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Evaluation of Nigerian Source of Kaolin as a Raw Material for Mullite Synthesis

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ABSTRACT

In the present study, a new source of kaolinitic clay ($Al_2O_3.2SiO_2.2H_2O$) collected from Abule Onikosin Road in Abeokuta area of Ogun State, Nigeria was first processed to remove the stony materials adhered to its surface and subsequently characterized with respect to its chemical analysis, TG-DTA, particle size spectrum and identification of mineralogical phases by XRD technique. The identified endothermic peak at 516.39°C for dehydroxylation in the DTA curve and observed deformed XRD profile confirm that the clay belongs to disordered kaolinitic clay. The high SiO_2 content (59.26 wt%) compared to theoretical value (46.54 wt%) of well-ordered kaolinite is due to excess silica and this has been revealed in XRD pattern as quartz peak. The compact samples of this processed clay powder on heating in the temperature range of 1400-1600°C resulted almost densified and impervious sample at 1600°C. The densification occurred by viscous flow mechanism. Silica together with impurity oxides (Fe_2O_3, TiO_2) in the clay forms glassy phase in the above temperature range and that accompany the formation of mullite ($3Al_2O_3.2SiO_2$) crystals. The XRD and FESEM studies conducted on heated samples revealed the formation of mullite needle, the amount and aspect ratio of which increases with increase in heating temperature. The EDAX studies confirm the presence of Al, Si, O as major elements which also support mullite formation in the heated compact samples. This new sources of kaolinitic clay identified in Nigeria is found to be suitable for mullite synthesis and it is advantageous due to its low temperature mullitization unique microstructure.

Keywords: Kaolinite, disordered structure, mullite, TG-DTA, phase transformation, sintering.

INTRODUCTION

Kaolinite, the most common clay mineral, has the theoretical formula $(OH)_4Al_2Si_2O_5$ (frequently expressed as $Al_2O_3.2SiO_2.2H_2O$). When pure, it has the composition (by mass) of alumina 39.56 %, silica 46.54 %, water 13.90 %, with a 1:1 sheet silicate structure composed of a $[Si_2O_5]^{2-}$ layer and an $[Al_2(OH)_4]^{2+}$ layer. Commercial kaolin contains 80 - 90% of the clay mineral, contaminated mainly with quartz and fined grade mica or hydrous mica but seldom with appreciable proportions of feldspar[1, 2].

Kaolin is usually produced by the weathering of pegmatites or micaceouschist. Pegmatite has been mentioned to contain kaolinised alkali-feldspar with quartz and abundant mica[3]. Hydrolysis, desilication and hydration are the typical reaction sequences for the formation of kaolin[4]. It is reported that the reactions continue not only by chemical means but also by colloidal transfer. Improper removal of potassium by weathering process may lead to the formation of illitic clays (2:1 sheet silicates) instead of kaolinite. Kaolin is found in two types of deposits[5, 6] namely (a) as residual kaolin, where the clay is found replacing their parent rock from which it was formed and (b) as sedimentary kaolin, composed of particles transported from the original point of formation by stream action and settled in deposits at the bottom of relatively quiet water, often with some alteration. The purity of residual kaolin depends on the purity of the parent rock, the completeness of decay, the amount of unwanted components lost by solution and the amount of impurities brought in from other sources. Sedimentary kaolin is seen as clay materials that have been washed out of rock masses and deposited in stratified layers by the action of water. Purification takes place both during transport and in the deposit. Both highly and poorly crystalline variety of kaolin occurs in different deposits. The degree of crystalinity of clays is generally expressed as the “Hinkley Index”[7]. The degree of crystalinity depends on extent of ionic substitution within the octahedral and tetrahedral layer of kaolinite lattice. Highly crystalline kaolin offers lower plasticity due to lower charge imbalance in the lattice, whereas poorer crystalinity kaolin offers considerably more plasticity.

Kaolinitic clay mineral is one of the major raw materials for the production of various types of ceramic products having certain valuable properties. Most important one is the formation of mullite crystals during heating at higher temperatures which has several applications in ceramic products by providing good mechanical strength to the body. The applications for many clay based ceramic products are determined by their physical properties which, in turn, may depend on their chemical and mineralogical composition and particle size[1]. Mullite crystallization is a common phenomenon involving the thermal transformation of kaolinite[8]. Nevertheless, the amount of SiO_2 together with the impurities in kaolinite forms a glassy phase and cristoballite to accompany the formation of mullite at a temperature higher than 1000°C[9, 10]. The quantity and development of mullite phase determines the final properties of the products to a great extent. The different phases formed during heating of kaolin at different temperatures have been reported by many authors and the summarized sequence of reactions is shown below[10]. After the removal of chemically combined water, kaolin is converted to metakaolin at above 600°C followed by formation of another metastable phase alumino-silico spinel ($2Al_2O_3.3SiO_2$). In the temperature range of 950 - 980°C, primary mullite ($3Al_2O_3.2SiO_2$) starts forming together with gamma alumina, another metastable phase and amorphous silica. It is reported that gamma alumina combine with amorphous silica and by chemical reaction forms mullite in the temperature range of 1200 - 1250°C[11]. At 1240 - 1250°C temperature, secondary mullite appears together with amorphous silica. Finally, in the temperature range of 1240 - 1350°C, amorphous silica converts to crystalline cristoballite.

