E_a - RT \quad (\text{III. 17})$$

$$\Delta G = \Delta H - T\Delta S \quad (\text{III. 18})$$

Table III.12 details the values of ΔG , ΔH , and ΔS . We note increasing the heating rate from 2 °C/min to 5 °C/min, free enthalpy (ΔG) of enstatite and forsterite partially decreases from 320.984 kJ.mol⁻¹ to 315.348 kJ.mol⁻¹ and from 324.231 kJ.mol⁻¹ to 316.450 kJ.mol⁻¹, respectively. The enthalpy (ΔH) of enstatite and forsterite crystallization slightly dropped from 40.230 kJ.mol⁻¹ to 470.096 kJ.mol⁻¹ and from 1054.958 kJ.mol⁻¹ to 1054.898 kJ.mol⁻¹, respectively. Enstatite and forsterite crystallization's entropy (ΔS) increased from 138.231 J.mol⁻¹K⁻¹ to 142.287 J.mol⁻¹K⁻¹ and from 665.657 J.mol⁻¹K⁻¹ to 668.498 J.mol⁻¹K⁻¹, respectively.

The average calculated values of ΔG , ΔH , and ΔS for enstatite crystallization were 319.177 kJ.mol⁻¹, 470.155 kJ.mol⁻¹, and 139.458 J.mol⁻¹K⁻¹, respectively. Forsterite crystallization average values of ΔG , ΔH , and ΔS were 320.62 kJ.mol⁻¹, 1054.922 kJ.mol⁻¹, and 666.488 J.mol⁻¹K⁻¹, respectively. ΔS result shows a positive value where $\Delta S > 0$. A positive ΔS value for both enstatite and forsterite crystallization indicates that the activated complex (crystallization state) is more disordered than the reactants, making the reaction easier to form and faster than the case in which $\Delta S < 0$ [62, 63]. The decrease in ΔG as a function of heating rate indicates that the crystallization process becomes favorable and spontaneous at higher heating rates.

Table III.12 Thermodynamic parameters (ΔG , ΔH , and ΔS) for enstatite and forsterite crystallization.

Thermodynamic parameters	Heat rate ϕ ($^{\circ}\text{C}/\text{min}$)				Average	
	2	3	4	5		
ΔG ($\text{kJ}\cdot\text{mol}^{-1}$)	320.984	320.523	319.853	315.348	319.177	Enstatite
ΔH ($\text{kJ}\cdot\text{mol}^{-1}$)	470.230	470.159	470.133	470.096	470.155	
ΔS ($\text{J}\cdot\text{mol}^{-1}\text{K}^{-1}$)	138.231	138.559	138.756	142.287	139.458	
ΔG ($\text{kJ}\cdot\text{mol}^{-1}$)	324.231	321.944	319.855	316.450	320.62	Forsterite
ΔH ($\text{kJ}\cdot\text{mol}^{-1}$)	1054.958	1054.929	1054.906	1054.898	1054.922	
ΔS ($\text{J}\cdot\text{mol}^{-1}\text{K}^{-1}$)	665.657	665.806	665.991	668.498	666.488	

**Part Four: Hydroxyapatite-
forsterite composites: A study
of thermal, mechanical,
microstructural and biological
properties**

In this section, hydroxyapatite-forsterite (HAF_x) composites were synthesized using a combination of prepared natural hydroxyapatite powder treated up to 800 °C and forsterite powder treated up to 1400 °C. The primary objective of this study is to evaluate the influence of forsterite as an additive, up to a maximum of 20 wt%, on the phase composition and densification behavior under sintering conditions and also study the antibacterial activity.

IV.1. Thermogravimetry (TG/DTG), Differential thermal analysis (DTA) and X-ray diffraction (XRD) analyses of bovine bone powder

To study the phase transformations and mass loss accruing in bovine bone (HAF_0) powder under heat treatment, the powder was thermally treated at 20 °C/min rate up to 1400 °C, using thermogravimetry and differential thermal analysis equipment. Figure III.31 (a, b) shows the TG/DTG and DTA curves.

Figure III.31 (a) shows multiple endothermic peaks. Between room temperature and 1000 °C, four endothermic peaks are detected. The first exothermal peak under 200 °C exactly at 173 °C with a mass loss of 7 %, which is associated with the evaporation of water (bone dehydration), while the second, at 354.84 °C with 23.22 %, corresponds to the decomposition of the organic matrix like collagen and protein. The last two endothermal peaks at 725.8 °C and 887.43 °C display the complete removal of carbonate from the bone samples, and the decarbonization process could continue up to 890 °C with a mass loss of 5.98 %. No mass loss was detected between 900 °C and 1000 °C, confirming that all the organic materials and carbonate were removed completely below 900 °C.

Figure III.31 (b) shows the DTA curve of bovine bone treated at 20 °C/min from room temperature to 1050 °C. Figure III.31 (b) shows one endothermic and three exothermal peaks. The first endo thermal peak at 173 °C is related to water removal, also noted in the TG/DTG curve. The first exothermal peak at 375.7 °C corresponds to the decomposition of organic matter in the bone, and the second exothermal peak at 737 °C displays the calcination of the bone and complete removal of carbonate. The decarburization process is approximately finished at 900 °C. The last exothermal peak was determined at 979 °C, corresponding to the hydroxyapatite phase's crystallization, as it aligns with the TG/DTG curve, which showed no mass change above 850 °C. Reports from **J. Manalu** et al. and others have been published confirming our study [64-66].

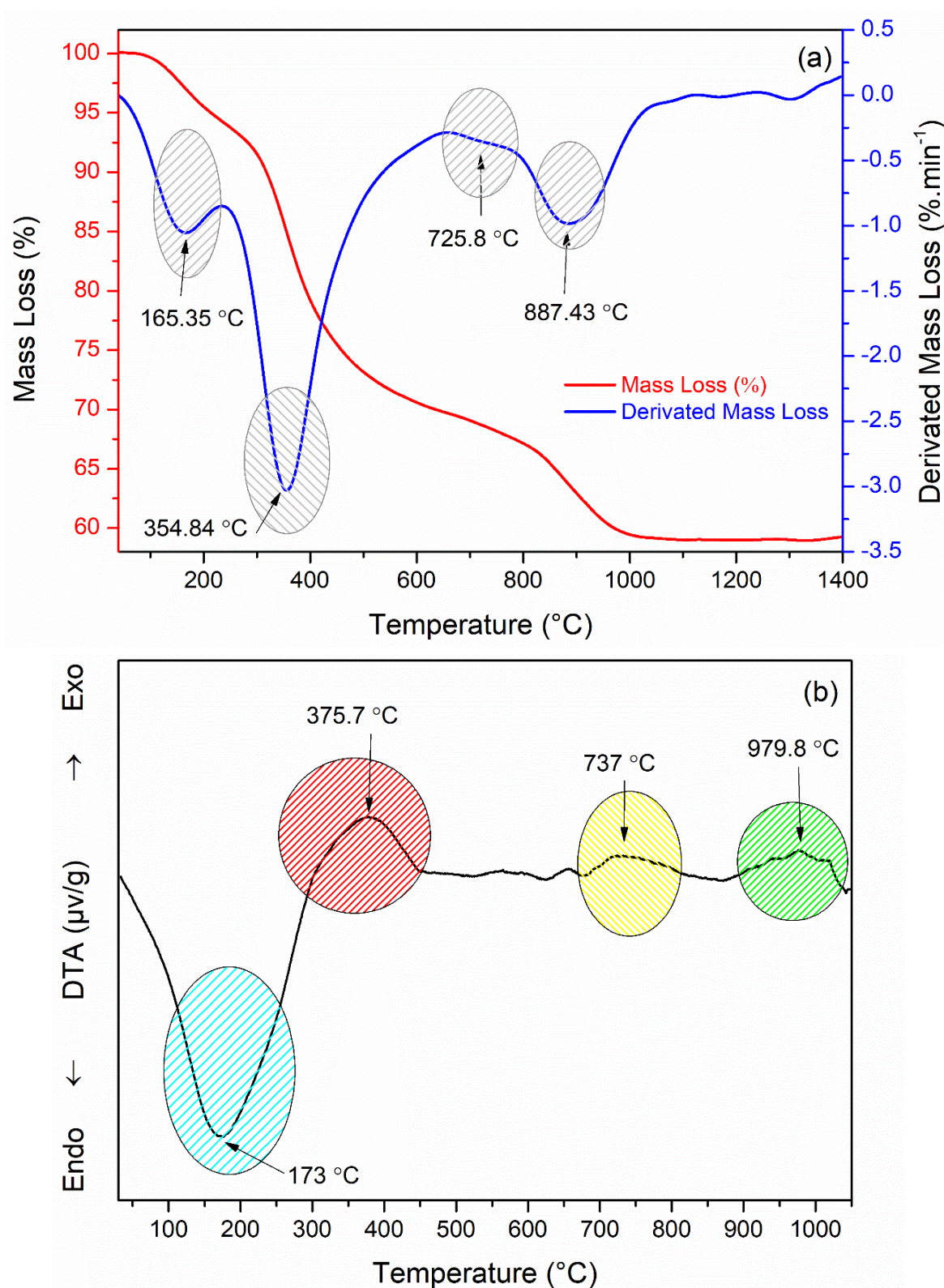


Figure III.31 (a) TG, DTG, and (b) DTA curves for bovine bone heated at 20 °C/min up to 1400 °C.

To identify the crystallized phases in the bone powder illustrated in DTA analysis in Figure III.31 (b), samples of the prepared bone powder were treated via DTA to different temperatures (230, 520, 610, 780, 1000, 1050, and 1400 °C) then an XRD analysis were performed to each sample. Figure III.32 shows the XRD spectra of heated bovine bone specimens up to 1400 °C. The XRD spectra up to 780 °C show weak peaks of the Apatite-CaOH phase, which confirms the peak of the decarburization process in the DTA curve at 737 °C. At 1000 °C, high-intensity hydroxyapatite peaks were detected. Further temperatures (1050 °C and 1400 °C) showed the increasing intensity of the hydroxyapatite phase. The results confirm that the previous DTA peak at 979.8 °C corresponds to the hydroxyapatite crystallization. The TG and DTA analyses confirmed that all the organic materials and carbonate are removed by heating to 800 °C to obtain pure hydroxyapatite.

