Synthesis of Al_2O_3 containing mullite from Algerian Kaolin and Boehmite

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In this work, mullite, an advanced structural, optical, and functional ceramic material, was synthesized from Algerian kaolin and boehmite. The appropriate amount of the two raw powders was ball milled for 5 hours and sintered between 1300 and 1600°C. A scanning electron microscope was used to characterize the raw powders and the microstructure of sintered samples. A dilatometer and x-ray diffractometer were used to analyze the formation and transformation of phases. The density and microhardness of sintered samples were measured using a densimeter and a microhardness tester, respectively. It was found that; mullite was the major phase present in the sintered samples besides small fraction of Al_2O_3. The increase of sintering temperature and sintering time increased the densification of samples; a highest relative density of 96 % was achieved at a sintering temperature of 1600°C and a sintering time of 1 hour. Also, the increase of sintering temperature increased mullite fraction and reduced the amount of Al_2O_3. The microhardness of samples increased with the increase of boehmite content.

1. Introduction

Recently, mullite became become a strong candidate for use as an advanced structural, optical, and functional ceramic [1, 2]. This is mainly due to its excellent thermal [3, 4], optical [5-8], and mechanical properties [9-11] besides to its stability under severe environments [1, 2]. Processing of clay [12-17] remains an economical way to prepare mullite with the desired properties [18]; where kaolin undergoes a series of reactions and finally forms mullite. The rate of formation was found to depend on the temperature of the reaction [12-17]. Raw kaolin from different countries such as Malaysia [19], France [20], Japan [21], Burkina-Faso [22], Georgia [23], Algeria [24], or commercial kaolin [25-27] was used to prepare mullite. In previous works we synthesized mullite through reaction sintering Algerian kaolin with pure alumina [24] and analyzed the kinetics of the dehydroxylation of Algerian kaolin through thermal analysis [28]. Also, we investigated the kinetics of mullite formation from Algerian kaolin and pure alumina and evaluated the temperature of formation, activation energies and growth morphology parameters [29]. The objective of the present work is to explore the possibility to synthesis mullite through reaction sintering Algerian kaolin and boehmite and characterize its microstructure and properties.

2. Experimental Procedures

Algerian raw kaolin (from Djabal Debagh) and boehmite was used in this investigation. The ball milling technique [30-33], was used to prepare a homogeneous mixture of kaoiln and boehmite. This technique is being used to develop many advanced materials including alloys, oxide-dispersion-strengthened alloys, composites, and nanocomposites. The boehmite was added to the kaolin to form a mixture of 48 and 52 wt.% of boehmite and kaolin, respectively. The mixture of the raw powders was charged into zirconia vials (250 ml in volume) together with 15 zirconia balls (10 mm in diameter). The ball-to-powder weight ratio was maintained as 10:1 and water was added at a ratio of 2:1. The ball-milling experiments were performed in a high-energy planetary ball mill (Fritsch P6) and were carried out at room temperature at a rotation speed of 250 rpm for 5 hours. The milled mixture was dried at 100°C for 6 hours then cold compacted at 75 MPa using uniaxial press. Cylindrical specimens of 13 mm diameter were produced. The green compacts were sintered in a furnace at 1300 to 1600°C. The heating rate was 10°C/min. For microstructure characterization the sample was polished and either chemically etched with a solution or thermally etched through heating it at a temperature 100°C less that the sintering temperature. X-ray diffraction (XRD) was used to identify phases formed in the sintered samples. XRD measurements were carried out on samples using a high resolution diffractometer MRD, PANalytical (ISM), with CuK_α radiation of a wavelength 1.5418 °A. The diffraction angle (2θ) range

was $15° \leq 2\theta \leq 50°$. Dilatometry experiments were performed on samples using a NETZSCH (Dil 402 C) equipment. The samples were heated from room temperature up to 1300°C, at heating rates of 5°C/min. The density of samples sintered at 1600°C for different sintering times was measured using a densimeter model KERN ARS 220-4 and quantified according to the Archimedes principle. Vickers microhardness of sintered samples was measured using a Zwick microhardness tester model 3210 and quantified using the equation Hv = $1.8544P/d^2$. A load of 500 g was used; this load was optimized through changing the load from 100 g to 500 g. It was found that with the increase of the load up to 400 g the microhardness decreased then remained almost unchanged for loads higher that 400 g, therefore a load of 500 g was used.

