Synthesis and Characterization of Cordierite from Talc, kaolin and silica for filter applications

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Abstract
The level of air pollution due to urban transport in most developing economies of the world is high and needs to be reduced. In this research, locally available raw materials namely kaolin, Talc and MgO have been used to synthesize cordierite which is one of the materials for the production of diesel particle filters used in automobiles. The samples were produced through the conventional ceramics processing method where the powders were mixed in their correct proportions, pressed and sintered at 1200^{o}C for 2 hours. Characterization tools like X-ray diffraction, differential thermal analyzer, compression testing machine etc. were used to evaluate the properties of the ceramics. As the talc content increased from 0 – 10%, there was no significant change in the density values as it remains at approximately 2.5 g/cm^3. A structure that is partially crystalline with some amorphous regions was observed in all the samples. The strength modulus of 9.89 MPa was obtained without talc while the thermal analysis shows that two endothermic peaks at 108.5^{o}C and 429^{o}C were observed for all samples corresponding to loss of absorbed water and kaolinite conversion to metakaolin respectively. The obtained properties from the produced samples show that filters for automobile applications can be produced from these locally available materials.

Keywords: Ceramics, Cordierite, Filter application, Talc

1.0 INTRODUCTION

Ceramics are usually prepared with the objective to obtain dense microstructure but there are situations which require that ceramics be deliberately made to be porous. Such ceramics usually have low thermal conductivity, high thermal shock resistance, low dielectric constant etc. As a result of these properties, they are used as materials for filters in automotive applications, membranes, catalyst converters etc. (Ewais *et al.*, 2009). Cordierite ceramics are known to be porous and based on the report by Korikovsky *et al.* (2009), cordierite can exist in three forms or polymorphs namely: α-cordierite also known as Indialite and stable between 1450^{o}C and 1460^{o}C, β-cordierite which is stable below 1450^{o}C and μ-cordierite which is a metastable phase. When a pure cordierite is obtained, the density is 2.53 g/cm^3 and its melting temperature is 1470^{o}C (Smart and Glasser, 1981).

Cordierite is a magnesium aluminium silicate compound with the chemical formula $Mg_2Al_4Si_5O_{18}$ which is composed of 13.7% MgO, 34.9% Al_2O_3 and 51.4% SiO_2 (Valaskova, 2015). Using raw materials from natural sources, a possible description of the chemical reaction that takes place when Talc ($3MgO{\cdot}4SiO_2{\cdot}H_2O$) (2.7 g/cm^3), kaolinite ($Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$) (2.65 g/cm^3) and Gibbsite ($Al(OH)_3$) (2.34 g/cm^3) are the starting materials at sintering temperature between 1200 and 1400^{o}C and normal atmospheric conditions shown is shown in equation 1.

$$4(3MgO{\cdot}4SiO_2{\cdot}H_2O) + 7(Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O) + 10Al(OH)_3 \rightarrow 6(2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2) + 33H_2O \quad (1)$$

The catalytic properties of cordierites make them highly important for use as honeycomb shaped catalyst carriers in the exhaust of automobiles. Different methods have been used to

synthesize cordierite ceramics in the literature. Zhu *et al.* (2012) used serpentine ($Mg_2Si_2O_5(OH)_4$), kaolin tailings and alumina in a solid-state processing where the samples were sintered at 1350^oC. A rhombic crystal structure was reported for the produced cordierite. Mai *et al.*, (2015), used kaolin as a substrate in the synthesis of cordierite to be applied as an auto exhaust catalyst. Addition of dolomite and aluminium hydroxide as precursors increased the surface area leading to higher loading and complete activity for the complete oxidation of CO. Shyam *et al.* (2015) investigated the effect of porosity and microcracking on the thermomechanical properties of cordierite. The reported results show that as the porosity increases, the mechanical properties decreases while there is no sensitivity to the thermal expansion coefficient. Albhilil *et al.* (2013) prepared and characterized cordierite-mullite ceramics from natural raw materials. The samples were sintered at temperatures between 1250 and 1500^oC while the thermal shock resistance was studied using consecutive heating and quenching of the samples. The crystallinity and grain sizes of the samples subjected to this test increased. Ewais et al. (2009) used silica fumes, bauxite and talc to prepare porous cordierite ceramics through the polymeric sponge replica technique. Sintering at 1350^oC for 2 h was deemed to be appropriate while 0.2% of sodium silicate and a suspension with a pH of 8 were suitable to keep the solution well dispersed. For optimum porosity (46.4%) and suitability for filter applications, polyurethane foams were added to the suspension. Gökçe *et al.*, (2004) investigated the microstructure of cordierite manufactured from both natural (kaolinite, sinter magnesite, talc and Pyrophyllite) and synthetic (Al_2O_3, MgO and SiO_2) powders. Solid state sintering was used to produce the cordierite at 1350^oC/1 h, 3h and 5h respectively. Cordierite from natural raw materials was observed to give denser microstructures compared to those from synthetic powders.

