

N.B. MUSTAPA¹, R. AHMAD^{1,2*}, M.M. AL BAKRI ABDULLAH^{2,3},
W.M. WAN IBRAHIM^{1,2}, M.A.O. MYDIN⁴, A.V. SANDU⁵

THE EFFECTS OF THERMAL EVOLUTION DURING SINTERING MECHANISM OF GEOPOLYMER-BASED CERAMICS

Ceramics have gained extensive utilisation across diverse industrial domains owing to their exceptional mechanical, thermal, and chemical characteristics. Nevertheless, the conventional manufacturing process of ceramics frequently entails substantial energy expenditure and notable carbon emissions. Geopolymers, as a contrasting option, present an eco-friendly prospect by harnessing industrial by-products and employing alkali activation mechanisms to engender a robust binding agent. Geopolymer-based ceramics, stemming from these precursors, have exhibited great potential concerning sustainability and mechanical performance. This article presents a comprehensive review of the thermal effects during sintering mechanism of geopolymer-based ceramics. Besides, the study offers valuable insights into the intricacies of the sintering process and the ensuing microstructural evolution of geopolymer-based nepheline ceramics, thereby advancing the comprehension of geopolymer-based ceramics. The findings also provide guidance for the rational design and fabrication of sustainable ceramics materials, fostering enhancements in their mechanical properties.

Keywords: Geopolymer; Geopolymer-based Ceramics; Ceramics; Sintering Mechanism

1. Introduction

Ceramics manufacturing holds significant importance in human civilization, exerting substantial influence across various sectors such as construction, electronics, automotive, and healthcare [1,2]. However, the conventional methods, specifically hot pressing and hot isostatic pressing required high sintering temperature up to 1800°C [3]. Besides the high in production cost, irregular grain growth, and furnace contamination, this conventional method also less environmentally friendly. Therefore, a new approach involves utilizing geopolymer as the precursor in ceramics manufacturing as it exhibits better mechanical properties, superior acid resistance, and its ability to accelerate strength development [4-8].

The term “geopolymer” were coined by Davidovits in 1970s, referred as an inorganic, typically ceramic material that forms long-range, covalently bonded, amorphous 3D networks, formed through a reaction between an aluminosilicate and alkali solution [9]. Fig. 1 shows the model for geopolymerization. The geopolymer network consist of SiO₄ and AlO₄ tetrahedra linked

by oxygen atoms [10]. Owing to two predominant advantages – minimal energy consumption and the absence of CO₂ emissions in the preparatory phase – geopolymers have garnered significant attention in contemporary scientific research [11]. The distinctive chemical composition and structural characteristics inherent in geopolymers confer numerous advantages when compared to conventional ceramics. These include lowered sintering temperature requirements, improved mechanical properties, increased resistance to chemical degradation, and a reduced environmental footprint.

Geopolymer-based ceramics are an innovative approach in producing ceramics with enhanced mechanical strength and low porosity by applying heat to the geopolymer green body. These ceramics benefit from lower sintering temperatures, yielding benefits to both environmental conservation and technological advancements [12]. Notably, geopolymer-based ceramics exhibit an elevated level of sustainability in contrast to conventional ceramics, given their utilization of waste materials as primary sources, release less carbon dioxide, and superior resistance to chemical and fire-related factors [13].

¹ UNIVERSITI MALAYSIA PERLIS (UNIMAP), FACULTY OF MECHANICAL ENGINEERING & TECHNOLOGY, 02600, ARAU, PERLIS, MALAYSIA

² UNIVERSITI MALAYSIA PERLIS (UNIMAP), CENTER OF EXCELLENCE GEOPOLYMER AND GREEN TECHNOLOGY (CEGEOGTECH), 02600, ARAU, PERLIS, MALAYSIA

³ UNIVERSITI MALAYSIA PERLIS (UNIMAP), FACULTY OF CHEMICAL ENGINEERING & TECHNOLOGY, 02600, ARAU, PERLIS, MALAYSIA

⁴ UNIVERSITI SAINS MALAYSIA, SCHOOL OF HOUSING, BUILDING AND PLANNING, GELUGOR 11800, PENANG, MALAYSIA

⁵ “GHEORGHE ASACHI” TECHNICAL UNIVERSITY OF IASI, FACULTY OF MATERIALS SCIENCE AND ENGINEERING, DEPARTMENT OF TECHNOLOGIES AND EQUIPMENT FOR MATERIALS PROCESSING, 700050 IASI, ROMANIA

