

# Effect of B<sub>2</sub>O<sub>3</sub> on Phase Transformation of Cordierite Synthesized from Algerian Kaolin and MgO

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In this study mixtures of Algerian kaolinite (kaolin Tamazarte (KT) and kaolin of Djebel Debbagh (DD1)) with magnesium oxide with and without boron oxide B<sub>2</sub>O<sub>3</sub> additive were investigated in order to obtain a dense cordierite also called indialite. The addition of B<sub>2</sub>O<sub>3</sub> has promoted the formation of  $\alpha$ -cordierite either by crystallization of the residual glass or by transformation of  $\mu$ -cordierite. The differential thermal analysis and thermogravimetric analysis experiments were carried out on ceramic samples in the temperature range between room temperature and 1300 °C at different heating rates. In order to determine the phases and their transformations in cordierite powders treated at different temperatures between 900 and 1300 °C with steps of 50 °C the X-ray diffraction analysis was used.

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## 1. Introduction

Cordierite (2MgO·2Al<sub>2</sub>O<sub>3</sub>·5SiO<sub>2</sub>) is the main phase of the ternary system MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>, along with mullite, enstatite, cristobalite, sapphirine, tridymite, forsterite, etc. [1]. Cordierite ceramics have been widely studied in recent years owing to their unique properties suitable for various industrial applications. It is characterized by extremely low dielectric constant and loss, high resistivity, low coefficient of thermal expansion, excellent thermal shock resistance, low density, stability at high temperature, good chemical stability and excellent insulation properties [1–13].

In view of these properties it is widely used for substrates in multilayer packaging and low temperature co-fire ceramic, for high frequency transportation, high speed applications, sound insulating boards, filters for separating solids from fluids, as substrate material for catalytic converters, kiln furniture, and thermal insulation materials requiring controlled porosity. It is also used for decades in various fields, ranging from substrate materials in microelectronic packaging industry to cookware, heat exchangers and, more recently in glazes for floor tiles [1–3, 5, 8, 9, 12, and 14].

Cordierite powders are easily synthesized by two major ways, either through the solid state reaction of stoichiometric amounts of oxides of magnesium, aluminum and silicon or through the recrystallization of molten glasses with a nominal composition of cordierite at high melting temperatures of around 1600 °C [1, 14].

Cordierite ceramics can be also fabricated through some specialized methods such as sol-gel and crystalliza-

tion of melt-derived glass. However in these routes, the starting materials are expensive and the production processes are difficult [5].

In order to synthesize the cordierite phase by solid state reaction, the mixtures of materials are generally submitted to thermal treatments between 1250 and 1350 °C. To lower the sintering temperature of cordierite ceramics and to increase the phase-transformation kinetics, B<sub>2</sub>O<sub>3</sub> was used as an additive [3–6, 14–16]. Boron oxide B<sub>2</sub>O<sub>3</sub> has some benefits compared to the other sintering aids due to its low melting point and less harmful effect on the insulating characteristics [5].

The objective of the present research was to produce cordierite ceramics from cheaper raw materials such as kaolin (kaolin Tamazarte (KT) and kaolin of Djebel Debbagh (DD1)) and also to add boron oxide to the mixture containing kaolin and magnesium oxide to study its effects on the sintering behavior and properties of cordierite ceramics.

Chemical composition of the minerals, TABLE I measured using XRF analysis (wt.%).

	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Na <sub>2</sub> O	SO <sub>3</sub>	K <sub>2</sub> O	MgO
KT	19.29	69.86	0.13	0.03	2.67	0.4
DD1	39.13	45.30	0.04	–	0.21	0.05
	CaO	MnO	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	rest	
KT	0.4	–	0.72	0.4	6.31	
DD1	0.15	0.02	0.07	–	14	

## 2. Materials and methods

The basic raw materials employed for the preparation of cordierite with the formula of 2MgO·2Al<sub>2</sub>O<sub>3</sub>·5SiO<sub>2</sub> were kaolin (kaolin Tamazarte KT (from Jijel, Algeria) and kaolin of DD1) (from Djebel Debbagh, Guelma, Algeria), synthetic powders of magnesium oxide MgO and

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boron oxide  $B_2O_3$ . Chemical compositions of the studied kaolin, determined by XRF analysis are shown in Table I.

