Synthesis of Mullite Powder from Aluminum Nitrate and Precipitated Silica using Sol-Gel Process

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ABSTRACT

In this work, a new route for possibility synthesizing high purity submicron size mullite ($3A1_2O_3.2SiO_2$) powder at relatively low temperature. Mullite precursor has been prepared from mixing precipitated silica powder with solution of aluminum nitrate nonahydrate ($Al(NO_3)_3.9H_2O$) through sol-gel process, in order to obtain composite powder. The formed precursor gel was calcined at temperatures of (1100, 1150, 1200 and 1250)°C for 1 hour. The influence of calcination temperatures of the mullite synthesis was discussed. The microstructure tests of calcined materials were investigated by x-ray diffractometer (XRD), scanning electron microscopy (SEM), and energy dispersive x-ray spectroscopy (EDX). X-ray analysis results identified the mullitization initiated at 1200°C, and the mullite phase was completely formed at 1250°C. The SEM micrographs show the microstructure of mullite powder had been aggregated in the regular and nearly spherical-like appearances with diameters in the range of (100-200) nm.

Keywords: Mullite, aluminum nitrate, precipitated silica powder, sol-gel process and XRD.

INTRODUCTION

Mullite ($3Al_2O_3.2SiO_2$) is a refractory aluminosilicate and it is the only stable phase in the $A1_2O_3.SiO_2$ binary system. Mullite is well-known as a superior engineering ceramic material because of their combined excellent properties such as low theoretical density, low thermal expansion, low thermal conductivity, low dielectric constant, chemical stability, thermal shock resistance and excellent high temperature strength [1–3].

Ceramics based on the mullite are candidate for advanced ceramic applications for structural, electronic and optical applications such as engine components, gas filters, thermal insulation parts, heat exchangers and substrates in fast electronic devices. Classical uses of mullite include refractories in the metallurgical industries for electric furnace roofs, hot metal mixers and low frequency induction furnaces [2,3].

In literature there is a wide variety of methods for mullite synthesis, including mixtures of reagents in solid state, co-precipitation of mixed salts in solution, spray pyrolysis, sol-gel process etc. [1]. The sol-gel method has the following advantages over the other techniques [4,5]:

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- High purity and high homogeneity multi-component ceramics and composite ceramics are obtained since the energy and the synthesis temperature is low enough,
- It is possible to prepare various special types of materials such as thin films, coatings and fibers because it is very easy to control on the reaction conditions.

Homogeneity of raw materials depends largely on the processing and synthesis method used, i.e. how to mix, precipitate, hydrolyses, or react of SiO_2 with Al_2O_3 components. The mechanism of mullite formation depends upon the method of combining the alumina- and silica-containing reactants [6].

There are many researchers have been synthesized mullite ceraimcs. Simon S. and Wasinton S., in 2012 [7], have been synthesized mullite from aluminum nitrate hydrate [$(Al(NO_3)_3.9H_2O$] and silica sol from rice husk. The formation of mullite was started at temperature of 1000°C. A. Sedaghata et al, in 2014 [8], have been synthesized nano powder of alumina-mullite composite with high homogeneity and high purity. Aluminum chloride ($AlCl_3.6H_2O$) and tetraethyl orthosilicate (TEOS) were used instead of alumina or mullite nano powder. The mullite formation starts from 1000°C and at 1200°C, it is completed.

The objective of this work is to synthesize mullite ceramic powders with fine microstructure and high homogeneity at somewhat low temperature via sol-gel process. Aluminum nitrate hydrate and precipitated silica powder were proposed as a source of alumina and silica respectively. Simultaneous XRD and microstructure analysis were performed for the characterization of the mullite powder formation.

Experimental Work

The starting materials used in this work were aluminum nitrate nonahydrate ($Al(NO_3)_3.9H_2O$) (BDH Chemicals Ltd Poole, England), as source of alumina and precipitated silica powder as source of silica. Mullite ceramic was prepared using the sol-gel method from suitable proportion of [$Al(NO_3)_3.9H_2O$]:[SiO_2] to produce the composite with molar ratio of Al_2O_3 to SiO_2 of (3:2). Silica sol was prepared by dispersed 3.36 grams of precipitated silica in 150 mL of (distilled water/ethanol) 1/1 wt%, and stirring under magnetic stirring for 30 min at 80°C. Alumina sol was prepared by dissolving 30 grams of $Al(NO_3)_3.9H_2O$ in 150 mL of ethanol under magnetic stirring for 30 min at 80°C. Both of alumina and silica solutions were mixed and stirred for 1 hour at 110°C to get homogeneous mixture. Adding of ammonium hydroxide drops to the mixed solutions until the white colored gel bed was formed. The gel formation begins at pH= 5 to 6. The prepared gel has been filtered, washing with distilled water, and then dried at 80°C for 3 hours in an electrical oven. The dried gel has been milled by mortar and pestle. This is followed by a calcination step. The calcination is carried out at (1100, 1150, 1200 and 1250)°C, with a heating rate of 7 °C/min and holding time at the specific temperature was 1 hour. The calcined powders were then characterized by x-ray diffraction (XRD), scanning electron microscope (SEM), and energy dispersive x-ray spectroscopy (EDX). The general flowchart for synthesizing of mullite powder in this work is shown in figure 1.

