

DEVELOPMENT OF ADVANCED CERAMIC MATERIALS

BY SPARK PLASMA SINTERING OF NANO-OXIDE

POWDERS

BY

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Dedication

Gratefully, I dedicate this work to Almighty Allah for His guidance and to my loving parents for their unwavering support. I also extend my heartfelt thanks to my dear family and friends for their encouragement throughout.

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LIST OF ABBREVIATIONS

MAS	:	Magnesium Aluminate Spinel
SPS	:	Spark Plasma Sintering
FCC	:	Face Centered Cubic
CZR0	:	Vickers hardness of pure cordierite
MgO	:	Magnesium Oxide
Al₂O₃	:	Aluminum Oxide
SiO₂	:	Silica
TEOS	:	Tetraethyl Orthosilicate
DC	:	Direct Current
DSC	:	Differential Scanning Calorimetry
DTA	:	Differential Thermal Analysis
XRD	:	X-Ray Diffraction
SEM	:	Scanning Electron Microscope
EDS	:	Energy Dispersive Spectroscopy
FESEM	:	Field Emission Scanning Electron Microscope

ABSTRACT

Full Name : [AHMED ALI ALGHANIM]

Thesis Title : [Development of Advanced Ceramic Materials by Spark Plasma
Sintering Nano-oxide Powders]

Major Field : [Material Science and Engineering]

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This thesis explores the single-step synthesis of fully dense spinel MgAl_2O_4 and pure cordierite materials through spark plasma sintering of nano-oxide powders and the impact of additive MgO on cordierite formation.

The research validated a novel approach for synthesizing spinel MgAl_2O_4 , achieving full densification and robust mechanical properties at a relatively low temperature of 1300 °C. This synthesis method promises potential advancements in the efficient production of cordierite materials.

This study demonstrates the successful synthesis of high-purity cordierite materials at a relatively low temperature via spark plasma sintering high-purity nanopowders in a single step. The sintering process yielded dense monolithic α -cordierite at 1150 °C, and the results contribute valuable insights into the synthesis, optimization, and mechanical properties of cordierite materials, indicating their potential for practical applications in various industries.

Additionally, this study investigated the effect of the MgO additive on cordierite formation. The results highlighted that the additive influenced the homogeneity of the powder mixtures, melting points, density variations, hardness, and fracture toughness of the resulting materials. These findings enrich our understanding of the role of additives in material synthesis and their influence on the mechanical properties of the final product.

ملخص الرسالة

الاسم الكامل: احمد علي الغانم

عنوان الرسالة: تطوير المواد السيراميكية المتقدمة باستخدام تفريغ بلازمي شراري لمساحيق النانو الأكسيدية

التخصص: علم المواد والهندسة

تاريخ الدرجة العلمية: December 2023

يستكشف هذا البحث إنتاج مواد السبيل $MgAl_2O_4$ والكورديريت النقية والتامة الكثافة في خطوة واحدة من خلال تلبيد مساحيق أكاسيد النانو باستخدام شرارة البلازما وكذلك تأثير مادة MgO المضافة على تشكل الكورديريت. أظهرت نتائج البحث إمكانية إنتاج السبيل $MgAl_2O_4$ ، وتحقيق التكثيف التام والخواص الميكانيكية الجيدة من خلال التلبيد باستخدام شرارة البلازما عند درجة حرارة منخفضة نسبياً تبلغ 1300 درجة مئوية. كذلك وجد أن التلبيد باستخدام شرارة البلازما طريقة فعالة لإنتاج مادة الكورديريت حيث أظهرت هذه الدراسة إمكانية إنتاج مواد الكورديريت عالية النقاء والتامة الكثافة عند درجة حرارة منخفضة نسبياً عن طريق تلبيد مساحيق نانوية نقية في خطوة واحدة. أسفرت عملية التلبيد عن إنتاج α -كورديريت كثيف متجانس عند 1150 درجة مئوية. بالإضافة إلى ذلك، بحثت هذه الدراسة في تأثير مادة MgO المضافة على تشكل الكورديريت. وأظهرت النتائج أن المادة المضافة أثرت على تجانس المساحيق الأولية، ودرجة حرارة الانصهار، وتغيرات الكثافة، وصلابة المواد الناتجة. وساهمت هذه النتائج في الفهم الجيد لدور المادة المضافة في تركيبة المواد التي تم الحصول عليها وتأثيرها على البنية المجهرية والخواص الميكانيكية للمنتج النهائي.

CHAPTER 1

INTRODUCTION

1.1. Overview of Spinel Ceramics:

The development of Magnesium Aluminate Spinel (MAS) ceramics has advanced significantly owing to the availability of nano-powders and improved powder metallurgy techniques. This progress has enabled the production of ceramics with customized microstructures and enhanced properties, although conversion to dense materials remains energy-intensive. To reduce costs and improve efficiency, researchers have focused on optimizing the furnace design, raw materials, production methods, and processing parameters.

MAS, with a cubic crystal structure (MgAl_2O_4), is notable for its exceptional thermal stability and corrosion resistance, which make it ideal for insulation, filtration, and optical applications. The process of forming MAS, known as spinellization, involves the reaction sintering of Al_2O_3 and MgO precursors, and is characterized by significant volume expansion, which presents challenges in densification.

The current research aims to synthesize low-cost, fully dense MAS using single-step reaction sintering of Al_2O_3 and MgO nano-oxides without sintering aids. This process involved preparing a stoichiometric nanopowder mixture, followed by SPS, and the final MAS properties were closely analyzed and compared with existing data. This approach underscores the potential of producing high-quality MAS ceramics in an efficient and cost-effective manner.

1.2.Overview of Cordierite Ceramics:

The synthesis of advanced ceramic materials, which was previously difficult using conventional methods, has become relatively easy as a result of innovative consolidation techniques. In addition, the production of nanoceramic powders has paved the way for the synthesis of advanced ceramics at relatively low temperatures. During the past decade, spark plasma sintering (SPS) has attracted significant attention from numerous researchers and has gained a reputation for the sintering of different powder materials. SPS is a direct, one-step, binderless process in which uniaxial stress and current are simultaneously applied. This low-cost process not only permits low sintering temperatures but also reduces sintering time, which enables the synthesis of novel materials with unique microstructures and excellent properties [1–4].

The ceramic cordierite phase is one of the various phases found in alumina-silica-magnesia systems. It has numerous advantages over the spinel and mullite phases. The key attributes of cordierite have been widely recognized, including, but not limited to, its excellent mechanical, thermal, and electrical properties. The low thermal ($1\text{--}2 \times 10^{-6} \text{ C}^{-1}$) and electrical conductivity and low thermal expansion with high thermal shock resistance and high melting temperature (1470 C°) with stable phase are some of the fundamental properties that are useful in high temperature applications such as refractories. It also has a low density (2.58 g/ cm^3) with a Young's modulus of approximately 139 GPa, excellent thermal shock resistance, and good stability under extreme conditions [5–8].

1.3.Motivation

This study focuses on the synthesis of advanced ceramic materials, specifically Spinel MgAl_2O_4 and Cordierite, using the spark plasma sintering (SPS) technique, owing to their unique advantages and applications.

Spinel MgAl_2O_4 Synthesis: The goal of synthesizing Spinel MgAl_2O_4 using Al_2O_3 and MgO nano-oxides via SPS was driven by the remarkable properties of the material. Spinel MgAl_2O_4 exhibits excellent mechanical strength, chemical stability, and optical properties. Traditional methods for creating this material typically require high temperatures and are time- and energy-intensive. In contrast, SPS allows the production of Spinel MgAl_2O_4 at lower temperatures and in shorter time frames. This method enhances densification, controls grain growth, and improves the overall mechanical properties of the materials.

Cordierite Synthesis: On the other hand, the synthesis of Cordierite through SPS aims to overcome the challenges posed by its scarcity in nature and the high costs associated with its conventional production methods. Typically synthesized at temperatures above 1400 °C, this study seeks to create pure cordierite at lower temperatures using nano-sized powders of Al_2O_3 , SiO_2 , and MgO . This approach is more economical and efficient, potentially replacing expensive precursors and processes. The use of SPS is expected to leverage the reactivity of the nano-powders, leading to a cost-effective and efficient route for cordierite synthesis suitable for various industrial applications.

This study aims to advance the field of materials science through innovative ceramic synthesis. This study seeks to develop materials with enhanced mechanical properties by exploring the synthesis of Spinel MgAl_2O_4 and Cordierite via spark plasma sintering (SPS) with nano-powders. These properties make these materials suitable for diverse high-

performance industrial applications. This approach emphasizes the use of nano-powders and underscores the importance of novel synthesis techniques for obtaining high-quality advanced ceramic materials.

|

CHAPTER 2

LITERATURE REVIEW

2.1 Background information on spinel materials

Spinel, with the general formula AB_2O_4 , represent a diverse and fascinating class of materials with a wide range of structural, chemical, and physical properties [9]. They exhibit cubic crystal structures with two distinct cation sites, tetrahedral (A site) and octahedral (B site), occupied by different metal ions. It consists of an FCC array of O^{2-} ions in which the A cation occupies one-eighth of the tetrahedral holes, and the B cations occupy half of the octahedral holes, as shown in Figure 1.

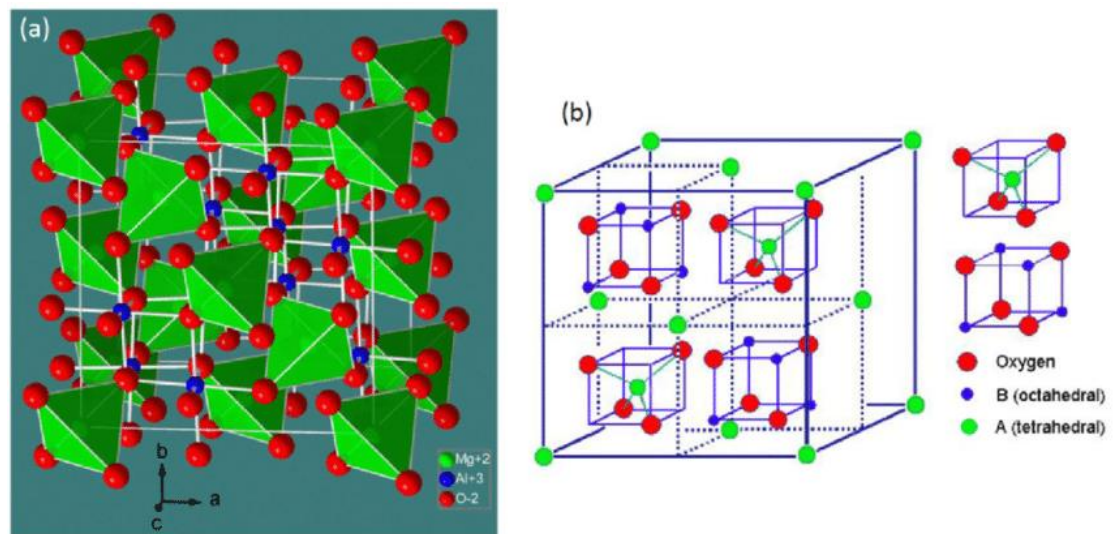


Figure 1. Crystal structure of spinel (AB_2O_4) [10]

This structural versatility, coupled with its ability to accommodate various elements, gives rise to a multitude of spinel compounds with unique properties. Spinel has a wide range

of applications in various fields owing to their unique properties such as high thermal stability, high hardness, and excellent chemical resistance [11].

Spinel materials can be synthesized using various techniques, each of which has distinct advantages and limitations. Common synthesis methods include the following:

- Solid-state reaction [12]: This method involves mixing and grinding precursor oxides, carbonates, or hydroxides, followed by heating at elevated temperatures to promote solid-state reactions and form the spinel phase.
- Sol-gel method [13]: This technique utilizes a sol-gel precursor solution typically containing metal salts and gelling agents to prepare spinel materials via hydrolysis and condensation reactions.
- Hydrothermal synthesis [14]: This method involves the reaction of precursor materials in a heated, pressurized aqueous environment, leading to the formation of spinel phases with a controlled particle size and morphology.
- Co-precipitation: This technique involves the simultaneous precipitation of metal ions from a solution using a precipitating agent, resulting in the formation of spinel nanoparticles.

The properties of the spinel depend on the composition and crystal structure of the material. These properties render these materials attractive for various applications. Their key properties are as follows:

- Electrical properties: Spinel materials can exhibit semiconducting, insulating, or conducting behaviors depending on their composition and doping.

- Magnetic properties [10] Spinel materials exhibit various magnetic properties, including diamagnetism, paramagnetism, ferromagnetism, and ferrimagnetism.
- Optical properties: Spinel materials can exhibit different optical properties, such as transparency, translucency, or opacity, depending on their composition and particle size.
- Catalytic properties: Spinel materials exhibit catalytic activity in various reactions, including oxidation, reduction, and reformation.
- Chemical stability: Spinel materials are chemically stable, resistant to corrosion and oxidation, and can withstand high temperatures.

Owing to their unique properties, spinel materials have applications in various fields, including;

- Electronics: Spinel materials are used in electronic devices, such as resistors, capacitors, and sensors.
- Magnetics Spinel materials are used in magnetic recording media, transformers, and magnets.
- Catalysis: Spinel materials are used as catalysts in various chemical processes such as petroleum refining and pollution control.
- Pigments and ceramics: Spinel materials are used as pigments in ceramics and paints.
- Biomedical applications: Spinel materials are used in biomedical applications such as drug delivery, bioimaging, and

2.2 Background information on cordierite materials.

Cordierite is a naturally occurring mineral that belongs to the silicate mineral group. It was named after French geologist and mineralogist Pierre Louis Antoine Cordier, who first described it in 1813. It has the chemical formula $(\text{Mg,Fe})_2\text{Al}_4\text{Si}_5\text{O}_{18}$ and belongs to the orthorhombic crystal system. Cordierite is commonly found in metamorphic and igneous rocks such as gneiss, schist, and granite. They often occur as prismatic crystals or grains embedded within rock matrices. The mineral exhibits a range of colors, including blue, blue-green, grey, and brown, and may display pleochroism, with different colors when viewed from different angles.

Cordierite is characterized by its unique crystal structure, which consists of chains of silica tetrahedra (SiO_4) linked by aluminum-oxygen octahedra (AlO_6). These chains are connected by magnesium or iron cations, giving cordierite its chemical composition. They have numerous advantages over mullite and spinel materials [15–20].

A notable property of cordierite is its high thermal stability and resistance to thermal shock. It has a low coefficient of thermal expansion, indicating that it undergoes minimal dimensional changes when exposed to rapid temperature variations [21, 22]. This property makes cordierite suitable for applications that require resistance to thermal cycling and high-temperature environments. In addition to its thermal properties, cordierite exhibits low electrical conductivity, chemical inertness, and good mechanical strength. These characteristics make them valuable for various industrial applications. For example, cordierite-based materials are widely used in catalytic converters for automobiles, where they provide thermal insulation and convert harmful exhaust gases into less harmful

substances. Cordierite is used in kiln furniture, refractory linings, electrical insulators, electronic substrates, and other applications.

The development of cordierite materials has resulted in advancements in synthesis methods and manufacturing techniques, as well as the exploration of doping and alloying strategies to enhance their properties. Ongoing research is aimed at further optimizing the performance of cordierite materials and exploring new applications in emerging fields.

2.3 Significance of cordierite materials in various industries

Cordierite materials are important in various industries because of their unique properties and versatile applications. Some of the key industries in which cordierite materials are widely utilized are as follows.

Automotive Industry: Cordierite-based materials play a crucial role in the automotive industry, particularly in the manufacturing of catalytic converters. Cordierite honeycomb structures are used as catalyst substrates to convert harmful pollutants in vehicle exhaust gases into less harmful substances. The high thermal stability, low thermal expansion, and chemical resistance of cordierite make it an ideal choice for this application [21–25].

Ceramics Industry: Cordierite materials are extensively used in the ceramic industry. Their low thermal expansion and excellent thermal shock resistance make them suitable for kiln furniture that supports ceramic ware during high-temperature firing. Cordierite-based kiln furniture helps ensure dimensional stability and prevents warping or cracking of ceramic products.

Refractory Applications: Cordierite materials are used in refractory applications in which high-temperature resistance is required. They are used in the linings of furnaces, kilns, and other thermal processing equipment to withstand extreme temperatures and provide thermal insulation. The ability of cordierite to maintain its structural integrity at high temperatures makes it the preferred material for such applications [26].

Electrical and Electronic Industries: The low electrical conductivity and excellent electrical insulation properties of cordierite make it valuable for electrical and electronic applications. It is used as an insulating material for electrical components such as spark plugs, igniters, and heating elements. Cordierite-based substrates have also been employed in the production of electronic circuits and sensors owing to their thermal stability and electrical insulation capabilities.

Chemical Processing: The chemical inertness and corrosion resistance of cordierite render it suitable for applications in the chemical processing industry. It is used in the construction of vessels, pipes, and reaction chambers that come in contact with corrosive chemicals. The high thermal stability of cordierite enables it to withstand harsh chemical reaction conditions.

Aerospace Industry: The lightweight nature and excellent thermal stability of cordierite make it attractive for aerospace applications. It is used as a thermal insulation material in aircraft engines and rocket propulsion systems where weight reduction and high-temperature resistance are crucial factors.

Environmental Applications: Cordierite materials are utilized in environmental applications such as gas filtration and particulate control. The porous nature of cordierite

allows for efficient gas flow while capturing and removing harmful particles from industrial exhaust streams.

The significance of cordierite in these industries stems from its unique combination of thermal stability, low thermal expansion, electrical insulation properties, chemical inertness, and mechanical strength. Ongoing research and development is aimed at further enhancing the properties of cordierite and exploring new applications to meet the evolving needs of various industries.

