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# $Al_2TiO_5$-Mullite Ceramic Using The Sintering Process

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Aluminum titanate ($Al_2TiO_5$)-mullite ceramics were prepared by a solid-state reaction using natural Algerian raw materials. A mixture of kaolin KT (45 wt.%), potassic feldspar (30 wt.%) and quartz (25 wt.%) was mechanically milled for 6 hours at room temperature in a high-energy planetary ball mill under an argon atmosphere. Various proportions of $TiO_2$ nanoparticles (0, 5, and 10 wt.%) were added to the mixture. The ball-milled powders were compacted into pellets and then sintered for 2 hours at 1200°C with a heating rate of 10°C/min. Microstructural, morphological and physical properties changes during the sintering process were characterized using X-ray diffraction, SEM, and physical property. The main crystalline phases revealed were mullite and quartz. The presence of $TiO_2$ in ceramic samples promotes densification and increases the physical and microstructural properties.

**Index Terms—**About Raw materials, $TiO_2$ addition, $Al_2TiO_5$.

## I. INTRODUCTION

Mullite-based-ceramics are renowned for their remarkable high-temperature chemical and physical properties. In addition to having a low dilatation coefficient, low thermal conductivity, and strong corrosion resistance, they exhibit good creep and thermal shock resistance [1]. Several studies have established the impact of ferrous and non-ferrous metal oxides as dopers on the sintering of porcelains used for electrical purposes. Esmaili et al. [2] noted that various metal oxides, including ZnO, $Cr_2O_3$, $MnO_2$, $Fe_2O_3$, $TiO_2$, and $ZrO_2$, have been examined. The addition of these oxides in small quantities allows (a) lowering the firing temperature, (b) promoting mullite formation, and (c) improving the mechanical strength as a result of reduced porosity.

We are interested in producing porcelain electrical insulators using local raw resources. As shown by Mebrek et al. [3], kaolin formed primarily of kaolinite undergoes successive structural and microstructural changes during its firing. The major crystalline phase and the only intermediate phase in the $Al_2O_3$-$SiO_2$ diagram that is stable under atmospheric pressure is mullite. It is thermally and chemically stable in air and under atmospheric pressure from room to the melting temperature [4]–[5]. Mullite material is used in classic and advanced ceramic applications as demonstrated by Schneider et al. [6].

In this work, titanium oxide was added to form aluminum titanate, one of the most promising ceramics with excellent properties, including low thermal conductivity (0.9-1.5 $Wm^{-1}K^{-1}$), low thermal expansion coefficient ($1.5x10^{-6}\,K^{-1}$), high-temperature resistance (with a melting point of 1860±10°C), low Young's modulus, and excellent corrosion resistance, as reported by Sarkar et al. [7]. These characteristics enable it to be used in the metallurgical and automotive industries as a refractory, structural, and insulating material and a thermal barrier coating that provides corrosion resistance and anti-oxidation under high temperatures. According to the work of Huang et al., Morishima et al., Kim et al. [8]–[10], mullite is a secondary phase that improves mechanical behaviour, especially the mechanical strength of the 1300–1450°C temperature range, which decreases microcracking and grain development in the $Al_2TiO_5$ phase.

## II. MATERIALS AND METHODS

### A. Raw Materials

The raw materials collected from the Algerian natural resources were kaolin clay, potassic feldspar, and quartz. The clays used were Tamazert Kaolin KT1 et KT2 from El-Milia of Jijel. Potassic feldspar was obtained from Annaba's Ain barber, while sand quartz was taken from El-Aouana of Jijel. $TiO_2$ nanoparticles were obtained from BioChem (purity 99%). Earlier research by Harabi et al. [11] determined the chemical composition of Tamazert kaolin KT2, feldspar, and quartz. Analyses show that kaolin KT2 and feldspar have a similar silica contents between 70 wt.% and 73 wt.%, while the $SiO_2$ contents in quartz are 94 wt.% and 2 wt.%, respectively. Alumina values in kaolin and feldspar range between 14 wt.% and 18 wt.%.

### B. Preparation of sample ceramic

The raw materials were sieved and dried at 100°C for 8 hours (Table 1). The powders were milled for 8 h at a rotation speed of 400 rpm in a high-energy planetary ball Fritsch Pulverizette 7 and then compressed into pellets using a uniaxial hydraulic press. The green samples were sintered at 1200°C for 2 hours at a heating rate of 10°C/min using a muffle furnace and air. Different $TiO_2$ proportions (0, 5 and 10 wt.% $TiO_2$) were added to enhance the microstructural and physical properties.