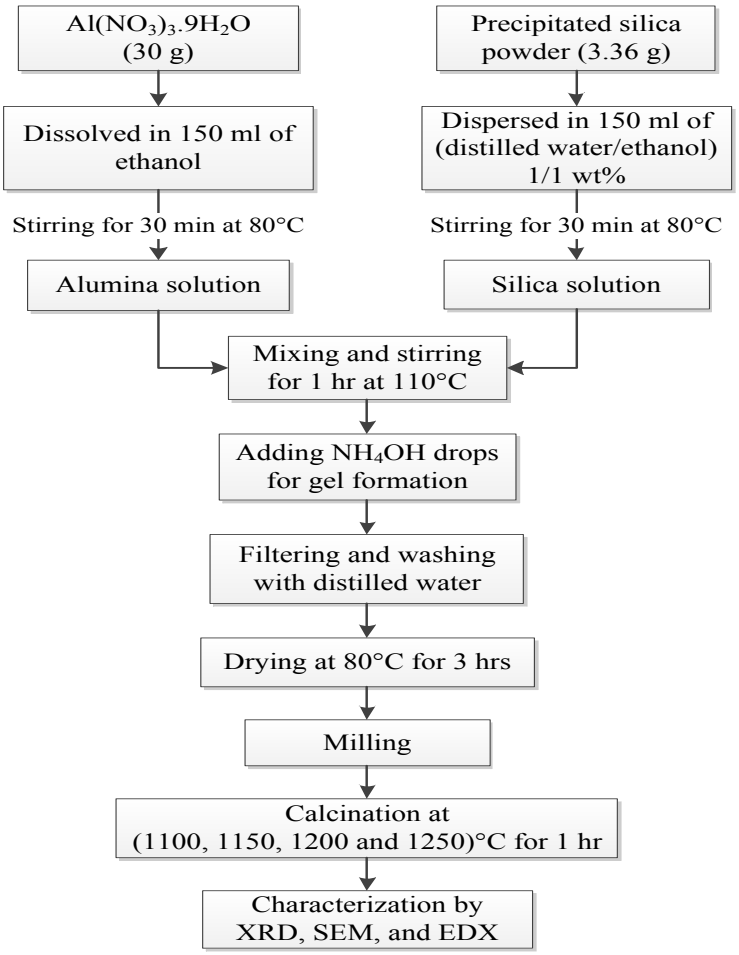


Figure (1): The General Flowchart For Synthesizing Of Mullite Powder In This Work

Results and Discussion

1. X-Ray Diffraction (XRD)

Figure (2) and figure (3-a, b and c) show the XRD analysis patterns of the obtained powders after calcinations of mullite precursors at (1100, 1150, 1200 and 1250)°C for 1 hour. It has been shown at calcinaion of 1100°C, figure (2), there is no clear diffraction peak appear and the XRD pattern are near to amorphous. At calcination temperatures of 1150°C and 1200°C, figure (3-a and b), only two small peaks of orthorombic mullite phase at 2θ = 16.3° (110) and 25.9° (120) have been observed at 1200°C calcination, corresponding to Joint Committee on Powder Diffraction Standards (JCPDS) card No. (15-0776), whereas the other phases present were identified to be α-alumina. The α-alumina phase appeared at 2θ = 25.6° (012), 35.2° (104), 43.3° (113), 52.5° (024) and 57.5° (116), corresponds to JCPDS card No. (46-1212). It also can be observed in the figure (3-a) the wide amorphous silica at 20°.

With increasing the calcination temperature up to 1250°C, the mullitization process was completely occurred as shown in XRD pattern figure (3-c). The XRD analysis indicates to present orthorombic mullite phase in the sample with the strong peaks of several mullite crystals planes at diffraction angles of 2θ = 16.4° (110), 26.1° (210), 33.2° (220), 35.3° (111) and 40.8° (121). Not only mullite phase is formed at 1250°C, but also there is some alumina phase has been detected in this sample.

