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Effect of B_2O_3 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_2O_3 additive were investigated in order to obtain a dense cordierite also called indialite. The addition of B_2O_3 has promoted the formation of α-cordierite either by crystallization of the residual glass or by transformation of μ-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 ($2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$) is the main phase of the ternary system $MgO\text{-}Al_2O_3\text{-}SiO_2$, 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 cofire 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 crystallization 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_2O_3 was used as an additive [3–6, 14–16]. Boron oxide B_2O_3 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.

TABLE I

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

	Al_2O_3	SiO_2	Na_2O	SO_3	K_2O	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_2O_3	TiO_2	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 $2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$) 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 rev min^{-1}. The slurry was dried at 150 °C for 24 h and then was crushed manually.

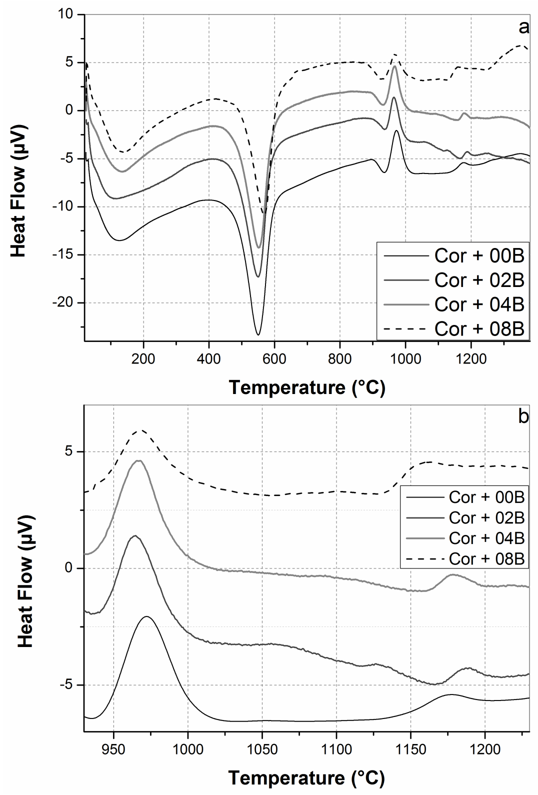

Fig. 1. (a): DTA curves of cordierite powder with B_2O_3 additive heated at 20 °C min^{-1}, (b): DTA curves of cordierite powder with 0, 2, 4 and 8 wt.% of B_2O_3 in temperature range of 900–1250 °C heated at 20 °C min^{-1}.

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 °C equipment) at heating rates of 10, 20, 30, 40 and 50 °C min^{-1} under flow of argon gas of 40 cm^3 min^{-1}. The crystalline phases precipitated in the parent powder were investigated using diffractometer system (XPERT-Pro) with Cu-K$_\alpha$ radiation with the wavelength of 0.15418 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 °C with heating rate of 20 °C min^{-1}. As a reference was used the sample of α-alumina with the same dimensions.

Two series of endothermic peaks at 130 °C and 560 °C and two series of exothermic peaks at 960 °C are present. The first series of endothermic peaks in the temperature range of 100–200 °C is attributed to humidity evaporation and dehydroxylation of kaolin to kaolinite.

The second series, which can be detected in the range of 450–600 °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 °C to 1100 °C a series of exothermic peaks reveals the formation of mullite phase. Another series of exothermic peaks, which start from 1100 °C and continue to 1250 °C are due to the formation of α-cordierite.

