

Preparation of ultra-homogeneous mullite precursor and evaluation of mullite formation

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The objective of this study is to present firstly the preparation of atomically ultra-homogeneous mullite precursors by ultrasonic spray pyrolysis technique and then to investigate the evaluation of mullite formation via calcination temperature and soaking time. At a temperature of as low as 500 °C for 15 days, the temperature was very close to the formation temperature of mullite (477 °C) is energetically possible; the structure of the precursor has been preserved as amorphous. It is possible to obtain single phase of mullite crystals at a temperature of 1000 °C without soaking time, while the crystallization required a temperature of 900 °C for 12 hours.

Key words: Amorphous, Mullite, Pyrolysis, Crystallization, Calcination.

Introduction

During the last decades a number of studies were conducted about the synthesis of 3 : 2 mullite powders via different techniques such as solid state reaction, sol-gel, crystallization from glasses (1-8) in which the synthetic mullite with a composition close to 3 : 2 was first synthesized by Sainte-Claire Daville and Caron in 1865 reported by Kleebe *et al.* [9]. Present studies show that the crystallization temperature of mullite powders is directly related to the precursor type. Ref [10] discusses two types of mullite precursors, namely type I and type II. Type I displays direct crystallization of mullite from the amorphous state at low temperature, while type II exhibits mullite crystallization by reaction of transient spinel-type alumina with silica above 1200 °C.

The type of mullite precursor is characterized by the homogenization degree of the cations where short-range order is required for type I. It is known that, alumina silicate glasses have short-range order and that it is possible to obtain mullite crystals below 1000 °C. However, the preparation of mullite glasses is very difficult since the glass forming ability of alumina silicate is low and extremely high quenching rates are required [10].

In this study, ultra homogeneous mullite precursors were prepared by ultrasonic spray pyrolysis technique. The obtained precursors were calcined at different temperatures and soaking times along with the evaluation of mullite formation were investigated. In

addition, mullite formation possibility at 500 °C is investigated which is slightly higher than the formation temperature of the energetically possible mullite.

Materials and Method

Mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) powders were obtained by a two stage reaction: preparation of high homogeneous precursor by ultrasonic spray pyrolysis and crystallization by post-sintering. The used ultrasonic spray pyrolysis system was given elsewhere [11], the system includes three main parts: preparation of aerosol droplets, formation of metal oxide powders and collection of the obtained powders. Tetraethylorthosilicate, TEOS (Fluka 98%), and aluminium nitrate nanohydrate- $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Merck extra pure) were used for the preparation of solutions with a molarity of 1.5 M. TEOS was added to distilled water and was mixed via a magnetic mixer at 500 rpm to form a clear solution after which 0.2 M HNO_3 was added to water. After obtaining a clear solution, aluminum nitrate nanohydrate was added and mixing was continued again via a magnetic mixer in order to obtain a clear solution. Clarity of solutions was measured by a turbidimeter and solutions were accepted to be clear when the turbidity value was below 0.1 NTU. The clear solution was placed in an ultrasonic nebulizer (frequency, 1.63 MHz) and aerosol droplets were obtained. The aerosol droplets were fed to a quartz tube (diameter-height, 5-120 cm) inside the hot reactor (temperature, 500 °C) by a carrier gas where the feed rate was 1.5 lt/min. The obtained metal oxide powders were collected by filtration by membrane filters (Schleicher & Schuell-NL 16) with a pore size of 0.2 mm. The obtained precursors were post-calcinated at different temperatures (500, 875, 900 and 1000 °C) for different soaking times (1 minute to

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15 days) where the heating and cooling rate of the furnace was 5 °C/min.

The crystalline phases of the prepared powders were determined by X-ray analysis (Rigaku-miniflex) at a speed of 2 °/min and 0.01 ° steps, by using CuK α radiation, between 10-70 °. Crystalline phases were also analyzed by using fourier transform infrared spectroscopy (FTIR, Burker Vertex 70). Particle size distributions were measured by a Zetameter (Malvern-Nano ZS). The morphologies of the powders were investigated by microscopic studies using scanning electron microscopy (Zeiss Supra 50 VP). The weight loss of the solution with time was determined using differential thermal analysis (DTA, Perkin Elmer-Diamond).

