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Study, with Different Characterization Techniques, of the Formation of Cordierite from both Natural and Activated Algerian DD3 Kaolin

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ABSTRACT

The work presented in this article deals with the synthesis of a cordierite ceramics, using a natural Algerian kaolin named DD3 of black colour, located in the region of Djbel Dbagh in Guelma. A synthesis was also carried out on bleached DD3 kaolin obtained by activation of hydrochloric acid on natural kaolin in order to eliminate the manganese oxide (which is responsible for the blackish colour) while enlarging the application field in industry (e.g. luxury porcelain). Preparation of this cordierite was carried out by adding the precipitated magnesium hydroxide and a silica deficit for each type of kaolin. Mixtures of pellet finely milled and pressed as pelleted powders were sintered at different temperatures (1150º, 1250º and 1350ºC) for 2 h before being characterized. The results obtained by X-ray diffraction showed that the cordierite phase crystallized at 1250ºC for both types of black and bleached samples, which was confirmed by Raman spectroscopy. Scanning electron microscopy was used to observe densification, homogeneity as well as the size of the sample constituents. Their coefficients of thermal expansion were respectively 1.95×10^{-6} and 1.69×10^{-6} ºC^{-1} between 23º and 800ºC, which allowed their use in automobile catalytic converters.

[Keywords: Natural kaolin, Activated kaolin, Cordierite, NMR spectroscopy, Thermal expansion]
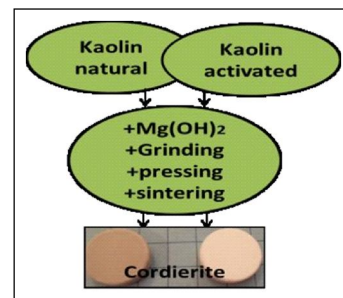
Introduction

Cordierite, $2MgO.2Al_2O_3.5SiO_2$, is a very important natural ceramic material with a stoichiometric composition of 13.7% MgO, 34.9% Al_2O_3 and 51.4% SiO_2.[1, 2] Cordierite is often used in kiln furniture, acoustical insulating panels, high temperature filters, integrated circuits and ceramic substrates. They are used as a support in the conversion of harmful gases emitted by car exhausts such as CO, HC into less harmful elements like CO_2 and H_2O.[3, 4] Such possibility is due to their high resistance to thermal shocks, their low coefficient of thermal expansion (from 2×10^{-6} to 6×10^{-6}.ºC^{-1}), their low dielectric constant, their high chemical durability and their high refractoriness.[5, 6] Several researchers prepared cordierite from raw materials because it is not abundantly present in nature.[7] Cordierite is synthesized from pure oxides or nitrates[8] or from natural raw materials such as kaolin, talc, diatomite, feldspar, sepiolite, andalusite, stevensite, rice husk, silica[9, 10] and from blast furnace slag.[11] In the literature, the synthesis of cordierite is made by several methods such as solid state, co-precipitation reactions, sol-gel and glass crystallization.[12, 13] Researchers are generally oriented towards the sol-gel technique because of its advantages in developing ceramics. Unfortunately, the cost and process of manufacturing ceramics is complicated from the alkoxides.[14]

For technical applications, cordierite is synthesized by the solid state method due to the lower cost of raw materials such as kaolin, which is generally used in the ceramic and refractory materials as high voltage insulators, applicable at high temperatures. In addition, kaolin features stability at high temperatures while containing a high amount in alumina and silica.[15–18]

This work aims to prepare a cordierite ceramics from a natural Algerian kaolin and from an activated kaolin by hydrochloric acid. This is in order to eliminate coexisting impurities, then to compare phase transformations and thermal expansion coefficients. The aim is also to improve the production of this cordierite which is used as substrates in catalytic converters and as refractories in different fields.

## Experimental Procedure
Synthesis Procedure

Chemical compositions of the two kaolins (natural DD3 and bleached DD3) used in this study are shown in Table I.

