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The effect of MgO and Cr_2O_3 on mullite formation from Nigeria sourced kaolin-calcined alumina sintered compacts

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Abstract. Mullite being one of the most important aluminosilicate materials has a lot of unique properties and industrial applications. Hence the need to produce via cheap and available starting materials is paramount. In this present study, mullite was synthesized from sintering of Nigerian sourced kaolin–alumina (high purity from Almatis) after reacting samples have been mixed in a high speed ball milling machine in the presence of MgO and Cr_2O_3 additives. The samples were uniaxially pressed in a mould to form compact and sintered at temperature of 1400-1600°C. Bulk density, apparent porosity, and modulus of rupture were investigated as a function of sintering temperature and presence of dopant. Microstructural studies using scanning electron microscope (SEM) and X-ray diffraction (XRD) studies were carried out on the kaolin-alumina sintered compacts. Results from the study indicate that mullite was successfully synthesized, as XRD pattern showed the presence of mullite as major phases at 1600°C without any trace of cristobalite (unreacted silica) or quartz. SEM studies showed the presence of needle-shaped mullite. The doped samples showed little improvement in the physico-mechanical properties of the aggregate. However, the degree of mullitisation for the doped samples at 1600°C far exceeds that of the undoped samples. Cr_2O_3 doped has 94.48% mullitisation while MgO has 79.96% mullitisation. The undoped sample has 59.19% degree of mullitisation. MgO doped was better densified.
Key words: Clay, alumina, sintering, MgO doping, Cr_2O_3 doping, mullite
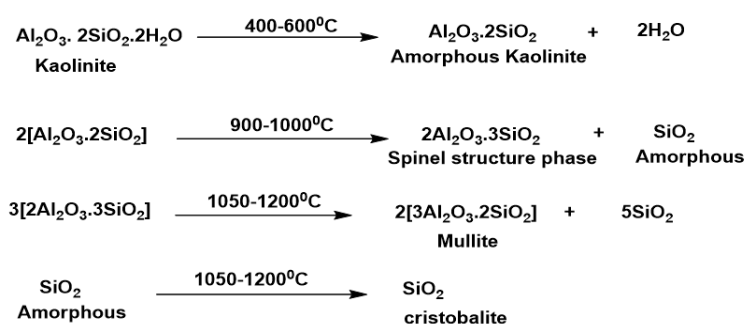
1. Introduction

Mullite ceramics ($3Al_2O_3.2SiO_2$) have recently generated a lot of interest due to its outstanding properties, such as low thermal expansion, low dielectric constant, high melting point, high thermal shock resistance and excellent creep resistance which has useful applications in the refractory industry [1, 2]. The composition of mullite is mostly denoted as $3Al_2O_3·SiO_2$ (71.83 wt.% Al_2O_3). However, the most relatively abundant form of mullite has about 71-76 wt.% Al_2O_3, 23-24 wt.% SiO_2, and minute amount of TiO_2, Fe_2O_3, CaO and MgO. The composition of mullites strongly depends on the starting materials and temperature treatment [3]. Several authors have carried out the synthesis of mullite through cost effective means [4, 5]. Materials such as clay, rice husk and other forms of naturally occurring aluminosilicate can be used as starting materials for mullite production. However, mullite synthesized from these sources do experience some limitations such as poor densification, low strength and high presence of impurity substance. Therefore, the choice of a synthetic method which will give a

high yield and also economically viable is important in mullite synthesis. The utilization of cheap and readily available alumina-silica starting materials, such as Nigeria kaolinite, will be of immense benefit in achieving the production of mullite.

Kaolin is very stable at high temperature and possess an excellent thermal shock resistance. Its refractoriness, porosity, permeability and plasticity are the qualities that makes it one of the most viable raw material for the production of certain ceramic materials such as mullite and porcelain. Nigeria as a country has massive deposits of kaolin and they are distributed all around the entire length and breadth of the nation. After some scientific studies was carried out on these kaolin deposits, a lot of them have been found to belong to the refractory clay group [6].

The development of synthetic approaches for mullite have been reported [7-9] but the most affordable of all is the thermal decomposition of kaolin which occurs at 1050-1500°C and kaolin plus alumina in the temperature range of 1400-1650°C [4, 10]. In the solid state sintering method of mullite synthesis, kaolin and all other materials are heated at an elevated temperature, to yield mullite and cristobalite as shown in the scheme 1.

