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**MATERIALS ENGINEERING | RESEARCH ARTICLE**

# Influence of transition metal ion (mn$^{4+}$) on mullite formation in a mixture of 50:50 Nigerian kaolin and calcined alumina

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**Abstract:** In the present investigation, 5 wt% chemical grade $MnO_2$ was added in a mixture of 50:50 Nigerian sources of kaolin and superfine calcined alumina powder and effect of this transition metal ion on their physico-mechanical properties, phase and microstructural evolution were studied during heating in the temperature range of 1,400–1,650°C. The heated samples were found to be highly porous (>30%) in this entire temperature range. The doping of 5 wt% $MnO_2$ in this mixture did not improved the densification, but resulted into higher flexural strength (26 MPa) at 1,400°C compared to 7 MPa in the undoped sample. At 1,650°C, the reverse trend was observed, the flexural strength of undoped sample was found to be higher (38 MPa) than doped sample (27 MPa). The XRD study revealed the formation of mullite as major and corundum as minor phases in both the samples. The microstructural study shown the presence of needle shaped mullite crystals and corundum grains. The presence of inter-granular and intra-granular pores in $MnO_2$ doped samples might have reduced the strength at 1,650°C. The aspect ratio of mullite needle at 1,650°C was found to be higher in doped sample. The theoretical and experimental value of >4 for $MnO_2$ ion has been validated.

## ABOUT THE AUTHORS

Our research group focuses on finding solutions to solid waste environmental issues and development of appropriate technologies that will guide industrial implementation.

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## PUBLIC INTEREST STATEMENT

This paper studies the performance in terms of densification, strength development, phase and microstructural evolution of mullite formation when kaolin-alumina mixture is doped with Mn$^{4+}$. The paper compares the differences of the undoped with the doped mixture at different temperatures. The results obtained revealed a non-improvement in terms of densification but inferred increased flexural strength at lower temperatures. The formation of well-developed needle shaped mullite and corundum crystals justifies the obtained flexural strength at lower temperatures in the presence of Mn$^{4+}$.

**Subjects: Chemistry; Physics; Manufacturing Engineering; Materials Science**

**Keywords: clay; alumina; sintering; $MnO_2$ doping; porous; mullite**

## 1. Introduction

Mullite is one of the most important phases in both traditional and advanced ceramics although it exists rarely in natural rocks. The importance of mullite is documented by the large number of publications. Its high thermal stability and the favorable properties like low thermal expansion and conductivity, high creep resistance and corrosion stability together with suitable strength and fracture toughness are some of the scientific and technical advantages for mullite based ceramic products. Depending on the synthesis procedure, different types of mullite crystals have been described by various authors (Anilkumar, Mukundan, & Warrier, 1998; Risbud & Pask, 1978). Sintered-mullites are produced by heat treatment of starting materials via solid-state reactions. These mullites are normally stoichiometric having chemical formula $3Al_2O_3 \cdot 2SiO_2$. The starting materials for the synthesis of sinter-mullite are primarily alumina plus silica, alumino-silicates of the composition $Al_2SiO_5$, clays, $Al_2O_3$-rich sheet silicates which are abundantly available in nature. Out of these, kaolinite and other clay-based materials offer additional advantages such as easy shaping of components in green state due to their high plasticity. In one of our earlier study, a Nigerian source of kaolinitic clay containing high $SiO_2$ together with impurities $Fe_2O_3$ and $TiO_2$ gives rise to needle shaped mullite on heat treatment at 1,400°C; itself and the mullite content increases with increase in heating temperature (Ajanaku, Aladesuyi, Pal, & Das, 2016). The presence of transition metal ions ($Fe^{3+}$ and $Ti^{4+}$) in this clay up to certain limit as impurities might have promoted mullite formation at lower temperature. A report (Gralik, Chinelattot, & Chinelatto, 2014) on the impurities present in clay, particularly $Fe_2O_3$ and $TiO_2$, indicated that impurities has phenomenal role during heating of clay and clay + alumina mixtures towards formation of mullite. Aladesuyi, Pal, Das, and Ajanaku (2017) also reported that when 25 wt% of very fine calcined alumina was added to this Nigerian clay powder, $Al_2O_3$ reacted with the excess $SiO_2$ and enhanced mullite formation. The authors observed that very little densification occurs at 1,400°C and alumina was mostly inert, however flaky primary mullite evolved from the kaolinite series of reactions. At 1,500°C, although densification did not improved much but needle shaped mullite formation nucleated at this temperature are grown and well crystallized at 1,600°C. After formation of mullite by the reactions of alumina and amorphous silica, the excess alumina recrystallized as corundum crystals. A study on the mullitization behavior of calcined clay–alumina mixture with different sources of alumina viz: reactive alumina, gibbsite and boehmite has been carried out and was found that mixture of calcined clay and reactive alumina exhibited better mullitization behavior compared to other combinations (Viswabaskaran, Gnanam, & Balasubramanian, 2003).

