

## Rapid synthesis of mullite powders

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This study covers the synthesis of high purity mullite powders using ultrasonic spray pyrolysis and the microstructural evaluation of bulk materials prepared by using this powder. Tetraethylorthosilicate and aluminum nitrate nanohydrate chemicals were used to prepare an aqueous solution and this solution was turned into aerosol droplets using an ultrasonic nebulizer with a resonance frequency of 1.63 MHz. These aerosol droplets were carried to the vertical tube furnace the temperature of which was set beforehand by using a gas with a flow rate of 1.5 L minute<sup>-1</sup>. Spherically shaped mullite powders were successfully synthesized at 1075 °C according to the results of XRD and FTIR. Bulk materials were obtained by sintering the pressed mullite powders at different temperatures (1500, 1550, 1600 and 1650 °C) with a soaking time of 5 hours. SEM images show that the particle shape changes with the sintering temperature of the bulk ceramic. For low temperature sintering, the particles are still quite spherical whereas they tend to form a rod-like structure with an increase in the sintering temperature.

**Key words:** Rapid synthesis, Mullite, Ultrasonic spray pyrolysis.

### Introduction

Due to its excellent high temperature strength and resistance to creep and thermal shock, low dielectric and thermal expansion constants, and good transmission at high temperatures in the mid infrared band, mullite is a promising candidate in electronic, optical and high temperature structural applications [1]. Some applications of pure mullite or mullite-based ceramics are as matrix materials for continuous fiber reinforced ceramic matrix composites that are used as thermal protection systems for combustion chambers in aircraft turbine engines and stationary gas turbines, heat exchanger parts, heat insulating parts, milling media, furnace center tube [2,3].

Pure mullite is a solid solution whose structural formula may be written as  $Al_2^{VI}(Al_{2+2x}^{IV}Si_{2-2x}^{IV})O_{10-x}$ . The symbols in the formula were IV and VI for tetrahedral and octahedral region cations, and x denotes the number of vacancies formed by the exsolution of oxygen atoms per average unit cell, respectively. The value of x lies within the limits  $0.17 \leq x \leq 0.6$ . It is generally accepted that mullite can be found in one of two chemical forms with a change in x: (i) the composition of  $3Al_2O_3 \cdot 2SiO_2$  phase ( $x=0.2$ ) and (ii) the composition of  $2Al_2O_3 \cdot SiO_2$  ( $x=0.4$ ) [4].

The production of high purity mullite by means of chemical methods, such as suspension combustion synthesis [5], a sol-gel process [6-7], an ion extraction

method [8], from molten salts [9], a flame spray pyrolysis process [10], is usually rather costly and the particle shape and size are hard to control. Ultrasonic spray pyrolysis (USP) has been used as a chemical method for obtaining ceramic powders during recent decades and there has been considerable interest in preparing several ceramic powders, such as mullite, PZT, zirconia [11-13]. The USP method is based on the preparation of aerosol droplets via an ultrasonic nebulizer of starting solutions and transportation of the aerosol droplets into the furnace at elevated temperatures. In spray pyrolysis, the aerosol droplets are transformed into microporous or dense particles. The advantage of this method is that the processes, such as solvent evaporation, precipitation and calcination occur in one step, as well as that each droplet/particle undergoes the same reaction conditions and no subsequent milling is necessary. Also, the method yields a powder with particles of a spherical shape in the submicron range, an arbitrary powder with hollow or dense particles, a powder synthesized at a relatively very low temperature and time [14].

The main purpose of this study was to produce mullite powder with a high purity at low temperatures in a short amount of time.

Due to its highest precursor homogeneity, the solution was mixed at the atomic level, the USP method was selected to achieve this purpose. The second purpose of this study was to produce mullite ceramic from spherical shaped mullite powders obtained by USP and research the microstructural evaluation of the ceramics by means of the particle shape.

