**Journal of Materials and Environmental Sciences**
**ISSN : 2028-2508**



**JMES, 2017 Volume 8, Issue 8, Page 2682-2838**

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# Phase and microstructural evolution during sintering of mixture of 75:25 Nigerian kaolin and calcined alumina powder compacts

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*Received 24 Aug 2016,*
*Revised 28 Sep 2016,*
*Accepted 04 Oct 2016*

*Keywords*

- ✓ kaolin,
- ✓ alumina,
- ✓ mullite,
- ✓ quartz,
- ✓ corundum,
- ✓ phase,
- ✓ morphology

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## Abstract

The microstructure progression of a uniformly mixed 75 wt% of Nigerian sources of kaolinite clay powder and 25 wt% finer grade of calcined alumina powder ($d_{50}$) of 6 - 8 mμ was investigated in this present work. The hydraulically compact samples of the mixture were heated in the temperature range of 1400 – 1600 $^{o}$C and their physical mechanical properties were evaluated. It was observed that 1400 and 1500 $^{o}$C heated samples did not show any major densification and resulted in higher apparent porosity in the range of 26 - 28%. The samples heated at 1600 $^{o}$C shows improved densification with significant reduction in apparent porosity (< 5.0%). The phase and microstructural evolution during heating of the samples were studied using XRD and SEM/EDAX technique. The results revealed the presence of quartz ($SiO_2$) and mullite ($3Al_2O_3.2SiO_2$) as major phases and corundum ($Al_2O_3$) as minor phase in the 1400 $^{o}$C heated samples while mullite, corundum as major and quartz as minor phases were identified in the 1600 $^{o}$C heated samples. The $Fe_2O_3$ present in the clay promoted the growth of the size of mullite needles. Due to the development of a largely dense compact microstructure at 1600 $^{o}$C, the flexural strength improved significantly to 45 MPa from 15 MPa obtained at 1400 – 1500 $^{o}$C. The aspect ratio of mullite crystals is higher in 1600 $^{o}$C heated samples compared to 1500 $^{o}$C heated specimen.

## 1. Introduction

Mullite ($3Al_2O_3.2SiO_2$) is known to be a very stable material at high temperatures and the low co-efficient of thermal expansion, high melting point, high thermal shock resistance and remarkable creep resistance makes it a superior material for thermal applications [1]. In addition, it has low dielectric loss property, and thus can be used to prepare electrical insulation components [2]. Several authors have adopted many approaches by which mullite could be prepared [2-11]. Chen *et al.* [2], Oluseyi *et al.* [3] and Viswabaskaran *et al.* [4] studied the mullitization behaviour of kaolin on sintering at high temperatures. The studies found that mullite is first formed at 1100 $^{o}$C and also stated that the size, shape and aspect ratio of mullite grains increased with increasing sintering temperature. Chen *et al.* [2], reported that the inter diffusion rates of $Si^{4+}$ and $Al^{3+}$ within the mullite lattice are relatively slow, the kinetics of mullite formation by reactive sintering depended strongly on the precursor mixing. The mullitization temperature for the solid state reaction between $Al_2O_3$ and $SiO_2$ powder is more than 1600 $^{o}$C [2, 5] and by coating amorphous $SiO_2$ on to the surface of γ-$Al_2O_3$ particles, the mullite can be formed at less than 1300 $^{o}$C [6]. As Si, Al, O are mixed at atomic level such as that prepared by sol-gel technique [7, 8], mullite is formed at 1150 $^{o}$C. Choudhury *et al.* [9] prepared transition metal ion doped mullite. Hydrothermal processing technique has been utilized by Somiya *et al.* [10] to prepare mullite at lower temperature while Hirata *et al.* [11] adopted Chemical Vapour Deposition (CVD) process to prepare purer grade mullite powder. The sol-gel, co-precipitation, hydrothermal and CVD processes produced chemically pure mullite powder, but these are all costly process which makes the mullite production cost to be very high.

