Green Synthesis of Calcium Magnesium Silicate (CMS-Akermanite) Using Natural Biowastes by Solid-State Sintering Route

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Abstract

The purpose of this study is to prepare dense bulk calcium magnesium silicate (CMS-akermanite, $Ca_2MgSi_2O_7$) for biomedical applications, using solid-state reaction of a mixture of biowaste materials i.e. cockleshell (as Ca source), dolomite (Mg source) and rice husk (Si source) with the stoichiometric ratio of Ca:Mg: Si 2:1:2 and subsequent heat treatment at 1150°C and 1250°C. The raw biowaste resource (initially calcined separately) were mixed in the planetary ball mill, then pellets were prepared and sintered. The X-ray diffraction (XRD), as well as Field emission electron microscopy (FESEM), was used to characterize the phase composition and surface morphology/microstructure of the sintered product. The XRD analyses confirmed CMS-akermanite as the main phase of the final product. In addition, FESEM showed a porous microstructure for sintered pellets at 1150°C. However, the reduction in porosity resulting from high shrinkage produced dense final product when the sintering temperature was raised to the temperature of 1250°C (however overfiring occurred at temperature above 1250°C). The optimum sintering temperature was 1250°C, showing densified microstructure with a relative density of 93.50%. The flexural strength and tensile strength were found to be 22.16 MPa and 8.21 MPa, respectively. The use of natural biowastes such as cockleshell and rice husk would be beneficial for biowaste management, while they could be considered as alternative source materials to synthesize valuable biomaterials.

Keywords: CMS-akermanite, Cockleshell, Rice Husk, Mechanical properties, Biowaste

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Introduction

Over the years, the focus on the management and reduction of biowaste materials has increased and become a priority. The reason is that the transformation of wastes into valuable products can lead to enhanced sustainable economic development and provide effective approaches for waste management [1]. Currently, there is demand for synthetic biomaterials for bone tissue engineering e.g. orthopedic implant and it is on the rise due to the growing aged population worldwide [2]. Therefore, the potential synthesis of biomaterials from natural biowastes can provide a better opportunity to meet future biomedical demands.

CMS-akermanite is ceramic that contains calcium (Ca), magnesium (Mg), and silicon (Si) ions that have shown excellent bioactivity both *in vitro* and *in vivo* [3]. It has also good mechanical properties and controllable degradability [4]. A previous study showed that the fracture toughness of CMS-akermanite was 1.83 $MPa.m^{1/2}$, which suggested better mechanical properties compared to hydroxyapatite (HA) [5].

Many natural bioresource materials can be investigated. Cockles are an important source of protein in the food industry as produced in canned food or fresh market, but it also produces an abundance of cockleshells as waste [6]. It was reported that the cockleshell contains 97.68% $CaCO_3$ [7]. For the past few decades, calcium-based biomaterials have been produced from biowaste (e.g. cockleshell) [8]. The industrial processing of rice, on the other hand, is one of the important food sources worldwide. It has almost 20 wt.% byproduct called rice husk (RH) that has very low nutritional value and requires a long time for decomposition [9]. It was found that RH contains 90% silica (SiO_2) [10]. Dolomite, in contrast, is comprised of ($CaMg(CO_3)_2$) and is naturally occurring mineral which can be found in sedimentary carbonate rocks. It can be used as a natural source of calcium (Ca^{2+}) and magnesium (Mg^{2+}) due to their low cost [11].

The concept of recycling biowastes has been used to produce calcium silicate ceramics such as diopside ($CaMgSi_2O_6$) [12] using eggshell biowaste which contains 94–96% calcium carbonate ($CaCO_3$). To our best of knowledge, there was no report on the synthesis of CMS-akermanite using a mixture of cockleshell, dolomite, and rice husk ash in the literature. The major objective of the present study is to synthesize and characterize CMS-akermanite ceramic by solid-state reaction route using cockleshell, dolomite, and rice husk as starting materials. The physicomechanical properties of CMS-akermanite produced by natural wastes were then evaluated.