2.4 Chemical composition and crystal structure of cordierite

The chemical composition of the cordierite is represented by the formula $(\text{Mg,Fe})_2\text{Al}_4\text{Si}_5\text{O}_{18}$. It is a complex silicate mineral with an orthorhombic crystal system. A typical crystal structure of β -cordierite with orthorhombic, (SiO_4) and (AlO_4) tetrahedrons constitute $[(\text{Si}_4\text{Al}_2)\text{O}_{18}]$ hexagonal rings and outside, (MgO_6) octahedral connected by (SiO_4) and (AlO_4) is shown in Figure 2. The crystal structure of cordierite consists of chains of silica tetrahedra (SiO_4) linked together by aluminum–oxygen octahedra (AlO_6) . These chains were connected by magnesium (Mg) or iron (Fe) cations, resulting in the formation of a three-dimensional network.

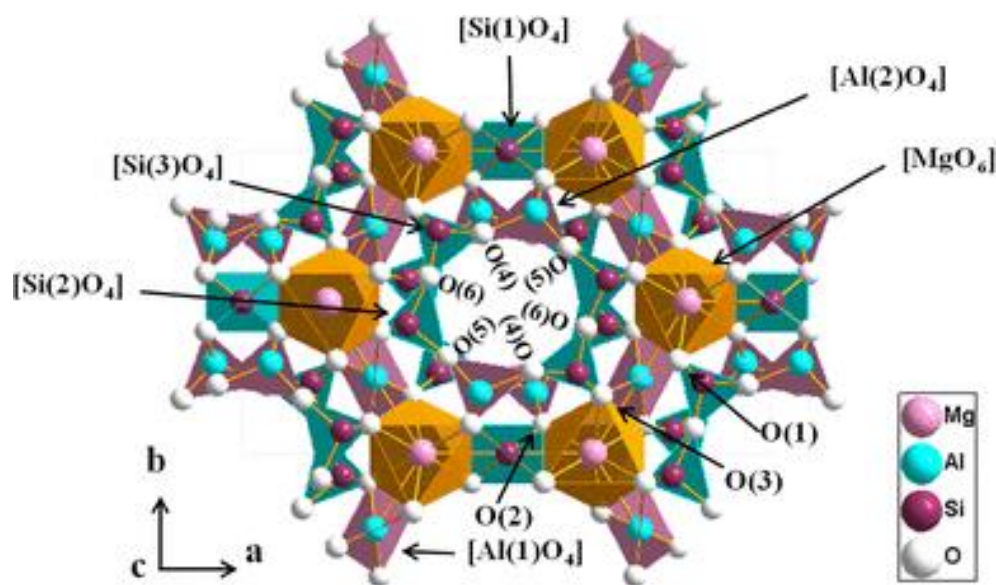


Figure 2. Crystal structure of β -cordierite with orthorhombic, (SiO_4) and (AlO_4) tetrahedrons constitute $[(\text{Si}_4\text{Al}_2)\text{O}_{18}]$ hexagonal rings and outside, (MgO_6) octahedral connected by (SiO_4) and (AlO_4) [27]

In the crystal structure of cordierite, each aluminum cation is bonded to six oxygen atoms, forming an octahedral coordination. The oxygen atoms are shared with neighboring tetrahedra, leading to the formation of double chains of linked tetrahedra. These chains run along the crystallographic b-axis of the cordierite structure.

The silica tetrahedra within the cordierite structure were characterized by the sharing of oxygen atoms with adjacent tetrahedra. This oxygen sharing creates a continuous tetrahedral framework throughout the crystal lattice.

Magnesium or iron cations are located between the double chains of the tetrahedra and occupy octahedral sites. The presence of these cations contributed to the overall charge balance of the cordierite structure.

The combination of Al, Mg, Fe, Si, and oxygen in the crystal structure gives cordierite unique properties, such as thermal stability, low thermal expansion, and chemical inertness, making it suitable for various industrial applications.

It is important to note that the specific chemical composition and crystal structure of cordierite can vary slightly depending on the presence of impurities and the substitution of cations within the mineral.

2.5 Physical and mechanical properties of cordierite

Cordierite exhibits several important physical and mechanical properties that make it suitable for various applications. The key properties of cordierite are as follows:

Density: Cordierite has a relatively low density, typically ranging from 2.5 to 2.7 grams per cubic centimeter (g/cm³) [28–30]. This low density contributes to its light weight, making it favorable for applications where weight reduction is important.

Thermal Expansion: Cordierite has a low coefficient of thermal expansion, typically is in the range of $1\sim3 \times 10^{-6} \text{ K}^{-1}$ (25–800 °C) and varies with the composition and manufacturing process [31]. This property enables the cordierite materials to resist dimensional changes and thermal cycling without significant cracking or distortion, rendering them suitable for high-temperature applications.

Thermal Conductivity: Cordierite exhibits a low thermal conductivity, typically in the range of 2-4 W/m·K. Compact α -cordierite has a thermal conductivity of about 3.5 W/m·K at room temperature [32]. This low thermal conductivity allows the cordierite materials to provide effective thermal insulation and reduce heat transfer, making them valuable for applications in which thermal management is crucial.

Mechanical Strength: Cordierite possesses good mechanical strength, which allows it to withstand mechanical stresses and loading conditions. The exact strength can vary depending on factors such as the material composition, microstructure, and manufacturing processes.

Hardness: Cordierite has a moderate hardness, typically ranging from six to seven on the Mohs scale. The Vickers hardness of pure cordierite (CZR0) is sensitive to the applied load during indentation testing; it is about 25.42 GPa for an applied load of 0.5 kg and decreases to 8.65 GPa for a 10 Kg load [33]. This hardness contributes to the resistance to scratching and abrasion.

Electrical Insulation: Cordierite exhibits excellent electrical insulation properties because of its low electrical conductivity. They are widely used as insulating materials in electrical components and devices.

Chemical Stability: Cordierite is chemically inert and resistant to several chemical reactions. It is not easily corroded by acids, alkalis, or other chemical substances, which makes it suitable for applications in corrosive environments.

Dielectric Properties: Cordierite has a low dielectric constant and dielectric loss, making it suitable for applications in the fields of electronics and telecommunications.

2.6 Physical and mechanical properties of cordierite

2.6.1 Traditional synthesis routes and their limitations

The traditional synthesis routes for cordierite materials typically involve solid-state reactions and high-temperature processes. The two common methods for synthesizing cordierite are as follows:

Solid State Reaction: In this method, a mixture of raw materials, typically magnesium oxide (MgO), aluminum oxide (Al_2O_3), and silica (SiO_2), is finely ground and compacted into the desired shape, such as pellets or blocks. The compacted samples were then heated to high temperatures (typically above 1300 °C) in a controlled atmosphere to induce solid-state reactions and the formation of cordierite. The heating process allowed for the diffusion of the constituent elements and the formation of the desired cordierite crystal structure. This process is time-consuming and requires a prolonged heating to ensure the complete reaction and formation of the desired phase. Selim et al. [34] utilized a mixture of kaolin and talc together with aluminum hydroxide to synthesize cordierite through a solid-state reaction. The raw materials were mixed such that 2:2:5 mol ratio of Al_2O_3 -MgO- SiO_2 is attained. In their study, the powders were ball milled and pressed uniaxially at 120MPa using a universal press. The pressed specimen was sintered at 1250, 1300, and 1350 °C with a 1h holding time while maintaining 10 °C/min heating rate. Their results indicated that the cordierite phase was formed at 1350°C with excellent crystallinity. Djaida et al. [35] reported on the use of kaolinite and synthetic magnesia. Kaolinite from two different sources was used as the sources of Al_2O_3 and SiO_2 . The raw materials were mixed in the ratio, 59,29,12% for SiO_2 , Al_2O_3 and MgO, respectively, for their work; the blended materials were ball milled and cold pressed at temperatures ranging from 900-1350 °C for

a total duration of 2h. The results showed that the sample possesses numerous phases for those that were sintered between 900-1150 °C. The crystallization of the cordierite phase began at 1200 °C, and a highly dense cordierite was formed at 1250 °C. Radu et al. [36] used refractory clay, steatite, Al₂O₃ gamma, 94% -Al₂O₃, amorphous silica, Al(OH)₃, quartz, and MgCO₃ and MgO mixed in various proportions, ball milled, and reaction sintered at 1250, 1350 and 1400 °C for a total duration of 1h. It was observed that cordierite phase formation increased with increasing temperature.

Sol-Gel Route: The sol-gel method involves the synthesis of cordierite from precursor solutions containing metal alkoxides or metal salts. The precursor solution undergoes hydrolysis and condensation to form a gel. The gel was then dried and heated at high temperatures to remove any remaining organic components and induce crystallization, resulting in the formation of cordierite. The advantage of this method is that it allows better control of the composition and particle size distribution of the cordierite powder. Several studies have been published with the aim of achieving a cordierite structure using the sol-gel method.

In earlier research work, Petrovic et al. [37] studied the effect of silica particle size on the crystallization and densification behavior of cordierite. The findings indicate that spinel crystallizes from the colloidal gels prior to cristobalite formation, and their reaction leads to the formation of β -cordierite, which is specific to three-phase gels. Reducing the size of silica particles results in a decrease in the crystallization temperature of cristobalite and the formation temperature of β -cordierite. In another study, Petrovic studied the effect of temperature on cordierite transformation [38]. It was observed that μ -cordierite crystallized within a temperature range of 950-1000 °C alongside small quantities of spinel; the μ -

cordierite transforms into α -cordierite at approximately 1100 °C, while the α -cordierite was further transformed into modulated β -cordierite at temperatures exceeding 1300 °C.

2.6.2 Co-precipitation:

The coprecipitation method involves the simultaneous precipitation of metal cations from their respective salts or precursors to form a homogeneous precursor solution. This solution was then subjected to further thermal treatment for conversion into cordierite. The coprecipitation method typically begins with the preparation of precursor solutions containing the necessary metal ions. For cordierite synthesis, aqueous solutions of magnesium, aluminum, and silicon salts were mixed under controlled pH and temperature conditions, and a precipitating agent, such as ammonium hydroxide or sodium carbonate, was added to initiate the formation of the cordierite precursor. The obtained gel is typically subjected to further thermal treatment for conversion into cordierite. The gel was then dried to remove excess moisture and calcined at elevated temperatures. Calcination facilitates the elimination of organic species, decomposition of precursors, and formation of intermediate phases [39].

Molten Salt Synthesis: In this method, a molten-salt mixture was employed as the reaction medium for the formation of cordierite crystals. The high-temperature molten salt facilitated solid-state reactions and enabled the crystallization of cordierite. This process involves the dissolution of the reactant salts in a molten salt medium at elevated temperatures. The reactants were allowed to react in the molten state to form cordierite crystals. The obtained product was cooled, crushed, and washed to remove the salt residue [40].

Spray Drying: Spray drying is a technique in which a liquid is rapidly converted into dry powder by spraying it into a hot gas stream. This results in the formation of small spherical particles. This technique involves preparing a slurry containing the desired precursors, followed by spray drying to obtain a fine powder. This process involves the creation of a precursor sol by hydrolyzing tetraethyl orthosilicate (TEOS) in an aqueous solution containing aluminum and magnesium nitrates. The solution was stirred thoroughly. Subsequently, the sol was spray-dried at a temperature of 200 °C. The next step in the process is calcination, where the spray-dried cordierite precursor powder is heated to a temperature of 750 °C. Calcination involves the subjection of a material to high temperatures to induce chemical and physical changes. In this case, calcination was used to initiate the crystallization of cordierite. The cordierite precursor powder crystallizes into α -cordierite via μ -cordierite but expands upon heating instead of sintering [41].

2.6.3 Limitations of Traditional Synthesis Routes

Traditional synthetic routes for the widely used cordierite ceramics have certain limitations that researchers have sought to overcome. These limitations include the following:

High Synthesis Temperatures: Many traditional methods require high temperatures for cordierite formation. This can lead to increased energy consumption and may limit the use of precursors or additives that cannot withstand high temperatures. Lowering the synthesis temperature without compromising the final properties of the cordierite is an ongoing challenge.

Prolonged Processing Time: Traditional synthesis methods often involve multiple processing steps such as calcination, grinding, and sintering, which can extend the overall

processing time. Lengthy processing times can increase production costs and hinder large-scale manufacturing.

Control over Composition and Stoichiometry: Achieving precise control over the composition and stoichiometry of cordierite using traditional synthesis methods is challenging. Variations in the starting materials, reaction conditions, and precursor properties can lead to deviations from the desired cordierite composition, thereby affecting the final properties of the material.

Particle Size and Homogeneity: Traditional synthesis methods may result in a wide particle size distribution and agglomerate formation. Nonuniform particle size and poor dispersion can lead to uneven densification and compromised mechanical properties of the final cordierite product.

Limitations in Microstructural Control: Traditional methods often exhibit limited control over the microstructures of cordierite ceramics. Grain growth during sintering can lead to larger grain sizes, affecting mechanical strength and other properties. Achieving a fine and homogeneous microstructure is crucial to achieving optimal performance in many applications.

Lack of Eco-Friendliness: Some traditional synthesis methods use toxic or hazardous chemicals that pose environmental and health risks. Additionally, the high-temperature processes employed in some methods contribute to carbon emissions and energy consumption, highlighting the need for more sustainable synthetic approaches.

Difficulty in Scalability: Traditional synthesis methods may face challenges when production is scaled up to meet industrial demands. Issues such as maintaining uniformity,

reproducibility, and consistency on a larger scale can arise and require further optimization and process adaptation.

2.7 Introduction to Spark Plasma Sintering (SPS) and nano powders

Spark Plasma Sintering (SPS) is an innovative powder consolidation technique that has attracted significant attention in materials science and engineering. It offers unique advantages over conventional sintering methods by utilizing pulsed electric current and pressure to achieve the rapid and efficient densification of powder materials. SPS has is widely used to fabricate advanced ceramics, metals, composites, and other materials with enhanced properties. The successful sintering of the materials resulted in the best densification by minimizing the number of pores. The densification process is influenced by factors such as the sintering temperature, duration, mechanism, average particle size of the powder, initial powder density, and size distribution of the particles within the powder [42].

2.7.1. Nano Powders:

Nano powders or nanopowders are powders consisting of particles with nanoscale dimensions typically ranging from 1 to 100 nanometres. These materials exhibit unique properties and behaviors compared to their bulk counterparts owing to their small sizes and high surface-to-volume ratios. Nano powders have attracted immense interest in various fields, including materials science, electronics, medicine, and energy, owing to their potential for tailoring properties and enhancing performance.

The combination of Spark Plasma Sintering (SPS) with nano powders has emerged as a promising approach for fabricating advanced materials with exceptional properties. The small particle size and high reactivity of nano powders enabled improved sintering kinetics and enhanced densification during the SPS. Additionally, the large surface area of nano

powders facilitated strong atomic bonding and promoted the formation of dense and homogeneous microstructures.

2.7.2. SPS Process:

The Spark Plasma Sintering (SPS) process involves the application of a pulsed direct electric current and uniaxial pressure to a powder compact inside a graphite die. The SPS setup consisted of a pulsed direct-current (DC) power supply, graphite die assembly, and a heating system. The powder compact was typically placed between two graphite electrodes, and pressure was applied to ensure intimate contact between the powder particles.

During the SPS process, the pulsed electric current passes through the compact powder, generating localized heating owing to the Joule heating effect. Rapid heating combined with applied pressure promotes the diffusion and rearrangement of atoms, resulting in the consolidation and densification of the powder material. A typical cycle of the SPS process is shown in Figure 3. The pulsed current propagates across the particle surfaces, as shown in Figure 4, preventing excessive grain growth and maintaining a fine microstructure in the final product. This process lowers the sintering temperature and reduces the sintering time of different material systems, enabling the synthesis of new materials with fine microstructures and unique properties [43–45].

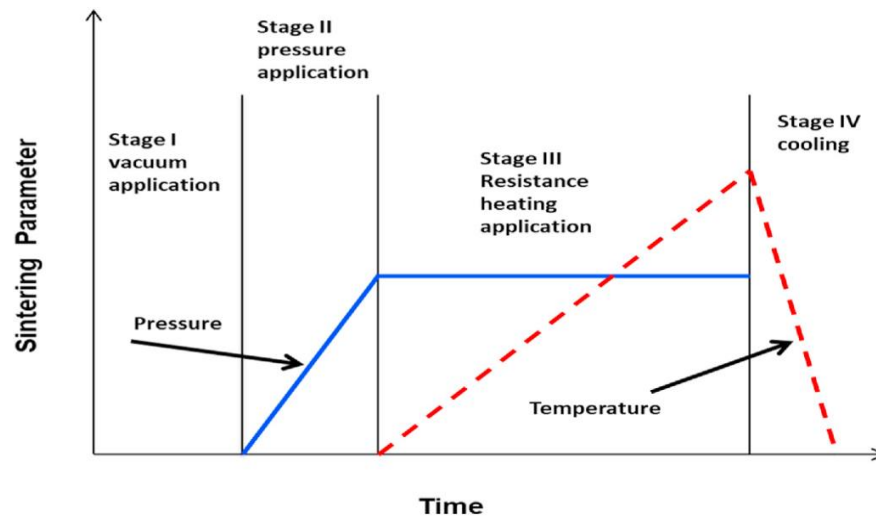


Figure 3. Typical stages of the SPS process [46]

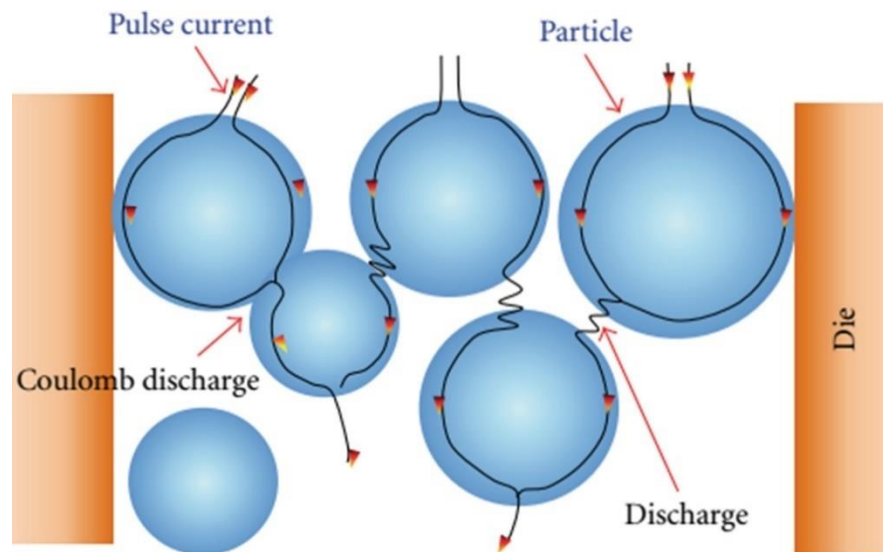


Figure 4. Pulsed current that flows through powder particles [42]

2.7.3. Advantages of SPS with Nano Powders:

- **Enhanced Densification:** The high reactivity and small particle size of nano powders facilitate improved densification during SPS, leading to higher relative densities and reduced porosity in the final product.