TABLE 1BATCH COMPOSITION OF PORCELAIN SAMPLES.

| Materials (wt.%) | M1 | M1- | M1- |
|---|---|---|---|
| Tamazert Kaolin | 45 | 45 | 45 |
| k-Feldspar | 30 | 30 | 30 |
| Quartz | 25 | 25 | 25 |
| $TiO_2$ | 0 | 5 | 10 |

C. Material characterization

- The microstructural characterization of the samples was performed using XRD on a Rigaku diffractometer with Cuα (λCu = 0.15406 nm) over a range (θ–2θ) and a step size of 0.01°. The lattice parameters (a, b and c), microstrains $<\sigma^2>^{1/2}$, crystallite size <L> and percentage of phases were determined from Rietveld refinement [12] using the material analysis using diffraction program (MAUD) [13].

- The microstructure and elemental composition of the samples were studied with a JEOL JDM-6830 scanning electron microscope coupled with a QUANTA 250-FEI instrument for energy dispersive X-ray analysis.
- The linear shrinkage (L. S. %) and bulk density (B. D) are calculated using the following equations:

$$\text{Linear shrinkage L. S. (\%)} = \frac{D1 - D2}{D2} \times 100 \qquad (1)$$

$$\text{Bulk density B. D. (g/cm}^{-3}) = \frac{M}{V} \qquad (2)$$

$D_1$ is the diameter of the porcelain sample before sintering (cm).
$D_2$ is the diameter of the porcelain sample after sintering (cm).
M is the mass of the porcelain (g).
V is the volume of the porcelain ($cm^{-3}$).

## III. RESULTS AND DISCUSSION

A. XRD analysis

The refinement Rietveld patterns of the samples sintered at 1200°C for two hours without and with $TiO_2$ addition are presented in Fig. 1. All the mixtures contain mullite and quartz phases and are accompanied by the formation of aluminum titanate ($Al_2TiO_5$) with a residual $TiO_2$ phase [14]–[15]. Mullite (ISCD n°: 7105575) crystallizes in an orthorhombic structure, with the Pbam space group and lattice parameters of $a_0$ = 0.7588 nm, $b_0$ = 0.7688 nm, $c_0$ = 0.28895

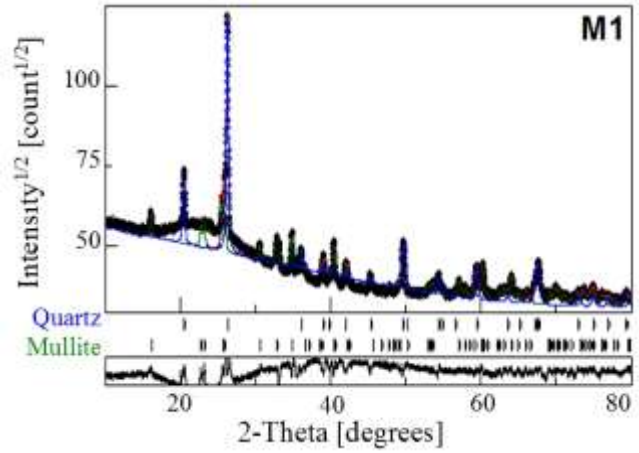
nm and $c_0/a_0$ = 0.38. Quartz (ICSD n°: 1011097) has a trigonal system, lattice parameters ($a_0$ = 0.4913 nm, $c_0$ = 0.5404 nm and $c_0/a_0$ = 1.10) and space group P3121.
According to Guedes-Silva et al. [16], the quantity of rutile ($TiO_2$) remained a residual phase suggesting that it is preferably consumed to form aluminum titanate. Rutile (ICSD n°: 9004144) has a tetragonal structure, space group P42/mnm and lattice parameters of $a_0$ = 0.4623 nm, $c_0$ = 0.2986 nm and $c_0/a_0$ = 0.65. The highest peak intensities of $Al_2TiO_5$ are detected at 2θ=18.56°, 26.28°, 33.30°, 47.22°, 50.42° and 61.82°, similar to the results of Violini et al., [17]. Hassan et al. [18] reported that increasing the calcination temperature to 1200°C allows the formation of the $Al_2TiO_5$ phase. The peak intensity of the $Al_2TiO_5$ phase increases, with increasing calcination temperature to 1300°C, indicating the complete formation of the phase. Aluminum titanate (ICSD n°: 2206495) crystallizes in an orthorhombic system, space group Cmcm and lattice parameters of $a_0$ = 0.3605 nm, $b_0$ = 0.9445 nm, $c_0$ = 0.9653 nm and $c_0/a_0$ = 2.68 [19].