* Corresponding author: romisuhani@unimapedu.my



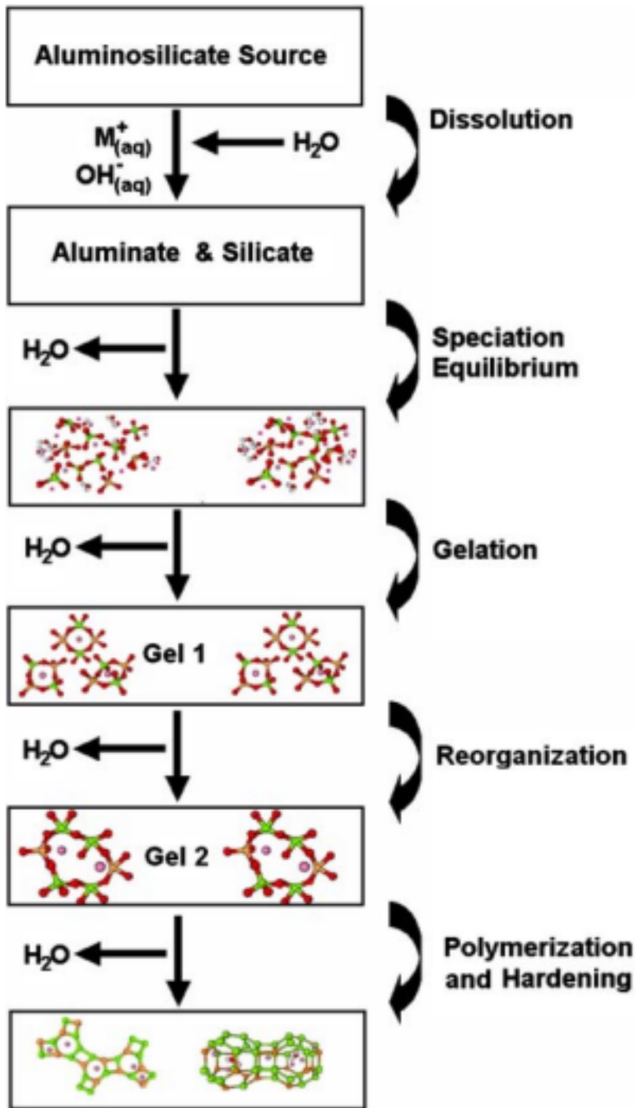


Fig. 1. Geopolymerization conceptual model

The sintering process, entailing the application of high temperatures to compacted ceramic material to facilitate densification and particle bonding, constitutes a crucial aspect of ceramic production. The sintering mechanism employed in this process plays a pivotal role in determining the resultant microstructure, density, porosity, and mechanical properties of the ceramic material. Therefore, this paper aims to provide a review that focusing on the effects of thermal evolution on the geopolymer-based ceramics during sintering mechanism.

2. Processing of Geopolymer for Ceramics Applications

Geopolymers, classified as inorganic materials and also recognized as alkali-activated materials (AAMs), have been explored as alternative options to Ordinary Portland Cement (OPC). This is mainly because of their low carbon dioxide emissions and performance advantages [14]. Raw materials used such as kaolin, slag, fly ash, and volcanic ashes were activated in an alkaline activator, under highly alkaline conditions, lead to polymerization process. During this process, reactive aluminosilicates rapidly dissolved, and free [SiO₄]⁻ and [AlO₄]⁻ tetrahedral units are released in solution. These units then linked to polymeric precursors by sharing oxygen atoms, thus forming polymeric Si-O-Al-O bonds [15]. Geopolymers have received considerable attention due to their cost-effectiveness, excellent properties, and eco-friendliness [16]. From the concept of geopolymer synthesis, geopolymer-based ceramics have become a notable alternative in ceramic manufacturing due to their ability to transform into ceramics when exposed to high temperature during sintering process.