Above 600°C,	$Al_2O_3.2SiO_2.2H_2O$ (kaolin)	$\longrightarrow$	$Al_2O_3.2SiO_2 + 2H_2O$ (metakaolin)
950-980°C,	$A1_2O_3.2SiO_2$	$\longrightarrow$	$3Al_2O_3.2SiO_2$ + c-Al_2O_3 + SiO_2 (Primary (gamma (amorphous mullite) alumina) silica)
1200-1250° C,	c-Al_2O_3 + SiO_2	$\longrightarrow$	$3Al_2O_3.2SiO_2 + SiO_2$ (secondary (amorphous mullite) silica)
1240-1350° C	SiO_2 (amorphous silica)	$\longrightarrow$	SiO_2 (crystalline cristoballite)

A survey of clay deposits carried out by the geological survey of Nigeria identified the principal clay deposits[12]. Although some of the deposits are small, there are many that are vast and can serve as the source of raw material for the building industry[13]. Such variety of clays with higher amount of impurity oxides such as Fe_2O_3, TiO_2, Na_2O and lower amount of Al_2O_3, SiO_2 may be suitable for manufacturing building bricks but not suitable for mullite synthesis due to inadequate $Al_2O_3 : SiO_2$ ratio and presence of higher amount of impurity oxides. In a typical properties in the phase analysis of ceramics materials indicates the importance of $Al_2O_3 : SiO_2$ ratio in the type of shapes that will encourage mullite formation[14]. Good quality kaolin is found in Kastina state of Nigeria and it is certified by mining experts as one of the best and cleanest kaolinitic mineral resources that lie beneath kankara soil[15,16]. The clay was characterized with X-ray diffraction studies and result shown that kaolinite is the dominant mineral phase with minor amounts of quartz, goethite and muscovite[16]. It was reported that low kaolinitic clays can also be used in the production of geopolymer bricks after calcination[17]. Ekiti state of Nigeria has shown sedimentary and secondary deposition of clays in very large quantities. Geologically, these clays were mainly found to be refractory clay group after some scientific examinations. A study exploited the characteristic properties of Ekiti-kaolin mineral and reported new areas of applications in glass matrix composites, reinforced particles in friction lining material in addition to the existing development of ceramic brake pad for automobile industry[18]. Several authors studied the suitability of Nigerian sources of kaolinitic clay minerals for the development of refractory products[19,20]. Another study examined the fundamental properties of different soil sample of clay from Ebonyi state of Nigeria[21]. The findings of the research work would help in oil prospecting operations, process modification and development of clay refractory products particularly for foundry[22].

In the present study, an attempt has been made to evaluate a particular source of kaolin collected from Abule Onikosin Road in Abeokuta area of Ogun state which is located within latitude 7°8'32" N and longitude 3°27'3" E south western part of Nigeria as a raw material for the synthesis of mullite ($3Al_2O_3.2SiO_2$) which is considered to be an important precursor for variety of ceramic products. The detail physico-mechanical properties, phase and microstructural evolution on heating this kaolin at higher temperatures have been investigated and various application possibilities of mullite thus obtained have been discussed.

EXPERIMENTAL

The kaolinitic clay mineral was collected from Abule Onikosin Road in Abeokuta area of Ogun State, Nigeria and it was dried and agglomerated lumps were broken to separate the stony materials adhered to the clay mass. After separating the stony materials, the clay was wet milled in a pot mill for four hours after which the clay slurry was sieved through 60 mesh BS sieve. The slurry passed through 60 mesh and was collected and dried in an oven till the moisture content reduced to less than 0.5 wt%. The dried mass was powdered and the following tests were conducted.

Chemical analysis

Different analytical techniques were used to determine the chemical constituents present in the above processed clay. SiO_2 and Al_2O_3 were estimated by volumetric method. CaO and MgO were determined complexometrically and Fe_2O_3 and TiO_2 were determined by spectrophotometry method[23]. Na_2O and K_2O were determined by flame photometry and loss on ignition by usual technique.

Thermo-gravimetric and Differential thermal analysis (TG-DTA)

The thermo gravimetric and differential thermal analysis of the processed clay sample was performed in a non-isothermal condition and in nitrogen atmosphere up to 1250°C at a heating rate

Table 1: Chemical analysis of the processed Clay

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

of 10 °C/min using simultaneous TG-DTA apparatus [NETZSCH STA 449].

Particle size analysis

The dry powdered sample was subjected to particle size distribution measurement using particle size analyzer [Microtrac S 3500].

X-ray Diffraction studies

The minerological phases present in the processed clay sample were determined using X-Ray diffractometer [PAN Anlytical], using CuKα radiation. The XRD data were recorded in step-scan mode with step size 0.05° (2θ) and step time 75 sec from 10-80°.