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Table I : Chemical compositions of two kaolins

Elements	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	ZnO	MnO_2	NiO	Cl
Natural DD3	52.5	41.6	0.15	0.357	0.707	0.05	0.085	0.613	0.14	3.41	0.14	–
Activated DD3	57.0	41.7	0.03	0.295	0.112	0.01	0.076	0.715	0.014	0.01	0.02	0.076

Clay of natural kaolin type DD3 black <20 μm was extracted from Djebel Debbagh in Algeria. Bleached DD3 <20 μm was obtained by activation of black kaolin with 37% HCl. The acid solution became black after 24 h of this activation, suggesting that the manganese was solubilized as chloride. The likely chemical reaction is:

$$MnO + 2HCl \rightarrow MnCl_2 + H_2O \qquad ..(1)$$
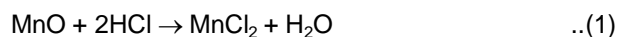
A white deposit was then formed. This deposit was subsequently washed several times until a neutral pH was obtained, then dried completely at 100°C.

Fine particles of $Mg(OH)_2$ were prepared by precipitation of $MgCl_2$ according to the following reaction:

$$MgCl_2.6H_2O + NH_4OH \rightarrow Mg(OH)_2 + NH_4Cl_2 + H_2O \quad ..(2)$$
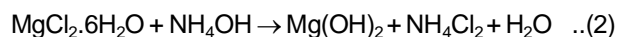
Then, each type of kaolin <20 μm was mixed with $Mg(OH)_2$ and SiO_2 <20 μm. This mixture was synthesized by solid state process to obtain stoichiometric cordierite composition $(2MgO. 2Al_2O_3.5SiO_2)$. In the rest of this article, the mixtures are mentioned as follows:

M1: the mixture of cordierite using 73.41 wt% of natural kaolin DD3, 20.12 wt% of precipitated hydroxide and 6.47 wt% of silica deficiency.

M2: the mixture of cordierite using 75.81 wt% of kaolin DD3 activated by HCl, 20.83 wt% of precipitated hydroxide and 3.35% of silica deficiency.

The obtained mixtures were dry mixed in an alumina ball mill for 3 h using 50% of ball and 40% of the mixture (the remaining 10% represent the vacuum). After drying in an oven at 100°C, the powders were uniaxially pressed at 150 MPa having 13 mm diameter and 40 mm thickness. The pellets were then sintered for 2 h in a furnace under air at 1150°, 1250° and 1350°C with a heating rate of 5°C/min (Fig. 1).
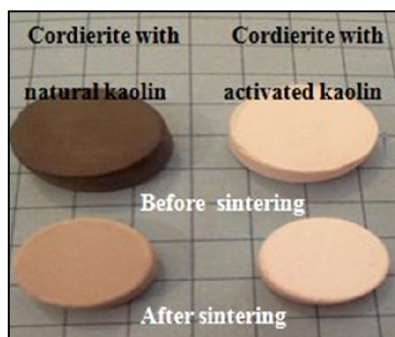

Fig. 1 – Photographs of cordierite pellets

Characterization Techniques

Chemical analyses of the two kaolins were performed using a Rigaku ZSX Primus X-ray fluorescence spectrometer. The particle size analysis of the mixtures was carried out by a laser scattering of type HORIBA LA-960. The powders were dispersed in water and shaken with ultrasound for 1 min and 34 s. Both the mixtures were analyzed by differential scanning calorimetry and thermogravimetry (DSC/TG) (NETZSCH STA 409PC/PG) from room temperature to 1400°C with a heating rate of 5°C/min. XRD crystallographic analysis was carried out using a Bruker D8 Advance (Kα1; λ=1.54060 Å) brand diffractometer. The scanned angular range was between 5° and 60° 2θ. Raman spectroscopic analysis was carried out using a micro-Raman spectrometer (Confocal LabRam HRevolution from Horiba Jobin Yvon) equipped with a UV-325 nm laser source (He-Cd) – 32 mW, featuring ×40 resolution and excellent spectral resolution due to its 800 mm focal length combined with a network of 1800 lines per mm (g.mm⁻¹). The cordierite morphology was determined by a scanning electron microscope (SEM) of type JSM-6360LV. Coefficient of thermal expansion (α) of the sintered ceramics of two mixtures (black and bleached) was measured in the range from room temperature to 800°C with a heating rate of 3°C/min. This was done using a dilatometer of type NETZSCH DIL 402C. Density and porosity of the sintered pellets were determined by the method of Archimedes. The setup described above allowed to obtain the results that are presented and discussed in the next section.