G¨unay (2011) focused on the sintering behaviour and properties of sepiolite-based Cordierite doped with 3 wt.% B_2O_3. The samples were sintered from 850-1200^oC and as the temperature increased to 1100^oC, the density of the cordierite increases. Further increase in temperature above 1100^oC led to a decrease in density. Multiple phases were revealed with X-ray diffraction because using natural raw materials; it is not easy to produce cordierite with a single phase which also has a low thermal expansion coefficient. Ning *et al.,* (2018) studied the effect of NH_4VO_3 on the structure and properties of cordierite ceramics. Talc, kaolin, calcined kaolin, Al_2O_3, $Al(OH)_3$ and amorphous SiO_2 are the starting raw materials. With 4% NH_4VO_3, low coefficient of thermal expansion was obtained but micro-cracks and uniform interconnected porosity appeared on the samples while the average particle size of the cordierite decreased.
Wu *et al.,* (2018) investigated the sintering process, phase transformation, microstructure evolution and properties of cordierite ceramics prepared from poor quality kaolin for electric heater support applications. The presence of K_2O led to the formation of a liquid phase during sintering. Sintering at 1320^oC resulted in the following properties for the cordierite: coefficient of thermal expansion (CTE) of 1.98×10^{-6}/℃ (500 ℃), bending strength of 90 MPa, apparent porosity of 15.1%, dielectric constant of 7.5 (100 Hz) and volume resistivity of 1.05×10^9 Ω·cm (100 Hz). Kaolin, Talc and Mg-containing minerals can be found in different parts of the country but their rate of utilization is very low. A lot of work has been done on synthesis of cordierite but most of these are focused on using an additive to improve the properties of the cordierite. The starting raw materials for these articles are mainly a combination of locally available materials and pure chemicals. To the best of the authors' knowledge, not much information exists about the effect of varying the content of Talc. The objective of this study therefore is to use locally available raw materials to produce cordierite as well as to investigate the effect of varying the amount of Talc on the properties of the synthesized cordierites.

2.0 MATERIALS AND METHOD

2.1 Sample Preparation

The raw materials used in the production of the cordierite include kaolin from Darazo, Talc from Oyo State and MgO procured from Ojota chemical market in Lagos. The raw materials were initially crushed using a jaw crusher (Broyeur Clero Hammer Mills type ODQ 1) to smaller particle sizes. This was carried out at the Federal Institute of Industrial Research Oshodi (FIIRO), Lagos. The specific amounts of the raw materials were measured and mixed in the following proportion as shown in Table 1. 1 kg of the powders was used for each composition synthesized. The basis for the mix ratio is the chemical formula for cordierite.

Table 1: Table showing the mix composition and percentages used in the production of composites

Composition	Talc Amount (g) / (%)	MgO amount (g) / (%)	Kaolin amount (g) / (%)
1	0 / 0	134 / 13.4	866 / 86.6
2	25.65 / 2.565	130 / 13	844.3 / 84.43
3	50 / 5	127.3 / 12.73	822.7 / 82.27
4	75 /7.5	123.9 / 12.39	801.05 / 80.1
5	100 / 10	120.6 / 12.06	779.4 / 77.94

The coarse powders were separately ball-milled for 3 hours (sne Foure, Limoges, France) also at FIIRO using hardened steel balls to fine powders in order to reduce their particle sizes and homogenize them. The powdered samples were sieved using a set of mesh sieves to ensure that only powders in the size range ≤ 80 µm were used for further processing. For easy pressing, they were mixed with distilled water in order to produce a paste which was vibrated and pressed with a stainless steel mould in a uniaxial pressing machine. The picture showing the samples after the pressing process is shown in Figure 1. The samples were dried in air for 48 hours and later heated in an automatic temperature-controlled gas-fired furnace to a temperature of 1200^{o}C at a heating rate of 400^{o}C/h and held at this temperature for 2 hrs. The samples were allowed to cool inside the furnace.