Table 2: Particle size distribution of the processed clay powder

Percentile	10.00	20.00	30.00	40.00	50.0 (d50)	60.00	70.00	80.00	90.00	95.00
Size (µm)	1.247	1.321	1.404	1.515	1.655	1.827	2.056	2.403	3.4	4.04

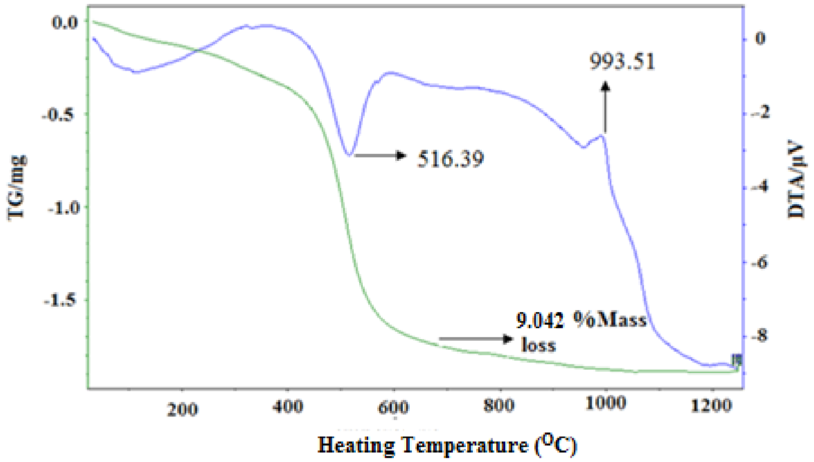

Fig. 1: Simultaneous thermo gravimetric and differential thermal analysis of processed clay

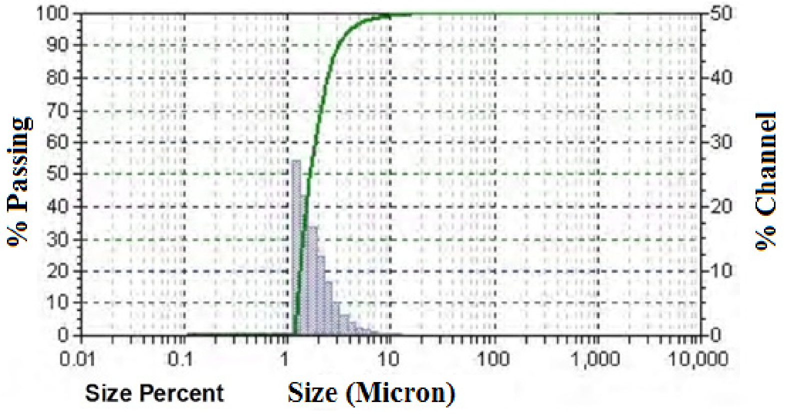

Fig. 2: Particle size analysis of processed clay powder

After characterization of the processed clay, the powder was moistened with 5- 6 wt% water and rectangular samples (65 mm × 14 mm × 5 mm) were prepared by compacting in a hydraulic press at a pressure of 350 Kg/cm^2. The pressed samples were dried in an oven at a temperature of 110°C for 24 hrs. The dried samples were then subjected to heating in the temperature range of 1400-1600°C. The heated samples were finally subjected to the following characterization: Percent Linear Shrinkage (%LS); Bulk density (BD); Percent Water absorption (%WA) and Percent Apparent porosity (%AP); Flexural strength; X-ray diffraction studies for phase identification; Field emission scanning electron microscopic study and energy dispersive X-Ray analysis (FESEM and EDAX).

The percent linear shrinkage was determined by measuring length of the sample before firing and after firing. Bulk density, percent water absorption and percent apparent porosity were measured by conventional water displacement

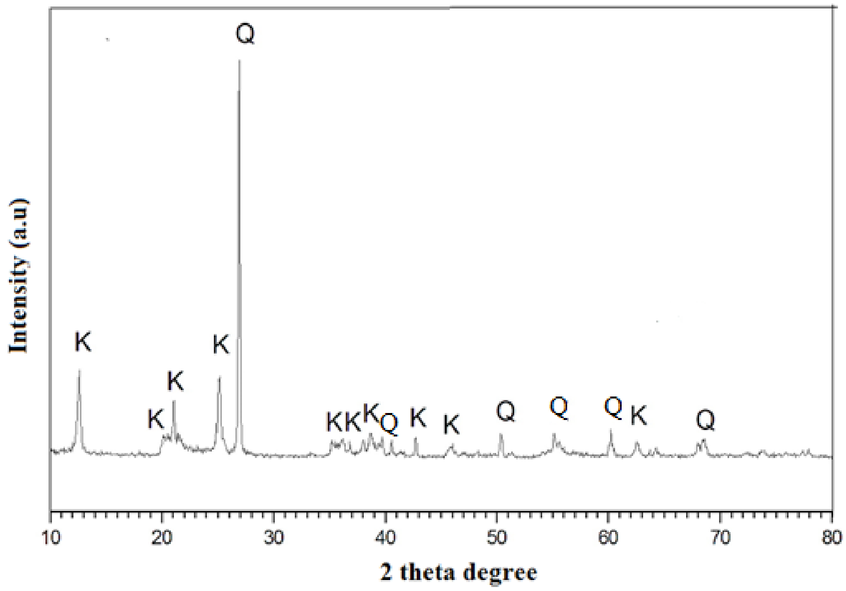

Fig. 3: X-Ray Diffraction pattern of processed Clay sample [K=Kaolinite, Q=Quartz]