Mullite has ability to form mixed crystals in a wide $Al_2O_3/SiO_2$ range and can incorporate a large variety of foreign cations into the structure depending on the synthesis temperature and atmosphere namely when added in differing amounts (Schneider, 2005) . The upper solubility limit is controlled by radii and oxidation states of the transition metal ions. Schneider (1990) reported that highest degree of incorporation are observed for $V^{3+}$, $Cr^{3+}$ and $Fe^{3+}$ followed by $Ti^{4+}$. Only very low amounts of $Mn^{2+}$, $Fe^{2+}$ and $Co^{2+}$ ions can enter the mullite structure. They also observed that transition metal ions preferably enter the octahedral position in mullite replacing Al. A low amount of tetrahedral-bound $Fe^{3+}$ has also been identified (Mack, Becker, & Schneider, 2005). $Fe^{3+}$ and $Mn^{2+}$ ions in the middle of the 3d transition metal series make an exception. These cations have stable $d^5$ electron configurations with nearly spherical symmetric charge distributions, similar to those of noble gases. Consequently $Fe^{3+}$ and $Mn^{2+}$ should exhibit no site preference and their incorporation behavior should mainly be controlled by the sizes of the cations. Actually a small amount of $Fe^{3+}$ does enter the oxygen tetrahedral in mullite at high temperature. On the other hand, $Mn^{2+}$ is obviously too large to be tetrahedrally incorporated in mullite (Schneider, 1990; Schneider & Vasudevan, 1989). The influence of transition metal ion on the formation of mullite with cases where $Mn^{4+}$ ion added in the form of $MnO_2$ in wear resistant high alumina ceramic compositions containing around 10 wt% kaolin has been studied (Das, 1998; Das, Ray, Mitra, & Gupta, 1993, 1999; Viswabaskaran et al., 2003). The authors observed that $MnO_2$ as sintering aids promoted sintering kinetics by increasing the

Al-diffusivity which is considered to be the rate controlling step in the sintering of $Al_2O_3$. The effects of $MnO_2$ on the physical, mechanical and microstructural properties of alumina was also studied where it was observed that the positive effect of $MnO_2$ addition on the hardness of alumina ceramics could be further enhanced with the increasing amount of $MnO_2$ addition and sintering temperature (Cheng, 2011). The author also found that small quantities of $MnO_2$ addition could lead to the enhancement of densification process. The grain growth would also be promoted by the addition of $MnO_2$, cause the formation of intra-granular and inter-granular pores while only inter-granular pores is observed on the undoped alumina ceramics. Moreover, the author did not found any secondary phase formation and this shows that $MnO_2$ is in solid solution of alumina. A colloidal technique during powder mixing process owing to the advantage of uniform distribution of the minor amounts of finer additive $MnO_2$ to alumina ceramics was recommended (Toy, Demirci, Onurlu, Sadik Tasar, & Baykara, 1995).

In the present investigation, an attempt has been made to study the influence of $Mn^{4+}$ in a mixture of 50:50 Nigerian kaolin and calcined alumina powder on mullite formation during heating at different temperatures. The densification behavior, strength development, phase and microstructural evolution were determined and discussed in this paper.

## 2. Materials and methods

Kaolinitic clay was collected at a location of latitude 7.08°N and longitude 3.27°E south-west Nigeria and it was processed to remove the grits as reported in earlier work (Ajanaku et al., 2016). High purity calcined alumina was obtained from ALCOA and chemical grade manganese di-oxide was procured from SD Fines and Chemicals. The chemical constituents present in the raw materials were determined by 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.