Boron oxide was added to 60 g of  $2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$  compositions with weight ratios of 59 wt.% DD1, 29 wt.% KT and 12 wt.% MgO. The batch compositions of the cordierite ceramics with different additive of boric oxide are given in Table II.

Batch compositions of cordierite ceramics with varied concentration of  $B_2O_3$ . TABLE II

Sample code	DD1 [g]	KT [g]	MgO [g]	$B_2O_3$ [g]
Cor+00 wt.% B	35.42	17.23	7.30	—
Cor+02 wt.% B	35.42	17.23	7.30	1.09
Cor+04 wt.% B	35.42	17.23	7.30	2.27
Cor+08 wt.% B	35.42	17.23	7.30	4.64

Raw material used for batch preparation were milled in a planetary ball mill using zirconia balls (15 mm in diameter) with ethanol as solvent for 5 h at a speed of  $250 \text{ revmin}^{-1}$ . The slurry was dried at  $150^\circ\text{C}$  for 24 h and then was crushed manually.

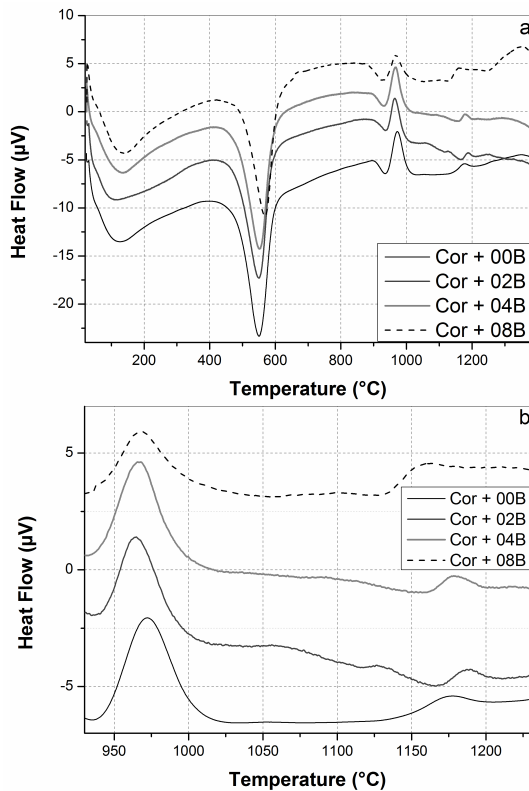


Fig. 1. (a): DTA curves of cordierite powder with  $B_2O_3$  additive heated at  $20^\circ\text{Cmin}^{-1}$ , (b): DTA curves of cordierite powder with 0, 2, 4 and 8 wt.% of  $B_2O_3$  in temperature range of  $900\text{--}1250^\circ\text{C}$  heated at  $20^\circ\text{Cmin}^{-1}$ .

The analysis of batch preparation was performed using analytical techniques of thermogravimetric analysis (TG) and differential thermal analysis (DTA), using

TG-DTA instruments (Setaram Labsys Evo TG-DTA  $1600^\circ\text{C}$  equipment) at heating rates of 10, 20, 30, 40 and  $50^\circ\text{Cmin}^{-1}$  under flow of argon gas of  $40 \text{ cm}^3 \text{ min}^{-1}$ . The crystalline phases precipitated in the parent powder were investigated using diffractometer system (XPERT-Pro) with  $\text{Cu-K}\alpha$  radiation with the wavelength of  $0.15418 \text{ nm}$ .

### 3. Results and discussion

Figure 1a shows the DTA curves of batch preparations (Cor 00, 02, 04 and 08 wt.% of  $B_2O_3$ ) heated from room temperature to  $1250^\circ\text{C}$  with heating rate of  $20^\circ\text{Cmin}^{-1}$ . As a reference was used the sample of  $\alpha$ -alumina with the same dimensions.