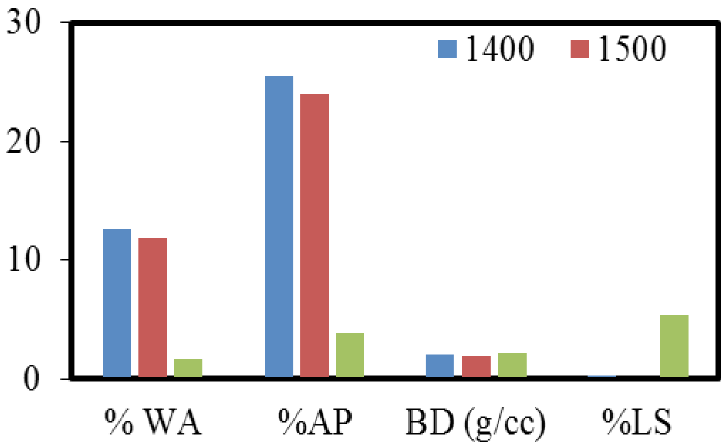

Fig. 4: Variation in LS, BD, WA and AP of fired Clay samples with heating temperature

method following Archimedes principle. The flexural strength of the heated samples were determined by three point bending method using INSTRON 5500R. For scanning electron microscope study, samples were grinded with SiC powder and water and then the samples were polished with diamond paste. The polished surfaces of each sample were with water and acetone followed by gold coating [Edwards, Scancoat]. Secondary electron image (SEI) of etched surface was observed by FESEM [Zeiss]. For EDAX analysis OXFORD was used.

RESULTS AND DISCUSSION

Characteristics of the processed kaolinitic clay

Table 1 provides the results of chemical analysis of the processed clay material. This clay contains higher amount of SiO_2 (59.26 wt%

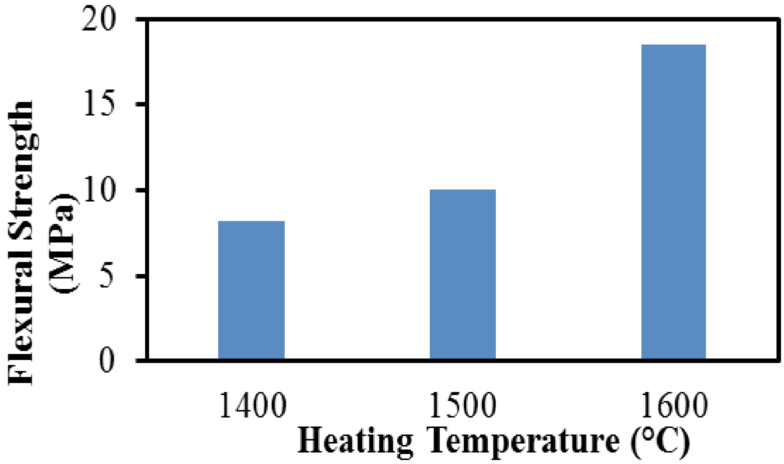

Fig. 5: Variation in flexural strength of fired clay samples with heating temperature