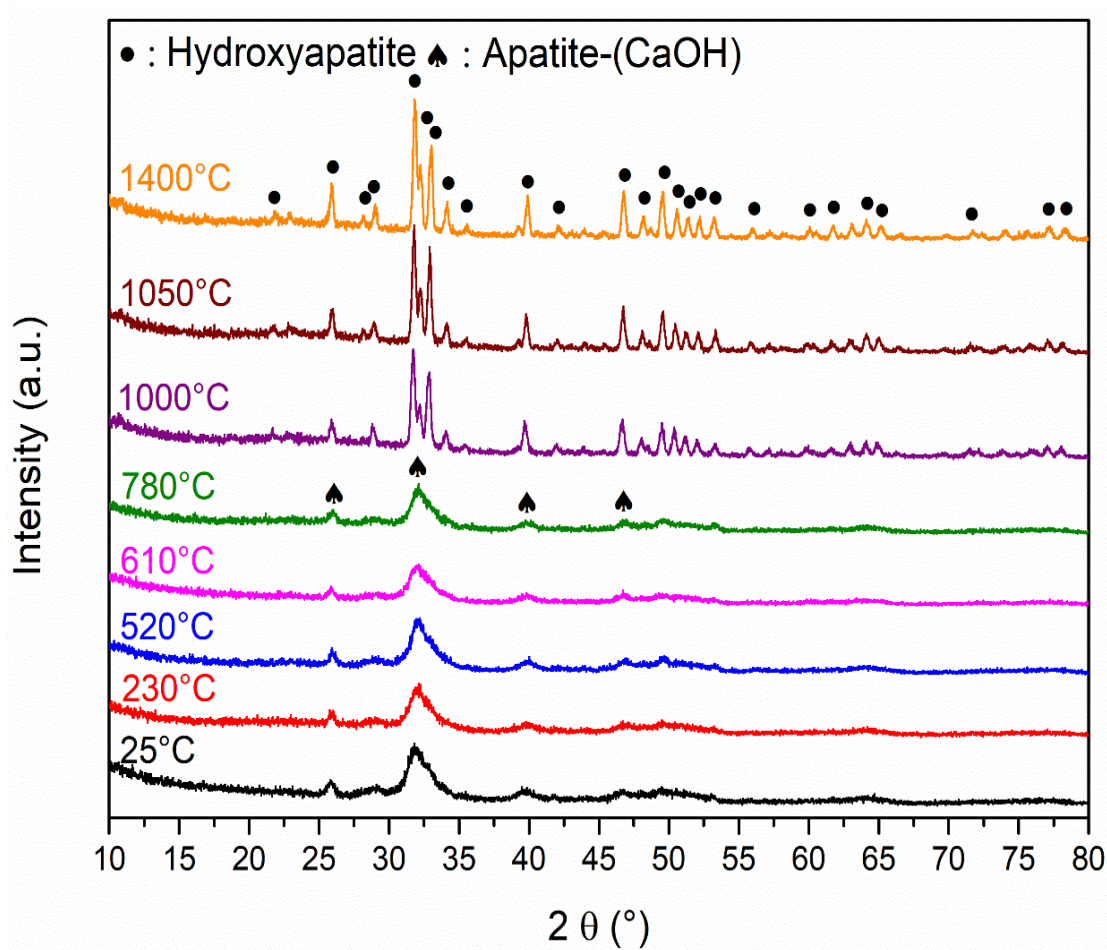


Figure III.32 XRD spectra of heated bovine bone specimens up to 230, 520, 610, 780, 1000, 1050, and 1400 °C.

IV.2. Analysis of shaped and sintered Hydroxyapatite-forsterite composites (HAF_x) samples

IV.2.1. X-ray analysis of Hydroxyapatite-forsterite composites (HAF_x) samples after sintering

Hydroxyapatite-Forsterite (HAF_x) samples were sintered for 2 hours at 1250, 1300, 1350, and 1400 °C and were heated at a 5 °C/min rate. Figure III.33 (a, b, c) shows the XRD spectra of samples

HAF₀, HAF₁₀, and HAF₂₀. The results were summarized as follows:

Figure III.33 (a) shows the crystallization of pure hydroxyapatite peaks only in sample HAF₀ at 1250 °C with no change in intensity or phase detected while increasing the sintering temperature to 1400 °C. The XRD results indicate that 1250 °C is sufficient for the sintering temperature to form the hydroxyapatite phase. Figure III.33 (b) shows that sample HAF₁₀ presents peaks of various detected phases. At 1250 °C, hydroxyapatite and β -TCP peaks are present in the same intensity as major detected peaks with secondary diopside, enstatite, and majorite peaks. From 1300 °C to 1350 °C, we noticed that the increasing sintering temperature decreased the hydroxyapatite diffraction peak intensity, accompanied by the β -TCP increasing peak intensity. The diopside phase disappears at 1350 °C. Some researchers have reported that hydroxyapatite doped with Mg decomposed to β -TCP and Ca₄Mg₅(PO₄)₆, [67, 68] and it was explained that the increasing of Mg prevents the formation of hydroxyapatite and aids the formation of secondary phases such as TCP [69, 70]. The increasing forsterite content in the HAF₁₀ sample may lead to the decomposition of hydroxyapatite and yield new secondary phases such as diopside and majorite. A report by **Salami** et al. demonstrated that Mg²⁺ ions significantly inhibit the growth of hydroxyapatite (HA). This inhibition is attributed to the adsorption of Mg²⁺ at active growth sites on the hydroxyapatite structure, which kinetically interferes with the nucleation process of hydroxyapatite [71]. At 1400 °C, low-intensity hydroxyapatite, enstatite, and majorite peaks were apparent. Figure III.33 (c) shows HAF₂₀ sample XRD spectra. We note that the same phases detected in sample HAF₁₀ are present in sample HAF₂₀, with an additional forsterite phase detected at 1250 °C. The forsterite phase increased while increasing the sintering temperature to

1350 °C. At 1400 °C, the HAF₂₀ sample showed peaks of weak of peaks hydroxyapatite, β -TCP, and enstatite only. Physically, the HAF₂₀ sample showed melting and bloating signs, which explains the decrease in the intensity of all phase peaks.

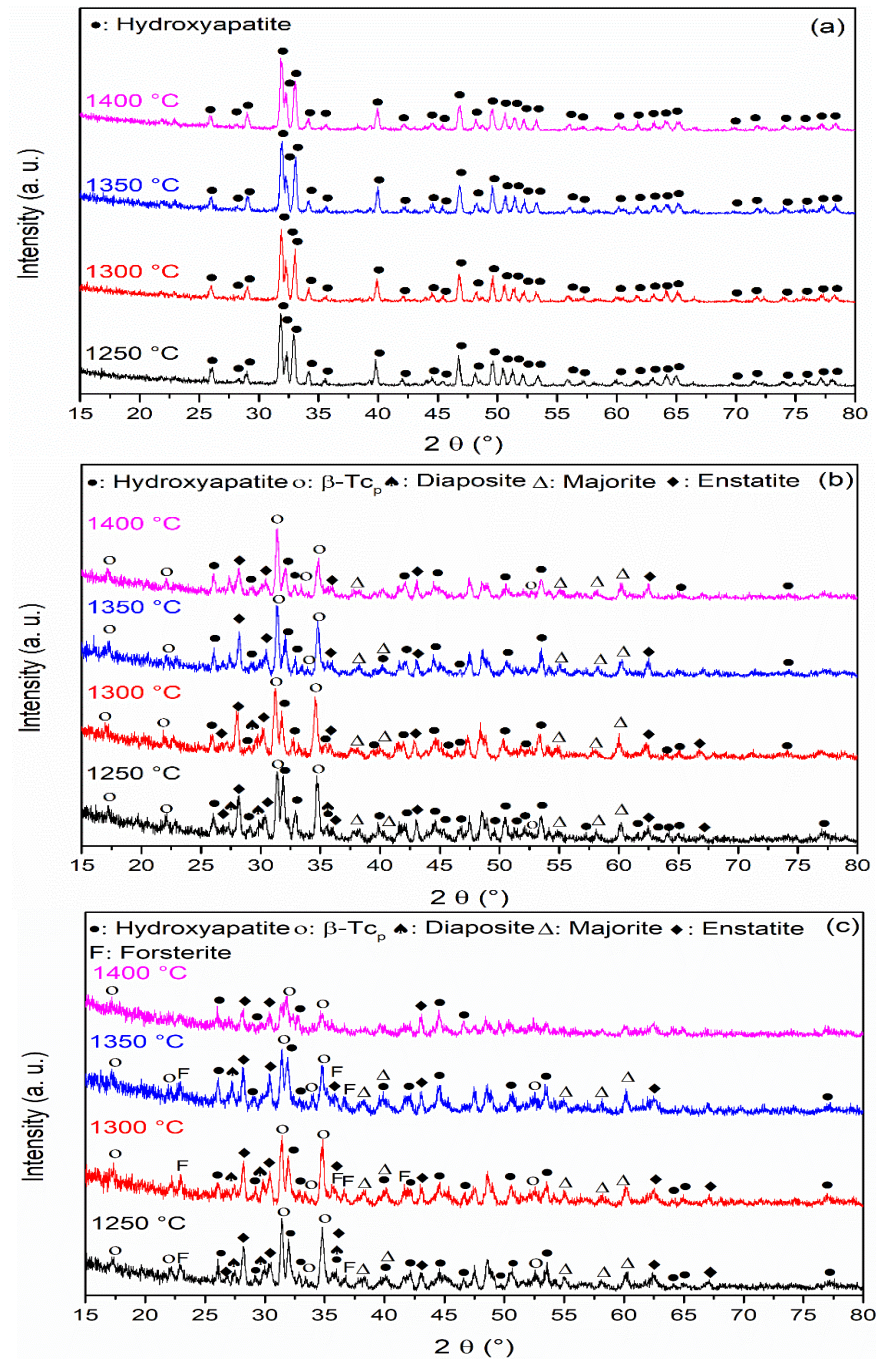


Figure III.33 XRD spectra of (a) HAF₀, (b) HAF₁₀, and (c) HAF₂₀ samples sintered at different temperatures.