$$Al_2O_3.\,2SiO_2.2H_2O \xrightarrow{\text{400-600}^0\text{C}} Al_2O_3.2SiO_2 \quad + \quad 2H_2O$$
$$\text{Kaolinite} \qquad\qquad\qquad \text{Amorphous Kaolinite}$$

$$2[Al_2O_3.2SiO_2] \xrightarrow{\text{900-1000}^0\text{C}} 2Al_2O_3.3SiO_2 \quad + \quad SiO_2$$
$$\qquad\qquad\qquad \text{Spinel structure phase} \quad \text{Amorphous}$$

$$3[2Al_2O_3.3SiO_2] \xrightarrow{\text{1050-1200}^0\text{C}} 2[3Al_2O_3.2SiO_2] \quad + \quad 5SiO_2$$
$$\qquad\qquad\qquad\qquad \text{Mullite}$$

$$\begin{array}{l} SiO_2 \\ \text{Amorphous} \end{array} \xrightarrow{\text{1050-1200}^0\text{C}} \begin{array}{l} SiO_2 \\ \text{cristobalite} \end{array}$$

Scheme 1. Phase transformation during heating of kaolinitic clay [11].

Addition of extra alumina reacts with amorphous silica to form mullite at a higher temperature usually 1400 to 1600°C [12]. Secondary mullite formation begins at 1400°C due to the transitory dissolution of alumina into liquids followed by mullite crystal formation [13]. Mullite formation is initially slow but becomes extremely fast at 1600°C [14], justifying the firing temperature of the aggregate between 1400-1600°C.

Various studies have revealed that the addition of certain additives such as transition metal ion and ions of group 1 and 2 elements through their oxides favours the formation of mullite from precursor materials [1, 3, 15]. It has also been established that oxides of transition metals such as V_2O_5, Nb_2O_5, Ta_2O_5, TiO_2 and Cr_2O_3 assist mullite formation [16]. The presence of these dopant ions reduces the mullitisation temperature and facilitates grain growth [1, 17].

In the present study, an attempt has been made to study the influence of Cr^{3+} and Mg^{2+} in a mixture of 50:50 (%) Nigerian kaolin and calcined alumina powder on mullite formation when sintered at different temperatures (1400-1600°C). The bulk density, strength development, phase and microstructural evolution were determined and discussed in this paper.

2. Experimental

The same source of processed kaolinitic clay (Abule Onikosin Road in Abeokuta area of Ogun State, Nigeria) which was utilized in our previous work [11] and reactive alumina, obtained from almatis (99% purity) were used for this study. Analytical grade chromium oxide and magnesium oxide was procured from Klinscent laboratory limited. The chemical constituents present in the starting materials were determined using different techniques namely: volumetric method for SiO_2 and Al_2O_3; complexometric method for CaO and MgO; spectrophotometry [LAMBDA-45, PerkinElmer, USA] for Fe_2O_3, TiO_2; flame photometry [PFP-7, Jenway, UK] for Na_2O and K_2O and loss on ignition (LOI) by heating the samples up to 800°C gravimetrically.

The kaolin used for this study was collected from Abule Onikosin Road in Abeokuta area of Ogun State, Nigeria. Abeokuta is located within latitude 7°8'32" N and longitude 3°27'3" E south western part of Nigeria. The kaolin was dried, thereafter agglomerated materials were broken and the stony materials adhering to the kaolin was separated. Afterwards the kaolin was wet ball milled in a high energy ball milling machine for about five hours and was made into a slurry. The resulting slurry was passed through a 60 mesh BS sieve. The sieved slurry was oven dried until minimal moisture content was achieved. The dried mass was grinded into powder.

The powdered clay samples after characterization was mixed with water in ratio of about 10:1 w/w and the moistened clay was the uniaxially pressed into rectangular bars with the help of a mould of dimension (65×8×8 mm) using a hydraulic press with pressure of 20 psi. The compacted samples were dried in an oven at a temperature of 110°C for 24 hours. The rectangular bars formed were sintered in a carbolite high temperature furnace in the range of 1400-1600°C for 2 hrs at a heating rate of 10°C/hr.

With the use of the above raw materials, three batches of 500 g each were prepared. The batch compositions are provided in table 1.

Table 1. Batch composition of materials for ball milling

Sample compositions	Sample L1 (grams)	Sample L2 (grams)
Kaolin	250	250
Alumina	250	250
Cr_2O_3	-	20
MgO	20	-

The apparent porosity (% AP), bulk density (BD), and flexural strength (FS) of the sintered samples were determined at three firing temperature of 1400°C, 1500°C and 1600°C. Bulk density and percent apparent porosity were measured by conventional water displacement method following Archimedes principle. The flexural strength of the sintered samples was determined by three-point bending method using INSTRON 5500R. The phase and microstructural analysis of the sintered samples were obtained via the X-Ray diffractometer (XRD) using CuKa radiation, SEM and EDAX (OXFORD) techniques. The XRD results of the samples (in powdery form) were recorded in step-scan mode with step size 0.05° (2θ) and step time 75 sec between 10-80°. For the microstructure evaluation of the sintered samples, the samples were grinded with SiC powder followed by water. Afterwards the samples were polished with diamond paste. Water and acetone were used in washing the surface of each of the polished samples followed by gold coating (Edwards, Scancoat).