- **Fine Microstructure:** The combination of SPS and nano powders enables the formation of fine-grained microstructures with improved homogeneity that can contribute to enhanced mechanical, electrical, and thermal properties.
- **Enhanced Mechanical Properties:** The presence of nanoscale grains and absence of grain growth during SPS with nano powders can result in superior mechanical properties, such as increased hardness, strength, and fracture toughness.
- **Reduced Sintering Temperature and Time:** SPS with nano powders allows lower sintering temperatures and shorter processing times than conventional methods, offering energy savings and the ability to process heat-sensitive materials.
- **Tailored Material Properties:** The use of nano powders in SPS enables the incorporation of dopants or additives at the nanoscale, allowing precise control over the material properties and the development of tailored functionalities.

2.7.4. Kinetics of cordierite formation

Investigations of cordierite formation by various researchers using different techniques and conditions have resulted in a wide range of reported activation energies. Donald et al. [8] utilized differential scanning calorimetry (DSC) and differential thermal analysis (DTA) under non-isothermal and isothermal conditions and found that the glass-to-cordierite transition occurred with energy values ranging from 532 to 574 kJ/mol. Kim et al. [34] examined cordierite crystallization from glass systems doped with CeO₂ using non-isothermal DTA and observed mean activation energies of 653 kJ/mol for the starting glass and 418 kJ/mol for the doped glass. Song et al. [36] prepared cordierite from potassium feldspar and used DSC to determine the activation energies in the ranges of 230 to 279 kJ/mol and 348–374 kJ/mol. Goel et al. [47] studied cordierite formation in Al₂O₃-TiO₂-

SiO₂-MgO under non-isothermal conditions and reported activation energies of 340 and 498 kJ/mol. Hu et al. [48] investigated the cordierite formation in the absence and presence of BaO using non-isothermal DTA and obtained activation energies of 366 kJ/mol and 290-487 kJ/mol, respectively. Silva et al. examined the kinetics of cordierite formation using nonisothermal DTA and observed an activation energy of 467 kJ/mol. Watanabe et al. [49] studied the kinetics of cordierite recrystallization from a glass with P₂O₅ and B₂O₃ additions using XRD and DTA, obtaining activation energy values of 303.5 kJ/mol and 301.9 kJ/mol, respectively. Rudolph et al. [50] characterized cordierite formation from glass modified with P₂O₅ using isothermal and non-isothermal DTA and reported activation energies of 469 kJ/mol and 300 kJ/mol, respectively. Boudchicha et al. [51] investigated cordierite crystallization in glass ceramics synthesized from dolomites and kaolin using non-isothermal XRD and found an activation energy of 45 kJ/mol. Miller et al. examined cordierite crystallization using non-isothermal and isothermal time-resolved powder diffraction DTA techniques and reported activation energy values in the range of 600-850 kJ/mol. Clark et al. [52] developed formulas to investigate cordierite crystallization in the presence and absence of Zn additives and determined activation energy values of 271 kJ/mol and 221 kJ/mol in the absence of Zn and 179 kJ/mol and 170 kJ/mol with Zn.

It is important to note that there is a significant disparity in the reported activation energy values for cordierite crystallization owing to variations in sample preparation methods, data collection, and analysis techniques. The composition, type of raw materials, additives, and presence of impurities were also found to significantly affect the kinetics of cordierite formation.

2.7.5. Previous research on cordierite synthesis using SPS and nano powders.

Several research works have been published on the use of the spark plasma sintering technique to synthesize cordierite materials. Cordierite was synthesized using Spark Plasma Sintering (SPS) in combination with nano powders. The aim was to achieve an efficient and rapid densification of cordierite. Researchers have explored various aspects of the synthesis process, such as the choice of starting materials, milling techniques for nano powder preparation, and SPS parameters for sintering. By utilizing the nanosized cordierite powder, the specific surface area and reactivity of the material can be enhanced, leading to improved densification during sintering.

Several studies have investigated the effects of different synthesis conditions, including temperature, pressure, and holding time, on the final properties of cordierite ceramics. SPS offers advantages in terms of reducing processing time and achieving high-density ceramics with fine-grained microstructures. The use of SPS in the synthesis of cordierite from nano powders has shown promising results in terms of enhancing densification kinetics, reducing grain growth, and improving the mechanical properties of the resulting ceramics. These advancements have the potential to expand the application range of cordierite-based materials in the automotive, aerospace, and electronics industries, where high-temperature stability and thermal insulation are desired. Rundans et al. [53] synthesized cordierite materials using alumina, silica, and magnesia, along with three types of dolomite. The synthesis process involved ball milling for 3 hours, followed by spark plasma sintering (SPS) at 1150 °C for 2 minutes. However, the authors also reported the formation of phases other than cordierite in their study. El-Buaishi et al. [54] utilized the sol-gel method to prepare cordierite powders, which were then consolidated by spark

plasma sintering (SPS). The alkoxide cordierite powder was spark plasma sintered at temperatures of 1400 and 1350 °C for 1 and 7 minutes, respectively. The authors reported various material properties, including a bulk density of 2.52 g/cm³, relative density of 99%, hardness of 8.5 GPa, and fracture toughness of 4 MPa m^{1/2}.

2.8. Aims and Objectives

This study aims to synthesize ceramic materials utilizing nano oxide pure powders and spark plasma sintering. In this study, the production of low-cost and highly pure cordierite materials at relatively low temperatures was investigated. This requires a deeper understanding of ceramics and composites, leading to the following objectives:

1. Synthesis of spinel materials from Al₂O₃ and MgO nano-oxides using SPS
2. To study the effect of processing parameters on the formation of the Spinel structure
3. Synthesis of cordierite from Al₂O₃, SiO₂, and MgO nano-oxides using SPS
4. To study the effect of processing parameters on the formation of the cordierite structure
5. To investigate phase transformation that leads to the formation of the cordierite structure.
6. To study the effects of the testing conditions, processing parameters, and characterization techniques on the hardness and fracture toughness.
7. To correlate the mechanical properties with the microstructure of the cordierite.

CHAPTER 3

MATERIALS AND EXPERIMENTAL PROCEDURE

3.1 Raw Materials

Three pure nano oxide powders, namely Al_2O_3 , SiO_2 , and MgO , were used in this study. Al_2O_3 procured from Chem PUR, Germany, with an average particle size of 150 nm and 99.85% purity. SiO_2 with an average particle size of 20-30 nm and 98% purity. MgO obtained from US Research Nanomaterials, with an average particle size of 60 nm and 99.95% purity.

3.2 Material Processing

The Spark Plasma processing route was used to process all samples used in this study. This involved mixing the powders, followed by sintering.

3.2.1 Blending

The calculated amount of powder was weighed with respect to the stoichiometric composition of cordierite (34.37 %wt. Al_2O_3 , 51.37 wt.% SiO_2 , and 13.7 wt.% MgO). The powder was then mixed by sonication. A sonicator (model VCX750, by Sonics & Materials Inc., USA) was used to mix the powders in ethanol at 450W for 30 min. The powder then was dried in a furnace for 12h at 100 °C.

3.2.2 Spark Plasma Sintering

The blended powder mixture was cold compacted using a 150Ton uniaxial hydraulic press. The loose powder was poured into the die cavity, and a pressure equivalent to 570MPa was applied in a single direction and held for 1min to form billets of 35-mm diameter and 40-

mm height. The compacted billet was then removed from the die. A schematic of the powder consolidation process is shown in.

A schematic of the spark plasma sintering process is shown in a. The sonicated powder was loaded into a 2 mm graphite die. The sintering was performed using a fully automated SPS system (FCT system, model HP D 5). During this process, pressure was kept at 50 MPa and at the heating rate of 100 °C/min. The current and uniaxial stress is applied to the sample at the same time '4'. The temperature was measured using both thermocouples inserted inside a hole in the graphite die, and pyrometer samples were sintered in vacuum at various temperatures between 900-1200 °C at 50 intervals for 30min.

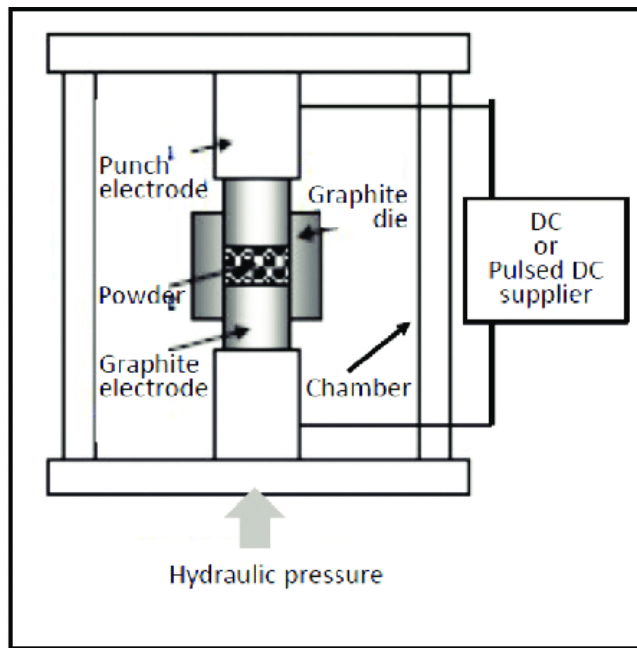


Figure 5: Schematic diagrams showing the spark plasma sintering process.

3.3. Material Characterization

3.3.1 Density Measurement

Density (ρ) measurements were performed on polished sintered samples and measured in accordance with Archimedes' principle [55] using an electronic densimeter, with an accuracy of ± 0.0001 g. The samples were carefully weighed in air and liquid (distilled water was used in this experiment). Equation 1 was used to calculate the experimental densities of the samples.

$$\rho_o = \left(\frac{A}{A-B} \right) * (\rho_l - \rho_a) + \rho_a, \quad \text{Equation 1}$$

where ρ_o = density of composite, ρ_l = Density of Liquid, A = Weight in Air, B = Weight in liquid and ρ_a = Density of Air

3.3.2 X-ray Diffraction Studies

X-ray diffraction analysis of monolithic and reinforced magnesium composites was conducted using an automated Bruker-AXS D8 Advance -40kv/40Ma diffractometer with Cu $K\alpha$ ($\lambda = 1.5418$ Å) radiation. Each specimen was scanned at a step size of 0.02° for a count time of 1s with the diffraction angles varying between 5° and 80° . The crystalline size of the samples was calculated using Scherrer's formula (Equation 2) [56].

$$W_{FWHM} = \frac{k\lambda}{D \cos \theta} \frac{180^\circ}{\pi}, \quad \text{Equation 2}$$

where λ is the wavelength = 0.15405 nm and the constant K = 0.49.

3.3.3 Microstructural Characterization

Microstructural characterization studies were performed on metallographically polished samples. High resolution FE-SEM images for pure powder, sonicated powder, and sintered samples were taken using FEI Quanta 250 attached with EDS 150 mm² to study the morphology of the samples and the composition and distribution of the nano powders. X-ray energy dispersive spectrometry (EDS) analysis of the powders and sintered samples was performed to analyze the elemental composition of the samples. Area mapping, Line Scanning, and Spot analyses were performed on the samples to confirm the presence and distribution of the powders.

3.4 Mechanical Characterization

3.4.1 Hardness Measurement

A hardness tester (ZHU250, Zwick-Roell, Germany) was used to indent the sintered samples by applying a load for 10 s. An average of 10 measurements was taken for each specimen, and the hardness value was obtained using Equation 3 [57, 58]:

$$HV = 1.854 * \left(\frac{P}{d^2} \right), \quad \text{Equation 3}$$

where HV is the Vickers hardness value (kgf/mm²). P is the applied load (kilogram-force); d is the length of the indentation diagonals (mm). The units of HV (kgf/mm²) were changed to GPa using equation 4 [59].

$$HV(GPa) = (9.81/1000) \times Hv(kgf /mm^2) \quad \text{Equation 4}$$

3.4.2 Fracture Toughness (K_{IC}) Measurement

The value of K_{IC} (in $\text{MPa}\cdot\text{m}^{1/2}$) was calculated using two methods; the Evans and Charles equation [60] was used in the first method (Equation 5), and the Anstis' formula [61, 62] was applied in the second method (Equation 6)

$$K_{1c} = 0.16 * \left(\frac{c}{a}\right)^{-\frac{1}{2}} \left(Ha^{\frac{1}{2}}\right) \quad \textbf{Equation 5++}$$

$$K_{1c} = 0.016 \sqrt{\frac{E}{H}} \frac{P}{C^{3/2}}, \quad \textbf{Equation 6}$$

where E is the elastic modulus (GPa), H is the Vickers hardness in GPa, P is the applied load (N), a is the indentation diagonal, and C is the diagonal crack length.

The K_{IC} value was used to calculate the GIC value using Equation 7 [63]:

$$G_{1c} = K_{1c}^2 \left(\frac{1 - \nu^2}{E}\right) \quad \textbf{Equation 7}$$

The value of the elastic modulus of stoichiometric single-phase spinel was taken as 273 GPa, while a value of 0.26 was used for Poison's ratio ν .

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 CHARACTERIZATION OF RAW POWDERS

4.1.1 Powder Morphology and Elemental Analysis

The scanning electron microscopy images of the as-received Al_2O_3 , SiO_2 , and MgO powders are shown in Figure 6. The Al_2O_3 powder shown in Figure 6a has an average particle size of 150 nm, whereas the SiO_2 powder shown in Figure 6b demonstrates a narrow particle size distribution ranging from 20 to 30 nm. The MgO powder in Figure 6c consists of particles smaller than 60 nm.

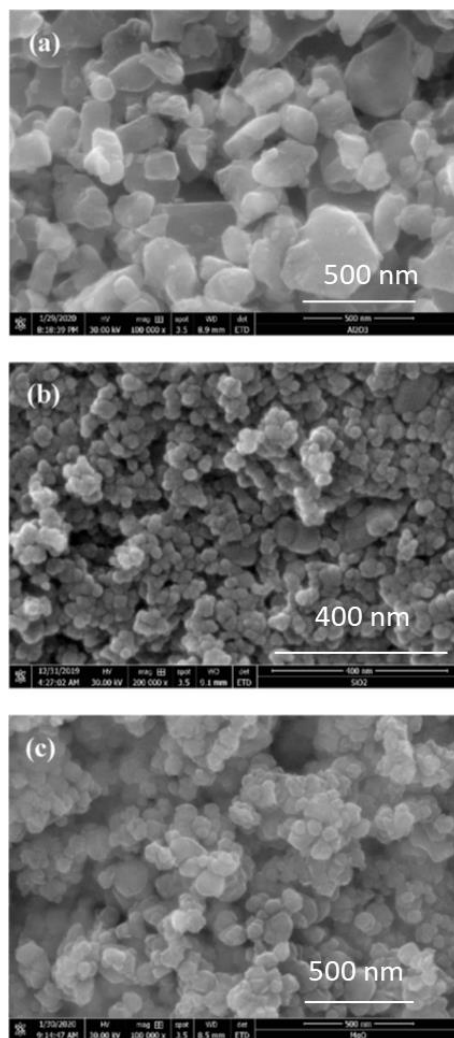


Figure 6. FE-SEM images of (a) Al₂O₃, (b) SiO₂, and (c) MgO nanopowders

4.1.2 X-RAY Diffraction Studies

The XRD patterns of the powders are presented in Figure 7. Notably, Figure 7(a) shows high-intensity peaks corresponding to crystalline alumina, whereas Figure 7(b) shows similar peaks for magnesia. On the other hand, Figure 7(c) reveals a broad diffraction peak indicating the amorphous nature of silica, observed within the 2θ range of 15 to 30°.

