#### A STUDY OF SOME PHYSICAL PROPERTIES OF COMPOSITION OF KAOLIN IN CLAY:

#### A COMPARATIVE STUDY ON ASAMANG AND AGONA CLAY.



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#### DECLARATION

I hereby declare that this submission is my own work towards the MPHIL and that, to best of my knowledge, it contain no material previously published by another person nor material which has been accepted for the award of any other degree of the university, except where due acknowledgement has been made in the text.



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#### DEDICATION

This thesis is dedicated to my parents, Mr. Kofi Yamoah and Gloria Kankam for their commitment, support and patience, not forgetting my uncles especially Dextor Anson, and my step – father Mr. Kwame Agyei – Nyarko.

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#### ABSTRACT

Some physical properties of the effect of composition of Kaolin on clay samples obtained from the Sekyere south district were studied. The raw clay samples were processed into powdered form, and a composite mixture of raw processed clay and kaolin were formed, with the kaolin composition increasing from 20 to 80 % in Agona and Asamang samples. The powdered raw clay samples were characterized using the X-Ray Diffraction analysis. The composite samples, together with the raw samples were further processed into cubic and cylindrical dimensions and finally fired at 1000 °C. Properties which include; Total shrinkage, water absorption, bulk density, specific gravity, cold crushing strength, weight loss, thermal conductivity, thermal resistivity, specific heat capacity and thermal diffusivity, were measured by the appropriate standard methods. The results show that the inclusion of kaolin in the samples affects the various properties of the samples: Porosity increases with percentage increase in kaolin across Agona and Asamang samples while thermal conductivity and thermal diffusivity reduced with percentage increase in kaolin. Optimum parameters were met by the various compositions and appropriate recommendations were prescribed for industrial implementations. The XRD – (phase analysis) showed the minerals as mainly Silicates and Alumina of various proportions. The mineral compositions of the clays outline their prospects of been used as alternative materials for various purposes of utilization; which include construction, due to their relatively high cold crushing strength coupled with their low thermal conductivity and refractory purposes, due to their low thermal conductivity.

#### TABLE OF CONTENTS

ACKNC	DWLEDGEMENTSiii	
ABSTR	ACTiv	
TABLE	OF CONTENTSv	
LIST OI	F FIGURESx	
LIST OI	f tablesxii KNUST	
<u>CHAPT</u>	<u>ER ONE</u>	
1.1.	Introduction	1
1.2.	Ceramic materials	.2
1.2.1.	A crystalline form of SiO <sub>2</sub>	.3
1.2.2.	Non-crystalline ceramics	3
1.2.3.	Ordinary ceramics	.3
1.3.	Bonding in ceramics.	4
1.3.1.	Ionic bonds	5
1.3.2.	Covalent bond	5
1.3.3.	Secondary bonds	6
1.4.	Ceramic structures	6
1.4.1.	Ceramic scope of materials	6
1.4.2.	Illustration of ceramic oxide structure	6
1.4.3.	Control of micro-structural imperfections	6
1.4.4.	The types of ceramic structures	7
1.5.	Ceramic crystal structures	7
1.5.1.	Magnesium oxide structure and iron –oxide structure	8

1.5.2.	Fluorite structure	9
1.5.3.	Perovskite structure	10
1.5.3.e	. The YBCO lattice structure	11
1.6.	Silicates	12
1.7.	Amorphous ceramics	12
1.8.	Imperfections in ceramics	14
1.9.	Intrinsic ionic disorder	15
1.9.1.	Frenkel defect	15
1.9.2.	Schottky defects	16
1.10.	Properties of ceramics	16
1.10.a.	The microstructure of ceramics	17
1.10.1.	Electrical properties	17
1.10.2.	Semi-conductor ceramics	17
1.10.3.	Ferroelectric ceramics	19
1.10.4.	Piezolelectric ceramics	19
1.10.5.	Insulating properties	19
1.10.6.	Electrical conductivity	20
1.10.7.	Superconducting ceramics	20
1.11.	Magnetic properties	21
1.12.	Thermal properties	22
1.13.	Optical properties	24
1.13.1.	Transparent ceramics	24
1.13.2.	Opaque ceramic materials	24
1.13.3.	Interaction of light with the particles in a ceramic material	25

1.14.	Mechanical properties	.25						
1.14.1.	Griffith law of stress superelevation conditions for failure26							
1.14.2.	How to overcome the brittle behavior2							
1.15.	Ceramic processing27							
1.15.1.	Traditional ceramic processing	.27						
1.15.2.	Advanced ceramics processing	.28						
1.16. R	Raw materials for traditional ceramics	.29						
1.17. B	uilding blocks of clay minerals	.30						
1.17.1.	The major crystal structures of clay	.30						
1.17.2.	Primary clay	.31						
1.17.3.	Secondary clay	.32						
1.18.	Properties of clay minerals	.32						
1.18.1.	Clay/ organoclay and organoclay/polymer nanocomposites	.33						
1.19.	Ceramic products	.34						
1.20.	Problem statement	.35						
1.21.	Main objectives	.36						
<u>CHAPTE</u>	R TWO							
2.0. Lit	erature review	38						
2.1. Re	eview of previous works on physical characterization of ceramics	.38						
2.2. Ok	ojectives of the research	51						

#### CHAPTER THREE

3.0.	Theoretical background	.53
3.1	Heat energy	.53
3.1.0.	Modes of heat transfer	.53
3.1.1.	Conduction	53
3.1.2.	Convection	54
3.2.	Thermal conductivity	57
3.2.	Factors influencing the thermal conductivity of a ceramic material	.60
3.3.	Mineralogy composition	60
3.4.	Effect of particle size	63
3.5.	Effect of heat treatment and temperature	64
3.6.	Effect of shrinkage	65
3.7.	Effect of water content	66
3.8.	Effect of texture and porosity	66
3.9.	Theory on the mechanical properties of ceramics	68
3.10.	Theory on specific heat capacity	71
3.11.	Theory on thermal shock resistance.	.72
3.12.	Theory of thermal conductivity measurements	73
3.12.1	. Transient state conduction	74
3.12.2	Steady state conduction	75
3.12.3	. The lee's disc experiment	76
3.13 effect	Theory on bulk density, apparent density, apparent density, apparent porosity, and ive moisture content	82

#### CHAPTER FOUR

4.1.	Methodology	83
4.1.	Formation of specimen samples	83
4.2.	Molding the samples	85
4.3.	Heat treatment of samples	87
4.4.	Measurement of some parameters	88
4.4.1	Measurement of shrinkage on firing	88
4.4.2.	Measurement of water absorption, bulk density, apparent porosity, and apparent	
specif	fic gravity for fired samples	20
opeon		
4.4.3.	Cold compression strength	91
4.4.3. 4.4.4.	Cold compression strength Thermal shock resistance	91 91
4.4.3. 4.4.4. 4.4.5	Cold compression strength Thermal shock resistance Measurement of weight loss on firing	91 91 91 92
4.4.3. 4.4.4. 4.4.5 4.4.6.	Cold compression strength Thermal shock resistance Measurement of weight loss on firing Measurement of specific heat capacity	91 91 92 92

#### CHAPTER FIVE

5.0.	Experimental results and discussion	96
5.1	Effect of composition on shrinkage	97
5.2	Effect of composition on water absorption	98
5.3	Effect of composition on weight loss	99
5.4	Effect of composition on cold crushing strength	.100
5.5	Effect of composition on porosity	101
5.6	Effect of composition on thermal conductivity and thermal resistivity	.103
5.7	Effect of specific heat capacity on composition	.104

Sture -

5.8	Effect of bulk density on composition	105
5.9	Effect of thermal diffusivity on composition	106
5.10.	Superimposed representative trend plots of important sample composition	
prop	erties	106
5.11.	. X-ray diffraction analysis of 100% clay samples	113

#### CHAPTER SIX

<u>CHA</u>	PTER SIX	<b>INN</b>	Ш	СТ	
6.1	Conclusion		U	<u> </u>	
6.2	Recommendations for future	projects			
REFI	RENCES				
APP	ENDICES			2	



#### LIST OF FIGURES

Figure 1.1	Crystalline and amorphous from of silicon dioxide	3
Figure 1.2	The rock salt structure (AX)	8
Figure 1.3	The Flourite structure (AX <sub>2</sub> )	9
Figure 1.4	The Perovskite structure (ABO <sub>3</sub> )	10
Figure 1.5	The YBCO lattice structure	11
Figure 1.6	The Soda glass structure	14
Figure 1.7	The frenkel and schottky defects	16
Figure 1.8	Ceramic processing steps	28
Figure 3.1	Theory on the lees disk apparatus	73
Figure 3.2	Schematic diagram on the flow of heat(steam)	.78
Figure 3.3 rate	Bad conductor on the brass disk with a thermometer to register the cooling	.79
Figure 3.4	Theoretical cooling curve of sample	.81
Figure 4.1 excess wat	The cylindrical mould and sample under formation and compression to get rid of er	86
Figure 4.2	Dried samples after sun drying and drying with an electrical dryer	86
Figure 4.3	Schematic diagram of the Lee's and Charlton's apparatus	95
Figure 5.1	Total shrinkage ass a function of composition	97
Figure 5.2	Water absorption as a function of composition	98
Figure 5.3	Weight loss as a function of composition	99
Figure 5.4	Cold crushing strength as a function of composition	100
Figure 5.5 I	Porosity as a function of composition	101
Figure 5.6	Thermal conductivity as a function of composition	103
Figure 5.7	Thermal resistivity as a function of composition	104

Figure 5.8 Heat capacity as a function of composition103
Figure 5.9 Bulk density as a function composition105
Figure 5.10 Variation of thermal diffusivity with composition106
Figure 5.11 Thermal conductivity as a function of water absorption properties varying with the percentage composition of kaolin107
Figure 5.12 Thermal conductivity and cold crushing strength properties varying with the percentage composition of kaolin
Figure 5.13 Total shrinkage and cold crushing strength properties superimposed on each other as percentage composition of kaolin increased108
Figure 5.14 Comparative plot of total shrinkage and apparent porosity properties, varying with kaolin com
Figure 5.15 Apparent porosity versus cold crush strength properties, varying with kaolin   composition position   109
Figure 5.16 Apparent porosity versus thermal conductivity properties, varying with kaolin composition
Figure 5.17 Specific heat capacity versus apparent porosity properties, with varying kaolin composition
Figure 5.18 Comparative plot of specific heat capacity with thermal diffusivity properties, with varying kaolin composition
Figure 5.19 X-RAY Diffraction pattern(phase analysis) of 100% Asamang sample
Figure 5.20 X-RAY Diffraction pattern (phase analysis) of 100% Agona sample114
WJ SANE NO

#### LIST OF TABLES

Table A.1.1.:	Table	showing	the	variation	of	shrinkage	values	with	
composition.									 126

Table A.1.4: Table showing thermal properties of samples with composition......129



#### CHAPTER ONE

#### 1.1. INTRODUCTION

The major concern of this thesis is to physically characterize and enhance the properties of some locally mined ceramic base materials in order to set an option for the local industry and the research database of the nation. Due to the types of bonding in these materials, which are mainly covalent and ionic bonds; they are primarily strong ,brittle, abrasive ,and are mostly bad conductors of heat and electricity. Their intrinsic and extrinsic properties results in their preferable qualities over other materials. Due to these complex qualities, especially: the transport phenomenon of both electricity and heat must be studied, with much emphasis on amorphous and crystalline ceramic materials, for instance an insight into how heat is transferred through such material is, of considerable importance in solving many applied and theoretical problems. In ceramics ,thermal conductivity and strength depends on the intrinsic properties of the material in question. Notably is it's lattice structure and the prevailing sintering temperature, In real world systems, heat transfer is virtually impossible to perfectly control and isolate; and due to the high cost of construction of the various technically driven systems of operations, both industrial and domestic. It is important for us to understand and control the flow of heat through these ceramic base materials so as to enable us describe our materials thermal performance by obtaining correct expressions for the thermal conductivity in relation to the user of the products. For example a furnace designer needs accurate data on the thermal conductivity of the different parts of a furnace; for instance the interior walls should be good thermal insulators whiles the muffles have high conductivity values. Before technicians make such a decisive and intelligent choice in selecting his materials or even predict their performance, a good knowledge of the material is of good importance. The rapid evolution of the ceramic based materials and its composites and the associated material technological

development, and supplying more data to the knowledge bank. As new materials and even newer technologies are developed; the methods of preparation and finishing are required to keep pace with the current trend rapid development which has necessitated this investigation.

#### 1.2. CERAMIC MATERIALS:

The word ceramic covers inorganic non-metallic materials which are formed by the action of heat and hydrothermal actions under the extreme pressures of the earth's crust. Ceramic materials are primarily hard, porous, brittle and chemically resistive to the actions of most solvents .They are also bad conductors of electricity and thermal variations and are composed of more than one element (eg.Al<sub>2</sub>O<sub>3</sub>) ceramics are most often crystalline or amorphous (Loeb 1954;Imura,et al,1978;Jakob 1957),although they also contain a combination of glassy and crystalline phases, which make fracture before any plastic deformation take place resulting in poor toughness. These materials tend to be porous due to the packing density of the material under study. The pores and microscopic act as stress concentrators, decreasing the toughness further and reducing the tensile strength.

They are harder and stiffer than steel; more heat and corrosion resistant than metals or polymers; less dense than most metals and their alloys; the aforementioned reasons combine to give catastrophic failures as opposed to the normally much more gentle failure modes of metals. In crystalline materials, a lattice point is occupied either by atoms or ions depending on the bonding mechanism. These atoms (or ions) are arranged in a regularly repeating patterns in three dimensions (i.e. they have long – range order). In contrast, in amorphous materials, the atoms exhibit only short- range order. Some ceramic materials, like silicon dioxide (SiO<sub>2</sub>), can exist in either crystalline or amorphous form.



Figure 1.1 Crystalline and Amorphous from of Silicon Dioxide

1.2.1. A crystalline form of  $SiO_2$ , as seen in fig.1.1 results when the material after heat treatment is slowly cool; also rapid cooling favours non-crystalline or amorphous formation since it is not allowed to cool slowly for ordered arrangements of atoms to form. Ceramic materials display a wide range of properties which facilitate their use in many different product areas. Crystalline ceramic materials are not amenable to great range of processing. Methods for dealing with them tend to fall into one of two categories –either makes the ceramic in desired shape, by reaction in situ, or by "forming" powders into the desired shape, and then sintering to form a solid body.

1.2.2. Non- crystalline ceramics, being glasses, tend to be formed from melts. The glass is shaped when either fully molten, by casting, or when in state of toffee-like viscosity by methods such as blowing to a mould. If later heat treatment causes this glass to become partly crystalline, the resulting material is known as glass ceramic.

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1.2.3. Ordinary ceramics, due to lack of "free" electrons such as those found in metals, are poor conductors of heat and electricity and therefore make excellent insulators. Unlike most metals, nearly all ceramics are brittle at room temperature: that is, when subjected to tension, they fail suddenly, with a little or no plastic deformation prior to fracture.

Despite such exceptions these structures and chemical compositions, though various, result in universally recognized ceramic-like properties of enduring utility, including the following: mechanical strength in spite of brittleness; chemical durability against the deteriorating effects of oxygen, water, acids, bases, salts and organic solvents; hardness, contributing to resistance against wear; thermal and electrical resistivity considerably higher than that of metals; low cost of raw materials and low cost of fabrication for some ceramics; ability to take decorative finish and the diverse tendency to develop composites with materials of the same family or other class of materials. The diversity in their properties emanates from their bonding and crystal structures. Underlying many of the properties found in ceramics are the strong primary bonds that hold the atoms together and form the ceramic material.

#### 1.3. BONDING IN CERAMICS

The bonding system of all ceramics are partially or totally ionic and can have combination of ionic and covalent bond types. The primary bonds of all these materials are composed and structured through these bonding systems with the exception of recently developed composites of ceramics materials, that may possess any other bonding type due to the processing technicalities, some ceramic materials can be doped with organic materials in order to enhance its peculiar property which is dictated by the scientist or the technician. The degree of ionic character depends on the difference of electronegativity between atoms which are ready to transfer bonding electrons from electropositive state, i.e. cation to electronegative atoms, i.e. anions. The larger the electronegativity difference between anion and cation (i.e. the greater the difference in potential to accept or donate electrons), the more nearly ionic is the bonding (i.e. the more likely are electrons to be transferred, forming positively charged cations and negatively charged anions).

1.3.1. Ionic bonds are entirely non-directional and "anisotropic". This non-directional nature allows for hard-sphere packing arrangement of ions into a variety of crystal structures, with some limitations; which includes: The relative size of the anions and cations. Anions are usually larger and closed packed, as in face-centered cubic (fcc) or hexagonal close-packed(hcp) crystal structures found in metals. Cations on the other hand are usually smaller, occupying interstices, or spaces, in crystal lattice between the anions.

The second limitation on the type of crystal structure that can be adopted by ionically bonded atom is based on a law of chemistry-that the crystal must remain electrically neutral. This law of electroneutrality results in the formation of very specific stoichiometry, .i.e. specific ratios of cations to anions that maintain a net balance between positive and negative charges. Anions are known to pack round cations, and cations around anions, in order to eliminate local charge imbalance. This phenomenon is referred to, as co-ordination.

1.3.2. Covalent bond involves the orbital sharing of electrons between the constituent atoms or ions. They are highly directional in nature, often dictating the types of crystal structure possible. The atoms that get involved in this bonds have similar electronegativity and the bond are also determined by valence- S and P orbitals dominate the bonding. The overall properties of ceramic

materials depend on the dominant bonding mechanism. Compounds that are either partially ionic or covalent have higher melting point, very high hardness or strength, good resistance to corrosion, high stiffness, low fracture toughness and poor machinability.

In summary, most primary chemical bonds found in ceramic materials are actually a mixture of ionic and covalent types. The larger the electronegativity difference between anion and cation (.i.e. the greater the difference in potential to accept or donate electrons), the more nearly ionic is the bonding (.i.e. the more likely are electrons to be transferred, forming positively charged cations and negatively charged anions). Conversely, small difference in electronegativity lead to a sharing of electrons, as found in covalent bonds.

1.3.3. Secondary bonds are also important in certain ceramics. For example, in diamond: a single crystal form of carbon, all bonds are primary, but in graphite, a polycrystalline form of carbon, there are primary bonds within sheets of crystal grains and secondary bonds between the sheets. The relatively weak secondary bonds allow sheets to slide past one another, giving graphite the lubricity for which it is well known.

1.4. CERAMIC STUCTURES:

1.4.1. Ceramic and related materials cover a wide range of objects. Ceramics are little more complex than metallic structures. Ceramics are basically classified as "an inorganic, non-metallic solid that is prepared from powdered materials and is fabricated into products through the application of heat. Most ceramics are made up of two or more elements or they have their basic composition as a compound. For example Alumina (Al<sub>2</sub>O<sub>3</sub>) is a compound made up of aluminium and oxygen atoms.

1.4.2. However it should be noted that the crystal structure of ceramics are many and varies across a wide range of materials with its specific lattice arrangements serving a wide range of technicalities. For example, while ceramics are perceived as electrical and thermal insulators, ceramics oxide(initially based on Y-Ba-Cu-O) is the basis for high temperature superconductivity. Diamond and silicon carbide have a higher thermal conductivity than aluminium or copper.

1.4.3. Control of micro-structural imperfections and limitations can help overcome inherent material flaws. This intrinsic properties offers the scientist or engineer a wide range of prospects to explore the materials to achieve and solve a specific technical problem. For example, control of the micro-structural cracks can overcome inherent stiffness to allow the production of ceramic springs, porous ceramics can be pillared to reduce the level of porosity and, ceramic materials can be doped to form ceramic composites which can have fracture toughness about half of steel. Also, the atomic structures are often of low symmetry that gives some ceramics interesting electromechanical properties, like piezoelectricity of which such materials are employed as sensors and transducers.

1.4.4. The structure of most ceramics varies from relatively simple to very complex. The microstructure can be entirely amorphous (glassy); entirely crystalline; or a combination of crystalline and amorphous. In later case, glassy phase usually surrounds small crystals, bonding them together. The main compositional classes of engineering ceramics are oxides, nitrides and carbides.

#### 1.5. CERAMIC CRYSTALL STRUCTURES:

Crystalline ceramic materials are not amenable to a great range of processing methods. They are formed through the standard processing methods; pressed or moulded into shapes and sintered. Normally they are allowed to cool to room temperature in order to attain crystalline form. Natural occurrence like hydrothermal actions and weathering can also yield such materials.