IV.2.2. Measurement of density and open porosity of Hydroxyapatite-forsterite composites (HAF_x) sintered samples

To evaluate the change in HAF_x samples' density and open porosity under different sintering temperatures using the Archimedes method, HAF_x powders were uniaxially pressed, shaped, and sintered at 5 °C/min up to 1250, 1300, 1350, and 1400 °C. Figure III.34 (a, b, c) illustrates the density and open porosity variation of HAF_x samples at different sintering temperatures.

From 1250 °C to 1400 °C, samples HAF₀ and HAF₁₀ exhibited an increase in density from 2.6 g.cm⁻³ and 2.15 g.cm⁻³ to 3.06 g.cm⁻³ and 3.06 g.cm⁻³, respectively. HAF₀ and HAF₁₀ sample's open porosity reached 0.14 % and 0.61 at 1400 °C, suggesting high densification of the HAF₀ and HAF₁₀ samples. The HAF₁₀ sample showed lower density than the HAF₀ sample at 1250 °C and 1300 °C, which could be due to the partial decomposition of the hydroxyapatite phase resulting in increasing porosity [72].

From 1250 °C to 1350 °C, the HAF₂₀ sample shows an increase in density from 2.19 g/cm³ to 2.86 g/cm³. The results of low density compared to the previous samples suggest that the formation of the forsterite phase caused an increase in density compared with the HAF₁₀ sample between 1250 °C and 1300 °C. With further increasing sintering temperature to 1350 °C, sample HAF₂₀ decreases in density to 2.86 g.cm⁻³ compared to the HAF₁₀ sample, possibly due to the decomposition of hydroxyapatite phase resulting in increasing the porosity while forsterite content is increased, as Figure 34 (c) confirms. Meanwhile, the open porosity was 0.82 % and remained similar to that of the HAF₁₀ sample. At 1400 °C, density decreased significantly to 2.01 g.cm⁻³ with a high open porosity of 25.37 %. Such results can be linked to the bloating of the HAF₂₀ sample due to the high sintering temperature, which was also noted in the sample XRD spectra in Figure III.33 (b).

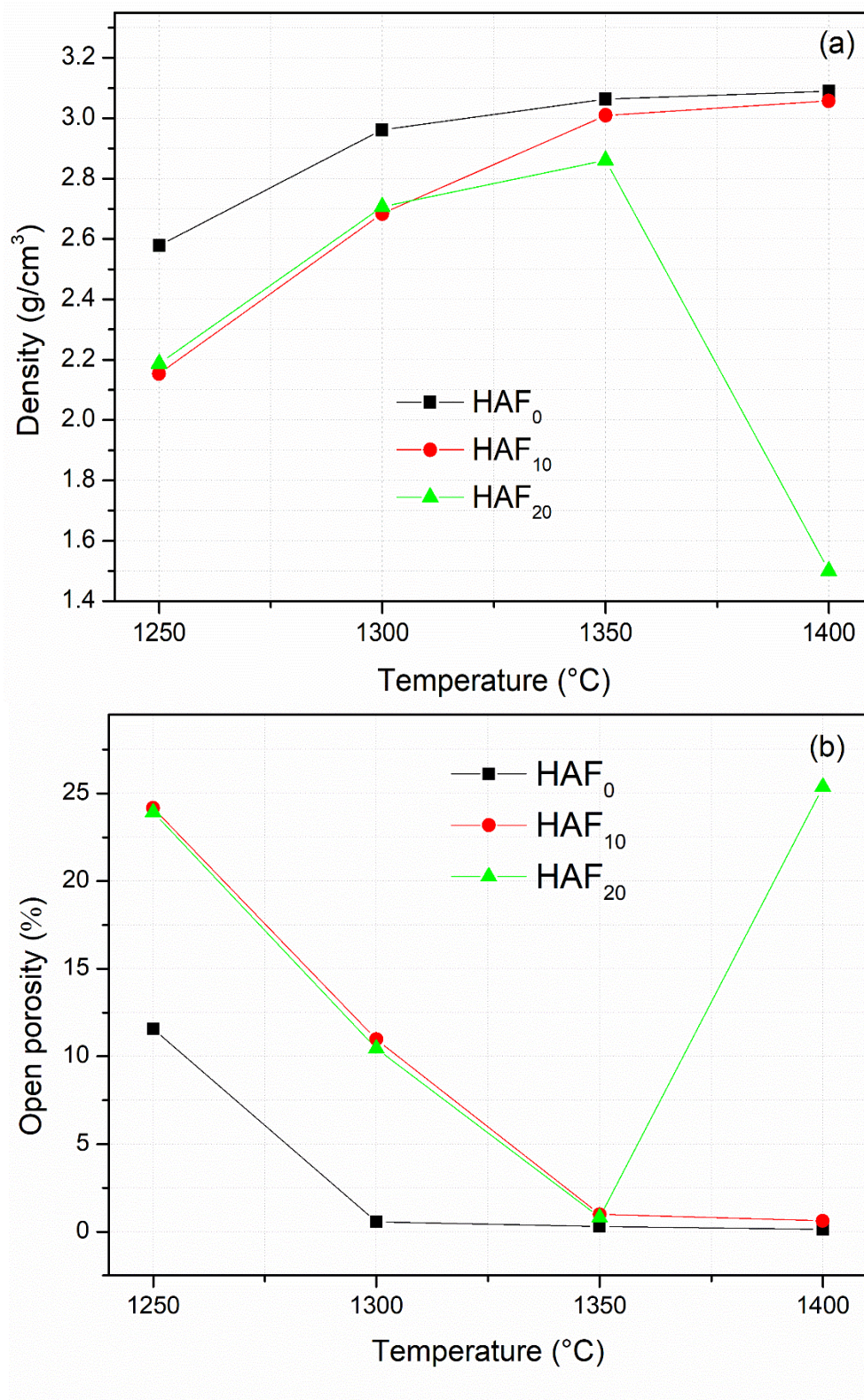


Figure III.34 (a) Density and (b) open porosity of HAF_x samples at different sintering temperatures.

IV.2.3. Micro-hardness measurement of HAF_x sintered samples

Table III.13 presents the variation in Vickers microhardness H_v of sintered samples with the lowest and highest forsterite content as a function of sintering temperature, ranging from 1250 °C to 1400°C. The observed hardness trend corresponded closely with the density trend, indicating that the hardness of all samples increased as the sintering temperature increased. Where the hardness of hydroxyapatite sample HAF_0 increased from 2.55 GPa at 1250 °C to 7.21 GPa at 1400 °C, which aligns with the densification results of the sample, other studies reported a range of 4.2-7.2 GPa for pure hydroxyapatite microhardness [73, 74]. At 1250 °C, it was 82 % and increased to 97.8 %, as shown in Figure III.34 (a). the hardness of HAF_{10} sample increased from 2.5 GPa at 1300 °C to 5.7 GPa at 1400 °C. The hardness of the HAF_{20} sample increased from 1 GPa at 1250 °C to 5.36 GPa at 1350 °C with densification of 91 %. Our results show a higher hardness value than previous studies, where values of 1.9 GPa to 20 % forsterite content samples treated at 1350 °C [72].

Table III.13 Microhardness of HAF_x samples sintered at different temperatures.

Sintering temperature	Hardness (GPa)		
	HAF_0	HAF_{10}	HAF_{20}
1250	2.55	/	1
1300	4.7	2.44	3.34
1350	6	4.51	5.36
1400	7.21	5.7	/

IV.2.4. Morphological analyses of HAF_x samples

Scanning electron microscope (SEM) equipped with an energy dispersive spectroscopy (EDS) facility was used to analyze the microstructure, morphologies, and elements distribution of HAF_x samples sintered at 1350 °C for 2 h, shown in Figure III.35, Figure III.36 (a, b), Figure III.37, Figure III.38 (a, b).

The SEM image and EDS of HAF_0 powder are shown in Figure III.35. The high sintering temperature of 1400 °C led to a homogenous grain shape, resulting in only a dense microstructure composed of hydroxyapatite. In Figure III.36 (a), the SEM/EDS image of various selected areas

in the HAF_0 sample sintered at 1350 °C. It was evident that the five chosen spectrums are similar and obtained clear elements of Ca, P, and O, proving the homogeneity of element distribution across the sample; no additional elements have been found indicating stoichiometric composition similar to that of the hydroxyapatite phase as reported in other studies [75, 76].

Figure III.36 (b) shows SEM/EDS elements distribution in the HAF_0 sample sintered at 1350 °C. A uniform elements distribution patterns of the Ca, P, and O mapping were dominated by green, yellow, and pink, confirming the previous results of one-phase crystallization in Figure III.36 (a).