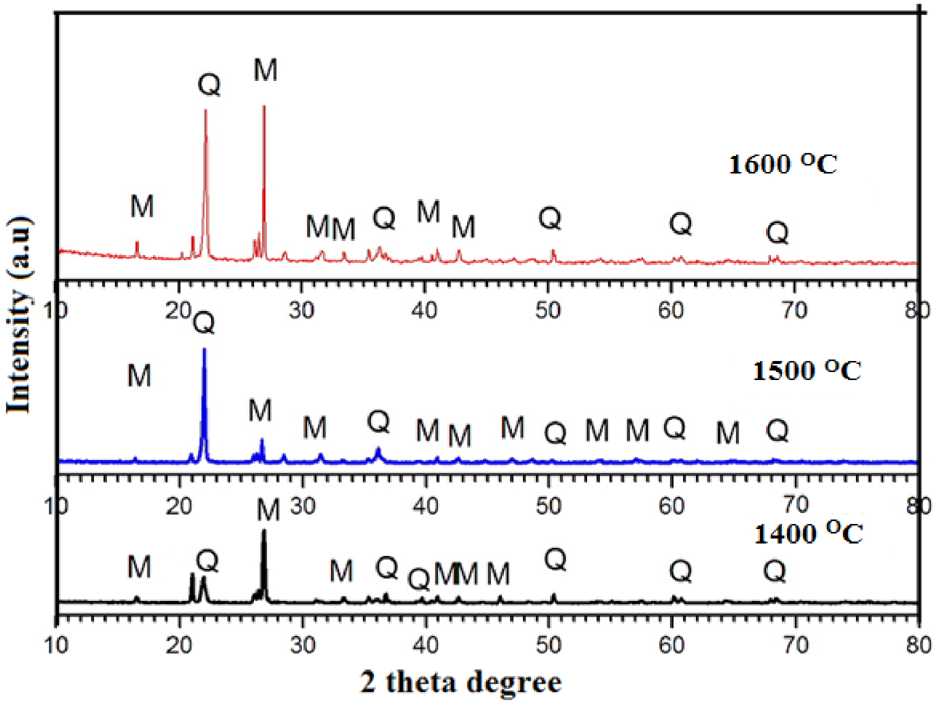

Fig. 6: XRD pattern of the fired Clay samples

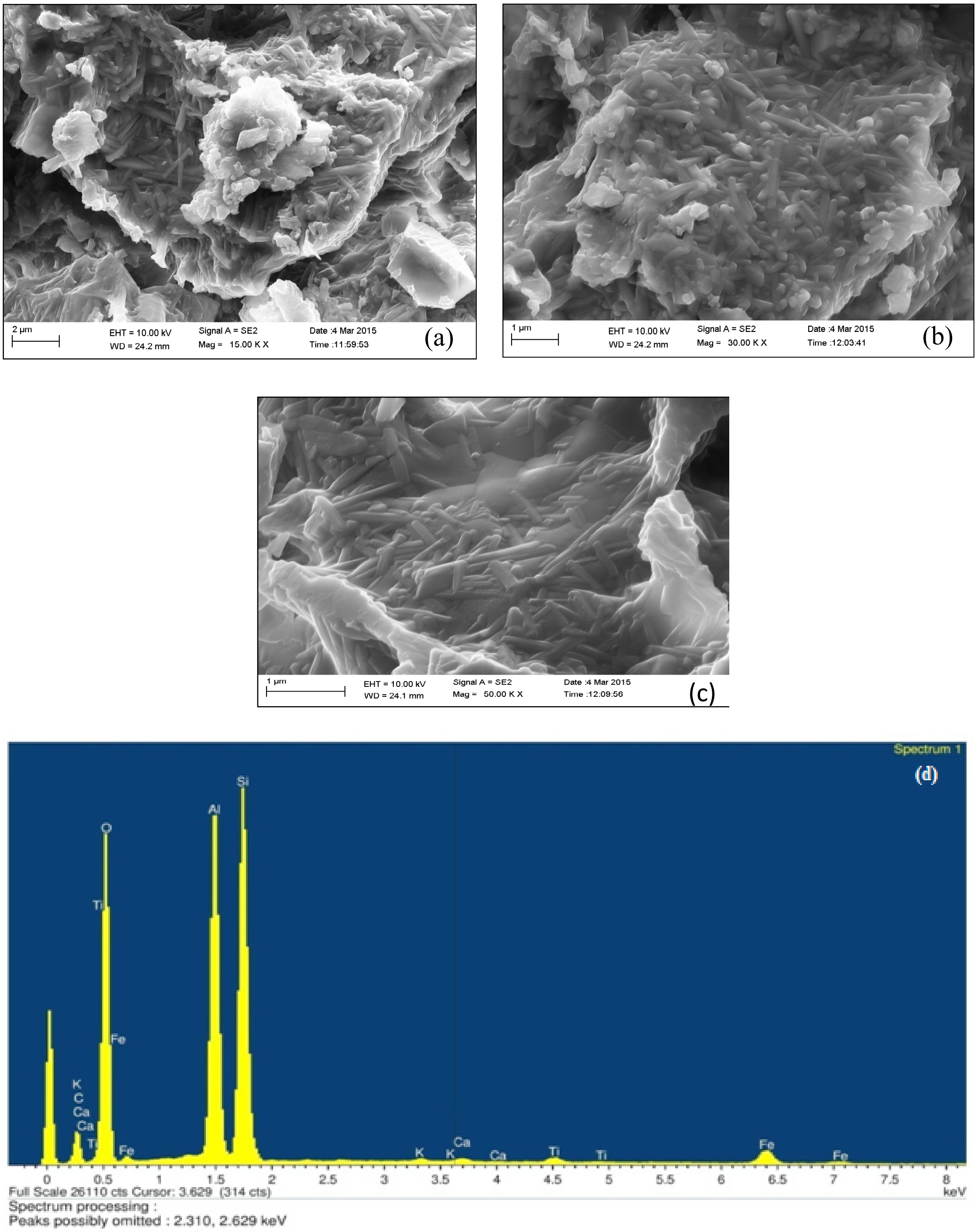

Fig. 7: Photomicrograph at 1400°C at different position and magnification

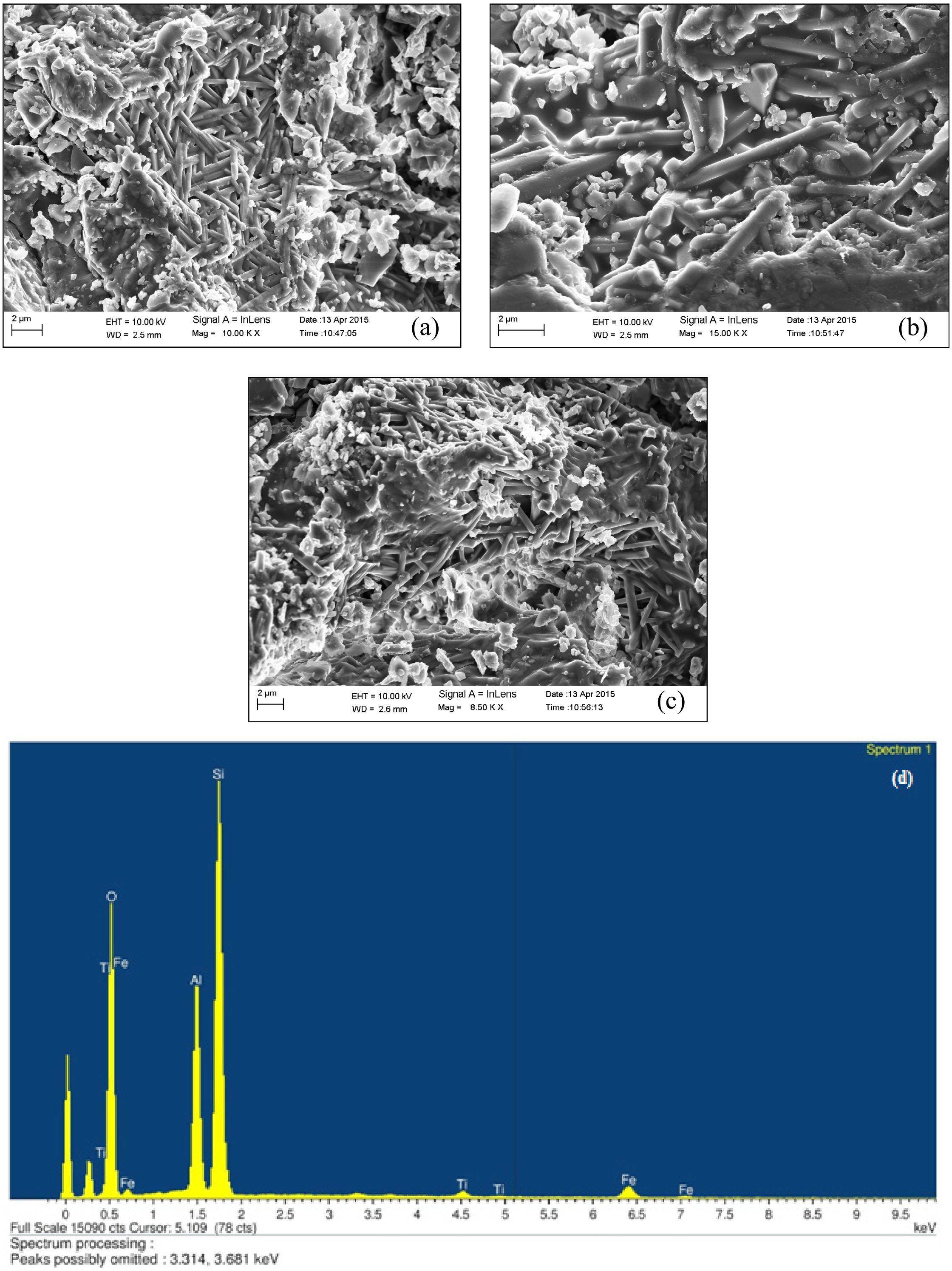

Fig. 8: Photomicrograph at 1500°C at different position and magnification

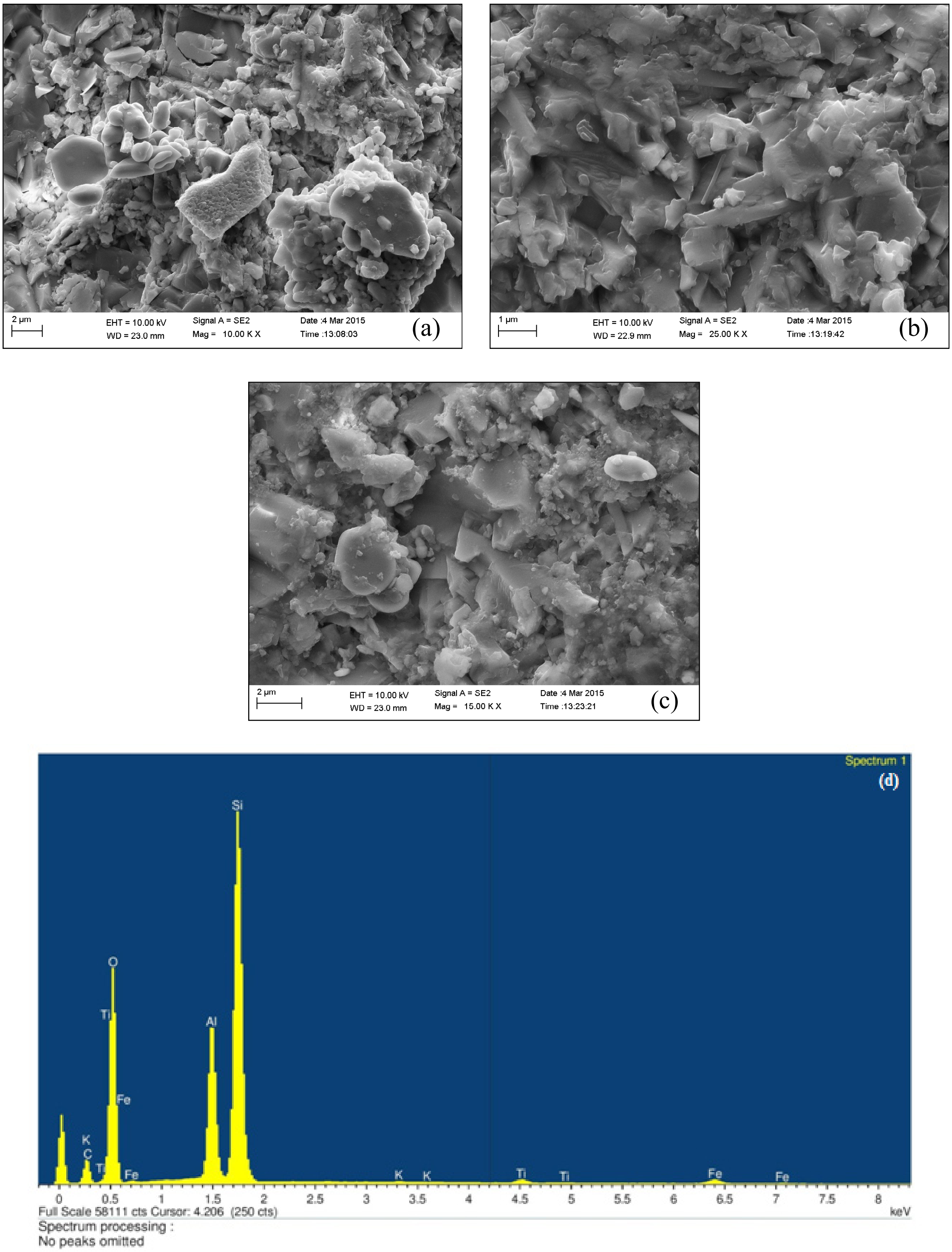

Fig. 9: Photomicrograph at 1600°C at different position and magnification

compared to a theoretical value of 46.5 wt% in pure kaolinitic clay), Fe_2O_3 and TiO_2 and lower amount of Al_2O_3. The obtained SiO_2 : Al_2O_3 ratio is also in correlation with what is obtainable in Zambia clay minerals[3]. The excess SiO_2 is due to presence of free quartz. The presence of Fe_2O_3 and TiO_2 in clay may promote sintering of the clay compact and formation of mullite at lower temperatures.

The TG-DTA study (Figure 1) revealed the presence of one endothermic peak at 516.39°C which is due to removal of water of crystallization (dehydroxylation). The temperature of