The building criteria for most crystal structures are to maintain charge neutrality and to achieve the closest packing. The Oxide structures forms an integral percentage of ceramic materials; they are characterize as often relatively close packed Oxygen in a lattice (FCC, HCP and others).

Their oxygen anions are much larger than metal cations and they are cations in the holes of the oxygen lattice.

Examples are the:

1.5.1. Magnesium Oxide structure and Iron –oxide structure, they have regular repeatable lattice orientation; as seen in figure 1.2 which is comparable to that of the sodium chloride.



Fig 1.2 The Rock salt structure (AX).

This structure is referred to as Rock salt structure because common salt (NaCl) has the same pattern. In the rock salt structure, each ion is surrounded by six immediate neighbors of opposite charge. Example the  $Mg^{2+}$  cation, which is surrounded by  $O^{2-}$  anions. This extremely packing

crystallize in this structure tend to have relatively high melting points. Magnesia is employed as refractory.

Some common ceramic structures and their stoichiometry are listed below. These are the basic building blocks of all crystal structures.

Note:



FCC structure with 3 atoms per lattice point

Figure 1.3 The Flourite Structure (AX<sub>2</sub>).

The structure is after the mineral (CaF<sub>2</sub>) which possess this structure. The material is comparable to Uranium dioxide(UO<sub>2</sub>). In the structure: as seen in figure 1.3, the oxygen anions are bonded to only four cations. Oxides with this structure are well known for the ease with which oxygen vacancies are formed. In Zirconia (Zirconium dioxide, ZrO<sub>2</sub>) which also possess this structure, a great number of vacancies can be formed by doping ,or carefully inserting ions of different element into the composition. These vacancies become mobile at high temperatures, imparting oxygen ion conductivity to the material and making it useful in certain electrical applications. The fluorite structure also exhibit considerable open space , especially at the center of the unit cell. In Urania, which is used as fuel element in nuclear reactors, this openness is believed to help accommodate fission products and reduce unwanted swelling.

1.5.3. PEROVSKITE STRUTURE:



The red spheres are X atoms(usually Oxygen), the blue spheres are B atoms (smaller metal cations, such as  $Ti^{4+}$ ) and the green spheres are A atoms (a large metal cation, such as  $Ca^{2+}$ )

Figure 1.4 The Perovskite structure (ABO<sub>3</sub>).

In most cases the perovskite structure is cubic – that is ,all sides of the unit cell are the same. However, in Barium Titanate (BaTiO<sub>3</sub>), the central  $Ti^{4+}$  can be induced to move off – center, leading to a non-cubic symmetry and to an electrostatic dipole, or alignment of positive and negative charges towards opposite ends of the structure, This dipole is responsible for the ferroelectric properties of Barium titanate, in which domains of neighboring dipoles lines up in the same direction. The enormous dielectric constant achievable with perovskite materials are the basis for many ceramic capacitor devices and recently developed solar cells. The non-cubic variations found in perovskite ceramics introduce the concept of anisotropy: i.e. an ionic arrangement that is not identical in all directions. In severely anisotropic materials, there can be great variation of properties. These cases are illustrated by Yttrium Barium Copper Oxide (YBCO-YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>) as shown in fig. 1.1.5.3.E



Figure 1.5. The YBCO lattice structure.

Yttrium barium Copper Oxide is a superconducting ceramic-it losses all resistance to electric current at relatively high temperatures. The structure consist of three cubes, with Yttrium or Barium at the centre; Copper at the corners , and Oxygen at the middle of each edge – with the exception of the middle cube, which has oxygen – vacancies at the outer edges. The critical feature

in this structure is the presence of two sheets of Copper-oxygen ions, located above and below the perpendicular to these sheets is not favoured, making the YBCO structure severely anisotropic. One of the challenges in fabricating crystalline YBCO ceramics capable of passing large currents is to align all the grains in such a manner that their copper-oxygen sheets line up.

#### 1.6. SILICATES

Silicon and Oxygen are the most common element on the planet. Due to the high reactive nature of silicon, it stabilizes itself by combining with other elements, they form basic structures like the silicon oxide structure, SiO<sub>2</sub> (silica): which exist as quartz, crystoballite and tridymit owing to the environmental condition during the formation. They have strong Si – O bonds which imply a high melting temperature (1710°C). Silicates are a combination of the basic SiO<sub>4</sub> tetrahedral structure by having them share corners, edges or faces. By this action, the material tend to exhibit high range of intrinsic and extrinsic qualities; the (SO) compound is unstable as it becomes a more complex stoichiometry; therefore it will have to stabilize itself through the actions of cations neutralization, which tends to provide the degree of ionic bonding to balance charge. Because, a net negative charge is associated with each (SiO4) unit, the negative charge is balance by an adjacent plane; rich in positively charged cations. Examples of these cations include  $Ca^{2+},Mg^{2+},Al^{3+}$ . Through the action of their ability to change counterions, they are able to alter their layer spacing and the layers to allow absorption of water. These phenomenons are known as the layered silicate structure or phylosilicates. They form the mineral base for many ceramic materials. Examples include:

Bentonites: which is used to seal wells so no polluted ground water seeps – in to contaminate water supply.

Micas (KAl<sub>3</sub>SiO<sub>10</sub>(OH)<sub>2</sub>): which is used as fire retarding chemical, insulators in heating systems

Kaolinites

Clay

#### 1.7. AMORPHOUS CERAMICS:

Non-crystalline ceramics tend to be formed from melts. The material composed of ceramic minerals is heat treated to the molten form, it is then shaped or casted when it attains the state of toffee-like viscosity and finally quenched rapidly. By this process the material can have its lattice arrangements being disordered as shown in fig.1.6. Ceramic materials that undergoes such a regime is known as glass – ceramic, these are widely used as cook-top and also as a glass composite material for nuclear waste disposal and window glass(fused or vitreous silica). Example , window glasses are produced by adding most oxides (e.g. CaO,Na<sub>2</sub>O) whose cations are incorporated within the SiO<sub>4</sub> network. The cations break the tetrahedral network and glasses melt at lower temperature than pure amorphous SiO<sub>2</sub>, because: A lower melting point makes it easy to form glass, for instance bottles. Some other oxides (TiO<sub>2</sub>,Al<sub>2</sub>O<sub>3</sub>) substitute for silicon and become part of the network.



Figure 1.6 The Soda glass structure.

#### 1.8. IMPERFECTIONS IN CERAMICS:

Imperfections include in ceramics include point defects, impurities, line defects and surface defects(grain boundaries). Their formation is strongly affected by the condition of charge neutrality (creation of unbalance charges requires the expenditure of large amount of energy). Nonstoichiometry refers to a change in composition so that the element in the ceramic are in the proportion appropriate for the compound (condition known as stoichiometry). To minimize energy, the effect of non-stoichiometry is a redistribution of the atomic charges. Charge neutral defects include the Frenkel and Schottky defects. Introduction of impurity atoms in the lattice is likely, in conditions where the charge is maintained. This is the case of electronegative impurities that substitute lattice anions or electropositive substitutional impurities. This is more likely for similar ionic radii since this minimizes the energy required for a lattice distortion. Defects will appear if the charge of the impurities is not balanced. Many properties of crystals are determined by imperfections. Electrical conductivity and diffusional transport in most ceramics is determined by the number and type of defects. Various optical properties; for instance, those giving rise to color and lasing activity, are caused by electronic absorption and emission processes at impurity ions and point defects. The rates of kinetic processes such as precipitation, densification, grain coarsening and high-temperature deformation determined by mass transport is due to defects. A principle difference between point defects in ionic solids and those in metals is that; all such defects can be electrically charged.

Ionic defects are point defects that occupy lattice atomic positions, including vacancies, interstitials, and substitutional solutes. Electronic defects are deviations from the ground state electron orbital configuration of a crystal, formed when valence electrons are excited into higher

orbital energy levels. Such an excitation may create an electron in the conduction band of the crystal.

#### 1.9. INTRINSIC IONIC DISORDER

Atomic defects are formed with expenditure of energy which is most commonly thermal, although radiation of various kinds can displace atoms. Two most common types of crystalline defects in ionic ceramic materials:

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#### 1.9.1. FRENKEL DEFECT:

# In ionic materials, both the cations and anion can undergo this kind of displacement. In metals and covalent compounds, frenkel defects can also form; they differ from those in ionic compounds only in that the defects need not be electrically charged. It is also known as a pair of cation (positive ion) vacancy and cation interstitial; see fig.1.7, it may also be an anion (negative ion) vacancy and anion interstitial. However anions are larger than cations and it is not easy for an anion interstitial to form.

1.9.2. <u>SCHOTTKY DEFECTS</u>: this is a pair of anion and cation vacancies. This vacancies must be formed in the stoichiometric ratio in order to preserve the electrical neutrility of the crystal. The total number of lattice sites is increased by one formula unit upon formation of schottky defect, unlike the frenkel defect, which conserves the number of lattice sites as shown in fig.1.7.



Figure 1.7 The frenkel and Schottky Defects

### 1.10. <u>PROPERTIES OF CERAMICS</u>

The physical properties of any ceramic material are a direct result of it's crystalline structure and chemical composition. Solid state physics reveals the fundamental connection between microstructure and properties such as localized density variations, grain size distribution, type of porosity and second -phase content, which can all be correlated with ceramic properties such as mechanical strength-  $\delta$  by Hall-Petch equation, hardness, toughness, dielectric constant, and optical properties exhibited by transparent materials. Physical properties of chemical compounds which provide evidence of chemical composition include; odour, colour, volume, density, melting point, boiling point, heat capacity, physical form at room temperature(solid, liquid, gas), hardness, porosity and index of refraction. The science of preparation ,examination and evaluation of microstructures is often implemented on similar spatial scales to that used in the emerging field of nanotechnology: from tens of angstroms (Å) to tens of micrometers (µm). This is typically somewhere between the minimum wavelength of visible light and resolution limit of the naked eye.

1.10.A. The microstructure includes most grain, secondary phases, grain boundaries, pores, microcracks, structural defects and hardness microindetions. Most bulk mechanical, optical, thermal, electrical, and magnetic properties are significantly affected by the observed microstructure. The fabrication method and processing conditions are generally indicated by the micro-structure. The root cause of many ceramic failures is evident in the cleaved and polished microstructure. Physical properties which constitute the field of material Science and engineering includes the following:

#### 1.10.1. ELECTRICAL PROPERTIES

The electrical properties of ceramic materials vary greatly with characteristic measures spanning over many orders of magnitude; with intrinsic and extrinsic electrical characters like: superconductivity, semi-conductivity, ferroelectricity, piezoelectricity, insulation properties, magnetic properties and dielectric properties. Though ceramics are considered as basically electrical insulators, due to their valence electrons not in the conduction band. However their conductivity can be altered by doping the material with impurities.

#### 1.10.2. <u>SEMI-CONDUTOR CERAMICS</u>

Some ceramic materials are semi-conductors. Most of them are transition metal oxides that are group2 and group6 semi-conductors, such as Zinc oxide. Exploring and technically manipulating the processing routings proofs that these materials show a grain boundary effect which makes them useful in many areas for technological advancements, they are widely used as varistor. These are devices that exhibit the property that; resistance drops sharply at a certain threshold voltage. Once the voltage across the device reaches the threshold, there is a breakdown of the electrical structure in the vicinity of the grain boundaries, which results in it's electrical resistance dropping from several mega ohms down to a few hundred ohms. The major advantage of these is that: it can dissipate a lot of energy, and they are self-reset-after the voltage across the device drops below the threshold, its resistance return to being high. This makes them ideal for surge protection applications; as there is control over the threshold voltage and energy tolerance and they are used

in all sorts of applications. The best demonstration of their ability can be found in electrical substations, where they are used to protect the infrastructure from lighting strikes. They have rapid response, have low maintenance, and do not appreciably degrade from use; making them virtually ideal devices for this application. Semiconducting ceramics are also employed as gas sensors and have prospects of mass – producing light emitting diode (LED). Ceramics which are believed to have a positive thermal coefficient show some grain boundary effect and suddenly become insulating upon an increase in temperature; they are mostly heavy metal Titanates and the critical transition temperature can be adjusted over a wide range by variations in chemistry. In such materials, current will pass through the material until joule heating brings it to the transition temperature, at which point the circuit will be broken and the current flow will cease. Such ceramics are used as self-controlled heating elements in, for example, the rear window defrost circuits of automobiles.

Also at the transition temperature, the materials dielectric response become theoretically infinite. While a lack of temperature control would rule out any practical use of the material near it's critical temperature, the dielectric effect is exceptionally strong even at much higher temperatures. Titanates with critical temperature far below room temperature are used for capacitors.

#### 1.10.3. FERROELECTRIC CERAMICS

Some ceramics materials also show ferroelectric effects, in which a stable electric dipole can be oriented or reversed by applying an electrostatic field. This effect, which is a necessary consequence of pyroelectricity can be used to store information in ferroelectric capacitors and ferroelectric Random Access Memory used in computers for information storage. An example includes Barium titanate.

#### 1.10.4. <u>PIEZOLELECTRIC CERAMICS</u>

A large number of ceramic materials also exhibit piezoelectric effect, in which there is an interconversion of electrical signals into mechanical response and vice-versa. An example is the quartz used to measure time in watches and other electronics. Such devices use both properties of piezoelectrics, using electricity to produce a mechanical motion (powering the device) and then using this mechanical motion to produce electricity (generating signal). Moreover, piezoelectric effect is generally stronger in materials that also exhibit pyroelectricity, and all pyroelectric materials are also piezoelectric. The materials can be used to inter-convert between thermal, mechanical, or electrical energy. For example, after synthesis in furnace, a pyroelectric crystal allowed to under no applied stress generally builds up a static charge thousands of volts. Such materials are used in motion sensors, where a tiny rise in temperature from a warm body entering the room is enough to produce a measurable voltage in the crystal.

#### 1.10.5. INSULATING PROPERTIES:

In contrast to metals, ceramics have low electrical conductivity due to ionic-covalent bonding which does not form free electrons. Most ceramics are used as electrical installation insulators.

#### 1.10.6. ELECTRICAL CONDUCTIVITY

This is the ability of the material to conduct electric current. The electrical conductivities differ by a factor as large as  $10^{12}$ .... $10^{21}$  between metallic and ceramic materials. Most ceramic materials are dielectric,(materials having very low electric conductivity, but support electrostatic field). Electrical conductivity of ceramics varies with the frequency of field applied and also with temperature. This is due to the fact that charge transport mechanisms are frequency dependent.

Further, the activation energy needed for charge career becomes mobile. Dielectric ceramics are used for manufacturing capacitors, insulators and resistors.

#### 1.10.7. <u>SUPERCONDUCTING CERAMICS</u>

In spite of very low electrical conductivity of most ceramic materials, there are ceramics that posses superconducting properties (near -to-zero electric resistivity). Lanthanum (Yttrium)barium-copper-oxide ceramic may be superconducting at critical temperature as high as 138K. These are known as high temperature superconductors, because of their relatively high critical temperature. This critical temperature is much higher, than the superconductivity critical temperature of other superconductors (up to 30K). Example, La<sub>2-x</sub>Ba<sub>x</sub>CuO<sub>4</sub>; this compound in its stoichiometry form La<sub>2</sub>CuO<sub>4</sub> is an antiferromagnetic insulator with Neel 240 K. The lanthanum has a valence of three and Cu a valence of two, so there is a perfect charge compensation between the electropositive and the electronegative atoms. The structure  $La_2CuO_4$  is orthorhombic and the bonding between the Cu and O ions is predominantly covalent. If La (which is always trivalent) is replaced by divalent Ba then the charge balance is disturbed, which leads to an electron deficient structure that demands one or more of the following changes: some Cu become trivalent, some O become monovalent and oxygen vacancies arise. In principle the oxygen concentration is maintained in order to prevent the formation of vacancies. Eventually; certain covalent bonds between copper and oxygen become broken and unsaturated when Ba replaces La. At sufficiently large Ba concentration, the system becomes metallic, the structure becomes tetragonal and superconductivity appears. Hall effect measurement show that the charge carries are holes. The measurement of the flux quantum in these substances show that the superconducting charge carriers have charge 2e, hence hole pairing. Although there is much discussion of the technical

application of these superconducting materials, high performance magnets are as yet the only major commercial development, and they have found use in the research laboratory. The one commercial exception is their use in nuclear magnetic resonance for chemical analysis and magnetic resonance tomography. Consequently, high  $-T_c$  superconductors can sustain much higher magnetic fields of about 100T. It is usually stated that the need to use large amount of expensive liquid helium as refrigerant is the major obstacle to the technical development of superconducting equipment, for example in superconducting power lines or rotating machinery.

#### 1.11. MAGNETIC PROPERTIES

Magnetic ceramics are prepared by sintering technology from Iron Oxide and Barium/strontium carbonate with small amounts of other metal oxides. Magnetic ceramics are known as ferrites, there are two types of magnetic ceramics (ferrites); Isotropic ceramic magnet with equal magnetic properties in all directions, and anisotropic ceramic magnets with magnetic properties in the direction f pressing. Ferrites combine good magnetic properties (high magnetization) with very low electrical conductivity. Low conductivity of ferrites allows reducing energy loss, caused by eddy currents, induced in the material when it works in high frequency magnetic fields. Therefore the widest field of application of ferrites is high frequency appliances: ferric antennas, speaker magnets, magnetic resonance Imaging (MRI), audio-visual recording heads and convergence coil cores.

#### 1.12. THERMAL PROPERTIES:

The tendency of a material to conduct, transmit and store heat energy describes a phenomenal property known as thermal property. The most critical thermal properties of ceramics to be discussed are heat, thermal conductivity, radiation and absorptivity in order to have well informed

knowledge of these materials in their areas of exploitations, such as their use as insulating materials, heat sinks and heat storage materials. Thermal energy can be either stored or transmitted by solid. In solid materials at temperatures above  $0^{\circ}$ kelvin, conduction of thermal energy is by microscopic diffusion and collisions of particles or quasi-particles within a body due to temperature gradient. The microscopically diffusing and colliding objects include molecules, electrons, atoms and phonons. They transfer microscopically disorganized kinetic and potential energy which are jointly known as internal energy. Whether by conduction or by thermal radiation, heat spontaneously flows from a body at higher temperature to a body at lower temperature. In the absence of external drivers, temperature difference decay over time and bodies approach thermal equilibrium. Also at 0°Kelvin, there is a constant vibration of the atoms at their lattice positions and these vibrations are also affected by the vibrations of adjacent atoms through bonding. Hence, vibration can be transmitted across the solid. The higher the temperature, the higher the frequency of vibration; and the shorter the wavelength of the associated elastic deformation. As temperature increases, the vibrational amplitude of the bonds increases. The elasticity of the waves is due to the fact that, the vibration of atoms affects the motion of neighbouring atoms. As temperatures (up to about 400 °C) energy travels through the material predominantly via phonons, elastic waves that travel at the speed of sound. Phonons are quantized lattice vibrations which increase in frequency and amplitude as temperature increases. Phonons travel through the material until they are scattered, either through phonon-phonon interactions or at lattice imperfections such as vacancies and interstitials. Phonon conductivity generally decreases with increasing temperature in crystalline materials as amounts of scattering increases. Amorphous ceramics which lack the ordered lattice undergo even greater scattering, and therefore are poor conductors. Those ceramic materials that are composed of particles of similar size and mass with simple structures (such as diamond BeO) undergo the smallest amount of scattering and therefore have the greatest conductivity. At higher
temperature, photon conductivity (radiation) becomes the predominant mechanism of energy transfer. This is a rapid sequence of absorptions and emissions of photons that travel at speed of light. This mode of conduction is especially important in glass, transparent crystalline ceramics, and porous ceramics. In these materials, thermal conductivity is affected by microscopic imperfections. The transmission of either type of wave (phonon or photon) is interrupted by grain boundaries and pores, materials that are more porous are better insulators. This is because at the normal dry conditions; the pores are occupied by air molecules and air is a bad conductor of heat due to the packing nature of its molecules. Also owing to the packing density of a material, it's mass, and surface area of the ceramic material: it can absorb and store heat energy; and transmit it at a slower pace through temperature fall, as compared to that of metals and other highly conductive materials. Ceramics of high density and porosity tend to have the ability to take up heat, store and have much more to get rid of through cooling. This phenomenon, known as the large heat capacity is one of the reasons why ceramics are better energy storing materials and hence their use as heat storage blocks in many systems around us. An example is the locally manufactured "Gyapa" Pot" and the locally manufactured blacksmith furnace.