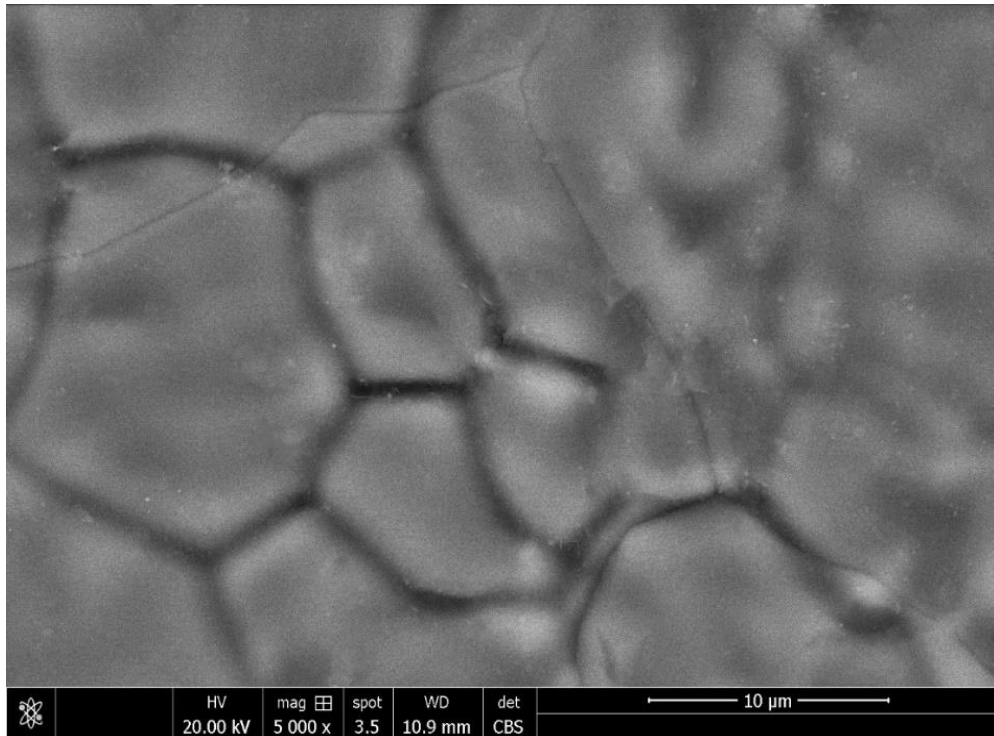


Figure III.35 SEM image of the HAF_0 sample sintering at 1350 °C.

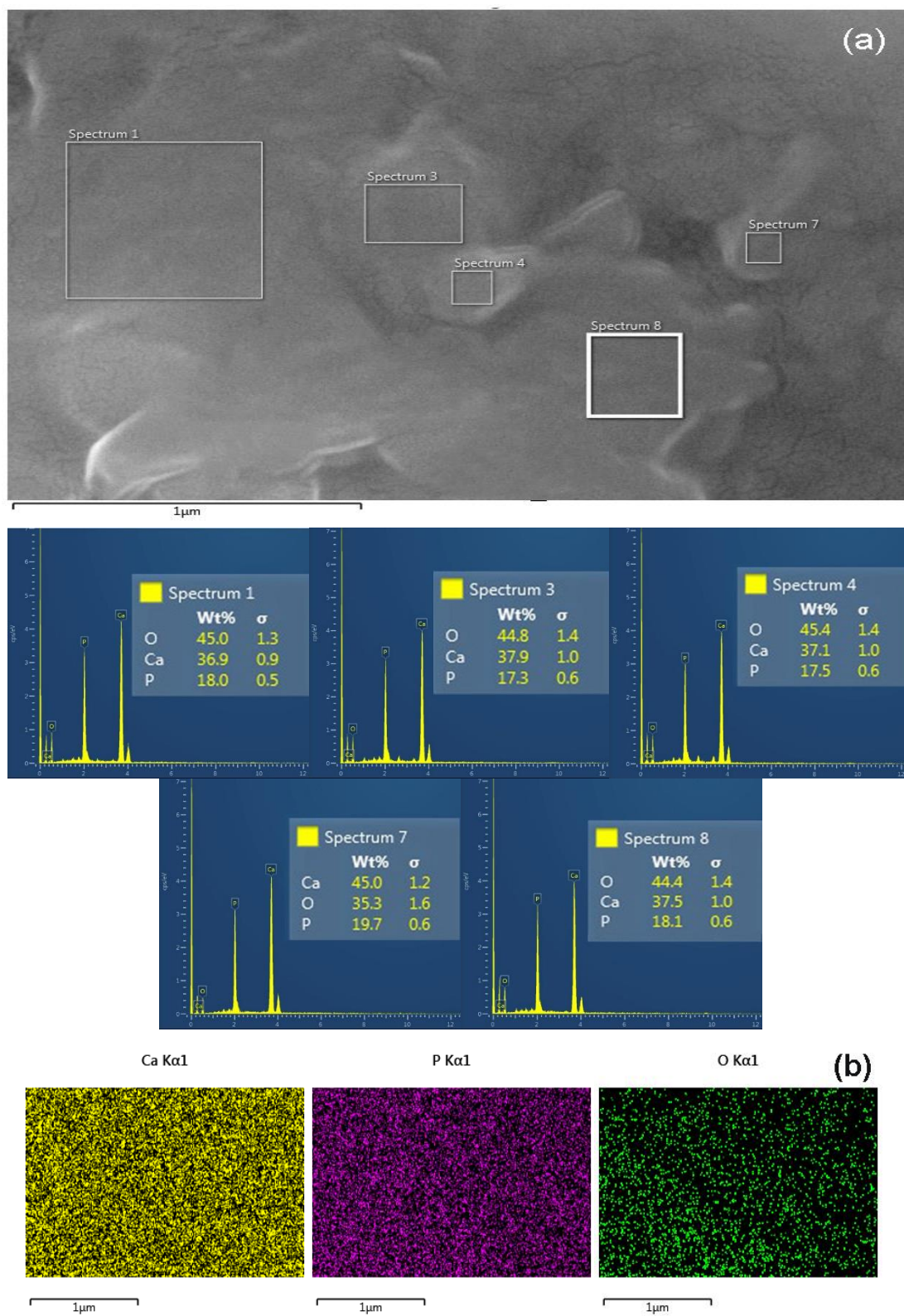


Figure III.36 (a) SEM image, (b) EDS, and (c) corresponding elemental mapping of calcium, phosphor, and oxygen of HAF₀ sample.

To investigate the effect of forsterite content on the hydroxyapatite morphology. SEM and EDS were used to analyze the microstructure and element distribution of the HAF₂₀ sample sintered at 1350 °C, as shown in Figure III.37 (a, b) and Figure III.38 (a, b).

Figure III.37 (a, b) shows that the HAF₂₀ sample morphology consists of a heterogeneous structure with more than three distinct grains: homogenous sintered morphology and secondary rod-like grains representing the enstatite phase, as previously confirmed in Figure III.17 (b). Also, a light-colored gathering of gains is observed. The XRD spectra confirm such results in Figure III.33 (c), which detects hydroxyapatite, forsterite, enstatite, β -TCP, and majorite peaks. Higher porosity is noted in the HAF₂₀ sample, aligning with the open porosity values in Figure III.34 (b). As illustrated in Figure III.37, the porous structure offers potential advantages for biomedical applications. This structural configuration facilitates tissue infiltration into the implant, thereby promoting enhanced fixation at the implantation site [77, 78].

The SEM/EDS image of five selected areas in the HAF₂₀ sample sintered at 1400 °C for 2 hours is shown in Figure III.38 (a). Significant differences exist in Ca, P, Mg, Si, and O weight percentages between spectra 22, 23, and 34. Such differences and the presence of Mg, Si, and O confirm the formation of forsterite, enstatite, and majorite, and the formed hydroxyapatite and β -TcP phases, as shown in Figure III.33 (c). The element distribution of the HAF₂₀ sample is shown in Figure III.38 (b). Ca and P mapping confirms homogenous distribution, whereas the Mg and Si mapping shows a heterogeneous distribution. In this case, the elements are unevenly distributed across the area, leading to variations in composition.

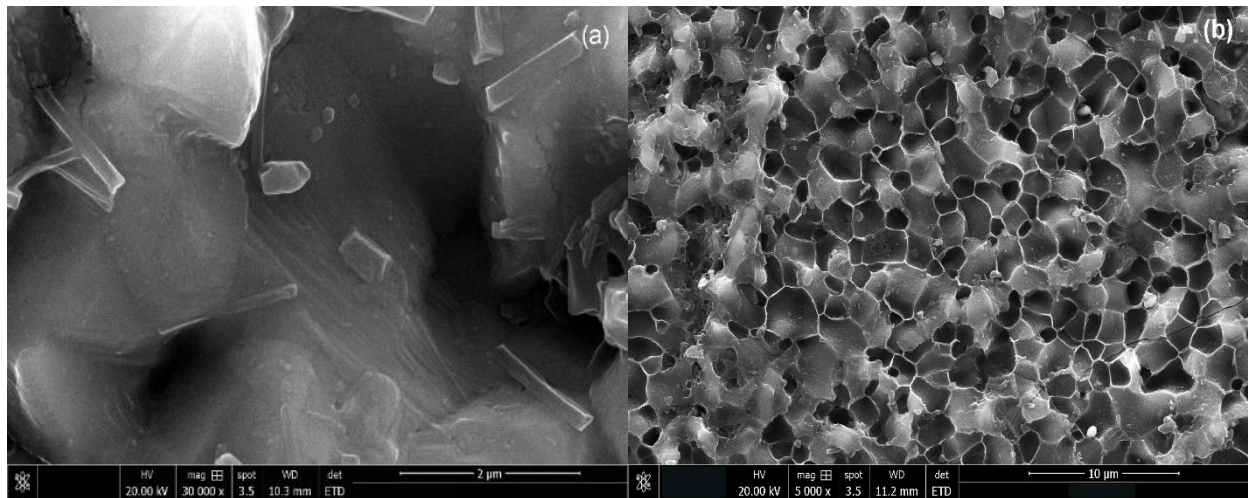


Figure III.37 (a, b) SEM image of the HAF₂₀ sample.