Sintering is a process which involves the consolidating materials through the application of heat and pressure without completely melting. During sintering, atomic migration among particles of the raw materials lead to the fusion into a solid structure. Fig. 2 shows the process flow during sintering [17]. This process facilitates the transformation of permeable materials into well-structured forms, resulting in functional and cohesive solids. The properties of polycrystalline ceramics, including their density, grain size, and the presence of variations, are inherently determined by their microstructure. Sintering conditions play a pivotal role in enhancing these ceramic properties. It is noteworthy that the transformation of geopolymer from an amorphous to a crystalline state is highly dependent on the sintering temperature employed in the process.

In a study by Ramli et al. [18], the influence of sintering temperature on the pore structure was explored. As in Fig. 3, Ramli et al. had study on the microstructure of both unsintered and sintered samples. Based on the outcome from the unsintered and sintered geopolymer to elevated temperatures of 900°C and 1100°C, notable occurrences of sizable pores were detected. These interlinked pores directly affecting the mechanical performance of the geopolymer ceramics produced to make it suitable for ceramic application.

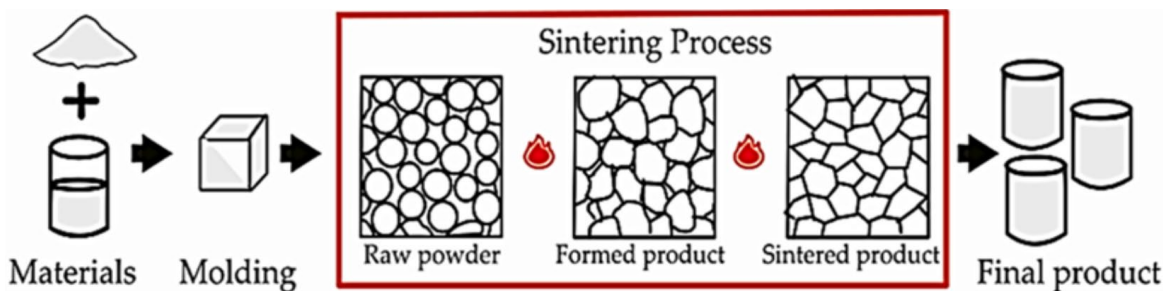


Fig. 2. Sintering process flow

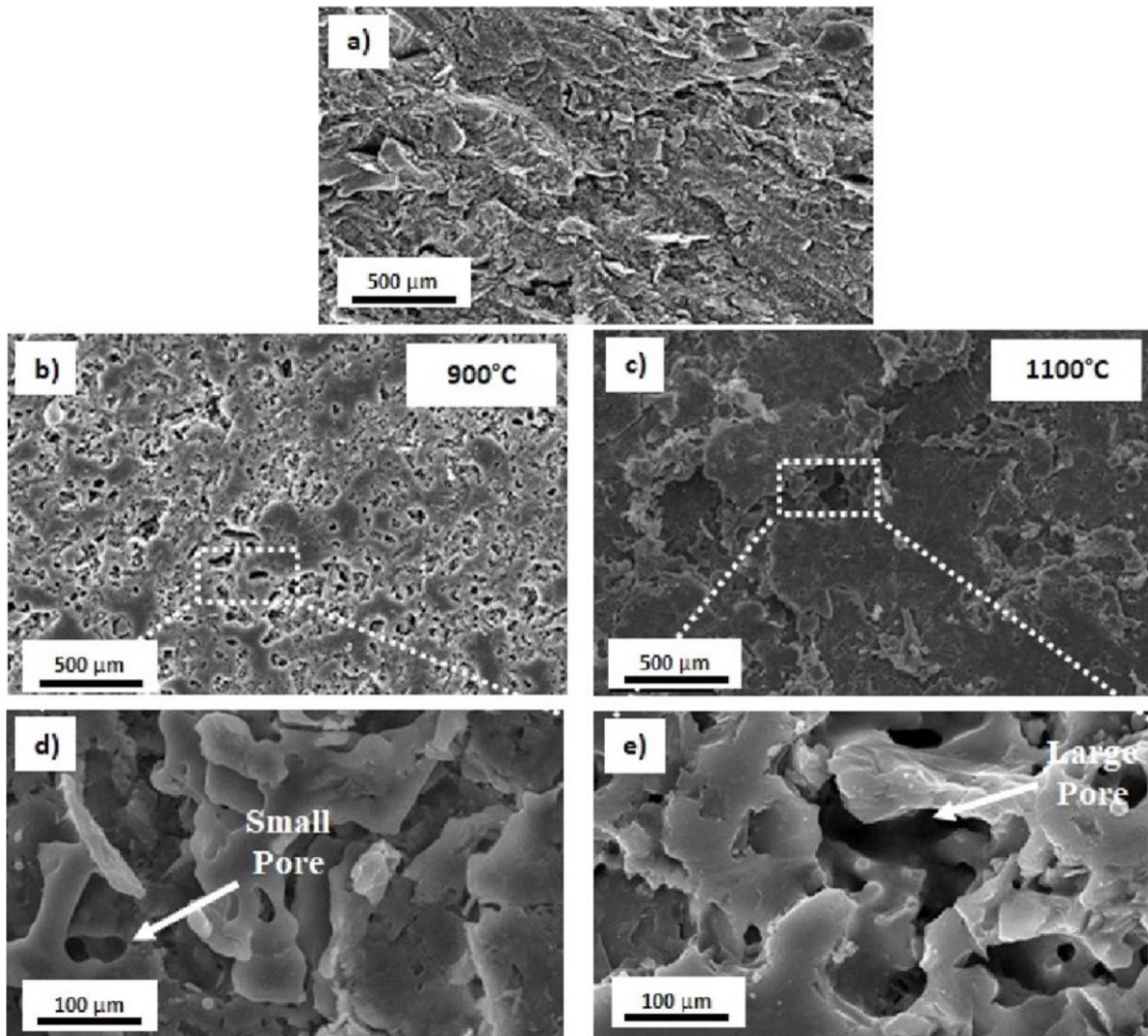


Fig. 3. SEM micrograph of (a) unsintered, (b,d) sintered at 900°C, and (c,e) sintered at 1100°C kaolin-based geopolymer

In another study by Polat et al. [19] geopolymer foams underwent exposure to diverse temperature levels, specifically 600, 700, 725, and 750°C, with the objective of evaluating the geopolymer's mechanical performance. When the temperature exceeded 700°C, the glass particles exhibited a semi-molten state, facilitating diffusion between them. The study outcomes elucidated that exposure to temperatures around 700°C initiated partial melting of the glass component within the sample. Moreover, surpassing this threshold temperature during the sintering process resulted in a reduction in density, attributed to the decomposition of thermonatrite, leading to the liberation of CO₂ gas.