3. Results and discussions

The chemical composition of kaolin and boehmite as determined by x-ray fluorescence (XRF) is shown in table 1. Fig. 1 (a) shows XRD spectrum of pure gibbsite which was heated at 300°C for 2 hours to yield boehmite as it is clear from its XRD spectrum shown in Fig. 1(b). The boehmite itself was transformed to Al_2O_3 through heating at 1200°C for 2 hours as it can be clearly seen in figure 1(c). Scanning electron micrographs of boehmite are shown in figure 2(a) and (b) at deferent magnifications. It is known that boehmite [34, 35], a partially dehydrated aluminum hydroxide, can be produced from aluminum hydroxides by controlled calcination [36-38]. Also, thermal calcination in air can convert gibbsite to boehmite [39, 40] which is frequently used as starting material for the synthesis of alumina phases [35]. SEM micrograph of kaolin and boehmite mixture milled for 5 hours is presented in figure 3. It can be noticed that ball milling has led to the decrease of the particle size of the mixture; this is due to the fact that ball milling as powder metallurgy processing technique [41] involves cold welding, fracturing and rewelding of powder particles. This finally leads to the formation of homogeneous mixture of kaolin and boehmite.

Table 1. Chemical composition of kaolin and boehmite as determined by XRF.

Elements	Kaolin	Boehmite
Al_2O_3	44.41	88.34
SiO_2	53.05	03.86
MnO	01.54	-
P_2O_5	00.03	-
SO_3	00.02	-
K_2O	00.02	00.07
Co_3O_4	00.13	-
NiO	00.09	-
ZnO	00.08	-
As_2O_3	00.37	-
CaO	00.17	00.18
Fe_2O_3	00.06	00.096

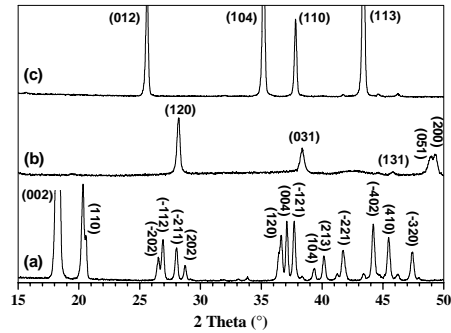|		
F	-	00.897
Na_2O	-	00.34
Ti_2O	-	00.08
LOI.	-	06

Fig 1. XRD patterns of (a) Gibbdite, (b) Boehomite and (c) α-Al_2O_3
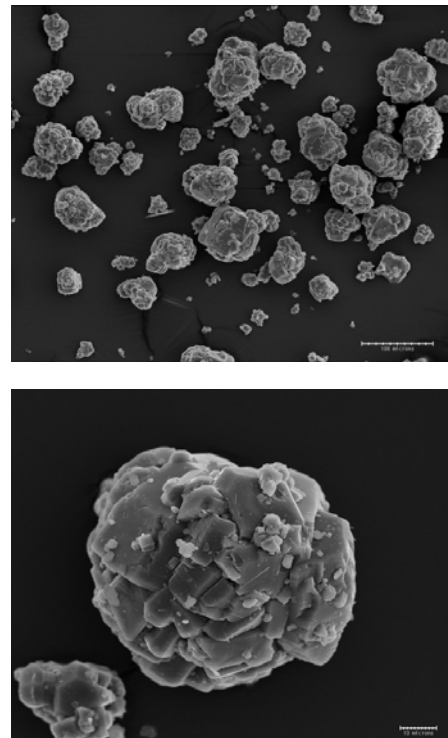

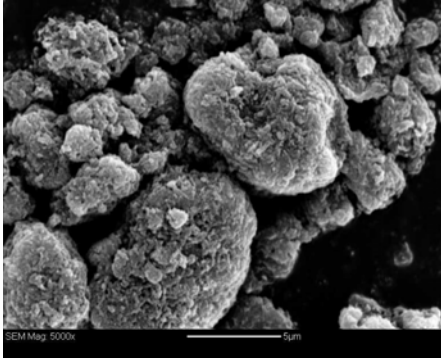*Fig 2. SEM micrographs of Boehmite at deferent magnifications.*

Fig 3. SEM of kaolin and boehmite mixture milled for 5 h.

