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Characterization and Potential Ceramic Applications of Kaolinite Clay from Okelele, Ilorin, Kwara State, Nigeria.

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Abstract

In this study, the characteristics of Okelele clay were investigated using microscopic and spectroscopic techniques for its potential ceramic applications. The raw clay sample was beneficiated by wet sedimentation and separated from impurities through a 63 µm standard sieve. The purified clay sample was characterized using X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy interphase with Electron Dispersive X-ray Spectroscopy (SEM/EDX) and Thermogravimetry/Differential Scanning Calorimetry (TGA/DSC) techniques. The XRD pattern revealed the purified clay to be composed of predominantly kaolinite (66.22%) with a substantial amount of quartz (29.76%) and a trace amount of sanidine and cowlesite. The clay morphology exhibits non-spherical particles of various sizes with thermal phase transition stability above 450 ^{o}C. The EDX analysis revealed high alumina and silica content with substantial concentrations of free silica and iron oxide that can improve mechanical properties and withstand thermal conditions. From the results of the chemical characterization, the clay offers potential applications for ceramics, porcelain, pottery production and high-temperature refractories applications.

Keywords: Ceramics, clay, kaolinite, mineralogical composition.

1.0 Introduction

Clay minerals are naturally occurring materials composed primarily of very tiny crystalline minerals resulting from the chemical weathering of granite and feldspathic rocks (Akwilapo and Wiik, 2003). They are very small, colloidal-sized crystals (diameter less than 1.0μm), and the individual crystals are in the form of tiny plates or flakes consisting of many crystal sheets which have a repeating atomic structure and the different types of clay minerals are determined basically by the structure (Aramide *et al*., 2014). Clay minerals are classified into groups on the basis of variations of chemical composition and atomic structure as kaolinite, illite, vermiculite, smectite and chlorite groups (Bergaya *et al*., 2006; Aramide *et al*., 2014).

Naturally occurring kaolinite clay is the oldest known ceramic material for making pottery and other earthenwares based on its plasticity. Kaolin, a white, soft, and plastic-hydrated aluminium silicate clay mineral ($Al_2Si_2O_5(OH)_4$) is the most important clay that offers a wide range of ceramic properties (Burst, 1991; Bergaya *et al*., 2006; Abu *et al*., 2018). Large deposits of clays mainly in the mineral form of kaolinite are found in Sub-Saharan Africa. Millions of metric tonnes of kaolin clay in deposits are found across the regions of Nigeria (Manukaji, 2013; Aramide *et al*., 2014). For ages, various products such as earth blocks fired bricks, and kitchen utensils have been produced from clay (Tiffo *et al*., 2015). Pottery technology is an ancient practice virtually in all major cultures worldwide. For decades, local pottery has been the traditional main utensils such as pots and local household ceramics containers in Nigeria (Aremu and Adeyemi, 2011). Clay is one of man's most ancient building materials and is still used extensively in infrastructure today. The ceramics industry, including the clay and concrete sectors, remained the world's biggest provider of industrial materials (Irabor *et al*., 2014). Kaolinite is a clay of choice in low-cost white ware ceramics because it is white or can be beneficiated to white in addition to its high alumina and low iron oxide content, low plasticity and high refractory properties (Burst, 1991; Ghosh *et al*., 2013).

High-engineering ceramic and technological advancement in recent decades has contributed immensely to the development of new ceramic products and more derivative products made with other materials including alumina, quartz, and polymeric membranes with little or no presence of clay. However, depending on the type of ceramics, clay is still a vital component of most ceramics, especially pottery, a minor component and additive in most advanced ceramics (Mefire *et al*., 2015). It constitutes 100% pottery and porcelain, 20 to 30% sanitary wares, and 70% stoneware tiles (Ndjigui *et al*., 2016). Apart from ceramics, the mineralogical and chemical composition of kaolin have widened its potential as a basic raw material in paper, catalyst, adsorbent for remediation of inorganic and organic pollutants, plastic, paint, ink, and pharmaceutical and cosmetics (Ahmet *et al*., 2007; Ferjani and Boudali, 2014; Lawal *et al*., 2020a).