Among available technologies, kaolinitic clay still remains the cheaper alternative source to mullite with alumina addition. In the kaolin-alumina system, it has been reported that below 1300 $^{o}$C, alumina was highly

inert and the dominant reactions were the kaolinite reaction series to form primary mullite, amorphous silica and cristoballite [12]. At above 1400 $^{o}$C, secondary mullite formation takes place from the transitory liquid phase, followed by precipitation of mullite crystals. The rate of secondary mullite formation was very slow at 1555 $^{o}$C and extremely fast at 1600 $^{o}$C due to strong effect of the eutectic liquid formation at 1550 $^{o}$C [13]. Viswabaskaran *et al.* [4] and Mcmanus [14] studied the mullitization behavior of some different sources of clays with three different sources of alumina namely reactive alumina, alumina hydrates such as gibbsite and bohemite. The results showed reactive alumina exhibited maximum mullitization, specimen with bohemite gave poor physical-mechanical properties and the impure variety clay with reactive alumina exhibited high strength but low density. The microphotographs shown mullite crystals are bimodal in size with particular clay from Neyveli, South India, when sintered with reactive alumina, resulted in mullite grains of tabular shape having rectangular faces with rounded ends [4]. Sainz *et al.* [15] studied the phase and microstructural evolution during sintering of kaolin and alumina mixtures. The study found that sintering temperature and proportionate mixture of kaolin and alumina plays important role on the phase formation and crystal morphology. Rezaie *et al.* [16] reported the differences in mullite evolution during reaction sintering of kaolin, kaolin + alumina mixture and sol-gel precursors. Mullite formation occurred at much less temperature from the sol-gel precursors [17]. The impurities present in clay particularly $Fe_2O_3$, $TiO_2$ has phenomenal role during heating of clay and clay + alumina mixtures towards formation of mullite. Presence of such impurities promotes mullite formation [17]. In one of our earlier research work [3], suitability of one Nigerian sources of kaolin was evaluated to synthesize mullite. It was observed that 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 $^{o}$C itself and mullite content increased with increase in heating temperature. Densification of the kaolin compacts took place through viscous flow mechanism and the highest densification was achieved at 1600 $^{o}$C.

In the present study, the suitability of mullite application with respect to densification and morphology development through firing of clay and clay + alumina mixture is investigated. This is achieved by mixing 75:25 kaolin and calcined alumina powder intimately, compacted in a hydraulic press and finally heated at three different temperatures in the range of 1400 – 1600 $^{o}$C. The heated compacts were subjected to the determination of physical-mechanical properties, phase and microstructural evaluation and the results are discussed in this paper.

## 2. Materials and methods

### *2.1. Experimental*

The same sources of processed kaolinitic clay (Abule Onikosin Road in Abeokuta area of Ogun State, Nigeria) which was utilized in previous work [3] and SRM-30 grade of calcined alumina supplied by Alcoa has been utilized in the present study. The characteristics of clay as evaluated in the previous work [3] and the properties of calcined alumina as provided by the supplier.

375 g of finer processed kaolin and 125 g of calcined alumina powder were intimately mixed first in dry condition and then in wet condition for a period of 30 minutes. The mixed slurry was taken in a porcelain container and dried slowly in an electric oven at 110 – 120 $^{o}$C for period of 24 h. The dried mass was powdered and 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 39.2 MPa. The pressed samples were dried in an oven at a temperature of 110 ± 5 $^{o}$C for 24 h. The dried samples were then subjected to sintering in the temperature range of 1400 – 1600 $^{o}$C. The sintered samples were finally subjected to the following characterization: Percent Linear Shrinkage (%LS); Bulk density (BD); 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 sintering and after sintering. 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 different phases formed in the sintered samples were determined using X-Ray diffractometer [PAN Analytical], using CuKa radiation. The XRD data were recorded in step-scan mode with step size 0.05° (2θ) and step time 75 sec from 10-80°. 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] and for EDAX analysis, OXFORD was used.

