A Study of Cordierite Ceramics Synthesis From domestic kaolin

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Abstract: This work aims to study the effect of chlorine ion on the formation of the cordierite phase (2MgO.2Al2O3.5SiO2) from domestic kaolin at various calcined temperatures. The cordierite phase was synthesized by a solid-state reaction technique from the mixture of kaolin, aluminum nitrate nonahydrate (Al(NO3)3.9H2O), and magnesium chloride hexahydrate (MgCl2.6H2O) which was designed to the stoichiometric composition of cordierite in the absence and presence of chlorine ion (NH4Cl). The structure and formation of cordierite phase were characterized by X-ray diffraction (XRD) and thermogravimetric – differential thermal analysis (TG-DSC). Phase composition of samples calcined at various temperatures was calculated by using Match! (Version 3.7.0) software. It is noteworthy that the presence of chlorine ion in the mixture declined the formation temperature of cordierite by 50 °C. The cordierite phase was calculated to be 61.3 wt.% and 5.5 wt.% at 1150 °C for the present and absent chlorine ion, respectively. The presence of chlorine ion affected the cordierite formation rate and suppressed the temperature of formation. Cordierite phase could be obtained up to 89.6 wt.% at 1250 °C and 30 wt.% NH4Cl. This investigation found that cordierite ceramic could be synthesized from domestic kaolin at lower temperature by using NH4Cl additive.

Key words: cordierite, domestic kaolin, ceramic methods.

1. Introduction

Cordierite ceramics are widely used in a variety of applications, including catalyst carriers [1], insulating materials [2], substrate material for integrated circuit boards [3] and kiln linings [2] due to cordierite ceramic has a low thermal expansion coefficient [4], good thermal stability [5], resistance to temperature fluctuations, high mechanical strength, and chemical stability [6]. The cordierite ceramics can be prepared by a various method as: sol-gel [7], solid-liquid dispersion [8], glass crystallization [9] and the conventional ceramic methods [9]. In the sol-gel technique, single phase cordierite can be produced from pure chemical sources at low calcined temperature. Einarsrud and co-works [9] have studied the synthesis of cordierite ceramics by sol-gel method from Mg(CH3COO)2.4H2O, tetraethoxysilane (TEOS) at low firing temperature range of 1000 -1300 °C. Cordierite materials are mostly synthesized by conventional ceramic methods using single oxides such as MgO, Al2O3, SiO2 [3] or compounds comprising MgO, Al2O3 and/or SiO2 such as talc, kyanite, and kaolinite [10] due to an especially simple to automate the manufacturing process for mass production [11]. Unfortunately, the drawback of conventional ceramic method is found to be the present of secondary phases [3] together with the main phase of cordierite in the final ceramic materials due to low diffusion of ions in solid during heated treatment. Therefore, cordierite producing from ceramic methods require a high calcination temperature to obtain considerable purity cordierite phase. Typically, Shi Zhiming et al. [12] synthesized cordierite ceramic with a high strength and a low thermal expansion coefficient from a mixture of MgO, Al2O3 and SiO2 oxides with additional small amount of Ce4+.
salt, at 1350 °C for 3 h. The obtained powder consists of α-cordierite and small amount of CeO₂ particles. According to author R.Goren et al. [3], single-phase cordierite was successfully synthesized from raw materials talc, diatomite and alumina at 1350 °C for 5h or 1400 °C for 1h. Impurities phase of Mg-Al spinel and α-alumina is observed in the synthesis process of cordierite ceramic from mixture of Al₂O₃, MgO and Kaolin even at high calcination temperature of 1400 °C for 4h [13]. To get market access and lower production costs, cordierite ceramic must be synthesized by a simple method from mineral resource at low calcination temperature. Therefore, it has been investigated of suitable materials and preparation method to produce single phase cordierite ceramic powder at lower calcination temperature. This study has been investigated the influence of the calcination conditions (temperature, time) on the formation of cordierite phase from MgCl₂.6H₂O, Al(NO₃)₃.9H₂O and domestic kaolin materials. Moreover, this study was also investigated the influence of amount of catalyst, NH₄Cl, to reduce calcination temperature of cordierite formation.