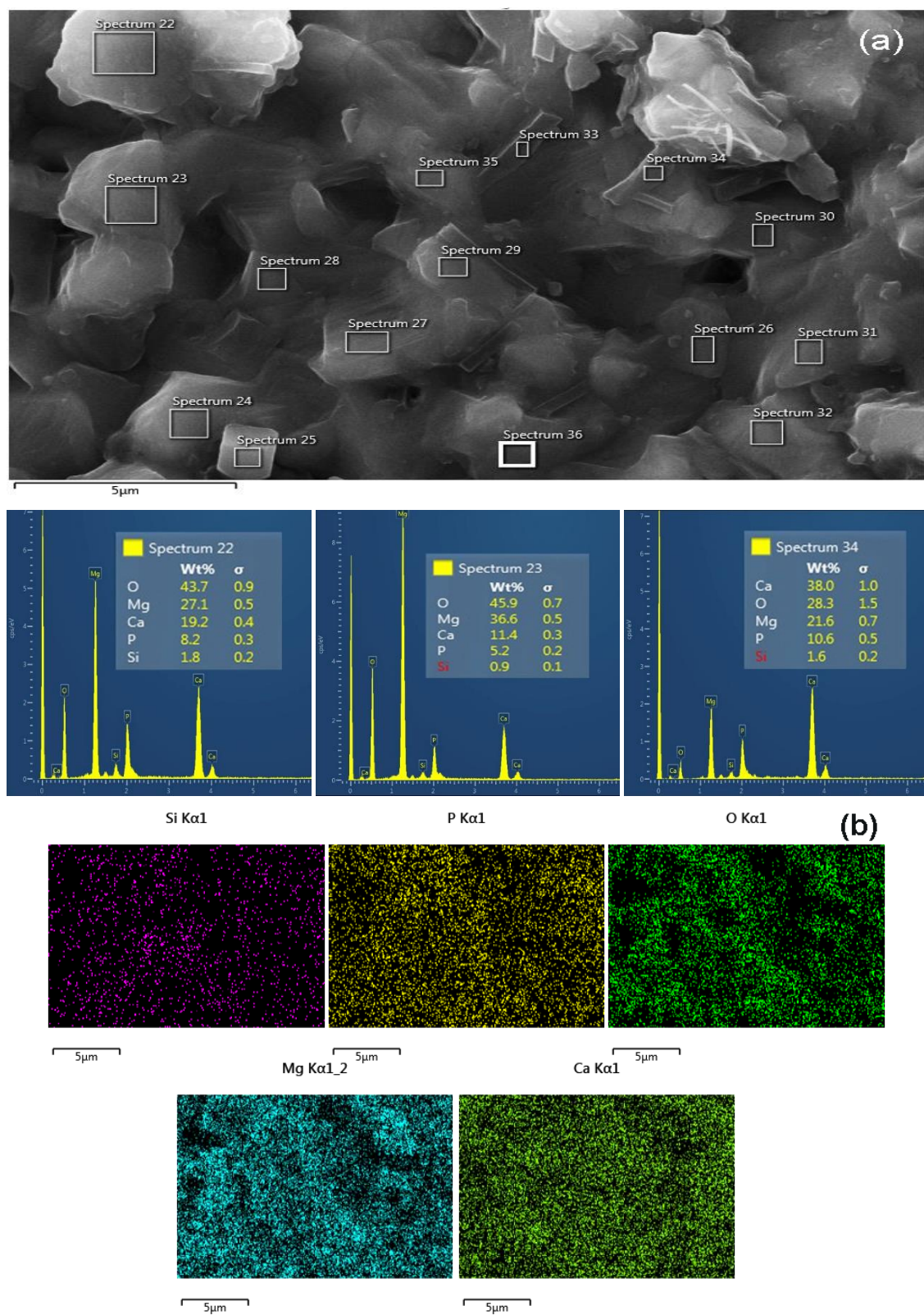


Figure III.38 (a) SEM image and (b) corresponding elemental mapping of calcium, phosphor, magnesium, silicon, and oxygen of HAF₂₀ sample.

IV.3. Antibacterial activity of HAF_x composition

The antibacterial activity of HAF_x composite samples treated at 1350 °C was evaluated against Gram-positive and Gram-negative bacteria using the disk diffusion method, as illustrated in Figure III.39. The study focused on two bacterial strains: *Pseudomonas aeruginosa* (Gram-negative) and *Staphylococcus aureus* (Gram-positive). The results demonstrated that the HAF₀, HAF₁₀, and HAF₂₀ samples exhibited no antibacterial activity against either bacterial strain. As previously discussed in part 2, which examined the antibacterial activity of the FS_x composition, this lack of activity could be attributed to the testing method employed, specifically the disk diffusion method, which was proven to give limited results compared to other methods under the applied experimental conditions.

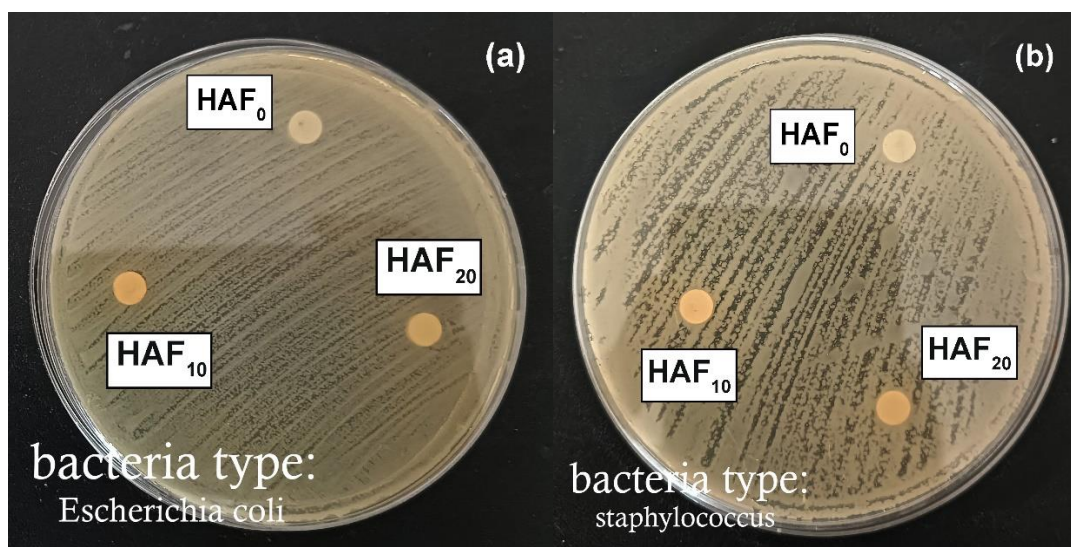


Figure III.39 Antibacterial disk diffusion test of HAF_x against two types of bacteria strain.

A wall diffusion test was conducted to confirm the accuracy of the previous findings. In this test, sterilized HAF₀ and HAF₂₀ powders were dissolved in 1 mL of DMSO at 8 mg/mL and 4 mg/mL concentrations and then applied against the *Pseudomonas aeruginosa* and *Bacillus* bacterial strains. The antibacterial activity of the HAF_x powders was compared to that of Ciprofloxacin (CLOP, 30 µg) and Pefloxacin (PEF, 5 µg) discs. The wall diffusion results of HAF_x solutions are presented in Figure III.40 (a, b, c, d). Figure III.40 (a, b) shows a clear inhibition zone of 19 mm in the 4 mg/ml HAF₀ solution with a weak non-distinguished inhibitory activity in the 8 mg/ml HAF₀ solution against *Pseudomonas* bacteria, suggesting that the prepared pure

hydroxyapatite shows antibacterial activity. The same non-distinguished inhibitory activity in 8 and 4 mg/ml HAF_0 solution is detected against the *Bacillus* bacterial strain, as summarized in Table III.14. Figure III.40 (c, d) shows that HAF_{20} solution of 8 mg/ml and 4 mg/ml concentrations except an inhabitation zone of 20 mm and 15 mm, respectively, against *Pseudomonas* bacteria strain and an inhabitation zone of 12 mm against *Bacillus* bacteria strain. Such an increase in antibacterial activity between HAF_0 and HAF_{20} solutions can be due to the formation of forsterite in the HAF_{20} sample, as indicated in Figure III.33 (b). Figure III.20 (a, b) and Table III.4 confirm that forsterite has excellent antibacterial activity against *Pseudomonas* and *Bacillus* bacteria stains at 8 mg/ml concentration.