## 3. Results and discussion

3.1. *Properties of processed kaolin*

The green and fired properties of processed kaolin used in this study are presented in Table 1. The data revealed that the Nigerian sources of clay is siliceous type and kaolinitic in nature. The XRD findings indicated that this kaolin is suitable for mullite synthesis on heating at higher temperatures. Along with mullite, quartz grain accompanied by some glassy phases are also identified which is undesirable for purer grade mullite which is stable at high temperatures in a crystalline matrix. Hence, a finer grade calcined alumina (d50 value 6 - 8 mμ) having more than 99.9% α-$Al_2O_3$ content was added to kaolin powder in the proportion of 75 wt% kaolin and 25 wt% calcined alumina and the mixed compacts were sintered at three different temperatures namely 1400, 1500 and 1600 $^oC$.

**Table 1:** Properties of kaolin used in the present study [3]

| Properties | Value |
|---|---|
| Chemical Analysis (wt%) | $SiO_2$ - 59.26, $Al_2O_3$ - 24.04, $Fe_2O_3$ - 3.87, $TiO_2$ - 1.46, CaO - 0.39, MgO - 0.14, $Na_2O$ - 0.74, $K_2O$ - 0.30, Loss on ignition - 9.40 |
| Av. Particle size ($d_{50}$), mμ | 1.655 |
| TG-DTA | 9.042% mass loss, one endothermic peak at 516.39 $^oC$ and one exothermic peak at 993.51 $^oC$. |
| Identified phases by XRD analysis | Kaolin and quartz as major mineralogical phases. |
| Fired properties at 1600 $^oC$<br>Bulk density, g/cc<br>Apparent Porosity, %<br>Flexural Strength, MPa | <br>2.40<br>3.80<br>19 |
| Identified phases on 1600 $^oC$ heated sample | Mullite as major and quartz as minor |
| SEM observation on 1600 $^oC$ heated specimen | Needle shaped mullite uniformly distributed in the matrix and quartz grains in a scattered manner accompanied by some glassy phases |

3.2. *Physical properties of fired samples*

The variation in % linear shrinkage, bulk density and % apparent porosity of the kaolin + alumina compacts in relation to heating at different temperatures are illustrated in Figures 1 and 2 respectively. From Figure 1, it may be observed that the kaolin + alumina compact experienced very little shrinkage (< 0.25%) at 1400 and 1500 $^oC$ compared to around 3% at 1600 $^oC$.

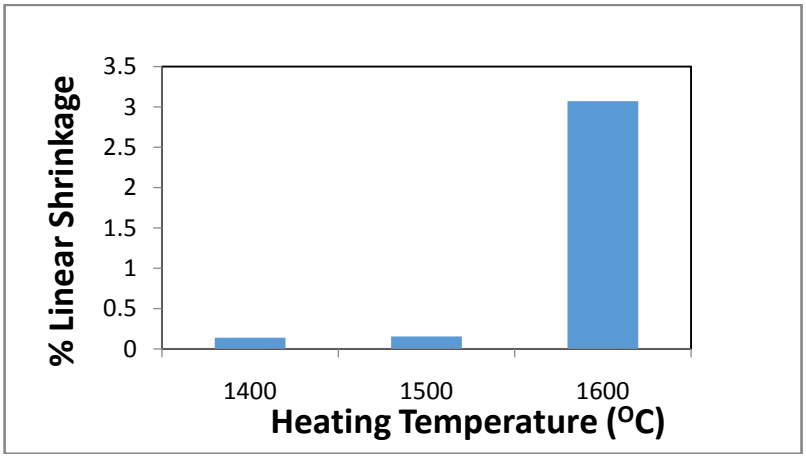


**Figure 1:** Variation in % Linear Shrinkage of kaolin + alumina compact in relation to heating temperatures.

The densification also shows significant improvement at 1600 $^oC$ where the porosity was drastically reduced to 4.8% from the value of 26 - 27% at 1500 and 1400 $^oC$ (Figure 2). This may be attributed to the fact that

alumina was largely inert within the temperature range 1400 – 1500 $^{o}$C and the dominant reactions were the kaolinite reaction series. At temperature more than 1500 $^{o}$C, the maximum densification was initiated from the reactions of kaolin and alumina. However, full densification did not occur at 1600 $^{o}$C, only 83% of theoretical density was achieved at this temperature with a porosity of 4.8%. This point to the fact that a higher temperature (>1600 $^{o}$C) is needed to get fully densified sintered product. Similar types of observations were made by other studies [12, 13] on kaolinite-alumina system.