dehydroxylation depends on the structural layer stacking order. It is known that disordered kaolinite dehydroxylate at less than 570°C and ordered kaolinite between 570-630°C[24]. Hence the kaolinite used in this study may be disordered type. This is confirmed by X-ray diffraction study. The exothermic peak at 993.51°C is attributed towards transformation of amorphous metakaolin ($Al_2O_3.2SiO_2$) to crystalline mullite ($3Al_2O_3.2SiO_2$). The TG curve shows 9.042% mass loss which supports the chemical analysis data.

The measurement of particle size distribution of the processed clay powder is shown in Figure 2. The nature of the curve confirms monomodal distribution with d50 value 1.655ìm. The detail particle size spectrum analysis calculated from the curve is provided in Table 2. The particle size distribution data of the clay powder provides important information for sintering the clay body. The spectrum data as obtained here confirms that the clay used in this study is finer in size and it will react faster to attain equilibrium phases.

X-ray diffraction pattern of the processed clay powder is shown in Figure 3. The XRD peaks obtained indicate that the clay used in this study mainly consists of kaolinite $Al_2Si_2O_5(OH)_4$ and quartz (SiO_2) as crystalline phases. However, when comparing the diffraction pattern with well-ordered kaolinitic clay, it may be observed that the diffraction pattern in the present kaolinitic clay is slightly deformed and this indicate that the kaolinite used in this study belongs to disordered type of kaolin which is also buttressed by the DTA result. Earlier study also revealed the disorder in the crystal structure cause deformation of X-ray diffraction profile[25]. Hence it may worthwhile to carry out a detail study on the structural disorder of these Nigerian sources of natural kaolinite using the model on computer simulation of XRD data[26]. The high intensity quartz peak observed in the diffraction pattern may be due to the presence of excess silica in the clay as found in chemical analysis.