Figure 1: Picture showing the samples after the pressing in a uniaxial press

2.2 Sample Characterization

The chemical composition of the starting raw powders was analyzed using an X-ray Fluorescence analyzer (Venarum Mines laboratory Limited Apapa, Lagos). 1g each of the samples was used for the analysis and the measurement was made with Au-Ag at a voltage of

40 kV and current of 50 mA. A table showing the results of the starting powders is shown in Table 2. The compositions of the powders are similar to those for same materials. The density of the samples was determined using Archimedes method where the mass of the samples was measured and then immersed in water after which they were dried and measured again.
To prepare the sintered samples for microscopic examination, they were cut using a circular blade incorporated with diamond particles and a saw equipped with a blade continuously water-cooled by spraying. The marks made by the saw were removed by grinding of the sample starting with a rough grit paper (size 320) to the fine grit paper (size 2000). To obtain a smooth finish, the samples were polished using aluminium slurry.

The samples for compression test were prepared according to the ASTM standard D412 using a dumb bell test material. They were placed in an INSTRON Universal Tester (INSTRON Series 3369) and then subjected to compressive load. This test was carried out at the Obafemi Awolowo University Ile-Ife. X-ray diffraction was used to determine the phases that were present in the samples. This test was carried out at the National Geosciences Research Laboratories in Kaduna. The measurement was made with Cu$k\alpha$ radiation with a wavelength of 1.5406 Å at a voltage of 45 kV and current of 40 mA.

Table 2: Table showing the chemical composition analysis of the starting raw powders using in producing cordierite

	Talc	MgO	Darazo kaolin
Analytes	**Content (wt.%)**		
SiO_2	58.06	1.45	46.48
MgO	29.02	86.13	0.08
CaO	3.11	3.52	0.11
Al_2O_3	1.03	3.41	39.91
Fe_2O_3	0.46	0.25	0.79
K_2O	1.32	-	0.36
TiO_2	0.04	0.02	1.99
Na_2O	0.51	-	0.75
BaO	0.001	-	0.01
P_2O_5	0.03	-	-
MnO	0.06	0.04	0.08
ZnO	-	-	0.04

3.0 RESULTS AND DISCUSSION

The bulk density values of the cordierite samples as a function of composition are shown in figure 2. Three samples for each composition were measured and the average value was recorded. For samples with composition 1 (no talc), the density value is 2.49±0.04 g/cm^3. With the introduction of talc (composition 2), the density value did not change very much (2.48±0.09 g/cm^3). With more addition of talc (composition 3), the density slightly decreased to 2.35±0.1 g/cm^3. As more talc was added, the density increases to 2.4±0.13 g/cm^3 and 2.64±0.15 g/cm^3 for compositions 4 and 5 respectively. Statistically, there is no significant difference in the obtained density values for most of the compositions. The density values from this study are slightly higher than that reported by Ewais *et al.* (2009) with a density of 2.18 g/cm^3 for samples sintered using similar temperatures. The difference in density values can be related to the difference in composition of the respective studies. It however is similar to the density value of 2.46 g/cm^3 reported by Shyam *et al.* (2015).