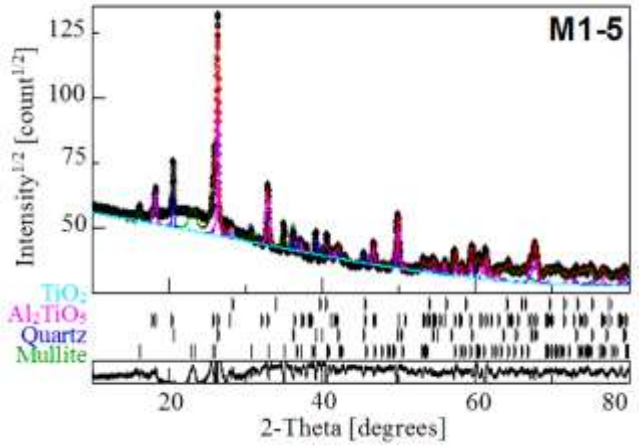
Table 2 summarizes the parameters obtained from Rietveld refinements, such as the phases, crystallite sizes, lattice parameters, relative deviation, microstrains and phase proportions of the porcelain sintered. The volume fraction of mullite without $TiO_2$ addition for mixture M1 is 73.52%, while that of quartz is 26.48%. $TiO_2$ (5 wt.%) leads to decrease in mullite to 66.39%, which continued to progressively decrease with an increase in $TiO_2$ to 10 wt.%, reaching values 37.62%. It is possible to correlate the decrease in the mullite phase with the notable increase in the $Al_2TiO_5$ volume fraction, which increased from 14.24% to 46.03% upon increasing the $TiO_2$ addition from 5 wt.% to 10 wt.%. This subsequently confirms that the presence of $TiO_2$ may favor the production of $Al_2TiO_5$. The average mullite crystallite size is 50 nm without $TiO_2$ addition. It drops considerably to a value of 5 nm when $TiO_2$ is added at 10 wt.%. This can be explained by the broadening of the diffraction peaks with a reduction in their intensity linked to the size of the crystallites at the nanometric scale. The contraction/expansion of the crystal lattice of the raw material powders, which may be measured by the relative deviation of the lattice parameters from those of the perfect crystal, can be related to the preparation procedure.

TABLE 2 PHASES, RELATIVE DEVIATION, CRYSTALLITE SIZE, MICROSTRAINS AND PHASE PROPORTION OF PORCELAIN.

| Mixture | Phase | Δa (%) | Δb (%) | Δc (%) | <L> ±4 (nm) | $<\sigma^2>^{1/2}$ x$10^{-4}$ | Volume fraction (%) |
|---|---|---|---|---|---|---|---|
| M1 | Mullite | 0.14 | 1.01 | 0.67 | 56.92 | 4.07 | 73.52 |
| | Quartz | 1.02 | − | 1.13 | 74.64 | 0.16 | 26.48 |
| M1-5 | Mullite | 0.01 | 0.01 | 0.00 | 16.75 | 0.29 | 66.39 |
| | Quartz | 0.01 | − | 0.00 | 75.89 | 0.25 | 18.12 |
| | $TiO_2$ | −0.04 | − | 0.09 | 90.37 | 0.17 | 1.25 |
| | $Al_2TiO_5$ | −0.01 | 0.02 | 0.02 | 27.68 | 0.36 | 14.24 |
| | Mullite | 0.00 | 0.01 | 0.00 | 4.48 | 0.54 | 37.62 |

| | | | | | | |
|---|---|---|---|---|---|---|
| M1-10 | Quartz | 0.01 | − | 0.00 | 80.08 | 0.20 | 10.59 |
| | $TiO_2$ | 0.06 | − | 0.10 | 96.47 | 1.85 | 5.76 |
| | $Al_2TiO_5$ | 0.00 | 0.01 | 0.01 | 75.71 | 0.13 | 46.03 |