Meanwhile, Kaze et al. [20] undergoes heat treatment to the 28-day-cured metakaolinite geopolymer (GPMK) series at 200, 400, 600, and 800°C to study on the thermal behavior and microstructural evolution upon sintering. Fig. 4 shows the difference in microstructure of the GPMK when exposed to heat. After heating, the micrograph of GPMK undergoes significant changes, with more porous and less dense when increasing the sintering temperatures ranging from 200 to 800°C. Notably, samples sintered at 600°C exhibit the emergence of micropores attribute to the liberation of water molecules bound structural

or chemically belonging to the geopolymer network. Upon reaching 800°C, the samples showed minor pores resulting from the destruction of the amorphous geopolymer binder network, consequently leading to poor adhesion between binding phase. These phenomena responsible to the drop of flexural strength as the sintering temperature increase.

It was expected that the pore structure of foam material would facilitate heat transport while mitigating thermo-mechanical degradation. The presence of porosity enabled rapid moisture elimination, thereby enhancing thermal insulating properties. This assertion was corroborated by Zhao & Sanjayan [21], wherein they emphasized that the internal pore structure facilitated the rapid dissipation of water vapor, leading to a reduction in pore pressure. The behavior of geopolymers under elevated temperatures was primarily influenced by the material's mass loss and thermal deformation caused by water vaporization. As temperature escalated, the mobility of structural water or water within pore voids accelerated, resulting in its evaporation from the material's surface [22]. An additional distinctive attribute of geopolymer pertains to its propensity for transformation into ceramics when subjected to elevated temperatures.