2 Materials and experiment

2.1 Materials and Preparation of powders

The raw materials such as kaolin (KLP-03, KL, Vietnam), aluminum nitrate nonahydrate (Al(NO₃)₃.9H₂O, ≥ 99 wt.%, AR, China), magnesium chloride hexahydrate (MgCl₂.6H₂O, ≥ 98 wt.%, AR, China) were weighted with proper ratio for the formulation of cordierite phase for the preparation of cordierite body. Then, the mixture was milled by wet-ball method in ethanol (C₂H₅OH, 99.5 wt.%) media for 12h, at 400 rpm rate, dried at 120 °C for 12h (mixture 1) prior subjected to make pellets at pressure of 50 MPa. Pellets (~ 3.0 g, 16 mm diameter) were sintered in air at 800 °C for 3h with heating rate 5 °C min⁻¹. The calcined pellets were pulverized by mortar and pestle; before milled by ball milling method and dried in oven at 100 °C for 12h. Final, the powder was then pelleted again and annealed in air at different temperatures (1100 – 1300 °C) for 4h at heating rate 5 °C min⁻¹. To study the effect of NH₄Cl on the formation of cordierite phase, amount of NH₄Cl was mixed with 800 °C calcined mixture 1 before ball milling step. After drying, the obtained mixture, named as mixture 2, was subjected to anneal at different temperatures (1100 – 1300 °C) for 4h at heating rate 5 °C min⁻¹.

2.2 Materials characterization

The phase compositions and crystal structures of samples were determined by X-ray diffraction (XRD) using a D2 Phaser (Bruker, USA) with CuKα radiation (λ = 0.15418 nm), a diffraction angle (2θ) from 5 to 80° and a step size of 0.02° at a scan rate of 4° min⁻¹. Match! 3 (Version 3.7.0) software was used to analyze the result of XRD to identify mineral species. Thermal analysis (TGA/DSC) of the precursor mixture were investigated by using simultaneous TG-DSC (Linseis, PT 1600) thermal analyser in a ramp temperature of 10°C min⁻¹ with air purge gas flow rate of 90 mlmin⁻¹ over a temperature range from ambient temperature to 1400 °C. 100 μL alumina pans were used for the experiments.

3. Results and discussion

3.1. Properties of kaolinite

Chemical composition of domestic kaolin is shown in table 1, provided SiO₂ and Al₂O₃ content for about 51 and 33 wt.%, respectively. Molar ratio of SiO₂/ Al₂O₃ is 2.63 and higher than that of stoichiometric ratio (2.0) in kaolinite (Al₂O₃.2SiO₂.2H₂O). The obtained results indicate that kaolinite contains amount of free silica. The influence of impurities on the structure [14], and formation of cordierite crystallization [15] can be ignored by the low content presented in kaolin material such as K₂O (0.1 wt.%), Na₂O (0.05 wt.%), and Fe₂O₃ (0.8 wt.%). X-ray diffraction pattern of domestic kaolin (figure 1) shows two major phases including kaolinite (Al₂Si₂O₅(OH)₄) JCPDS card 96-900-9235, quartz (SiO₂) JCPDS card 00-046-1045 and minor impurities phases with low intensity.
3.2 Thermal analysis
The thermal behavior of the mixture 1 preparing for cordierite synthesis was measured by TGA/DSC method, ranging from room temperature to 1400 °C in air at a heating rate of 10 °C/min as shown in figure 2(a). As shown in Figure 2(a), TGA curve shows two main stages with total weight loss of 28.4 wt.% in ranging from 30 to 800 °C. DSC curve shows endothermic peaks in the temperature range of 124 - 496 °C due to the dehydration of kaolinite [16], the dehydration and decomposition of aluminum nitrate Al(NO$_3$)$_3$·9H$_2$O [17] and magnesium chloride MgCl$_2$·6H$_2$O [18], and of any remaining liquid water expelled from the mixture. The endothermic peaks between 550 °C and 650 °C are attributed to the dehydration of kaolinite [19] and phase transition of α-quartz to β-quartz [20].
Figure 2. TGA/DTA diagram of (a) dried mixture and (b) NH$_4$Cl-dried mixture from 30 °C to 1400 °C

The exothermic peak at 994 °C is attributed to the formation of spinel MgAl$_2$O$_4$ as presented in reaction (1) and sapphirine (4MgO.4Al$_2$O$_3$.2SiO$_2$) as presented in reaction (2) [21]. The formation of spinel and sapphirine is confirmed in the XRD pattern when calcining at 1100 °C (figure 3). The exothermic peak at 1266 °C is assigned to the formation of main phase cordierite as presented in reaction (3) and reaction (4) [22]. A small weight loss at 1350 °C can be attributed to the release of oxygen by oxides at high temperatures.