Akwilapo and Wiik (2003), investigated the ceramic properties of Pugu kaolin clays. The chemical analysis results indicated the presence of high levels of iron oxide (1.43%) which could adversely affect the translucency of whitewares. Mineralogical, physical and mechanical features of ceramic products of the alluvial clastic clays from the Ngog-Lituba region, Southern Cameroon have been carried out using X-ray diffraction (XRD), scanning electron microscopy (SEM), thermal and physico-mechanical analyses (Ndjigui *et al*., 2016). From XRD analyses, it is found that above 900 °C, the major product of the clay is mullite which favors densification of the ceramic bodies. Other crystallized minerals content are cristobalite and hematite and the low content in fluxing agents limits the vitrification. Mefire *et al*., 2015, characterized Koutaba (west Cameroon) kaolinite clays in order to evaluate their potential use as raw materials for ceramics.

From the results, the main clay minerals were kaolinite (32–51%) and illite (up to 12%) in addition to other major phases including quartz (32–52%), goethite (6–7%) and feldspars (0–4%). The chemical composition showed variable amounts of SiO_2 (60–72%), Al_2O_3 (15– 20%) and Fe_2O_3 (1–9%), in accordance with the quartz abundance in all of the samples studied.

In this study, the characterization of purified Okelele clay was carried out using microscopic and spectroscopic techniques to determine its mineralogical and chemical composition and to evaluate its potential industrial applications beyond local pottery. The utilization of Okelele clay for making of making pottery materials including bricks, roofing tiles, cooking utensils, and other household items has been reported in the literature (Oladimeji *et al*., 2015).

Okelele is a settlement known for hosting several pottery workshops where traditional techniques are used in making the pottery material. The techniques used for the chemical characterization of the clay sample include X-ray Diffraction

(XRD), Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy/Electron Dispersive X-ray (SEM/EDX), and Thermogravimetry coupled with Differential Scanning Calorimetry Analyzer (TGA-DSC).

2.0 Materials and Methods

2.1 Clay sample Collection: The clay sample was collected from the traditional potter's excavation site, Okelele, Ilorin, Kwara State Nigeria (8.5122^o N and 4.5477^o E). Representative samples from the deposit site were taken using the cone and quartering techniques (Gerlach *et al*., 2002).

2.2 Sample Purification

The clay sample obtained was pulverized, sun-dried and sedimented in deionized water for 24 hours. The clay suspension was stirred to disperse the clay particles. The slurry obtained was sieved using a British standard sieve of mesh 63 µm to separate the fine clay particles from impurities. The filtrate was allowed to stand in a separation funnel for 3 hours to separate the clay particles (upper layer) from silt at the lower layer. The resulting clay particles in the upper layer were centrifuged for 30 minutes at the rate of 3000 revolutions per minute. The clay sediment obtained was oven-dried for 1 hour at a temperature of 105 ^oC and pulverized into fine particles (Lawal *et al*., 2020b).

2.3 Characterization

The clay composition of the purified Okelele clay was characterized using BRUKER, AXS D8 Advance XRD equipped with copper Kα radiation (1.5406 Å) with a scanning speed of 0.5 seconds per step at 2 theta range. The Infrared spectrum of the purified clay was recorded using a Tensor 27 Platinum ATR-FTIR working in the wavenumber range of 4000 - 400 cm^{-1}. The purified clay sample morphological image and elemental composition were studied using TESCAN VEGA TS 5136LM Scanning Electron Microscope interphase with Electron Dispersive X-ray Spectrometer (SEM/EDX). The SEM photograph was obtained from the clay sample coated with a thin film of gold and the EDX spectrum was obtained from an uncoated sample using the same instrument. The clay's thermal stability and phase changes were determined using SDT Q600 Thermal Gravimetry/Differential Scanning Calorimeter (TGA/DSC).