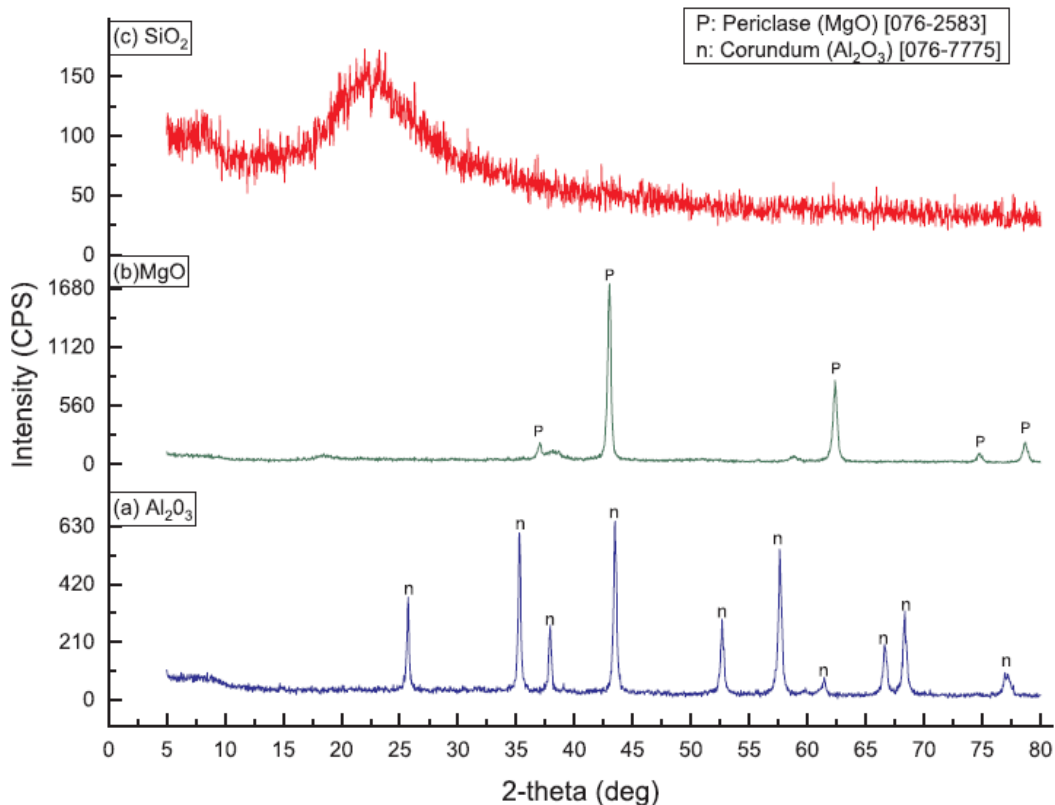


Figure 7. XRD spectra of raw nanopowders

4.2 SINGLE-STEP SYNTHESIS OF FULLY DENSE SPINEL MgAl_2O_4 BY REACTION SPARK PLASMA SINTERING Al_2O_3 AND MgO NANO-OXIDES

4.2.1 Characterization of Mixed Al_2O_3 and MgO Powder

The FE-SEM images shown in Figure 8(a) and (b) provide the low- and high-magnification views of the dried powder mixture. These images indicate that there were no significant particle agglomerates, suggesting a less agglomerated powder mixture. This observation is further supported by the X-ray maps of Al (Figure 9(a)) and Mg (Figure 9(b)), which

correspond to the low-magnification images shown in Figure 8(a). The dispersion of the aluminum and magnesium spots on the maps indicates a less agglomerated powder mixture at the microscale. Similar patterns can be observed in the Al and Mg X-ray maps presented in Supplementary Figure 13(a) and 2(b), respectively, which correspond to the high-magnification images shown in Figure 14(b). This revealed a less-agglomerated powder mixture at the nanoscale level. Fig. 15 shows a representative EDS spectrum of the sonicated powder mixture, where signals of aluminum, magnesium, and oxygen are detected at 1.48, 1.25, and 0.52 keV, respectively. Three different areas were scanned to determine the mass fractions of the elements and their oxides; the results are listed in Table 1. The obtained composition values closely matched those of stoichiometric MAS, with deviations of approximately 1.16% for MgO and 0.46% for Al₂O₃ between the standard and actual compositions. It is important to note that the scan was performed in a single plane [64]. The small deviation in the composition is believed to be due to the dispersion of the oxides at the micro and nanoscales.

These observations and measurements confirm that the powder mixture used in this study exhibits a relatively uniform distribution of particles and a composition close to the desired stoichiometric MAS composition, indicating the successful preparation of the cordierite material.

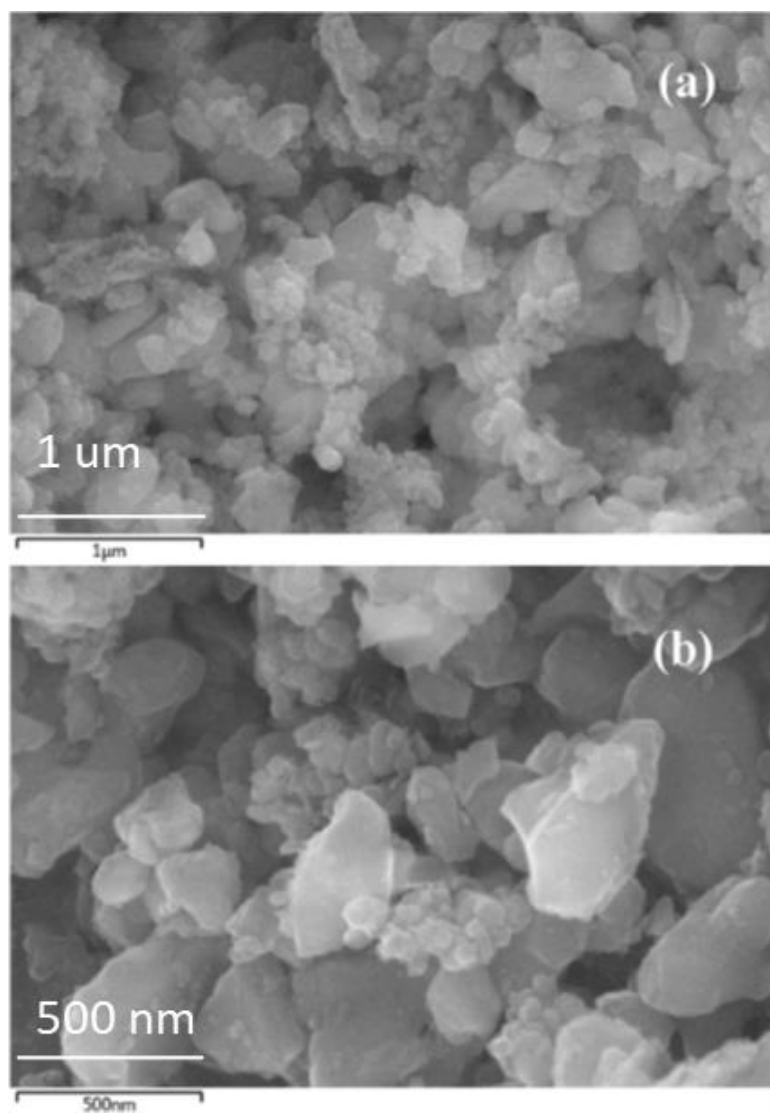


Figure 8. FE-SEM images of the sonicated powder mixture at (a) low and (b) high

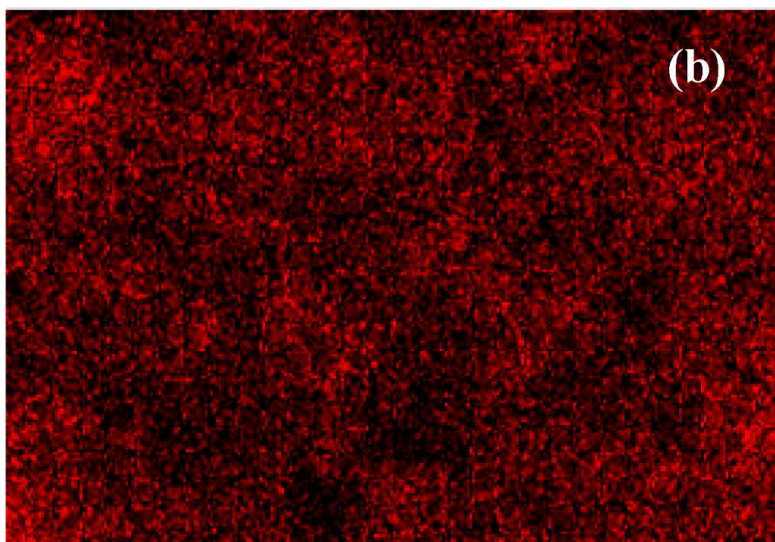
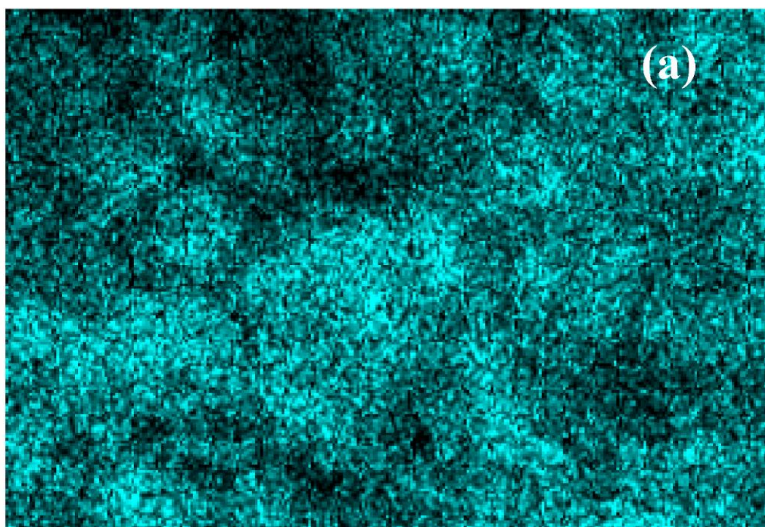


Figure 9. X-ray maps showing distribution of (a) aluminum and (b) magnesium.

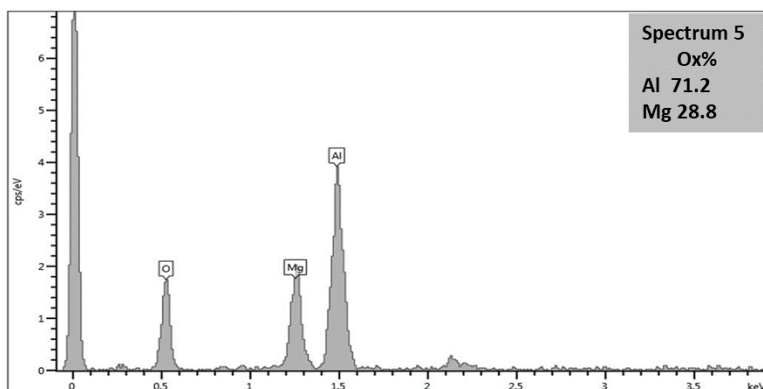


Figure 10. Typical EDS spectrum of the sonicated powder mixture

4.2.2 Effect of Sintering Temperature on spinel formation

The XRD patterns of the sintered specimens are shown in Figure 11. The amount of spinel (MgAl_2O_4) increased with the temperature, ranging from 1000 to 1200 °C. Eventually, at sintering temperatures of 1300 and 1400 °C, only monolithic MAS (MgAl_2O_4 spinel) could be detected. In conventional methods, stoichiometric MgAl_2O_4 spinel is typically formed by the reactive sintering of aluminum oxide (Al_2O_3) and magnesium oxide (MgO). This process is known to involve a relatively high-volume expansion of 5-8% due to spinellization. However, the present results demonstrate the possibility of synthesizing fully dense and single-phase MAS through spark plasma sintering of elementary magnesia and alumina nano-oxides in a single step, without the use of a sintering aid, at a temperature of 1300 °C for 30 minutes. This finding suggests that spark plasma sintering can effectively facilitate the concurrent synthesis and densification of cordierite materials, resulting in the formation of dense and homogeneous monolithic structures. The absence of a separate spinel phase in the XRD spectra confirmed the successful synthesis of single-phase MAS under the specified sintering conditions.

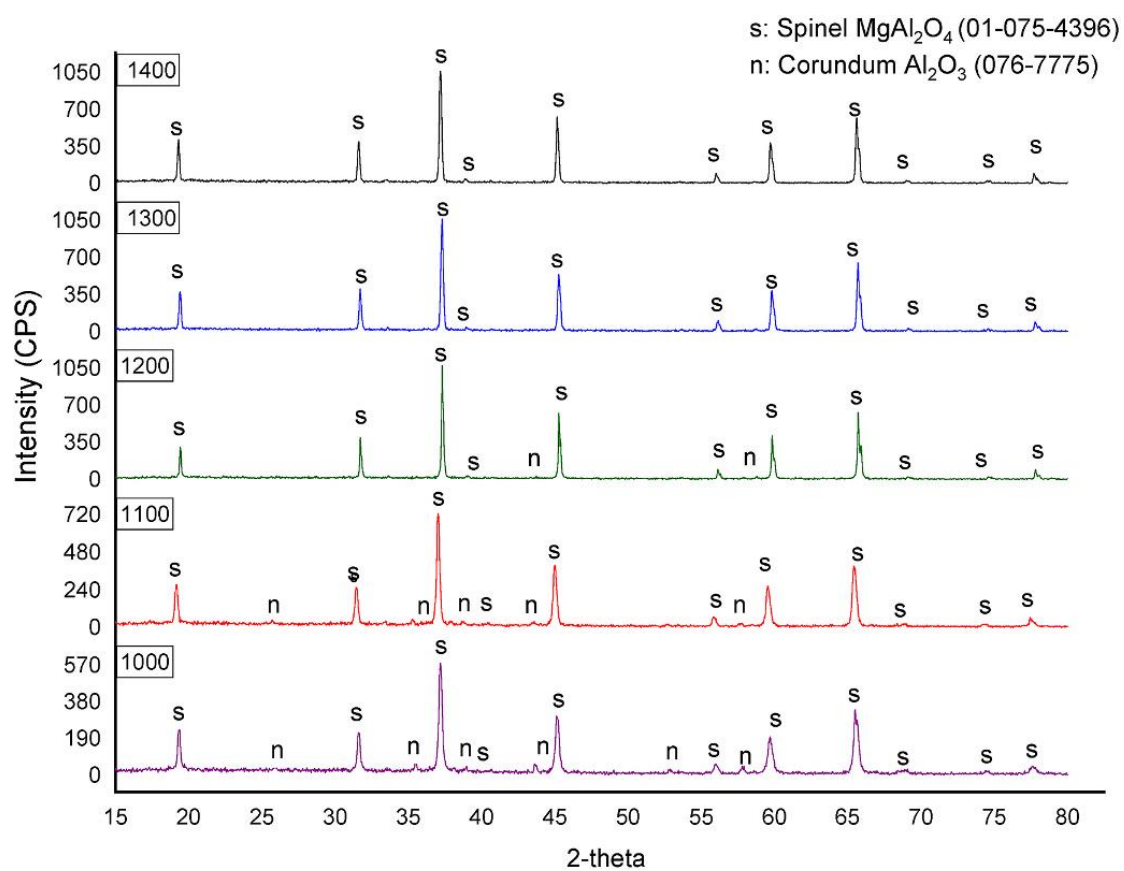


Figure 11. XRD spectra of samples sintered for 30 min

4.2.3 Effect of Sintering Temperature on Densification

The density values of the specimens consolidated at various temperatures (1000 to 1400 °C for 30 minutes) are provided in Table 2. As the temperature increased from 1000 to 1300 °C, the density of the specimens increased from 2.4762 to 3.57 g/cm³, corresponding to a relative density increase from 69.17% to approximately 100% ($\approx 100\%$). No further change in density was observed when the temperature was increased to 1400 °C, indicating the complete formation of fully dense MAS at 1300 °C.

This observation agrees with the XRD results discussed earlier and the microstructural analysis. The achieved sintering temperature of 1300 °C in this study was comparable to the 1275 °C reported for spinel formation by sintering calcined sol-gel precursors [65, 66]. However, it is lower than the sintering temperatures reported for MAS formation from micron-sized alumina and magnesia via two-step pre-sintering and furnace post-sintering at 1600 °C for 3 hours with or without the aid of La₂O₃ [67], or by furnace reaction sintering of Al₂O₃ and MgO nanopowders at 1400 °C for 2 hours [68]. Furthermore, it is lower than the sintering temperatures of 1400 °C and 1500 °C achieved for sintering composite granules [69].

The successful full densification of the spinel in this study can be attributed to the characteristics of the nano-powder precursors, including their sinterability and reactivity, owing to their small particle size. Additionally, the sintering pressure and current applied during the spark plasma sintering process likely play significant roles in achieving full densification.

Table 1. Density and grain size of samples sintered for 30 min.

Temperature (°C)	1400	1300	1200	1100	1000
Density (g/cm ³)	3.5806	3.5742	3.2398	2.7222	2.4762
Relative density (%)	100	99.84	90.5	76.04	69.17
Grain size (nm)	41.527	40.925	34.042	27.429	24.819

4.2.4 Mechanical Properties

The HV, KIC, and GIC values of the samples consolidated at 1200, 1300, and 1400 °C are listed in Table 2. The HV increased from 10.88 ± 0.345 to 17.29 ± 0.185 GPa as the temperature was raised from 1200 to 1300 °C and reached a value of 17.45 ± 0.167 GPa at 1400 °C. The fully dense specimens sintered at 1300 and 1400 °C exhibited KIC values of approximately $2.14 \text{ MPa m}^{1/2}$ (calculated using equation (5)) and $1.82 \text{ MPa m}^{1/2}$ (calculated using equation (6)). The specimen sintered at 1200 °C had relatively high KIC values of 2.89 and $3.12 \text{ MPa m}^{1/2}$ obtained from equations (5) and (6), respectively.

For GIC values, the fully dense specimens sintered at 1300 and 1400 °C showed values of around 15.58 J/m^2 (equation (5)) and 11.40 J/m^2 (equation (6)). The specimen sintered at 1200 °C had relatively higher GIC values of 28.58 and 33.35 J/m^2 calculated using equations (5) and (6), respectively.