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## Experimental

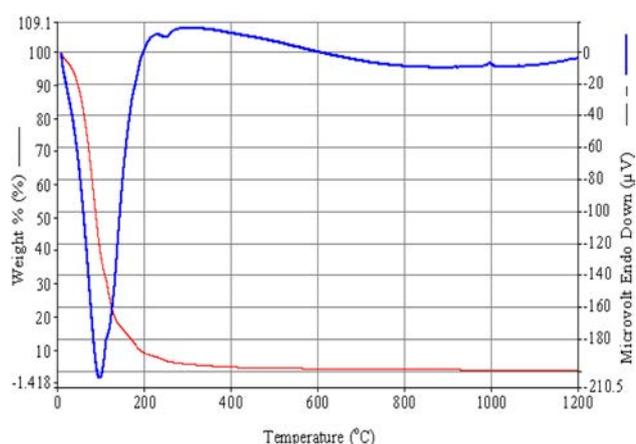
The ultrasonic spray pyrolysis system includes three main parts: preparation of aerosol droplets, formation of metal oxide powders and collection of the powders obtained. Tetraethylorthosilicate (Fluka 98%) and aluminium nitrate nanohydrate (Merck extra pure) were selected as starting materials to prepare a solution mixed at the atomic level with a molarity of 1.5 M. Tetraethylorthosilicate (TEOS) was added to distilled water and was mixed via a magnetic mixer at 500 rpm to form a clear solution where 0.2 M  $\text{HNO}_3$  was added to the water. After a clear solution was obtained, aluminum nitrate nanohydrate ( $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) was added and mixing was continued again via a magnetic mixer in order to obtain a clear solution. The clarity of the 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 small aerosol droplets were produced. The aerosol droplets produced were carried with an air flow rate of  $1.5 \text{ L minute}^{-1}$  through a quartz tube placed in a vertical furnace, with a diameter/length ratio of 5/120 cm. The temperature of the tubular furnace was fixed at 1000, 1025, 1050, 1075 and  $1100^\circ\text{C}$ . The pyrolyzed powders were collected by filtration using membrane filters (Schleicher & Schuell-NL 16) with a pore size of  $0.2 \mu\text{m}$ .

The pyrolyzed powders were shaped by a uniaxial press to form disks,  $1 \text{ cm } \varnothing$ ,  $0.5 \text{ cm}$  height, the disks were placed in an alumina support and then sintered in air at 1500, 1550, 1600 and  $1650^\circ\text{C}$  for 5 hours with a heating and cooling rate of  $5^\circ\text{K minute}^{-1}$ .

Phase analyses on the pyrolyzed powders were performed by an X-ray diffractometer (Rigaku MiniFlex,  $\text{CuK}\alpha$  radiation,  $2\theta = 15$  to  $45^\circ$ , scanning speed  $1^\circ \text{ minute}^{-1}$ ). Particle size distributions were measured by a Zetameter (Malvern-Nano ZS). Thermal decomposition of the solution was studied by TG/DTA (Perkin Elmer-Diamond) under an air atmosphere at a constant heating rate of  $10^\circ\text{K minute}^{-1}$ . The molecular structure was characterized by a Bruker Vertex 70 series Fourier Transform Infrared Spectrometer (FTIR) in transmittance mode from  $400$  to  $1400 \text{ cm}^{-1}$ , with 2 mg samples using a standard KBr method (sample to KBr ratio equal 1:100). Particle morphologies were examined using a JEOL scanning electron microscope (SEM).

## Result and Discussion

The TG/DTA pattern of the clear solution which was used to obtain mullite powders containing Al and Si species mixed at the atomic scale, heat treated in an air atmosphere to  $1200^\circ\text{C}$  at a rate of  $10^\circ\text{K minute}^{-1}$  is presented in Fig. 1. The DTA curve shows two



**Fig. 1.** The DTA pattern of the solution used for the preparation of mullite powders.

endothermic peaks and one exothermic peak at  $125^\circ\text{C}$ ,  $250^\circ\text{C}$  and  $990^\circ\text{C}$ , respectively. The first endothermic peak corresponds to the loss of  $\text{H}_2\text{O}$ , nitric acid, decomposition of TEOS and loss of some molecules of water from the aluminum nitrate without loss of nitrate groups. The breaking of the nitrate groups and the completion of the decomposition of aluminum nitrate nanohydrate proceeds at  $250^\circ\text{C}$  where the reaction is indicated by the second endothermic peak [15]. The exothermic peak ( $\sim 990^\circ\text{C}$ ) indicates that the atomic scale solution prepared by mixing Al and Si species was converted directly to mullite [7,16,17]. According to this result we thought that it may be possible to obtain some mullite powders at around  $990^\circ\text{C}$ .