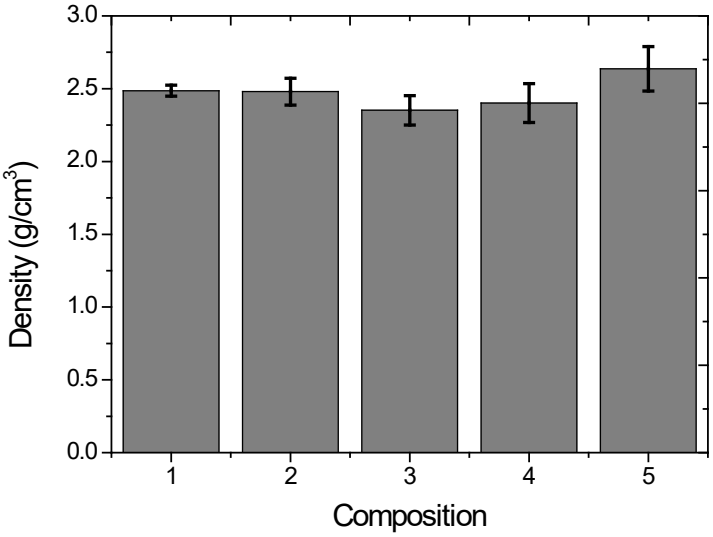


Figure 2: A plot of bulk density as a function of sample composition of the cordierite samples

The plot of intensity as a function of diffraction angle for the cordierite samples are shown in figure 3. Diffraction patterns that are only slightly crystalline with some amorphous phases were obtained for all the samples. The intensities and position of the various diffraction peaks are however different with composition. The possible reasons why the patterns are slightly crystalline may be traced to the sintering temperature used for the samples. Cordierite peaks are observed at the following Bragg angles: 21°, 27°, 31° etc. but they were not fully formed. Reports by Ewais *et al.* (2009) and Zhu *et al.* (2012) show that sintering cordierite at temperatures between 1300°C and 1350°C enables the phases to completely form as opposed to the lower temperature that was used in this work. At temperatures below 1200°C, it has been reported that the main crystalline phases present include quartz, forsterite and enstatite (Zhu *et al.*, 2012). The Scherer equation which relates broadening of X-ray beam to the size of a crystal has been used to estimate how crystalline the samples are. It is given by the formula in equation 2.

$$\beta = k\lambda/t \cos\theta \qquad (2)$$

where β represents sample broadening, k is a correction factor (approx. 1), λ is the wavelength of the X-ray, t is the crystallite size and θ is the incident angle. Using the angles at 42.86° and 59.95°, average crystallite size of 5.96 Å and 8.87 Å were obtained respectively. As the angle of measurement increases, the crystallite sizes increase.

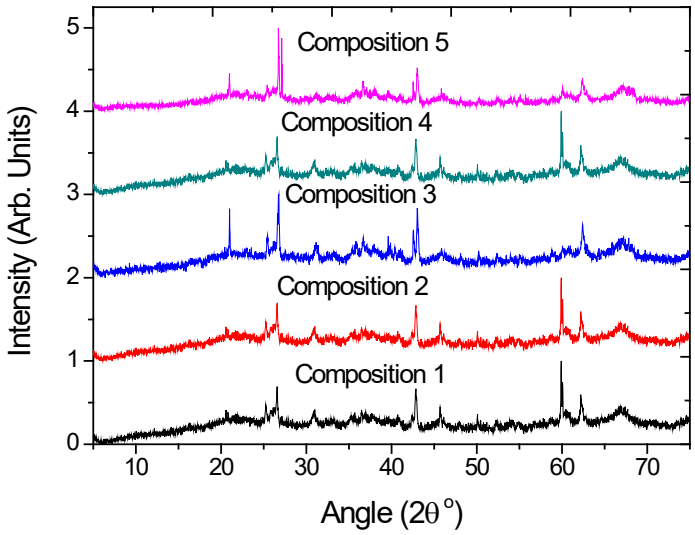


Figure 3: A graph of X-ray diffraction patterns for the cordierite samples

The graph of compressive stress as a function of compressive strain for the cordierite ceramics is shown in figure 4. The linear portion of the graphs was used to calculate the modulus values of the graphs. There was no defined trend or pattern in the moduli obtained. For sample 1, the modulus is 9.8937 ± 0.175 MPa and decreases to 6.758 ± 0.05 MPa. As the talc content of cordierite increases, the modulus slightly increases to 7.057 ± 0.1 MPa. For sample 4, the modulus decreases to 6.189 ± 0.076 MPa and for sample 5, the modulus values increase to 8.2339 ± 0.2 MPa. An increase in the modulus values of the samples is expected to increase the fatigue life cycle of the cordierite and vice versa.