Results and Discussions

Spherical mullite precursors were formed in three steps: formation of droplets, formation of metal oxide particles and recovery of the particles. One precursor was produced from one droplet. All steps have great importance on the physical and chemical properties of the precursor, however, the crystalline phase, particle structure and morphology of the particle was determined by the evaporation and decomposition reactions within the hot reactor. So for the successful synthesis of mullite precursor, the determination of reaction temperature is required.

Figure 1 shows the differential thermal analysis/thermal gravimetry analysis results obtained from the thermal decomposition of solution used for obtaining mullite precursors by ultrasonic spray pyrolysis. The curve shows two endothermic peaks with peak points at 97 and 249 °C. During the first reaction the peak and extreme points were at 97 and 198 °C, the solution lost about 90.8 wt % of its mass. The mass loss corresponds to the evaporation of water, nitric acid, decomposition of TEOS and loss of some molecules of water from aluminum nitrate without loss of the nitrate groups. The breaking of the nitrate groups and the

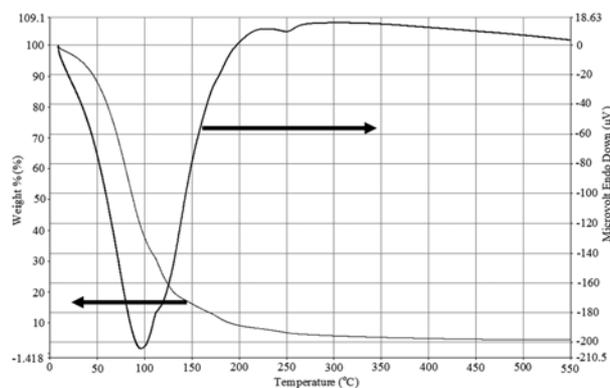


Fig. 1. Differential thermal analysis/Thermal gravimetry analysis of the solution used for the preparation of mullite precursor.

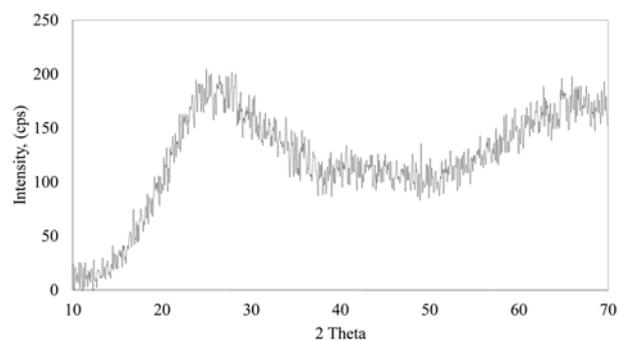


Fig. 2. X-ray pattern of the precursor.

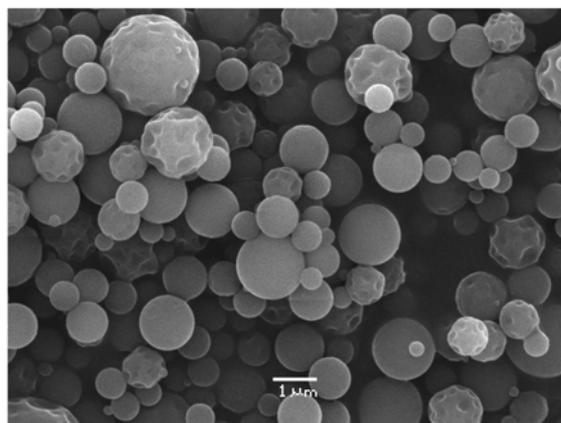


Fig. 3. Scanning electron microscopy picture of the precursor.

completion of the decomposition of aluminum nitrate nanohydrate proceeds at 220-450 °C where the reaction is signed by the second endothermic peak [12]. According to the results, it is possible to obtain mullite precursor by ultrasonic spray pyrolysis technique at a reactor temperature of 500 °C which is higher than the temperature of all the decomposition reactions completes with the total weight loss of 95.39% wt.

Phase analysis and particle morphology of the precursor have been given in Figure 2 and 3, respectively. The obtained precursor has an amorphous structure and the particles have spherical shapes. Also the particle size of the sample is narrow with a mean size of about 1.1 μ m.