The presence of alumina phase within the mullite could be explained on the transformation of mullite can be observed as decomposition according to the following reaction: $2(2Al_2O_3.SiO_2) \rightarrow 3Al_2O_3.2SiO_2 + \alpha\text{-}Al_2O_3$ [7]. Furthermore the role of raw materials is governed on the formed phases in the final mullite powder.

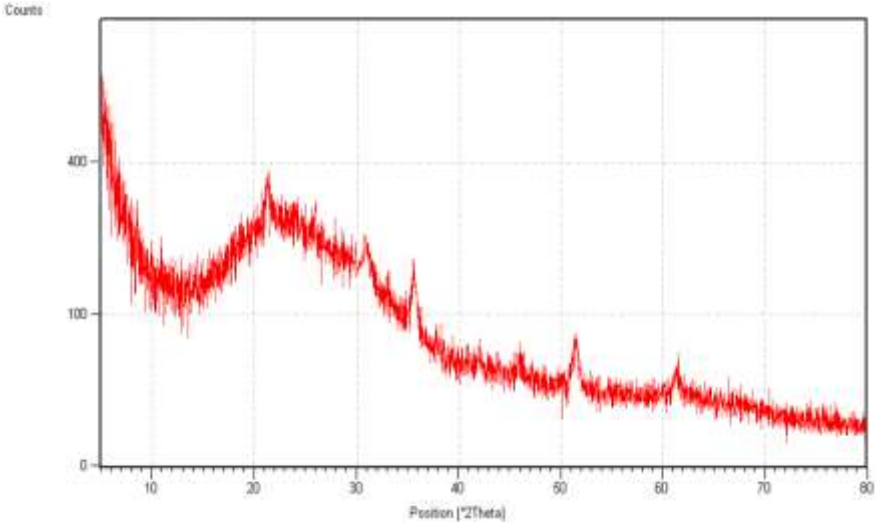
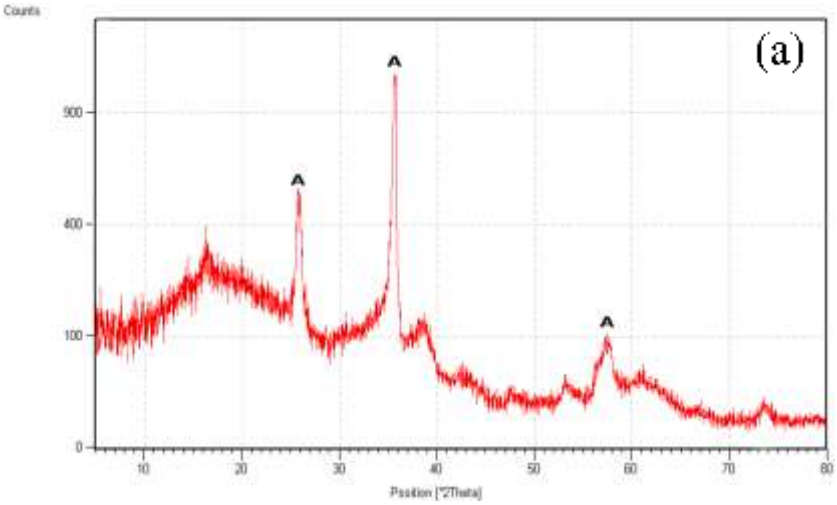


Figure (2): XRD analysis pattern of the mullite precursor after calcination at 1100°C.