# 1.13. OPTICAL PROPERTIES:

The optical property of a ceramic material describe the way it reacts to the exposure to light. When light energy hits a ceramic material, it may transmit, absorb, or reflect. Ceramic materials vary in their ability to transmit light, and are usually described as transparent, translucent or opaque.

1.13.1. Transparent ceramics, which is used in the military sector as high-strength, robust materials has the capability to transmit light(electromagnetic waves) in the visible (0.4 - 0.7 mm) and mid-infrared(1 - 5 mm) regions of the spectrum. These materials are used as transparent bullet proof windows, transparent Amor; including next-generation high speed missiles and pods, and

protection against improvised explosive devices. Examples of such materials are aluminium Oxide (alumina); which could be made translucent upon right manufacturing conditions. During the processing the microscopic pores in the ceramic materials; upon the formation of it polycrystalline phase, which are trapped at the junctions of microcrystalline grains is reduced. This is basically done through further exploitation of the particle size of the material. Also in the formation of polycrystalline materials(metals and ceramics) the size of the crystalline grains is determined largely by the size of the crystalline particles present in the raw material during formation(or pressing) of the object, moreover; the size of the grain boundaries scale directly with particle size. Thus a reduction of the original particle size below the wavelength of visible light(0.5 micrometers for shortwave violet) eliminates any light scattering, resulting in a transparent material. Engineers ensure the volume of fraction of these microscopic ores to be less than 1% in order to achieve such level of transparency.

1.13.2. Opaque ceramic materials do not transmit light. Their opacity results from the incoherent scattering of light at the surfaces and interfaces. In addition to pores, most of the interfaces in typical metal or ceramic objects are in the form grain boundaries which separate tiny regions of crystalline order.

1.13.3. Mechanism for the interaction of light with the particles in a ceramic material:

There are two important mechanisms for the interaction of light with particles in a solid. They are electronic polarization and transitions of electrons between different energy states. Polarization is described as the distortion of the electron clouds of an atom by electric field. In this case the electric field of light. As a result of polarization, some of the energy may be absorbed, that is: converted into elastic deformations (phonons), and consequently heat. Alternatively, the polarization may propagate as a material bound electromagnetic wave with different speed than

light. When light is absorbed and re-emitted from the surface at the same wavelength, it is called reflection and transmission of light from one medium into another, such as from air into glass: is called refraction – which is the apparent bending of light rays that result from the change in speed of the light wave owing to the packing density of the two materials under study. The change In speed is the result of electronic polarization. On the other hand the transitions of electrons between different energy states which is by virtue of the fact that the energy levels of electrons are quantized, i.e. each electron transition between levels requires a certain specific amount of energy. The absorption of energy results in the shifting of electrons from the ground state to a higher excited state. The electron that fall back to the ground state is accompanied by the remission of electromagnetic radiation.

# 1.14. MECHANICAL PROPERTIES:

ceramic materials are usually ionic or covalent bonded materials, and can be crystalline or amorphous. A material held together by either type of bond will tend to fracture before plastic deformation takes place, which results in poor toughness in these materials. Additionally, because these materials tend to be porous, the pores and other microscopic imperfections act as stress concentrators, decreasing the toughness further, and reducing the tensile strength. These combine to give catastrophic failures, as opposed to the normally much more gentle failure modes of metals. This is why they are considered as brittle fractured materials. These materials do show plastic deformation. The plastic deformation in ceramics is by stip, which is difficult due to the structure and the strong local (electrostatic) potentials. However, due to the rigid structure of the crystalline materials, there are very few available slip systems for dislocation to move, and so they deform very slowly. With the non-crystalline (glassy) materials, viscous flow is the dominant source of plastic deformation, and also very slow. It is therefore neglected in many applications of ceramic materials. The brittle fracture of ceramics limits its applications. It occurs due to unavoidable presence of microscopic flaws (micro-cracks, internal pores, and atmospheric containments) that result during processing. The flaws heeds to crack formation, and crack propagation (perpendicular to applied stress) is usually transgranular along the cleavage planes.

1.14.1. Griffith law of stress superelevation conditions for failure:

it states that; all materials exhibit a natural defect population due to production, defects differ in size, form and orientation, and brittle materials fail if nominal strength is overcome by defect related stress peak. He further explained that: Brittle materials can not diminish stress superelevation at crack tip by plastic deformation; small defects weaken brittle materials and failure occurs in brittle materials of theoretical strength lee than defect related stress peak.

 $\delta.\sqrt{x}.c \geq \sqrt{2}.Y.E$ ,

Where;

 $\delta$ , C Applied stress < defect related stress peak.

2,Y surface created, intrinsic surface energy of material.

E Young modulus

1.14.2. To overcome the brittle behaviour, ceramic materials development has introduced the class of ceramic matrix composite materials, in which ceramic fibres are embedded into the material, and they form fibre bridges across any crack. This mechanism substantially increases the fracture toughness of such ceramics. An example is the ceramic disk brake and ceramic springs. The compressive strength of ceramics is typically ten times the tensile strength. This makes ceramics good structural materials under compression (e.g. bricks in houses and tiles), but not in

conditions of tensile stress, such as under flexure. Finally A.A Griffith, upon his study of microstructural imperfections, like cracks, in brittle materials described "ceramics are strong in compression and weak in Tension".

# 1.15. CERAMIC PROCESSING:

The processing of ceramic materials describes the way in which ceramic object (e.g. porcelain, glass windows, optical fiber, bearing etc.) are produced. The processing has can be grouped into

a) Traditional processing

b) Advanced processing

Both have individual steps and the level of sophistication in obtaining a particular ceramic relates it to the above mentioned categories.

# 1.15.1. TRADITIONAL CERAMIC PROCESSING

The basic raw material is obtained through sustainable mining process and it is carefully sorted to get rid of other unwanted macro-particles. Another step is to reduce the particle size of the raw material through grinding and other necessary procedures to achieve a uniform fine powder (diameter  $< \mu m$ ). To achieve a tendency to cast into shape, and design(plasticity), additives is added in a process known as forming; Appropriate drying mechanism are employed to achieve a good level of dryness and the materials is subsequently sintered to achieve the desired ceramic material. Sintering at high temperature (800°C to 1800°C) causes densification, which gives the ceramic product its strength and desired properties. During this process, the individual ceramic particles coalese to form a continuous solid network and pores are created as combustible matter in the product burns out. Typically, the microstructures of sintered product contains dense grains, where an individual grain is composed of many starting particles. See fig.1.8 for basic ceramic processing steps.



# Figure 1.8 Ceramic processing steps.

High temperature superconductors: Solid-state thermochemical reaction involving mixing, calcination and sintering. This is the mechanism employed by scientist and engineers to achieve ceramic products of desired technical qualities. Basically the raw material is subjected through chemical deposition to achieve the appropriate amounts of precursor powders. The powders are mixed thoroughly using a ball mill, solution chemistry processes such as coprecipitation, freedrying and sol-gel methods are alternative ways for preparing a homogeneous mixture. The powders are repeatedly; calcined, cooled, reground at several hour intervals at temperature range from 800°C to 950°C in order to get rid of impurities and absolute homogeneous material. The powders are subsequently compacted to pellets and sintered. The sintering environment such as temperature, annealing time, atmosphere and cooling rate play a very important role in getting good high-T<sub>c</sub> superconducting materials. For example the  $YBa_2Cu_3O_{7-x}$  compound is prepared by calcination and sintering of a homogeneous mixture of  $Y_2O_3$ , BaCuO<sub>3</sub> and CuO in the appropriate atomic ratio. Calcination is done at 900°C-950°C, whereas sintering is done at 950°C in oxygen atmosphere. The oxygen stoichiometry in this material is very crucial for obtaining a superconducting YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> compound. At the time of sintering, semiconducting tetragonal

 $YBa_2Cu_2O_6$  compound is formed; which, on slow cooling in oxygen atmosphere, turns into superconducting  $YBa_2Cu_3O_{7-x}$ . The uptake and loss of oxygen are reversible in  $YBa_2Cu_3O_{7-x}$ . A fully oxidized orthorhombic  $YBa_2Cu_3O_6$  by heating in a vacuum at a temperature above 700°C.

## 1.16. RAW MATERIALS FOR TRADITIONAL CERAMICS

Mineral silicates, such as clays of various compositions, and silica, such as quartz and alumina, are among the most abundant substances in nature and constitute the principal raw material for traditional ceramics. These solid crystalline compounds have been formed and mixed in earth's crust over time by complex geological processes. Silicon stabilizes itself by combining with other minerals like oxygen, potassium, Aluminium and others to form silicates. The various combinations of silicon with other minerals yield the six common minerals and mineral group. They include; Quartz, feldspar, mica, ferromagnesian minerals, clay minerals and calcites. The basic raw material of ceramics is the clay related minerals. Clay mineral family include; Kaolinites group, Illite group, Smectite group and vermiculate group. They are formed through weathering and hydrothermal actions of silicon based rock mineral groups. The basic lattice structural unit of all silicates is the  $SiO_4$  (silicon oxygen tetrahedron), which is a pyramid with triangular base. In some silicates, these units occur as single ions linked by positive metal ions lying between them. Three dimensional networks of SiO<sub>4</sub> units also occur. The number and variety of silicate mineral are due to many different ways in which the basic  $SiO_4^{4-}$  units can combine with metal ions to form stable crystal structures. Clay minerals are phyllosilicates, (they are layered in structure); all of them have layers of silicon tetrahedral and layers of Aluminum, Iron, Magnesium octahedral. The silica tetrahedral can be arranged into chains or sheets by the sharing of oxygen between the adjacent silica tetrahedral. Clay variety depend on bonding

1 sheet of SiO<sub>4</sub> tetrahedral yields the kaolinite group

2 sheets of SiO<sub>4</sub> tetrahedral yields the montmorilloite

Clay varieties are also products of alteration from original silicates. Water molecules fits readily into the layered structure of clay minerals such as kaolin. When heat treated, the clay body loses it's content and becomes vitrified due to the formation of silicates that bind together the clay particles.

# 1.17. Building blocks of clay Minerals: NUST

Clay minerals are essentially composed of two types of sheets, the silica tetrahedral sheet and the alumina or magnesia octahedral sheet. These sheets are joined together in various arrangements to form the plate-like structures of clay minerals. The clay minerals are classified according to the number and the arrangements of silica tetrahedral sheets. Generally the recognized structures are (1:1) types and (2:1) types.

1.17.1. The major structures are kaolinite, vermiculite, illite and chlorite.Classification of clay minerals:

(1:1) type: layers in which the tetrahedral sheet is bonded to one octahedral sheet. The theoretical structures (without deformations) both types of layers depend on the hexagonal symmetry of the tetrahedral and octahedral sheets which are linked to each other. The apical oxygens of the tetrahedral unite with the vertices of the octahedral in a 1:1 layer are formed by 40H<sup>-</sup> radicals and 2 apical oxygens of the tetrahedral (Meunier 2005)

2:1 type: layers in which one octahedral sheet is sandwiched between two tetrahedral sheets. The commonly used layered silicates belong to the same general family of 2:1 layered or phylosilicates. Their crystal structures consist of layers made up of two tetrahedrally coordinated silicon atoms

fused to an edge-shared octahedral sheet of either aluminum or magnesium hydroxide. The layer thickness is around 1nm, the lateral dimensions of these layers may vary from 30nm to several microns or lager, depending on the particular layered silicate. Stacking of the layers leads to a regular van-der waals gap between the layers called the interlayer or gallery(Sinha Ray and Okamoto 2003). Isomorphic substitution within the layers (for example Al<sup>3+</sup> replaced by Mg<sup>2+</sup> or by Fe<sup>2+</sup> and also Mg<sup>2+</sup> replaced by Li<sup>+</sup>) generates negative charges that are counter balanced by alkali or alkaline earth cations situated in the interlayer(Sinha Ray and Okamoto 2003).

# 1.17.2. PRIMARY CLAY:

Kaolinite is the simplest type of clay mineral. They are classified as primary clays due to their location of deposit and their structure. It is composed of one aluminium hydroxide sheet and one silicon tetrahedral sheet in which each apical oxygen of the silicon tetrahedral sheet replaces one hydroxyl group of the aluminium hydroxide sheets and forms 1:1 type structure. Kaolinite has a low shrink-swell capacity and low cation exchange capacity. It is soft, earthy, usually white mineral (dioctahedral phyllosillicate clay), produced by the chemical weathering of aluminum silicate minerals like feldspar. In many parts of the world, it is coloured pink-orange-red by oxide, giving it a distinct rust hue. Rocks that are rich in kaolinite are known as kaolin. Kaolin is used extensively in the ceramic industry, where it's high fusion temperature and white burning characteristics make it particularly suitable for the manufacture of whiteware; kaolin is generally used alone in the manufacture of refractory. Substantial tonnages of kaolin are used for filling rubber to improve its mechanical strength and resistance to abrasion. Kaolin is an important ingredient in ink, organic plastics and many other products where it's very fine particle size, whiteness, chemical inertness and absorption properties gives it particular value.

# 1.17.3. SECONDARY CLAY:

There are a number of clay bodies which is used as the base material of most ceramic materials. They include the various forms of secondary clay bodies. Example include: Ball clay, Earthenware clay, stoneware clay etc. These forms of clay have the trace of at least two or more of the clay minerals. Basically, they are formed at their silicate-rich rock weathering site and then carried to particular locations by the agents of erosion. The process of their formation: they mix up with organic humus which make the clay body plastic when mixed with solvents. The level of plasticity is the property of clay that allows it to change shape without rupturing when force is applied to it. Clay particles are attracted to each other by weak electrostatic forces, water conducts these forces. Thus; dry clay mixed with fifth of its weight in water becomes plastic.

# 1.18. PROPERTIES OF CLAY MINERALS:

Cation exchange capacity (CEC): This is the ability of clay to absorb cations, and water molecules and form ionic double layer. The cation exchange reaction results mainly from unsatisfied bonds of charges due to isomorphous replacement of silicon and aluminum that give a large number of exchange sites and high exchange capacity. Others include; Flocculation, Dispertion and basal spacing.

# 1.18.1. CLAY/ ORGANOCLAY AND ORGANOCLAY/POLYMER NANOCOMPOSITES:

Since Ancient times, clay minerals have been investigated because of their importance in Agriculture, ceramics, building(Holeman 1965) and other uses such as intercalation, quasi-twodimensional magnetism, structural phase transition, fractal characteristics, mixed-crystal behaviour and so on(Wada and Kanitahara1991). In past few decades, the natural clay minerals such as montmorillonite(MMT), kaolinite(Murray 2000), and Palygorskite(attapulgite) (Galam 1996), are widely used in catalysis(cavani et. Al 1991; Harvey and Murray 1997; Guomois et al,2002 as absorbent, (Huh et al 200;Li et al 2004, Jaber et al,2005) in Nanocomposites (Giannelis 1996, Le Barron et al 1999; Morgan and Dubois 2000, Ray and Okamoto 2003) in sensors (Darder et al 2005) electrode (Zen 2004); as antibacterial materials, nuclear waste storage, pesticides carriers and so on. Nowadays, surface modifications of clay minerals have received an intensive attention because it allows the creation of new materials and new applications. Organically modified layered silicates can be produced by replacing the cations originally present in the galleries with organic cations. Ion exchange with alkylammonium ions is well-known and preferential method to prepare organoclays(de Paiva et al, 2008). As a result; the study of clays and organoclays are large field and shows an immense potential to be explored. The physical and chemical properties of clay minerals determine their practical use in the process industry. Especially the development of inorganic-organic hybrid materials was widespread in the few decades(Ruiz-Hitzky and Meerbeek 2006) are essential to develop polymer nanocomposites. Nanocomposites constitute one of the most developed areas of nanotechnology (de Paiva et al, 2008).

# 1.19. CERAMIC PRODUCTS:

Clay construction products – bricks, clay mortar, clay pipe and tiles. Refractory ceramics – ceramics capable of high temperature applications such as furnace walls, crucible and moulds.

Cement used in concrete – used for construction and roads.

Whiteware products – pottery, stoneware, fine china, porcelain, and other table ware, based on mixtures of clay and other minerals.

Abrasives – aluminium oxide and silicon carbide.

Glass - bottles, glasses, lenses, window pane and light bulbs

Glass fibers – thermal insulating wool, reinforced plastics (fiberglass), and fiber optic communication lines.

Cutting tool materials - tungsten carbide, aluminium oxide, and cubic boron nitride.

Ceramic insulators – electrical transmission components, spark plugs and microelectronic chip substrates.

Magnetic ceramics - computer memories, ceramic permanent rotors

Nuclear fuels based on uranium oxide(UO<sub>2</sub>)

Bioceramics - Artificial teeth and bones.

Motivation: The project seeks to find concrete solutions to some major problems facing most of the developing countries of which Ghana is part.

1.20. <u>PROBLEM STATEMENT</u>: Owing to nations over-dependence on Portland cement based materials for all forms of construction, the building industry and the consumers of such infrastructure are suffering huge financial set-backs in terms of rent and construction cost due to the subsequent increment in the price of cement products locally. Also our local cement demand deficit calls for an import of cement and its related materials from other countries which has also lead to the pressure on our local currency to fall to the other foreign currencies. Moreover ,The nation has also been importing all our porcelain cook-ware, toiletry facilities and porcelain tiles for the various construction purposes.

The local pottery, foundry, artisans and catering industries has been facing the problem of energy loses in their operations. This is because they spend more energy and huge financial cost in their operations due to the inadequate and under-functioning thermal insulation mechanisms of their various kilns, ovens , and furnaces.

Clay bodies mined from the Atwima District have an environmental degradation effect on the wet lands around river bodies. Agricultural activities are on the slum, crops that rely heavily on clay soil like sugar cane, water cocoyam and other crops has seen a decline since the vegetation is used for the prospecting of clay. Another issue to talk about within the industry is the high cost of transporting the clay and It's finished goods from the industries around to the various destinations.

The poultry industry has been incurring huge loses and also under-performance of poultry breeds due to the poor way of husbandry of chicks from the hatchery. Because the materials they use in constructing most of the brooder pens are good conductors of heat or may not sustain the heat within its environs for a long time. They most of the time end up spending huge sums of money in the provision of heat energy and also the inevitable loss of higher number of the chicks during the brooding period. Another point to talk about is the under-production of breeds due the fact that the chicks do not get the required range of temperature all the time.

The nation also uses a lot of fossil related fuel for its domestic and commercial purposes and we go through a lot of uneasiness when there is a shortage in the supply. We also spend sums of foreign exchange on importing these form of unsustainable fuel.

#### 1.21. MAIN OBJECTIVES:

The motive behind the study is to give the best form of alternatives, backed by scientific proves in our quest to find absolute solutions to the problems aforementioned. They are;

To investigate the technical viabilities of our local ceramic bodies in the construction of stronger and durable edifice in order to reduce our dependence on Portland cement and also to deal with the issue of getting a proper national plan on constructions using most of our locally based material. This can also go a long way in solving our fiscal economic problems. Also the research can give the industry players an overview of the raw material available, which can serve as the bench mark in developing modernized ceramic industry to curve for the importation of the low standard ceramic materials which do not stand the test of pressure.

To give our entrepreneurs and the local engineers the best body ceramic composition that will help solve the issue of heat loss in their various activities. Not forgetting the tendency of the clay bodies vitrifying at a lower temperature. This type of clay bodies if proved can go a long way in helping the pottery industry to save cost since they will be using less energy to bake the clay bodies.

The research will give the local industry another competitive alternative in prospecting of clay. This can go a long way to create jobs for the people within and around the Sekyere South District and also give a shifting cultivation plan for the locations in Mfensi and Afari to have their wet land regain its fertility and also to pave way for the re-deposition of more plastic and strong bodied clay that has been sustaining the industry till now. To investigate the viability of the clay body in the construction of energy saver cooking ware and also for the production of clay briquettes that will utilize the wood waste from our timber industries.

To improve on the thermal insulation properties of our burnt bricks to help in the construction of efficient heat retaining poultry infrastructure. And also to check on the possibility of using the best insulating body for the construction of the lining of locally manufactured incubators and brooding pens.

In this study, efforts were made to mine clay from two locations in the Sekyere – South district of the Ashanti Region of Ghana. Deposits from the Agona-Oyon river beds and Asamang township where taken, giving the first phase processing after mining and taken to the ceramics department of the Kwame Nkrumah University of Science and Technology for sample preparation and some of characterization. An initial test was done on the samples to get a prior knowledge the sample. And another effort was made to improve on these qualities by the introduction of other ceramic raw materials. Example was the introduction of kaolin to improve on the thermal conductivity of the sample and also the use of the clay as a binder in the production of clay briquettes.