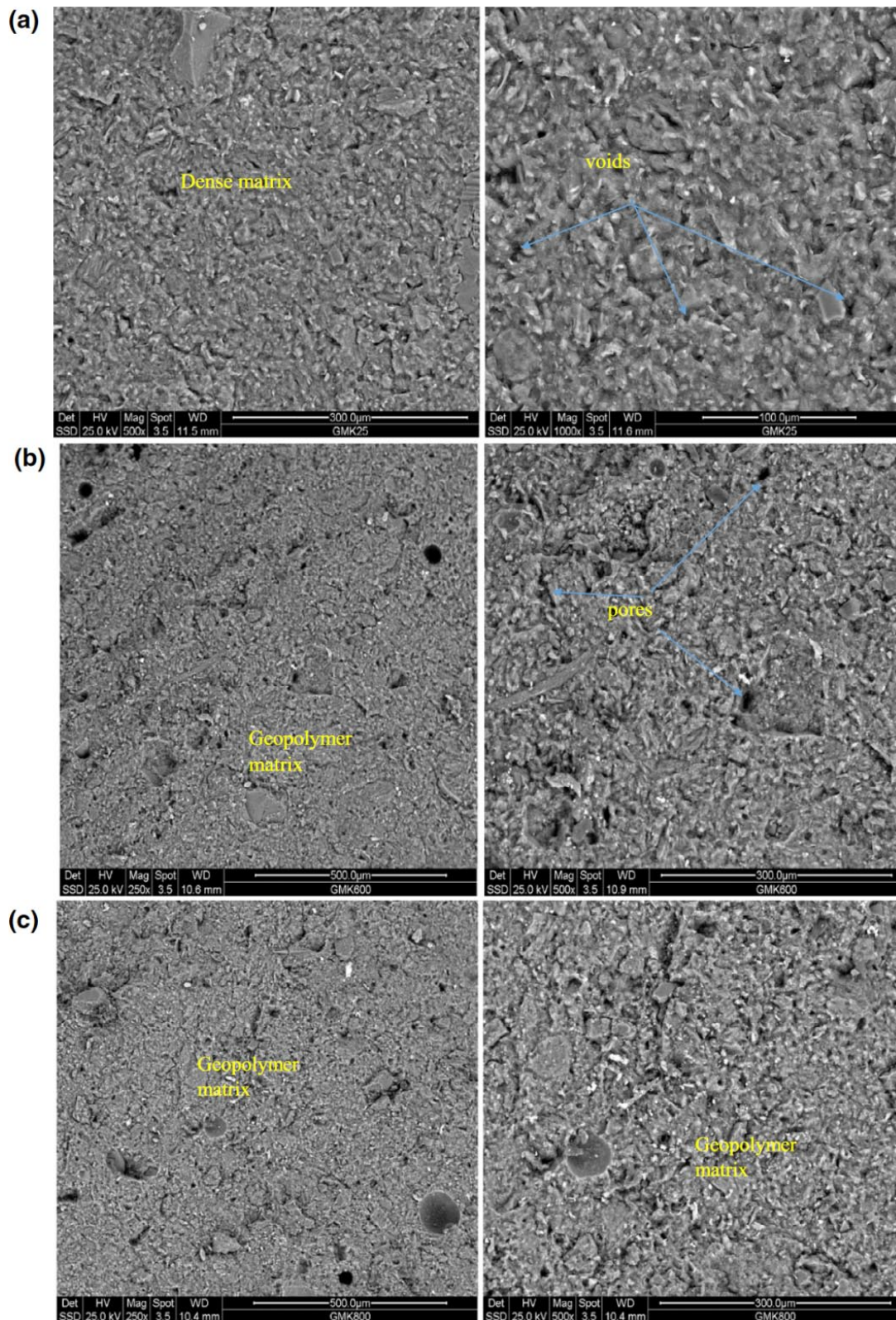


Fig. 4. SEM images of geopolymer GPMK25 (a), GPMK600 (b) and GPMK800 (c) specimens