3. Result and Discussion

The chemical constituent of the processed Nigeria Kaolinite is shown in table 2.

Table 2. Chemical constituent of processed Nigeria clay [11]

Constituents (wt %)	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	LOI
	59.26	24.04	3.87	1.46	0.39	0.14	0.74	0.3	9.4

As revealed in our earlier work Ajanaku *et al.* [11], compacted clay samples sintered at 1400–1600°C, yielded a partially densified material at 1600°C. The XRD pattern showed mullite as minor phase and silica in form of quartz as major phase. At the aforementioned temperature range of sintering, impurity oxides present in the clay forms a glassy phase together with the formed mullite. In another of our previous work Aladesuyi *et al.* [18] the processed kaolin combined with reactive alumina at composition of 50:50% showed mullite as major phase in the XRD and cristobalite as minor phases. This is an indication that the quantity of added alumina is sufficient enough for mullite formation. The effects of the two dopant ion employed as sintering additives are discussed in the next section.

3.1. Effect of Chromium oxide doping in Mullite synthesis

3.1.1. Physico-mechanical properties of Cr^{3+} doped mullite aggregate. The apparent porosity, bulk density and flexural strength of the Cr_2O_3 doped and undoped synthesized mullite aggregate crystals were determined at three firing temperature of 1400°C, 1500°C and 1600°C as shown in Fig. 1. The incorporation of ions of transition elements into mullite's interstices is controlled mainly by ionic radii, oxidation states and sintering condition [3]. Therefore, the incorporation of Cr^{3+} ions into the mullite lattice will occur as a result of any of the aforementioned reasons. As a result of the large cationic size and high tetrahedral crystal field splitting parameters of most transition element there exist a preference for octahedral substitution in the mullite crystal lattice rather than tetrahedral substitution [1-3, 7].

(a)

(b)

(c)
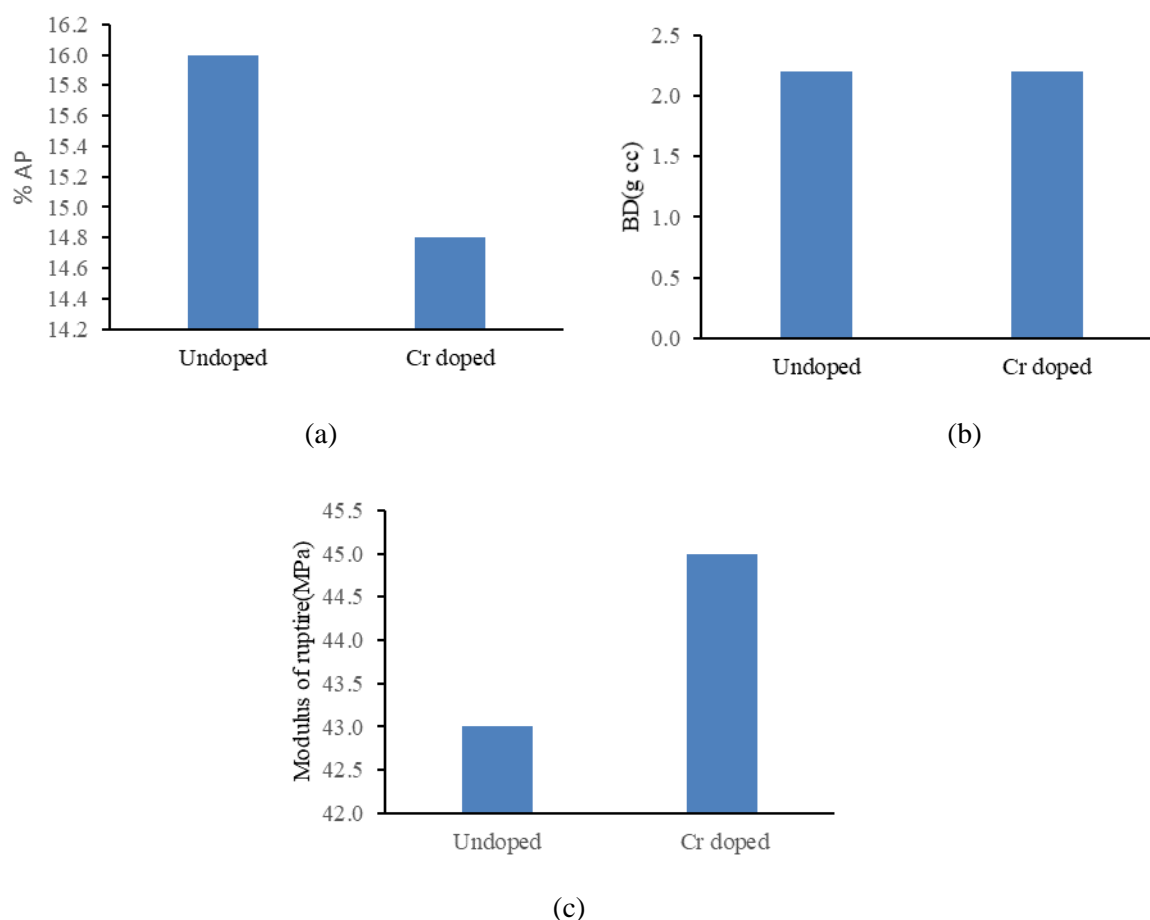
**Figure 1.** Variation in (a) AP, (b) BD, and (c) MOR of sintered Cr2O3 doped samples at 1600°C temperature