## CHAPTER TWO

# LITERATURE REVIEW

Previous studies has been made on investigating the technical and scientific viability of the various ceramic component materials in order to ascertain it's competitive advantage over other types of materials for the purposes of domestic and commercial use. With qualitative and quantitative scientific qualities like; thermal properties, specific heat capacity, weight loss, shrinkage, apparent porosity, bulk density, mechanical properties, and thermal diffusivity.

For example knowledge of thermal conductivity of a material is therefore of major importance for materials used in applications where thermal properties influenced the functionality in the products. The relevance of a knowledge on some of these key important scientific quantities gives the basic understanding of the underlying mechanisms and also some information of the structure as well as indications of factors like phase change and change of state. The various forms of studies and characterization have led technology into the discovery of many qualities of ceramic bodies; with preferable and competitive properties like superconductivity, and heat capacity.

# 2.1. <u>REVIEW OF PREVIOUS WORKS ON PHYSICAL CHARACTERIZATION OF</u> <u>CERAMICS.</u>

SUNDAY E. ETUK et al,(2003) studied the comparison of thermal properties of clay samples as a potential walling material for naturally cooled building design. This work was to investigate and compare the various clay bodies in order to establish their suitability as building material from the energy conservation point. The specific heat capacity for each sample was determined through the method of cooling correction, the weighing and displacement method was used for the determination of bulk density. The thermal conductivities were determined for each of the clay

samples using the steady state method; which involved the use of the improvised Lee's disc apparatus. Hence the thermal diffusivity and absorptivity were also calculated through a mathematical relation. In the end, the experimental results proved that, Kaolin has the least solar radiation absorptivity as well as the least thermal conductivity, hence high thermal resistivity. A model was devised for the prediction of temperature variation with the thickness of the samples. The model proved that kaolin would during the hottest time of the day record a lower temperature than the other clay samples. He concluded that kaolin would make a better choice over other clay material in the design of a naturally cooled building.

S.K. Nimo,(2009), studied on improving the thermal insulation properties of some locally mined clay in the Atwima District of Ghana. He composed two body blocks of kaolin from Teleku Bokasso in the Western Region of Ghana, and clay from two known sources namely; Afari and Mfensi. The bricks were sintered at a temperature of 1000°C. The clay samples were also characterized in terms of their particle size and chemical composition. It was proved that a percentage increment in the kaolin concentration improved on the thermal insulation properties of the samples. The Afari composition had an average of 1% more resistant than those of Mfensi. Afari with 40% Teleku bokasso was recommended for the construction of local furnace because it had it's strength more than doubled (105%) and was by 2% more resistant to heat than that same composition with Mfensi. All the samples were proved to have low weight loss levels , low water absorption , good linear shrinkage and compressive strength.

M.O.Ojo et al,(2009) embarked on the analysis of thermal and electrical properties of some clay samples from different locations in the Ondo town, Nigeria. They analyzed the sample through the determination of thermal conductivity, electrical resistivity and sedimentation. The standard experimental procedures used were the Lee's disc method, law of floatation and the simple

voltmeter – ammeter method. The results analysis revealed that, the samples texture were more of silt and clay and are yellowish in colour. The results further showed that the clay samples have different thermal conductivities and rates of cooling. They used the relation after (Tyler,1975) to calculate the thermal conductivity after going through the procedures of the Lee's disc experiment. Hence, calculated the thermal conductivity for the various clay samples

Samples	Thermal conductivity $(Wm^{-10}C^{-1})$
Red	3.82 × 10 <sup>-2</sup>
Yellow	
Grey	$1.457 \times 10^{-1}$
White	$7.05 \times 10^{-2}$
R	1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1

The study showed that grey sample has the highest thermal conductivity and emissive power while white clay sample has the lowest thermal conductivity and emissive power. The results also revealed that the clay samples had low electrical conductivity due to the low salt content. Voltmeter – ammeter results showed that grey sample has very high resistivity value 2.296 ohm-cm, followed by red sample with a resistivity value of 1.269 ohm-cm. It was observed further that yellow sample has a resistivity value of 1.140 ohm-cm while white sample has the least value of 0.7226 ohm-cm. The practical implications of the general characteristics of the clay samples and their potential as local building material were subsequently discussed.

F.O. ARAMIDE et al,(2012). Worked on the production and characterization of porous insulating fired bricks from Ifon clay(Nigeria) with varied sawdust admixture. The study was to investigate the effect of sawdust admixture in creating more pores and eventually affecting the thermal conductivity of such bricks. The clay was first processed to very fine particles and characterized using SEM/EDX, XRD and XRF to study the microstructures and mineral phases present in the

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samples. Physical properties which include; thermal shock resistance, bulk density, cold crushing strength, porosity and thermal conductivity were obtained by the appropriate standard test methods. The ASTM standards for measuring thermal shock resistance, bulk density, cold crushing strength and porosity were used, with the exception of the thermal conductivity, which they used the calorimetric principle that involves the Ibrahim's Apparatus. The results show that the amount of sawdust admixture affects the properties variously; porosity increased with percentage increase in sawdust admixture while the thermal conductivity and other properties of the sample reduced with the percentage increase in sawdust admixture. They concluded that for structural insulating bricks where compressive strength is important the sawdust admixture should not exceed 10 to 15 per cent. Some of the findings in terms are; fig.1 X-ray diffraction pattern (phase analysis), that shows the percentage by peaks of elemental compounds present in the clay; with the two major components being silica and Aluminium oxides. Table 1. Presents the XRD showing the percentage of minerals present and the percentage phase composition. There is also a the variation of thermal conductivity with the sawdust admixture and the relationship suggest that as the sawdust admixture increases, thermal conductivity of the samples reduced which subsequently proves an increase in the thermal resistivity of the samples. Fig.2 displays the SEM/EDX of Ifon clay samples; showing the morphorlogy of the minerals and its chemical composition; with oxygen and W J SANE NO BROW silicon being the most abundant elements.



Figure 1. X-ray diffraction pattern (phase analysis) of the ifon clay sample.



Sawdust admixture(%)



Figure 2. Typical SEM/EDX of ifon clay sample; showing the morphology of the minerals and its chemical composition.

Tayfun Cicek and Mehmet Tanriverdi [2007] experimented the fly ash-sand-lime bricks and obtained the compressive strength, unit weight, water absorption and thermal conductivity under optimum test conditions as 10.25 MPa, 1.14 g/cm<sup>3</sup>, 40.5% and 0.34 W m<sup>-1</sup> K<sup>-1</sup> respectively. They suggested that it was possible to produce good quality of light weight bricks from the fly ash of Seyitomer power plant, Turkey. The unit volume weight of the fly ash bricks prepared with quartz sand addition was 1.15 g/cm<sup>3</sup>, whereas the unit volume weight of the bricks with river sand addition was 1.27 g/cm<sup>3</sup>. Thus, the unit volume weights of the fly ash bricks were much lower than that of the traditional clay bricks. The water absorption of the fly ash-sand-lime bricks ranged from 30% to 40%. The thermal conductivity of the fly ash-sand-lime bricks was found to be 0.34–0.36 Wm<sup>-1</sup>K<sup>-1</sup> which was lower than that of the traditional clay bricks. The fly ash-sand-lime bricks produced were suitable for use as construction material. The production of fly ash bricks

contributes to the recycling of the fly ash and hence minimizes the negative impact of the fly ash landfills on the environment. On the other hand, the reduction in clay usage for the production of conventional clay bricks helped to protect the environment. Furthermore, the hazardous emissions from the clay brick burning kilns were reduced. The considerably low volume weight and low thermal conductivity of the fly ash bricks will reduce the construction and heating/cooling costs of the buildings.

Jose Luis Vivancos et al [2009] discussed that the energy consumption of a specific building depends mainly on the building type, climatologic conditions, building construction, occupancy behaviour, installations for heating, cooling, production of domestic hot water and lighting. Heat flux evolution on different types of clay and concrete bricks was studied using a guarded hot- plate. From the data collected a new model to study heat flux was proposed. This model was based on the shape of the typical sinusoidal curves observed for the time dependent heat flux evolution. The heat flux evolution on different types of clay and concrete bricks was studied using a guarded hot-plate based on standards. The model allowed the determination of the thermal resistance ( $R_B$ ), the heat flow for a finite wall thickness in the steady-state ( $\Phi$ G) and the time necessary to achieve half of  $\Phi$ GD( $t_B$ ). The proposed model helped to determine the value of  $t_B$  in the simple way. The value found showed a linear correlation with the square root of the product between the thermal diffusivity and the geometric characteristics of the bricks.

Michele et al (2004) outlined the thermal conductivity of clay and physical or micro-structural parameters which affect their thermal behaviour most significantly. A comparison of the correlation between the thermal conductivity data collected from the literature and those obtained in the present work with the bulk density highlighted that the dependence of thermal conductivity on bulk density, quoted by several authors was not always very obvious and was not able to

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describe accurately the thermal behaviour of clay bricks. Through a statistical treatment of data, some trends regarding the relationships among the thermal conductivity and the main mineralogical and micro-structural variables of bricks were revealed. The simple linear binary correlations and the multivariate analyses (factor analysis and multiple linear regression analysis) highlighted the role played by some mineralogical components, in particular Ca-rich silicates (wollastonite and melilite), quartz and amorphous in improving the insulating properties of clay bricks. On the other hand, among the micro-structural parameters, the role of open porosity in improving the thermal performances of bricks was found to be predominant.

Gangadhara Rao et al (1998) made an effort to evaluate the thermal resistivity of class F fly ash using a laboratory thermal needle/probe. The effect of density of compaction and the moisture content on the thermal response of the fly ash were studied. Fly ash was used in conjunction with aggregates to design a proper backfill material. Soil as such was not a good conductor of heat when compared to the metals (normal conductors). Soil thermal resistivity was a measure of the resistance offered by the soil to the passage of heat. Thermal stability was normally related to the ability of moist soil to maintain a relatively constant thermal resistivity when subjected to an imposed temperature difference. Thermal instability occurs when a soil was unable to sustain a rate of heat transfer; to overcome this; the native soil was replaced by materials (backfills) with better thermal properties. When water was added to the ash, it formed a thin film around the fly ash particles that eased the conduction of heat (i.e.) increasing its conductivity and reducing its resistivity. This attributed to the fact that the thermal resistivity of air (equal to 4000 °C-cm/ W) was higher than that of the water (equal to 165 °C-cm/W). The addition of water to the fly ash resulted in decrease in the air voids (and hence the density increases) and as such the thermal resistivity of the fly ash in the near vicinity of its optimum moisture content attained almost a constant value that is the minimum value of thermal resistivity the fly ash can exhibit. At this situation the resultant resistivity of the fly ash, known as —critical moisture content, was more dependent upon the resistivity of the pore water. There was a rapid increase in the thermal resistivity of the soil, with a small reduction in moisture content as less than the critical moisture content. This critical moisture content depends on the particle size distribution and the density of compaction. From the resistivity-moisture content variations, another important observation was that as compaction density increased, critical moisture content decreased. The critical moisture content values for fly ash were obtained in the range of 28–32%.

Turning attention to soils, the thermal conductivity of soil under a given set of conditions is most important as it relates to the soil's microclimate. The early growth and development of a crop may be determined to a large extent by microclimate. As a result, a lot of works have been done in that field; notably among them is the investigation performed by christoph et al.(2000). who worked on the thermal conductivity of soil and rocks using theoretical models and came to the conclusion that for modest temperatures and pressures there is great variation of thermal conductivity which depends on the specific rock base on it's mineral content, porosity, pore fluid, and anisotropy but they observed a significant decrease for temperature and pressure above 300 °C and 20 MPa, respectively.

The effect of soil density and water content on the apparent thermal conductivity of four selected soils with different textures (sand, sandy loam, loam, and clay loam) was investigated through laboratory studies by Nidal et al.(2000). In addition they also investigated the effects of two common salts (NaCl and CaCl<sub>2</sub>) and organic matter(peat moss) on apparent thermal conductivity of clay loam soil taken from Jordanian soil. The thermal conductivity of the soils were measured using the single probe methodology. Their observation was that, for the soils studied, the thermal

conductivity increased with increasing soil density and moisture content, which was as a result of particle-contact enhancement as porosity was decreased. Increasing water content completed water films around sand particles, which are relatively larger than silt and clay, and thus increased the contact area between sand particles that causes the thermal conductivity to increase rapidly. Their results also showed that an increase in the amount of salts in other words, increasing the salt concentration in solution at given moisture content decreased thermal conductivity. These results were similar to those of Noborio and McInne (1993). Values of thermal conductivity at a given solution content for sandy soil were higher than those for clay loam soil at all salt concentrations in solution.

Noborio et al.(1993), explained that for the soils with significant amount of clay, flocculation and aggregation might be strongly influenced by the interactions of clay particles with salt ions. The less ordered the structure of clay (i.e., more flocculated), the lower the thermal conductivity. Increasing the percentage of soil organic matter also decreased thermal conductivity. They therefore concluded that thermal conductivity varies with soil texture, water content, salt concentration, and organic matter content. For all soils studied, an increase in bulk density at a given moisture content increased thermal conductivity. Thermal conductivity for clay loam soil decreased with increasing organic matter(peat moss) content. Their results suggest that: solution – clay interactions significantly affect the thermal conductivity by altering the microstructure of clayey soils.

Other authors have also dealt with the problem of determining the effective thermal conductivity of porous ceramics. The effect of pressure, temperature, and porosity on the effective thermal conductivity, the behaviour of fluid-saturated porous mica ceramics with open pores was measured over temperature range of 275 to 423K and at a pressure of up to 400 MPa using a steady-state

parallel-plate apparatus with argon and water as pore saturants was studied by by Abdulagatov et al.(2002). They observed a sharp increase in the effective thermal conductivity for porous mica ceramic with gas (Ar) saturated at low pressures(between 0.1 and 100 MPa) along various isotherms, while for the same sample saturated with water, the pressure dependence of effective conductivity displayed very weakly.

Wag (1993), worked on the porosity and grain – size dependence of thermal conductivity calculated in terms of a power law; with the exponent of the power law depending on skewness of grain – size distribution. He compared that formalism with experimental results for isometric spherical – pore distribution in alumina, random-pore distribution in alumina, uranium dioxide and yttria-stabilized zirconia, sedimentary rocks and bricks, and found that good agreements existed between the experimental results and predictions based on the microstructure of the materials and their porosity dependence of the elastic modulus.

Materials synthesized from nitrides are effective high-temperature electric insulators operating in corrosive media. That prompted Miyashiro et al.(1990) to focus on the basic properties of aluminum nitride(AlN) and problems with AlN from the manufacturing process point of view and focused on four problem areas: the realization of highest thermal conductivity by sintering, pin/lead brazing, the metallization problem for co-fired case and the post-fired case, and polishing for a thin-film circuit, but as compared to JÚNIOR et al.(2004) they did a more detailed work by seeking to explain the variation in thermal conductivity when polycrystalline AlN is compared to it's single crystal version. The thermal conductivity of polycrystalline ceramics in general, exhibit lower thermal conductivities than their associated single crystals; so by Maxwell(Dondi) in 1904 and later modified by Euken to describe thermal conductivity(JÚNIOR; Kingery et al.,1976; Nye,1985; Baranda,1991) they reached the conclusion that the variation which was observed was strongly

dependent upon the purity of the starting materials and the details of the fabrication process since it influences the microstructure and thus influences the conduction mechanism. From their perspective, the thermal conductivities of polycrystalline AlN could be enhanced by:(a) reduction of powder impurities, namely oxygen and silicon,(b) appropriate selection of sintering additives, and (c) utilization of controlled sintering conditions.

Emerging needs for decrease in device size, the use of molecular level theories in device design and modelling has become more and more important, one particular issue that needs to be addressed in nano-electronic device modelling is the thermal transport properties of the components. Hence, the study of the thermal conductivity of nanotubes and its dependence on structure, defects and strain is of critical importance and has drawn the attention of many Mohamed (2001) and Depaak et al.(2001) who focused on the thermal researchers like conductivity of several single-wall carbon nanotubes calculated over a temperature range of 100-500K using molecular dynamics simulations with the Tersoff - Brener potential for C - Cinteractions. In all cases, starting from similar values at 100K, they observed that the thermal conductivity showed a peaking behaviour before falling off at higher temperatures. The peak position shifts to higher temperatures for nanotubes with larger diameters and no significant dependence on the tube chirality was observed. They showed that this phenomenon was due to the onset of Umklapp scattering, which shifts to higher temperatures for nanotubes with larger NO JSANE diameters.

Jianwei et al.,(2002) tried to understand the lattice thermal transport properties for carbon nanotubes, by using equilibrium molecular dynamics simulations to calculate carbon nanotubes thermal conductivities and its dependence on vacancies and defects. Green-Kubo (GK) relation derived from linear response theory was used to extract the thermal conductivity from heat – current correlation functions. The high value of thermal conductivity they obtained was for pure and defect free carbon nanotubes. As they expected, the thermal conductivity decreased as vacancy concentration increased. However, the rate of decreasing in thermal conductivity was quite unexpected, so more detailed analysis will be needed to understand the origin of this behaviour. In addition , more accurate interaction potentials need to be developed to quantitatively study the nanotube bundles and nanostructures.



### 2.2. OBJECTIVES OF THE RESEARCH

The behaviour of any ceramic material will undoubtedly greatly depend on its properties. Like all materials it's behaviour is dedicated by the types of atoms present i.e. their shape and size, the types of bonding between the atoms and the way the atoms are packed together (Dietrich). However it is difficult to determine how each particle affects the other or even which mode of combination are most important because there exist some unavoidable microscopic flaws.(i.e. micro-cracks, internal pores, atmospheric contaminants and grain boundaries) that results during cooling from melt. The flaws cannot be closely controlled in manufacturing which leads to large discrepancies regarding the data published by different authors in different laboratories mostly caused by the difficulties in accurate measurements as reported by Nunes et al. (2003). Yet the data on physical characterization of ceramic material do still appear similar but none of the available literature has really taken into consideration, physical characterization of locally mined ceramic materials.

Therefore the objective of this research is to:

- Basically characterize the material in terms of the physical characteristics like; apparent porosity, loss on ignition, density, linear shrinkage, cold crushing strength, thermal conductivity, specific heat capacity and chemical composition and characterization test
- Enhance the properties by the introduction of another locally mined ceramic material: Kaolin to form Clay-Kaolin composites.

- To investigate the mineral phase composition of these materials in order to have knowledge of the basic material constituents.
- Determine whether the new material has any appreciable change in terms of these characters, and performance in serving the purpose of the researcher and the Technician.



## CHAPTER THREE

# 3.0. THEORETICAL BACKGROUND:

# 3.1 <u>HEAT ENERGY</u>

Heat is the process of energy transfer from a system to another due to a variation in temperature. Thermodynamics is the study of the conversion of energy into work and the accompanying heat, it is related to macroscopic variables such as temperature and pressure. Heat transfer is a path function(process quantity), as opposed to a point function (state quantity). Heat is known to flow between systems that are not in thermal equilibrium with each other. It spontaneously flows from the areas of high temperature to areas of low temperature. When two bodies of different temperature come into thermal contact, they exchange internal energy until their temperatures are equalized; that is, until they reach thermal equilibrium. The adjective hot is used as a relative term to compare the object's temperature to that of the surroundings. In the absence of work interactions, the heat that is transferred to an object ends up getting stored in the object in the form of internal energy.

3.1.0. Heat can be transferred from one place to another by three methods: conduction in solids, convection in fluids (liquid or gases), and radiation through anything that will allow radiation to pass.

3.1.1. Conduction is the transfer of energy and distribution of heat energy through matter; from particle to particle. In other words, heat is transferred by conduction when adjacent atoms vibrate against one another, or as electrons move from atom to another. In solids, thermal conduction results from conduction by lattice vibrations and conduction by electrons. In insulating materials, the conduction is by lattice waves. In pure metals, the lattice contribution is negligible and the

heat conduction is primary, due to electrons. In many alloys, impure metals, and semi conductors, both conduction mechanisms contribute. In superconductors at temperatures below the critical temperature, the electronic conduction is reduced; at sufficiently low temperatures, the thermal conductivity becomes entirely due to lattice waves and is similar to the form of the thermal conductivity of an insulating material. Conduction is greater in solids, where atoms are in constant contact; as packing density decreases so does conduction. Therefore fluids(and especially gases) are less conductive. This is due to the large mean free path between atoms in gases: fewer collisions between atoms means less conduction and the conductivity of gases increases with temperature.