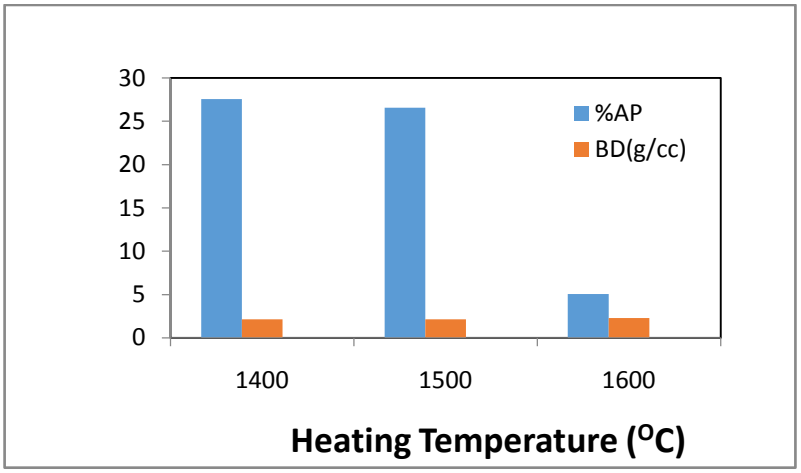


**Figure 2:** Variation in bulk density and apparent porosity of kaolin + alumina compact in relation to heating temperatures.

The gradual development of flexural strength of kaolin + alumina compacts with increase in heating temperature is shown in Figure 3. There was significant improvement in strength observed at 1600 $^{o}$C (close to 45 MPa) from a value of around 15 MPa obtained at 1500 $^{o}$C. This threefold increase in strength, even though it is not fully sintered, was due to increased densification and formation of well crystallized needle shaped mullite and corundum phases. It has been reported [3] that kaolin compact samples without alumina addition developed only 19 MPa strength at 1600 $^{o}$C which explains why alumina addition becomes essential component to kaolin for producing high strength alumino-silicate-based composites.

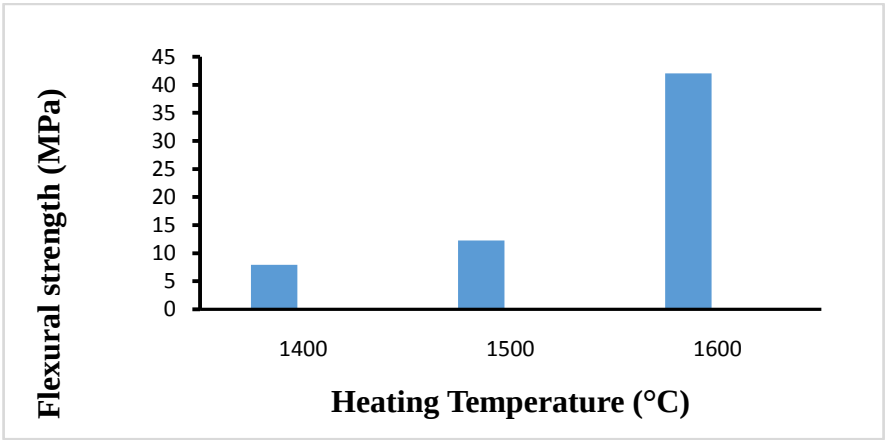


**Figure 3:** Variation in flexural strength of kaolin + alumina compacts in relation to heating temperature.

3.3. *FESEM and Energy dispersive X-ray analysis*

Figure 4 represents the XRD patterns of the kaolin + alumina composites heated at 1400 and 1600 $^{o}$C. The XRD patterns of the heated sample at 1400 $^{o}$C confirm the presence of quartz as major phase (Q) with mullite (M) and corundum (Co) as minor phases. This is because the added alumina did not react with the free quartz in the clay at this particular temperature. At 1600 $^{o}$C, mullite and corundum was observed as major phases and very few quartz peaks were seen at low intensity. This explains that alumina reacted with the free quartz present in kaolin and formed more mullite and the remaining alumina recrystallized as corundum.