The apparent porosity of the doped kaolin-alumina compacts decreased with increasing temperature, and across the three firing temperatures, the Cr-doped samples is less porous than the undoped mullite compact as shown in Fig.1. The reason for this can be explained on the basis of preferential substitution of Al^{3+} by Cr^{3+} ion at the octahedral position as Cr^{3+} is likely to substitute Al^{3+} in the crystal structure of the synthesized mullite to form CrO_6 octahedral due to the smaller ionic radius of Cr^{3+} (53.5) as against that of Al^{3+} (73.5). Also, as the temperature approaches 1600°C densification is reaching completion with little or no glassy phase and cristobalite phase is present together with the mullite phase.

However, in Fig. 1, it was observed that doping with Cr^{3+} does not improve the bulk density of the mullite aggregate across the sintering temperature. This may be as a result of inhomogeneous grain

growth during sintering. Also it may be due to the formation of Cr^{3+}-Cr^{3+} cluster in the melt leading to the partial entry of Cr^{3+} ions into the interstices. The relatively high porosity value also shows inadequate densification.

At 1600°C, the modulus of rupture of the doped samples increased to about 45 MPa from 38 MPa. The increase in strength at 1600°C can be as a result high level of inter-diffusion of Al^{3+} and Cr^{3+} ions due to closeness in ionic radii of Cr^{3+} to that Al^{3+} and also as a result of the lower melting temperature of Cr_2O_3 when compared to that of Al_2O_3. The presence of the Cr_2O_3 in the melt causes a reduction in the amount of glassy phase at high temperature leading to increase in strength. Therefore, at 1600°C Cr^{3+} doping will result to an increase in strength in solid state sintered mullite.

3.1.2. Microstructure and XRD Analysis of Chromium Doped Mullite Aggregate. The SEM and EDAX Micrograph of chromium doped compacted samples at 1600°C are shown in Fig. 2 and 3 respectively.
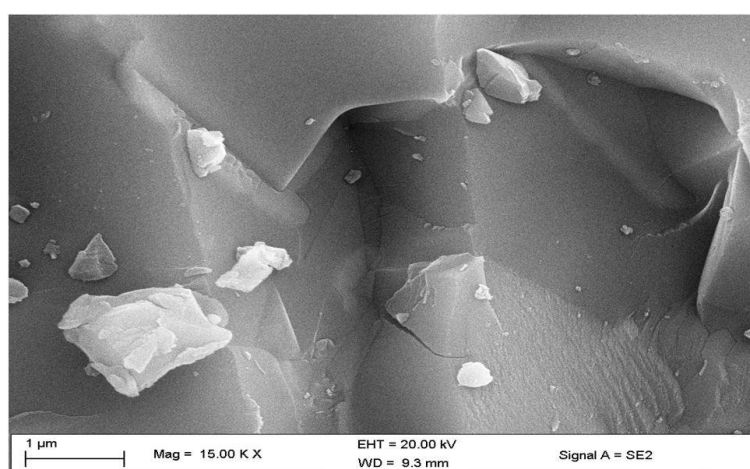
Figure 2. SEM Micrograph analysis of Cr_2O_3 doped L1 samples heated at 1600°C.
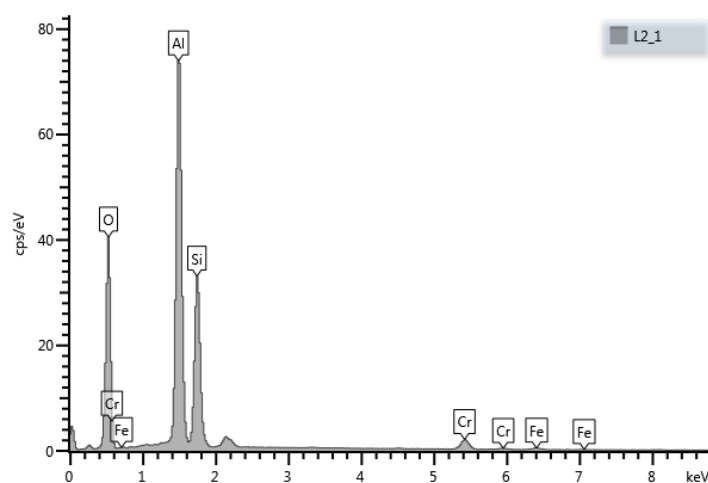

Figure 3. EDAX images of chromium-doped L1 samples at 1600°C heating temperature

The presence of well-formed solid structure of secondary mullite grains in the SEM micrograph (Fig. 2) is an indication of complete mullitisation at 1600°C. However, increased sintering temperature can also allow the formation of larger grain sizes and polygonisation of the mullite crystals [15].