3.1.2. The second mode of heat transfer: convection depends on the mass motion of a fluid or gas to convey the heat. Convection is the transfer of heat energy between a solid surface and the nearby liquid or gas in motion. It involves the flow of a fluid, the conduction of heat into or out of the fluid; the flow of heat across a solid boundary. The presence of bulk motion of fluid enhances the heat transfer between the solid surface and the fluid. The accepted formula used to describe the convective heat transfer is Newton's Law of cooling/heating given by the relation:

$$q = hA (T_s - T_b)$$

Where A is the surface area,  $T_s$  is the surface temperature and  $T_b$  is the temperature of the fluid at bulk temperature. However  $T_b$  varies with each situation and is the temperature of the fluid "far" away from the surface. The h is the constant heat transfer coefficient which depends upon physical properties of the fluid such as temperature and the physical situation in which convection occurs. Convective heat transfer is not effective in solids.

(3.1)

Both conduction and convection require matter to transfer heat. Radiation is a method of heat transfer that does not rely upon any contact between the heat source and the heated object. Radiation is the only form of heat transfer that can occur in the absence of any form of medium(i.e., No mass exchange and no medium is required). Thermal radiation is a direct result of the movements of atoms and molecules in a material. Since these atoms and molecules are composed of charged particles (protons and electrons), their movements result in the emission of electromagnetic radiation, which carries energy away from the surface. At the same time, the surface is constantly bombarded by radiation from the surroundings, resulting in the transfer of energy to the surface. Since the amount of emitted radiation increases with increasing temperature, a net transfer of energy from higher temperature to lower temperature results. All objects with temperature above absolute zero radiate energy at a rate equal to their emissivity multiplied by the rate at which energy would radiate from them if they were a black body. A black body is a hypothetic body that completely absorbs all wavelengths of thermal radiation incident on it. Such bodies do not reflect light, and therefore appear black if their temperatures are low enough so as to be self-luminous. All black bodies heated to a given temperature emit radiation. The radiation energy per unit time from a black body is proportional to the fourth power of the absolute temperature and can be expressed with Stefan – Boltzman Law as

$$q = \delta T^4 A$$
 (3.2)

Where:

q = heat transfer per unit time (W),  $\delta = 5.670310^{-8}$  (W/m<sup>2</sup>K<sup>4</sup>) – The Stefan - Boltzman constant,

T = absolute temperature in Kelvin (K), A = area of the emitting  $body(m^2)$ 

For objects other than ideal black bodies ('grey bodies') the Stefan – Boltzman Law can be expressed as:

$$q = \varepsilon \,\delta \,T^4 A \tag{3.3}$$

Where:

 $\varepsilon$  = emissivity of the object (one for a black body)

If a hot object is radiating energy to its surroundings the net radiation heat loss rate can be expressed as:

$$q = \varepsilon \delta \left( T_h^4 - T_c^4 \right) A_c$$
(3.4)

Where:

 $T_h$  = hot body absolute temperature (K),  $T_c$  = cold surroundings absolute temperature(K),  $A_c$  = area of the object (m<sup>2</sup>)

Both reflectivity and emissivity of all bodies is wavelength dependent. The temperature determines the wavelength distribution of the electromagnetic radiation as limited in intensity by Plank's law of black-body radiation. For all bodies, the reflectivity depends on the wavelength distribution of incoming electromagnetic radiation and therefore the temperature of the source of the radiation. The emissivity depends on the wavelength distribution and therefore the temperature of the body itself.

# 3.2. THERMAL CONDUCTIVITY

Thermal conductivity is the amount of heat a particular substance can carry through it per unit time. Usually expressed in W/m K, the units represent how many Watts of heat can be conducted through a one meter thickness of the said material with one Kelvin temperature difference between the two ends. The basic equation for thermal conductivity is given by the Fourier conduction equation for one dimensional flow:

$$\frac{dQ}{dt} = -kA\frac{dT}{dx}$$
(3.5)

Where:

dQ is the amount of heat flowing normal to the area A in time dt

In general the thermal conductivity is not simply related to the individual clay components, because the conduction of heat occurs through all kinds of sequence of the conducting materials, both in series and in parallel. The above equation assumes only one situation in layered profiles, that is in series. The heat flow is proportional to the temperature gradient  $-\frac{dT}{dx}$ , the proportionality factor being a material constant and k is the thermal conductivity. equation (3.5), under steady-state conditions can be used for particular shapes of interest.

For a heat flux  $q = \frac{dQ}{dt}$  through a slab, the equation becomes;

$$q = -kA \frac{T_2 - T_1}{X_2 - X_1} \tag{3.6}$$

For radial heat flow, out through a cylinder, tube or pipe of length(l), inner diameter  $D_1$  and outer diameter  $D_2$ :

$$q = -k(2\pi l) \frac{T_2 - T_1}{\ln D_2 - \ln D_1}$$
(3.7)

If the temperature is not constant, it's rate of change with time depends on the ratio of the thermal conductivity to the heat capacity per unit volume  $\rho C_p$ . The rate of change of temperature of a volume element dxdydz is therefore derived as equal to



The heat equation is used to determine the change in internal energy function(U). the heat equation is a consequence of Fourier's law of conduction. It is an important partial differential equation which describes the distribution of heat(or variation in temperature) in a given region over time. This function changes over time as heat spreads through space.
For a function T(x,y,z,t) which describe the temperature at a given location (x,y,z), the heat equation is:

$$\frac{\partial T}{\partial t} = \frac{k}{\rho C_p} \nabla^2 T$$
(3.9)

or equivalently for a rectangular coordinate the equation becomes:

$$\frac{\partial T}{\partial t} - \frac{k}{\rho C p} \left( \frac{d^2 T}{dx^2} + \frac{d^2 T}{dy^2} + \frac{d^2 T}{dz^2} \right)$$
(3.10)

For sphere, the thermal diffusion equation becomes:

$$\frac{\partial T}{\partial t} = \frac{k}{\rho C p} \frac{1}{r^2} \frac{\partial}{\partial r} \left( r \frac{2dT}{dr} \right)$$
(3.11)

If the system has reached steady state, it's properties are not time - dependent.

This includes the temperature, so

$$\frac{\partial T}{\partial t} = 0$$
(3.12)
Hence in this case, the thermal diffusion equation reduces to

$$\nabla^2 \mathbf{T} = 0 \tag{3.13}$$

That is, Laplace's equation; this equation is describing steady state flow.

# 3.2. <u>FACTORS INFLUENCING THE THERMAL CONDUCTIVITY OF A CEREMIC</u> MATERIAL.

There are several factors that significantly influence the rate of flow of heat through a ceramic material. Notably among them are:

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- Mineralogy composition
- Effect of Temperature and heat treatment
- Shrinkage
- Water and Oxide content
- The texture and porosity of the material
- Effect of particle size

#### 3.3. MINEROLOGY COMPOSITION

Heat conduction in insulators can be considered as diffusion of phonons from the hot to the cold end. Non-metallic solids transfer heat by lattice vibrations, so as atoms vibrate the more energetically at one part of a solid and transfer that energy to less energetic neighbouring atoms. Numerous attempts have been made to explain the property of thermal conductivity in terms of this theoretical reasoning. The most basic in considering the effect of composition on thermal conductivity is Debye's model. Debye's model estimates the phonon contribution to the specific heat capacity in a solid. It treats the vibration of the atomic lattice(heat) as phonons in a box. In contrast to Einstein model, which treats the solid as many individual , non-interacting quantum harmonic oscillators. The Debye model correctly predicts the low temperature dependence of heat capacity, which is proportional to  $T^3$  – the Debye  $T^3$  law. But due to simplifying assumptions, it's accuracy suffers at intermediate temperatures. The approximation that the frequency is inversely proportional to the wavelength(giving a constant speed of sound) is good for low energy phonons but not or high – energy phonons. This is one of the limitations of the Debye model, and corresponds to the incorrectness of the results at intermediate temperatures, whereas both at low temperatures and also at high temperatures they are exact.

A good knowledge of the rate at which phonon can transfer heat along the body of the crystal is therefore important. The classical theory of gases gives the thermal conductivity as:

(3.14)

 $\mathbf{K} = \frac{1}{3} \mathbf{c} \mathbf{v} \mathbf{l}$ 

Where:

c - is the heat capacity per unit volume,

v - the velocity and 1 - is mean free path.

The only difference in solids is that Phonons replace the molecules so that the heat capacity, velocity and mean free path refer to phonons instead of gaseous molecules. Since heat capacity is constant at high temperatures and varies as  $T^3$  at low temperatures, the conductivity therefore basically depends on mean free path.

In a system made up of ideal harmonic oscillators, the various normal modes of oscillation of the system are completely independent of one another, there are no coupling whatsoever between the different normal modes. In other words, phonons corresponding to different normal modes do not interact. Therefore, for a harmonic lattice, the harmonic waves do not give rise to thermal

resistance. This is the situation with phonons in crystals at low temperatures. At low temperatures (up to 400°C), energy travels through the material predominantly via phonons; elastic waves that travel at the speed of sound. Phonons are the quantized particle vibrations which increase in frequency and amplitude as temperature increases. Phonons travel through the material until they are scattered, either through phonon-phonon interactions or at lattice imperfections. Phonon conductivity generally decreases with increasing temperature in crystalline materials as the amount of scattering increases. Amorphous ceramics which lack the ordered lattice undergo even greater scattering, and therefore are poor conductors. However at high temperatures, anharmonicity becomes appreciable and phonon-phonon interactions give rise to thermal resistance thereby reducing the thermal conductivity. At higher temperatures, photon conductivity (radiation) becomes the predominant mechanism for energy transfer. This is a rapid sequence of absorptions and emissions of photons that travel at the speed of light. This mode of conduction is especially important in glass, transparent crystalline ceramics, and porous ceramics. In these materials, thermal conductivity increases with increased temperature. The electron mechanism of heat transport is relatively unimportant in ceramics because the charges are localized. This mechanism is very important, however, in metals which have large numbers of free (delocalized) electrons as freely moving valence electrons transferring not only electric current but also heat energy. However, the general correlation between electrical and thermal conductance does not hold for the other materials, due to the increasing importance of phonon carriers for heat in non-metals.

A phonon-phonon interaction is another consequence of asymmetry in the interaction potential between atoms. When different phonons overlap at the location of a particular atom, the vibrational amplitudes superimpose. Hence the atom has the tendency to vibrate with a different frequency, which produces a different phonon. Although the thermal conductivity is affected by faults or defects in the crystal structure, the transmission of either type of wave (phonon or photon) is interrupted by grain boundaries and pores, so the more porous materials are better insulators. Ceramics generally have strong bond and light atoms. Thus they can have high frequency vibrations of the atoms with small disturbances in crystal lattice. The result is that they typically have both high heat capacities and high melting temperatures.(kittel,1996; Blundel et al.,2006, Ashcroft et al.,1976;Schroeder,2000)

#### 3.4. EFFECT OF PARTICLE SIZE

Grain boundaries are effective obstacles to heat flow. In the case of high conductivity ceramics, large grain sizes are needed in order to minimize both grain boundary scattering, and effect of grain boundary phases. However the thermal conductivity of ceramics is generally inversely related to the square root of the grain size. This implies the smaller the grain size, the greater the thermal conductivity. This works well at low temperatures. At elevated temperatures, due to radiant heat transfer through the voids, the thermal conductivity increases with increasing particle size (Mcglinchey 2005; sivakugan,2000; ASTM C136-06 standard).

#### 3.5. EFFECT OF HEAT TREATMENT AND TEMPERATURE

Heat flow through porous composite materials such as clay bodies, is more complicated than flow through solids because of the varying combination of phases and densities of the clay components. Nevertheless, the same fundamental features of heat flow operate in both types of materials. As illustrated by equation 3.14, for non-metallic solids, the heat transfer is viewed as being transferred via lattice vibration, as atoms vibrate more energetically at one part of a solid transfer that energy to less energetic neighbouring atoms. This can be enhanced by cooperative motion in the form of propagating lattice waves, for crystalline materials the thermal conductivity decrease with increasing temperature since anharmonicity of the lattice vibration decreases the mean free path.

For amorphous materials on the other-hand an increase in temperature results in an increase in thermal conductivity since the decrease in thermal conductivity due to anharmonicity at elevated temperature is off-set by an increase in transmission in radiant energy and a considerable decrease in gas conductivity.

For most clays during sintering, at temperatures below 600°C, dehydration takes place. Below that temperature the organic matter is volatized. Solvents usually evaporates at temperatures below about 100°C and solutes evaporate at temperatures below about 450°C. At 500°C, the clay is completely dehydrated. It no longer slake or disintegrate in water, it has lost all plasticity. An irreversible change has taken place- dehydration and this is not accompanied by any shrinkage. The colour of the clay becomes light at that stage whiles porosity, shrinkage and strength increase with a decrease in weight. Oxidation starts at 350°C and is not complete until the

temperature has reached about 900°C and all the matter has been removed(Matter, such as carbon, inorganic carbonates and sulphates). During that stage if the clay has Fe<sub>2</sub>O<sub>3</sub> the colour of the clay becomes strong whiles on the other –hand if the clay has combustible materials the colour becomes weak. At that stage porosity increases since the loss of the solute and solvent leaves pores in the green body whiles there is slight decrease in both strength and weight. As sintering advances, the dissociation point of the compound is reached and the carbon or sulphur is driven off. As the temperature increases beyond 900°C the colour becomes stronger and vitrification occurs. Vitrification gives the fired clay it's characteristics: hard, dense, durable and rocklike properties. This includes the gradual elimination of porosity, which is typically accompanied by a net shrinkage and overall densification of the component. Thus, the pores in the object may close up, resulting in a denser, stronger product. The more plastic a clay is , the more strength it will develop in the dry state. Vitrification proceeds gradually as temperature increases and becomes increasingly hard, up to a point of melting and deformation.

## 3.6. EFFECT OF SHRINKAGE

Ceramic components undergo shrinkage at several steps in the manufacturing process. Clay body shrinkage refers to the loss of size that occurs throughout the total drying and firing process. Major shrinkage occurs during sintering as pores are gradually reduced or eliminated. There are three distinct periods of shrinkage. The first is when the ''air-dries'' to become bone dry, the second is during bisque firing and the third is during glaze firing. Shrinkage is the result of mechanically and chemically combined water being driven off from a material. Mechanical or ''free'' water is driven off during the initial stages of firing, from 100 to 200°C, and the chemically combined water begins to leave the clay structure in the 450 to 600°C range. As the

temperature increases, organic matter is oxidized or driven off, and the clay body begins to sinter or form itself into the first stage melting. The shrinkage rate varies both with the clay body and the temperature to which it is fired. In general: the higher the temperature, the greater the shrinkage. The more plastic a clay body is, the more it shrinks. Clay with finer particles absorbs more water, expands more, and when the water is forced out by drying or firing, they shrink more. If the clay is heated too quickly, steam will build up within the piece causing it to crack or explode in the dryer or kiln.

#### 3.7. EFFECT OF WATER CONTENT

An increase in the water content of the material slightly increases the thermal conductivity of the ceramic, due to water replacing air in the voids between soil particles. At complete dryness, the heat flow passes mainly through the clay particles and has to bridge the air-filled gaps between the particles and around their contact points, as a result the magnitude of the thermal conductivity at complete dryness is low since the contact areas are small and the thermal conductivity of air is low owing to the packing density of the air molecules as compared to that of liquids and solids. At low water content the clay particles are covered by thin water layer that acts as binders and thermally couples the particles so as the water content increases it causes the contact areas to expand which significantly increase the thermal conductivity.

#### 3.8. EFFECT OF TEXTURE AND POROSITY

Ceramics are, by nature, generally porous materials with varying degrees of porosity. The porosity of a material describes the fraction of void space in the material, where the void may contain, for example, air or water. The volume fraction occupied by voids, i.e. the total void

SANE

volume divided by the total volume occupied by the solid matrix and void volumes, is called porosity. Each void is connected to more than one other pore(interconnected), connected only to one other pore(dead end), or not connected to any other pore(isolated). Fluids flow through the interconnected pores only. The volume fraction of the interconnected pores is called effective porosity. Open porosity refers to a material that permits a fluid to move from one surface to an opposing surface in the material through a convoluted pathway of interconnecting networked channels. Whiles closed porosity refers to those pores that have become sealed within the grain structure. Ceramics do have varying degrees of porosity. Pores can be very large or very small (of the order of atomic or molecular size). Well sorted (grains of approximately, all of one size) materials have higher porosity than similarly sized poorly sorted materials (where smaller particles fill the gaps between larger particles), because smaller grains can effectively fill the pores (where all water flow takes place), drastically reducing porosity. Less porous clay absorbs less water, shrinks less and also withstand better the effect of thawing better than porous clay. Pores affect the strength of ceramics in two ways; first, they act as stress concentrators. once the stress reaches a critical level, a crack will form and propagate. Because ceramics possess no plastic-deformation attributes to absorb any energy transferred to these materials once a crack is initiated, it propagates until fracture occurs. On the other side, pores(i.e. their size, shape, and amount) reduce the strength of ceramics because they reduce cross-sectional areas over which a load can be applied and consequently, lower the stress that these materials can support(Encyclopaedia Britannica 2009, Kaviany 1995).

### 3.9. THEORY ON THE MECHANICAL PROPERTIES OF CERAMICS

The rate at which energy is released while a crack is formed, can be obtained from the energy difference at the beginning and end of the crack( $\Delta X$ ) respectively.

$$G = \lim_{\Delta x \to 0} \frac{2}{\Delta x} \int_0^{\Delta x} \frac{\sigma}{2} U_{yy} d_x$$
 KNUST<sup>1</sup>

For purely brittle solids, equation  $(1) = 2\gamma$ 

The Irwin correlation showed that this simple relation exist between the stress intensity factor and energy release rate.

$$G = \frac{K_I^2}{E} = \frac{dU_M}{dc}$$
  
Where,  
$$G = \text{ energy release rate}$$
$$U_M = \text{ mechanical energy}$$

 $U_E =$  released energy

And if Load is constant:

Combining equation 2 and 3

$$\frac{K_I^2}{E} = \frac{d\left[\frac{\sigma^2.\pi.c^2.t}{2.E.2}\right]}{dc}$$

 $K_I = \sigma \cdot \sqrt{c} \cdot Y$ 

Therefore  $K_I$  depends on

- externally applied stress (σ)
- size of the crack
- Y-factor defined by geometry of crack.

The Y-factor predicts the intensity and distribution of a stress field around a defect in the material of a component caused by an external load. The strength of ceramics depends on this equation. The units for the various relations are;

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$$K_{IC} = \sigma_c \;.\; \sqrt{c}$$
 . Y

Where,

$$[K_{IC}] = MPa\sqrt{m}$$
$$[\sigma_c] = MPa$$
$$[C] = m$$

No material and component is free of defects due to the purity and homogeneity of raw

material, processing, machining, handling etc. These defects are;

Volume defects such as pores, large grains

Surface defects such as cracks, pits, chipped edges, machining marks.

The conclusions made are;

 $K_{IC}$  – indicates how well a specific material under stress is able to withstand the extension of a crack, this is taken into consideration in designing most mechanically biased materials. The higher the  $K_{IC}$ , the more difficult it is for a crack to advance in a material.

The strength at failure  $\sigma_c$  is characteristic of a sample, part, or component.

In designing a material, one has to consider the effects of fracture toughness, strength, creep, sub-critical growth, and other technological tests and also consider the explanations of Griffith Laws to get an intuitive knowledge on the type of mechanical failure mode of the material.

Griffith law of stress superelevation conditions for failure:

it states that; all materials exhibit a natural defect population due to production, defects differ in size, form and orientation, and brittle materials fail if nominal strength is overcome by defect related stress peak. He further explained that: Brittle materials can not diminish stress superelevation at crack tip by plastic deformation; small defects weaken brittle materials and failure occurs in brittle materials of theoretical strength less than defect related stress peak.

 $\delta.\sqrt{\pi.c} \ge \sqrt{2.Y.E}$ 

Where,

 $\delta$ , C applied stress < defect related stress peak.

2,Y surface created, intrinsic surface energy of material.

E Young modulus.

The compressive strength of ceramics is typically ten times the tensile strength. This makes ceramics good structural materials under compression (e.g. bricks in houses and tiles), but

not in conditions of tensile stress, such as under flexure. Finally A.A Griffith, upon his study of micro-structural imperfections, like cracks, in brittle materials described ''ceramics are strong in compression and weak in Tension''.

#### 3.10. THEORY ON SPECIFIC HEAT CAPACITY

Heat Capacity is amount of heat required to raise material temperature by one unit.