Results and Discussion
Particle Size Analysis

The two prepared mixtures of cordierite ceramic powder (M1 and M2) were first finely milled for 3 h and characterized by laser granulometry. Particle size distributions of the two mixtures M1 and M2, shown in Figs. 2a and 2b, respectively, are relatively broad and show particle sizes ranging between 0.01 and 1000 μm. The mixture M1 shows a monodal distribution with only a maximum point, whose average size is 11.84 μm and median diameter (D_{50}) is 10.37 μm. This indicates agglomeration of the particles. For M2, the mixture has a bimodal distribution. The average size and median diameter are 40.01 and 17.36 μm, respectively. These two results show that the particle sizes of M1 are smaller than M2. This may be due to the activation of DD3 kaolin by hydrochloric acid.
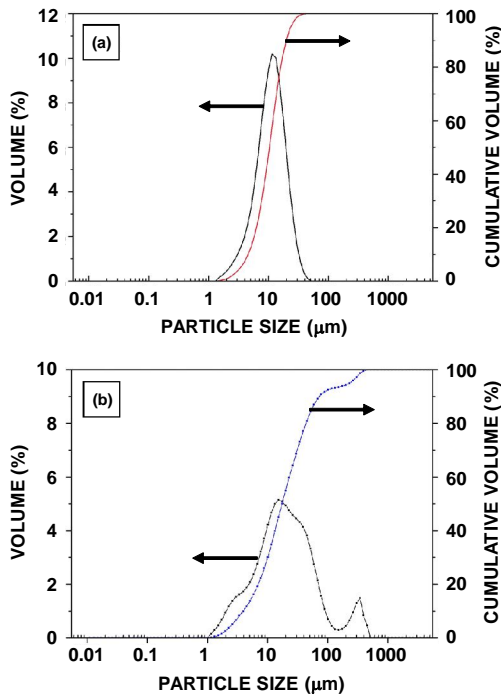
Fig. 2 – Particle size distribution of: (a) M1 cordierite mixture, and (b) M2 cordierite mixture

DSC/TG Analysis

The DSC/TG analyses of the two cordierite mixtures (M1, M2) are shown in Fig. 3. The DSC (Fig. 3a) for the black colour mixture M1 shows five peaks: the first endothermic peak is in the vicinity of 90.7^{o}C, which is caused by the evaporation of adsorbed water; the second endothermic peak is at 391.1^{o}C and corresponds to the
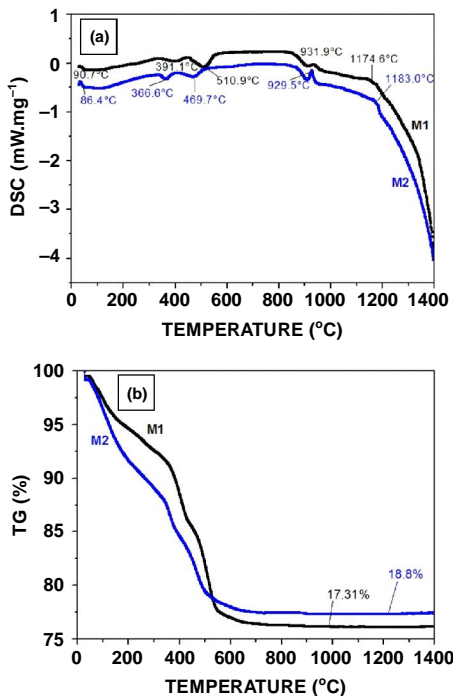

Fig. 3 – (a) DSC and (b) TG of the cordierite mixtures M1 and M2

dehydroxylation of magnesium hydroxide; the third endothermic peak observed at 510.9^{o}C corresponds to the dehydroxylation of kaolinite; the fourth exothermic peak at 931.9^{o}C indicates the crystallization of μ cordierite; the fifth exothermic peak observed at 1174.6^{o}C corresponds to the transformation from μ to α cordierite or indialite (this is in agreement with the work of Kobayashi et al.[19]).