The X-ray diffraction (XRD) patterns of the pyrolyzed droplets at temperatures ranging from  $1000^\circ\text{C}$ , slightly higher than the crystallization temperature of mullite according to DTA, to  $1100^\circ\text{C}$  with an increase of  $25^\circ\text{C}$  are shown in Figure 2. The powders pyrolyzed at  $1000^\circ\text{C}$  had an amorphous structure. Mullite peaks appeared at  $1025^\circ\text{C}$  and the crystalline mullite content increased significantly with an increase in the temperature to  $1050^\circ\text{C}$  (Fig 2c). No amorphous and/or secondary phases were observed at temperatures higher than  $1050^\circ\text{C}$ , the pyrolyzed powders at  $1075$  and  $1100^\circ\text{C}$  were completely mullite. This temperature ( $1075^\circ\text{C}$ ) was slightly higher than the crystallization temperature ( $\sim 990^\circ\text{C}$ ) shown in the DTA curve. This is not surprising because it should be noted that the reactions/crystallizations may require higher temperature using the USP method depending on a very short residence time (a few seconds) of the droplet/powder within the hot reactor [18].

It is known that some crystalline or semicrystalline structures can be detected by Fourier transform infrared spectroscopy analysis while it is not possible to do so by X-ray analysis [37,41]. The FTIR spectra of the pyrolyzed mullite precursor powders at different temperatures are shown in Figure 3. In the literature, the fundamental bands assigned to  $\text{SiO}_4$  ( $482$ ,  $988$ ,

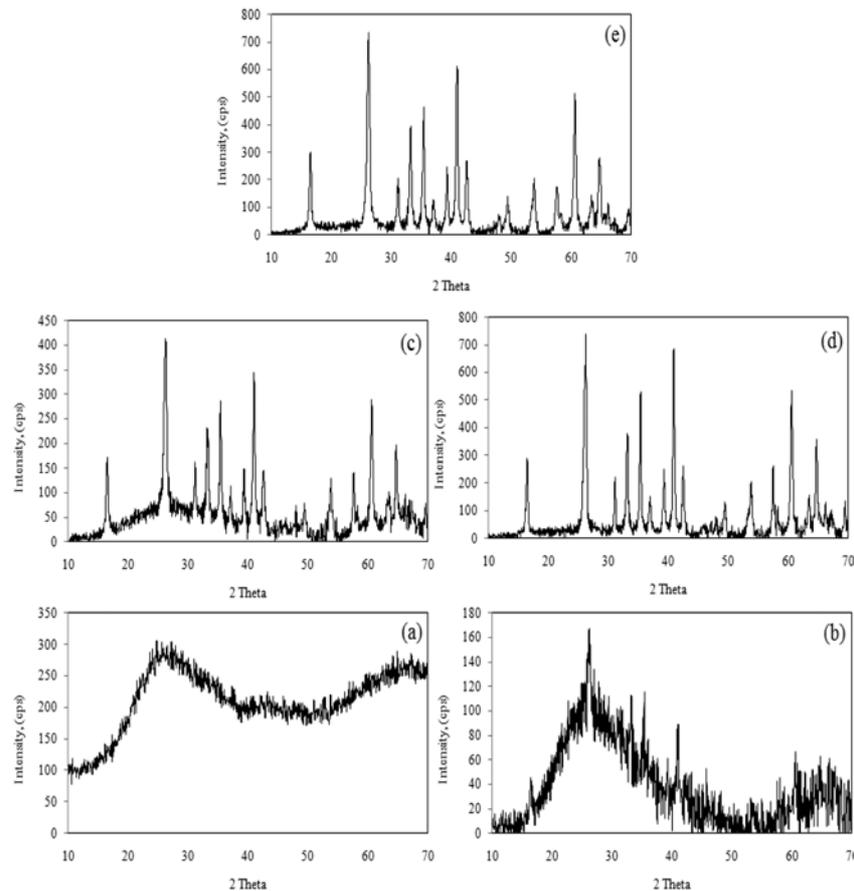


Fig. 2. XRD patterns of mullite powders obtained as different temperatures: a)1000 °C, b)1025 °C, c)1050 °C, d)1075 °C and e)1100 °C.