\[
MgO + Al_2O_3 \xrightarrow{944 ^\circ C} MgO\cdot Al_2O_3
\]

(1)

\[
4MgO + 3Al_2O_3 + Al_2O_3\cdot 2SiO_2 \xrightarrow{944 ^\circ C} 4MgO\cdot 4Al_2O_3\cdot 2SiO_2
\]

(2)

\[
2(MgO\cdot Al_2O_3) + 5SiO_2 \xrightarrow{1266 ^\circ C} 2MgO\cdot 2Al_2O_3\cdot 5SiO_2
\]

(3)

\[
4MgO\cdot 4Al_2O_3\cdot 2SiO_2 + 8SiO_2 \xrightarrow{1266 ^\circ C} 2(2MgO\cdot 2Al_2O_3\cdot 5SiO_2)
\]

(4)

To investigate the influence of chlorine ion on the enhancement of cordierite formation rate, the mixture 2, is measured TGA/DSC thermal analyzed and shown in figure 2(b). Interestingly, the exothermic peak is shifted to lower temperature at about 943 °C (Fig. 2(b)) from 994°C (Fig. 2(a)) due to the faster formation of spinel and sapphirine in the presence of chlorine ion. The produced gas from decomposition of NH$_4$Cl during calcinating lead to produce smaller particle size of spinel, sapphirine and SiO$_2$, resulting shorter diffusion paths and a greater area of grain boundaries. Consequently, rate of formation of cordierite from the reaction of spinel or sapphirine and silica is also increase, resulting higher amount of cordierite at lower annealing temperature, for instance 1192 °C (Fig. 2(b)) instead of 1266 °C (Fig. 2(a)).

3.3 XRD analysis

To study the effect of the calcinating temperatures on the formation of cordierite phase, the mixtures after ball-milling and drying, were calcined at various temperatures of 1100, 1150, 1200, 1250 and 1300 °C for 4 h and evaluated by using XRD method. Figure 3 shows XRD patterns of calcined samples with no obvious diffraction peaks cordierite phase when calcined at 1000 °C.
Figure 3. XRD patterns of dried samples calcined at different temperatures.

However, the calcination temperature is increased to 1150 °C, distinct diffraction peaks appeared at 10.43° and 28.41° indicating that the cordierite phase was formed at temperature higher than 1100 °C. At 1150 °C, the samples contain mainly sapphirine (PDF 96-900-0183), quartz at 2θ = 21.84° (PDF 96-901-0145) and spinel Al₂O₃·MgO at 2θ = 18.98; 31.23; 36.84; 44.82° (PDF 96-900-5768) phases. The result of this study is similar to that of Yuichi Kobayashi’s research [23]. In addition, the presence of cristobalite can be related to the amorphous silica at sufficiently high temperatures. Obviously, the intensity of the cordierite peaks are enhanced at elevated temperature, and the diffraction peaks become sharper. The intensity of unexpected spinel phase decreases and disappears at calcined temperature 1250 °C. Samples calcined at 1250 and 1300 °C exhibited a nearly single phase of α-cordierite (92.8 wt.%) representing at 2θ = 10.43; 18.10; 21.71; 28.41°, and no trace impurity phase was detected. Moreover, figure 3 shows that the XRD diffraction patterns of the samples, calcined at 1250 °C for 8 h and at 1300 °C for 4 h, are similar. The obtained results revealed that the heating time has a significant effect to the cordierite formation.

To estimate quantity of phase composition at various calcination temperatures, Match! (Version 3.7.0) software was used and tabulated in table 1. It can be seen that amount of cordierite phase is calculated only about 5.5 wt.% at 1150 °C calcination temperature and increase dramatically at higher calcination temperature, about 60 wt.% at 1200 °C, or 84 wt. % at 1250 °C associating with decreasing amount of main impurity phases of spinel, sapphirine and mullite. It can be remarked that cordierite is formed mainly from the reaction between sapphirine, spinel and SiO₂ [24].
Figure 4. XRD patterns of dried samples calcined at 1250 °C for 8h and at 1300 °C for 4h