The FESEM photographs of the kaolin + alumina compact samples heated at 1400, 1500 and 1600 $^{o}$C are shown in Figures 5 a, b, c respectively. At 1400 $^{o}$C, flaky shaped primary mullite and quartz grains are seen as

major crystalline phases along with unreacted alumina (corundum) and few needle shaped secondary mullite distributed in the matrix in a scattered manner. This also confirms that at 1400 $^{o}$C, alumina was mostly inert and mostly kaolin series of reactions produces mullite. At 1500 $^{o}$C, needle shaped mullite crystals gradually appeared. Bundles of mullite crystals are also seen in some other region of the same sample. At 1600 $^{o}$C, a densified compact microstructure with well crystallized mullite needles of higher aspect ratio was seen to be uniformly distributed in the matrix.

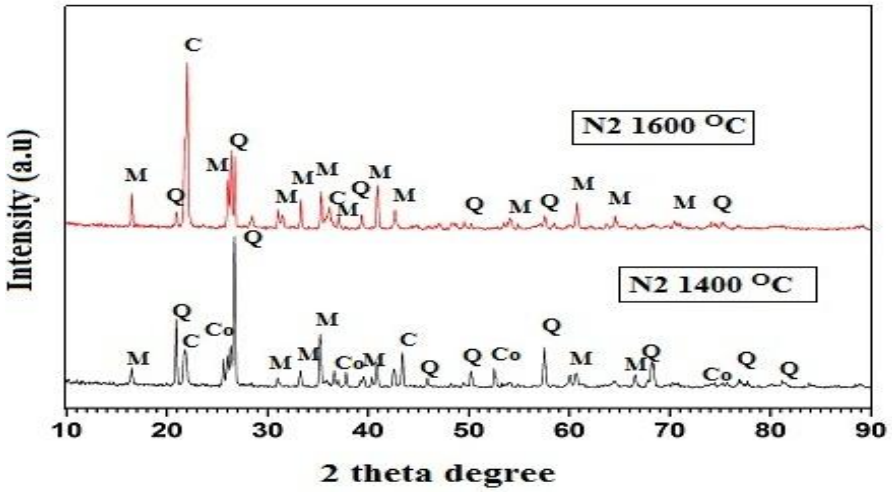


**Figure 4:** *X*-Ray diffraction pattern of 1400 and 1600 $^{o}$C heated kaolin + alumina sample.
Key: M = Mullite; Q = Quartz; C = Cristobalite; Co = Corundum