For the second bleached colour mixture M2 (Fig. 3a), phenomena similar to M1 occurs during heating. However, the onset of crystallization of μ-cordierite differs for M1 and M2 (931.9^{o} and 929.5^{o}C for M1 and M2, respectively). This phase, which crystallizes at 929.5^{o}C with a clearer exothermic peak, implies that the M2 mixture contains less oxides and impurities due to the activation of kaolin by hydrochloric acid. At 1183.0^{o}C, it is the transformation of μ-cordierite into α-cordierite.

Mixtures M1 and M2 show mass losses of 17.31% and 18.8% (Fig. 3b), respectively. From these different observations, it can be deduced that the synthesis of cordierite is clear and possible for both types of mixtures.

X-ray Diffraction Analysis (XRD)

XRD patterns of M1 and M2 samples obtained after sintering at different temperatures are shown in Figs. 4a and 4b, respectively. At 1150°C, the diffractogram corresponds to the α-cordierite phase, with the presence of sapphirine for both types of samples M1 and M2. Shu et al.[14] explained this result as a consequence of the
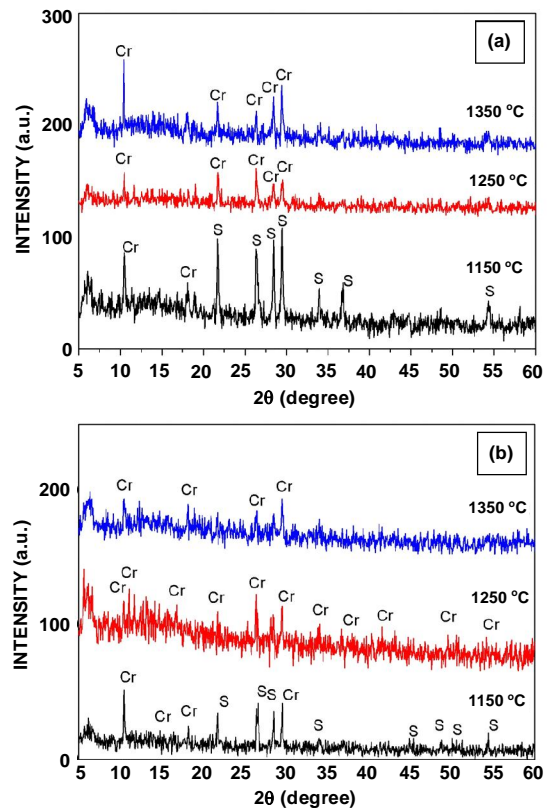

Fig. 4 – XRD patterns of: (a) M1 pellets, and (b) M2 pellets treated for 2 h at 1150°C, 1250°C and 1350°C (Cr: α-cordierite, S: Sapphirine)

formation of sapphirine, $Mg_4Al_4(Al_4Si_2)O_{20}$, that probably results from the reaction between crystalline cristobalite and the intermediate phase (spinel). The sintering temperature was increased in order to ensure that there is no other phase co-existing with the cordierite α. At 1250°C, α-cordierite becomes the major phase and sapphirine disappears for M1 (Fig. 4a) and M2 (Fig. 4b). α-cordierite is formed by the reaction between sapphirine and residual amorphous silicate.[14] According to Xingrong et al.[11], as the temperature increases, magnesium oxide reacts with SiO_2, sapphirine and amorphous aluminium to form α-cordierite. At 1350°C, all peaks of the M1 samples (Fig. 4a) correspond to α-cordierite. For M2 (Fig. 4b), a small amount of α-cordierite was detected; it is certainly due to the appearance of a vitreous phase.