Table 1. The calculated phase composition versus calcined temperature

| Phases name   | Phase composition (wt.%) |
|---------------|--------------------------|
|               | 1100 °C  | 1150 °C  | 1200 °C  | 1250 °C  | 1250 °C  | 1300 °C  |
|               | 4h       | 4h       | 4h       | 4h       | 8h       | 4h       |
| Cordierite    | 2.5      | 5.5      | 60.1     | 84.4     | 91.7     | 92.8     |
| Spinel        | 39.7     | 21.3     | 6.6      | 5.5      | 1.2      | 2.7      |
| Sapphirine    | 22.7     | 43.4     | 21.8     | 4.4      | 2.9      | 2.1      |
| Quartz        | 21.8     | 8.6      | 2        | 0.8      | -        | 0.3      |
| Proto-enstatite| 1.1      | 2.7      | 0.8      | 0.8      | 0.2      | 0.5      |
| Cristobalite  | 3.7      | 6.3      | 0.6      | 0.2      | -        | 0.2      |
| Mullite       | 5.1      | 11.8     | 7.9      | 3.7      | 3.9      | 1.1      |
| Corundum      | 3.4      | 0.3      | 0.2      | 0.2      | 0.1      | 0.3      |
Figure 5. XRD patterns of samples calcined at different conditions, (a) 1150 °C, 0 wt.% NH₄Cl, (b) 1150 °C, 20 wt.% NH₄Cl, (c) 1150 °C, 30 wt.% NH₄Cl, (d) 1200 °C, 30 wt.% NH₄Cl and (e) 1250 °C, 30 wt.% NH₄Cl.

Table 2. The calculated phase composition of samples calcined at different conditions for 4h

| Phases name     | 1150 °C, 0 wt.% NH₄Cl | 1150 °C, 20 wt.% NH₄Cl | 1150 °C, 30 wt.% NH₄Cl | 1200 °C, 30 wt.% NH₄Cl | 1250 °C, 30 wt.% NH₄Cl |
|-----------------|------------------------|------------------------|------------------------|------------------------|------------------------|
| Cordierite      | 5.5                    | 7.4                    | 61.3                   | 79.4                   | 89.6                   |
| Spinel          | 21.3                   | 12.3                   | 15.5                   | 12.1                   | 7.5                    |
| Sapphirine      | 43.4                   | 46.7                   | 7.8                    | 1.4                    | 1                      |
| Quartz          | 8.6                    | 20                     | 11.6                   | 1                      | 0.1                    |
| Proto-enstatite | 2.7                    | 1.6                    | 0.5                    | 1.4                    | 0.5                    |
| Cristobalite    | 6.3                    | 8.8                    | 0.2                    | 0.3                    | -                      |
| Mullite         | 11.8                   | 0.9                    | 1.5                    | 2.6                    | 0.9                    |
| Corundum        | 0.3                    | 2.2                    | 1.7                    | 1.6                    | 0.4                    |
Figure 5 shows the effect of chlorine ion on the rate of cordierite formation. Figure 5(a) (sample with a 20 wt.% NH4Cl content, calcined at 1150 °C) shows a very weak peak of cordierite phase as 10.43°. The diffraction peak intensity of cordierite is strongly increased by the addition of 30% NH4Cl content in the mixture. The cordierite phase is obtained 61.3 wt.% (at 30 wt.% NH4Cl, 1150 °C) as in table 2 and higher than that of sample prepared at 20 wt.% NH4Cl at the same calcination temperature, 1150 °C. In addition, the obtained cordierite phase content increases from 79.4 to 89.6 wt.% with the heating temperature increase from 1200 °C to 1250 °C, respectively. Interestingly, the sample with 30 wt.% NH4Cl calcined at 1150 °C contents about 61.3 wt.% cordierite phase, which was higher than that of sample without using NH4Cl, 5.5 wt.%) at 1150 °C or 60 wt.% at 1200 °C. The cordierite phase is formed at high calcination temperature (1300 °C) [24, 25] in the absence of NH4Cl addition. Finally, it is noted that NH4Cl has a significant influence on cordierite formation, chlorine ion faster the cordierite formation rate.

4. Conclusion
We have synthesized purities cordierite ceramic from domestic kaolin by solid state reaction. The use of MgCl2.6H2O and Al(NO3)3.9H2O as MgO and Al2O3 sources instead of oxide lead to reduce temperature of cordierite formation, at 1200 °C rather than 1300 °C for conventional method. The combination of domestic kaolin, magnesium salt, aluminum salt and calcinating additive NH4Cl was investigated. In this case, cordierite was formed at 1150 °C, which was decreased by 50 °C compared to the case of without using NH4Cl, and decreased by 150 °C compared to conventional method, using oxides only.

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