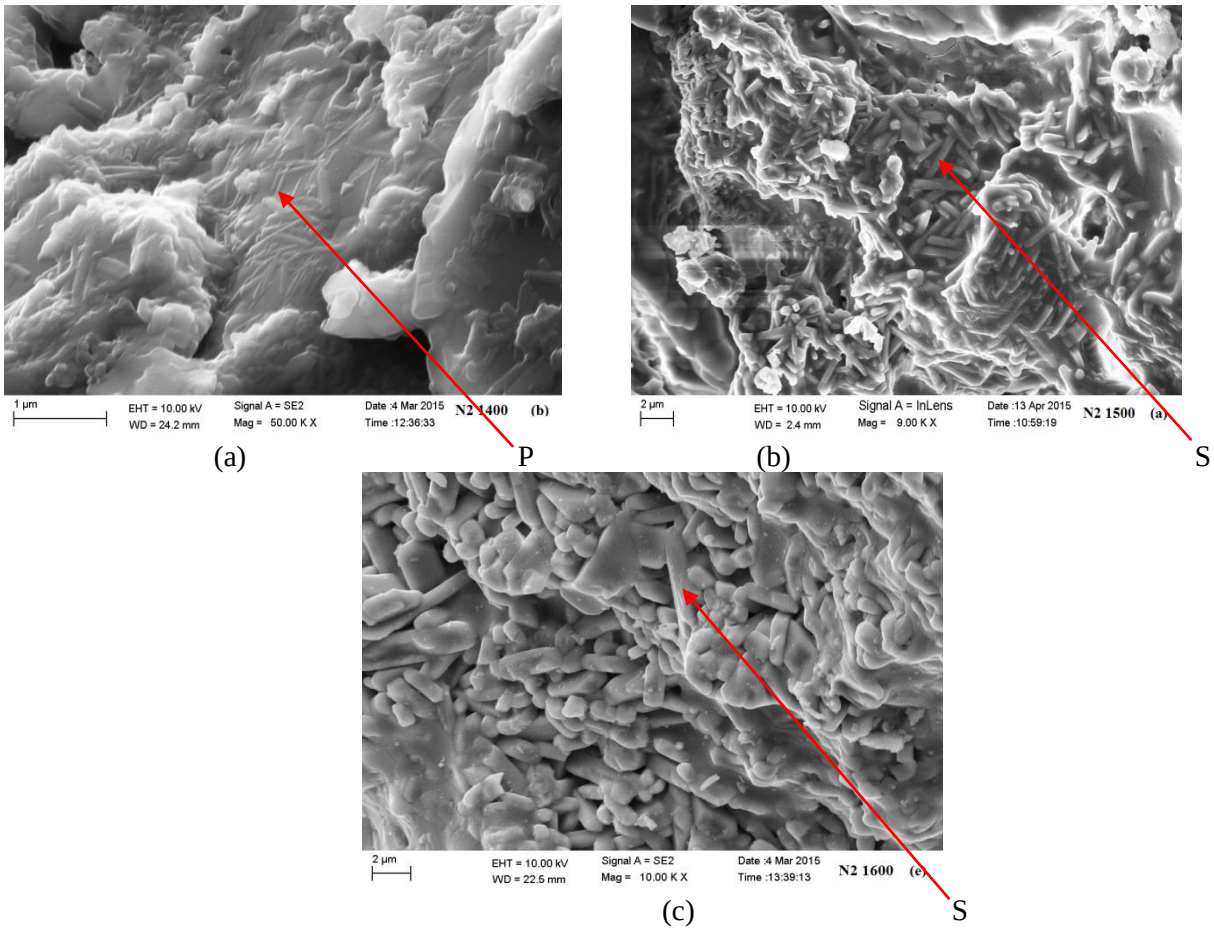


**Figure 5:** FESEM photographs of heated kaolin + alumina sample heated at (a) 1400 $^{o}$C (b) 1500 $^{o}$C and (c) 1600 $^{o}$C.
Key: S = Secondary mullite; P = Primary mullite

Few unreacted alumina recrystallized as corundum are also seen in the matrix. Due to the development of this compact microstructure consisting of mullite and corundum at 1600 $^{o}$C, the flexural strength was observed to increase threefold at this temperature than what was obtained at 1400 and 1500 $^{o}$C heated samples. The Nigerian kaolin used in this study contains around 3.7% $Fe_2O_3$ which might have contributed to the structural re-organization stage of the material, when mullite is nucleated [18]. The iron quantity attained a saturation of Fe/Al ratio between 0.3 and 0.4 depending on the crystallinity of the raw kaolin. The kaolin used in this study is a poorly crystallized material and that has resulted in the faster nucleation and growth of mullite [19]. Chakraborty [20] also confirmed that iron usually promote the growth of the size of mullite. There are no significant changes observed in the EDAX spectra of the samples heated at different temperatures (Figure 6).