It has been established by several authors that the incorporation and sintering behaviour of transition metals in sintered mullite is mainly determined by the oxidation state and the ionic radii of the dopant ion, the highest degree of incorporation is experienced by trivalent ions [1, 3, 7, 15]. Due to the closeness in ionic radii between Cr^{3+} and Al^{3+}, incorporation of chromium into the mullite lattice occurs mainly by Al^{3+} replacement [1]. These two aforementioned factors of ionic radii and oxidation state of chromium ion will definitely promote grain growth and ensure a high degree of mullitisation as observed in the SEM micrograph and XRD studies at 1600°C.

The presence of Cr^{3+} ions substituting Al^{3+} also reduces the viscosity of the melt during solid state sintering. Nucleation growth and microstructure development are controlled by low viscous phases in solid state sintering [7]. Another reason for the high level of mullite formation experienced in Chrome doped mullite can be attributed to the formation of Cr_2O_3–Al_2O_3–SiO_2 system during sintering. The Cr_2O_3–Al_2O_3–SiO_2 system have been found to have inherent characteristics that promote microstructure development and grain growth [1, 3, 7].

As shown in the XRD pattern (Fig. 4), it is evident that mullitisation has been completed at 1600°C as there was not any form of cristobalite, quartz or α-alumina in the XRD pattern. The degree of mullite formation was also very high, about 94.48%, that is a difference of about 35% more than that of the undoped sample. Also, the peak splitting around 2θ (26) indicates a transformation from the primary mullite to secondary mullite. This is also corroborated in the SEM micrograph in Fig. 2 which clearly shows the presence of secondary mullite. In addition, the peaks of the doped mullite were more intense indicating crystallinity of the doped mullite.
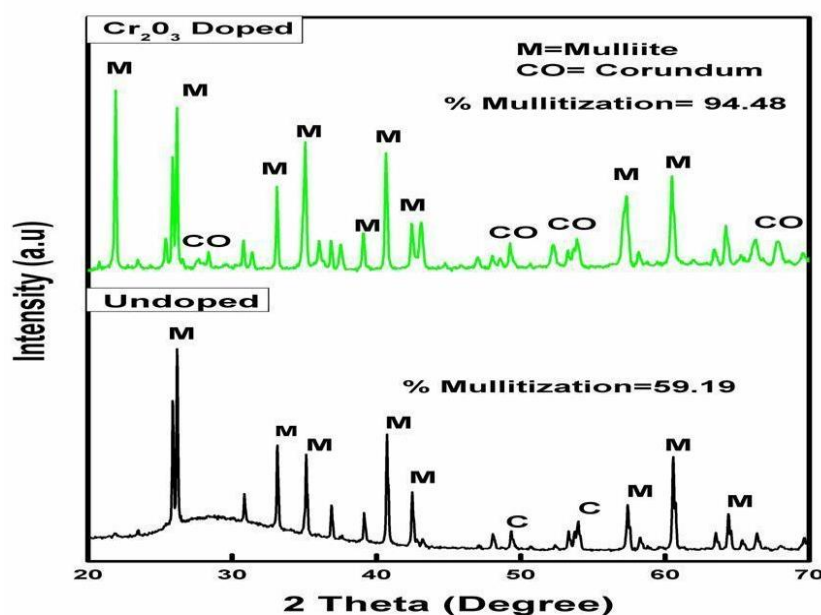

Figure 4. XRD pattern of undoped and Cr_2O_3 doped (L1) Clay-alumina samples sintered at 1600°C temperature.

Mullite formation via solid state reaction sintering, takes place through dissolution-precipitation reaction mechanism. In this mechanism, Al_2O_3 atoms dissolves in the already co-existing SiO_2 liquid (due to their lower melting point) until a critical Al_2O_3 concentration is attained [19, 20]. On attainment of this critical concentration of Al_2O_3 a reduction in viscosity of the melt is experienced due to the presence of Cr^{3+} ions thereby enhancing the rate of dissolution of alumina silica flux. The major increase in the rate of alumina dissolution is the reason for the major increase in the degree of mullitisation observed at 1600°C, when mullite formation is expected to have been completed. Another factor that may have contributed to the high degree of mullite formation in the Cr^{3+} doped sample is due to the fact

that its oxidation state and atomic radii fits best with that of Al^{3+} [1]. As result there is ease of replacement of Al^{3+} in AlO_6 octahedra by Cr^{3+} which in turn aid the inter-diffusion of Si^{4+} and Al^{3+} thereby accelerating grain growth of mullite.