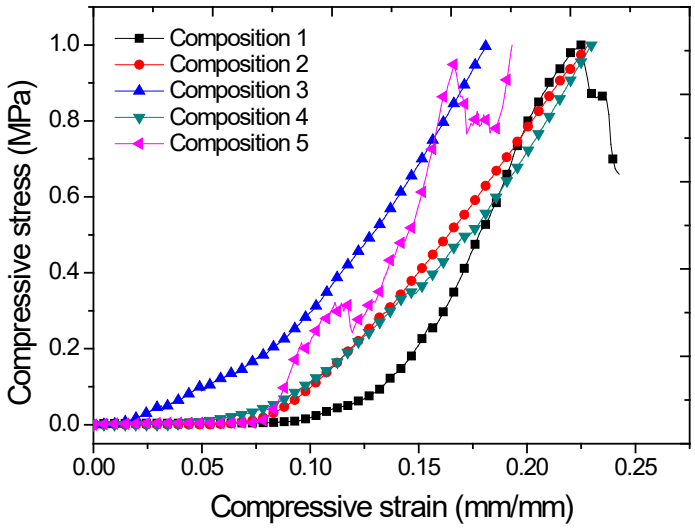


Figure 4: A plot of compressive stress as a function of compressive strain for cordierite ceramics

The thermal analysis graph of the samples using a differential thermal analyzer which measured on heating is shown in figure 5. As the samples were heated, their heat content continued to increase up to a temperature of about 1000°C. Two endothermic peaks were observed as the heating took place. The first occurred at a temperature of approximately 108.5°C and is associated with the loss of physically adsorbed water (Wu *et al.*, 2018). The second endothermic peak occurred over a range of temperatures with the peak being

observed at a temperature of 492°C and is associated with the conversion of kaolin to metakaolin. At a temperature of 892°C, it is believed that the talc decomposes to begin the formation of cordierite.

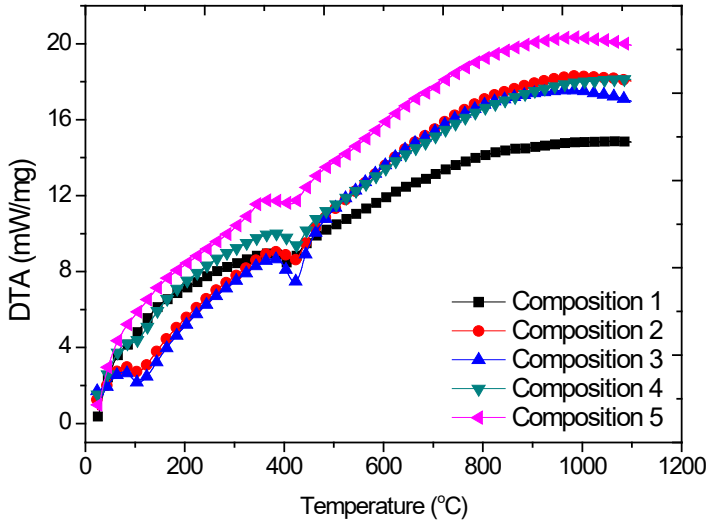
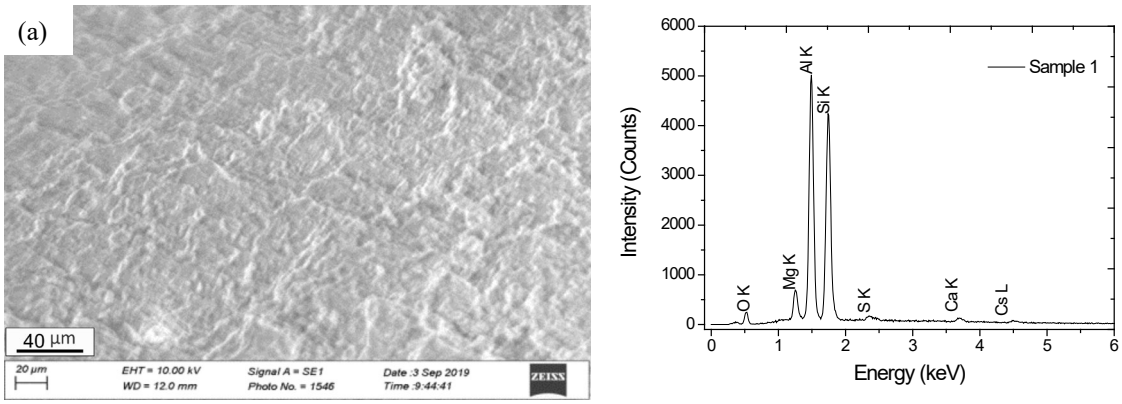


Figure 5: Differential thermal analysis plots as a function of temperature for the cordierite samples measured on heating.