Materials and methods

Extraction of calcium from cockleshell waste

To prepare $CaCO_3$ from the cockleshell, the shells were first collected from the restaurants and cafeteria. Then they were washed with water to remove dirt and impurities followed by boiling in water for 30 min to remove unwanted protein coatings and microorganisms from the shells. Then, the waste shells were dried in the oven at 100°C overnight. Finally, the dried shells were calcined in chamber furnace (Lenton, UK) at 900°C with a heating rate of 10°C/min for 4 h. The calcined solid were crushed using agate mortar and pestle.

Extraction of silica from rice husk

To prepare silica from rice husk, the husk was first collected from Kahang Organic Rice Eco Farm in Johor. Then, the husks were washed to remove dirt and impurities and dried in the oven at 100°C overnight. The dried rice husks were acid leached by boiling in 3% (v/v) hydrochloric acid (HCL) and 10% (v/v) sulphuric acid (H_2SO_4) for 2 h. The leached husks were then washed thoroughly by distilled water and further dried in the oven at 100°C overnight. Finally, the dried husks were calcined at 600°C to obtain the silica powder.

Synthesis of CMS-akermanite powder

High-energy planetary ball milling was used to synthesize CMS-akermanite powders using biowastes as the raw materials. The synthesis of the powder was designed based on the stoichiometric ratio of CMS-akermanite, Ca: Mg: Si as 2:1:2 (Table 1), according to the following reaction [5]:

$$2CaO + MgO + 2SiO_2 \rightarrow Ca_2MgSi_2O_7$$

Briefly, dolomite was brought by Batu Reput local region in Perlis. Then, the batch of calcined cockleshell, calcined rice husk ash, and dolomite was weighed, and the mixture was milled for 4 h in zirconia vials in a planetary ball mill (PM 400-Reutch), containing zirconia balls. The ball-to-powder weight ratio was 10:1. The vial speed was set at 200 rpm. The as-prepared milled powders were sieved. Then, the powders were pressed into pellets, using a stainless-steel die with a diameter of 13 mm by and a uniaxial hydraulic press (24T Laboratory hydraulic Press, Cooperation) at a pressure of 200 MPa for 1 min. To analyze the temperature to synthesize single-phase akermanite, three sintering temperatures were chosen [13]. Thus, the ceramic compact was then sintered in a chamber furnace (Lenton, UK) at three different sintering temperatures of 1150°C, 1200°C, and 1250°C with a dwelling time of 4 h and a heating rate of 5°C/min.

Table 1. The starting materials used to produce CMS-akermanite ceramic in the present study

Starting materials	Molar ratio	Weight (g)
Cockleshell	2	6
Dolomite	1	11
Rice Husk Ash	2	7

Characterization

Phase analysis of calcined powders and sintered pellets

The phase composition of powders calcined at 600°C and 900°C and pellets sintered at 1200°C and 1250°C was determined by X-ray diffraction (XRD, D8 Bruker Advance Diffractometer, England), with $CuK_{\alpha 1}$ radiation (λ=1.541 Å at 20 kV and 30 mA) in diffraction angles (2θ) between $10° \leq (2\theta) \leq 90°$. The crystallite size and lattice constants (a and c) were estimated by the modified Scherrer equation and Nelson–Riley function [14]. In addition, X-ray Fluorescence analysis (XRF, PW2404, Netherlands) was used to characterize the elemental chemical composition in the calcined cockleshell and rice husk ash powders.

Microstructural analysis of sintered pellet

The microstructure of sintered pellets at 1150°C, 1200°C and 1250°C was observed by field emission scanning electron microscopy with energy dispersive spectroscopy (FESEM, Zeiss SupraTM35VP, Germany). For this purpose, the pellets were coated with a thin layer of gold (Au) by sputtering (EMITECH K450X, England).