3. Sintering mechanism of geopolymer-based Ceramics

Frueh et al. [23], conducted research focusing on the factors influencing the precision of master sintering curve (MSC) used for the comprehensive analysis of ceramic powder sintering

profiles. Their findings indicated that employing high heating rates within the range of 35-150°C/min resulted in a reduced $Q = 290$ kJ/mol. Meanwhile, as documented by Shao et al. [24], a notably higher Q value of up to 1064 kJ/mol was recorded for granulated and dry-pressed alumina powders. This elevation was ascribed to the effect of densification associated with slower

heating rates of 0.5 and 5°C/min. This phenomenon attributed to the study of the optimum heating conditions for surface and grain boundary diffusion in a material, where heating rate was identified as part of factor influencing densification. Gradual heating was observed to promote surface diffusion and particle coarsening. Consequently, materials exposed to slower heating rates spent more time at lower temperatures, leading to more pronounced particle coarsening before reaching the temperature range suitable for crystal densification.

Shen et al. [25] carried out an investigation to examine the intricate interplay between debonding and sintering profiles in the context of transparent ceramics. Within this study, three distinct sintering schemes were meticulously devised, each executed at an equivalent sintering temperature of 1800°C. Notably, these sintering profiles varied in terms of sintering rates (5 and 10°C/min) and holding times (5 and 10 hours). The results show the correlation between the heating rate and the resultant transmittance properties of the ceramics. When adopting a lower sintering heating rate, an appreciably higher degree of transmittance was observed. This phenomenon can be attributed to the gradual and uniform heating of the green bodies, effectively mitigating internal stresses. Additionally, lower heating rate helped the crystallization process inherent to geopolymer ceramics, ensuring a controlled and gradual phase transformation. This transformation was characterized by the diffusion of the amorphous phase, ultimately culminating in the formation of the ceramics' definitive crystalline structure. The deliberate employment of a slow heating regime enabled precise control over the crystal growth rate, ensuring the attainment of a desired grain size while concurrently eliminating existing porosity.

4. Effects of Thermal on the geopolymer-based Ceramics

In a study by Asadikiya et al. [26], the influence of sintering temperature, heating rate, and holding time of sintered spark plasma had been investigated from the result of the density and the hardness. It is found that the increment of sintering temperatures producing a denser ceramic in a fixed phase region. The same result was obtained by Mazaheri et al. [27] as when hydroxyapatite (HA) nanopowder compacts were exposed to the temperature of 950°C to 1100°C, a slight density enhancement of 5% is achieved. This may be due to the e pressure effect of insoluble gas in the closed pores followed by the collapse of pores.

Meanwhile, Zawrah et al. [28] conducted research focused on optimizing the characteristics of geopolymer derived from kaolin and examined the effects of gradual sintering at temperatures of 800, 1000, and 1200°C. an increased proportion of nepheline ceramics was observed in contrast to the predominant presence of quartz at 800°C. Elevating the sintering temperature resulted in a higher formation of nepheline, consequently enhancing the ceramics' strength.

The performance of ceramics is intricately governed by their chemical, microstructural, and crystallographic compositions.

The meticulous control of morphology and crystallographic arrangements becomes imperative to craft microstructures comprising grains with precise chemical compositions. In turn, the efficacy of processing principles and the selection of appropriate sintering techniques are contingent upon the underlying kinetic mechanisms. Sintering parameters such as heating rate, sintering temperature, and holding time wield a decisive influence on the ultimate density and mechanical attributes of the sintered specimen.

6. Conclusions

In conclusion, it is noted that the sintering mechanism helps in the performance of the geopolymer ceramics, makes them versatile product in engineering field. The densification of ceramic materials occurred upon raising the sintering temperature to 1100 °C in accordance with the optimal sintering profile. This was attributed to heightened grain diffusion and densification processes. Consequently, an increase in flexural strength was observed with the rising sintering temperature. Moreover, the elevation in sintering temperature led to the formation of new pores, serving as stress concentrators that aid in preventing cracks within the structure, thereby enhancing mechanical performance. A further study on the chemical and physical reaction of the ceramic body is needed for deeper understanding. With further development, this will give the ability to design geopolymers with specific applications in mind.

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