Characterization of fired kaolinitic clay compacts

Densification study and strength development

The results of LS, BD, WA and AP are shown in Figure 4. It may be observed that %LS and BD increases with increase in heating temperature and %WA and %AP decreases with increase in heating temperature due to densification. No significant variation is observed in the temperature range of 1400 - 1500°C. However, at 1600°C, the samples are almost densified and %AP considerably reduced to 3.80% from a value of 24% at 1500°C. It can be inferred that the densification of a clay body at higher temperature proceeds by forming a viscous alumina-silicate liquid phase that permeate the pores and pull the grains together leading to consolidation of the clay matrix. Different impurity oxides namely Fe_2O_3 and TiO_2 present in the clay used in this study might have entered the glassy phase, decreasing its viscosity and made this glass more fluidised resulting in higher shrinkage at 1600°C.

Figure 5 illustrates the variation in flexural strength of the fired clay samples in relation to heating temperature. It may be revealed that with the increase in heating temperature flexural strength steadily increases and reaches its highest value (≈19MPa) at 1600°C. This is due to higher densification of the clay body at this temperature. The XRD and FESEM results discussed in later section confirm the presence of well-developed mullite crystals in the 1600°C heated samples and this has contributed towards strength development.

Phase identification and microstructural study

X-ray diffraction study was carried out to identify the crystalline phases formed during heating of the kaolinitic clay compacts at three different temperatures (1400, 1500 and 1600°C) and the pattern is provided in Figure 6. At all temperatures, quartz and mullite are the major crystalline phases observed from this XRD pattern. The effect of temperature on the mullite formation is not very significant in the lower temperature range but an increasing trend is observed at higher temperatures and it is more pronounced at 1600°C. The extent to which mullitization process proceeds depends upon the extent of order of the kaolinite. It has been reported that well-ordered kaolinite affords maximum opportunity for the formation of mullite since the proper alignment of octahedral elements carried over into metakaolinite is in accord with the requirements imposed by the mullite lattice[27]. Since the kaolinite used in the present study is disordered type, its mullitization behaviour on heating is different from well-ordered kaolinite. In the present investigation, mullitization occurred also in presence of foreign ions (Fe^{+3}, Ti^{+4}) which help to form mullite from the glass by replacing Al^{+3} in its structure.

The microstructural studies on the samples heated at three different temperatures was conducted using Field Emission Scanning Electron Microscope (FESEM) technique. The microphotographs have been shown in the Figures 7, 8 and 9 for 1400, 1500 and 1600°C heated samples respectively along with their EDAX results. Clusters of well-developed mullite needles were observed in 1400°C heated compact itself due to the presence of large amount of liquid phase (Figure 7). The existence of liquid phase encourages the exposure of low-energy crystallographic faces. Mullite needles which exhibit low-energy faces are therefore formed. The aspect ratio of mullite crystals increases with increase in heating temperature. The mullite needles observed in 1500°C heated compacts is larger than 1400°C specimen (Figure 8). An earlier study examined the microstructure evolution of mullite during sintering of kaolin powder compacts and observed almost similar findings in their 1400 and 1500°C heated specimens[28]. However, very well crystallized mullite needles were seen throughout the matrix in their samples without any quartz grains which may be due to use of well-ordered pure variety kaolinitic clay. Due to the presence of excess silica in the presently used kaolinitic clay, few quartz grains are also observed in the matrix. The EDAX analysis reveals the presence of Si, Al, O as major element which supports the formation of mullite.

The microstructure of 1600°C heated specimen looks more compact (Figure 9) due to maximum densification. The matrix is wetted by formation of more liquid phases at this temperature. Another study investigated the microstructure evolution and phase transformation of different sintered kaolin powder compacts and found that densification of kaolinite compact take place through viscous flow during heating at high temperatures as we observed in our present study[29]. The EDAX analysis of 1600°C heated specimen also confirms the presence of Si, Al and O and support the formation of mullite.

The mullite synthesized from the Nigerian kaolin in the present study may be tried in its aggregate form of different size fractions for the production of medium duty refractory products.

CONCLUSION

A Nigerian source of Kaolin used in this study is a disordered type of kaolinitic clay as confirmed by DTA and XRD results. High SiO_2 together with the impurities Fe_2O_3 and TiO_2 in the kaolin forms glassy phase to accompany the formation of needle shaped mullite at 1400°C itself and mullite content increases with increase in heating temperature. Densification of the kaolin compacts takes place through viscous flow mechanism and the highest densification is achieved at 1600°C. The mullite needles are formed in-situ within the compacts during sintering. The study revealed that the mined kaolin can be utilized for the synthesis of mullite after physical beneficiation. Advantages of using this presently available Nigerian source of kaolin powder as the starting material for mullite synthesis are (1) low temperature mullitization and (2) unique microstructure. Attempts will be made in future work to increase the mullite content further by adding very fine calcined alumina to this processed clay powder which will react with excess SiO_2 and form mullite. Selective dopants will also be utilized to stimulate sintering process.

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