Specific Heat Capacity is amount of heat required to raise temperature of unit mass of material by one unit:

SANE

$$c = \frac{\Delta Q}{(m\Delta T)}$$

#### Where:

c -specific heat capacity;

 $\Delta Q$  – amount of heat;

m – material mass;



Specific Heat Capacity of ceramic materials is higher, than that of metals.

## Compare:

"c" of alumina = 0.203 BTU/(lb\*°F) (850 J/(kg\*K)).

"c" of steel =  $0.115 \text{ BTU}/(\text{lb*}^{\circ}\text{F}) (481 \text{ J}/(\text{kg*}\text{K})).$ 

#### 3.11. THEORY ON THERMAL SHOCK RESISTANCE

Thermal Shock Resistance is an ability of material to withstand sharp changes in temperature. If a ceramic material is rapidly cooled, its surface reaches the temperature of cooling environment and tends to contract (thermal contraction). Since the interior regions of the material are still hot, thermal contraction of the skin surface is impossible.

This leads to formation of tensile stress (thermal stress) in the skin. Such thermal stresses may cause cracks and consequent failure.

Thermal shock resistance of a material may be estimated in accordance to the formula:

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$$\mathbf{Rs} = (\lambda^* \sigma F) / (\alpha^* E)$$

Where:

Rs – thermal shock resistance;

 $\lambda$  - thermal conductivity;

 $\sigma F$  – flexural strength

 $\alpha$  -coefficient of thermal expansion (CTE); E – modulus of elasticity. Sensitivity of ceramic materials to thermal shock may be also determined by experimental method (Hasselmann Method).

In this method a specimen (flexural test specimen) is heated to a specified temperature and then quenched. The specimen cools rapidly by temperature  $\Delta T$  (the difference between the specimen temperature before and after cooling).

After quenching the flexural strength of the quenched material is measured by standard flexure (bending) test.

The test results are plotted on the graph of Strength vs.  $\Delta T$ .

When  $\Delta T$  reaches a certain value the specimen strength falls sharply.

This value of  $\Delta T$  is a parameter indicating thermal shock resistance of the material. Some ceramic materials have very low coefficient of thermal expansion therefore their resistance to thermal shock is very high despite of low ductility (e.g. fused silica).

#### 3.12. THEORY OF THERMAL CONDUCTIVITY MEASUREMENTS

The fundamental methods that has been developed for determining the thermal conductivity of ceramic materials are; steady state methods and Transient state methods and theoretical predictions; also, several mathematical models have been proposed for calculating the thermal conductivity of ceramics differing in composition (Terry, 2004).

Thermal conductivity is thus a second order tensor, but in a material with cubic isotropy it reduces to a scalar. It is an intensive property (changing the amount of material does not change

its thermal conductivity) and is a function of both pressure and temperature. The thermal resistance R of a layer of a material of thickness (d) and of thermal conductivity k is given by:

$$R = \frac{a}{k}$$

The greater the value of R, the greater the resistance to the flow of heat.

# 3.12.1. Transient state conduction KNUST

In general, during any period in which temperatures are changing in time at any place within an object, the mode of thermal energy flow is termed transient conduction. Another term is "non steady-state" conduction, referring to time-dependence of temperature fields in an object. Nonsteady-state situations appear after an imposed change in temperature at a boundary of an object. They may also occur with temperature changes inside an object, as a result of a new source or sink of heat suddenly introduced within an object, causing temperatures near the source or sink to change in time. When a new perturbation of temperature of this type happens, temperatures within the system will change in time toward a new equilibrium with the new conditions, provided that these do not change. After equilibrium, heat flow into the system will once again equal the heat flow out, and temperatures at each point inside the system no longer change. Once this happens, transient conduction is ended, although steady-state conduction may continue if there continues to be heat flow. If changes in external temperatures or internal heat generation changes are too rapid for equilibrium of temperatures in space to take place, then the system never reaches a state of unchanging temperature distribution in time, and the system remains in a transient state. An example of a new source of heat "turning on" within an object which causes transient conduction is an engine starting in an automobile. In this case the transient thermal

conduction phase for the entire machine would be over, and the steady state phase would appear, as soon as the engine had reached steady-state operating temperature. In this state of steady-state equilibrium, temperatures would vary greatly from the engine cylinders to other parts of the automobile, but at no point in space within the automobile would temperature be increasing or decreasing. After establishment of this state, the transient conduction phase of heat transfer would be over. The transient techniques is based on the fact that any material submitted to a constant strength heat source of a given geometry in a given position, undergoes a transient behaviour, that is the temperature of a given point changes with time in accordance with the materials physical characteristics and it's thermal conductivity. Transient-state of thermal conductivity measurement generally makes use of either a line source of heat or plane source of heat. In both categories, the usual procedure is to apply a steady heat flux to the specimen, which must be in thermal equilibrium initially, and to measure the temperature rise at some point in the specimen resulting from this applied flux. The equation governing the temperature increase is expressed as a series of exponential terms, most of which can be ignored except at very small values of the time variable. Thus by avoiding the initial period, the duration of which depends upon the material dimensions of test specimen, a reasonably simple temperature relationship may be used. Non-steady-state methods to measure thermal conductivity do not require the signal to obtain a constant value. Instead, the signal is studied as a function of time. The advantage of these methods is that they can in general be performed more quickly, since there is no need to wait for a steady-state situation. The disadvantage is the mathematical analysis of the data is terser.

#### 3.12.2. STEADY STATE CONDUCTION:

This is the form of conduction that happens when the temperature difference(s) driving the conduction are constant, so that (after an equilibration time), the spatial distribution of temperatures (temperature field) in the conducting object does not change any further. Thus, all partial derivatives of temperature with respect to space may either be zero or have nonzero values, but all derivatives of temperature at any point with respect to time are uniformly zero. In steady state conduction, the amount of heat entering any region of an object is equal to amount of heat coming out (if this were not so, the temperature would be rising or falling, as thermal energy was tapped or trapped in a region). For example, a bar may be cold at one end and hot at the other, but after a state of steady state conduction is reached, the spatial gradient of temperatures along the bar does not change any further, as time proceeds. Instead, the temperature at any given section of the rod remains constant, and this temperature varies linearly in space, along the direction of heat transfer. Steady state method is based on the measurement of the constant heat flux in a sample of known thickness and flow area, under a constant imposed temperature gradient applied to the sample boundaries. Under these conditions, temperatures within the sample are functions of position only. The most common steady state methods of measuring thermal conductivity in our part of the world is the Lee and Charlton(1896) method(Lee's disk experiment) and the simple calorimetric method of which the Ibrahim's apparatus is an example.

3.12.3. The Lee's Disc experiment determines an approximate value for the thermal conductivity k of a poor conductor like glass, ceramic, cardboard, etc. The procedure is to place a disc made of the poor conductor, radius r and thickness x, between a steam chamber and two

good conductivity metal discs (of the same metal) and allow the setup to come to equilibrium, so that the heat lost by the lower disc to convection is the same as the heat flow through the poorly conducting disc. The upper disc temperature  $T_2$  and the lower disc temperature  $T_1$  are recorded. The poor conductor is removed and the lower metal disc is allowed to heat up to the upper disc temperature  $T_2$ . Finally, the steam chamber and upper disc are removed and replaced by a disc made of a good insulator.

The metal disc is then allowed to cool through  $T_1 < T_2$  and toward room temperature  $T_0$ . The temperature of the metal disc is recorded as it cools so a cooling curve can be plotted. Then the slope  $S_1 = \Delta T/\Delta t$  of the cooling curve is measured graphically where the curve passes through temperature  $T_1$ .



Fig. 3.1 Schematic diagram of the Lee's Disc apparatus and a theoretical graph showing the cooling rate of the metal disc with the insulator.

At the steady state, rate of heat transfer (H) by conduction is given by;

$$H = kA \left[ \frac{T_2 - T_1}{x} \right]$$

Where,

k - Thermal conductivity of the sample **NUST** 

A - Cross sectional area,

- $T_2 T_1$  -Temperature difference across the sample.
- x -Thickness of the bad conductor (see figure.1)

The sample is an insulator . It is in the form of a thin disc with large cross sectional area ( $A = \pi \times 0.5D^2$ ) compared to the area exposed at the edge ( $a = 2\pi rx$ ) in order to reduce the energy loss. Rate of energy transfer across the sample can be increased by keeping 'x 'small and 'A 'large. Keeping x small means the apparatus will reach a steady state quickly.



Fig.3.2. A schematic of steam chamber, brass disc A and disc B with the sample specimen with thickness X and direction of steam flow.

The thin sample of disc is sandwiched between the brass disc and brass base of the steam chamber (see figure 2). The temperature of the brass disc is measured by thermometer  $T_1$  and the temperature of the brass base is measured by thermometer  $T_2$ . In this way the temperature difference across such a thin disc of sample can be accurately measured.



Fig.3.3. A schematic diagram of heat loss due to cooling from the bottom of the brass disc by air convection.

The temperatures  $T_1$  and  $T_2$  are constant when the apparatus is in steady state. Then the rate of heat conducted through the brass disc must be equal to the rate of heat loss due to cooling from the bottom of the brass disc by air convection. By measuring how fast the brass disc cools at the steady state temperature  $T_1$ , the rate of heat loss can be determined. It shown in figure 3. If the disc cools down at a rate,  $\frac{dT}{dt}$  then the rate of heat loss is given by:



Where,

m- mass of the brass disc

c - specific heat capacity of brass.

At steady state, heat conducted through the bad conductor per second will be equal to heat radiated per second from the exposed portion of the metallic disc.

$$kA\left[\frac{T_2 - T_1}{x}\right] = mc\frac{dT}{dt}$$

$$k = \frac{mc\frac{dT}{dt}}{A\frac{(T_2 - T_1)}{x}} \quad \text{KNUST}$$

Where;

- k Coefficient of thermal conductivity of the sample,
- A Area of the sample in contact with the metallic disc,
- x Thickness of the sample,
- T<sub>2</sub>- T<sub>1</sub> -Temperature difference across the sample thickness,
- m Mass of the metallic disc,
- c The Heat capacity of the metallic disc,
- $\frac{dT}{dt}$  Rate of cooling of the metallic disc at T<sub>2</sub>



Figure. 3.4. Cooling curve of sample specimen on the metal disc B

#### TOTAL SHRINKAGE

The drying shrinkage, firing shrinkage and the total shrinkage is calculated for each test specimen using the following formula [4]:



where: OL means original length; DL stands for dry length and FL is fired length.

The drying shrinkage indicates to some degree the plasticity of the mixture. A large drying shrinkage means that mixture could absorb much water, which in turn indicates fine mixture particles. The firing shrinkage indicates how fusible the mixture is. A high shrinkage normally means a lower melting point. The total shrinkage of refractory bodies tells the degree of

reduction in the wet structure so that an information on the technical characteristics and a qualitative decision can be agreed on.

# BULK DENSITY, APPARENT DENSITY, APPARENT DENSITY, APPARENT POROSITY, AND EFFECTIVE MOISTURE CONTENT

The respective bulk density, apparent density, apparent porosity, and percentage water absorption were calculated using the formulae:

Bulk Density 
$$= \frac{D}{(W-S)} (g/cm^3)$$
 (4)  
Apparent Density  $= \frac{D}{(D-S)} (g/cm^3)$  (5)  
Apparent Porosity  $= \frac{(W-D)}{(W-S)} \times 100$  (6)

where: D = Weight of fired specimen, S = Weight of fired specimen suspended in water, and W = Weight of soaked specimen suspended in air

Effective moisture content:

Effective moisture content for the brick samples were calculated using the formula:

% Moisture content = 
$$\frac{(A-B)}{A} \times 100$$
 (7)

Where:

A =Wet weight of brick, and B = Dry weight of brick

#### CHAPTER FOUR

#### 4.1. <u>METHODOLOGY</u>:

The clay samples were mined from their individual deposit sites. They were sun dried for two weeks and during that period all the macro-impurities were sorted out. The clay were ground to the finest particle size and then moved into the ball mill for further reduction in particle-size. This is referred to as primary crushing. The initial processing stage known as preparation consist of transforming the clay rock into plastic mouldable material by a process of grinding and mixing with water to produce homogeneous, plastic clay mass. The clay samples were prepared by; the formation of raw samples and subsequently the kaolin was introduced to form admixture compositions of clay-kaolin in different ratios of percentage weight to the nearest kilogram. Each raw composition was mixed to contain 20 to 30% water by weight to form green or wet plastic, and mouldable bodies as Seen in table 4.1 and 4.2

## 4.1. FORMATION OF SPECIMEN SAMPLES:

Sample	% Kaolin	% Asamang	Ratio
As. 1	W 2500	100	0:5
As. 2	20	80	1:4
As. 3	40	60	2:3
As. 4	60	40	3:2
As. 5	80	20	4:1

 Table 4.1. Sample One: Composition of Kaolin with Asamang

Sample	% Kaolin	% Agona	Ratio
Ag. 1	0	100	0:5
Ag. 2	20	80	1:4
Ag. 3	40	UST	2:3
Ag. 4	60	40	3:2
Ag. 5	80	20	4:1

Table 4.2. Sample Two: Composition of Kaolin with Agona

The samples were moulded into three different shapes to meet the criteria for the standards for each test performed, and also in conformity with the equipment employed in performing the various experiments. They were;

Rectangular - 4cm  $\times$  7cm molded specimen for the shrinkage test

Cubic -7cm  $\times$  7cm molded specimen for the mechanical property test

Cylindrical moulded sample were used for the Thermal conductivity, bulk density, porosity, specific heat capacity and weight loss.

#### 4.2. MOULDING THE SAMPLES

them out evenly from inside out.

The rectangular and square shaped samples were prepared from standard metal moulds and the mould was oiled after the formation of each specimen, and care was taken in the pressing state to ensure uniform size and distribution of weight of the moulds.

The cylindrical shaped specimen samples were prepared by a costumed mould specifically designed to meet the shape of the standard Lee's disk apparatus.

Two cardboard slabs of thickness 0.5cm each was placed beneath the inner portion of the mould and on top of the sample after it has been filled. Rubber was used to line the mould to improve lubricity and easy movement of the sample after formation. To ensure compactness and elimination of cracks, the sample was pressed with a clamp to a point near the maximum wet crushing limit and at that point most of the entrapped excess water would be gushing from the base of the mould. This condition was maintained for some time until the sample could be moved out of the mould without breaking. The samples were dried at room temperature for two days and then taken to an electric drier which operated at a temperature range of 150°C for six hours. This process was necessary because firing the samples with some water content within it would cause an explosion of the samples, because the kiln extreme temperature could force out the moisture. Drying involves the removal of water from the wet brick in such a way as to dry If the exterior section of the brick dries first it becomes impossible for the moisture inside to escape. The sample slightly shrink when dried as the clay particles come together and they become strong enough to be stacked. See figures 4.1, 4.2 for sample preparation and the dried bodies.



Fig. 4.1 The cylindrical mould and sample under formation and compression to get rid of excess water.



Fig. 4.2 Dried samples after sun drying and Drying with an electrical dryer

#### 4.3. <u>HEAT TRAETMENT (SINTERING AND COOLING)</u>

The last stage of sample formation process was the drying and sintering(firing). After the pressing and moulding of the green body, the dried samples were arranged in a kiln, whose temperature was gradually raised for eight hours until a temperature of 1000°C was reached. Obviously the samples cannot suddenly be subjected to these temperatures so firing was in three stages.

- Pre heating This ensures total dryness of the sample and the combusting gases in the kiln raise the brick temperature.
- Firing An electric kiln was used to raise and maintain the temperature to the required level for the stipulated period.
- Cooling After the temperature has peaked and is maintained for a prescribed time, the cooling process begins. Cooling is an important stage in the processing of sample because it has an effect on the colour of the final sample.

Firing temperatures vary considerably between different clay types and are often quite critical. During firing , the sample undergoes a physical change. Clay particles and impurities are fused together to produce hard, durable and weather resistant product; any residual water evaporates, some minerals melt, blend, and fuse, and organic matter oxidizes. The hardness of the sample increases and colour develops. This is called vitrification. This was accompanied by further shrinkage and a colour change.

#### 4.4. MEASUREMENT OF SOME PARAMETERS:

The clay composition samples were subjected to the following test and measurements.

#### 4.4.1 MEASUREMENT OF SHRINKAGE ON FIRING

The purpose of this test is to obtain values of shrinkage after drying and firing of clay bodies or both, under various processing conditions to enable designers to determine the proper size of mould or die so as to produce a predetermined size of fired and unfired ware.

The samples dimensions was taken after preparing, this was done by marking a 5cm plastic length on each sample studied. The dimension was read after sun drying and firing, and the distance between the shrinkage reference marks on the dried and fired samples was read to the nearest (0.1mm) with callipers of suitable accuracy. An average of six specimen was recorded for each sample composition.

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#### Calculation

The percentage linear shrinkage on firing and drying was calculated as follow.

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$$S_{d} = \frac{L_{p} - L_{d}}{L_{p}} \times 100$$

Where:

 $S_d =$  linear drying shrinkage,

 $L_p$  = plastic length of test specimen

 $L_d = dry length of test specimen$ 

The total linear shrinkage after firing of the specimen as a percentage of plastic length was calculated as follows:

$$S_{t} = \frac{L_{p} - L_{f}}{L_{r}} \times 100$$

$$4.2$$

Where:

 $S_t = total linear shrinkage after drying and firing, %,$ 

 $L_p$ = plastic length of test specimen, and

 $L_f = fired length of test specimen$ 

# 4.4.2. <u>MEASUREMENT OF WATER ABSORPTION, BULK DENSITY, APPARENT</u> POROSITY, AND APPARENT SPECIFIC GRAVITY FOR FIRED SAMPLES

The measurement of density, porosity, and specific gravity is a tool for determining the structural properties that may be required for a given application. The porosity in this research was determined by using ASTM procedure C373, which is based on Archimedes' principle. This principle states that the weight of an object in a fluid equals its dry weight minus the buoyant force (or the weight of the fluid displaced). The apparent porosity was measured by taking only three measurements – the object's dry weight, its net saturated and suspended weight, and from that the porosity of the samples was calculated.(Kaviany,1995)

The specimen after drying at 150°C, followed by cooling and the dry mass, D was taken to the nearest 0.01g. They were placed in a large pan of distilled water and was boiled for 5hours and was allowed to soak for additional 24hours. After this impregnation of the sample, the sample

was suspended with a wire loop and immersed into a beaker filled with three quarter of water. The suspended mass, S was noted.

The specimen was blotted after the determination of the suspended mass with a cotton cloth to remove all excess water from the surface and the saturated mass, M, to the nearest 0.01g was noted. An assumption was made that  $1 \text{ cm}^3$  of water weighs 1g.

The exterior volume, V, in cubic centimetres was calculated as follows:

$$\mathbf{V} = \mathbf{M} - \mathbf{S} \tag{4.3}$$

The volume of open pores  $V_{op}$  and impervious portions  $V_{ip}$  in cubic centimetres was calculated as follows:

$$V_{\rm op} = M - D \qquad 4.4$$

The apparent porosity, P, expressed as the percentage of the relationship of the volume of the open pores of the specimen to the exterior volume was calculated as follows:

4.5

$$\mathbf{P} = \left[\frac{(M-D)}{V}\right] \times 100$$

The water absorption, A, expressed as a percentage of the relationship of mass of water absorbed to the mass of the dry specimen was calculated as follows:

$$A = \left[\frac{(M-D)}{D}\right] \times 100$$
 4.6

The apparent specific gravity, T, of the specimen that was impervious to water was calculated as follows:

$$T = \frac{D}{(D-S)}$$
 4.7

The Bulk density, B, in grams per cubic centimetre of the specimen sample is the quotient of dry mass divided by the exterior volume, including pores was calculated as follows:

$$\mathbf{B} = \frac{D}{V} \tag{4.8}$$

#### 4.4.3. Cold Compression Strength

Cold compression strength test is to determine the compression strength to failure of each sample, an indication of its probable performance under load. The cubic shaped samples of clay blends with kaolin were dried in an oven at a temperature of 150°C, allowed to cool and then placed between two plates of the compression strength tester. This was followed by the application of a uniform load to it. The load at which a crack appears on the sample was noted and the cold compression strength (CCS) is calculated from the equation:

 $CCS = \frac{Load \ to \ fracture}{Surface \ Area \ of \ sample} \ KG.cm^{-1}$ 

4.9

#### 4.4.4. Thermal Shock Resistance

Each sample of the clay/saw dust blend was placed in an electrically heated furnace to attain the test temperature of 1000°C for over 3 hours. Each sample was then with- drawn from the furnace and held for 10 minutes. The procedure was repeated until an appearance of a crack was visible. The number of cycles necessary to cause a crack was recorded for each of the samples and taken as a measure of its thermal shock resistance.