3.2. Effect of Magnesium oxide doping in Mullite synthesis

3.2.1. Physico-mechanical properties of MgO doped mullite aggregate. Fig. 5 illustrates the variation in porosity, bulk density, linear shrinkage and modulus of rupture of the MgO doped and undoped synthesized mullite compacts at the sintering temperature 1600°C. The porosity of the undoped compacts did not show any appreciable difference across the three sintering temperatures. This is an indication of poor densification of the mullite aggregates.

(a)

(b)

(c)
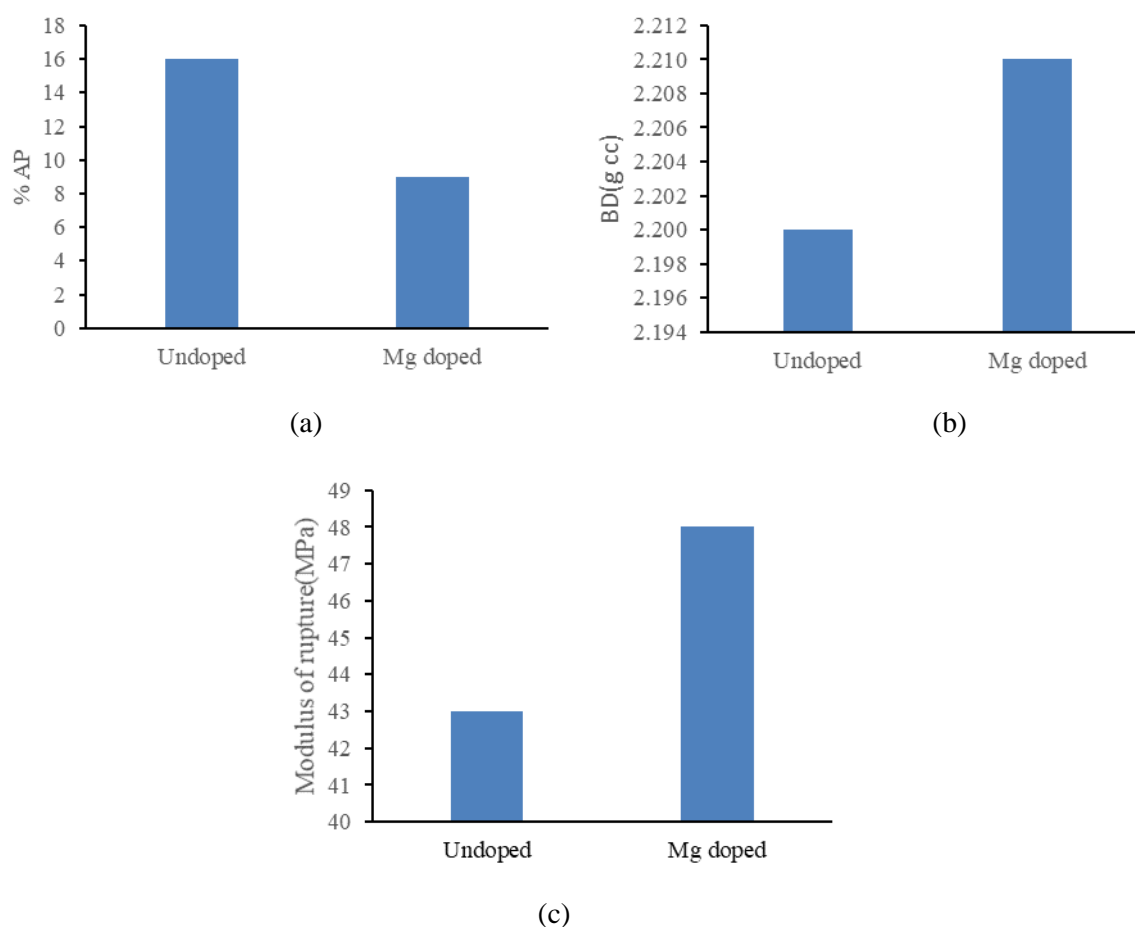
**Figure 5.** Variation in (a) AP, (b) BD and (c) MOR of sintered MgO doped (L2) samples at 1600°C.

However, there was a significant difference in the apparent porosity of the doped compacts. The porosity of the Mg doped compacts reduced drastically at sintering temperature of 1600°C. At 1600°C the apparent porosity was reduced to 9% as against 30% observed in the undoped compact. The reduction in the apparent porosity values shows that Mg ions contributed to the reduction in the amount of pores. This reduction in porosity is may be as a result of spinel formation during incorporation of Mg^{2+} ions into the mullite structure as shown in the phase evolution and microstructure.