Two batches were prepared using the above raw materials. The batch compositions are provided in Table 1. The batches, 250 gm of each were prepared by using the common ceramic processing technique such as wet mixing of raw materials in a pot mill, drying of slurry and powdering, granulation using 5–6% moisture. The bar samples (65 × 7 × 7 mm size) were fabricated in a hydraulic press [Carver Laboratory Press, 2698, India] at 400 kg/cm$^2$. The compact bar samples were dried in air first and then in an electrically heated furnace at 100 ± 10°C till the moisture content reduced to less than 0.5 wt%. Then the dried samples were heated in an electrically operated furnace at temperature in the range of 1,400–1,600°C for a soaking period of 30 min. Standard method was applied to evaluate percent apparent porosity (%AP) and bulk density (BD) of the heated samples. Flexural strength of the samples were measured by universal testing machine (INSTRON 5500R, UK). The phase and microstructural analysis were performed using X-ray Diffraction [PAN analytical, ALMELO, X'Pert Pro MPD, Netherland], FESEM [Zeiss, Germany] and EDAX [Oxford, UK] technique. X-ray diffraction pattern of the powdered samples were recorded in the range of 10–80° in step-scan mode with step size 0.05° (2θ) and step time 75 s. For microstructural analysis of the vitrified samples, the samples were ground with SiC powder and then were polished with 6, 3 & 1 micron finish. The polished surface was chemically etched with 5% HF solution, washed with water and acetone followed by gold coating.

| Table 1. Batch compositions | | | |
|---|---|---|---|
| **Composition Code** | **Raw materials (wt%)** | | |
| | **Processed Nigerian kaolin** | **Calcined alumina** | **MnO$_2$** |
| LSK-1 | 50 | 50 | Nil |
| LSK-2 | 47.5 | 47.5 | 5 |

## 3. Results and discussions

The chemical analysis of the processed kaolin used in this study is given in Table 2.

It was observed in our earlier study that the compact samples of this processed clay powder on heating in the temperature range of 1,400–1,600°C resulted almost densified and impervious product at 1,600°C. Silica together with impurity oxides ($Fe_2O_3$, $TiO_2$) in the clay forms glassy phase in the above temperature range and that accompanying the formation of mullite ($3Al_2O_3 \cdot 2SiO_2$) crystals. Alumina content in the calcined alumina is >99.8 wt% and it is very fine with average particle size (d50) in the range of 6–8 μm. The assay content of $MnO_2$ powder was found to be 80%. The oxide compositions of the prepared batches are provided in Table 3.

It may be seen that oxide constituents of both the batches are more or less same except $SiO_2$ and $Al_2O_3$, which are slightly higher in LSK-1. $MnO_2$ is specially added as dopant to LSK-2 batch in order to study the influence of $Mn^{4+}$ ion on physico-mechanical properties and mullite formation in the mixture of kaolin and calcined alumina. It was observed that both the compositions shown negligible shrinkage in the entire heating range of 1,400–1,650°C and ultimately leads to poor densification and higher porosity. Table 4 provided the variation in bulk density (BD), percent apparent porosity (%AP) and modulus of rupture (MOR) strength in relation to the heating temperatures.

| Table 2. Chemical analysis of the processed kaolin (Ajanaku et al., 2016) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 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 |

| Table 3. Oxide composition of the batches | | |
|---|---|---|
| Chemical constituents (wt%) | LSK-1 | LSK-2 |
| $SiO_2$ | 29.63 | 28.54 |
| $Al_2O_3$ | 61.92 | 58.93 |
| $Fe_2O_3$ | 1.93 | 1.83 |
| $TiO_2$ | 0.73 | 0.69 |
| CaO | 0.19 | 0.18 |
| MgO | 0.07 | 0.06 |
| $Na_2O$ | 0.41 | 0.38 |
| $K_2O$ | 0.18 | 0.16 |
| $MnO_2$ | Nil | 4.05 |
| LOI | 4.75 | 4.46 |

| Table 4. Physico-mechanical properties of the heated samples | | | | | | |
|---|---|---|---|---|---|---|
| Heating Temperature (°C) | LSK-1 | | | LSK-2 | | |
| | BD (gms/cc) | %AP | MOR (kg/cm²) | BD (gms/cc) | %AP | MOR (kg/cm²) |
| 1,400 | 2.20 | 31.50 | 70 | 1.78 | 35.50 | 260 |
| 1,500 | 2.18 | 31.40 | ND | 1.80 | 36.50 | ND |
| 1,650 | 1.98 | 30.70 | 380 | 1.88 | 34.50 | 270 |

Note: ND = not determined.