Raman Spectroscopy

Figures 5a and 5b show nuclear magnetic resonance (NMR) spectra of the black densified (M1) and bleached (M2) pellets, respectively, sintered for 2 h at 1150°, 1250° and 1350°C. For M1 and M2 sintered at 1150°C, peaks are observed at 253.462 cm^{-1} (Fig. 5a) and 256.461 cm^{-1} (Fig. 5b), respectively, and are attributed to sapphirine. Other peaks of both the mixtures are characterized by cordierite. At 1250° and 1350°C, intense peaks appear at 257, 367, 564, 669, 973, 1014 and 1190 cm^{-1} for black mixture samples and at 256, 369, 563, 676, 976, 1102 and 1191 c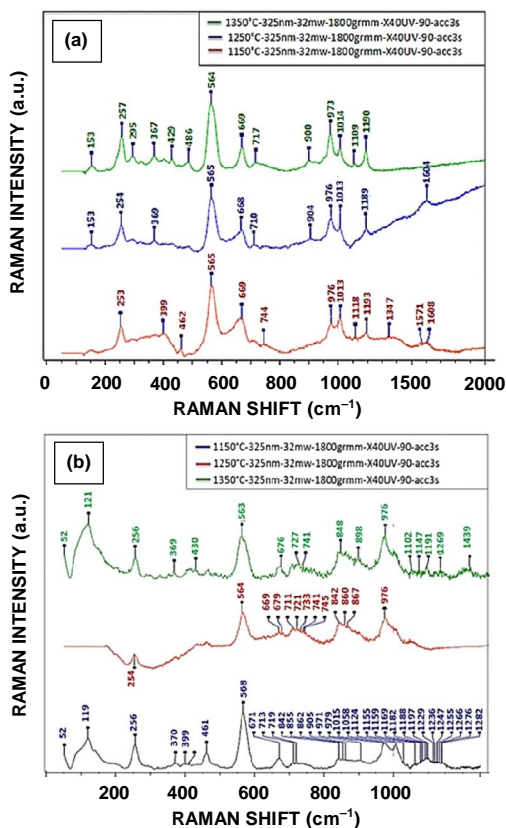m^{-1} for the bleached mixture samples. All these peaks of M1 and M2 correspond to the cordierite phase. These results confirm that the total formation of cordierite is at 1250°C and 1350°C for M2 and M1, respectively. This is possible due to raw reactive materials. Phuc et al.[20] used Raman spectroscopy and Raman mapping to study the formation of cordierite from stoichiometric oxides. They proved that the formation of cordierite was rather favoured for the sintered samples at 1400°C for 2 h by a reaction between alumina and magnesium silicate than by that between silica and spinel. The obtained results of the present experiment have been enhanced as shown in Figs. 5a and 5b.

SEM Observation

In order to perform these observations, pellets of the two blends (black and bleached) were finely polished, then coated with 5 nm layer of gold-palladium using a SEM metallizer of type Cressington 108 sputter coaters. Figure 6 shows different morphologies of the samples observed at different temperatures for 2 h. For the pellets of mixture M1 sintered at 1150°C (Fig. 6a), the grains are dispersed in a heterogeneous manner with a beginning of cordierite nucleation, which can be confirmed by the results obtained with XRD and NMR. At 1250°C, the sample has a homogeneous microstructure with a uniform grain distribution (Fig. 6b), indicating the formation of a dense cordierite ceramics. Such a structure was observed by Bejjaoui et al.[9] where the morphology and formation of dense cordierite at 1250°C was confirmed from both the Moroccans stevensite and andalusite. At 1350°C (Fig. 6c), presence of pores of different sizes (47.29, 50 and 70.5
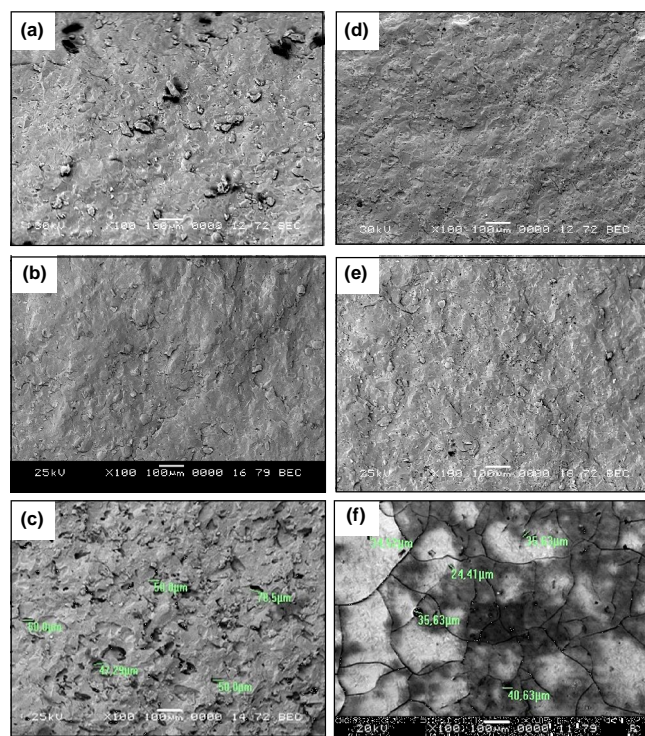