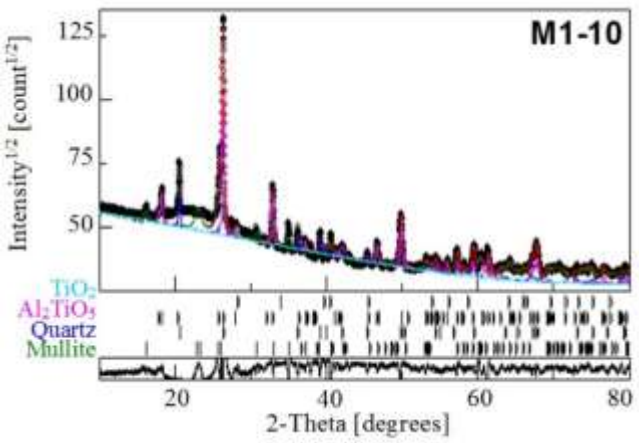
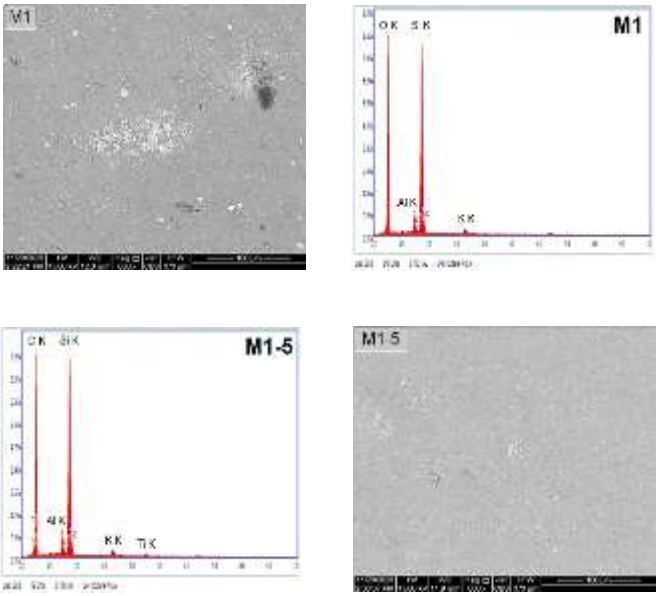



Fig. 1. Rietveld refinement of the mixtures without and with $TiO_2$.

B. SEM observations

Fig. 2 shows the microstructures of the samples sintered without and with $TiO_2$. Many pores were observed in the microstructure of the sintered samples. The high average atom weight in the BSE (backscattered electron) mode shows a bright contrast. The bright gray region reflects the $Al_2TiO_5$ phase, whereas the dark gray region indicates the mullite phase [10, 17]. EDS analysis revealed the presence of the principal element oxygen (O = 75.97 at. %) with silicon (Si = 19.29 at. %) and aluminum (Al = 3.46 at. %).



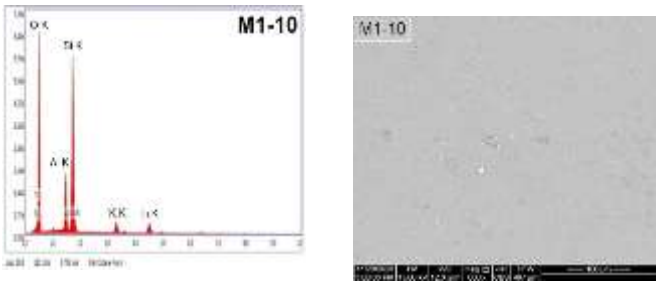



Fig. 2. SEM micrographs and EDS analysis of the mixtures without and with $TiO_2$

C. Bulk density and shrinkage

The density and shrinkage of the samples sintered at 1200°C are shown in Fig. 3. $TiO_2$ addition slightly enhances the bulk density, with a value of 2.33 $cm^{-3}$. The shrinkage increased gradually to 13% then decreased when the addition of $TiO_2$ reached 10 wt. %. As reported by Esmaili et al. [2], the addition of (5) wt.% $TiO_2$ improved the bulk density, which enhanced the mechanical properties.

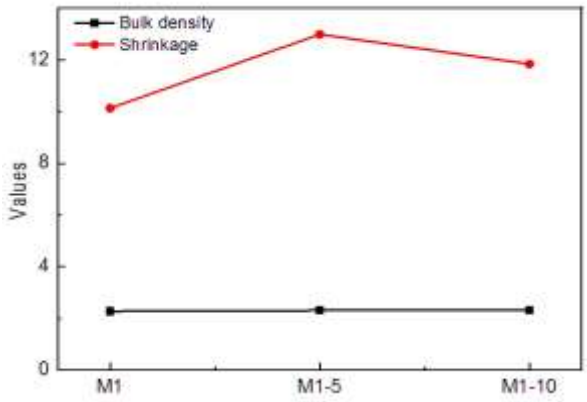



Fig. 3. Bulk density and shrinkage of the mixtures without and with $TiO_2$.

## IV. CONCLUSION

Aluminum titanate ($Al_2TiO_5$)-mullite ceramics were synthesized using sintering from natural Algerian raw materials and $TiO_2$. The phases obtained from the sintered sample were mullite and quartz. The porcelain mixture containing 45 wt. % kaolin KT2, potassic feldspar (30 wt. %), and quartz (25 wt.%) with the addition of $TiO_2$ (10 wt. %) exhibited good properties. The presence of $TiO_2$ promoted densification and increased the physical and microstructural properties of the porcelain sample**.**

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