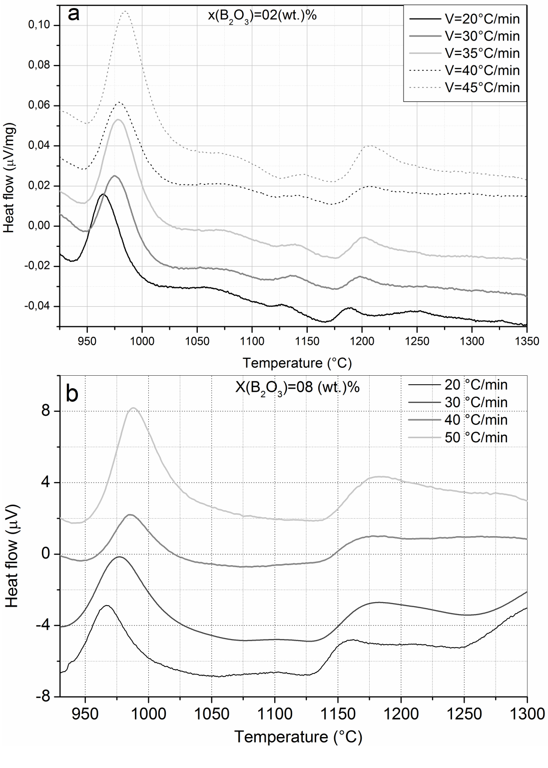

Fig. 2. DTA curves of cordierite powder with 2 wt.% (a) and 8 wt.% of B_2O_3 (b), heated at different heating rates.

Figure 2a and b presents the DTA curves of batch preparations of cordierite powder with 2 wt.% of B_2O_3 and cordierite powder with 8 wt.% of B_2O_3, 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 α-cordierite. The curve shows clearly that the increase of heating rate from 20 to 45 °C min^{-1} or from 20 to 50 °C min^{-1} 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_2O_3 and Cor+08 wt.% B_2O_3 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), μ-cordierite (PDF#96-900-5807) and α-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_2O_3 and Cor+08 wt.% B_2O_3.

TABLE III

XRD results for the different crystalline phases (A: magnesium silicate, E: enstatite, M: mullite, S: sapphirine, C: cristobalit, μ: μ-cordierite and α: α-cordierite).

Sample code	900 °C	950 °C	1000 °C	1050 °C
Cor+00%B_2O_3	E+A	E+A	E+A+M	E+M+A
Cor+08%B_2O_3	E+A+M	E+M+A	S+E+α	S+E+α
	1100 °C	1150 °C	1200 °C	1250 °C
Cor+00%B_2O_3	E+M+S	C+S+μ+α	C+S+μ+α	α
Cor+08%B_2O_3	S+C+α	C+α	α	α