3.0 Results and Discussion

3.1 Characterization Results

XRD: The XRD pattern for the faces of Okelele clay particles revealed basal peaks of 001, 002, 003, and 004 at interlayer spacing observed at 2θ values of 12.4, 20.4, 36, and 51^o (Figure 1). The edges prism peaks were 020, 110, 130, and 202 at 2θ values of 20.4, 25, 35, and 38.5^o respectively. These peaks confirm kaolinite (66.22%) as the main clay mineral (Semiz, 2017; Lawal *et al*., 2022). A substantial amount of quartz (29.76%) with diffraction peaks at 2θ values of 21.0, 26.5, 50.0, and 60^o were revealed. Other minor minerals identified in the sample were sanidine (3.34%) and cowlesite (2.0%) respectively. Cowlesite $[Ca(Al_2Si_3)O_{10}.5\text{-}6H_2O]$, a calcium-rich zeolite appeared at diffraction peaks of 6.0, 11.5, 21, 23.5 and 29^o 2θ values. Sanidine $[(K,Na)(Al,Si)_4O_8]$, a feldspar alkali group that exhibits a completely random distribution of Al and Si ions among the two distinct tetrahedral layers was revealed at diffraction peaks of 13.8, 15.2, 19.5, 21.5, and 30^o 2θ values (Bernado *et al*., 2006).

FTIR: The infrared absorption bands of the clay sample is shown in Figure 2. The bands observed at 3694.66 and 3620.32 cm^{-1} represent the stretching vibration of surface hydroxyl groups and inner hydroxyl groups between the tetrahedral and octahedral sheet of the kaolinite network (Hafid and Hajjaji, 2015; Gomathy *et al*., 2021). The absorption bands located at 3429.32 and 1651.07 cm^{-1} represent the stretching vibration of H-O-H. The bands at 1114.39, 995.22, 910.17, 779.32, and 748.0 cm^{-1} indicate stretching vibration of Si-O-Si, Si-OH, deformation bands of Al-OH, and Al-O respectively. Vibration bands at 524 and 450 cm^{-1} were attributed to the Si-O-Si and Si-O-Al fingerprints of the quartz in the clay (Djomgoue and Njopwouo, 2013; El-Kasmi *et al*., 2016).