The Vickers hardness values of the specimens consolidated at 1300 and 1400 °C were comparable to the values of 17 and 18 GPa achieved for spinel produced by sintering composite granules at 1500 and 1400 °C, respectively [69]. However, they were

significantly higher than the value of 12.71 GPa reported for spinel obtained by sintering a calcined sol-gel precursor [70]. The fracture toughness of the fully dense spinel obtained in this study is higher than that reported in another study by a different researcher [69].

Table 2. Hardness, fracture toughness, and critical strain energy release rate of samples sintered at different temperatures.

Temperature (°C)	1200		1300		1400	
HV (GPa)	10.88 ± 0.345		17.29 ± 0.185		17.45 ± 0.167	
K _{IC} (Mpa.m ^{1/2})	Equation 5	Equation 6	Equation 5	Equation 6	Equation 5	Equation 6
	2.891 ± 0.138	-	2.129 ± 0.106	1.825 ± 0.085	2.143 ± 0.1	1.828 ± 0.082
G _{IC} (J/m ²)	28.584		15.488	11.384	15.681	11.418

The micrographs of the fracture surface of a specimen sintered at 1400 °C are presented in Figure 12. The average grain size of the spinel phase in the samples sintered at 1300 and 1400 °C was measured to be 40.92 and 41.52 nm, respectively. This indicates that grain growth was inhibited due to the use of the Spark Plasma Sintering (SPS) method. Upon examining the microstructure of the samples, several observations can be made: (i) there is only one phase present, which is a monolithic spinel; (ii) no pores are observed, indicating full densification; and (iii) transgranular fracture dominates the fracture behavior.

Random Energy Dispersive spectroscopy (EDS) analysis of different areas of the specimen sintered at 1400 °C confirmed that the stoichiometry of the sample was preserved after

sintering. Table 3 lists the mass percentages of aluminum and magnesium oxides, which were similar to those of monolithic MAS. There were slight deviations of -9.98% and +3.49% in MgO and Al₂O weight percentages, respectively, between the standard and actual compositions. Similar results were observed for the specimen consolidated at 1300 °C. The values of HV, KIC, and GIC of the samples consolidated at 1300 °C showed similar results, indicating consistent mechanical properties between the specimens sintered at 1300 and 1400 °C.

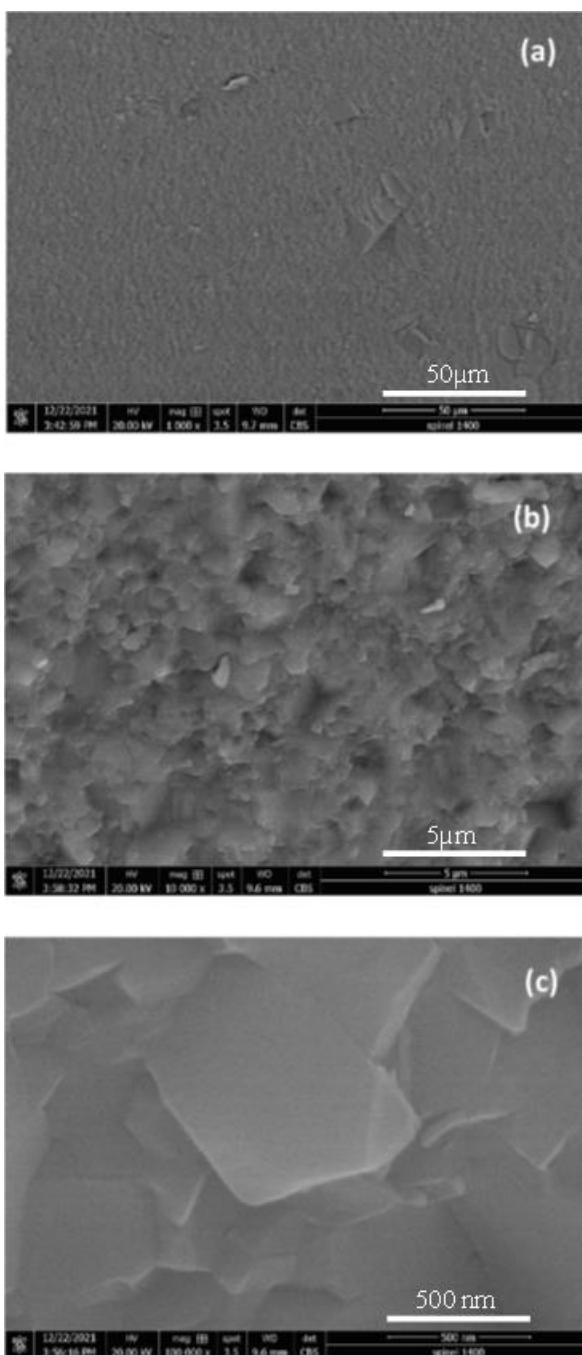


Figure 12. FE-SEM images of fracture surface of sample sintered for 30 min at 1400 °C (a) X1000 (b) X10000, and (c) X100000.

4.3 SYNTHESIS OF PURE CORDIERITE MATERIALS BY SPARK PLASMA SINTERING OF Al_2O_3 , SiO_2 , and MgO NANO-OXIDE POWDERS

4.3.1 Characterization of Mixed Al_2O_3 , SiO_2 , and MgO

Figure 13(a) shows a representative FE-SEM image of the sonicated powder mixture captured at high magnification. The image shows a homogeneous blend without significant agglomerates of the Al_2O_3 , SiO_2 , and MgO particles. To further examine the uniformity of the powder mixture at the microscale, X-ray maps of Al, Si, and Mg are presented in Figure 13(c), (d), and (e), respectively, obtained at low magnification. These maps exhibit a consistent distribution of the three powders, as evidenced by the even dispersion of spots in the Al-, Si-, and Mg-dot maps. To confirm the homogeneity of the powder mixture and its uniform distribution on the nanoscale, additional FE-SEM images were captured at high magnification, followed by X-ray mapping.

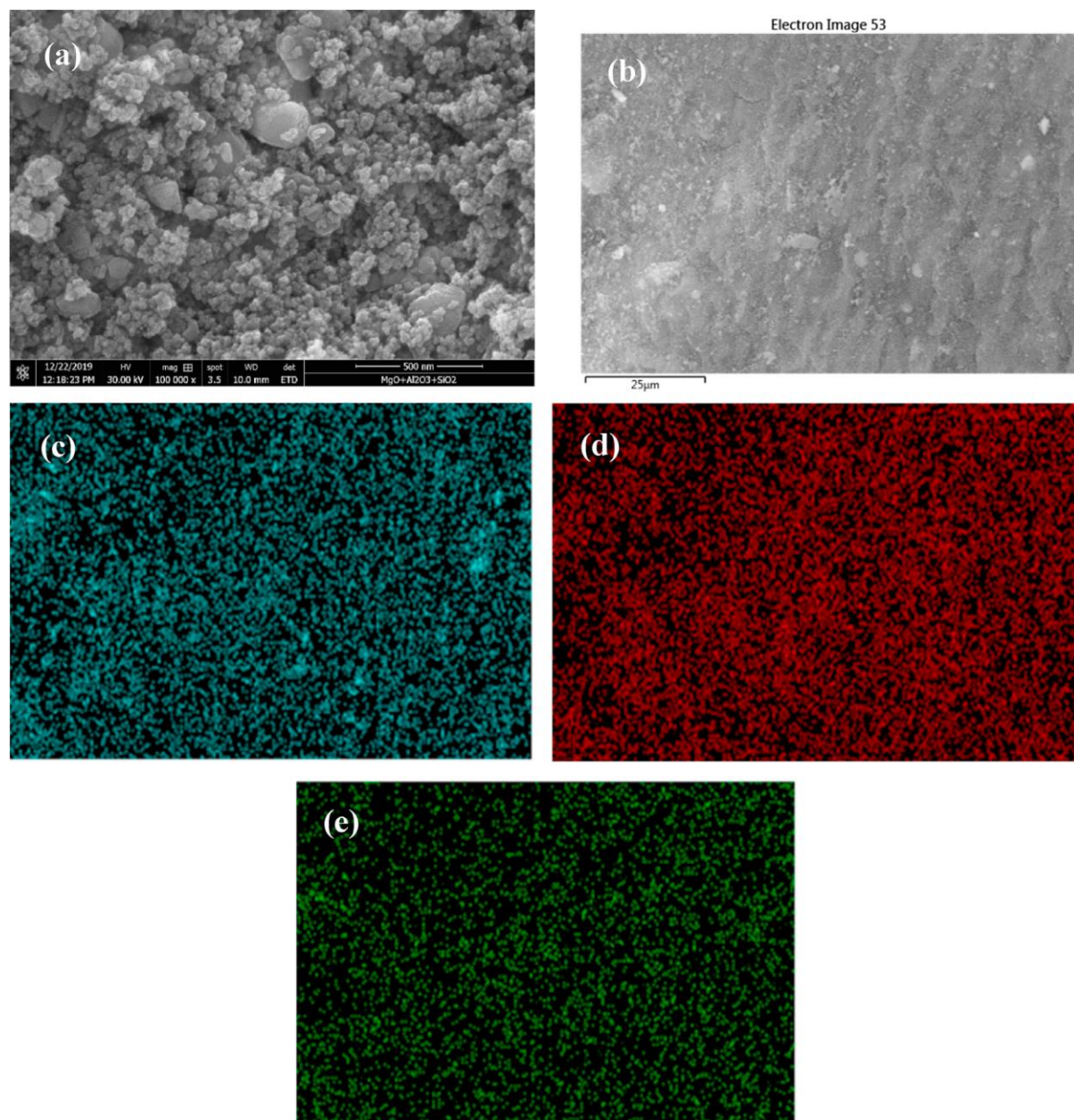


Figure 13. FE-SEM images of the sonicated powder mixture at (a) high and (b) low magnification. X-ray maps showing distribution of (c) aluminum, (d) silicon, and (e) Mg

Figure 14 shows a representative image along with the corresponding X-ray maps. The uniform distribution of aluminum (Figure 14b), magnesium (Figure 14c), and silicon (Figure 14d) spots in the maps clearly indicates the even dispersion of the three powders at the nanoscale. Additionally, the EDS spectrum depicted in Figure 14e reveals signals for Al (~1.48 keV), Mg (~1.25 keV), Si (~1.74 keV), and O (~0.52 keV). Mass fraction (wt. %) of elements and oxides in two different scan areas are provided in Table 1. The obtained values closely aligned with those of stoichiometric cordierite. The deviation (%) of the actual composition from the standard composition is as follows: MgO (+1.45%), Al₂O₃ (-1.51%), and SiO₂ (+0.64%). These results indicate that the oxide content was close to the composition of monolithic cordierite, considering that the scan was conducted in a single plane [71]. This small deviation is deemed acceptable and can be attributed to the homogeneity and uniform distribution of oxides achieved not only at the microscale, but also at the nanoscale.

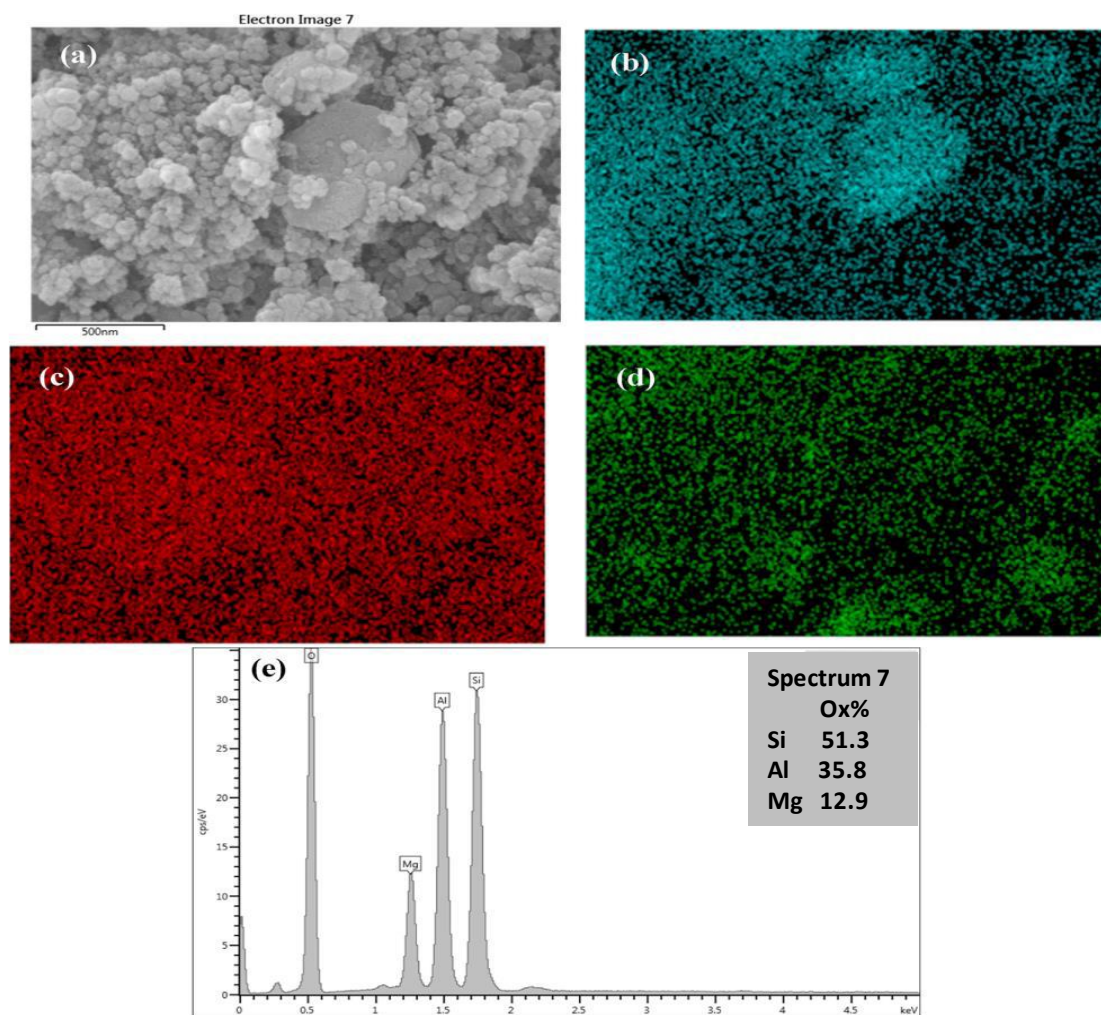


Figure 14. (a) High magnification FE-SEM image of the sonicated powder; corresponding x-ray maps (b) aluminum, (c) silicon, (d) magnesium, and (e) EDS spectrum

Table 3. Mass fraction (wt.%) of elements and oxides in different scan area in the sonicated powder mixture

Elements	Area 1	Area 2	Oxides	Area 1	Area 2	Average	Standard Cordierite	Deviation
Al	14.6	13.7	Al ₂ O ₃	35.3	33.5	34.4	34.93	-1.51
Mg	6.6	7.4	MgO	13.1	14.7	13.9	13.7	1.45
Si	17	16.9	SiO ₂	51.6	51.8	51.7	51.37	0.64
O	61.8	62.1						

4.3.2 Effect of Sintering Temperature on Cordierite Formation

The sonicated powders were sintered via SPS at different temperatures of 900, 950, 1000, 1050, 1100, 1150, and 1200 °C for a duration of 30 minutes. The resulting samples were analyzed by X-ray diffraction (XRD) to confirm the developed phases. The results of the XRD analysis are shown in Figure 15. In the spectra of the specimens sintered at 900 and 950 °C, characteristic peaks of α -alumina (corundum) and forsterite (Mg₂SiO₄) are observed. Additionally, a broad peak representing amorphous silica can be observed in the lower 2 θ range. The presence of forsterite below 950 °C can be attributed to the reaction between magnesia and a portion of silica. At 1000 °C, forsterite disappears, enstatite (MgSiO₃) emerges, amorphous silica crystallizes into cristobalite (SiO₂), and the intensity of α -alumina (corundum) peaks diminishes. Subsequently, at 1050 °C, enstatite vanishes, cristobalite decreases, and the phases of sapphirine (Mg_{3.5}Al₉Si_{1.5}O₂₀) and α -cordierite (Mg₂Al₄Si₅O₁₈) appear, with only weak peaks of α -alumina (corundum) observed. As the

temperature reaches 1100 °C, traces of α -alumina (corundum) are observed, while cristobalite and sapphirine sharply decrease, with α -cordierite becoming the major phase. Finally, at 1150 and 1200 °C, only α -cordierite is present in the consolidated samples.