Density/porosity measurement

The ASTM B962-17 was used to calculate the relative density and apparent porosity of sintered samples at 1200°C and 1250°C [15]. The relative density of the samples was measured by applying the theoretical density of akermanite (2.944 $g.cm^{-3}$) [5].

Mechanical properties of sintered pellet

The diametral tensile strength (DTS) is an indirect method to measure the tensile strength of brittle materials and can be used to determine the bone tensile behavior [16]. For this purpose, the following formula was used to calculate the diametral tensile strength of the pellets sintered at 1200°C and 1250°C using universal experimental instrument (INSTRON 3367) with a speed rate loading of 0.5 mm/min:

$$\sigma_t = \frac{2P}{\pi dh} \tag{1}$$

Where σ is tensile strength (MPa), P is maximum at ample break (N), d is the sample diameter (mm), h is sample height (mm). Then, the correspondent between the measured tensile strength (σ_t) and its equivalent 3-point flexural strength is established based on the formula proposed by Harabi [17].

$$\sigma_f (MPa) = 2.7 \times \sigma_t (MPa) \tag{2}$$

Results and discussion

Phase analysis of calcined cockleshell and rice husk ash (RHA)

The XRD pattern of cockleshell after calcination at 900°C is shown in Fig.1. The narrow peaks with high intensity observed in the pattern of calcined cockleshell powders indicated that the material was in crystalline form after calcination. The raw cockleshell is rich in calcium and was characterized as the aragonite ($CaCO_3$), i.e. orthorhombic polymorphs of $CaCO_3$ [18]. The calcination at 900°C caused the $CaCO_3$ compound to decompose to CaO. The emergence of reactive CaO was accompanied by the presence of calcium hydroxide ($Ca(OH)_2$) (ICDD 44–1181) which was attributed to moisture absorbance by the powders from the environment [19]. The presence of a small amount of $CaCO_3$ in the calcined powder could be possibly due to insufficient calcination temperature of the cockleshell powders [20]. The average crystallite size of calcined cockleshell powders was 69.44 nm.

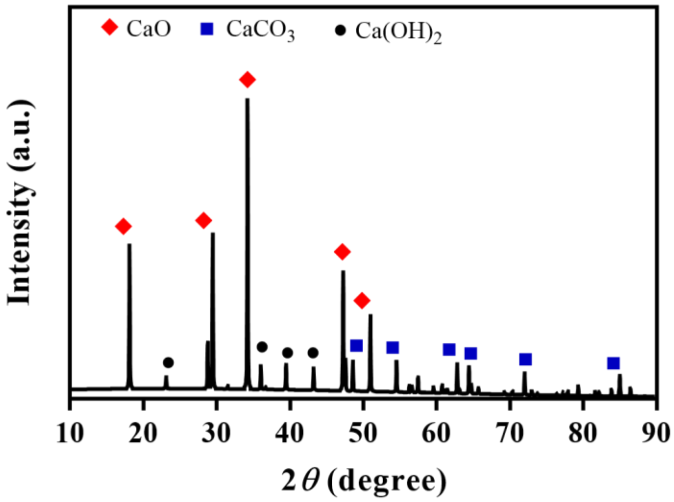

Fig.1. The XRD pattern of cockleshell after calcination.

The XRD pattern of rice husk ash (RHA) after calcination at 600°C is depicted in Fig.2. The presence of a broad diffraction peak (2θ=20–40°) suggest that the RHA obtained after calcination was amorphous in nature. The high intensity peak corresponding to (101) lattice planes at the peak position of 2θ=21.22° indicated the silica phase [21]. A similar result was found for the synthesis of bioactive glass [22] and bioactive ceramic [23] using rice husk ash as the Si source. The phase was cristobalite silica (ICDD 82–0512). The crystallite size of calcined rice husk powder was 2.55 nm.