Two series of endothermic peaks at  $130^\circ\text{C}$  and  $560^\circ\text{C}$  and two series of exothermic peaks at  $960^\circ\text{C}$  are present. The first series of endothermic peaks in the temperature range of  $100\text{--}200^\circ\text{C}$  is attributed to humidity evaporation and dehydroxylation of kaolin to kaolinite.

The second series, which can be detected in the range of  $450\text{--}600^\circ\text{C}$ , corresponds to the dehydroxylation of kaolinite and the formation of metakaolinite. On the high temperature side on the DTA curve, as shown Fig. 1b, in temperature range from  $900^\circ\text{C}$  to  $1100^\circ\text{C}$  a series of exothermic peaks reveals the formation of mullite phase. Another series of exothermic peaks, which start from  $1100^\circ\text{C}$  and continue to  $1250^\circ\text{C}$  are due to the formation of  $\alpha$ -cordierite.

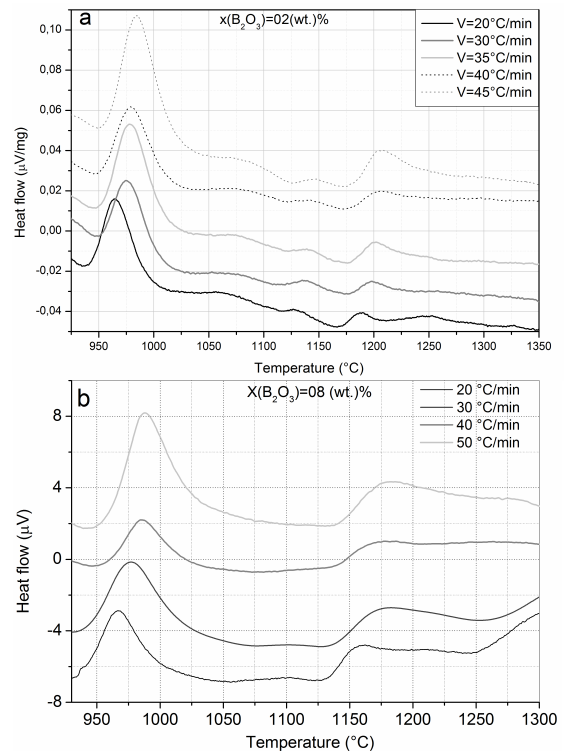


Fig. 2. DTA curves of cordierite powder with 2 wt.% (a) and 8 wt.% of  $B_2O_3$  (b), heated at different heating rates.

Figure 2a and b presents the DTA curves of batch preparations of cordierite powder with 2 wt.% of B<sub>2</sub>O<sub>3</sub> and cordierite powder with 8 wt.% of B<sub>2</sub>O<sub>3</sub>, respectively, heated at various heating rates. Two series of exothermic peaks are observed clearly. The first exothermic peak in the temperature range of 950–1050 °C is due to the formation of mullite phase. This peak gradually shifts to higher temperatures when the heating rate is increased.

Within the range of 1200–1250 °C, a series of exothermic effects were detected due to the formation of  $\alpha$ -cordierite. The curve shows clearly that the increase of heating rate from 20 to 45 °Cmin<sup>-1</sup> or from 20 to 50 °Cmin<sup>-1</sup> shifts the temperature of the maximum of the exothermic peak position to higher temperature from 1216 °C to 1245 °C.

Figure 3 reveals the XRD pattern curves of Cor+04 wt.% B<sub>2</sub>O<sub>3</sub> and Cor+08 wt.% B<sub>2</sub>O<sub>3</sub> powders heat treated under different temperatures from 900 to 1250 °C in steps of 50 °C for 2 h. The following crystalline phases were determined: magnesium silicate (PDF#01-089-1625), enstatite (PDF#96-901-0242),

sapphirine (PDF#96-901-3490), mullite (PDF#96-900-1568), cristobalite (PDF#96-900-8230),  $\mu$ -cordierite (PDF#96-900-5807) and  $\alpha$ -cordierite (also known as indialite) (PDF#96-900-6272). Table III shows the results of the XRD analysis and the difference in crystalline phases between Cor+00 wt.% B<sub>2</sub>O<sub>3</sub> and Cor+08 wt.% B<sub>2</sub>O<sub>3</sub>.