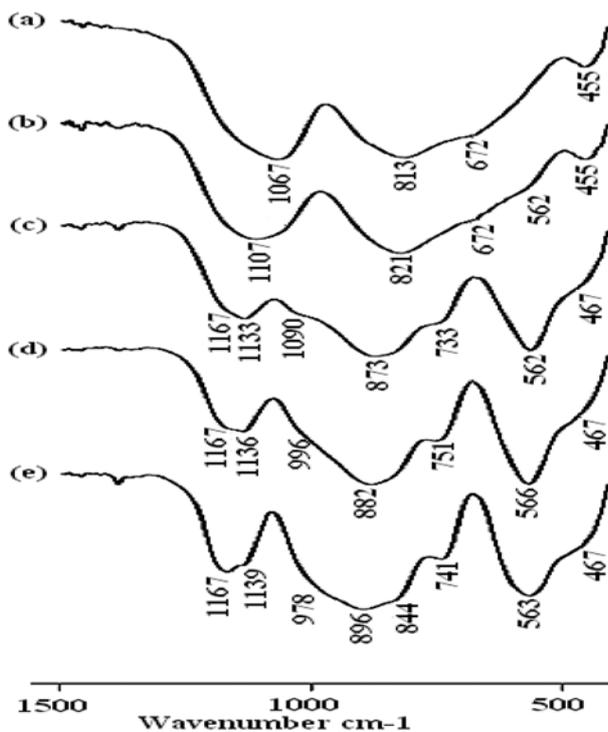
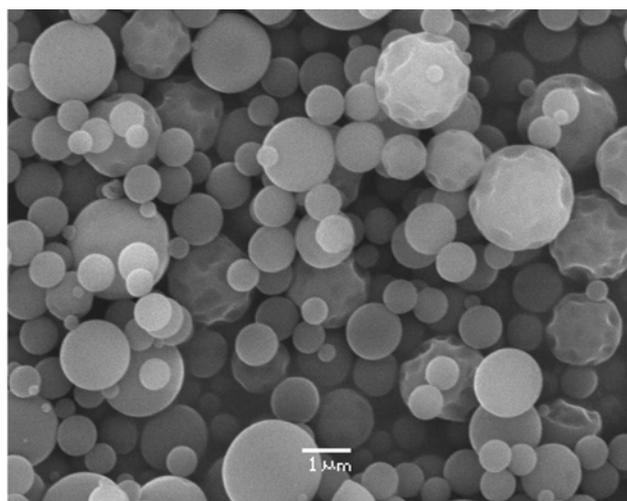


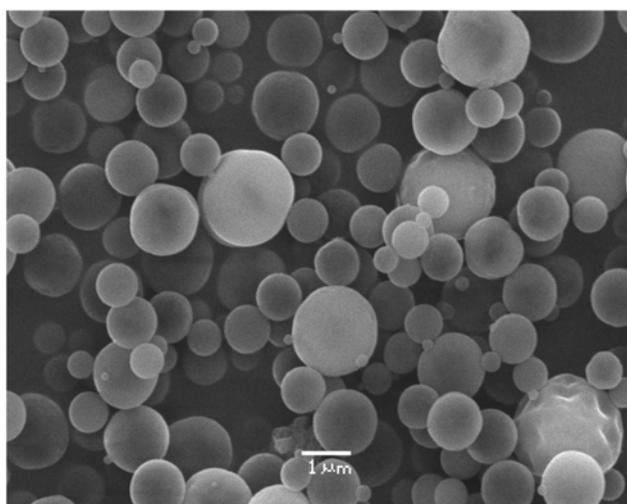
Fig. 3. The IR band positions ( $\text{cm}^{-1}$ ) of the powders obtained at different temperatures: (a) 1000 °C, (b) 1025 °C, (c) 1050 °C, (d) 1075 °C and (e) 1100 °C.