The SEM images and the corresponding EDX plots of samples with composition 1 and 3 are shown in figure 6. The sample without talc content has a dense microscope with small spherical pores observed at the grain boundaries. The surface of the sample is not smooth because the measurement was carried out on the fracture surface. The EDX shows the presence of elements like O, Mg, Si, Al, S, Ca and Cs. Al and Si however have the strongest peaks which correspond to their contents as shown in the chemical composition of the samples. The sample containing talc also has the same elements. The difference between the two samples however can be found in the intensity of the Mg peak. It is observed that when there was no talc in the cordierite, the intensity of the peak is low but when talc was present, the peak intensity increases. The micrograph of the sample containing talc indicates the presence of protrusions that may result in pores if the sintering temperature is increased to 1300°C.



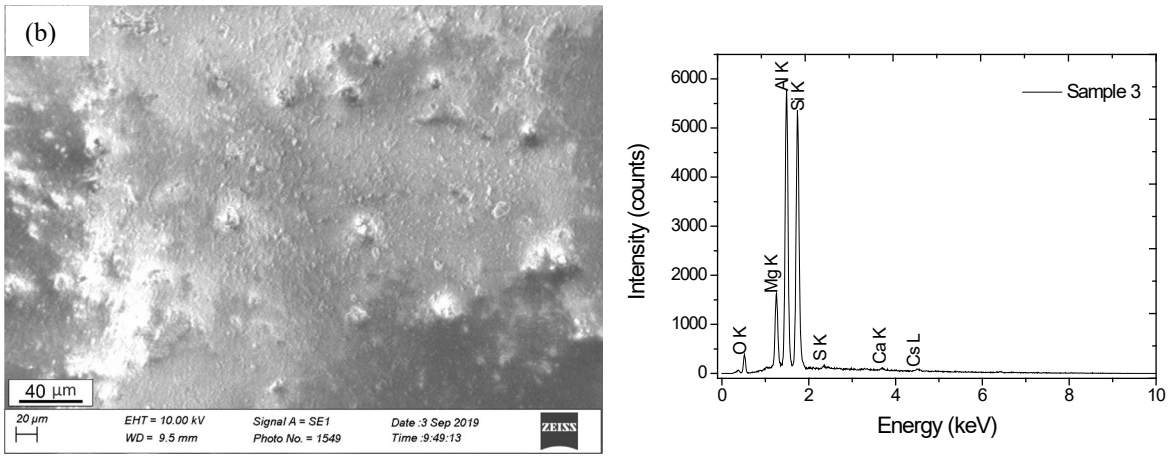


Figure 6: Scanning electron microscope images and the corresponding energy dispersive spectroscopy graphs for (a) Sample 1 and (b) Sample 3.

4.0 CONCLUSION

Cordierites ceramics with different talc contents have been produced using the mixed oxide synthesis method. As the talc content of the samples increases, the density of the samples did not change as the average density is 2.5 g/cm^3. Moderately crystalline diffraction patterns were obtained for the samples indicating that the temperature used for the samples could be higher to achieve higher crystallinity. The compression test on the samples show that modulus values from 6.7 MPa to 9.9 MPa were obtained. The thermal analyses on the samples show that two endothermic peaks corresponding to removal of physically adsorbed water and conversion to metakaolin were obtained on heating. The morphology of the sample indicate that talc addition tends to introduce porosity to the samples while the EDX showed the presence of O, Mg, Si, Al, S, Ca and Cs in the samples. The density, compressive moduli, microstructural results obtained from this work indicates that the locally available materials are suitable for cordierite production.

5.0 REFERENCES

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