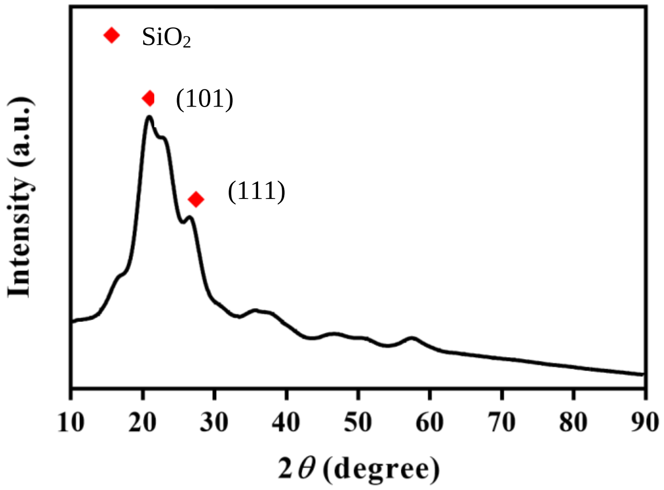

Fig.2. The XRD pattern of rice husk ash after calcination.

Elemental chemical composition of calcined cockleshell and rice husk ash (RHA)

The XRF was used to quantitatively estimate the chemical composition in the calcined cockleshell powders at 900°C (Table 2). It was demonstrated that the calcined cockleshell powders are generally comprised of CaO (98.93 wt.%). The large presence of CaO in the XRF result is attributed to the presence of $CaCO_3$ as the main constituent of cockleshell biowaste, which is in agreement with the XRD result. The calcined cockleshell contained a small quantity of trace elements of strontium oxide (SrO), sodium oxide (Na_2O), silica (SiO_2), and iron oxide (Fe_2O_3), which is insignificant in the CMS-akermanite composition.

The XRF results of calcined rice husk ash (RHA) after calcination at 600°C are also presented in Table 2. It shows that the calcined rice husk contains a high amount of silica SiO_2 (96.11 wt.%). The calcined rice husk also contains small quantity of other oxides including potassium oxide (K_2O), calcium oxide (CaO), phosphorus pentoxide (P_2O_5), sulfur trioxide (SO_3) and chromium oxide (Cr_2O_3).

Table 2. The chemical composition of calcined rice husk powders at 600°C.

Compound	Concentration at 600 °C (wt.%)	Concentration at 900 °C (wt.%)
SiO_2	96.11	0.14
K_2O	1.42	–
CaO	0.66	98.93
P_2O_5	0.65	–
Cr_2O_3	0.28	–
SO_3	0.28	–
SrO	–	0.43
Na_2O	–	0.14
Fe_2O_3	–	0.17

Phase analysis of sintered CMS-akermanite pellet

The XRD patterns of CMS-akermanite pellets produced by using biowastes resources of rice husk and cockleshell and sintered at 1200°C and 1250°C are depicted in Fig.3. It was seen that a single-phase crystalline CMS-akermanite was successfully formed using natural biowaste. In this study, there were no secondary phases detected, although natural bioresources being used. However, the presence of some phase impurities such as merwinite was observed at a lower sintering temperature below 1200°C [13]. The major characteristic peaks are related to CMS-akermanite, thus suggesting the use of these calcined biowaste materials is feasible. The highest intensity peak corresponding to (121) lattice planes at the peak position of $2\theta=31.85°$ confirmed the CMS-akermanite phase (ICDD 035–0592) [5,13]. The crystallite size and lattice volume of sintered CMS-akermanite at 1250°C were found to be higher than that of 1200°C which indicates an increase in crystallinity (Table 3).