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It may be observed from the above table that the bulk density of LSK-2 samples is significantly dropped by the addition of 5 wt% $MnO_2$ in the mixture of kaolin and calcined alumina. This might be due to the increasing amount of porosity in the kaolin and alumina mixture as the concentration of $MnO_2$ addition is more than certain limit that could diminish its effect in enhancing the densification of the present experimental body. Cheng (2011) in his study also found that addition of $MnO_2$ from 0–1.5 wt% increased the relative density of the alumina ceramics. However, further addition of $MnO_2$ up to 5 wt% caused the relative density of the alumina ceramics to drop to a certain level. Wet pot milling technique which was used during preparation of batches in the present study might have limitations when doping submicron particles. Toy et al. (1995) suggested employing colloidal technique which allows a uniform distribution of minor amounts of $MnO_2$ within the alumina ceramic. It is interesting to note that $MnO_2$ doped sample (LSK-2) developed better strength (26 MPa) at 1,400°C compared to 7 MPa in undoped sample (LSK-1). This may be attributed to better bonding between the grains at lower temperature in presence of $MnO_2$. On the other hand, it may be observed that at 1,650°C, LSK-1 (undoped) sample developed higher strength (38 MPa) compared to 27 MPa in $MnO_2$ doped sample (LSK-2). These differences in strength development at 1,650°C will be better explained later while discussing microstructure evolution. Figure 1 illustrates the XRD pattern of both 1,650°C heated samples. Both patterns look almost similar. The phases identified were mullite and corundum.

The microstructures of 1,650°C heated undoped sample (LSK-1) in different regions are shown in Figure 2 along with the EDX analysis and it looks to be homogeneous with uniform grain growth. The structure is full of needle shaped mullite crystals embedded in glassy matrix and corundum grains all over.

**Figure 1. XRD pattern of LSK-1 and LSK-2 samples heated at 1,650°C temperature.**

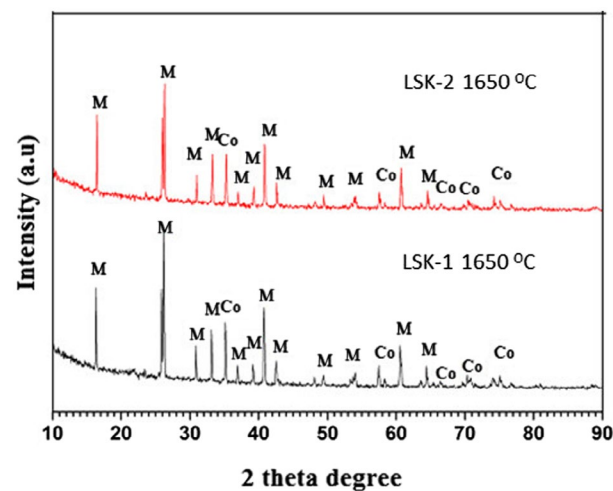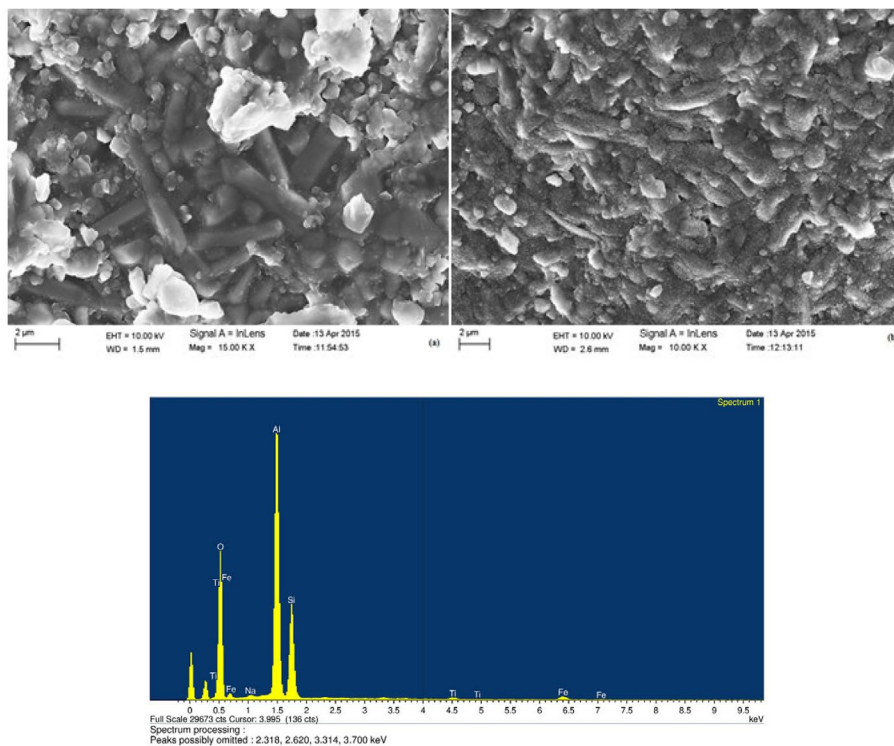Notes: M = Mullite,
Co = Corrundum.