During the preparation of mullite precursor the solution lost a huge amount (95.39% wt) of mass due to a series of reactions such as evaporation of water, decomposition of TEOS and dehydration, hydrolysis and breaking of nitrate groups of aluminum nitrate nanohydrate. Hence, the determination of the precursor formation from solution and the crystallization of the formed precursor (only 4% wt of solution) by a single DTA/TG analysis are difficult. Therefore the crystallization of the precursor was determined separately and results were given in Figure 4. The curve shows an exothermic peak with peak points at 982 °C which is the crystallization temperature of mullite. The relatively big weight loss of up to 900 °C is related to

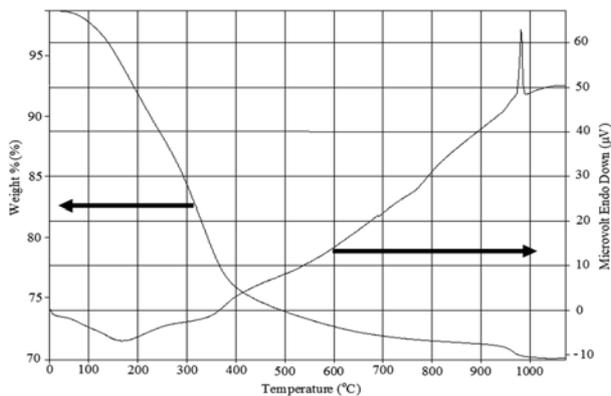


Fig. 4. Differential thermal analysis/Thermal gravimetry analysis of the mullite precursor.

the breaking up of OH groups and the removal of H₂O from the system. These phenomena have been discussed in detail in literature [15-15].

The mullite precursor was calcined at above (1000 °C) and below (900 °C and 875 °C) the crystalline temperature with and without soaking times varying between 1 hour and up to 15 days. The crystalline phases of the calcined powders were determined by X-ray analysis and the results were given in Figure 5-7. The calcination at highest temperature (1000 °C), which is slightly higher than the crystallization temperature of the precursor determined by differential thermal analysis (see Fig. 4) without any soaking time indicates mullite crystallization with no detectable impurities such as amorphous, silica or alumina based structures (Figure 5). Besides, obtaining of mullite structure without any impurity phase at a lower temperature (900 °C) required a soaking time of 12 hrs (Figure 6). For short soaking times, an amorphous

phase that increases with decreasing soaking time was present in mullite crystallization. The calcination at 900 °C for a soaking time of less than 4 hours did not indicate any mullite crystallization detectable by X-ray analysis. On the other hand, only a trace amount of mullite crystallization was detected for the calcinations that took place at a temperature of 875 °C for 60 hours where there is no mullite crystallization for a soaking time of 24 hours.

Janackovic et al. [16] synthesized mullite powders by the same technique and reported that mullite was formed at 1200 °C by reaction of silica and γ -alumina formed at 1100 °C. However, in this study the amorphous structure directly transforms to mullite structure at lower temperatures. This phenomenon can be explained with the homogeneity degree of cations. When the ultra-homogeneous cation mix was achieved, the amorphous structure transforms to mullite without formation of any transient phases. Otherwise, mullite was crystallized with the solid state reaction of transient γ -alumina and amorphous silica.

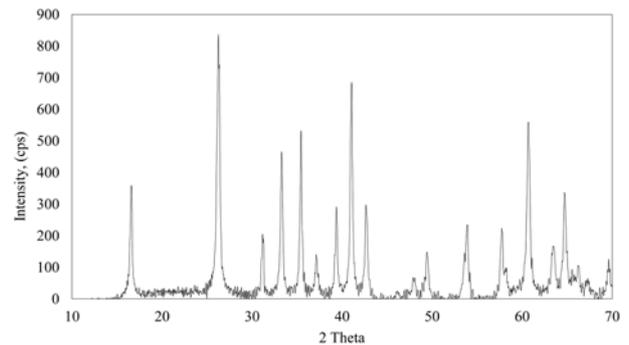


Fig. 5. X-ray analysis of the powder calcined at 1000 °C without any soaking.