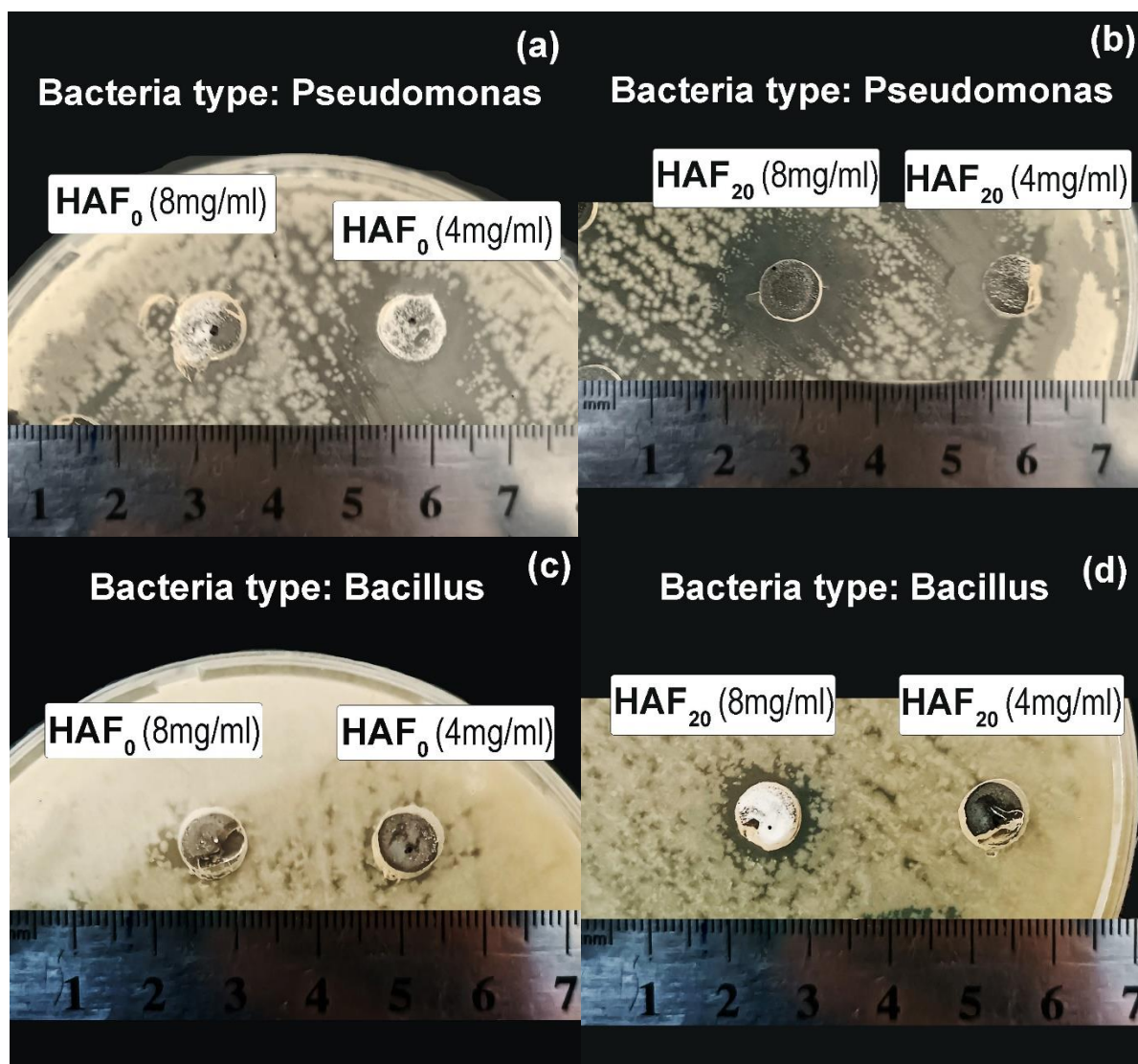


Figure III.40 Antibacterial wall test of HAF_x against two types of bacteria.

Table III.14 Inhibition zone in mm of different clinical pathogens by HAF_x composites using wall dilution technique.

Samples	Type			
	Pseudomonas (-)		Bacillus (-)	
Concentration	8 mg/ml	4 mg/ml	8 mg/ml	4 mg/ml
HAF ₀	/	19	/	/
HAF ₂₀	20	15	12	0

To quantitatively evaluate the antibacterial activity of HAF₀ and HAF₂₀, the broth dilution method was employed to determine the Minimum Inhibitory Concentration (MIC) and Minimum Bactericidal Concentration (MBC). Four dilutions of HAF₀ and HAF₂₀ powders (0.5 mg/mL, 1 mg/mL, 2 mg/mL, and 4 mg/mL) were prepared and tested against *Pseudomonas* and *Bacillus* bacterial strains using a 96-well plate. The plates were incubated at 37°C for 24 hours, and the samples from each concentration were subsequently streaked onto sterile agar plates and incubated under the same conditions. The results are summarized in Table III.15. The Minimum Inhibitory Concentration (MIC) for HAF₀ and HAF₂₀ solutions was determined to be 4 mg/mL against both *Pseudomonas* and *Bacillus* bacteria. The Minimum Bactericidal Concentration (MBC) was observed to be 4 mg/mL for *Pseudomonas*, while for *Bacillus*, it was greater than 4 mg/mL. These results indicate that the solutions exhibit both bacteriostatic and bactericidal properties at the same concentration against *Pseudomonas* while requiring concentrations exceeding 4 mg/mL to achieve bactericidal effects against *Bacillus*. The improved antibacterial efficacy observed between HAF₀ and HAF₂₀ in Figure III.40 (a, b, c, d) and Table III.15 is likely attributed to the presence of Mg²⁺ ions, which have been reported to exhibit bactericidal properties [79]. This aligns with findings by **J. Sawai**, who noted that the antibacterial activity of MgO is comparable to that of CaO [80].

Table III.15 MIC and MBC test values of HAF_x powders.

Samples	Type			
	Pseudomonas (-)		Bacillus (-)	
	MIC	MBC	MIC	MBC
HAF ₀	4	4	4	> 4
HAF ₂₀	4	4	4	> 4

Reference

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Conclusion

Conclusion

In this work, we successfully synthesized forsterite and Forsterite-Silica composites (FS_x) using varying ratios of MgO and SiO_2 non-oxides powder, where we studied the thermal, mechanical, microstructural antibacterial and kinetic properties. Additionally, we prepared natural hydroxyapatite and developed Hydroxyapatite-Forsterite composites HAF_x and investigated their crystallization, mechanical, microstructural, and antibacterial properties. These results were achieved by using the solid-state reaction method.

The raw materials demonstrated high purity, uniform morphology, and thermal stability. XRD and FT-IR analyses validated all materials' phase purity and functional group integrity. These findings demonstrate the raw materials' thermal stability, reactivity, and structural consistency, making them ideal for advanced composite applications.

In part two, Forsterite- Silica composites (FS_x) were synthesized with varying SiO_2 content (up to 6 wt.%) and sintered. Forsterite formation began at 860 °C and fully crystallized at 1300 °C, with added SiO_2 reducing sintering temperatures and improving densification but introducing the weaker enstatite phase. FS_0 (pure forsterite) achieved the highest densification (94.35 %), 7.64 GPa microhardness at 1500 °C, and $10.24 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ thermal expansion coefficient, while FS_6 showed increased porosity and lower mechanical strength. SEM/EDS analysis revealed FS_0 's dense and uniform microstructure, contrasting with FS_6 's heterogeneous rod-like grains and dual-phase structure. Antibacterial tests demonstrated FS_0 's significant activity against Gram-negative *Pseudomonas* bacteria (23 mm inhibition zone), attributed to Mg ions creating an alkaline environment, while FS_6 showed no antibacterial activity due to the enstatite phase. These results balance the benefits of SiO_2 addition or cost-effective sintering and its impact on mechanical, thermal, and antibacterial properties.

Part three studied forsterite and enstatite phase formation kinetics using DTA under 2-20 °C/min rates. Activation energy values were calculated using Kissinger, Ozawa, and Boswell methods, revealing that forsterite formation required higher activation energy (1028-1073 kJ/mol) compared to enstatite (472-88 kJ/mol), reflecting the greater thermal stability of forsterite. The crystallization of forsterite and enstatite phases by the growth of spherical particles controlled by diffusion and nucleation followed by linear nuclei growth, respectively, both phases are described

by the Šesták-Berggren model. Thermodynamic analysis showed that forsterite and enstatite crystallization became more favorable at higher heating rates, as indicated by decreasing Gibbs free energy (ΔG) and increasing entropy (ΔS). Simulations of crystallization kinetics closely matched experimental data, confirming the model's accuracy. These findings provide a detailed understanding of the mechanisms and energy requirements for phase formation, enabling precise control over the thermal processing of forsterite.

Part four examined Hydroxyapatite-Forsterite composites (HAF_x) with varying forsterite content (up to 20 wt.%) sintered at different temperatures (1250-1400 °C). XRD analysis revealed that pure hydroxyapatite (HAF_0) remained stable up to 1400 °C, while composites with forsterite (HAF_{10} and HAF_{20}) showed phase transformation, including hydroxyapatite decomposition into β -TCP, enstatite, and other phases. Density increased with sintering temperature for HAF_0 and HAF_{10} , peaking at 3.09 g.cm⁻³ (1400 °C), while HAF_{20} exhibited structural instability and bloating above 1350 °C, reducing density (2.01 g.cm⁻³). Microhardness followed a similar trend, with HAF_0 reaching 7.2 GPa at 1400 °C and HAF_{20} peaking at 5.4 GPa at 1350 °C before declining due to porosity. SEM/EDS analysis showed uniform grains in HAF_0 and heterogeneous microstructures in HAF_{20} . With increased porosity, the porous structure in our sample facilitates tissue infiltration into the implant, thereby promoting enhanced fixation at the implantation. Antibacterial tests (MIC and MBC) revealed significant antibacterial potential for HAF_x composites, where forsterite as an additive enhanced the antibacterial activity. These findings highlight that while forsterite enhances mechanical and antibacterial properties, excessive amounts lead to structural instability at higher sintering temperatures.

We can confidently state that the primary objective of this thesis has been achieved: the successful preparation and characterization of pure forsterite and the investigation of its aspect as ceramic and bioceramics for various high-temperature and medical applications.

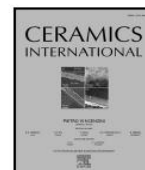
Future Work

Investigate using dopants like Zn to improve antibacterial properties while maintaining mechanical strength. Investigate the bioactivity of forsterite- silica (FS_x) and hydroxyapatite-forsterite (HAF_x) composites using simulation body fluid (SBF). Explore alternative synthesis methods, such as sol-gel or mechanochemical approaches, to reduce energy consumption during sintering.



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Kinetics of formation, microstructure, and properties of monolithic forsterite (Mg_2SiO_4) produced through solid-state reaction of nano-powders of MgO and SiO_2

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ABSTRACT

The synthesis of forsterite can be challenging because the initial oxides react slowly and undesirable compounds like enstatite (MgSiO_3) can form instead of forsterite (Mg_2SiO_4). Although several methods have been developed to overcome these challenges, the synthesis of forsterite using the solid-state reaction of nanopowders has not been investigated. This study aims to explore the possibility of producing forsterite by reacting MgO and SiO_2 nano-powder. The initial oxides were wet ball milled, dried, and reaction sintered. Spectroscopy and microscopy methods were used to analyze the formed phases and study the formation kinetics. The density, coefficient of thermal expansion (CTE), and hardness of sintered samples were measured using a densimeter, a dilatometer, and a hardness tester, respectively. The results demonstrated that it is possible to synthesize forsterite by solid state reaction of pure MgO and SiO_2 nano-powders. The reaction between the two compounds begins at a temperature as low as 860°C and leads to the formation of forsterite by a two-step formation mechanism. The first reaction involves the reaction of MgO and SiO_2 to form enstatite, and the second one produces forsterite as a result of enstatite reacting further with MgO . The activation energy values ranged from 1028.89 to 1105.655 kJ/mol for the formation of forsterite, and from 456.316 to 488.08 kJ/mol for the formation of enstatite. Monolithic forsterite was completely formed at a low temperature of 1200°C for a relatively short duration of 2 h. The sample sintered at 1400°C for 2 h, had a density of 2.96 g/cm^3 , a Vickers hardness of 7.64 GPa, and a coefficient of thermal expansion of $10.24 \times 10^{-6}/\text{K}$ measured in the temperature range of $200\text{--}1300^\circ\text{C}$.