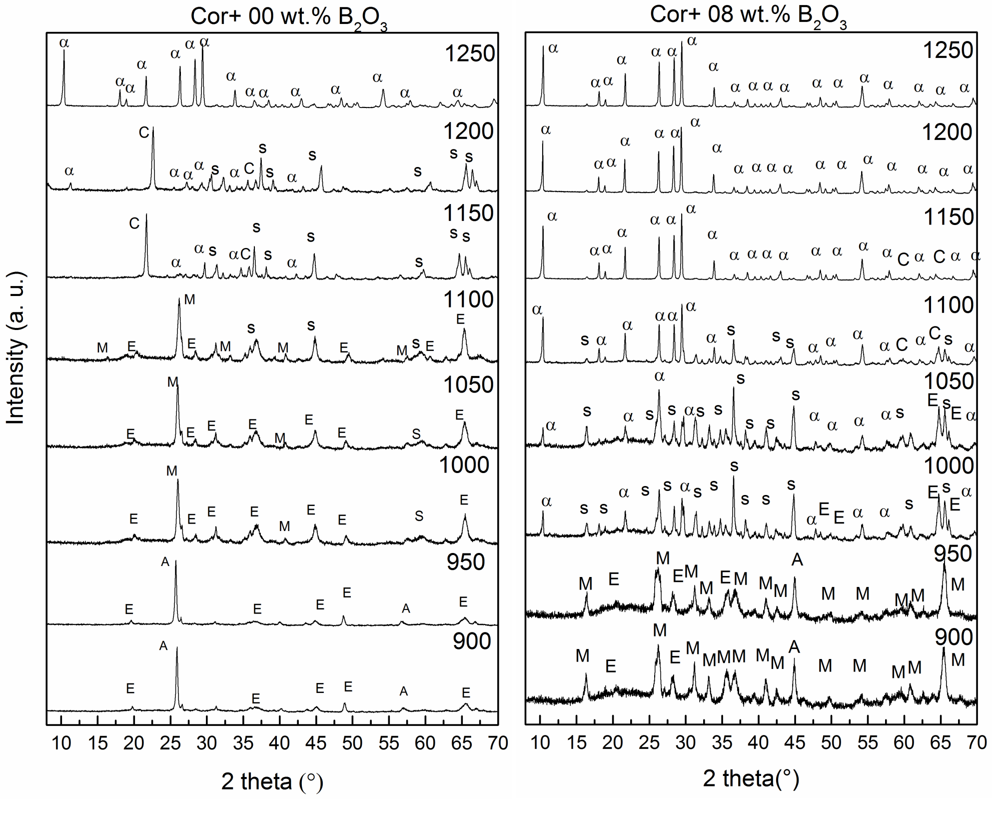

Fig. 3. XRD patterns of cordierite with 0 and 8 wt.% of B_2O_3 treated at different temperatures (A: magnesium silicate, E: enstatite, M: mullite, S: sapphirine, C: cristobalit, μ: μ-cordierite and α: α-cordierite).

Figure 4 shows the plot of $\ln[\varphi/T_{\mathrm{p}}^2]$ versus temperature for various studied concentrations of B_2O_3 (wt.%). The values of activation energies of cordierite powder with different concentrations of B_2O_3 can be calculated from these curves by Kissinger method based on Eq. (1) [17, 18]:

$$\ln\left(\frac{\varphi}{T_{\mathrm{p}}^2}\right) = -\frac{E_{\mathrm{A}}}{RT_{\mathrm{p}}} + C_1. \qquad (1)$$

Here C_1 is a constants, φ 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.

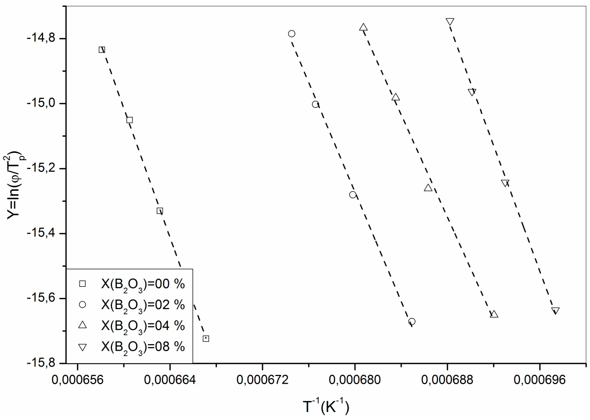

Fig. 4. Plot of $\ln[\varphi/T_p^2]$ versus inverse temperature for various concentrations of B_2O_3 additive (wt.%).

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 kJmol^{-1}, respectively [16].

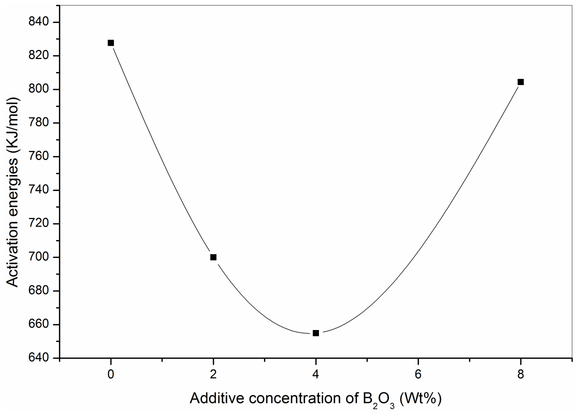

Fig. 5. The activation energy of crystallization as a function of concentration of B_2O_3 additive.

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 μ-cordierite and accelerated the crystallization of α-cordierite.

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