TABLE III

XRD results for the different crystalline phases (A: magnesium silicate, E: enstatite, M: mullite, S: sapphirine, C: cristobalite,  $\mu$ :  $\mu$ -cordierite and  $\alpha$ :  $\alpha$ -cordierite).

Sample code	900 °C	950 °C	1000 °C	1050 °C
Cor+00%B <sub>2</sub> O <sub>3</sub>	E+A	E+A	E+A+M	E+M+A
Cor+08%B <sub>2</sub> O <sub>3</sub>	E+A+M	E+M+A	S+E+ $\alpha$	S+E+ $\alpha$
	1100 °C	1150 °C	1200 °C	1250 °C
Cor+00%B <sub>2</sub> O <sub>3</sub>	E+M+S	C+S+ $\mu$ + $\alpha$	C+S+ $\mu$ + $\alpha$	$\alpha$
Cor+08%B <sub>2</sub> O <sub>3</sub>	S+C+ $\alpha$	C+ $\alpha$	$\alpha$	$\alpha$

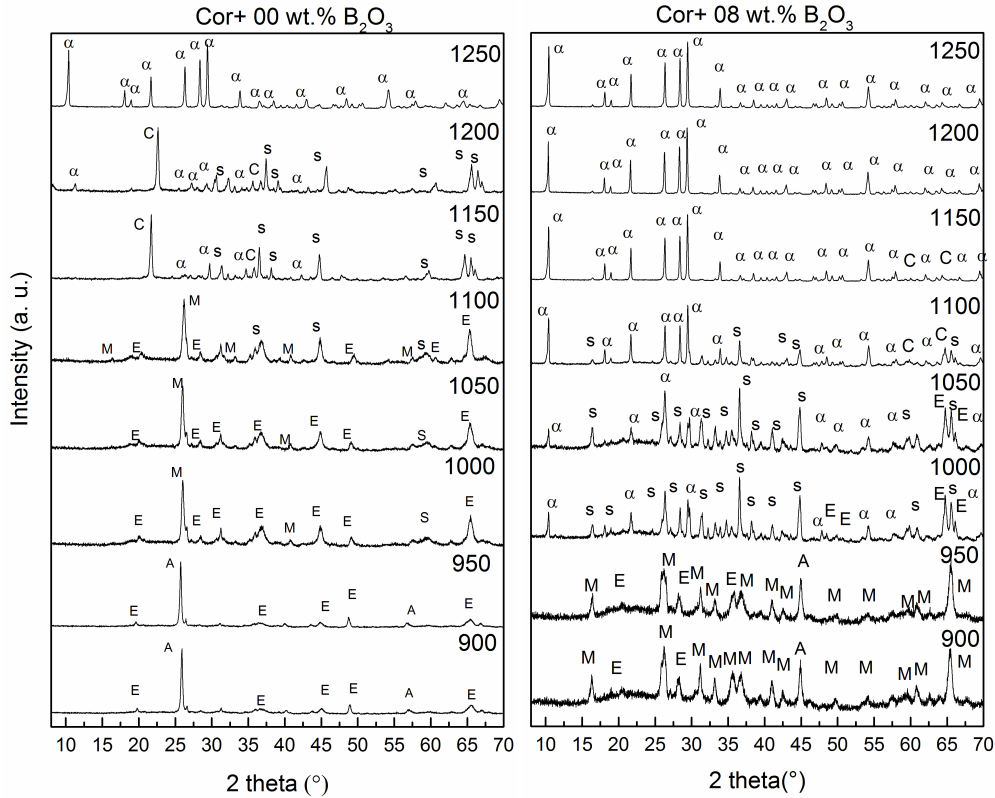


Fig. 3. XRD patterns of cordierite with 0 and 8 wt.% of B<sub>2</sub>O<sub>3</sub> treated at different temperatures (A: magnesium silicate, E: enstatite, M: mullite, S: sapphirine, C: cristobalite,  $\mu$ :  $\mu$ -cordierite and  $\alpha$ :  $\alpha$ -cordierite).