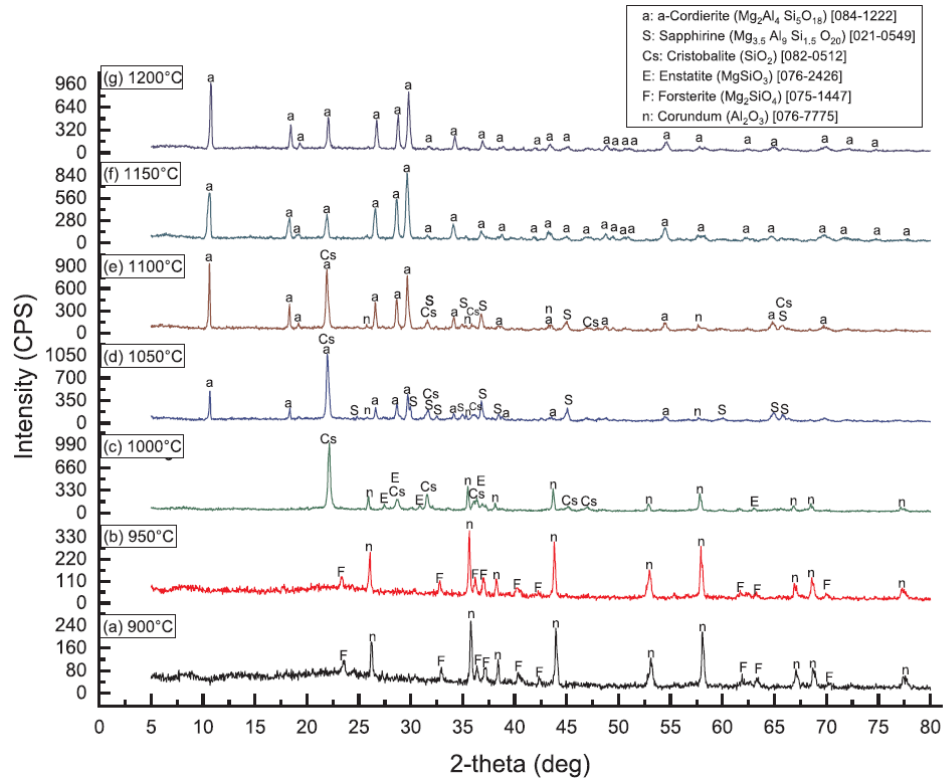


Figure 15. XRD spectra of samples sintered for 30 min.

4.3.3 Effect of Sintering Time on Cordierite Formation

To investigate the impact of the sintering time on cordierite formation, additional samples were subjected to different sintering conditions. Specifically, samples were sintered at 1150 and 1200 °C for 10 and 20 minutes, and at 1050 and 1100 °C for 60 minutes. The resulting XRD patterns are shown in Figure 16. At 1050 °C, the spectra exhibit reflections from cristobalite, sapphirine, α -cordierite, and weak peaks of corundum. Upon increasing the

temperature to 1100 °C, the reflections from cristobalite and corundum disappear, leaving only characteristic reflections of sapphirine and α -cordierite. When sintered at 1150 °C for 10 minutes, the sample predominantly consists of μ -cordierite, along with small amounts of cristobalite and sapphirine. Extending the sintering time to 20 minutes leads to a decrease in the intensity of cristobalite and sapphirine peaks, and the transformation of μ -cordierite into α -cordierite. In the case of sintering at 1200 °C for 10 minutes, the sample contains cristobalite, sapphirine, and α -cordierite, while at 20 minutes, α -cordierite becomes the major phase with a small amount of sapphirine. Notably, μ -cordierite, which is a metastable form of cordierite, is only observed in the sample sintered at 1150 °C for 10 minutes, and it transforms into the stable α -cordierite after 20 minutes. These findings indicate that the rate of cordierite formation and the occurrence of intermediate phases are not solely dependent on the temperature but are also influenced by the sintering time.

The XRD analysis of spark plasma-sintered MgO, Al₂O₃, and SiO₂ nano-oxide powders reveals the formation of several phases, including forsterite, enstatite, sapphirine, μ -cordierite, and α -cordierite. The formation of α -cordierite can be attributed to several reactions or transformations, such as the interaction between compounds like alumina and enstatite [72], the conversion of μ -cordierite to α -cordierite, and the direct formation from the oxides. These findings align with those of Shon et al. [73], who demonstrated the thermodynamic feasibility of MgO, Al₂O₃, and SiO₂ interactions leading to the formation of the Mg₂Al₄Si₅O₁₈ phase. They prepared a stoichiometric nanostructured mixture of oxides through the high-energy ball milling of microscale powders for 10 hours and consolidated the mixture using pulsed current-activated sintering. Additionally, direct cordierite formation from oxides has been observed in samples with a high degree of

mechanochemical activation [72]. The formation of spinel (MgAl_2O_4) as an intermediate phase occurs when magnesia reacts with alumina, and the subsequent reaction between spinel and silica yields cordierite [74]. However, the XRD results of this study did not indicate the presence of a spinel phase. Previous studies have shown that spinel formation may be suppressed in samples with a high degree of mechanochemical activation [72]. It is believed that the high reactivity of the nano-oxide powders used in this study contributed to the suppression of spinel phase formation.

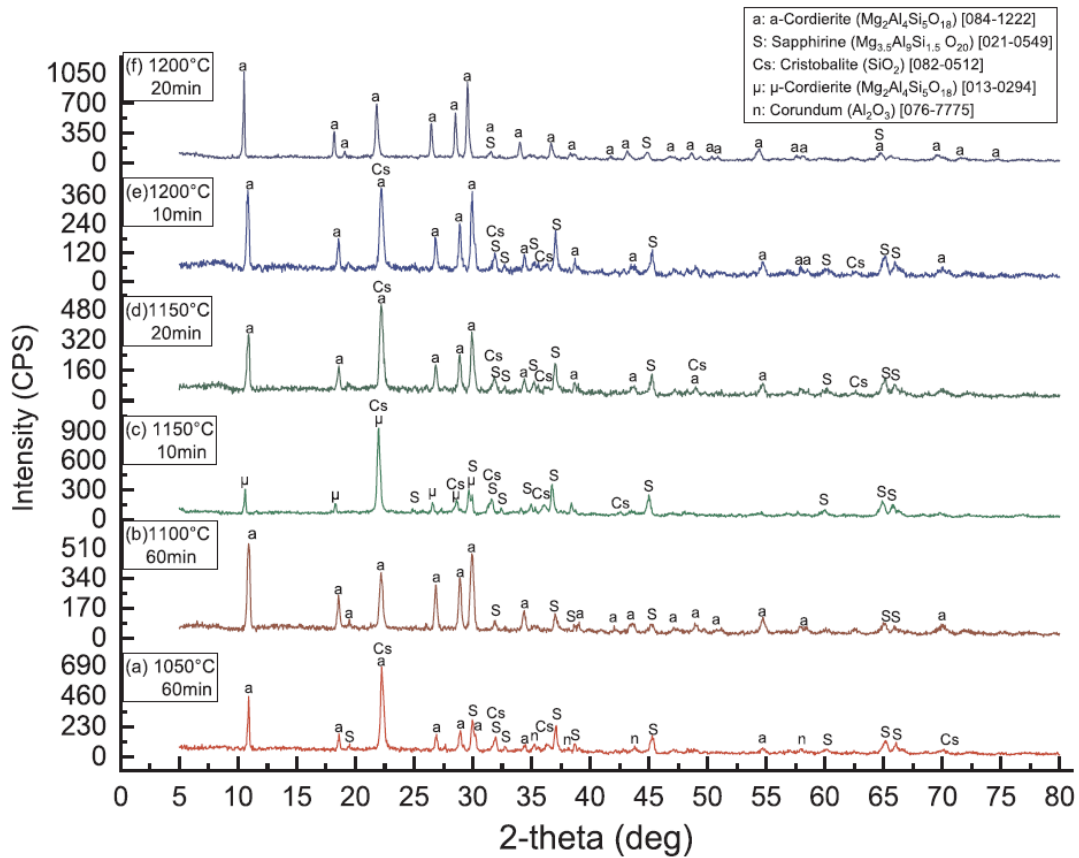


Figure 16. XRD spectra of samples sintered at different temperatures for different times.

Based on the XRD results, the optimum conditions for the synthesis of pure α -cordierite are a sintering temperature of 1150 °C and a sintering time of 30 minutes. This differs from the findings of Rundans et al. [75], who used alumina, silica, and magnesia with dolomite to synthesize cordierite. They conducted ball milling for 3 hours, followed by spark plasma sintering at 1150 °C for 2 minutes. In their study, cordierite was not formed, and the observed phases were enstatite, spinel, and clinoenstatite, with small fractions of anorthite and quartz. An insufficient sintering time of 2 minutes at 1150 °C may explain the absence of cordierite formation in their study. In contrast, the present study employed a lower sintering temperature and shorter sintering time than other studies that synthesized cordierite using higher temperatures and longer durations [54, 76].

Cordierite is known to exist in three forms: α -cordierite and β -cordierite, which are stable at high and low temperatures, respectively, and metastable μ -cordierite [77]. The XRD results confirmed that cordierite formation is a complex process influenced primarily by temperature and time. Notably, the results indicate the possibility of synthesizing dense α -cordierite directly from pure nano-oxide powders using spark plasma sintering at a relatively low temperature of 1150 °C, eliminating the need for sintering aids. This approach offers a solution for the challenges associated with the development of highly pure and dense cordierite ceramics [71, 76]. Previous studies have highlighted the difficulty, if not impossibility, of achieving dense cordierite materials without the use of sintering aids during the sintering process. This is mainly due to the narrow temperature range (25–30 °C) required for sintering below the melting temperature of cordierite [71]. In addition, raw oxide powders, particularly alumina, exhibit low reactivity [76]. However,

the sol-gel method often involves expensive raw materials and complex production processes, making it economically unfeasible and less attractive for cordierite synthesis. Furthermore, regardless of the chosen processing route, the use of impure raw materials can lead to the formation of undesired phases, such as cristobalite, increasing the sintering temperature of cordierite and reducing its purity [71]. Overall, the findings suggest that spark plasma sintering of pure nano-oxide powders at 1150 °C provides a promising approach for the efficient and cost-effective synthesis of dense α -cordierite ceramics, circumventing the challenges associated with traditional methods and improving the material's purity.

4.3.4 Effect of Sintering Temperature and Time on Densification

The density measurements are presented in Table 2. When examining specimens sintered for 30 minutes in the temperature range of 900-1200 °C, it was observed that the density increased with rising temperature. The highest density value of 2.85 g/cm³ was reached at 1000 °C, followed by a decrease to 2.58 g/cm³ at 1150 °C. Further increasing the temperature to 1200 °C did not affect the density. Considering that different theoretical density values ranging from 2.51 g/cm³ [78] to 2.66 g/cm³ [64, 79] have been reported for cordierite, an average value of 2.58 g/cm³ was adopted in this study. Thus, it can be concluded that the formation of dense monolithic α -cordierite was achieved at 1150 °C, corroborating the XRD and FE-SEM findings discussed above.

To investigate the influence of sintering time on cordierite formation, additional samples were sintered at 1150 °C and 1200 °C for 10 and 20 minutes, and at 1050 °C and 1100 °C for 60 minutes. At 1150 °C, the density decreased from 2.71 g/cm³ to 2.58 g/cm³ as the

sintering time increased from 10 to 30 minutes. A similar trend was observed at 1200 °C, with the density decreasing from 2.65 g/cm³ to 2.58 g/cm³. These results indicate that a sintering time of 10 or 20 minutes is insufficient to achieve the density value of 2.58 g/cm³, which is characteristic of pure α -cordierite. Furthermore, the density values of 2.72 g/cm³ and 2.60 g/cm³ obtained at 1050 °C and 1100 °C, respectively, suggest that the formation of cordierite was incomplete at these temperatures even with an extended sintering time of 60 minutes. The densities obtained in this study are in close agreement with those reported by other researchers [25, 55-58] who synthesized cordierite materials using various raw materials and methods. Reported densities include 2.33 g/cm³ [28], 2.4 g/cm³ [30], 2.52 g/cm³ and 2.58 g/cm³ [28], 2.53 g/cm³ [76], and 2.58 g/cm³ [29].

Table 4. Density of sintered samples.

Temp	(°C)	1200			1150			1100		1050		1000	950	900
Time	(min)	30	20	10	30	20	10	30	60	30	60	30	30	30
Density	(g/cm ³)	2.58	2.65	2.65	2.58	2.56	2.71	2.63	2.6	2.72	2.72	2.85	2.76	2.76

4.3.5 Mechanical properties

To ensure the accurate determination of hardness and fracture toughness, two methods were employed to measure the length of the indentation diagonals: an indenter camera and FE-SEM. The evaluation of the fracture toughness involves two approaches. The first approach utilizes the Evans and Charles equation [80], whereas the second approach employs the Anstis equation [81, 82]. It is important to

note that the former approach relies solely on hardness, whereas the latter incorporates hardness, indentation load, and modulus of elasticity.

To determine the load condition at which hardness becomes independent of the load, a range of loads from 0.981 N to 98.1 N was applied to the sample sintered at 1150 °C for 30 minutes, which exhibited complete densification and the formation of α -cordierite. As shown in Figure 17, the hardness initially exhibits load-dependent behavior until it reaches a seemingly constant plateau. Hardness is a measure of the resistance of a material to deformation and is defined as the ratio of the applied load to the projected indentation area. In the low-load region, the size of the impressions was related to the applied load, with smaller loads or harder materials resulting in smaller indentations [83]. Equation (3) suggests that smaller indentations associated with lower loads lead to higher hardness values. However, the dependence of hardness on the load in the low-load region continues to be a topic of discussion among researchers [84, 85].

In the present study, hardness decreased from 11.7 ± 0.231 GPa to 8.7 ± 0.128 GPa as the load increased from 0.981 N to 9.81 N, and then remained nearly constant at around 8.4 GPa for loads ranging from 29.43 N to 98.1 N. The independence of hardness from the load in the high-load region is believed to be associated with the initiation of extensive cracking around and beneath the indentation [83]. Consequently, a threshold load of 29.43 N was selected to test the other samples. Table 4 presents the hardness (HV), fracture toughness (KIC), and critical strain energy release rate (GIC) values for samples consolidated at 1150 °C and 1200 °C for 30 minutes. The hardness values obtained using FE-SEM for samples sintered at 1150 °C and 1200 °C were 8.46 ± 0.188 GPa and 8.25 ± 0.158 GPa, respectively, which were slightly higher than the values of 8.43 ± 0.139 GPa

and 8.15 ± 0.429 GPa obtained using the indenter's camera. The values obtained from the FE-SEM measurements were considered more accurate because of the clear indentations observed under the microscope, enabling precise measurement of the diagonal lengths. Increasing the temperature from 1150 °C to 1200 °C resulted in a small decrease of 2.48% in hardness. Both samples achieved the same level of densification and consisted solely of α -cordierite in their microstructures. The decrease in hardness can be attributed to a 17.93% increase in grain size. The obtained hardness value of 8.46 ± 0.188 GPa for monolithic cordierite in this study is higher than the values reported by other researchers. For instance, researchers who prepared cordierite through furnace sintering of pure α -cordierite nanopowder at 1300 °C achieved a hardness of 6.7 GPa [86], while pulsed current activated heating of ball-milled MgO-SiO₂-Al₂O₃ mixture for 1 minute resulted in a hardness of 6.73 GPa [73]. Furthermore, conventional sintering at 1430 °C for 2 hours yielded a hardness of 7.5 GPa [76]. The obtained hardness value is also higher than the standard hardness value of 8.2 GPa [87]. It is important to note that, for the comparison of hardness results with the literature, the value of 8.46 ± 0.188 GPa measured using a load of 29.43 N, at which hardness became almost constant, was used instead of the maximum value of 11.7 ± 0.231 GPa obtained at a load of 0.981 N.

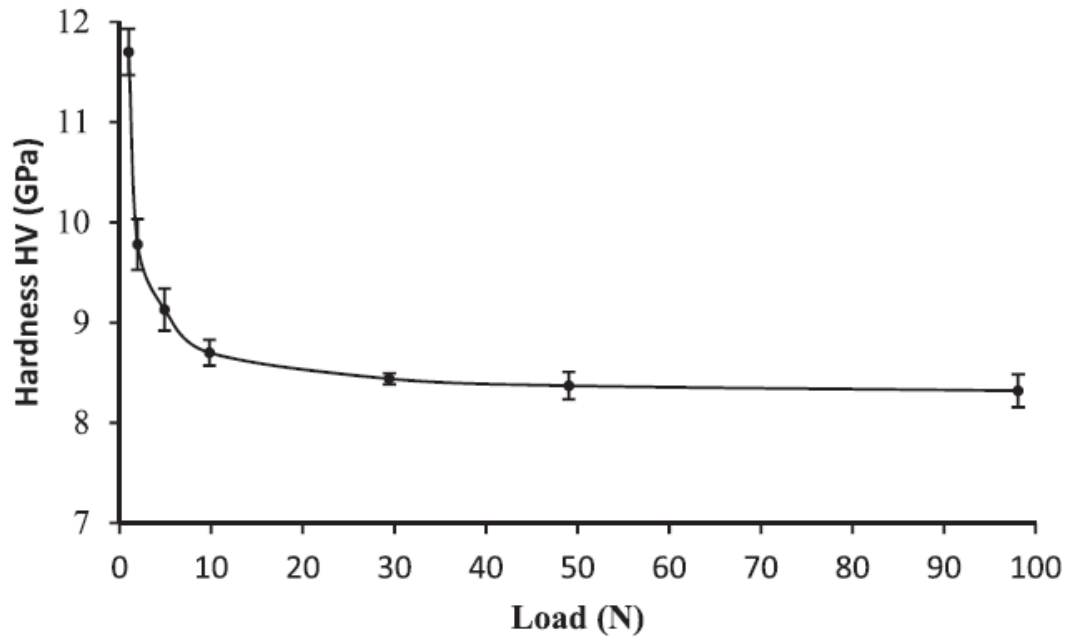


Figure 17. Influence of load on hardness of the sample sintered at 1150 °C for 30 min.

The fracture toughness (KIC) values for the sample sintered at 1150 °C ranged from 1.96 ± 0.2 to 2.7 ± 0.340 MPa m^{1/2}, while for the sample sintered at 1200 °C, the values varied from 1.96 ± 0.129 to 2.25 ± 0.345 MPa m^{1/2}. The hardness values calculated using the lengths of the indentation diagonals measured using FE-SEM were slightly higher than those obtained using the indenter camera. However, the opposite trend was observed for the KIC values calculated using equation (5), where the values obtained from the indenter camera were higher. Furthermore, the KIC values calculated using equation (6) were slightly lower than those calculated using equation (5).