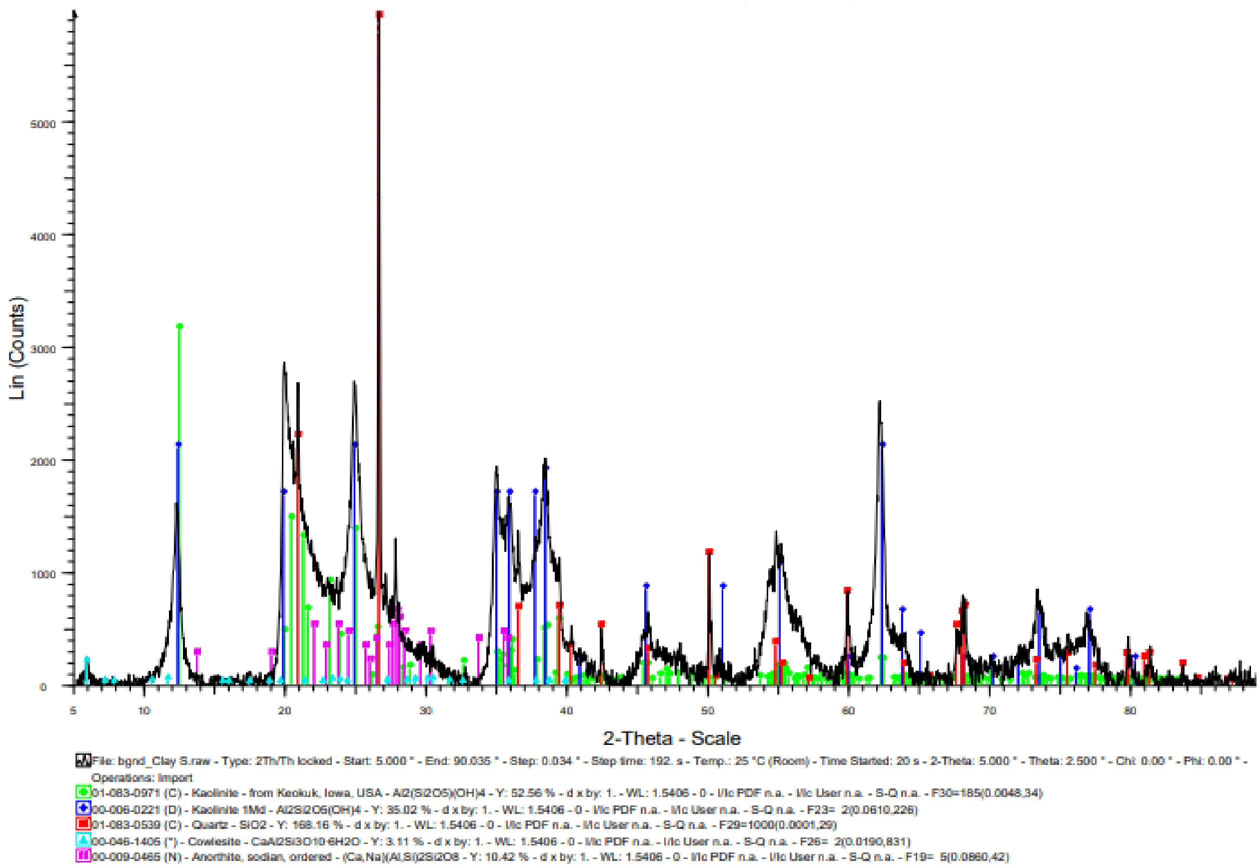

Figure 1. XRD pattern for Okelele clay

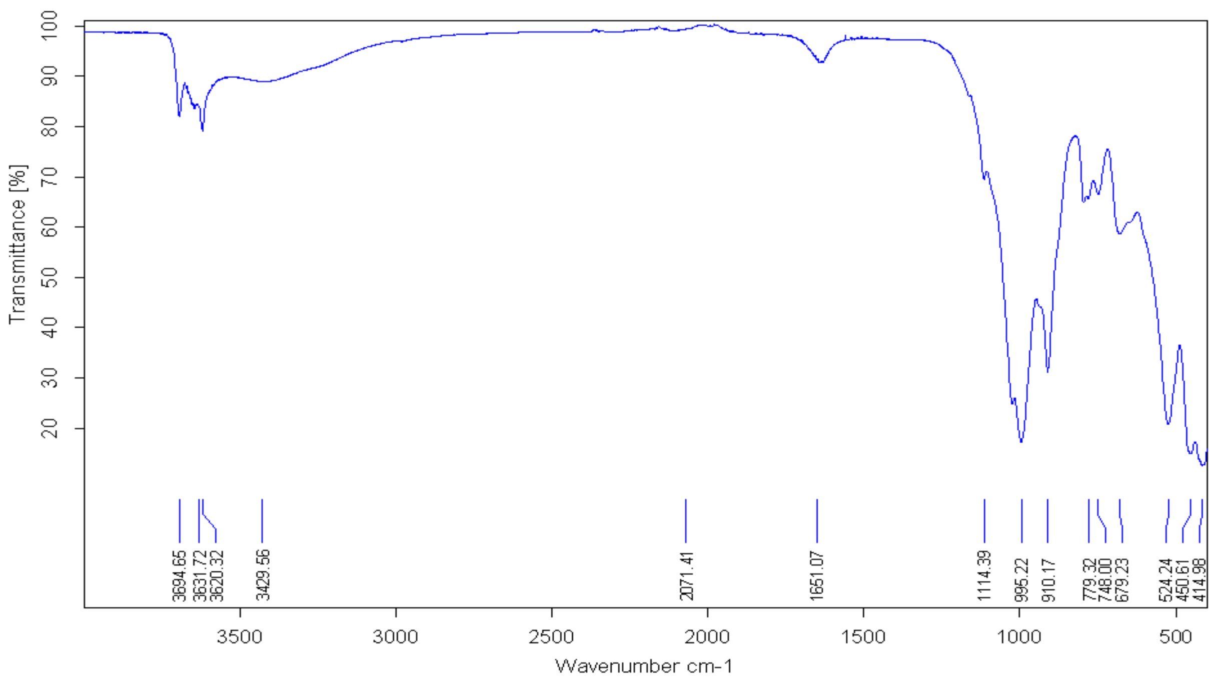

Figure 2. FTIR spectrum of Okelele clay

SEM-EDS: The SEM photographs and elemental composition of the clay (Figure 3), revealed that the structural orientation of the clay exhibits highly dispersed non-spherical particles of various sizes. The elemental composition of the clays obtained from the electron diffraction spectrum shows the predominant elements as aluminium, silicon carbon, and oxygen, and calcium, iron, and titanium as the minor elements (Figure 4, Table 1). Similar morphology and elemental composition have been reported in the literature for kaolinite (Nwosu *et al*., 2018; Lawal *et al*., 2020b).

TGA-DSC: The TGA/DSC thermal analysis measurement of the clay from ambient to 600 ^{o}C at a heat flow rate of 10 ^{o}C/min are presented in Figure 5. An initial rapid loss in weight of 5% at a temperature of up to 125 ^{o}C indicates the loss of adsorbed water molecules on the clay's surface and interlayer lattice space. The second rapid weight loss of 15% between the temperature ranges of 375 to 550 ^{o}C represents the dehydroxylation in the octahedral layer. The DSC endothermic peak at 50 ^{o}C was assigned to the structural change that occurs as a result of the dehydration of water held at the clay crystals' interlayer space.

The second endothermic phase corresponds to dehydroxylation resulting from the conversion from kaolinite to meta-kaolinite crystals at 450 ^{o}C. The temperature range at which the dehydration and dehydroxylation occur is associated with kaolinite thermal phase transition (Ndjigui *et al*., 2016; Lawal *et al*, 2022).