**Figure 2. FESEM and EDAX analysis of LSK-1 samples heated at 1,650°C.**



The addition of $MnO_2$ in LSK-2 body resulted in homogenous grain growth as observed in the different regions of the sample (Figure 3). Few inter-granular and intra-granular pores could also be observed in the microstructures of the samples doped with $MnO_2$. The lower strength in 1,650°C heated LSK-2 sample (27 MPa) compared to LSK-1 (38 MPa) is due to the presence of these pores. Larger size mullite needles with higher aspect ratio are seen in LSK-2 sample due to grain growth in presence of $MnO_2$. Corundum crystals are also distributed in the matrix of LSK-2 sample.

A comparative study of the chemical analysis and oxide composition of the constituents were illustrated in Figure 4. This is done to adequately propose a model for understanding the transition metal ion participation in mullite formation. The active constituents as seen in Figure 4 were $SO_2$, $Al_2O_3$, $K_2O$ and $Fe_2O_3$. The thermal deactivation model that was derived by Benjamin, Reznik, Benjamin, and Williams (2007) was adopted to understand the number of transition metal ion (N). The modified formula for this study becomes:

$$N(T) = (A_1T^3 + B_1T^2 + C_1T + D_1)k_{exp} \tag{1}$$

where $A_1$, $B_1$, $C_1$ and $D_1$ are coefficients that describes the concentration of metal ion, $k_{exp}$ is the experimentally measured rate coefficient given by Su and Chesnavich (1982) when they calculated the ion-polar molecule collision rate constant by parameterization. The value of the coefficient is determined by the polynomial curve-fit of the active constituents illustrated above. The processes for