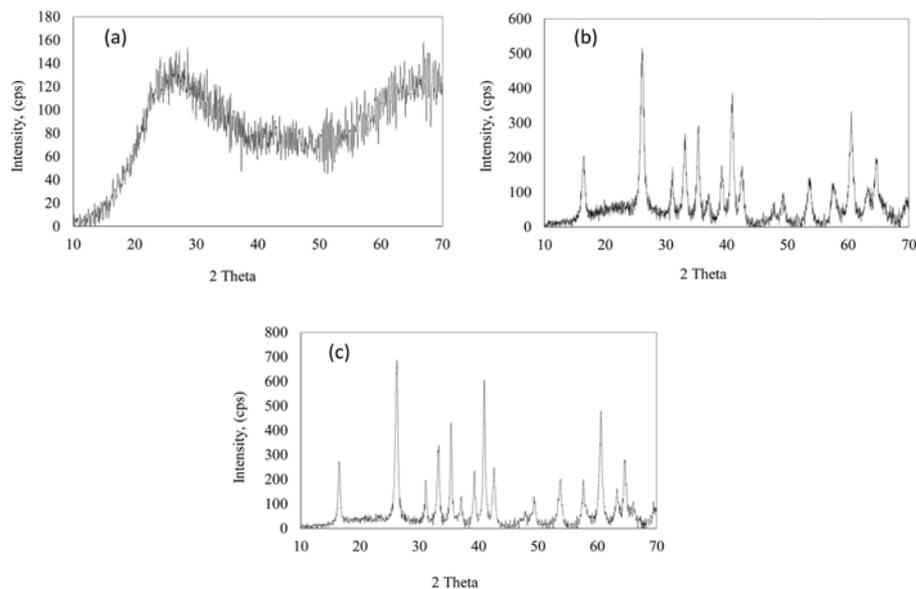


Fig. 6. X-ray patterns of the powders calcined at 900 °C for different soaking times: 1 hour (a), 8 hours (b) and 12 hours (c).

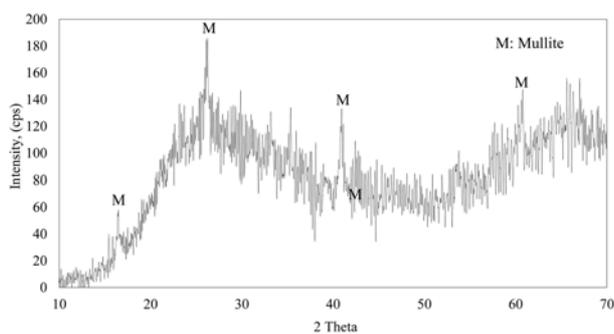


Fig. 7. X-ray pattern of the powder calcined at 875 °C for 60 hours.

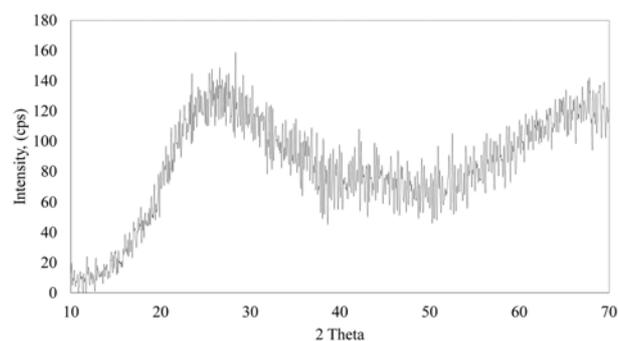


Fig. 9. X-ray pattern powder calcined at 500 °C for 15 days.

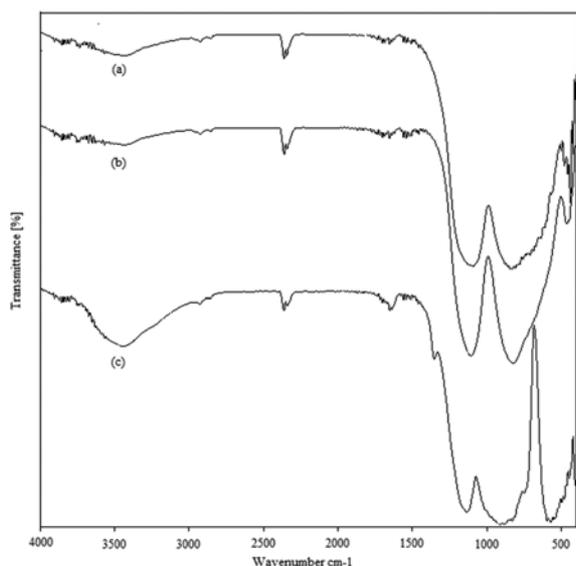


Fig. 8. Fourier transform infrared spectroscopy spectra of the powders calcined at 900 °C for different soaking times: 1 hour (a), 8 hours (b) and 12 hours (c).