#### 4.4.5 Measurement of weight loss on firing

The purpose of this test was to determine the weight lost by each sample after drying and sintering stage. The loss of the solute and solvent during drying leaves pores in the cold pressed body. At peak firing temperatures, the glassy phase melts, a certain amount of sintering of the clay particles occurs and there is a resulting filling of the voids or densification of the bodies. It is this densification which is a factor in weight lost. After forming the green body and allowing it to solidify by sun drying, its weight was measured using an electronic balance. Then the weights of the sample were again taken after the firing process to determine how much water and combustive matter it has lost. The measurement was taken for six samples per composition and the average taken. The difference gave the weight lost; which was expressed in terms of percentage by the equation presented;

4.10

Weight Loss (%) =  $\left(\frac{W_p - W_f}{W_p}\right) \times 100$ 

Where :

 $W_p$  = weight of plastic body and  $W_f$  = weight of fired body

#### 4.4.6. MEASUREMENT OF SPECIFIC HEAT CAPACITY

The specific heat capacity(c) of a material is the energy needed to raise the temperature of 1 kg of it by 1 °C. Some materials needs larger amounts of energy than others to produce an increase in temperature. These materials are better at storing thermal energy and so have much more to get rid of when they are cooling.

The electrical method was used in the measurement of the specific heat capacity of the sample. An electrical source of known quantity of heat(Q) was used to provide a constant source of energy to the setup. The heat source was at a button of a well lagged system that has the thermocouple inserted halfway into the cylindrical specimen. The initial temperature  $(T_1)$  and final temperature after the heater has being switched off through the heating period was noted as  $(T_2)$ . A stop clock was used to note the time interval t (seconds) from the time the heater was switched of to the point where it passes its maximum temperature  $(T_2)$ . The relation presented as follow was used in the measurement of the quantity.

$$Q = m c \Delta T$$

Where:

Q is the quantity of heat which is the product of Voltage of source, Current supplied and the time(seconds)

M is the mass of sample in (Kg)

 $\Delta T$  is the change in temperature during the period.

# 4.4.7. MEASUREMENT OF THERMAL CONDUCTIVITY

Thermal is the intrinsic property of a material which relates its ability to conduct heat.

Thermal conductivity is a useful design parameter for the rate of heat transfer through a material. The results of this method may be used for design purposes, service evaluation, manufacturing control, research and development, and hazard evaluation. In this research the experimental approach employed is the Lee's and Charlton's method for determining the thermal conductivity of insulating materials. The experiment involves two major sections; the statical section: which involves the measurement of the mass of the cast iron metal disc, the diameter of

the specimen slab S with a scale, the thickness (d) of specimen slab was measured with the help of a micrometer screw gauge and, Hence the cross sectional area was calculated. Thermal contact of specimen slab S with metal disk was improved by the moistening the surface with grease. The apparatus setup was screen off from the external heat the burner was transmitting with a cardboard. Steam was passed from a distant water container (pot) into steam chamber and temperatures  $T_1$  and  $T_2$  of metal disk A and B were measured with digital thermometers. The thermometers were watched respectively and carefully. When it was about to become steady,  $T_1$  and  $T_2$  are recorded until they remained constant. When a steady state is reached (temperatures  $T_1$  and  $T_2$  changed by less than 0.5 Celsius in 1 minute), a note of  $T_1$  and  $T_2$  was taken. The supply of steam was stopped and the steam chamber with the upper metal disc was removed. The specimen slab S still was left on top of metal disc B, and was heated by moving the burner under it until the temperature raised to about 10°C above the steady state temperature T<sub>2</sub>. Then the burner was removed and allowed metal disc B to cool. The temperature was noted every half a minute until the temperature fell about 10°C from steady state temperature T<sub>2</sub>. The cooling rate was noted and a graph was drawn with the time of cooling as abscissa and the temperature of metal disc B as ordinate. A tangent was drawn at steady state temperature  $T_2$ . The slope of the tangent gave the rate of cooling as;  $\frac{\partial Q}{\partial t}$  at steady state temperature T<sub>2</sub>. The major precautions taken was that the specimen slab was well lagged at the edge to reduce massive heat loss due to a slight increase in the thickness of the slab due to the relatively brittle nature of the material and also the high tendency of crack development in processing ceramics of such small thickness. See figure 4.12 for a schematic view of the Lee's and Charlton's Apparatus and Figure 4.13 for the experimental setup.


3. Cast iron stand ring 4. steam chamber 5. Cast iron metal disc A(upper) 6.sample slab S 7.Cast iron metal disc B(lower) 8,9 thermometers

Fig.4.12 Schematic diagram of the Lee's and Charlton's apparatus



#### CHAPTER FIVE

#### 5.0. EXPERIMENTAL RESULTS AND DISCUSSIONS

The chapter discusses the experimental results of some physical characterization of the ceramic raw material samples: clay, obtained from Agona and Asamang together with Kaolin obtained from Teleku Bukaso in the western Region of Ghana. The effect of these composition on Thermal conductivity, total shrinkage, water absorption, weight loss, cold crushing strength, porosity, specific heat capacity, bulk density and thermal diffusivity has also been investigated.

The chapter also discusses the variation of some pertinent quantities on the samples against one another along with the relative change in the composition of the percentage of Kaolin. These variation of such pertinent quantities with each other as a percentage change in composition of additives enhances a change in quantity has been reported by Atanda P. et al,(2012). The mathematical calculation procedure has been reported by M. Alam et al, (2012). The results and the procedures are shown in the Appendix A1.1 - A1.10. The summary of results: Tables,(A.1.1 - A.1.4) and cooling curve are also shown in the appendix (figures A.1- A.10).



#### 5.1 EFFECT OF COMPOSITION ON SHRINKAGE

Shrinkage occurs during water elimination by diffusion towards the surface and evaporation is the critical character of the drying stage. High shrinkage normally causes destruction of samples both in firing and drying stages of production. The Firing shrinkage results of the samples with varying composition are shown in table A.1.1 (see appendix)



Fig.5.1 Total shrinkage as a function of composition.

Figure 5.1 presents the effect of varying composition on total shrinkage. A highly linear relation occurred between volume shrinkage and percentage composition. The percentage total shrinkage of the samples generally decreases as percentage composition of the kaolin was increased, therefore at 1000°C, the total shrinkage of the two samples varies from 17.40% to 5.80% for the Asamang composition and 14.40% to 3.60% for the Agona composition. It was evident that the Agona composition generally has lower shrinkage values at any ratio of the two compositions. This is because the kaolin inhibits shrinkage and the reason could be attributed to the vitrification level and the subsequent formation of strengthened three-dimensional polymeric network which helped to resist further contraction.

#### 5.2 EFFECT OF COMPOSITION ON WATER ABSORPTION

The average water absorption determined by submersion of the sample in water for 12 hours must be less than 18 percent (Turkish Standards Institution, 1979). In this study water absorption for some of the samples produced at 1000°C met the criteria specified by the Turkish standards institute (Turkish standard Institution). Water absorption results of samples with varying composition are listed in table A.1.2 (see appendix). Figure 5.12 presents the result of water absorption of the sintered samples for various compositions.



Fig.5.2 Water absorption as a function of composition

The graph depicted by figure 5.2 is the result for water absorption which was sintered around 1000°C. Averagely Asamang absorbed more water than Agona composition. This is due to the less plastic nature of the composition of Asamang with Kaolin as compared to Agona Kaolin composition, by virtue of that , more water was probably needed to bind the Asamang composition together. As porosity increases the rate of water absorption also increases. As temperature increases, percentage water absorption decreases. This goes to buttress the argument that temperature increase leads to shrinkage of pores, which subsequently leads to the disappearing of many pores, the result of this, is less water absorbed by the samples. In general water absorption increases in both cases with the highest compositions of kaolin content: the more kaolin content, the less plastic the material that explains why shrinkage was

decreasing with increasing kaolin content[*see fig*. 5.1 *and fig* 5.2]. As.5 and Ag.5 had the least shrinkage but absorbed relatively more water which implies that, it used more water to help remain bound. Compositions Ag.1, Ag.2 and Ag.4 met the standard set by the Turkish standard institute, therefore these compositions can be recommended for industrial applications. High values of water absorption obtained indicate that the compositions were relatively porous.



# 5.3 EFFECT OF COMPOSITION ON WEIGHT LOSS

Fig. 5.3 Weight loss as a function of composition

The figure 5.3 presents the result of weight loss of the sintered sample for various compositions. The graph depicted by fig.5.3 is the results for weight loss of the samples which was sintered in a kiln for up to a temperature of 1000°C. This high temperature of firing resulted in the weight loss. Basically the weight loss on firing for the sample compositions are good for technical applications in which strength and light weight materials are involved, sample As.1 has the highest weight on loss on firing 10.42%. The reason for such property is the presence of high combustible matter in the samples.

#### 5.4 EFFECT OF COMPOSITION ON COLD CRUSHING STRENGTH

The graph depicted by fig. 5.4 is the result of cold crushing strength as a function of composition. The samples in their raw states had appreciably high strength, sample As.1, Ag.1 as compared to sample As.2 and Ag.2 which was very minimal, the reason being the low temperature vitrification rate of the two samples. The introduction of the smaller ratio of kaolin gave smaller strength values for samples As.2, Ag.2, As.3, and As.4, the reason may be due to the packing process of the composition, at the highest composition of kaolin, the samples had the highest strength values and it was due to the presence of high Alumina content in the composition as the highest ratio of kaolin was introduced which led to optimal densification of sample As.5 and Ag.5. (Bhatnagar et al, 2002) attributed the sharp increase in strength to the enhanced compressive strength to the enhanced vitrification in the clay materials. Increase in compressive strength is due to decrease in porosity and increase in bulk density with increasing temperature (sedat et al, 2006).



Fig. 5.4 Cold crushing strength as a function of composition

#### 5.5 EFFECT OF COMPOSITION ON POROSITY

The variation in porosity as a function of composition is given in table A.1.2 (see appendix). Fig.5.5 shows the result of porosity of the sintered sample for various compositions. Porous ceramic materials have applications in many industrial areas, such as catalyst support for heterogeneous chemical reactions, filters, membranes, thermal insulators and bioceramics. (F.O. Aramide et al, 2012). These applications require an optimal pore-size distribution, the porous microstructure and other important properties such as chemical inertia and resistance to thermal and/or mechanical shock. (L.H. Van Vlack, 1991). The presence of pores (holes) in a material can render itself all sorts of useful properties that the corresponding bulk material would have. (J.D.F. Ramsey, 1993). Pores are the volume of air entrapped in a material. The more the percentage of pore additives, the more porous the material is, because heat cannot pass through the motionless air which trapped in the pores. This trapped air is what acts as insulators.

The graph depicts the result for apparent porosity of samples with varying compositions which were soaked for 24 hours.



Fig. 5.5 Porosity as a function of composition

The average percentage apparent porosity of Asamang was more than that of Agona composition. The plastic nature of the two compositions with their high Alkaline content lead to the glass formations thereby sealing the pores. This resulted in the less porous nature of the sample compositions Ag.4, Ag.2,Ag.3,Ag.1,and As.2. Sample As.5 and Ag.5 had the highest porosity values due to the level of kaolin content in the samples. The obtained values seem to have a similar pattern to the values obtained from the water absorption test. (See figure 5.2). Materials with high water absorption values do mostly have high porosity values. This might be

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due to loss of crystallized water and organic matters in both samples that had occurred below 800°C, causing an increase in porosity of the body. Also porosity increases in both cases with an increase in kaolin content, this may be due to the packing density that is the well sorted nature of kaolin resulting in lack of very fine particles to fill the pores. In conclusion; the greater the porosity, the weaker the strength of the material that is why "pores have traditionally been avoided in ceramic products to increase crack resistance". (F.O. Aramide, 2012.)

## 5.6 EFFECT OF COMPOSITION ON THERMAL CONDUCTIVITY AND THERMAL RESISTIVITY

Fig 5.6 presents the variation of thermal conductivity with the kaolin plastic clay composition from the two locations. The variation of thermal conductivity with composition is given in table A.1.4 (see appendix). It was evident that the thermal conductivity decreased as there was a gradual introduction of kaolin content. Thermal conductivity decreases as porosity increases. The porosity of the samples generally increases with the kaolin admixture ratio and this level of refractoriness exhibited by kaolin on its own as a pure refractory material induces an appreciable degree of thermal resistivity as the ratio of kaolin increases. These empty space or voids (though may contain air) insulate the thermal flow hence, the reduction in thermal conductivity of the sample as the percentage of kaolin increases. This explanation is applicable to fig 5.5, where the apparent porosity of the samples on the average, varied with increasing kaolin composition for all Asamang samples. The influence of texture and porosity may be considered together because, the principal effect on the thermal conductivity is a relation between the amount of solid and air which the heat has to transverse in passing through the material. Since air is much a better insulator than any solid material, the larger the proportion of air, the lesser will be the thermal conductivity and conversely a greater thermal resistivity power of the material. Consequently a fine grained, closed-textured material with a coaser open texture. For example Agona which is more plastic and finer has relatively greater thermal conductivity than Asamang at any ratio of kaolin plastic clay composition.



Fig. 5.6.a Thermal conductivity as a function of composition.

The relatively lower level of thermal conductivity and subsequent high thermal resistivity of all Asamang sample composition is due to the high presence of mica, which is physically evident in the clay raw state, averagely high porosity and the high level of combustible matter though it was less plastic in nature. Subsequently the thermal resistivity of the sample composition increased across this argument of increase in porosity to entrap more air to serve as an insulator. Fig 5.6.b presents the thermal resistivity of the samples. Thermal conductivity of insulating materials has been found to vary with: density, moisture content, temperature, direction of heat flow with respect to grain for fibrous presence of defects in materials and porosity. (Rajput, 2005).



Fig. 5.6.b Thermal resistivity as a function of composition

#### 5.7 EFFECT OF SPECIFIC HEAT CAPACITY ON COMPOSITION

The graph depicted by figure 5.8 is the result of specific heat capacity as a function of composition. A high specific heat capacity value, means there is a high tendency for heat retention and hence good insulating materials should have a high specific heat capacity. The averagely large specific heat capacity of Asamang is because of the high porosity and density of the Asamang sample composition. This directly relates to the high thermal resistivity and low thermal conductivity of the Asamang composition. Asamang sample also has some level of mica present which suggests its high level of insulation, for this reason; heat will take longer periods in transversing across, and subsequently heating to achieve a reasonable temperature change will require higher amounts of thermal energy. The eventually stored energy can be recovered when the temperature of the material falls, and because of the high heat capacity nature of Asamang samples, it stores much better thermal energy and readily have much to get rid of when they are in the process of cooling down. (see appendix: Cooling curves for Asamang compositions). In summary; though Asamang compositions are considered as relatively higher specific heat capacity material, the level of consistency exhibited by the Agona composition also make it desirable in many applications.



Fig. 5.7 Heat capacity as a function of composition

The direct relationship between the two results of the sample composition seems to back the argument that thermal resistivity is a reciprocal of thermal conductivity.

#### 5.8 EFFECT OF BULK DENSITY ON COMPOSITION

The graph depicted by fig. 5.9 is the result of Bulk density as function of composition. It was observed that the generally low densities of the sample compositions contributed to the comparatively low thermal conductivity of the sample. The fact that the bulk density did not linearly decrease as the ratio of pore additive was introduced was due to the inability of the samples to the inconsistent weight levels attained by the composition during the process. Sample As.3 had the highest Bulk density of 2.51 g/cm<sup>3</sup> and sample As.4 had the lowest 1.42g/cm<sup>3</sup> as compared to that of Agona.



Fig. 5.9 Bulk Density as a function composition.

#### 5.9 EFFECT OF THERMAL DIFFUSIVITY ON COMPOSITION

Thermal diffusivity measures the ability of a material to transmit a thermal disturbance. It indicates how quickly a material will change. Thermal diffusivity increases with the ability of a body to conduct heat and decreases with the amount of heat needed to change the temperature of a body. From the graph (fig5.10), the thermal diffusivity of Agona sample composition linearly decreases as the kaolin composition ratio increases with a subsequent decrease in thermal conductivity. The Asamang sample composition also had an appreciable level of diffusivity and it could also serve as a comparative material if the other preferable qualities like the high specific heat capacity is considered. Materials with high thermal diffusivity are employed as heat exchange membranes. Figure 5.10 presents the variation of thermal resistivity as a function of composition.



Fig. 5.10 Variation of thermal diffusivity with composition.

5.10. The following figures show superimposed representative trend plots of important sample composition properties of compared to each other in order to get proper blend of properties.

This is a comparative approach of some important sample properties compared to each other in order to get the best combination of properties of the samples in order to meet standards in product fabrication.



Fig. 5.11A and fig.5.11B present a comparative plot between the thermal conductivity trend and the water absorption trend as the percentage composition of kaolin increased. These results tallies with most technical specifications, sample As.2,As.3,Ag1,Ag.2,Ag.3 and Ag.4 had the acceptable values, with Agona having the average lower values. The samples could be used to produce roofing tiles because their water absorption levels are lower than the limit (20%) suggested for such application (Veira et al,2001) and their relatively low thermal conductivity values suggest they can support any partially cooled building and roofing setup.



Fig. 5.12A and fig.5.12B presents the comparative plot of thermal conductivity and cold crush strength as the kaolin composition increases, the raw samples had appreciably good blend of thermal conductivity and cold crush strength. The cold crush strength started decreasing as small amount of kaolin was introduced at As.2 and Ag.2 but generally started increasing as good proportion of kaolin and plastic clay samples were composed from As.3 and Ag.3 and thermal conductivity had a linear decrease as the percentage kaolin composition increased. Samples As.1, As.5, Ag.1, Ag.4 and Ag.5 met the standard for the construction of refractory materials. A refractory should have low thermal conductivity and high strength to withstand the conditions they will be subjected to in service conditions.



Figure 5.13A and fig.5.13B presents total shrinkage and cold crushing strength properties superimposed on each other. It showed that as shrinkage decreased, cold crushing averagely increase from sample As.3 and Ag.3. The raw samples had an appreciable blend of total shrinkage and cold crush strength. The optimum balance was achieved for samples As.1, As.5, Ag.4 and Ag.5. These optimum blend of sample properties suggest that the sample can be employed in construction as the sample averagely shrunk less and can withstand a high degree of compressive load.



Figure 5.14A and fig.5.14B presents the total shrinkage and apparent porosity properties of the samples with increasing Kaolin content. It showed there is a smooth linearity of increasing porosity with a decreasing total shrinkage for all Asamang samples but a non-linear increase in apparent porosity of Agona samples with a decreasing total shrinkage. Optimum parameters where met for sample As.3,As.4,As,5,Ag,3 and Ag.5 for the constructing cell membranes for the development of microbial fuel cells.



Fig.5.15A and fig. 5.15B Presents a superimposed graph of apparent porosity versus cold crush strength varying with kaolin composition, the raw samples had appreciable porosity and cold crush strength values but there was a decrease as 20% amount of kaolin was introduced, this was as a result of weak composition formed. Apparent porosity with cold crushing strength ]]generally increased from samples As.3 and Ag.4.

Optimum parameters were met for the raw samples As.1 and Ag.1 and composition samples As.5, ag.5, Ag.4 and Ag.3 for the construction of refractory materials and low energy furnace walls.



Figure 5.16A and fig.5.16B presents Apparent porosity and thermal conductivity properties, varying with percentage kaolin composition. It showed that porosity averagely increased with thermal conductivity decreasing as the kaolin composition increased. As porosity increases, a refractory material is less resistant to the eroding action of penetrants. Also, the entraped air pockets reduce thermal conductivity. An optimum parameter is reached for samples As.3 and As.4 for the construction of the inner linning of low energy furnace, blacksmith furnace and brooder room interior walls.



Figure 5.17A and fig.5.17B presents superimposed plots of specific heat capacity with apparent porosity properties varying with percentage kaolin composition. It showed that the samples had an appreciable high heat capacity with an increasing porosity for Asamang samples, a relatively lower heat capacity for Agona samples but a non-linear increase in porosity. These implies that the samples had averagely low thermal conductivity due to the relatively high porosity and high heat capacity because materials with high thermal resistivity needs more heat to change it's temperature. All levels of composition proved to be viable in the construction of inner walls of furnace and general construction owing to the specification and the degree of service for the technician.