**Figure 3. FESEM and EDAX analysis of LSK-2 samples heated at 1,650°C.**
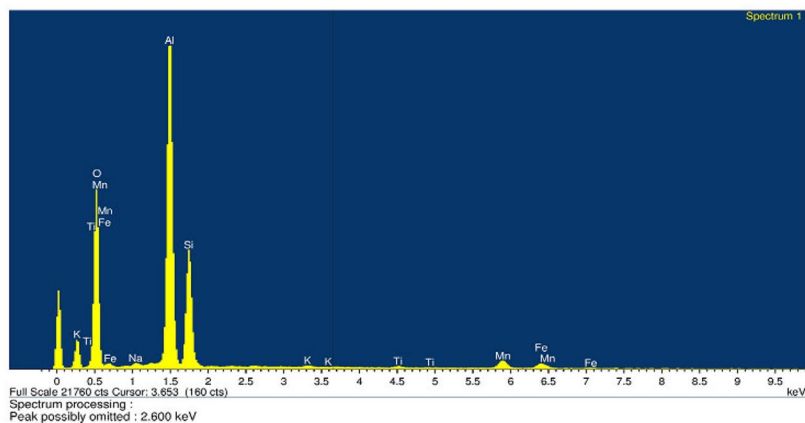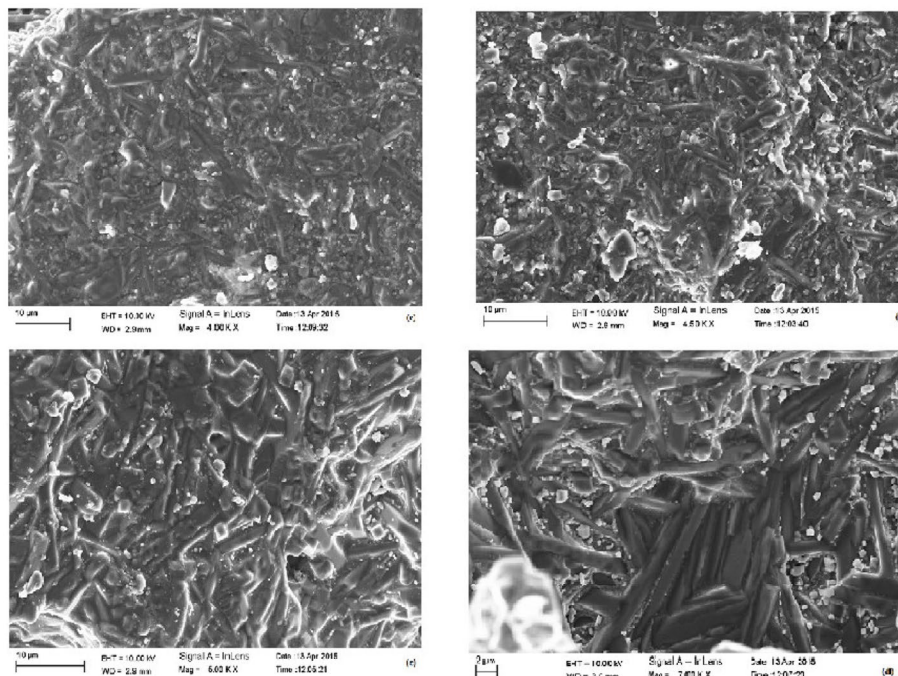


**Figure 4. Comparative analysis of the chemical analysis and oxide composition.**
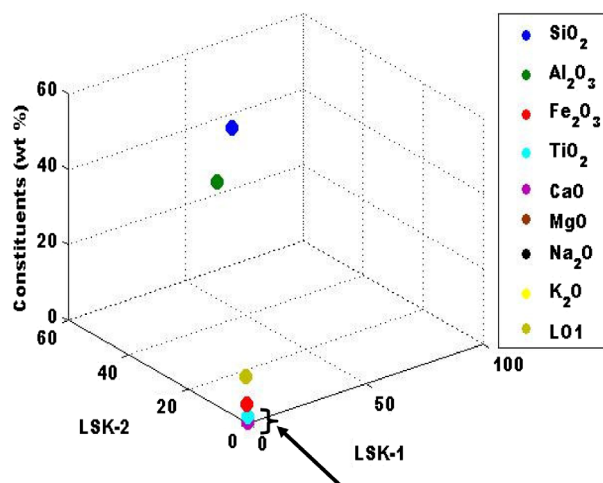
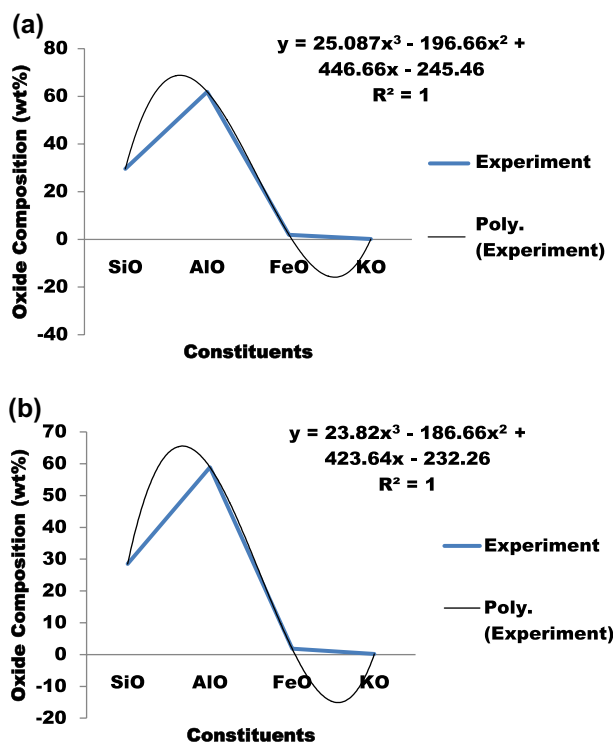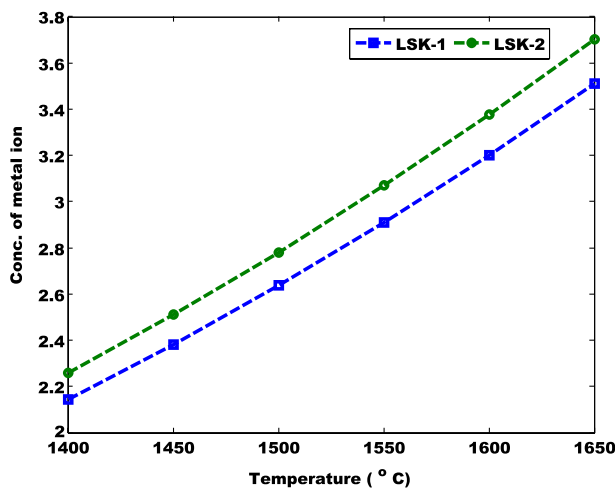**Figure 5. Analysis for the determination of transition metal ion coefficients.**