The highest fracture toughness value obtained in this study for monolithic cordierite, 2.7 ± 0.340 MPa m^{1/2}, is relatively larger than the standard value of 2.3 MPa m^{1/2}. However, it is lower than the values of 3.5 and 2.9 MPa m^{1/2} reported in Ref. [73, 76], respectively. It

is worth noting that the fracture toughness reported by Ogiwara et al. was evaluated using the indentation fracture method, where they used a higher Young's modulus of 281 GPa for cordierite than the standard value of 139 GPa used in this study to calculate the fracture toughness using the Anstis equation.

The critical strain energy release rate (GIC) values for the sample sintered at 1150 °C ranged from 25.98 to 48.90 J/m², while for the sample sintered at 1200 °C, the values varied from 25.69 to 33.95 J/m². The relatively low GIC values indicate that pure α -cordierite is a brittle phase, which is consistent with the fracture toughness results. The GIC value of 25.98 J/m² (corresponding to KIC of 1.96 ± 0.2 MPa m^{1/2}) is comparable to the value of 22.7 J/m² reported for spark plasma sintered alumina, which has a fracture toughness of 2.38 MPa m^{1/2}.

An analysis of the results presented in Table 4 indicates that the mechanical properties of cordierite depend on the measurement and calculation methods employed. Therefore, the accurate measurement of hardness, appropriate selection of the calculation method, and use of suitable stiffness values are crucial for the accurate evaluation of fracture toughness and critical strain energy release rate.

Table 5. The hardness, fracture toughness, and critical strain energy release rate of samples sintered for 30 minutes.

Temperature(°C)	1150				1200			
HV(GPa)	Indenter's Camera		SEM		Indenter's Camera		SEM	
	8.43±0.139		8.46±0.188		8.15±0.429		8.25±0.158	
K _{IC} (MPa·m ^{1/2})	Equatio n 5	Equatio n 6	Equatio n 5	Equatio n 6	Equatio n 5	Equatio n 6	Equatio n 5	Equatio n 6
	2.7±0.3	2.45±0.	2.25±0.	1.96±0.	2.25±0.	2.01±0.	2.2±0.1	1.96±0.1
	4	306	238	2	345	361	58	29
G _{IC} (J/m ²)	48.90	40.26	33.95	25.98	33.95	27.15	32.46	25.69

This investigation demonstrates the possibility of producing high-purity cordierite materials at relatively low temperatures through spark plasma sintering of high-purity nanopowders in a single step without the need for sintering aids. Cordierite materials are widely used in industrial applications owing to their low cost, low thermal expansion, and high thermal-shock resistance.

4.4 EFFECT OF ADDITIVE MgO ON THE CORDIERITE FORMATION

The effect of the MgO additive on cordierite formation was studied using two different compositions of 4wt% designated as ASM4M and 8wt% designated as ASM8M. The analyses of the two compositions are as follows:

1.1.1 4.4.1 Characterization of Mixed MgO+(Al₂O₃, SiO₂, and MgO) Powders

Figure 18 (a) shows the representative FE-SEM image of the sonicated powder mixture for the ASM powder without any additive MgO and ASM4M with 4wt% additive MgO, and ASM8M with 8 wt. % additive MgO. The FESEM image reveals a homogeneous mixture with minimal agglomerates, indicating a successful and uniform distribution of the MgO additive in the ASM4M and ASM8M samples. This uniformity is crucial as it can significantly influence the material's properties and performance. The EDS analysis was performed to confirm the presence of the elements in the mixture. The results of the EDS analysis confirmed that additional MgO was added to the ASM4M and ASM8M powders. Specifically, the composition of MgO in the original ASM powder is 12.9%. However, with the addition of MgO, the compositions increase to 16.3% in ASM4M and 19.5% in ASM8M, respectively. These values closely correspond to the targeted MgO additions (4 wt. % and 8 wt.%) for ASM4M and ASM8M, respectively. The slight deviation might be due to the inherent measurement limitations of the EDS or minor variations during the mixing process.

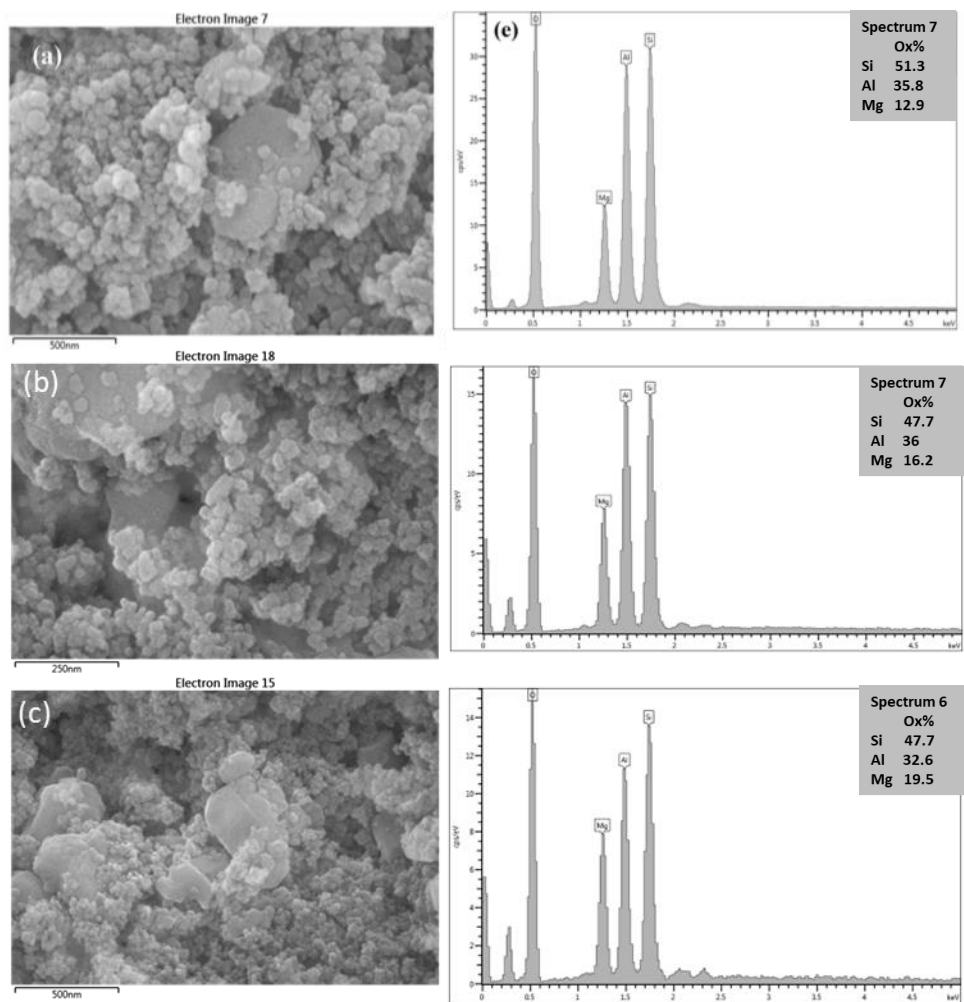


Figure 18. FE-SEM images and their corresponding EDS analysis of the sonicated powder mixture for (a) ASM (b) ASM4M and (c) ASM8M

4.4.2 Effect of Sintering Temperature on Cordierite Formation

The ASM4M and ASM8M sonicated powders were sintered via SPS at different temperatures ranging from 900 °C to 1150 °C for a duration of 30 minutes. The resulting samples were analyzed by X-ray diffraction (XRD) to confirm the developed phases. Figure 19 presents the XRD patterns of the ASM4M and ASM8M samples sintered at various temperatures (900 °C-1150 °C) for 30 minutes using SPS. These patterns reveal the evolution of the crystalline phases present in the samples as a function of the sintering temperature and MgO content. Analysis of the evolving peaks in the spectra allowed us to understand the phase formation sequence during sintering.

At 900 °C, the dominant peaks in ASM4M correspond to α -alumina (corundum) and cristobalite (SiO_2). This suggests that the starting materials had not yet fully reacted. Similar to ASM4M, α -alumina peaks were observed in ASM8M. However, additional peaks indicate the formation of forsterite (Mg_2SiO_4) owing to the reaction between MgO and SiO_2 , facilitated by the higher MgO content in ASM8M.

At 950 °C sintering temperature, the cristobalite (SiO_2) phase disappeared in the ASM4M samples, and Magnesium aluminum silicate ($\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$) appeared due to a possible reaction between the silica and magnesia at a higher temperature [88]. In the ASM8M samples, the forsterite (Mg_2SiO_4) completely disappeared and transformed into enstatite (MgSiO_3) at 950 °C [88]. The transformation into enstatite occurred later in the ASM8M samples compared to the ASM4M samples where enstatite was present at lower temperatures of 900 °C.

At 1000 °C, both samples exhibited significant shifts. Peaks corresponding to forsterite, enstatite, α -alumina, and other secondary phases diminish, while prominent cordierite

($\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$) peaks emerge. This indicated the successful formation of the desired cordierite phase with minimal unwanted secondary phases such as sapphirine ($\text{Mg}_{3.5}\text{Al}_9\text{Si}_{1.5}\text{O}_{20}$). As the temperature increased further, the sapphirine peaks diminished, leading to a nearly pure cordierite phase [89, 90]. It should be noted that for the ASM8M samples, there was complete melting of the sample at 1150 °C; hence, no analysis could be done for the samples beyond 1100 °C. This melting behavior is consistent with the theory that the first visible sign of melting does not necessarily occur at the eutectic temperature and is not observed until approximately 10-20% of the sample has melted. These findings highlight the complex phase transformations that occur during the sintering process and the significant roles played by composition and temperature in these transformations [91, 92]. The formation and disappearance of various phases such as forsterite, enstatite, α -alumina, cordierite, and sapphirine at different temperatures provide valuable insights into the reactivity and stability of these materials under high-temperature conditions [89, 93]. The XRD results highlighted the influence of the MgO content and sintering temperature on the phase evolution. The presence of additional MgO in ASM8M promoted the formation of forsterite at lower temperatures but appeared to delay the transformation to the enstatite phase compared to ASM4M. At higher temperatures (1000 °C and above), both samples exhibited successful cordierite formation. However, the complete melting of ASM8M at 1150 °C suggests potential limitations associated with the higher MgO content. These findings emphasize the importance of optimizing both the MgO content and the sintering temperature to achieve the desired cordierite phase formation without encountering unwanted melting phenomena.

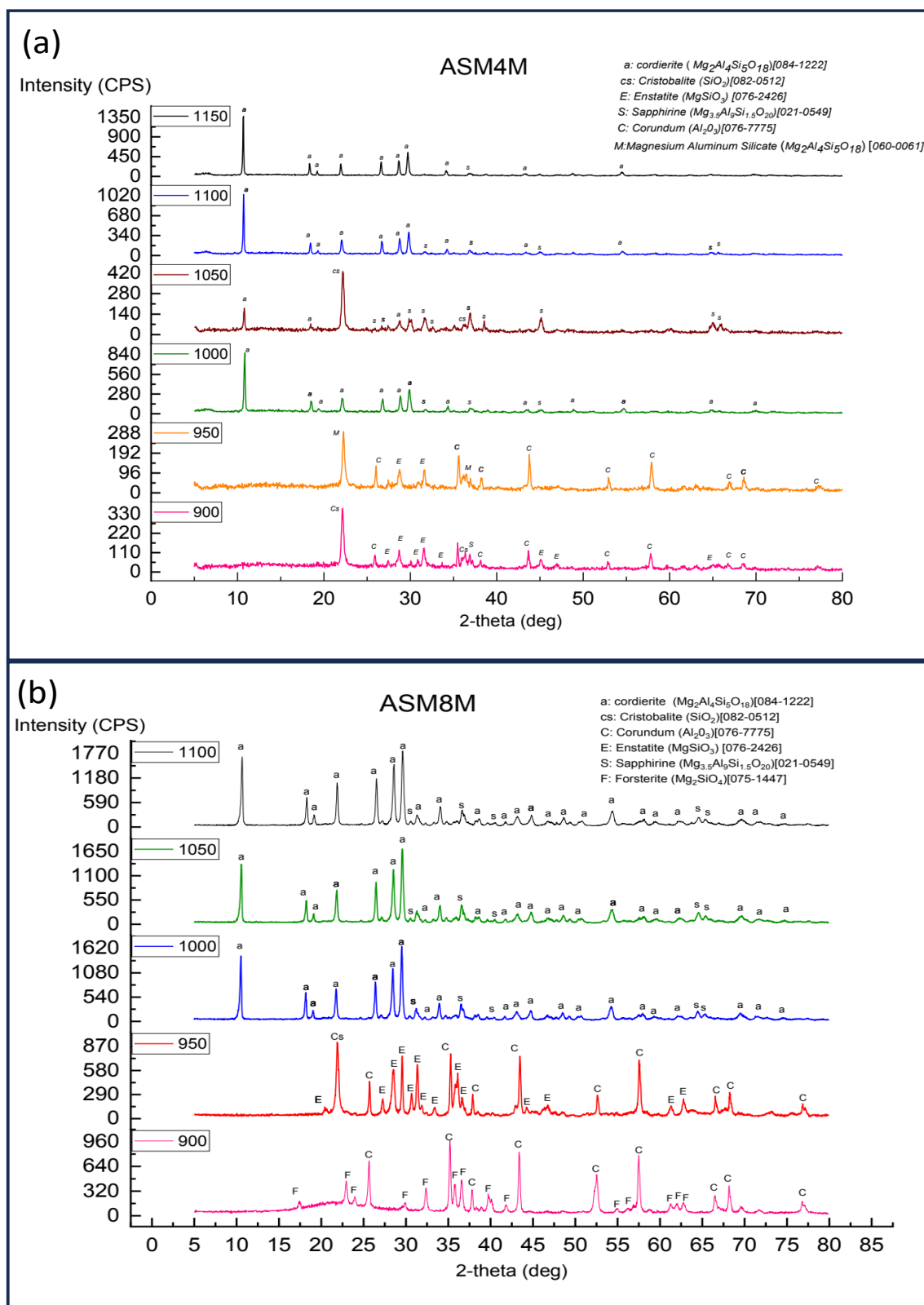


Figure 19. XRD Spectrum of samples sintered at different temperatures for (a) ASM4M and (b) ASM8M.

The density measurements depicted in Figure 20 offer crucial insights into the sintering behavior and the resulting material properties of the ASM4M and ASM8M samples across different temperature regimes. Significantly, the ASM8M samples experience complete melting at a temperature of 1150 °C, which highlights the crucial significance of precise temperature regulation during the sintering process to prevent unfavorable consequences such as sample melting and modified material properties. Analysis of the density data provided in the accompanying table revealed intriguing trends regarding the impact of MgO content on the sintering behavior of the two materials. At lower sintering temperatures, such as 900 °C, ASM4M exhibited a relatively high density of 2.82 g/cm³, indicating a significant degree of densification during the sintering process. However, as the temperature increases, the density of ASM4M gradually decreases, suggesting potential densification issues or structural changes at higher temperatures. In contrast, the density variations observed in the ASM8M samples at different sintering temperatures were more erratic and less predictable. Starting at a density of 2.67 g/cm³ at 900 °C, ASM8M demonstrates a substantial increase in density to 2.97 g/cm³ at 950 °C before experiencing a subsequent decrease at 1000 °C. This erratic behavior suggests a more complex interplay between the MgO content and the sintering temperature, leading to unpredictable densification outcomes. The observed differences in the density variations between ASM4M and ASM8M highlight the distinct sintering behaviors induced by varying the MgO content within the cordierite-based materials. Whereas ASM4M demonstrated a more consistent densification trend, ASM8M's density fluctuations underscore the intricate nature of the sintering processes influenced by the MgO content and temperature dynamics. Density measurements provided valuable information about the effectiveness of the sintering process and the influence of the MgO content. Understanding the interplay

between the MgO content, sintering temperature, phase evolution, and microstructure development is crucial for optimizing the sintering process to achieve cordierite ceramics with high density and desired properties. The observed differences in density behavior between ASM4M and ASM8M can be attributed to several factors: Phase evolution: As seen in the XRD analysis shown in Figure 19, the presence and transformation of various phases (α -alumina, forsterite, enstatite) during sintering can influence packing efficiency and density. The higher MgO content in ASM8M may lead to a more complex reaction pathway, affecting the densification behavior. Microstructure development: Further analysis using Scanning Electron Microscopy (SEM) revealed microstructural differences between the samples. The grain size, porosity distribution, and presence of secondary phases can influence the density. Sintering mechanisms: Investigating the dominant sintering mechanisms, such as diffusion and grain boundary movementv at different temperatures for both compositions can provide further insights into the observed density variations. Moreover, conducting mechanical tests, such as hardness and fracture toughness assessments, on sintered samples can complement density measurements, offering comprehensive insights into the structural integrity and mechanical performance of ASM4M and ASM8M materials at different sintering temperatures. This holistic approach to characterization and analysis will facilitate the development of optimized sintering protocols for the production of cordierite-based ceramics with tailored properties suitable for various applications.