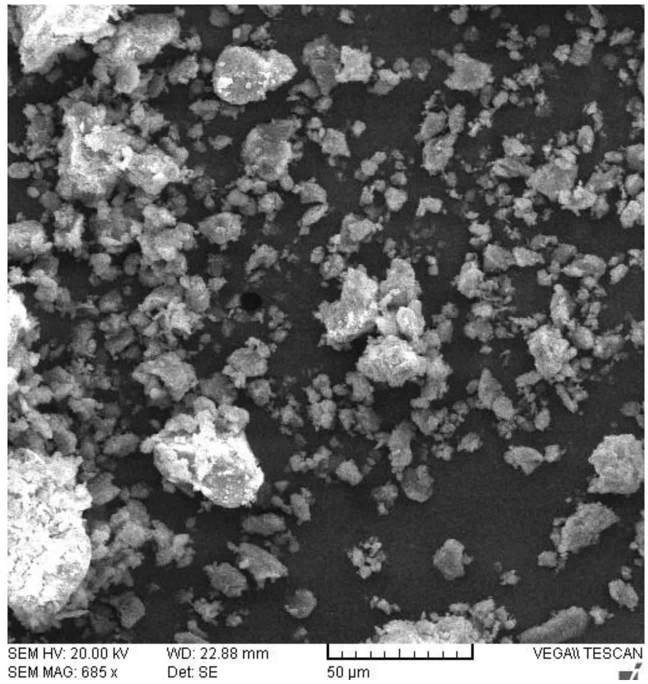

Figure 3. SEM image of Okelele clay

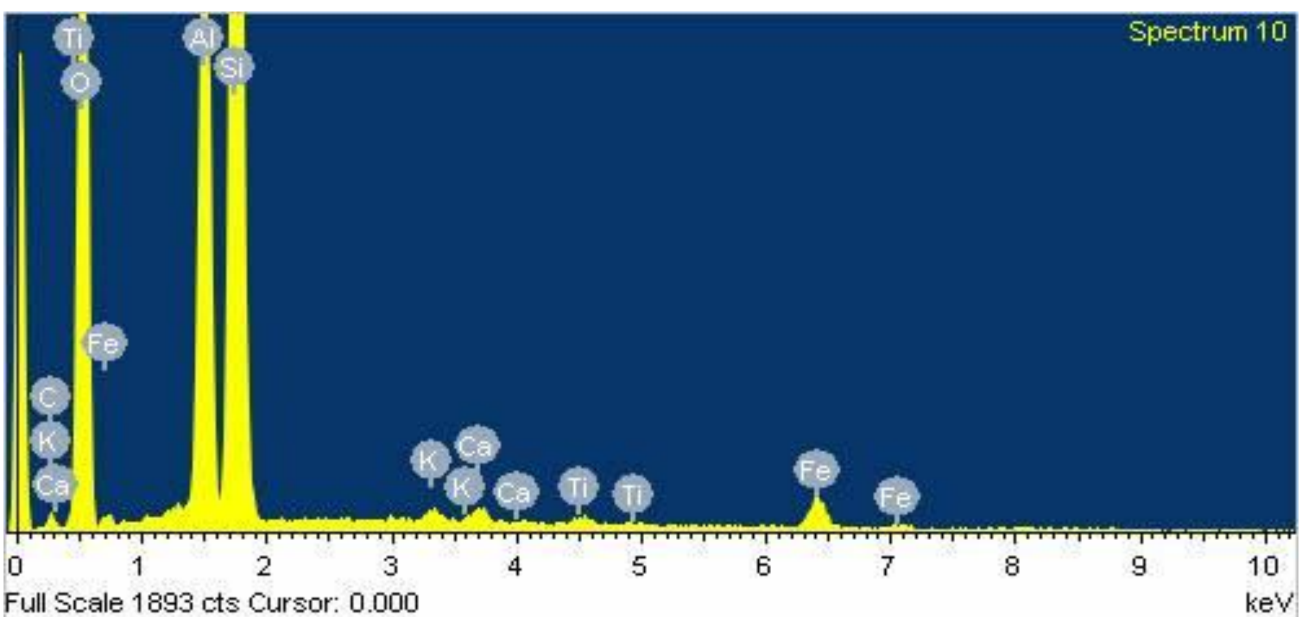

Figure 4. EDX spectrum of Okelele clay

Table 1. Elemental composition of Okelele Clay

Element	Weight%	Atomic%
C K	0.00	0.00
O K	53.01	67.16
Al K	12.57	9.45
Si K	29.91	21.59
K K	0.41	0.21
Ca K	0.57	0.29
Ti K	0.44	0.18
Fe K	3.09	1.12
Totals	100.00	

3.2 Potential Application of Okelele Clay

The chemical characterization of Okelele clay has shown it to be of satisfactory quality in pottery making and a wide range of other ceramic products. The kaolinite content and presence of quartz as revealed in the diffractogram and IR absorption bands showed the clay meets the thermal stability criteria required for porcelain, wall title ceramics (Iyasara *et al*., 2014) and pottery making; a major traditional product obtained from Okelele clay (Oladimeji *et al*., 2015). The quartz content of the clay (29.76%) conveys its usability as recommended for the porcelain industry (Akwilapo and Wiik, 2003) and the high alumina content (12.57%) basically showcases its usefulness in fire clay refractory products (Burst, 1991; Zhang *et al*., 2019; Xu *et al*., 2020).

The low alkaline and iron content and low dehydroxylation temperature of the clay make it a vital material for bio-ceramics (Liu *et al*., 2001; Manoharan *et al*., 2012; Ramli *et al*., 2022). The 0.51% by weight of calcium obtained from the EDX result shows the clay is non-calcareous. A calcium content of less than 10% by weight a required for non-calcareous pottery (Dey *et al*., 2020).