1107, 1131 and  $1168 \text{ cm}^{-1}$ ),  $\text{AlO}_4$  ( $620, 828$  and  $909 \text{ cm}^{-1}$ ),  $\text{AlO}_6$  ( $578$  and  $482 \text{ cm}^{-1}$ ) and T-O-T ( $\text{TO}_4$ ) ( $737 \text{ cm}^{-1}$ ) show the presence and/or formation of mullite [19].

The main (sharp) bands for the powder pyrolyzed at 1000 °C were 455, 813 and  $1067 \text{ cm}^{-1}$ , which are the bands assigned to Si-O bonding. The bands at 813, 1067 and  $455 \text{ cm}^{-1}$  are assigned to amorphous silica, the vibrational mode of the asymmetric stretch of Si-O-Si and bending of Si-O-Si, respectively. For 1025 °C, the peaks were nearly the same as the spectrum of the powder pyrolyzed at 1000 °C. For 1025 °C, a band at  $\sim 560 \text{ cm}^{-1}$  (as a shoulder) was observed, correlating to randomly distributed ( $\text{AlO}_6$ ) octahedra. Besides these peaks, both spectra show a band at  $\sim 670 \text{ cm}^{-1}$  relating to the formation of O-Al-O ( $\text{AlO}_4$ ) and (Si,Al)-O-(Si,Al) ( $\text{TO}_4$ ) bending vibration modes in the region  $737\text{-}620 \text{ cm}^{-1}$  [8]. According to the XRD pattern shown in Fig. 2b, the powder pyrolyzed at 1025 °C includes both amorphous and mullite phases. The bands at  $\sim 562 \text{ cm}^{-1}$ ,  $821 \text{ cm}^{-1}$  and  $1107 \text{ cm}^{-1}$  are assigned to the  $\text{AlO}_6$ ,  $\text{AlO}_4$  and  $\text{SiO}_4$  groups, respectively [20]. The transmittance band at  $821 \text{ cm}^{-1}$  could also be assigned to amorphous silica. Thus, the FTIR results are in good accordance with the X-Ray results. Although DTA analysis provides exothermic peaks at 990 °C, the mullite phase



(a)



(b)

**Fig. 4.** SEM micrograph of the powders obtained at lowest (a) and highest (b) temperatures.

has just started to form at 1025 °C according to the XRD pattern. While the DTA curve which is used to find the reaction temperature was obtaining at a heating rate of 10 °K minute<sup>-1</sup>, the preparation of oxide powders by the ultrasonic spray pyrolysis technique is completed in a few seconds. So, the reactions occur at higher temperatures than obtained by DTA.

For the FTIR spectra of the precursors pyrolyzed at 1050, 1075 and 1100 °C, all the peaks were nearly the same as the spectrum of ideal mullite reported in the literature [3]. For the pyrolyzed powders at these temperatures, all the characteristic bands of mullite at 1168, 1131, 988, 750 and 482 cm<sup>-1</sup> are observed. According to the DTA, X-Ray and FTIR results, the molecular level mixture was directly transformed with atomic interactions to primary mullite at 990 °C, and then it was evolved to crystalline mullite at temperatures > 990 °C. New bands at ~750 cm<sup>-1</sup> and ~560 cm<sup>-1</sup> were