There was no appreciable increase in the bulk density of the MgO doped at 1600°C sintering temperature. This is an indication that addition of MgO does not really add to the densification of the

mullite aggregate at 1600°C. Kong *et al.* [21] in their study also observed that although MgO doping promotes anisotropic grain growth but does not really enhance densification during mullite synthesis. As shown in Fig. 5, the modulus of rupture of the MgO doped increased across the sintering temperature. At 1600°C the Strength of the MgO doped compact increased (45 MPa) compared to the undoped compact (38 Mpa). The increase in strength can be due to the reduction in the amount of pores and better densification of the compact. It could also be as a result of the interlocking and bonding of the mullite grains. MgO incorporation in mullite is most effective between 0.1–5% addition [22]. Therefore, addition of 4% MgO as carried out in this study will have maximum incorporation into the mullite's interstices. Kong *et al.* [21] also observed that MgO addition at maximum incorporation forms a very dense spinel of MgO-Al_2O_3-SiO_2. The MgO doped sample exhibited better physico-mechanical property when compared to the Cr_2O_3 doped sample. The reason for this can be explained on the basis of spinel formation as shown in the XRD.

3.2.2. Phase Identification and Microstructural study of MgO Doped Mullite Aggregate. The SEM and EDAX spectrum of MgO doped samples are shown in Fig. 6 and 7 respectively at 1600°C.
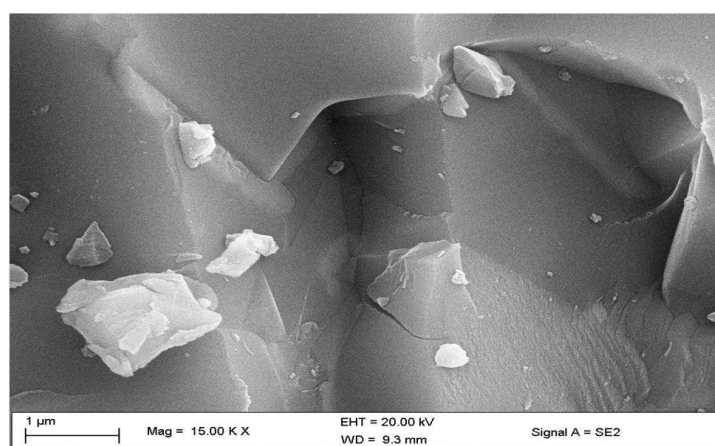
**Figure 6.** SEM Micrograph analysis of MgO doped L3 samples heated at 1600°C
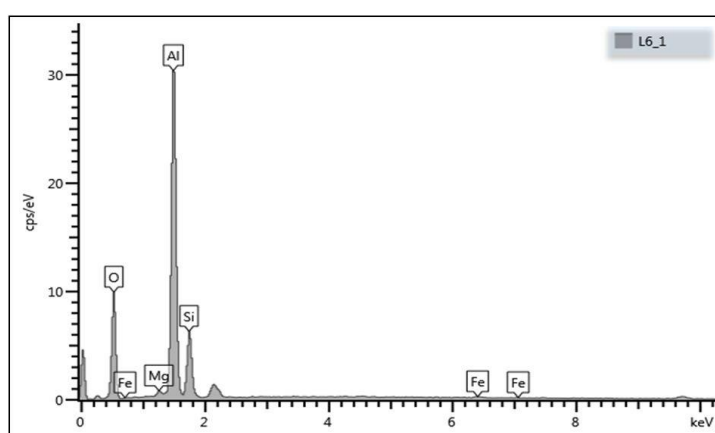
Figure 7. EDAX images of MgO doped L1 samples at 1600°C heating temperature.

At 1600°C sintering temperature, the morphology of the mullite changed from equiaxed to acicular indicating the presence of more secondary mullite grains. The formation of mullite via solid state sintering is determined by the dissolution-precipitation mechanism [3, 18, 21]. During the process of

sintering, SiO_2 liquid layer is first formed due to its lower melting point followed by the dissolution of the alumina rich layer. Crystallisation into mullite follows as the alumina reaches a critical level. The presence of this liquid layer enhances sintering and densification. This phenomenon is known as the viscous transient flow sintering. However, if densification takes place after mullitisation, whiskers are formed. If the reverse takes place, densed equiaxed grains will be formed [21]. In other to ensure continuous mullitisation after densification, the raw materials are subjected to very high temperature so as to ensure continuous dissolution of alumina in the liquid layer. The continuous dissolution of Al_2O_3 will therefore lead to continuous grain growth and effective mullitisation.