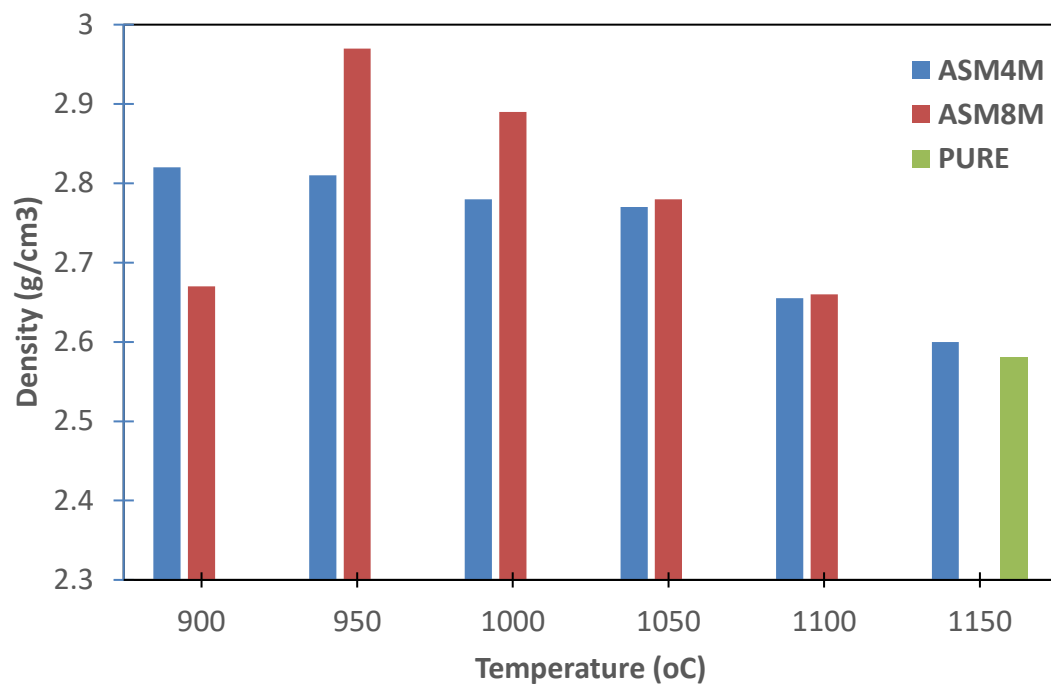


Figure 20. Density measurement of ASM4M and ASSM8M samples at different sintering temperatures.

4.4.3 Effect on Sintering Temperature on Mechanical Properties

The hardness values depicted in Figure 21 provide valuable insights into the mechanical properties of ASM4M and ASM8M sintered at different temperatures. Hardness, a fundamental mechanical property, quantifies the resistance of a material to indentation, thereby reflecting its ability to withstand external forces and maintain structural integrity. The analysis of the hardness data for ASM4M revealed intriguing trends across a range of sintering temperatures. Initially, at 900 °C, ASM4M exhibited a hardness of 8.03 GPa, indicating a moderate resistance to indentation. As the sintering temperature increases to 950 °C, the hardness substantially improves to 9.11 GPa, suggesting enhanced material densification and structural integrity. However, at 1000 °C, the hardness slightly decreases to 8.77 GPa before experiencing a subsequent increase to 9.13 GPa at 1050 °C. This fluctuation in hardness may be attributed to complex phase transformations and microstructural changes occurring within the material matrix. Despite minor fluctuations, the overall hardness remains relatively stable across the temperature range, indicating consistent mechanical properties [94–96].

In contrast, ASM8M demonstrated more pronounced variations in hardness with changing sintering temperatures. Beginning at a relatively low hardness of 1.84 GPa at 900 °C, ASM8M undergoes a substantial increase in hardness to 8.75 GPa at 950 °C, indicating significant improvement in material hardness and resistance to indentation. At this low temperature, the material may be poorly sintered with high porosity, leading to low hardness. Furthermore, XRD analysis suggested the presence of forsterite at 900 °C for ASM8M. This phase may have been relatively soft, contributing to its low initial hardness. However, at 1000 °C, the hardness decreases to 7.87 GPa, possibly due to phase transitions

or microstructural alterations induced by the elevated temperatures. Subsequently, at 1050 °C, the hardness dramatically increases to 9.27 GPa, suggesting further enhancement of material hardness and mechanical strength [97, 98]. This coincides with the transformation of forsterite to enstatite observed in the XRD analysis. Enstatite may be a harder phase, leading to a significant improvement in hardness. The absence of data for ASM8M at 1150 °C precludes a comprehensive assessment of its hardness behavior at higher temperatures. The observed variations in hardness underscore the intricate relationship between the sintering temperature, microstructural evolution, and mechanical properties of ASM4M and ASM8M [91–93].

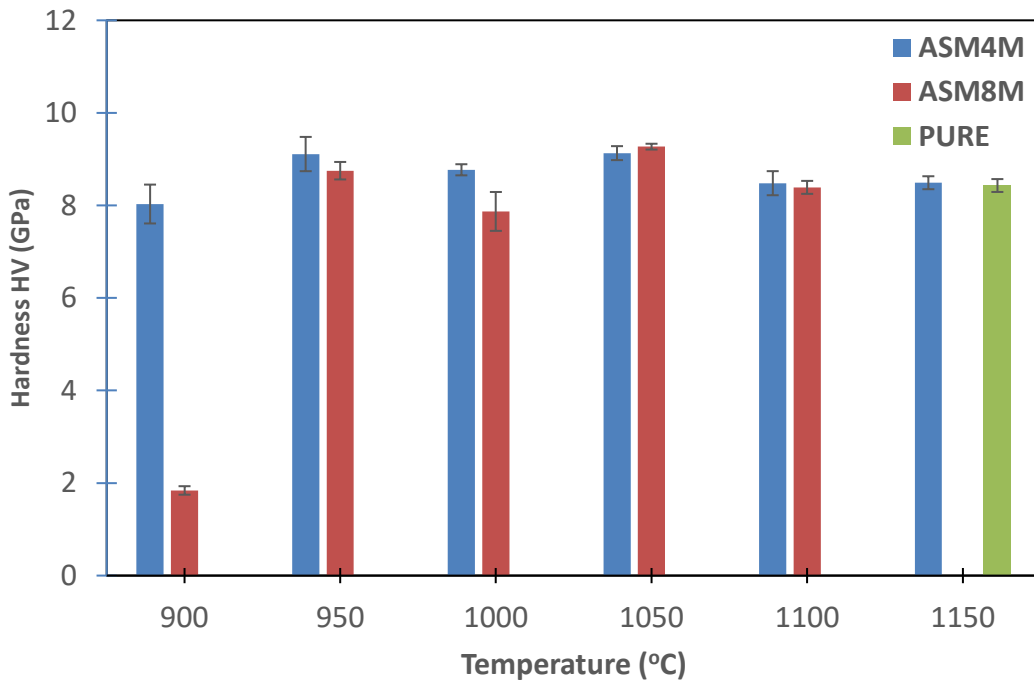


Figure 21. Hardness Value for ASM4M and ASM8M Samples at different sintering temperatures.

The fracture toughness (KIC) values depicted in Figure 22 offer critical insights into the resistances of ASM4M and ASM8M to crack propagation at different sintering

temperatures. Fracture toughness is a fundamental mechanical property that quantifies the ability of a material to resist crack initiation and propagation, making it essential for structural applications where reliability and durability are paramount. Analysis of the fracture toughness data for ASM4M revealed notable variations across the sintering temperature range. At 900 °C, ASM4M exhibited a fracture toughness value of 3.17 MPa.m^{1/2}, indicating moderate resistance to crack propagation. As the sintering temperature increases to 950 °C, the fracture toughness substantially improves to 4.5 MPa.m^{1/2}, suggesting enhanced crack resistance and improved structural integrity. However, at 1000 °C, the fracture toughness experiences a significant decrease to 2.31 MPa.m^{1/2}, indicating decreased resistance to crack propagation and potential degradation of material properties. This downward trend continues as the temperature increases further, with fracture toughness values declining to 2.6 MPa.m^{1/2} at 1050 °C, 2.3 MPa.m^{1/2} at 1100 °C, and 1.72 MPa.m^{1/2} at 1150 °C. The observed variations in fracture toughness underscore the complex interplay between the sintering temperature, microstructural evolution, and mechanical behavior in ASM4M materials.

Similarly, ASM8M's fracture toughness values exhibit fluctuations with the sintering temperature. Beginning at 1.757 MPa.m^{1/2} at 900 °C, ASM8M demonstrates improved fracture toughness with increasing temperature, reaching 2.89 MPa.m^{1/2} at 950 °C. However, at 1000 °C, the fracture toughness decreases to 2.45 MPa.m^{1/2}, indicating reduced crack resistance and potential structural vulnerabilities. The fracture toughness values exhibit a slight increase to 2.508 MPa.m^{1/2} at 1050 °C before data becomes unavailable for ASM8M at 1100 °C and 1150 °C due to melting. The observed trends highlight the sensitivity of the ASM8M fracture toughness to variations in sintering

temperature, emphasizing the importance of optimizing the processing parameters to achieve the desired mechanical properties. The contrasting KIC behavior between ASM4M and ASM8M can be attributed to several factors. Examining the microstructure using SEM at different sintering temperatures can provide insights into grain size, porosity distribution, and the presence of cracks or secondary phases. These features significantly affect fracture toughness. Phase composition: Similar to the hardness, the type and amount of phases present, as identified by XRD, can affect the overall KIC. The higher initial MgO content in ASM8M may lead to the formation of less tough phases at lower temperatures, thereby affecting the initial KIC. Fracture mechanisms: Understanding the dominant fracture mechanisms at different temperatures is crucial. Different mechanisms, such as intergranular or transgranular fractures, can be influenced by factors such as grain size and the presence of secondary phases.

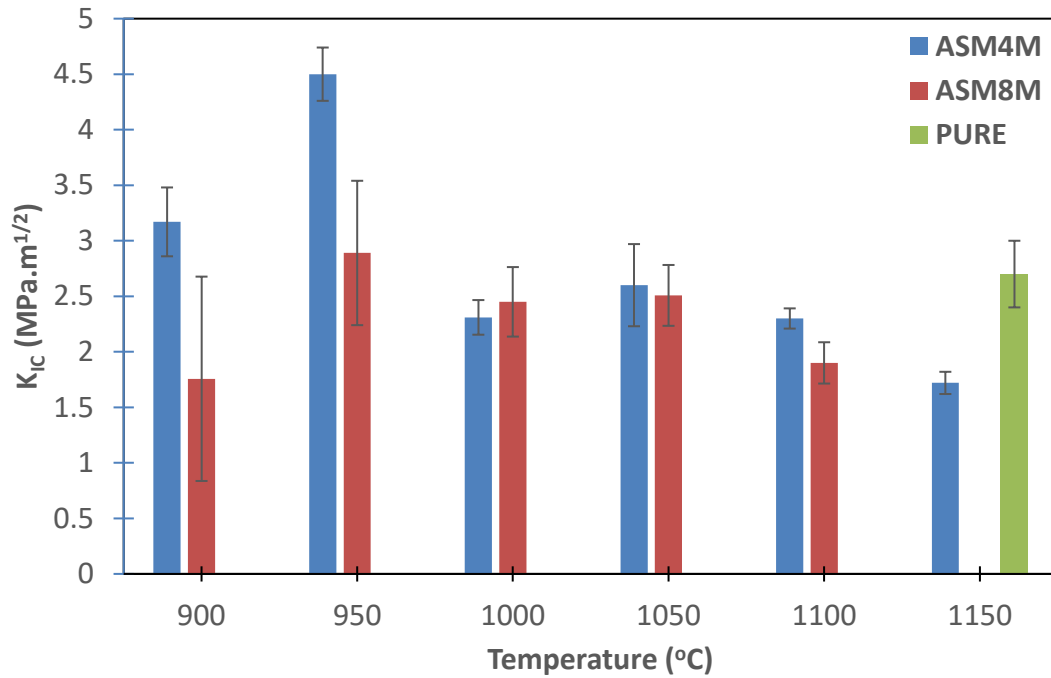


Figure 22. Fracture toughness Values ASM4M and ASM8M Samples at different sintering temperatures.

Figure 23a and b provide detailed insights into the fracture surfaces of ASM4M and ASM8M at 1050 °C, showcasing both high and low magnifications alongside their respective energy-dispersive X-ray spectroscopy (EDS) analyses. These images offer valuable information about the microstructural features and elemental compositions of the fracture surfaces, shedding light on the underlying mechanisms influencing the material behavior. Upon examination, the fracture surfaces of both ASM4M and ASM8M revealed the presence of multiple phases, corroborating the XRD analysis findings. This multifaceted composition suggests a complex interplay between chemical reactions and phase transformations during the sintering process. Of particular note is the higher concentration of the sapphirine phase observed in ASM4M than in ASM8M [99]. This distinctive feature can be attributed to the presence of MgO as an additive, which

accelerated the phase transformation kinetics and promoted the formation of cordierite [100]. The enhanced formation of the sapphirine phase in ASM4M underscores the pivotal role of MgO in catalyzing phase transitions and influencing the final microstructure of the material. MgO plays a crucial role in tailoring the properties of ASM4M by facilitating the nucleation and growth of specific crystalline phases, thereby imparting desirable characteristics for various applications [101, 102]. Furthermore, EDS analyses provided quantitative data on the elemental composition of the fracture surfaces, offering valuable insights into the distribution of key constituents within the materials. This information can be instrumental in elucidating the mechanisms governing the fracture behavior, phase evolution, and microstructural development of ASM4M and ASM8M. Overall, the comprehensive analysis of the fracture surfaces coupled with EDS investigations enhances our understanding of the complex microstructural features and phase transformations that occur in ASM4M and ASM8M during sintering. These findings contribute to the optimization of processing parameters and development of tailored materials with enhanced performance and functionality for diverse applications.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATION

5.1 CONCLUSIONS

Pure cordierite materials were successfully synthesized via spark plasma sintering using Al_2O_3 , SiO_2 , and MgO nano-powders. The following conclusions are drawn based on the different sections:

Synthesis of Fully Dense Spinel MgAl_2O_4 :

- A single-step spark plasma sintering process using Al_2O_3 and MgO nano-powders successfully achieved fully dense Spinel MgAl_2O_4 (MAS) at 1300 °C.
- Uniform particle distribution and elimination of sintering aids were confirmed.
- Microstructure analysis and mechanical property tests (hardness and fracture toughness) demonstrated successful synthesis and robust material properties.

Synthesis of Pure Cordierite Materials:

- Spark plasma sintering of Al_2O_3 , SiO_2 , and MgO nano-powders achieved pure α -cordierite at a relatively low temperature (1150 °C) in 30 minutes.
- This method eliminates the need for sintering aids and offers a promising solution to the challenges of conventional synthesis.
- Dense α -cordierite with stoichiometric composition was obtained.

Effect of Additive MgO on Cordierite Formation:

- The MgO additive affected the homogeneity, melting points, density variations, and mechanical properties (hardness and fracture toughness) of the resulting cordierite materials (ASM4M and ASM8M).
- MgO content affected cordierite formation temperatures and the presence of intermediate phases.
- ASM4M exhibited more stable mechanical properties across temperatures compared to ASM8M.
- This study highlights the importance of MgO content in tailoring the properties of cordierite for specific applications.

5.2 RECOMMENDATIONS

The present work led to the development of pure cordierite materials through spark plasma sintering techniques. The effects of the additional MgO additives on the microstructure and mechanical properties were also examined. Further analysis of the developed materials is recommended. This may include:

- The effects of varying the sintering duration on the microstructure and mechanical properties were explored to optimize the process.
- The performance of the synthesized Spinel MgAl_2O_4 was tested for potential applications such as high-temperature structural components or wear-resistant materials.

- The spark plasma sintering process parameters (pressure and dwell time) were optimized for different cordierite compositions to further improve the efficiency and tailor the properties.
- The influence of nanopowder characteristics (size and morphology) on the final cordierite microstructure and properties was investigated.
- We explored the possibility of using this method to synthesize other complex ceramic materials in addition to cordierite.
- A more in-depth study of the reaction mechanisms between MgO and other starting materials should be conducted to fully understand their impact on cordierite formation and phase evolution.
- Explore the effects of the MgO contents beyond 4% and 8% used in your study to identify a wider range of achievable cordierite properties.
- The long-term stability and performance of cordierite materials with varying MgO contents under different environmental conditions were investigated.

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PUBLICATIONS

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PROFFESIONAL EXPERIENCE

Siemens Energy

2023 to current

- **Metallographic Analysis:** Conducted detailed analyses and prepared test reports, ensuring accuracy and clarity.
- **Team Support:** Provided essential support to the coating staff, including troubleshooting, maintaining logs, and assisting with projects.
- **Inventory Management:** Managed laboratory inventory effectively, ensuring supplies were well-stocked and orders were placed and verified in a timely manner.
- **Equipment Maintenance:** Maintained and operated laboratory equipment, following operating instructions, performing preventive maintenance, and arranging for necessary repairs.
- **Documentation:** Kept detailed daily logs and records, contributing to the accurate documentation of laboratory activities.
- **Quality Control:** Actively participated in quality assurance processes, analyzing data and implementing corrective actions.
- **Collaboration and Development:** Assisted in project completion and team meetings, and stayed updated with industry trends through technical publications.

- **Reputation Enhancement:** Committed to enhancing the laboratory's reputation by accepting new challenges and identifying opportunities for improvement.

King Fahd University of Petroleum and Minerals (KFUPM)

2016 to 2023

Working in Material Science Lab:

- Supervised undergraduate, MS, and Ph.D. students as well as researchers in performing various experiments, including Metallography, Hardness Test, Tensile Test, Impact Test, Bending Test, Heat Treatment, X-Ray Diffraction (XRD), and Diffraction Scanning Calorimetry (DSC).
- Assisted students and researchers with metallography analysis, including sectioning, mounting, grinding, polishing, and etching for grain boundary relief.
- Conducted training sessions for instructors on experiment procedures.
- Managed over 20 lab sections per semester, supervising more than 400 students weekly and preparing test specimens for them.

Br. C.A.T International Company Limited 2015 to 2016

Pipeline Project under ARAMCO Supervision

- Successfully worked under the supervision of ARAMCO on a significant pipeline project for a duration of one year.
- Collaborated with a dedicated team, contributing to the successful implementation and execution of the project.

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