1. Introduction

Forsterite, a phase in the $\text{MgO}\text{--}\text{SiO}_2$ binary system, with the chemical formula $2\text{MgO}.\text{SiO}_2$ and chemical composition Mg_2SiO_4 [1], is an important ceramic with various applications. It has a chemical composition consisting of 42.71 wt% SiO_2 and 57.29 wt% MgO , and a crystal structure that belongs to the orthorhombic system. The structure of forsterite is defined by SiO_4 tetrahedra oriented in opposite directions, with six oxygen atoms octahedrally coordinating Mg atoms. The density of forsterite is 3.27 g/cm^3 [2–5]. Forsterite possesses desirable thermal and mechanical properties, including a high melting point of 1890°C , a low thermal expansion coefficient, good chemical stability [6,7], and a

high hardness of 7.68 GPa [8]. It is versatile and finds application in the medical field, displaying good bioactivity, aiding in bone adhesion, contributing to bone implantation, and producing nanometer-scale fibers [6,9–16]. Forsterite also serves as an essential component in the refractory and electronic industries, particularly in electrical insulating substrates for electronic applications [17–19]. Its uses extend to ceramic coating, thermal coating against thermal corrosion [20,21], solid oxide fuel cells (SOFC) due to its stability and matching thermal expansion coefficient value with fuel cell components [22], optical devices [23, 24], and heat-resistant materials such as bricks within furnaces [25–28], wave insulation applications such as microwaves [29], and as an active medium for compression laser rays [18,30].

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Dense, Hard, and Thermally Stable $\text{Al}_6\text{Si}_2\text{O}_{13}$ – $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$ Composite Material for Silicon Substrate Applications

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Abstract

One of the key problems to overcome, in the development of electronic substrates, is that of thermal distortion because of thermal mismatch between silicon and the substrate. The aim of this work is to design a mullite-cordierite composite material, with coefficient of thermal expansion tailored to silicon substrate applications. Dense, hard, and thermally stable $\text{Al}_6\text{Si}_2\text{O}_{13}$ – $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$ composite was produced by sintering amorphous precursor powder synthesized through the sol–gel method. $\text{Si}(\text{C}_2\text{H}_5\text{O})_4$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were used, as source of SiO_2 , Al_2O_3 , and MgO oxides, respectively, to prepare mullite-cordierite precursor powders. Fourier-Transform Infrared spectroscopy (FTIR), Thermogravimetry (TG), Dilatometry, Differential Thermal Analysis (DTA), and X-ray powder Diffraction (XRD) methods were used to characterize the synthesized amorphous powder and its crystallization. The microstructure of specimens sintered at 1600 °C for 1 h was analyzed using a scanning electron microscope (SEM). The hardness (HV) and coefficient of thermal expansion (CTE) of the composite sintered at 1600 °C were measured by using a hardness tester and a dilatometer, respectively. The results show the increase in density and decrease in open porosity with the increase in temperature and equivalent amount of cordierite. For specimens sintered at 1600 °C, the increase in cordierite content from 0 to 40 wt.% increased the HV from 9.18 to 13.08 GPa; a further increase to 50 wt.% decreased it to 11.15 GPa. Sample containing 40 wt.% cordierite had the highest value of hardness (HV = 13.08 GPa), representing an increase of 42.48% with respect to monolithic mullite. The CTE of the composites (in the range 50–1000 °C) showed continuous decrease from 5.23×10^{-6} to $2.26 \times 10^{-6} \text{ K}^{-1}$ with the increase in cordierite content from 0 to 50%. Sample containing 50 wt.% cordierite displayed the lowest thermal expansion (CTE of $2.26 \times 10^{-6} \text{ K}^{-1}$), representing a decrease of 56.78% with respect to monolithic mullite.

Keywords Mullite-cordierite composite · Thermal expansion · Thermal distortion · Thermal mismatch · Silicon · Electronic substrates

1 Introduction

The Al_2O_3 – SiO_2 – MgO ternary phase diagram is of great significance to ceramic development. Mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) and cordierite ($2\text{Al}_2\text{O}_3 \cdot 2\text{MgO} \cdot 5\text{SiO}_2$) are two extremely important phases of this diagram. The former has high thermal and chemical stability, low thermal conductivity, and good mechanical properties but its thermal-expansion coefficient is high, and it has poor thermal-shock resistance [1–6]. The latter is characterized by outstanding thermal shock resistance, low dielectric constant and thermal expansion, low electrical conductivity, excellent chemical resistance, but low mechanical properties [5–10]. Furthermore, mullite and cordierite have theoretical density values of about 3.16 and 2.61 g/cm³, respectively [5]. These attributes paved the way for the design of mullite-cordierite

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Kinetics of mullitization from sol-gel synthesized precursors

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A B S T R A C T

The aim of this study is to shed more light on the formation of mullite and the kinetics of mullitization from sol-gel synthesized precursors. Tetraethylorthosilicate (TEOS) and aluminum nitrate nonahydrate (ANN) were used, as a source of silica and alumina, respectively, for the synthesis of homogenous mullite precursor powder. The mullitization process was characterized by thermogravimetry (TG), differential thermal analysis (DTA), thermogravimetric analysis (TGA), and x-ray powder diffraction (XRD) techniques. It was found that mullite started to crystallize at temperatures of 1050, 1200, and 1241 °C as determined by XRD, DTA, and TGA, respectively. Mullite crystallization kinetics was thoroughly investigated under isothermal and non-isothermal conditions using DTA. The activation energy for mullite formation was calculated, for different crystallization fractions, following the Friedman, Kissinger, Boswell, and Ozawa methods. The average values were found to be 1282.92, 1324.30, 1336.93, and 1283.09 kJ/mol, respectively. The kinetic parameters and the crystallization mechanism were determined and the results were compared with those available in the literature. The Sestak Berggren SB(m,n) model was found to be the most suitable for the determination of mullite crystallization mechanism. The calculated average values of the Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) for mullite formation, at different heating rates, were 433.98 kJ/mol, 1294.20 kJ/mol, and 566.23 J/mol.K, respectively.

1. Introduction

Mullite [1–3], an important phase in conventional and advanced ceramics, has outstanding thermal characteristics, and excellent resistance to thermal shock, creep, and corrosion [1–6]. Traditional mullite ceramics are usually produced from cheap and abundant raw materials. They are extensively used for pottery, whiteware, porcelain, and refractories [3]. Advanced mullite ceramics such as single-phase mullite ceramics, mullite films and coatings, mullite fiber, and mullite composites are usually produced from sol-gel-derived gels [3]. Monolithic mullite ceramics are widely used for numerous functional, structural, and biomedical applications [1–3,7–12].

Selection of starting materials and procedures to synthesize and/or process mullite ceramic materials generally depends on the end application and cost. Mullite processing methods include “solid-state, liquid-state, sol-gel, hydrothermal, chemical vapor deposition, and spray pyrolysis approach” [13]. Because of its versatility and good reproducibility, the sol gel process remained the most efficient method for the production of high purity mullite for advanced applications [13–16]. The precursor materials and the methods employed greatly influence mullite formation [14,16]. Mullite was produced, at temperatures between 850 and 1350 °C, from chemically synthesized precursors. The

homogeneity of the later determines the formation mechanism and crystallization temperature. A high degree of homogeneity, leads to low crystallization temperature, from 1000 to 1350 °C, compared with 1500–1700 °C reported for other methods such as reactive powder mixture [14–21]. Two types of mullite precursors could be prepared i.e. monophasic and diphasic. In the first, precursor materials are directly transformed to mullite at temperatures lower than 1000 °C [13,22,23]. In the second, mullitization takes place at a temperature above 1200 °C [13,24,25].

Many researchers used diverse starting materials and methods to study the kinetics of the mullitization process [13,26–40]. The starting materials include Tetraethylorthosilicate (TEOS) + aluminum nitrate nonahydrate (ANN) [4,22,26,28,30], TEOS + aluminum isopropoxide (AIP) [13], TESO + pseudoboehmite [32], TESO + boehmite [33], ANN + colloidal silica [34], Algerian kaolin [35], kaolin [36], fumed silica nanopowder + boehmite sol [37], commercial glass fiber [27], commercial mullite powder [29], aluminum carboxylates + silica sol [31], kaolinite and boehmite [38], kaolinite [2,39], and raw kaolin + alumina [40]. The kinetics of mullitization was investigated using DTA [13,28,30,34–37], DSC [26,29,31], XRD [13,27,32,33], and TGA [2,38]. Researchers reported mullite activation energy values of 1053 kJ/mol [26], 1200 kJ/mol [27,28], 892 and 1333 kJ/mol [29], 1202 kJ/mol

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Title: Preparation and characterization of forsterite (Mg_2SiO_4) from SiO_2 and MgO nanopowders

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ABSTRACT

Keywords:

bioceramics

forsterite (Mg_2SiO_4)

differential thermal analysis

ceramics

The focus of this work is on the synthesis of forsterite (Mg_2SiO_4) bioceramics from SiO_2 and MgO nanopowders. The used raw materials powders (initial powders) were mixed, ball milled and sintered within the temperature range of 1100–1500 °C for 2 h. Differential thermal analysis, dilatometry, Thermogravimetry, thermodilatometric analysis and x-ray diffraction, complementary techniques were used to study the sintering behavior and The crystalized phase during the thermal treatment. X-ray diffraction method was used to characterize the specimens heat-treated in both the dilatometer and furnace. The results shows that the forsterite bioceramic synthesized from pure nano-oxide powders begin to crystallize at 900 °C and completed at 1400 °C for the heat-treated specimens by furnace.