Figure 4 shows the plot of  $\ln[\varphi/T_p^2]$  versus temperature for various studied concentrations of B<sub>2</sub>O<sub>3</sub> (wt.%). The values of activation energies of cordierite powder with different concentrations of B<sub>2</sub>O<sub>3</sub> can be calculated from these curves by Kissinger method based on

Eq. (1) [17, 18]:

$$\ln\left(\frac{\varphi}{T_p^2}\right) = -\frac{E_A}{RT_p} + C_1. \quad (1)$$

Here  $C_1$  is a constants,  $\varphi$  is the heating rate,  $E_A$  is the activation energy,  $T_p$  is the absolute peak temperature in

DTA curves and  $R$  is the ideal gas constant. This values increase with the increasing temperature.

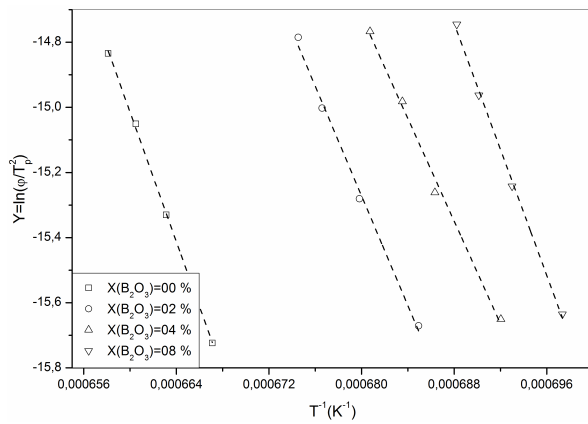


Fig. 4. Plot of  $\ln[\varphi/T_p^2]$  versus inverse temperature for various concentrations of  $B_2O_3$  additive (wt.%).

Figure 5 illustrates the calculated activation energy as a function of concentration of the  $B_2O_3$  additive (wt.%). It can be seen that the activation energies of the crystallization depend strongly on the amount of additive used. The activation energies of samples with 0 wt.%, 2 wt.%, 4 wt.% and 8 wt.% of  $B_2O_3$  were determined to be 830, 700, 650 and 800  $\text{kJmol}^{-1}$ , respectively [16].

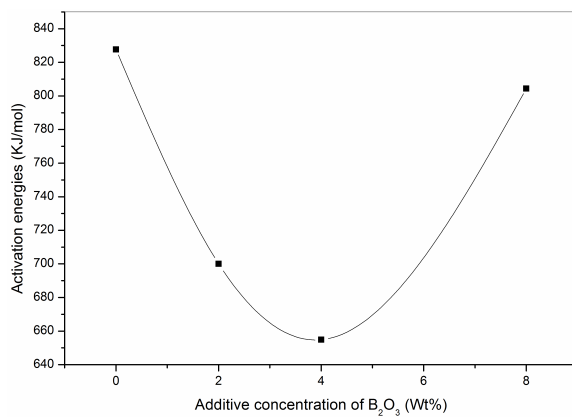


Fig. 5. The activation energy of crystallization as a function of concentration of  $B_2O_3$  additive.

#### 4. Conclusions

In this study, cordierite ceramics was produced using the Algerian raw kaolinite (KT, DD1) and the synthesized magnesium oxide  $MgO$  with different additive concentrations of boron oxide  $B_2O_3$ . In order to control the crystallization and to decrease the sintering temperature of cordierite,  $B_2O_3$  was added to stoichiometric cordierite. Results show that the addition of  $B_2O_3$  to pure cordierite lowers the sintering temperature, retards

the crystallization from amorphous to  $\mu$ -cordierite and accelerated the crystallization of  $\alpha$ -cordierite.

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