Fig. 5 – Raman spectra of: (a) M1 pellets, and (b) M2 pellets sintered at different temperatures

Fig. 6 – SEM images of M1 and M2 pellets sintered at: (a, d) 1150°C, (b, e) 1250°C, and (c, f) 1350°C

µm) in the structure of cordierite is observed. For pellets of the M2 mixture sintered at 1150°C (Fig. 6d) and 1250°C (Fig. 6e), results similar to the M1 samples have been obtained, while, for pellets of M2 sintered at 1350°C (Fig. 6f), the presence of microcracks and some white areas on the surface of the cordierite indicates that the cordierite phase begins to vitrify from this temperature. There is also appearance of some pores of different sizes varying between 24.41 and 40.36 µm. These results were confirmed by Wang et al.[21] The black areas represent the cordierite phase while the white ones correspond to the vitreous phases.

Thermal Expansion Coefficients of Cordierite Ceramics

Figure 7 and Table II show the thermal expansion coefficients (TEC) of the cordierite ceramics M1 and M2 sintered at different temperatures (1150°, 1250° and 1350°C) for 2 h. TECs were measured from 23° to 800°C.

As shown in Fig. 7a, the TEC of cordierite sample M1 decreases with increasing sintering temperature ($2.83 \times 10^{-6}.°C^{-1}$ at 1150°C to $1.95 \times 10^{-6}.°C^{-1}$ at 1350°C; Table II), which is comparable with the data (($1-2 \times 10^{-6}.°C^{-1}$) between 20° and 800°C) of cordierite.[22] TEC values decrease with increasing α-cordierite content, which has also been confirmed by Kobayashi et al.[19] For M2, the obtained results (Fig. 7b) show that the lowest TEC is that of the sample sintered at 1250°C ($1.69 \times 10^{-6}.°C^{-1}$; Table II), which is due to the reduction of impurities such as MnO_2, Fe_2O_3, ZnO and Na_2O. This indicates that the presence of impurities in

Fig. 7 – Coefficient of thermal expansion of sintered pellets: (a) M1, and (b) M2

Table II : Thermal expansion coefficients (TEC's) of the cordierite samples after sintering at various temperatures for 2 h

Sintering temperature (°C)	TEC ($23°-800°C) \times 10^{-6}.°C^{-1}$ of sample	
	Black cordierite (M1)	White cordierite (M2)
1150	2.83	1.97
1250	2.16	1.69
1350	1.95	2.25

the clay influences the TEC.[23] At 1350°C, the TEC increases to $2.25 \times 10^{-6}.°C^{-1}$ due to decrease in the crystallization rate of the cordierite phase and beginning of the formation of a vitreous phase. These results agree with those of Wang et al.[21] that a small amount of vitreous phase increases the TEC to some extent. Among the works dealing with the TEC of dense cordierite ceramics, Sembiring et al.[24] found a TEC value of $3.3 \times 10^{-6}.°C^{-1}$ of a sintered cordierite sample at 1350°C using amorphous rice husk silica. They explained that such decrease is due to the decrease of the amount of both spinel and cristobalite. In an another study, Bejjaoui et al.[9] found that the TEC of cordierite prepared from Morrocan stevensite and andalusite was $5.3 \times 10^{-6}.K^{-1}$ at 25°-1300°C.

Figures 7a and 7b show that the obtained TEC values are lower than those given in the literature, which is an enhancement of the previous related works.