Fig. 4 shows linear shrinkage of kaolin-boehmite mixture heated at a rate of 10°C/min. This shrinkage curve shows reactions that could take place during heating and are discussed below. Relative expansion at a temperature lower that 160°C due to the evaporation of adsorbed water where kaolin is transformed to kaolinite, and the rate of evaporation is maximum at around 94°C. A relative shrinkage which starts at 500°C and ends at 670°C where the rate of shrinkage is maximum at 628°C. This shrinkage is due to the dehydration of the kaolinite which transforms to metakaolinite. A third relative shrinkage as a result of the transformation of spinel (Al-Si) to silica in the form of cristobalite and primary mullite at 1185°C and this reaction ends at a temperature lower that 1300°C.
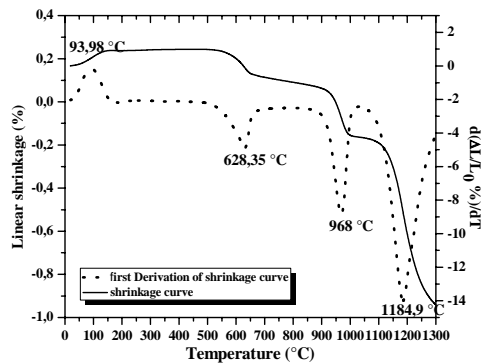

Fig 4. Linear shrinkage of kaolin-boehmite mixture heated at 10°C/min.

XRD spectra of kaolin-boehmite sample sintered between 1300 and 1600°C for 1 hour; are presented in figure 5. It can be noticed that mullite is the major phase present in addition to small fraction of Al₂O₃. The later decreases with the increase of sintering temperature as it can be clearly seen from the decrease of the intensity of its peaks. Figure 6 shows XRD patterns of kaolin-boehmite sample treated at 1600°C for different sintering times. For a sintering time of 5 minutes reflections from Al₂O₃ phase are clear, however, increasing sintering time beyond 10 minutes the intensity of these reflections is sharply reduced. The Al₂O₃ did not disappear completely even after a sintering time of 1 hour. This clearly indicates that the end product is made of mullite and a small fraction of alumina.
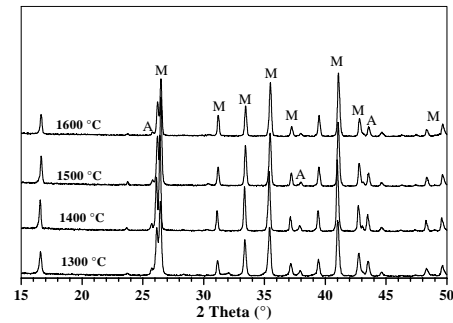

Fig 5. XRD spectra of kaolin-boehmite sample treated at different temperatures for 1 hours. M, Mullite; A, Alumina.
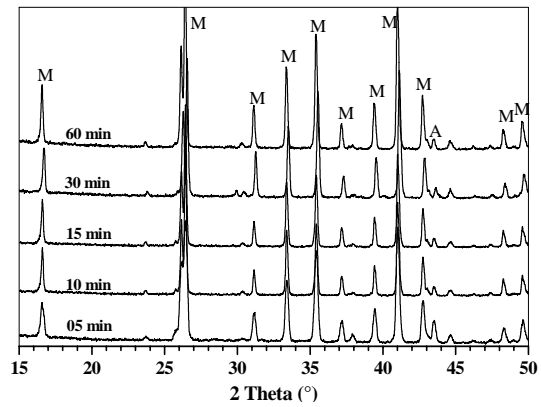

Fig 6. XRD patterns of kaolin-boehmite sample treated at 1600°C for different sintering times. M, Mullite. A, α-Al₂O₃.

Fig. 7 shows the bulk density and relative density of kaolin-boehmite sample sintered at 1600°C for deferent sintering times. The relative density was evaluated on the basis that mullite formation is full and that the theoretical density of mullite is 3.16 g/cm³. The density of samples decreased with the increase of sintering time up to 10 minutes, after that it increased with the increase of sintering time. Also, it can be noticed that the rate of increase decreases with the increase of sintering time until it reach zero at a sintering time of 30 minutes; this shows that this sintering time is enough to reach the highest density of 96%. The increase of density is usually attributed to the elimination of pores during sintering. However, the decrease of density between 05 min and 10 min is due to the existing phases mullite, alumina, and cristobalite; as the time increases, the mullite fraction increases until complete formation at 30 min. Because mullite density is less of about 4% than the density of its components, the density decreases between 05 min and 10 min [19, 24]. Although sintering of mullite powder to high densities normally requires relatively high sintering temperatures because of the low bulk and grain-boundary diffusion coefficients for mullite; a high relative density of 96% was achieved at relatively lower sintering time of 60 min. This density is close to the maximum density of 98% obtained with the addition of 5 wt.% boehmite and pressureless sintering at 1200°C [42]. Fig. 8 shows SEM