High energy ball milling can reduce the reacting starting materials used in solid state to the nearest minimum, even up to the nano scale. This reduction in size of the starting materials to the nano scale can achieve mullite formation at a lower temperature, below that which is required for densification [23]. Therefore, mullitisation can be achieved at a much lower scale during solid state sintering when the particle size of the starting precursors is reduced to the nanometer scale. The $MgO–Al_2O_3–SiO_2$ system formed when kaolin-alumina compacts are doped with Mg^{2+} ions from MgO behave in a like manner as the high energy ball milled $Al_2O_3–SiO_2$ system [21]. This is therefore the reason for the similarity in the microstructure of both MgO doped and undoped samples and also the reason for the relatively high level of the degree of mullitisation observed for MgO doped samples in this particular study despite the relatively large atomic size of Mg^{2+} ions.

Fig. 8 shows the XRD pattern of undoped and MgO doped 50:50 kaolin-reactive alumina sintered compacts at 1600°C. Both of the XRD patterns have mullite has the major phase with no trace of cristobalite or α-alumina.
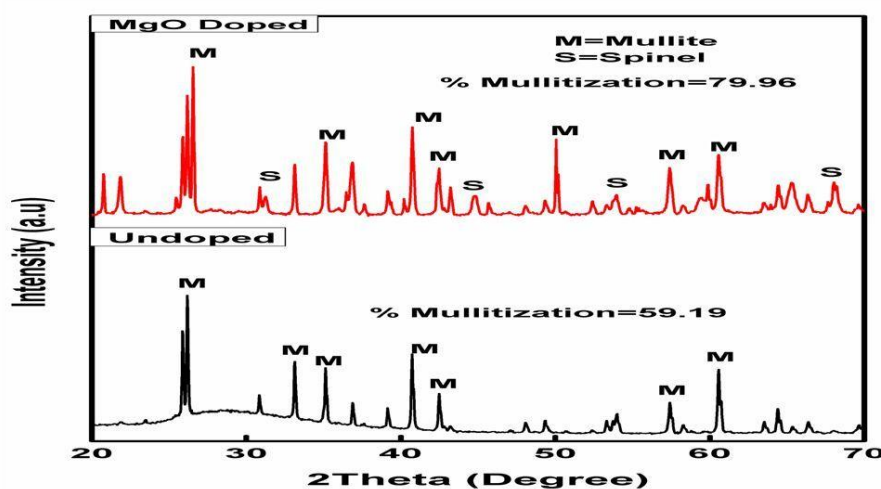
Figure 8. XRD pattern of MgO doped and undoped mullite aggregate.

This is an evidence that mullitisation has been completed at 1600°C and with raw material ratio of 50:50 kaolin-reactive alumina. Almost a single phase mullite was achieved. The splitting of peaks was observed around (2θ) 26° for both the doped and undoped samples. It was however more prominent for the doped sample. This splitting peak might be as a result of abrupt mullite composition change from primary mullite $2Al_2O_3.SiO_2$ (aluminium rich) to secondary mullite $3Al_2O_3.2SiO_2$ [10, 23]. In addition, observed in the doped sample is the presence of $MgO-Al_2O_3$ spinels. The spinel is mainly magnesium aluminate. From the $MgO-Al_2O_3-SiO_2$ phase system, MgO has the ability to produce Mg-Al spinel at very high temperature [24]. Meanwhile in aluminosilicates, when the peritectic point (1587°C) is exceeded, the equilibrium phases observed are mullite, α-alumina and a liquid phase. There is usually no occurrence of spinel above 1587°C according to the phase diagram [24]. Therefore, the occurrence of spinel as seen in the XRD pattern of Fig. 8 could have been as a result of the devitrification of the liquid phase during the cooling of the samples. Studies have however shown that mullite grain growth

is enhanced during devitrification and entrapment of precipitates [10, 25]. This is the reason for the 35% increase in mullitisation observed upon doping with MgO (4%).

In addition, the spinel formation as observed in the XRD may also be as result of the difficulty experienced in the inter-diffusion of Mg^{2+} and Al^{3+} ions due to the former's relatively large ionic size, thereby leading to the formation of magnesium aluminate ($MgAlO_6$) alongside the mullite. However, the presence of this spinel causes a decrease in viscosity in the melt during sintering which in turn causes an increase in the liquid phase. This increase in liquid phase observed promotes grain growth and increases the aspect ratio of the formed mullite and also increase the amount of mullite formed as shown in the XRD (Fig. 8).

4. Conclusion

Mullite was successfully synthesized via solid state sintering of Nigeria sourced Kaolin at 1400-1600°C. The presence of MgO and Cr_2O_3 dopants positively affected the degree of mullitisation of the sintered mullite. The presence of these additives also improve the physico-mechanical properties of the sintered mullite owing to enriched microstructure and positive phase evolution. However, the MgO doped sintered mullite showed better mechanical properties when compared to the Cr_2O_3 doped mullite owing to spinel formation as observed in the phase composition.

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