Figure 5.18A and fig.5.18B present a superimposed plot of specific heat capacity and thermal diffusivity, with varying kaolin composition. The samples has an appreciable high level of heat capacity and a non-linear decrease in thermal diffusivity. This implies that the samples are relatively good thermal insulators and such materials demand a large amount of heat to change it's temperature and relatively low thermal diffusivity implies that after the samples has accumulated the heat energy, it will take longer time to give off the heat, refer to the cooling rate of the various samples (see appendix). These property makes the material viable in the production of heat storage materials, refractories and the construction of passively cooled building materials. The level of kaolin composition will determine the degree to which a technician would want to employ to suit his demand. For example sample Asamang compositions stands as a good material in the production of energy efficient clay briquets and good linning material for brooder pens.

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#### 5.11. X-RAY DIFFRACTION ANALYSIS

Ceramic materials are identified by their major chemical constituents, which govern their qualities and properties. It is essential to carry out complete chemical analysis of these materials for its quality assessment. As a thumb rule, it is known that the higher the Alumina content, the better its properties. However, it is obvious that while the major chemical constituents of a ceramic material do play the most important role in determining its ability to perform, the minor constituents- mainly impurities also play a very important role in its performance.

Most ceramics; especially refractory materials, are normally Oxide having a tendency to react with another at high temperature to form different compounds with different crystal structures. The mineralogical formation and crystal structures of the same chemical constituents will vary depending upon the extent of heat treatment/thermal exposure the material receives in manufacturing or operating conditions. The crystal structure that forms will decide the performance of the refractory as the resistance to corrosion/erosion behaviour depends on it.

Figures 5.29 and 5.30 presents the X-ray diffraction analysis(phase identification) of samples AS.1 and AG.1(100 % Asamang and Agona samples). The peaks reveals the chemical compounds that constitute the phases of clay minerals that are present in these material.

Clay is composed of Silica(SiO<sub>2</sub>), Alumina(Al<sub>2</sub>O<sub>3</sub>) and water(H<sub>2</sub>O) plus appreciable concentration of Oxides of Iron, alkali and alkaline earth, and contains groups of crystalline substances known as clay minerals such as quartz, feldspar and mica.(Folaranmi,2009)



Figure 5.19 X-ray Diffraction pattern(phase analysis) of 100% Asamang sample.



Figure 5.20 X-ray diffraction pattern(phase analysis) of 100% Agona sample.

The levels of Alumino-silicate presents these materials as Alumino-Silicate presents these materials as Alumino silicate refractories; as established by (Folaranmi,2009) that Fire clay composes of essentially; two basic Oxides Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> with its associated impurities oxides of TiO<sub>2</sub>, FeO<sub>3</sub>, MgO, CaO, Na<sub>2</sub>O and K<sub>2</sub>O forms about 2-10% when put together.



#### CHAPTER SIX

#### CONCLUSIONS AND RECOMMENDATIONS:

#### 6.1 CONCLUSION

Some investigations have been undertaken to reveal and understand the physical and chemical properties of these ceramic raw materials and an effect tampering exercise has been done; by composing an admixture of Kaolin-raw clay bodies to understand its adverse effect it had on the sample composition.

With the results obtained, it can be concluded that, Asamang sample composition generally produced better results in terms; of thermal conductivity, weight loss but could not match the cold crushing strength of Agona sample composition. It was revealed that the raw sample: (AS.1,AG.1) had appreciable levels of qualities in terms of most of the quantities measured. Asamang sample composition generally had high levels of thermal resistivity which subsequently proved their generally high levels of heat capacity and low thermal diffusivity as compared to that of Agona sample composition.

There were linear and non-linear correlations between the comparative quantitative approach of the sample compositions; Apparent porosity generally increased as thermal conductivity decreased for all samples, as the percentage composition of kaolin increased. Asamang sample composition has a non-linear decrease in thermal diffusivity and an increase in specific heat capacity as the percentage composition of kaolin increased.

The XRD-Analysis (phase identification) revealed that the samples are composed of high amounts of Oxides, Alumina and Silicon related clay compounds. The high percentage of these compounds makes the samples suitable for the production of some category of Refractory materials. These standards as suggested by the Swiss Agency for Development and cooperation, Competence Network for small and Micro Learning Enterprises, and Energy and Resources Institute.

All the sample compositions have good mechanical behavior after sintering at 1000 °C temperature range. Sample composition (AS.3,AG.4) had high specific heat capacity and low thermal diffusivity coupled with appreciable levels of weight loss and total shrinkage, recommends these materials for the manufacture of strong, light weight and less porous roofing tiles.

All sample compositions had an appreciable level of cold crushing strength, and low thermal conductivity levels, they can serve all purpose of refractory and construction materials owing to the specification of the technician or the end-user. For example, the optimum parameter for the purpose of strong and good brick oven, industrial furnace lining construction; sample (AS.3,AG.3) can serve such purposes. Sample composition AS.1, AG.1, AG.2, AS.2 can be used in the manufacture of clay briquettes, due to their good level of plasticity; which will serve as a good binder. Their appreciable low levels of thermal conductivity, high specific heat capacity and low thermal diffusivity present them as good materials for the construction of energy saving clay briquettes, ''Gyapa'' lining and heater base for electric stoves.

The samples meets the standards already outlined by the BIS (Bureau of Indian Standards) covering standard dimensions, physical and chemical properties; and can be recommended for Red bricks, IS-6 and IS-8 fireclay refractory bricks. These sample compositions can also serve the purpose of passively cooled building structures in hot climatic conditions and also the construction of temperature controlled environment like Brooding pens for poultry, and tiles for incubator lining.

#### 6.2 <u>RECOMMENDATIONS FOR FUTURE PROJECTS</u>.

In order to improve the knowledge base of these materials, further advanced efforts should be made to support and create a competitive material base for our building industry.

A comprehensive computerized modelling should be created to further investigate the physical and chemical properties in order to get a more comprehensive knowledge of these ceramic materials. For example, an effort to understand the mode of radiant heat transmission through the transient method of thermal conductivity measurement and the behaviour of such materials in certain weather conditions like our hot climate will lead to a more informed decision in using these materials.

An advanced effort should be made in developing advanced ceramic based Nano-materials, and Polymer Nanocomposites can help solve many industrial situations in the country; for example to serve the purpose of sustainable catalyst for organic transformations and as membrane for biofuel systems.

The influence of other factors such as thermal shock resistance, other mechanical test like flexural strength test, effect of chemicals on the body(corrosive test) and thermal expansion of these materials should be considered.

Other Admixture compositions, like the formation of multi body samples should be encouraged to enhance the physical and chemical properties of the materials. An effort should also be made in the inclusion of organic waste materials like; sawdust, rice peels, palm kernel fiber, coconut fiber and grass in these bodies to further enhance its insulating, mechanical and chemical properties should be considered.

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#### APPENDIX A.1

#### TABLES OF VALUES FROM VARIOUS EXPERIMENTS:

TABLE A.1.1.: TABLE SHOWING THE VARIATION OF SHRINKAGE VALUESWITH COMPOSITION.

sample	Original	Dry	Fired	Dry	Fired	Total	Temperature
	length	length	length	shrinkage	shrinkage	shrinkage	(°C)
	(cm)	(cm)	(%)	(%)	(%)	(%)	
As.1	5	4.63	4.50	7.4	10.0	17.4	1000
As.2	5	4.68	4.62	6.4	7.6	14.0	1000
As.3	5	4.70	4.68	6.0	6.4	12.4	1000
As.4	5	4.84	4.76	3.2	4.8	7.8	1000
As.5	5	4.88	4.86	2.4	2.8	5.8	1000
Ag.1	5	4.68	4.60	6.4	8.0	14.4	1000
Ag.2	5	4.74	4.66	6.8	6.8	13.6	1000
Ag.3	5	4.84	4.78	3.2	4.4	7.6	1000
Ag.4	5	4.88	4.86	2.4	2.8	5.2	1000
Ag.5	5	4.96	4.86	ANE N	2.8	3.6	1000

TABLE A.1.2.: TABLE SHOWING THE VARIATION OF PERCENTAGE APPARENT POROSITY, WATER ABSORPTION, BULK DENSITY, SPECIFIC GRAVITY VALUES WITH COMPOSITION.

Sample	Fired	Suspended	Soaked	Apparent	Water	Specific	Bulk
	weight	Weight	weight	porosity	Absorption	gravity	density
	(g)	(g)	(g)	(%)	(%)		(p) g/cm <sup>3</sup>
As.1	179	116	227	43.24	26.82	2.84	1.61
As.2	202	131	243	36.61	20.30	2.24	1.80
As.3	209	143	250	42.27	19.62	1.84	2.51
As.4	190	134	268	58.21	41.05	3.28	1.42
As.5	200	170	269	69.70	34.50	1.98	2.02
Ag.1	239	138	280	28.87	17.15	2.37	1.68
Ag.2	221	129	251	24.59	13.57	2.40	1.56
Ag.3	218	131	262	33.59	20.18	2.51	1.66
Ag.4	227	130	244	11.81	7.49	2.40	1.99
Ag.5	198	163	290	72.00	46.60	5.68	1.85
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### TABLE A.1.3: TABLE SHOWING THE VARIATION OF MECHANICAL PROPERTIES AND WEIGHT LOSS WITH COMPOSITION.

sample	Cold crushing	Dry weight	Fired weight(g)	Weight loss(%)		
	strength (KN/cm <sup>2</sup> )	(g)	<b>OT</b>			
As.1	163.27	192	172	10.42		
As.2	failed	193	173	10.36		
As.3	40.82	198	179	9.60		
As.4	40.82	224	206	8.04		
As.5	363.53	210	182	13.32		
Ag.1	469.39	251	230	8.36		
Ag.2	40.81	229	213	6.98		
Ag.3	122.45	217	205	5.5		
Ag.4	163.27	214	203	5.14		
Ag.5	540.82	210	187	10.95		
BADHES BADHES						
	13	SANE NO				

TABLE A.1.4: TABLE SHOWING THERMAL PROPERTIES OF SAMPLES WITH COMPOSITION.

sample	Thermal	Thermal	Specific h	eat	Bulk density	Diffusivity	
	conductivity	resistivity	capacity		ho (kg/m <sup>3</sup> )	$\lambda(m^2/s)$	
	W/mK		J/kg.k <sup>-1</sup>			×10 <sup>-5</sup>	
As.1	0.1389	5.04	3098.47	5	1.61	2.73	
As.2	0.1267	5.52	2845.36	)	1.80	2.47	
As.3	0.1069	6.55	2795.48		2.51	1.52	
As.4	0.0977	7.16	2995.61	2	1.42	2.30	
As.5	0.0845	8.24	2791.62	Ś	2.02	1.50	
Ag.1	0.1823	3.29	2299.58		1.68	4.72	
Ag.2	0.1403	4.28	2502.52	1	1.56	3.59	
Ag.3	0.1318	4.55	2467.13	Ň	1.66	3.22	
Ag.4	0.1291	4.64	2691.63	1	1.99	2.41	
Ag.5	0.0899	7.79	2459.58		1.85	1.98	
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#### APPENDIX. 2

Lee's and Charlton's Method for investigation of thermal conductivity of Insulating Materials

A.2.1 Specimen Ag.1

Mass of metal disc B, m=1021g = 1.21kg

Specific heat capacity of the material of metal disc B, s = 0.390 kJ/KgK

Diameter of specimen slab S, D= 10.224cm

Area of cross-section,  $\alpha = \pi \times (0.5 D^2)$  sq.cm

$$= \pi \times (\times 10.22410^{-2})^2$$

 $= 0.0082098 \text{ m}^2$ 

Thickness of specimen Ag.1, d=0.6cm=  $6 \times 10^{-3}$  m



Fig.4.1: Temperature vs. Time for Sample Ag.1
From the Cooling Curve, fig. 4 the slope of the tangent at 73°C

 $\frac{dQ}{dt} = \frac{height of ordinate}{height of abscissa}$ 

 $=\frac{73-48}{2250-0}$ 

= 0.0111°C/sec

At steady state  $T_1 = 94$ °C ,  $T_2 = 58$ °C KNUST

Calculation: the thermal conductivity of Sample Ag. 1 is measured as follow:



Specific heat capacity of the material of metal disc B, s = 0.390kJ/KgK

Diameter of specimen slab S, D= 10.145cm

Area of cross-section,  $\alpha = \pi \times (0.5 \text{ D}^2) \text{ sq.cm}$ 

$$=\pi \times (0.5 \times 9.533 \times 10^{-2})$$

$$= 0.0071375 \text{ m}^2$$

Thickness of specimen Ag.2, d= 0.6cm =  $6 \times 10^{-3}$ m



Calculation:

Thermal conductivity of sample Ag.2 is measured as follow:

$$K = \frac{ms \frac{dQ}{dt}}{\alpha (\frac{T}{2}) \frac{1}{d}} W/mk$$

$$= \frac{1.21 \times 0.390 \times 1000 \times 0.01026 \times 0.006}{0.0071375 \times (95-66)} W/mk$$

$$= 0.14034 W/mk$$
A.2.3 specimen Ag. 3  
Mass of metal disc B, m=1021g = 1.21kg  
Specific heat capacity of the material of metal disc B, s= 0.390kJ/KgK  
Diameter of specimen slab S, D=10.116cm  
Area of cross-section, =  $\pi \times (0.5 D^2)$  sq.cm  

$$= \pi \times (0.5 \times 10.116 \times 10^{-2})^2$$

$$= 0.008037 m^2$$

Thickness of specimen Ag.3, d= 0.6cm= 0.006m



Fig. A.3: Temperature vs. Time for sample Ag. 3

From the cooling curve, fig4.3 the slope of the tangent at 66°C



The thermal conductivity of sample Ag.3 is measured as follow:

$$K = \frac{ms \frac{dQ}{dt}}{\alpha \times (\frac{T_1 - T_2}{d})} W/mk$$
$$= \frac{1.21 \times 0.390 \times 1000 \times 0.01009 \times 0.006}{0.008037 \times (93 - 66)} = 0.13178 W/mk$$

## A.2.4 Specimen Ag. 4

Mass of metal disc B, m=1021g = 1.21kg

Specific heat capacity of the material of metal disc B, s = 0.390 kJ/KgK

Diameter of specimen slab S, D= 10.335cm

Area of cross-section,  $\alpha = \pi \times 0.5 \text{ (D}^2) \text{ sq.cm}$ =  $\pi \times (0.5 \times 10.335 \times 10^{-2})^2$ 

= 0.008389

The thickness of the specimen Ag.4, d = 0.6cm= 0.006m



Fig. A.4: Temperature vs. Time for specimen Ag.4

From the cooling curve, fig. 4.4 the slope of the tangent at 65°C

 $\frac{dQ}{dt} = \frac{height of ordinate}{height of abscissa}$  $= \frac{66-41}{2250-0}$ 

At steady state  $T_1 = 95^{\circ}C$ 

Calculation:

The thermal conductivity of sample Ag.4 is calculated as follow:

 $\mathbf{K} = \frac{ms \frac{dy}{dx}d}{\alpha(T_1 - T_2)} \quad \mathbf{W}/\mathbf{mk}$ 

 $= \frac{1.21 \times 0.390 \times 1000 \times 0.0111 \times 0.006}{0.008389(95-66)}$  W/mk

= 0.1291 W/mk

A.2.5 Specimen Ag.5

Mass of metal disc B, m=1021g = 1.21kg

Specific heat capacity of the material of metal disc B, s= 0.390kJ/KgK

Diameter of specimen slab S, D= 10.145cm

Area of cross-section,  $\alpha = \pi \times 0.5$  (D<sup>2</sup>) sq.cm

 $=\pi \times (0.5 \times 10.145 \times 10^{-2})^2$ 

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 $= 0.008083 \text{ m}^2$ 

Thickness of the specimen, d = 0.6cm = 0.006m



Fig. A.5: Temperature vs. Time for specimen Ag.5

From the cooling curve, fig.4.5 the slope of the tangent at 63°C



The thermal conductivity of sample Ag.5 is measured as follow:

$$K = \frac{ms \frac{dQ}{dt}}{\alpha (T_1 - T_2)} \quad W/mk$$
$$= \frac{1.21 \times 0.390 \times 1000 \times 0.0077}{0.008083(93 - 63)} \, w/mk$$

= 0.08990 W/m

A.2.6. Specimen As.2

Mass of metal disc B, m=1021g = 1.21kg

Specific heat capacity of the material of metal disc B, s = 0.390 kJ/KgK

Diameter of specimen slab S, D= 10.935cm Area of cross-section,  $\alpha = \pi \times (0.5 \text{ D}^2) \text{ sq.cm}$ 

$$=\pi \times (0.5 \times 10.935 \times 10^{-2})^2$$

 $= 9.391 \times 10^{-3} \text{m}^2$ 

The thickness of the sample 0.7cm=0.007m





$$\frac{dQ}{dt} = \frac{height of ordinate}{height of abscissa}$$

cooling

 $=\frac{00}{2010-0}$ 

the

From

 $= 0.01045^{\circ}C/sec$ 

Calculation:



slope

of the

tangent at 69 °C

The thermal conductivity of sample As.2 is measured as follow:

curve, fig 4.7, the

$$\mathbf{K} = \frac{ms \frac{dQ}{dt}d}{\alpha \times (T_1 - T_2)} \,\mathbf{W}/\mathbf{mk}$$

= <u>1.21×0.390×1000×0.01022×0.007</u> W/mk 0.009391×(95–66)

= 0.1267W/mk

A.2.7. Specimen As. 1

Mass of metal disc B, m=1021g = 1.21kg

Specific heat capacity of the material of metal disc B, s = 0.390 kJ/KgK

Diameter of specimen slab S, D= 10.223cm

Area of cross-section,  $\alpha = \pi \times (0.5 \text{D}^2)$  sq.cm

$$=\pi \times (0.5 \times 10.233 \times 10^{-2})^2$$

$$= 8.224 \times 10^{-3} m^2$$

Thickness of the specimen, d=0.7cm=0.007m



Fig.A.6: Temperature vs. time for sample As.1

From the cooling curve, Fig 4.6, the slope of the tangent at 66.23°C



= 0.1389 W/mk

A.2.8 Specimen As.3

Mass of metal disc B, m=1021g = 1.21kg

Specific heat capacity of the material of metal disc B, s = 0.390 kJ/KgK





From the cooling curve, fig 4.8, the slope of the tangent at 66°C

 $\frac{dQ}{dt} = \frac{height of ordinate}{height of abscissa}$  $= \frac{62-43}{2040-0}$  $= 0.009314^{\circ}C/sec$ 

Calculation:

The thermal conductivity of sample As.3 is measured as follow:

$$K = \frac{ms\frac{dQ}{dt}d}{\alpha \times (T_1 - T_2)} W/mk$$

$$= \frac{1.21 \times 0.390 \times 1000 \times 0.009314 \times 0.007}{8.7185 \times 10^{-3} \times (95 - 62)} W/mk$$

$$= 0.10694 W/mk$$
A.2.9 Specimen As.4
Mass of metal disc B, m=1021g = 1.21kg
Specific heat capacity of the material of metal disc B, s= 0.390kJ/KgK
Diameter of specimen slab S, D= 10.335cm
Area of cross-section,  $\alpha = \pi \times (0.5D^2)$  sq.cm
$$= \pi \times (0.5 \times 10.335 \times 10^{-2})^2$$

$$= 0.008389 m^2$$
The thickness of the sample slab As.4, d = 0.7 = 0.007m



Fig A.9: Temperature vs. Time of specimen As.4

From the cooling curve, fig 4.9, the slope of the Tangent at 61°C



= 0.09767 W/mk

## A.2.10 Specimen As.5

Mass of metal disc B, m=1021g = 1.21kg

Specific heat capacity of the material of metal disc B, s = 0.390 kJ/KgK

Diameter of specimen slab S, D= 10.235cm

Area of cross-section,  $\alpha = \pi \times (0.5D^2)$  sq.cm =  $\pi \times (10.235 \times 10^{-2})^2$ = 0.0082275 m<sup>2</sup>

Thickness of the sample slab As.5, d = 0.7 cm = 0.007 m



Fig A.10: Temperature vs. Time of sample As.5

From the cooling curve, fig 4.10, the slope of tangent at 57°C,

 $\frac{dQ}{dt} = \frac{height of ordinate}{height of abscissa}$ 

$$=\frac{57-38}{2580-0}$$
$$= 0.007364^{\circ}\text{C/sec}$$

Calculation:

n

The thermal conductivity of sample As.5 is measured as follow:

