



**UNIVERSITI PUTRA MALAYSIA**

***EFFECTS OF SINTERING ATMOSPHERE AND TEMPERATURE ON  
PHYSICAL PROPERTIES OF MULLITE- BASED CERAMIC FROM  
BLACK RICE HUSK ASH AND ALUMINA MIXTURE***

**NURZILLA BT MOHAMED**

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PHYSICAL PROPERTIES OF MULLITE- BASED CERAMIC FROM BLACK  
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**By**

**NURZILLA BT MOHAMED**

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in  
Fulfillment of the Requirement for the Degree of Master of Science**

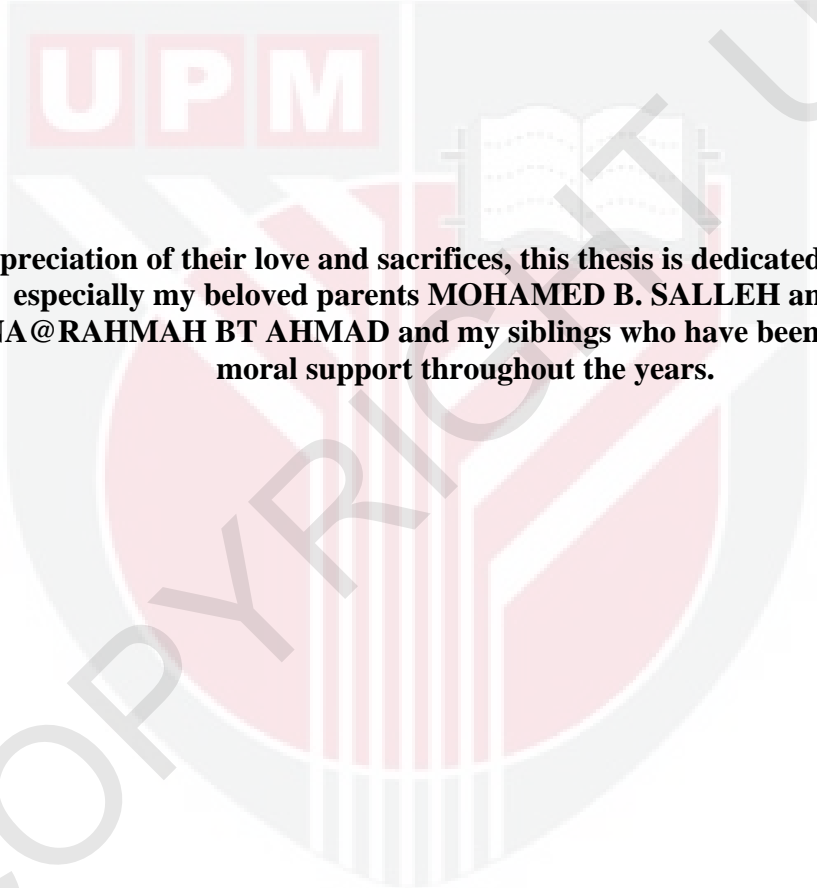
**February 2014**

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**In appreciation of their love and sacrifices, this thesis is dedicated to my family especially my beloved parents MOHAMED B. SALLEH and CHE HASNA@RAHMAH BT AHMAD and my siblings who have been giving me full moral support throughout the years.**

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the Degree of Master of Science

**EFFECTS OF SINTERING ATMOSPHERE AND TEMPERATURE ON PHYSICAL PROPERTIES OF MULLITE BASED- CERAMIC FROM BLACK RICE HUSK ASH AND ALUMINA MIXTURE**

By

**NURZILLA BT MOHAMED**

**February 2014**

**Chairman: Khamirul Amin Matori, PhD**

**Institute: Science**

Mullite ( $3\text{Al}_2\text{O}_3\text{-}2\text{SiO}_2$ ) is well known as a thermal insulator material because of its excellent electrical insulating ability and has been used for various applications. This research was an attempt to study the physical, structural and thermal diffusivity properties of mullite based ceramic prepared by mixing

Black Rice Husk Ash (BRHA) and commercial alumina ( $\text{Al}_2\text{O}_3$ ) mixture.  $\text{Al}_2\text{O}_3$  powder of purity 99.995% was added to BRHA at 60 % and 80 % percent composition and labeled as samples A (60 wt.%  $\text{Al}_2\text{O}_3$ -40 wt.% BRHA) and B (80 wt.%  $\text{Al}_2\text{O}_3$ -20 wt.% BRHA) respectively. The two types of compositions were separately mixed via ball milling for 24 hours. The combinations of BRHA with  $\text{Al}_2\text{O}_3$  were pressed into pellets using uniaxial die pressing with an applied pressure of 5 tons to produce the pellets. Samples A and B were sintered in air and nitrogen atmospheres at different temperatures for 2 hours using an electric furnace. The mullite ceramic derived from samples A and B were characterized for physical, structural and thermal diffusivity properties using X-ray diffraction (XRD), X-ray fluorescent (XRF), Fourier transform infrared spectroscopy (FTIR), Field emission scanning electron microscopy (FESEM) micrographs and Laser flash analysis (LFA).

The bulk density of samples A sintered in air was increased ( $2.45 \text{ g/cm}^3$  to  $2.83 \text{ g/cm}^3$ ) with increasing sintering temperature from 1200 to 1450 °C. However the bulk density of samples A sintered in nitrogen decreased within the range of  $2.70$  to  $2.54 \text{ g/cm}^3$  with increasing sintering temperature from 1350 to 1400 °C. Besides that, the bulk density of samples B in both air and nitrogen were increased with increasing sintering temperature. It is noted that the shrinkage percent of sample increased with increase in bulk density of sample. The weight loss of samples sintered in nitrogen is slightly lower compared than samples sintered in air. The bulk density of samples B was found to be higher than

samples A which was expected because the quantity of  $\text{Al}_2\text{O}_3$  in samples B was higher compared to samples A. The largest linear shrinkage was observed in samples A and this was attributed to the larger amount of BRHA. This variation due to the increase in weight loss for samples A was because of the higher composition of BRHA and hence a larger surface area when compared to samples B. The XRD results revealed that samples A sintered in air at  $1450\text{ }^\circ\text{C}$  for two hours exhibiting the best results in terms of mullite content. FTIR spectroscopy showed that mullite formation occurred at  $1175\text{ cm}^{-1}$ . It was evident from the FESEM micrographs that, samples A sintered in air had a rod-like mullite form with an average grain size increase to  $0.25\text{ }\mu\text{m}$ . In contrast, the XRD results of other samples showed a smaller amount of mullite. The results of LFA showed the highest thermal diffusivity at  $1450\text{ }^\circ\text{C}$ . However, thermal diffusivity sharply decreases with increasing measured temperature from  $27$  to  $500\text{ }^\circ\text{C}$ .

It was also observed that, the mullite content increased with decreasing  $\text{Al}_2\text{O}_3$  addition and increasing of sintering temperature. Thermal diffusivity of samples was diminished due to the presence of impurities in the starting material which contributed to the glassy phase formation.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Master Sains

**KESAN PERSINTERAN ATMOSFERA DAN SUHU KE ATAS SIFAT FIZIKAL  
DARIPADA MULLITE BERASASKAN CAMPURAN ABU SEKAM PADI DAN  
ALUMINA**

Oleh

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Mullite ( $3\text{Al}_2\text{O}_3\text{-}2\text{SiO}_2$ ) terkenal sebagai bahan penambat haba kerana ciri penambat elektrik yang sangat baik dan telah digunakan dalam pelbagai aplikasi. Kajian ini dilakukan untuk mengkaji sifat fizikal, struktur dan kemeresapan haba seramik berasaskan mullite daripada campuran abu sekam padi hitam (BRHA) dan alumina komersial ( $\text{Al}_2\text{O}_3$ ).

Serbuk  $\text{Al}_2\text{O}_3$  dengan kejituan 99.995% telah ditambah kepada BRHA pada 60 % dan 80 % peratus komposisi dan dilabelkan masing-masing sebagai sampel A (60 wt.%  $\text{Al}_2\text{O}_3$ -40 wt.% BRHA) dan B (80 wt.%  $\text{Al}_2\text{O}_3$ -20 wt.% BRHA). Kedua-dua jenis komposisi ini dicampur secara berasingan melalui bebola pengisar selama 24 jam. Kombinasi BRHA dan  $\text{Al}_2\text{O}_3$  telah ditekan dan dibentuk menjadi pelet dengan menggunakan alat penekan dengan tekanan 5 tan untuk menghasilkan pelet. Sampel A dan B disinter di dalam udara dan nitrogen atmosfera dengan menggunakan relau elektrik pada suhu yang berbeza selama 2 jam. Mullite seramik diperolehi daripada sampel A dan B dicirikan bagi sifat-sifat fizikal struktur dan kemeresapan terma menggunakan pembiasan sinar-X (XRD), pendarfluor sinar-X (XRF), spektroskopi infra merah (FTIR), mikroskop pengimbas medan elektron (FESEM) dan analisis laser flash (LFA).

Ketumpatan pukal sampel A disinter di dalam udara meningkat ( $2.45 \text{ g/cm}^3$  sehingga  $2.83 \text{ g/cm}^3$ ) dengan kenaikan suhu persinteran daripada 1200 sehingga 1450 °C. Walaubagaimanapun, ketumpatan pukal sampel A disinter di dalam nitrogen menurun dalam lingkungan julat dari 2.70 sehingga  $2.54 \text{ g/cm}^3$  dengan kenaikan suhu persinteran daripada 1350 sehingga 1400 °C. Selain itu, ketumpatan pukal bagi kedua-dua sampel B di dalam udara dan nitrogen telah meningkat dengan kenaikan suhu persinteran. Didapati bahawa, peratusan pengecutan sampel telah meningkat dengan kenaikan ketumpatan pukal sampel. Kehilangan berat sampel disinter di dalam nitrogen adalah rendah sedikit berbanding sampel yang disinter di dalam udara. Didapati ketumpatan

pukul sampel B lebih tinggi daripada sampel A kerana kuantiti  $\text{Al}_2\text{O}_3$  di dalam sampel B adalah lebih tinggi berbanding dengan sampel A. Pengecutan linear terbesar pada sampel A diperhatikan dan hal ini merujuk kepada jumlah BRHA yang lebih besar. Perubahan ini membawa kepada peningkatan kehilangan berat sampel A kerana komposisi BRHA yang lebih tinggi dan menyebabkan luas permukaan yang lebih besar jika dibandingkan dengan sampel B. Keputusan XRD menunjukkan bahawa sampel A disinter di dalam udara selama dua jam pada  $1450\text{ }^\circ\text{C}$  memperolehi keputusan yang baik dari segi kandungan mullite. Spektroskopi FTIR menunjukkan pembentukan mullite terjadi pada  $1175\text{ cm}^{-1}$ . Hal ini dibuktikan oleh mikrograf FESEM bahawa sampel A yang disinter di dalam udara mempunyai mullite berbentuk rod dengan purata saiz butiran meningkat kepada  $0.25\text{ }\mu\text{m}$ . Sebaliknya hasil keputusan XRD bagi sampel yang lain menunjukkan pembentukan mullite adalah kecil. Keputusan LFA menunjukkan kemerapan terma meningkat pada  $1450\text{ }^\circ\text{C}$ . Walaubagaimanapun, kemerapan terma berkurangan dengan peningkatan suhu pengukuran dari  $27$  sehingga  $500\text{ }^\circ\text{C}$ .

Didapati bahawa, kandungan mullite meningkat dengan penurunan kandungan  $\text{Al}_2\text{O}_3$  dan kenaikan suhu persinteran. Kemerapan terma bagi sampel berkurangan berikutan kehadiran bendasing di dalam permulaan bahan yang menyumbang kepada pembentukan fasa kaca.



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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfillment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

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## LIST OF ABBREVIATIONS

BRHA	Black Rice Husk Ash
RH	Rice Husk
XRD	X-ray Diffraction
FESEM	Field Emission Scanning Electron Microscopy
EDX	Energy Dispersive X-ray
FTIR	Fourier Transform Infrared Spectroscopy
XRF	X-Ray Fluorescent
LFA	Laser Flash Analysis
DTA	Differential Thermal Analysis
Wt.%	Weight percent

# CHAPTER 1

## INTRODUCTION

### 1.1 Background of Mullite

Over the last decades, mullite has been discovered at the contact of superheated magma intrusion with  $\text{Al}_2\text{O}_3$  rich sediments as on the Island of Mull (Scotland) where mullite was first named (Schneider et al., 2008). Mullite is one of the most important phases in both traditional and advanced ceramics since it is a stable intermediate compound ( $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ) formed with the  $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$  system. Mullite has many advantages, including high melting point, low coefficient of thermal expansion and thermal conductivity, high chemical inertness, insoluble in hydrogen fluoride, excellent high temperature creep resistance, good chemical resistance, infrared transparency, low dielectric constant, unique resistance to thermal shocks and high strength at high temperature (Park et al., 2007). Mullite can be prepared using synthesis methods, including sol-gel processing, co-precipitation, hydrothermal process, chemical vapor deposition, sintering of silica-coated alumina micro and nanopowders and solid state sintering (Bernardo and Colombo 2006).