**(a)**

$$y = 25.087x^3 - 196.66x^2 + 446.66x - 245.46$$
$$R^2 = 1$$

**(b)**

$$y = 23.82x^3 - 186.66x^2 + 423.64x - 232.26$$
$$R^2 = 1$$

**Figure 6. Expected progression of the transition metal ion i.e. (LSK-1 and LSK-2) at varying temperatures.**

acquiring the coefficients are shown in Figure 5. The ranges of $A_1$, $B_1$, $C_1$ and $D_1$ are 23.8 to 25.1, −186 to −196.7, 423.6 to 446.7 and −232.3 to −245.5 respectively. Hence, the thermal model for the understanding of the influence of the transitional metal ion between 1,400–1,650°C is shown in Figure 6. The expected progression of the transition metal ion i.e. (LSK-1 and LSK-2) at varying temperatures is shown in Figure 6. Also, a case where the first coefficient of the first term of Equation (1) was considered to be dynamic was considered as shown in Figure 7. This assumption is to ascertain if the

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**Figure 7. Validation of unperturbed calculation of coefficient rate.**
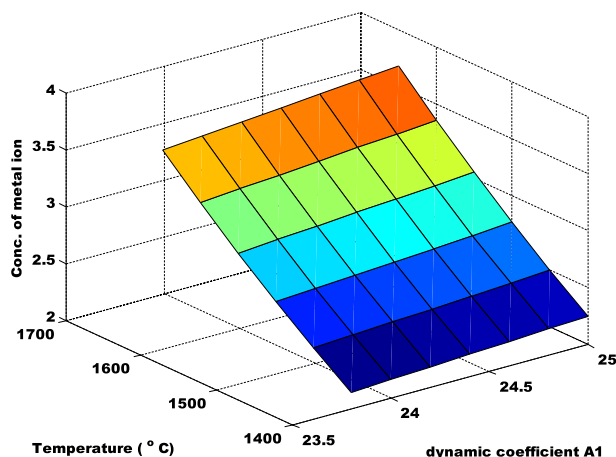


experimentally measured coefficient rate would shift. It was observed that it had no significant changes. Hence the theoretical and experimental value of >4 for $MnO_2$ has been validated.

## 4. Conclusions

From the present study, it may be concluded that a compact of 50:50 Nigerian clay and calcined alumina powder resulted in porous samples when heated in the temperature range of 1,400–1,650°C. The doping of 5 wt% $Mn^{4+}$ ion as $MnO_2$ in this mixture did not improved densification, but increased the flexural strength at 1,400°C, while at 1,650°C, the strength dropped due to inhomogenous grain growth and generation of inter-granular and intra-granular pores. The XRD pattern and SEM photographs revealed the presence of well-developed needle shaped mullite and corundum crystals.

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