Apparent Density and Porosity

Bulk density and porosity values of pellets sintered at 1250° and 1350°C for 2 h are presented in Table III. The obtained values show that the apparent density of sintered M1 pellets at 1250°C is 2.586 g.cm^{-3}, which means good densification. Also these pellets have fewer pores (1.83%) than those of M2 which are less dense (2.483 g.cm^{-3}) and more porous (4.98%). This may be due to the fineness of the black colour mixture (M1) particles compared to the bleached colour mixture (M2). With the increase of temperature to 1350°C, a decrease in the density is noticed for both the mixtures (M1 and M2) which become 2.539 and 2.343 g.cm^{-3}, respectively, with a slight decrease of the porosity. This means that the sintered cordierite ceramic pellets at 1350°C begin to vitrify. According to the literature, many researchers have studied dense cordierite.

Table III : Sintering Characteristics of specimens fired at 1250°-1350°C for 2 h

Temperature (°C)	Sample	Bulk density (g.cm^{-3})	Apparent porosity (%)
1250	M$_1$	2.586	1.83
	M$_2$	2.483	4.98
1350	M$_1$	2.539	1.81
	M$_2$	2.343	3.26
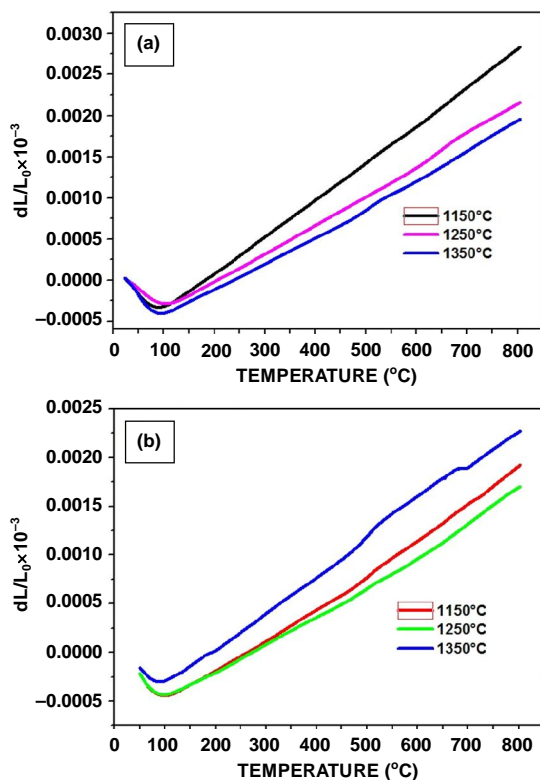
Tunç and Demirkiran[25] showed that the density of cordierite ceramics obtained from a mixture of zeolite, MgO and Al_2O_3 sintered at 1250°C for 0.5 h was 2.583 g.cm^{-3} and the density of the samples treated for 2 h was 2.525 g.cm^{-3}. They explained that the reason for this decrease in density was due to the increase in the content of the vitreous phase. Redaoui *et al.*[26] reported a density of 2.50 g.cm^{-3} for cordierite ceramics obtained for samples prepared from kaolnite and magnesia sintered at 1250°C for 2 h. In this regard, the density of ceramics of the sintered M1 samples at 1250°C obtained in this work is improved while it is close to the theoretical value of the cordierite which is 2.6 g.cm^{-3}.[25]

Conclusions

In the present study, the cordierite ceramics was prepared using natural Algerian DD3 kaolin (M1) and a hydrochloric acid activated kaolin (M2). The results are summarized as follows:

- The cordierite phase begins to crystallize at 1150°C for both types of samples. It is favoured at 1350°C for M1 and 1250°C for M2. The TEC of cordierite M1 which is sintered at 1350°C is 1.95×10^{-6}.^{o}C^{-1} while that of M2 is 1.69×10^{-6}.^{o}C^{-1} for the cordierite sintered at 1250°C. This value is the lowest, due to the removal of impurities from the kaolin. To the best of our knowledge, this is the first time to obtain the lowest TEC using activated kaolin.

- The lowest density of 2.343 g.cm^{-3} is obtained for the activated sample sintered at 1350°C, whereas the highest value of 2.586 g.cm^{-3} is obtained for the non-activated sample.

- Cordierite ceramics obtained from both natural and activated kaolin can be used in the manufacture of automotive catalytic converters.

Due to the absence of impurities in the activated kaolin and its bleached colour, ongoing studies are focusing on applications targeting both paper and luxury porcelain manufacture.

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