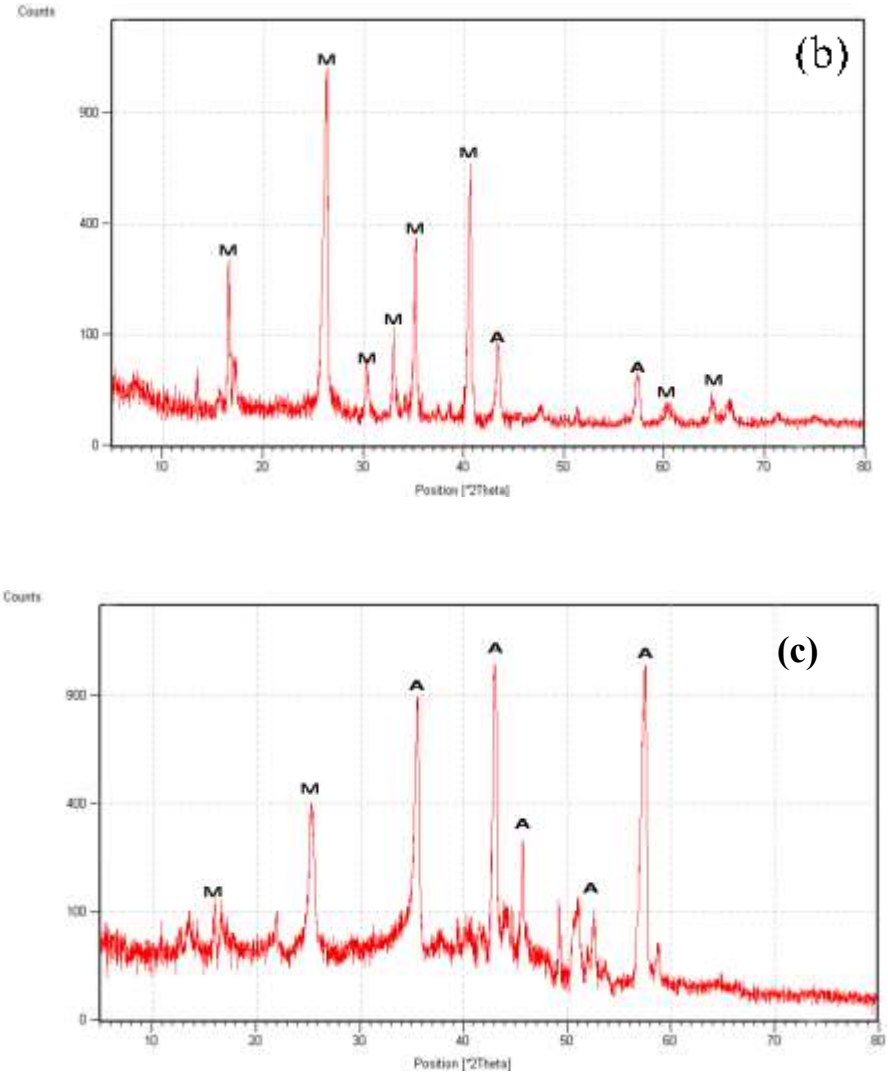


Figure (3): XRD analysis patterns of the mullite precursors after calcinations at: (a) 1150°C, (b) 1200°C and (c) 1250°C. Where (M, mullite; A, alumina).

2. Microstructure analysis

Scanning electron microscopy (SEM) imaging has been conducted for the mullite powder prepared at 1250°C, in order to observe the morphology of the powders and the particle size. Figure (4) shows the SEM images of the mullite powder with different magnifications. As seen in these figures, the morphology of the mullite powder had been aggregated in the regular and nearly spherical-like appearances. The spherical mullite powder particles in this work have a good sinter property and will

improve the mechanical properties. In addition notice the mullite particles have somewhat narrow size distribution with diameters in the range of (100-200) nm. The particles agglomeration refers to the adhesion of the particles to each other because of Vander Walls force of attraction which are significantly higher in nanoparticles.

The mullite particle morphology in this work seems to be different with most of previous literatures. A. Sedaghat, et al. [8] and Jagannath Roy, et al. [9], have been prepared mullite powders on the platy- and needle-like appearances through using sol-gel process. This different in the resulting mullite particle shape reflect to the role of raw materials in governing the formation of particles shape in the final mullite powder. The mullite precursor here was prepared as composite powder form by coating the precipitated silica particles with aluminum hydroxide through sol-gel process. The mullitization of the composite powder precursor and the miscibility of alumina and silica were expected at such calcination temperature.