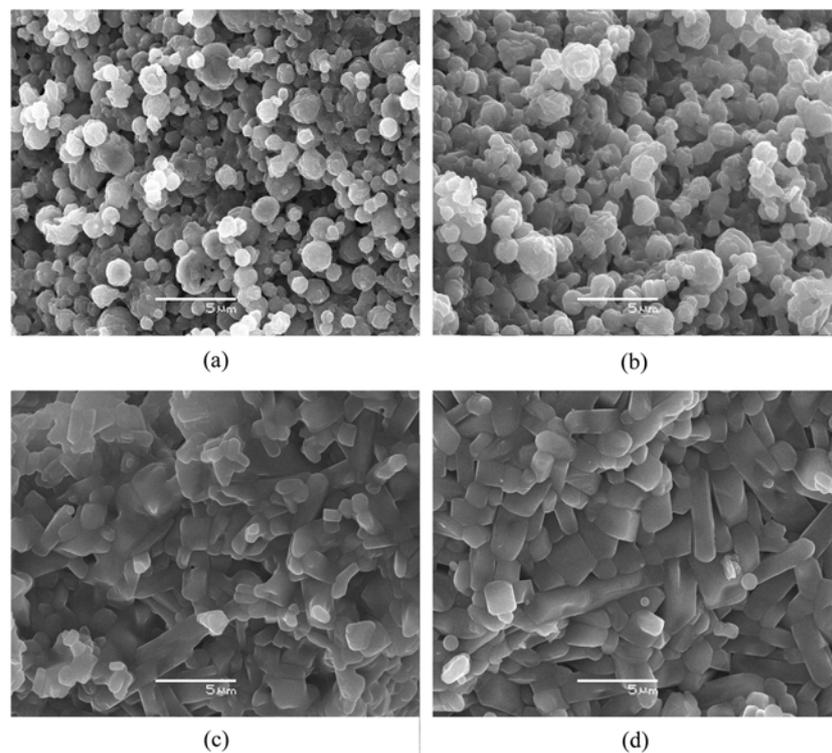
assigned to the AlO<sub>4</sub> bending and AlO<sub>6</sub> stretching modes, respectively. The band at ~670 cm<sup>-1</sup> (as a shoulder) may be assigned to the (Si,Al)-O-(Si,Al) linkage bending modes. This assignment is in agreement with the proposed T-O-T (TO<sub>4</sub>) bending mode for the band at ~737 cm<sup>-1</sup> in mullite.

SEM micrographs of the mullite powders obtained by the USP method at 1000 °C and 1100 °C are shown in Figures 4a and b, respectively. It is obvious from the figures that the reactor temperature has no significant effect on the particle shape and size. The powders prepared at both temperatures were spherical with smooth surfaces and they were nonagglomerated. The mean particle diameters were 0.82 μm and 0.88 μm for the particles prepared at 1000 °C and 1100 °C reactor temperatures, respectively. Their particle size distribution is also relatively narrow which is advantageous for several applications.

The second purpose of this study was to produce mullite ceramics from spherically shaped mullite powders obtained by the USP method and research the microstructural evaluation of the ceramics by means of particle shape. The microstructures of the samples sintered at 1500, 1550, 1600 and 1650 °C are given in Figure 5 a, b, c and d, respectively. At 1500 °C, (see Fig 5a), the sintered particles are still quite spherical. By increasing the sintering temperature to 1550 °C (see Fig 5b), neck connections between spherical particles start to form. When the temperature reaches 1600 °C, nearly all the single particles contact to each other forming a bulk material. Finally at 1650 °C rod like particles can easily be seen on the microstructure where the aspect ratio of some particles is over 5. This is interesting when it is noted that the particles used for the preparation of the ceramic were fully spherically shaped. Also as expected the porosity of the sintered ceramic decreases with an increase in the sintering temperature. According to the SEM results, it may be said that the spherically shaped mullite powders obtained by the USP method tend to form a rod like-structure above 1550 °C.

## Conclusions

The synthesis of mullite powder was made by an ultrasonic spray pyrolysis technique. High purity, spherically shaped powder was successfully obtained without any impurities or amorphous phase at 1075 °C. According to the XRD results, the powder synthesized at 1000 °C was amorphous, however, FTIR showed that the powder included a mullite phase. It could also be said that amorphous mullite was achieved at a temperature as low as 1000 °C. Besides these significant results, it is observed that the spherically shaped powders transformed to rod like structures where the aspect ratio of some particles was over 5 at 1650 °C.



**Fig. 5.** The microstructure of the sintered samples at different temperature: (a) 1500 °C, (b) 1550 °C, (c) 1600 °C and (d) 1650 °C.

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