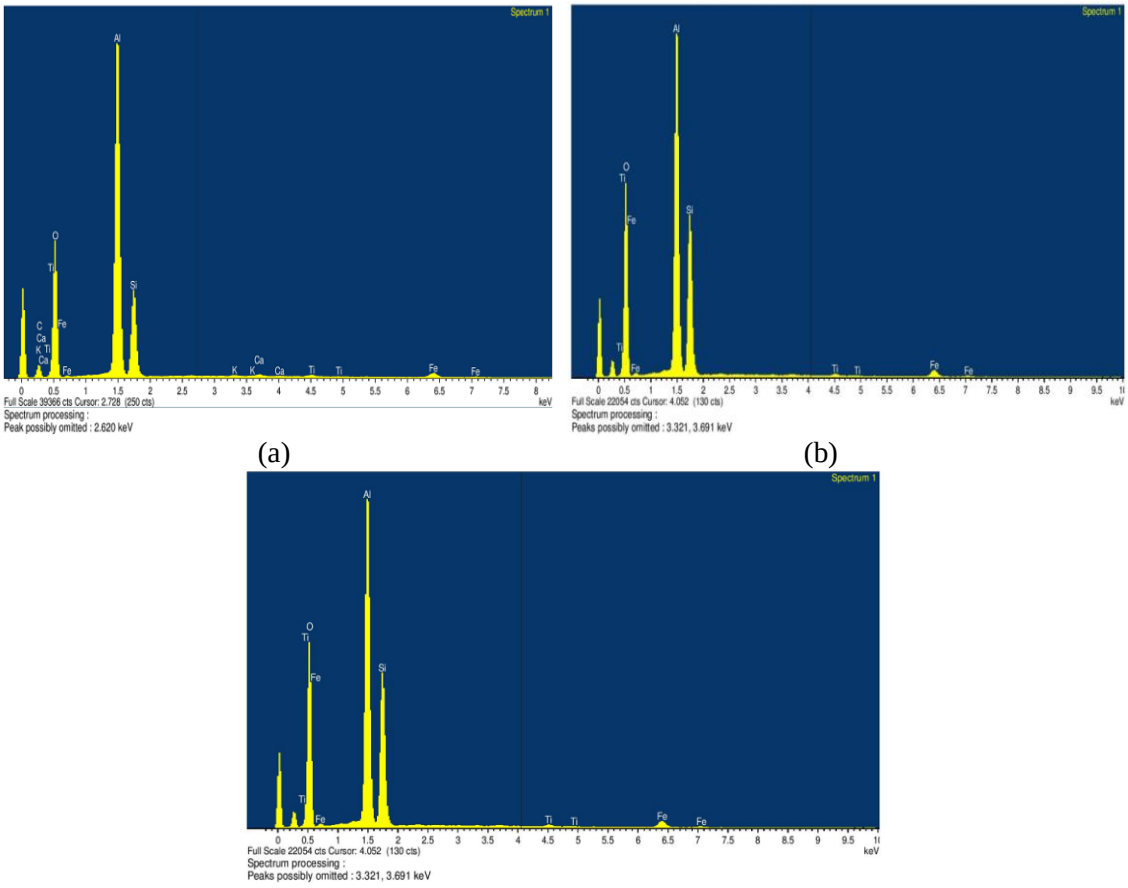


Figure 6: EDAX analysis of kaolin + alumina compact sample heated at (a) 1400 $^{o}$C (b) 1500 $^{o}$C and (c) 1600 $^{o}$C

## Conclusions

In the present investigation, a composite consisting of mullite and corundum crystals has been prepared by reaction sintering of a mixture of 75 wt% Nigerian kaolinite and 25 wt% calcined alumina powder at three different temperatures of 1400, 1500 and 1600 $^{o}$C. It was observed that very little densification occurs at 1400 $^{o}$C and alumina was mostly inert, however flaky primary mullite evolved from the kaolinite series of reactions. At 1500 $^{o}$C, although densification did not improve much, but needle shaped mullite formation nucleated at this temperature and it grew and crystallized very well at 1600 $^{o}$C. After formation of mullite by the reactions of alumina and amorphous silica, the excess alumina recrystallized as corundum crystals. Due to the development of a largely dense compact microstructure at 1600 $^{o}$C, the flexural strength has improved significantly to 45 MPa from a value of about 15 MPa obtained at 1400 – 1500 $^{o}$C. The mullite-corundum composite developed in the present study will be highly suitable in the form of aggregates for manufacturing high temperature monolithic.

## Acknowledgements

The authors are grateful to the Head of Unit, Ceramic Engineering, Calcutta University for the analysis of the samples.

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(2017) ; http://www.jmaterenvironsci.com