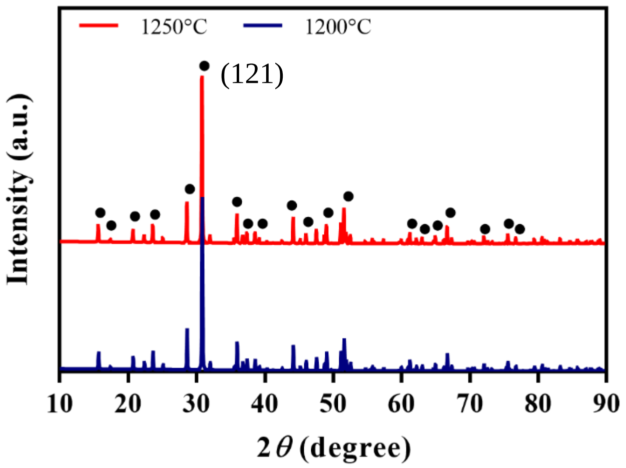

Fig.3. The XRD pattern of CMS-akermanite sintered at 1200°C and 1250°C.

Table 3. The crystallographic data obtained for sintered CMS-akermanite samples.

	Sintering temperature(°C)	
Sample	1200	1250
a(Å)	7.832	7.833
c(Å)	5.006	5.006
V($Å^3$)	307.069	307.147
Crystallite size (nm)	46.73	49.43

Microstructural analysis of sintered pellet

The microstructural evolution of the synthesized CMS-akermanite sample sintered at 1150°C, 1200°C and 1250°C is shown in Fig.4. A porous structure was observed for samples sintered at 1150°C when compared to samples sintered at 1200°C and 1250°C. However, by increasing the sintering temperature to 1200°C and beyond this temperature, densification with the elimination of porosity was observed. Nevertheless, although a highly densified CMS-akermanite sample was obtained, samples sintered at 1250°C, showed glassy phase due to melting of grain. In addition, the intergranular fracture (blue arrow) was mainly observed at 1200°C while it changed to transgranular (red arrow) fracture particularly at 1250°C, suggesting a typical failure of brittle ceramics. It is suggested that the strong particle bonding at high sintering temperature would lead to a change in fracture mode from intergranular to transgranular mode [24]. It is known that the microstructural changes could affect the mechanical properties of ceramics. The strength between the grain boundaries could be reinforced by this change in fracture mode of CMS-akermanite ceramic which enhances the mechanical properties of CMS-akermanite ceramic [25].

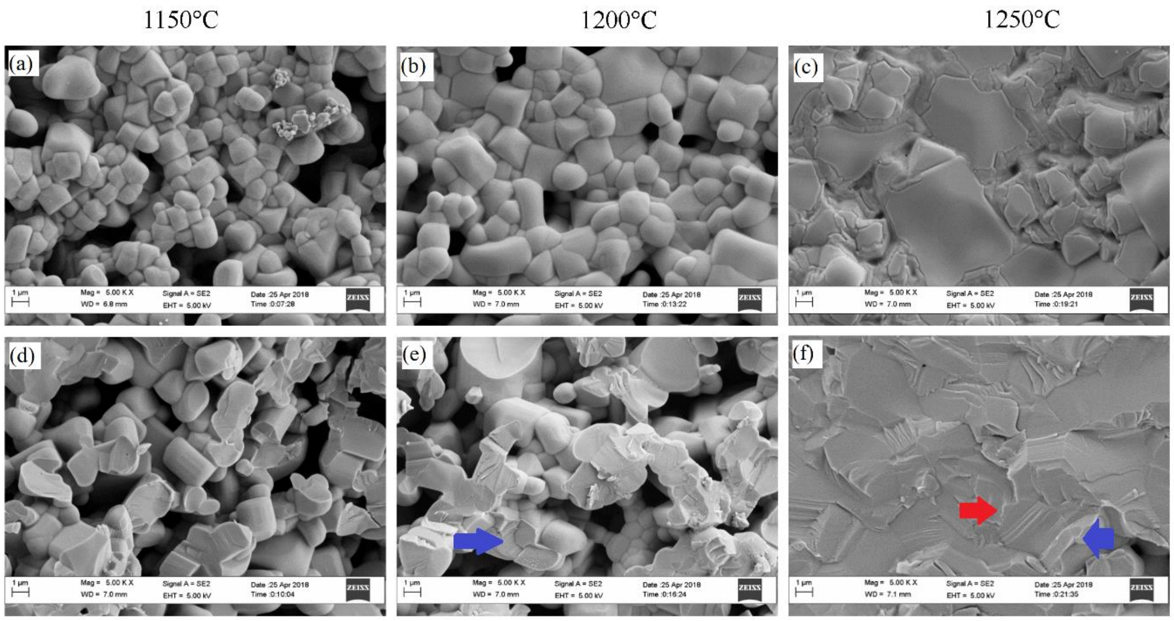

Fig.4. The FESEM micrograph of (a–c) surface microstructure and (d–f) fracture surface of sintered CMS-akermanite at different sintering temperatures.