1. Introduction

forsterite is an intermediate compound in the MgO - SiO_2 phase diagram with chemical formula $2\text{MgO} \cdot \text{SiO}_2$ [1], Pbnm as space group, orthorhombic crystal system, and structure parameters $a=5.19$, $b=4.754$, and $c=10.19$ Å. Forsterite has many attractive properties, such as: melting point (1910 °C), high creep resistance at high temperatures, low thermal/electric conductivity, and high corrosion resistance against molten iron and neutral slag, therefore making it an excellent candidate for high-temperature applications such as refractory materials.

To synthesize forsterite powders, various preparation methods have been devised, including co-precipitation, sol-gel, solid-state reaction, self-spread synthesizing method, and so on. [1-3], Traditional solid state reaction processes are more convenient and desirable for large-scale manufacturing comparing to the techniques listed above. However, the generated MgSiO_3 (secondary phase) and residual MgO in the prepared Mg_2SiO_4 directly result in low density, high porosity, poor sinterability, and other inferior qualities during the calcination process.

2. Materials and Procedures

high purity nano powders of MgO and SiO_2 were used to synthesize forsterite bioceramic. yield stoichiometric forsterite content of oxides was selected to (42.70 wt % SiO_2 and 57.29 wt % MgO). The SiO_2 and MgO powders mixture, distilled water, PVA at 1 %, and ZrO_2 balls were emptied in ZrO_2 vials. The

experiments were follow through using a Fritsch P6 planetary ball mill for 3 h at 180 rpm, the furnace condition for drying the slurry are 120°C for 1 day. The LABSYS EVO DTA/DSC-TG SETARAM equipment was used obtain the TG and DTA studies. The samples were heated to 1300 °C under 40 cm^3/min of argon gas flow. The heating rates were 20 °C/min. NETZSCH (Dil 402 C) equipment was used in the dilatometry studies up to 1500 °C, at heating rate of 5 °C/min. Identical dimensions of a reference sample manufactured from Alumina were utilized. The raw powders and sintered samples were characterized using XPERT-Pro diffractometer equipment with Cu-K radiation of wavelength 0.15418 nm. Applying the water immersion procedure, the bulk density of samples was determined using a KERN densitometer.

3. Results and discussion

3.1 Phase formation analysis

Forsterite formation is a multistage process, which is mainly influenced by temperature and time. Therefore, it is essential to analyse the kinetics of forsterite formation using DTA and TDA methods. The phase transformations leading to forsterite formation for the samples heated in the DTA equipment and dilatometer were characterized by XRD, then, the kinetic analysis was performed.

Figure 1 shows DTA/TG/DTG curves of the sample heated from room temperature to 1200 °C at 20 °C/min. based on the figure, it can be observed that there are two endothermic peaks in the DTA curve accompanied by a decrease in mass in the TG curve.



7th International Conference on Smart Materials and Spectroscopy July 04-06, 2024, Monastir, TUNISIA



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Effect of SiO₂ Addition on The Thermal and Mechanical Properties of Forsterite from MgO and SiO₂ Nano-powders

Pr. GARGOURI Mohamed

Date

05-07-2024





Department of Science Physics in cooperation
with the Laboratory of Mathematics and
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Has made **Poster** presentation Titled:

**" Thermal analysis of Hydroxyapatite-Forsterite compound synthesized via bovine bone and nano-oxides
powders "**

In this national conference held at Higher Normal School of Bousaada, Algeria,

(NCPA2023) 02 December 2023

Co-author. **Foudil SAHNOUNE, Hanan BEN SHANIT, Amar DJENI**





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Smail Lamara Physics and Chemistry of Materials Lab, Department of Physics, University Mohamed Boudiaf of M'sila, Algeria Physics Department, Faculty of Science, University Mohamed Boudiaf of M'sila, 28000 M'sila, Algeria

Pour sa (leur) participation au **SÉMINAIRE INTERNATIONAL SUR LES SCIENCES DE LA MATIÈRE (PHYSIQUE ET CHIMIE)** en ligne (webinaire), organisé par Algerian Journal of Engineering, Architecture and Urbanism le 17 et 18 Septembre 2021, avec une **communication orale** intitulée:

Crystallization kinetics and characterization of forsterite (Mg₂SiO₄) bioceramics Synthesized from Nano-powder oxides

Oran, Algerie

18/09/2021





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Co-authors: DILMI Zeyneb LAMARA Smail SAHNOUNE Foudil HERAIZ Menad SAHEB Nouari

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Co-authors: Foudil Sahnoune, Smail Lamara and Nouari Saheb

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Co-authors: *Khadija Laziri, Zeyneb Dilmi, Smail Lamara, Foudil Sahnoune and Menad Heraiz*

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Characterization of Cordierite/Mullite Composites Prepared By sol-gel Technique

Co-author (s): Menad Heraiz , Sahnone Foudil , Lamra Ismail , Laziri Khadidja



Dr. Ammar ZOBEIDI



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Co-author (s): Foudil Sahnoune, Amar Djemli



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DE PARTICIPATION

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A participé activement au séminaire et a présenté une communication **Affiche (Poster)**

Intitulée: **The effect of magnesium silicate on the thermal and other properties of forsterite ceramics from nano-powder**

Co-auteurs : Foudil Sahnoune, Amar Djemli, Nouari Saheb

Le Président du Séminaire
Dr. Abdelhakim KHENICHE



Le Doyen de la Faculté des Sciences
Pr. Ettayib BENSACI



Abstract

The synthesis of high-purity forsterite (Mg_2SiO_4) is challenging due to the slow reaction of the precursor materials involved and the potential formation of other phases, such as enstatite (MgSiO_3) and periclase (MgO). Although various methods have been approaches to overcome these challenges, the solid-state reaction method using nanopowders remains insufficiently unexplored. This study aims to evaluate the feasibility of synthesizing pure forsterite through reacting MgO and SiO_2 nanopowders. The phases identification and grain size of the raw materials were analyzed using X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FT-IR). Forsterite was synthesized via a solid-state reaction and characterized using thermogravimetric analysis (TG), differential thermal analysis (DTA), XRD, and dilatometry (DL). Furthermore, the influence of excess silica on forsterite properties was investigated by preparing a series of powder mixtures with different ratios of silica processed through a planetary ball mill. The formation of forsterite and the effect of the silica on phases transformation were examined using XRD and scanning electron microscopy with energy-dispersive spectroscopy (SEM/EDS). To determine the reaction mechanism, DTA experiments were conducted at different heating rates to determine the kinetic parameters, reaction model, crystallization mechanisms, and thermodynamic parameters associated with the forsterite and enstatite formation. Additionally, the effect of forsterite as an additive on hydroxyapatite crystallization, bulk density, open porosity, microhardness, microstructure, and antibacterial activity was studied.

Keywords

Phase transformation, Kinetic parameters, Microhardness, Coefficient of thermal expansion, Forsterite, hydroxyapatite.

المخلص

إن تحضير الفورستريت (Mg_2SiO_4) عالي النقاوة يعد تحدياً لعدة أسباب منها بطيء التفاعل للمواد الأولية الداخلة في تركيبه وإمكانية تكون أطوار أخرى غير الفورستريت مثل الأنستاتيت والبيريكلاس، وعلى الرغم من إتباع عدة طرق تجريبية للتغلب على هذه التحديات إلا أنه لا تزال طريقة تفاعلات الحالة الصلبة باستخدام مواد أولية نانومترية غير مستكشفة بشكل أعمق. يهدف هذا البحث إلى تقييم إمكانية تحضير الفورستريت النقي من خلال تفاعل مسحوق أكاسيد المنغنيزيوم وأكسيد السيليكا النانويين. تم تحليل الأطوار وحجم الحبيبات للمواد الخام باستخدام حيود الأشعة السينية (XRD) وتحليل الأشعة تحت الحمراء بتحويل فورييه (FT-IR). تم تحضير الفورستريت عن طريق تفاعل الحالة الصلبة، وتمت دراسته باستخدام التحليل الحراري الكتلتي (TG)، والتحليل الحراري التفاضلي (DTA) وحيود الأشعة السينية (XRD)، وجهاز التمدد الطولي الحراري (DL). بالإضافة إلى ذلك، تم دراسة تأثير إضافة السيليكا على خصائص الفورستريت من خلال تحضير سلسلة من الخلائط بنسب وزنية مختلفة من السيليكا بواسطة السحق الألي التصادمي. تم فحص تبلور الفورستريت وتأثير إضافة السيليكا على التحولات الطورية باستخدام حيود الأشعة السينية (XRD)، والمجهر الإلكتروني الماسح المزود بمطيافية تشتت الطاقة (SEM/EDS). ولتحديد آلية التفاعل، تم إجراء تجارب التحليل الحراري التفاضلي (DTA) بإستعمال سرع تسخين مختلفة لتحديد كل من العوامل الحركية ونموذج التفاعل وآلية التبلور والمعاملات التارموديناميكية المرتبطة بتكوين الفورستريت والإنستاتيت. زيادة على ذلك، تم دراسة تأثير الفورستريت كمادة مضافة على تبلور الهيدروكسيأباتيت، والكتلة الحجمية، ونسبة الفراغات المفتوحة، والصلادة المجهرية، والبنية المجهرية، والنشاط المضاد للبكتيريا.

كلمات مفتاحية

التحولات الطورية، العوامل الحركية، الصلادة المجهرية، معامل التمدد الطولي الحراري، الفورستريت، الهيدروكسيأباتيت.