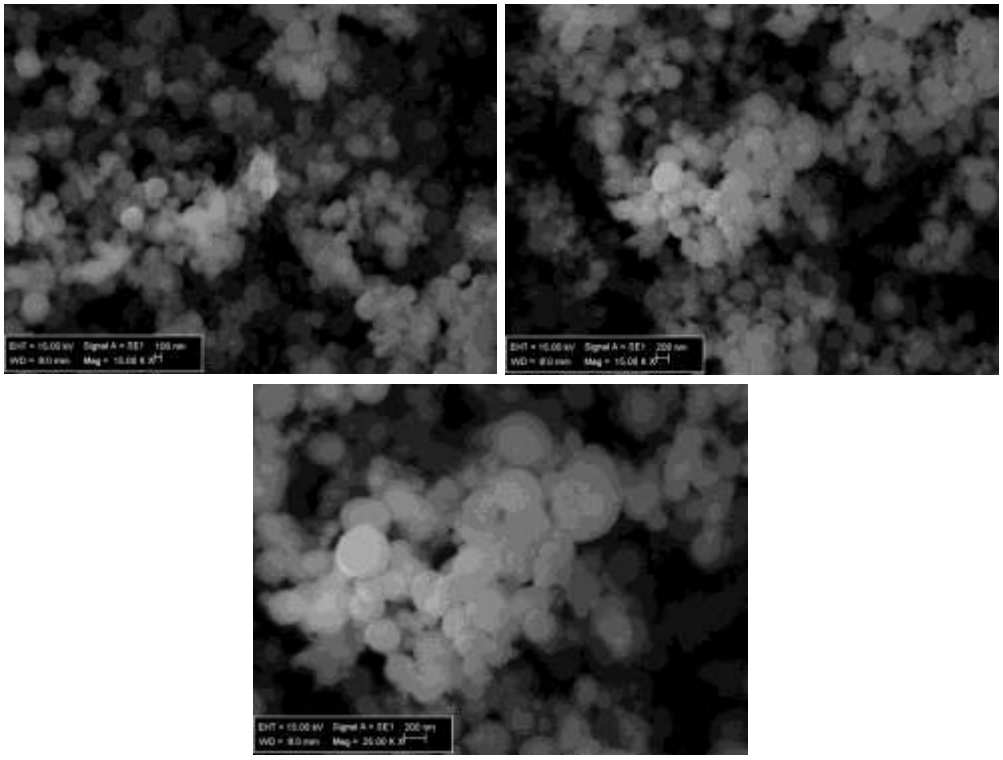


Figure (4): SEM photographs with different magnification of mullite powder calcined at 1250°C.

Energy dispersive x-ray (EDX) composition analysis of the prepared mullite powder is shown in figure (5). It can be seen that composition mainly contains of O, Al and Si with a very small amount of C and S as impurity. The gold (Au) element was measured in EDX analysis image due to the sample was coated of gold before the analysis. The quantitative analysis through EDX spectroscopy shows that their weight percent scale of the prepared mullite powder was containing O (39.41%), Al (43.07%) and Si (17.52%). The EDX analysis result is consistent with XRD analysis, demonstrating to formation of mullite phase. The formation mechanism of present

mullite phase can be explained by inter-diffusion of aluminum and silicon ionic species under high calcination temperature in the alumina–silica contact zone.

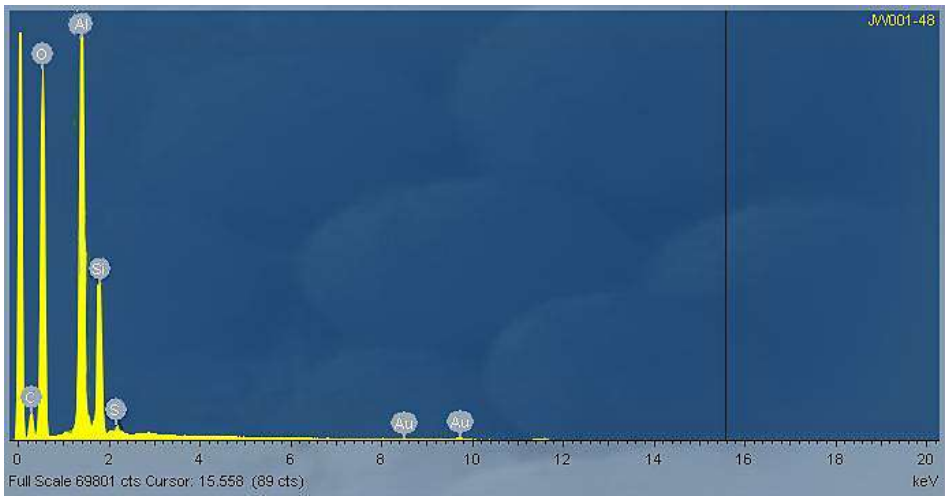


Figure (5): EDX analysis of the prepared mullite powder at 1250°C.

CONCLUSIONS

In this work, mullite ceramics powder in submicron size has been successfully synthesized at relatively low temperature from using precipitated silica powder and aluminum nitrate nonahydrate through sol-gel processing. The use of precipitated silica particles coupled with aluminum nitrate solution proved very effective for the preparation of mullite ceramics. XRD analysis results identified the mullitization process initiated at 1200°C, and the mullite phase was completely formed at 1250°C. Preparing of the mullite precursor as composite powder form by coating precipitated silica particles with aluminum hydroxide has significant effect on the resulting mullite particle shape and on the formed mullite phases. SEM micrograph shows the microstructure of the mullite powder had been aggregated in the regular and nearly spherical-like appearances with diameters in the range of (100-200) nm.

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