micrograph of kaolin-boehmite sample sample sintered for 1 hour at 1600°C. We note a more homogeneous structure with a uniformly distributed porosity. This sample is composed of irregularly and round-shaped large mullite grains. Vickers microhardness of samples containing different percentage of boehmite sintered 1 h at 1600°C is presented in Fig. 9. The increase of boehmite content has increased the hardness of samples. This due to the fact that the increase of boehmite content increases the fraction of remaining Al_2O_3 in sintered samples.
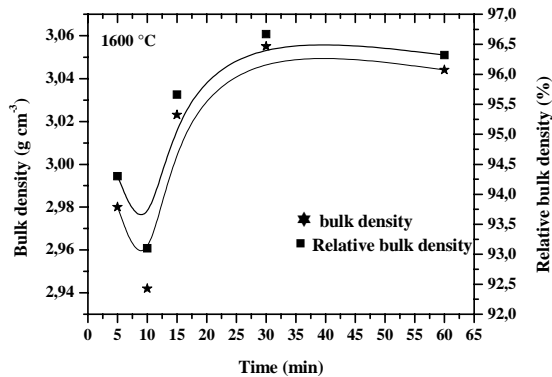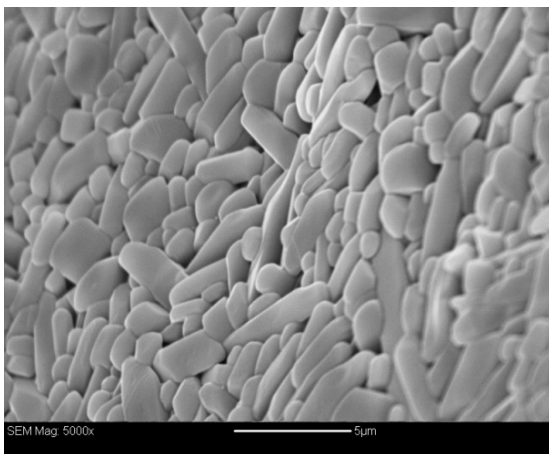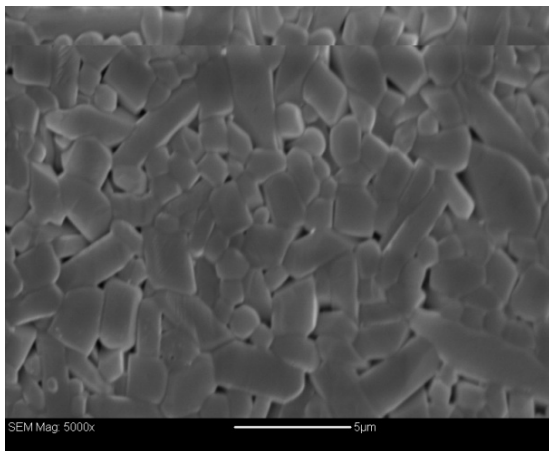

Fig 8. SEM micrographs of kaolin-boehmite sample sintered at 1600°C for 1 hour.
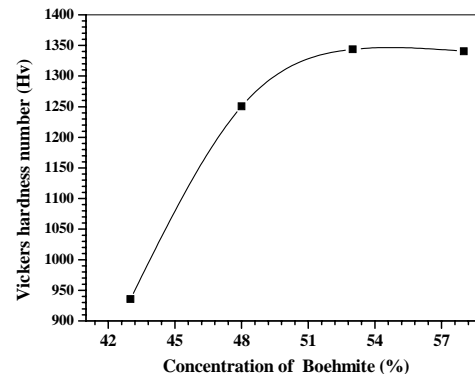
Fig 9. Vickers microhardness as function of boehmite content of samples sintered 1 h at 1600°C.

Fig 7. Density of kaolin-boehmite sample sintered at 1600°C for deferent sintering times.

4. Conclusion

Algerian kaolin and boehmite were suitable raw materials for the synthesis of Al_2O_3 containing mullite through reaction sintering. It was found that; mullite was the major phase present in the sintered samples besides small fraction of Al_2O_3. The increase of sintering temperature and sintering time increased the densification of samples; and a highest relative density of 96 % was achieved at a sintering temperature of 1600°C and a sintering time of 1 hour. Also, the increase of sintering temperature increased mullite fraction and reduced the amount of Al_2O_3. The microhardness of samples increased with the increase of bohemite content.

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