Relative density/porosity of sintered pellet

It is known that densification and grain growth occur during sintering [26]. The open pores and closed pores are the two types of porosity in ceramic materials. After sintering, the porosity of ceramics will be decreased [26]. It is generally accepted that the mechanical properties of ceramic material increase by decreasing porosity [27]. In the present study, the relative density was increased due to a decrease in porosity and an increase in sintering shrinkage when sintering temperature was raised from 1200°C to 1250°C (Table 4). A relative density of 81% and 93% was obtained after sintering at 1200°C and 1250°C, respectively which is consistent with FESEM micrographs in Fig.4. In addition, the melting of the CMS-akermanite was observed.

Table 4. The density and porosity of sintered CMS-akermanite samples

	Sintering temperature(°C)	
Sample	1200	1250
Relative density (%)	81.50±0.64	93.50±0.54
Open Porosity (%)	32.24±0.34	7.40±0.33

Mechanical properties of sintered pellet

Increasing the relative density and decreasing the grain size would improve the ceramic strength [26]. In this study, the CMS-akermanite sintered at lower temperature 1150°C showed a low tensile strength of 3.73±0.2 MPa which could be ascribed to its low relative density. The tensile strength of sintered CMS-akermanite was increased to 4.51±0.44 MPa and 8.21±42

MPa, after increasing sintering temperature to 1200°C and 1250°C, respectively. The results showed a steady increase in tensile strength of sintered CMS-akermanite produced by using biowastes cockleshell and rice husk as shown in Table 5, which is in a good agreement with the density of samples. This increase in mechanical strength of CMS-akermanite is due to a decrease in porosity which is consistent with the empirical equation of the correlation between mechanical strength and porosity of ceramic material as follows [27]:

$$S = S_0 \exp(-bp) \tag{3}$$

In which, S is the mechanical strength of porous material, S_0 is the ideal mechanical strength with no porosity, P is the porosity of the material and b is the empirical constant. The tensile strength and flexural strength of CMS-akermanite sintered at 1200°C and 1250°C were found to be (4–8 MPa) and (9–22 MPa which are close to that of human cancellous bone (1.5–38 MPa) and (10–20 MPa), respectively [28]. The flexural strength of dense CMS-akermanite was found to be below 35 MPa which is similar to the result reported in the previous study [29].

Table 5. The mechanical properties of sintered CMS-akermanite samples

	Sintering temperature(°C)	
Sample	1200	1250
DTS	4.51±0.44	8.21±0.42
Flexural strength (MPa)	9.02±0.44	22.16±0.42

Conclusion

The cockleshell, dolomite and rice husk ash were used for the first time as the calcium, magnesium and silica source to prepare dense single-phase CMS-akermanite ceramic. This study shows that natural biowastes can be employed to produce valuable ceramics. A highly-densified CMS-akermanite was obtained with a relative density of 93.50%. In addition, the tensile strength and flexural strength of CMS-akermanite were 9.02 MPa and 22.16 MPa, respectively which are in the range of human cancellous bone. The results postulated that CMS-akermanite ceramics could be used as potential bone graft substitutes in the non-load-bearing site.

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Author contributions

All authors contributed toward data analysis, drafting and critically revising the paper and agree to be accountable for all aspects of the work.

Disclosure of conflict of interest

The authors have no disclosures to declare.

Compliance with ethical standards

The work is compliant with ethical standards.

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