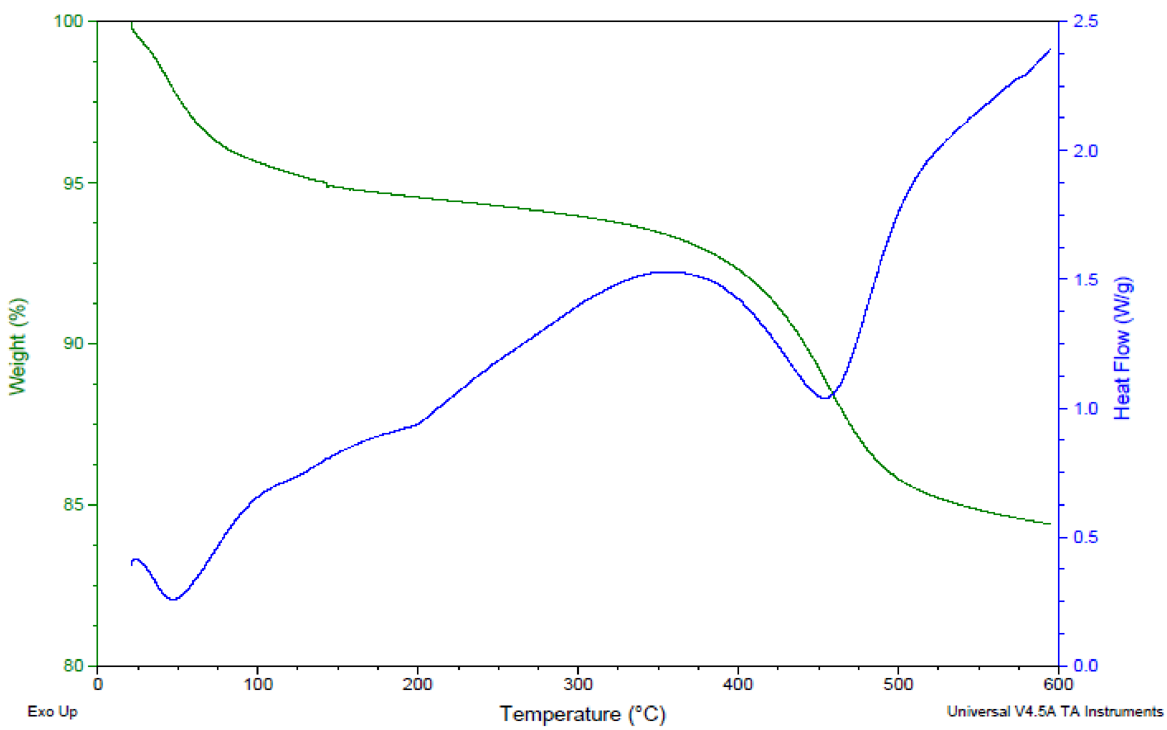

Figure 5. TGA/DSC thermogram of Okelele clay

The presence of titanium oxide (0.44%) suggests that the clay contains rutile or anatase which contributed to the red-coloured ceramic products obtained from Okelele kaolinite in addition to the presence of iron oxide (Tiffo *et al*., 2015). The clay is considered not suitable for sanitary ware because of the presence of iron oxide (3.09 weight %) whose concentration is high enough to affect the translucency. Kaolinite with iron oxide content above 1% is considered unsuitable for sanitary wares (Akwilapo and Wiik, 2003), However, the clay is considered useful for making refractory bricks and glass which requires iron oxide content in the range of 0.5 to 3.0% by weight (Elimbi *et al*., 2014; Semiz, 2017; Abuh *et al*., 2018). Also, the presence of iron oxide at a relatively high concentration improves the ceramic products' mechanical properties (Obada *et al*., 2020; Liu *et al*., 2021).

4.0 Conclusion

The Okelele kaolinite was found to be composed of principally kaolinite and quartz, and a trace amount of cowlesite and sanidine. The small amounts of fluxes such as alkali and iron oxide in the sample indicate the densification of the fired products would appear at higher temperatures. The mineralogical and elemental composition, morphology, thermal stability, alumina and silica iron content and low alkaline properties obtained from the chemical characterization satisfy its multiplicity of applications for a wide range of ceramic products beyond its local application as earthen wares and cooking utensils.

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