Mullite processing, as well as properties and applications are well reported in the literature (Schneider et al., 1994). Several works have been carried out to prepare mullite ceramics using various starting materials and chemical methods all of which follow different mullitization routes on heating. Generally, mullite is a common reaction product of most aluminium silicates at high temperatures (Aksay et al., 1991). In order to get a significant amount of mullite in alumina ceramics, two techniques may be considered. The first technique involves addition of a mullite-containing material with a lower content of glassy phase forming ingredients. The second technique involves the use of a proper silicate based material as an additive. Using high temperature transformation with this material and the after reaction between silica and alumina, mullite and residual crystalline phases will be obtained (Medvedovski, 2006). It has been known that the crystal structure of mullite is closely related to that of siliminite. This has been proven by the characterized chains of edge-connected  $\text{AlO}_6$  octahedra running parallel to the crystallographic *c*-axis (Schneider et al., 2008)

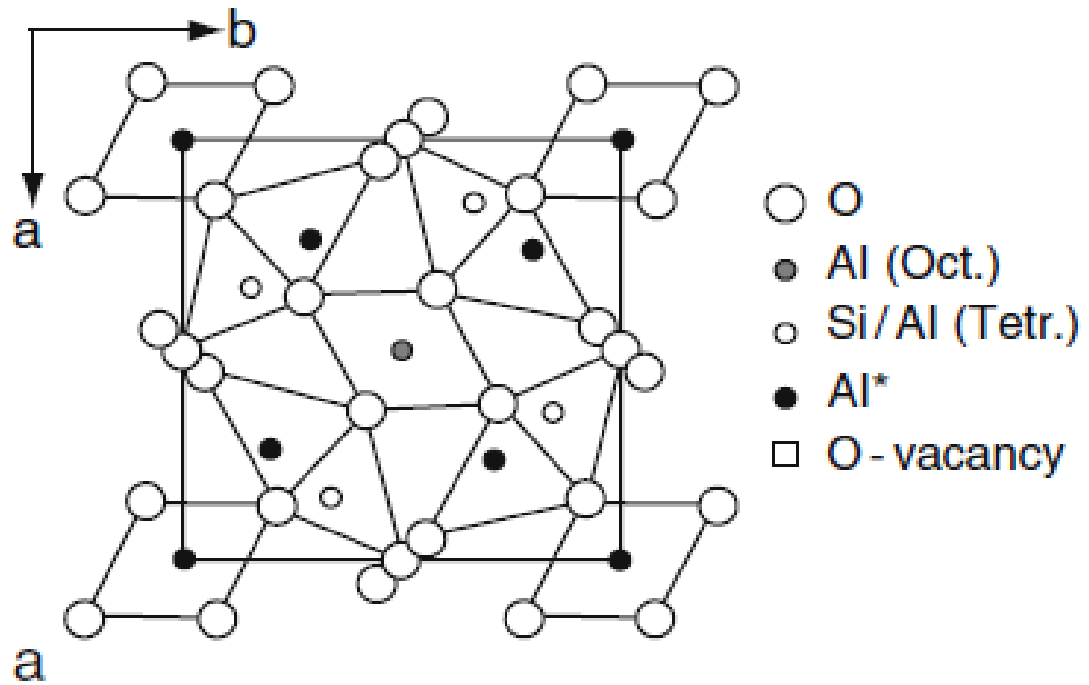
### 1.2 Crystal structure of Mullite

Theoretically, mullite has a structural similarity with siliminite proven by the X-ray diffraction (XRD) pattern. Angel and Prewitt (1986) noted that the crystal structure of mullite was orthorhombic with the space group  $\text{Pbam}$  and unit cell dimensions of  $a = 0.7540$  nm,  $b = 0.7680$  nm and  $c = 0.2885$  nm (Figure 1.1). Scientific and technological developments related to mullite are a solid solution compound with structures consisting

of chains of distorted edge-sharing Al–O octahedra at the corners and center of each unit cell running parallel to the *c*-axis. Besides that, mullite is a solid solution compound with stoichiometries ranging from relatively high silica  $3\text{Al}_2\text{O}_3\text{-}2\text{SiO}_2$  (3:2 mullite) to high alumina  $2\text{Al}_2\text{O}_3\text{.SiO}_2$  (2:1 mullite). It was also observed that the crystal structure of mullite can be modified with increased alumina content obtained by replacing Si with Al so that the overall charge neutrality will be maintained. According to  $2\text{Si}^{4+} + \text{O}^{2-} \Rightarrow 2\text{Al}^{3+} + \text{vacancy}$ , mullite stoichiometry is achieved by substituting  $\text{Si}^{4+}$  ions with  $\text{Al}^{3+}$  ions in the tetrahedral sites of the alternating aluminum and silicon columns and the vacancy is created to maintain charge neutrality. Burnham (1964) reported that structural defects can cause distorted Al-O octahedral which run parallel to the *c* axis of the orthorhombic unit cell. Meanwhile, random distribution of silica and alumina tetrahedral occur when the chains are linked by discontinuous double chains of Al-O and Si-O tetrahedral in the unit cell (Kriven et al., 1998). Hence, this can caused movement of distorted alumina tetrahedral in an oxygen-deficient tricluster in the normal position. The coordination of the remaining oxygen atoms is increased and forced into new positions which is slightly different from their original locations. It is noted that defects are more likely to cluster with short-range order along specific crystallographic directions. On the other hand, less directional correlation of oxygen vacancies occur when alumina concentration is lower. Freimann and Rahman (2001) revealed that lattice parameter *a*, and to a lesser extent *b* is moved parallel by oxygen vacancies, and the result could be used to interpret thermal expansion behavior of mullite. However, the elemental composition of mullite is known as a defect structure as follows:



where *x* is the amount of missing oxygen per average unit cell, *VI* and *IV* represent the four and six fold coordination of aluminium. In this case, the value of *x* is in the range of 0.17 until 0.59 (70.5-83.6 wt.%). Based on structural studies, the effects of kinetics, temperature and composition, in the presence or absence of alumina are important factors that determine development of various forms of mullite structures. The development of metastable forms of mullite depends on all of these factors.



**Figure 1.1: Crystal structure of the alumina silica system** (Duval et al., 2008)

### 1.3 Applications of Mullite

It is well known that, mullite is an important material in various applications especially as a thermal insulator in electronic, optical and high temperature structural applications. It is known that a single crystal can be grown in to polycrystalline and polyphase ceramics. There are three types of polycrystalline mullite ceramics which are commonly used into structural ceramic applications as discuss below:

#### i) Monolithic mullite ceramics

Mullite has achieved outstanding significant as a material for both traditional and advanced ceramics because of its characteristics. Products from monolithic mullite include tableware, porcelain, construction and engineering ceramics, refractories, creep resistant materials, substrates for catalytic convertors, electronic devices, and other advanced ceramics.

#### ii) Mullite coatings

Many metals and ceramics are susceptible to degradation due to oxygen exposure and harsh chemical environments at high temperature. In order to protect materials under such the required conditions, surface coating known as Environmental Barrier Coating, (EBCs) is the best method to overcome these problems. Besides that, the mullite EBCs

have been successfully applied for multiple uses in oxide or nonoxide-based ceramic structures such as furnace tubes.

### **iii) Mullite matrix composites**

The group which includes mullite matrices and mullite fibers is called mullite matrix composites. An expected outcome in the field of mullite composites is the reduction in the inherent brittleness of systems through improvement in their toughness. Mullite matrix composites display a large variety of applications including are components and structures for gas turbine engines, high duty kiln furnitures, burner tubes, and heat shields for re-entry space vehicles.

## **1.4 Problem statement**

Mullite has attracted a lot of attention in recent years due to its wide application in thermal and electrical insulation components. However, it is still difficult to produce mullite free from the glassy phase has been reported in the literature. The presence of impurities, homogeneity of mixing and the nature of the starting materials are the main reasons for the existence of this glassy phase. These reasons tend to influence the performance of mullite ceramics. Therefore, solid state sintering is required for producing engineering ceramic components from mullite with little glassy phase. Although the sintering reaction between silica and alumina to produce mullite has been investigated, little research was devoted to sintering in different atmospheres. Hence, the purposes of this research were mainly to study the effect of the reaction in different atmospheres on the characterization of mullite obtained from BRHA and alumina mixtures.

## **1.5 Objectives**

This research deals with the preparation and characterization of mullite using two types of different batch compositions carried out in air and nitrogen gas at various temperatures. The main objectives of this research are summarized as follows:

- i. To prepare a low cost mullite from Black Rice Husk Ash (BRHA) and alumina powder mixtures via solid state sintering.
- ii. To determine the effect of the reaction atmospheres (sintered in air and nitrogen gas ) and the raw material composition on the physical, structural and thermal diffusivity properties of mullite.
- iii. To investigate the effect of sintering temperature on the thermal diffusivity of mullite formation.



## 1.6 Thesis outline

The general introduction of mullite, its crystal structure and applications of mullite are presented in Chapter 1. Chapter 2 describes the related literatures on mullite synthesis methods, mullite phase equilibrium diagram, effect of composition, reaction atmospheres and microstructure on the mullite properties and also the basic theories of infrared spectrum and thermal diffusivity of mullite. In Chapter 3 the methodologies employed for the preparations and characterization of the sintered mullite are discussed. The results of the different batch combinations carried out in air and nitrogen gases at the various temperatures are explained in Chapter 4. Finally, the conclusions and suggestions for future research are presented in Chapter 5.





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