These findings were in accordance with other fourier transform infrared spectroscopy (FT-IR) studies. In Figure 8, it is shown that the FT-IR spectra of powders calcined at 900 °C for different soaking times varied between 1 and 12 hours in which the shortest and longest soaked samples have amorphous and fully mullite, respectively. For the mullite sample, five main spectra were present where the bands at 1168 and 1134 cm^{-1} were assigned to Si-O stretch (tetrahedral), 845 cm^{-1} to Al-O stretch (tetrahedral), 749 cm^{-1} to T-O-T bend (tetrahedral), 550 cm^{-1} to Al-O stretch (octahedral) and 460 cm^{-1} to O-Si-O bend (tetrahedral) and Al-O-Al bend (octahedral). These results were in good accordance with the peaks of mullite given in literature [17]. When the soaking time decreased a band at 670 cm^{-1} appeared which was assigned to Al-OH band and the bands at 1168 and 1134 cm^{-1} shifted to lower wavelengths. Besides, α -alumina or similar phases were not detected. According to both X-ray and FT-IR results, it is possible to state that an ultra-homogeneous cation mix with amorphous structure was achieved and the amorphous phase was directly transformed to the mullite phase.

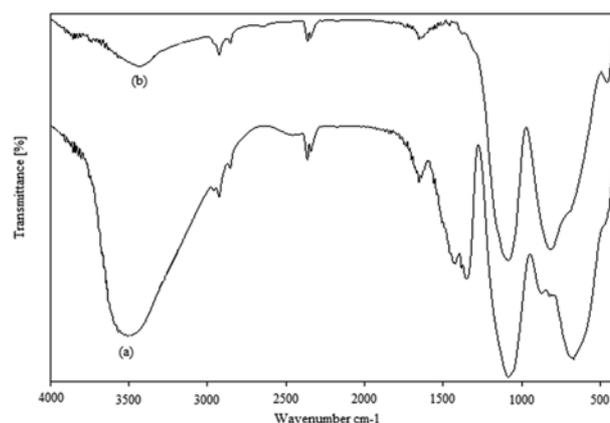


Fig. 10. Fourier transform infrared spectroscopy spectra of the precursor (a) and powder calcined at 500 °C for 15 days (b).

In addition, the possibility of formation of mullite structure at a temperature of 500 °C is investigated which is slightly higher than the formation temperature of mullite (477 °C) is energetically possible [18]. Figure 9 shows that the X-ray pattern of the precursor was calcined at 500 °C for 15 days. The powders have amorphous structure and there is no significant difference between the patterns of the calcined powder and precursor (see fig. 2). However, the FT-IR results of the powders were different (see Figure 10).

The main differences between the two FT-IR spectras are the bands at 670 cm^{-1} which were assigned to the Al-OH band in which the bands were absent for the calcined powder while they are present for the precursor. Besides, the bands of the calcined powder were in good accordance with the characteristic mullite bands mentioned above. According to the results, it can be stated that mullite formation was achieved for a long soaking time (15 days) at 500 °C. This formation can be detected by the FT-IR analysis while it is not possible to do so by X-ray analysis. This phenomenon can be described such that: mullite structure was achieved but the crystalline size of the structure was so small that X-ray analysis gave amorphous structure in which it is reported that these type structures can be detectable by FT-IR ~~fourier transform infrared spectroscopy~~ whereas it is not possible to do by X-ray

[19]. It is clear that the grain growth requires high calcination temperatures or requires a very long time at low temperatures.

Conclusions

Ultra-homogeneous mullite precursor has been prepared by ultrasonic spray pyrolysis technique and the evaluation of mullite formation from the precursor depending on the calcination temperature and time has been investigated. Mullite formation is directly related to the calcination temperature and the time in which the mullite precursor directly transforms to mullite at and above the temperature of 1000 °C without soaking time. When the temperature decreases, the completion of mullite formation requires soaking time. It is possible to obtain a fully crystalline mullite powder by calcination of the precursor at 900 °C for 12 hours. Also in this study amorphous mullite powder was obtained for the first time by calcination of the ultra-homogeneous mullite precursor obtained at a calcination temperature of as low as 500 °C for 15 days in which the temperature was very close to the formation temperature of the energetically possible mullite. This mullite structure has been detected by FT-IR analysis whereas X-ray analysis indicated amorphous structure. It is clear that in such cases the FT-IR results are more reliable than the X-ray results.

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