Cordierite Ceramic Through Glass and Ceramic Routes From Kaolin And Talc

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Abstract

Based on kaolin and talc, cordierite was prepared through melt quench and ceramic process of two compositions. The sintering process of ceramics between 1000 and 1300 °C shows mainly the manifestation of cordierite with little ratios of spinel, enstatite, mullite and cristobalite. However, the sintering of their corresponding glasses between 1100 °C and 1200 °C shows the crystallization of cordierite as the main phase with little cristobalite and spinel. In microstructure, the sintering of the ceramic samples revealed nano size rounded- or rod- crystals either free or in clusters in glassy matrix. Whereas, sintering of the corresponding glasses showed clear euhedral to subhedral tetragonal to hexagonal crystals in submicron scale that spread in the residual glassy matrix. The density of the sintered ceramic samples was in the range of 1.96 and 2.43 g/cm³ corresponding to porosity of 29.34 and 5.46 % respectively. While the density of the sintered glasses was 1.90 and 2.35 gm/cm³, corresponding to porosity of 36.20 and 3.30 % respectively. The sintered glass samples presented low and negative coefficient of thermal expansion (CTE) of 1.63 and -2.93 × 10⁻⁶ °C⁻¹ (in the range ~ 24 -500 and 700 °C). The microhardness values were between 468 and 577 Kg/mm². As a result, the prepared cordierite ceramic may be possibly used as refractoriness in electric heater supports, such as electric stove or heater cooling plate and ceramic heater base.

Keywords: Ceramic, glass-ceramic; cordierite; CTE; hardness

1. Introduction

Materials based on magnesium aluminum silicate (MAS) system have many industrial applications. Some minerals such as cordierite, mullite, osmumite, spinel and proto pyroxene were detected within such ternary diagram MgO-Al₂O₃-SiO₂ [1-2]. Cordierite (Mg₂Al₄Si₂O₁₀) and osmumite [(K,Na)(Fe,Mg)₃ (Al,Fe₂)(Si,Al)₂O₁₀] glass-ceramic and ceramic have low thermal expansion coefficient, high mechanical , chemical stability and low dielectric constant [3]. Their properties make it a promising candidate for many industrial applications, such as floor tiles, substrate material for solar cell, electric heater supports (such as electric stove, ceramic heater base, and electric heater cooling plate) [4].

There are different methods for the synthesis of aluminosilicate phases in the MgO-Al₂O₃-SiO₂ system such as melt quench, ceramic, sol-gel or wet and composite routes [5-10]. Among these methods, we are going to use powder method by solid-state and melt quench routs. However, the raw materials usually contain a quantity of Fe₂O₃, CaO, TiO₂, ... etc. As it is well known that these oxides enhance the nucleation in ceramic and glass industry, which in turn have influence on the crystallization process [11 – 16]. Impurities based on cordierite ceramic batch, such as TiO₂, Fe₂O₃, CaO, K₂O and Na₂O have influence on the developed phases and their properties [15]. It is well known that kaolin-talcic system was usually used in the preparation of cordierite ceramics [7]. Cordierite containing glass-ceramic in nanoscale microstructure have very low thermal expansion coefficient prepared from kaolin- magnesite containing impurities of TiO₂ and Fe₂O₃ [6, 16]. Likewise, presence of Na₂O and K₂O would lower the refractoriness of the cordierite ceramics and enhance their thermal expansion [13].

In the present research, cordierite ceramics and glass-ceramics were fabricated using talc, kaolin,
commercial alumina. Sintering behavior, phase compositions, microstructure, physical, mechanical and thermal properties were studied. Furthermore, some properties of ceramics and glass ceramics are given to see the potential application of them.

2. Experimental

The starting materials are mainly talc (South Eastern desert, Egypt) and kaolin (Southern Sinai, Masbh salama, Egypt), in addition to commercial alumina. Table 1 demonstrates the chemical analyses of raw materials. Talc and kaolin were subjected to grinding and pulverizing through ball mill to develop powder (grain size < 63 μm). The batch composition was based on cordierite Mg₂Al₄Si₅O₁₈ talc was represented as source of MgO, kaolin and commercial alumina are sources of Al₂O₃ and both talc and kaolin are the source of SiO₂. Through melt quenching process, the admixed batches were melted in a platinum crucible at 1400 °C in an electric gloubar furnace for two hours. Molten glasses were quenched in distilled water. The glass frit samples were ground in a planetary mill for 5 minutes (650 rpm for 1 minute). For preparation of ceramic batch, green powder was mixed and milled in an agate ball mill grinder (650 rpm for 1 minute) then dried overnight.

Table 1. Chemical analysis of the starting raw materials

<table>
<thead>
<tr>
<th>Raw Material</th>
<th>SiO₂</th>
<th>TiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>MgO</th>
<th>CaO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>P₂O₅</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Talc1</td>
<td>47.94</td>
<td>0.38</td>
<td>6.64</td>
<td>8.62</td>
<td>21.84</td>
<td>7.47</td>
<td>0.22</td>
<td>0.05</td>
<td>0.09</td>
<td>6.16</td>
</tr>
<tr>
<td>Talc2</td>
<td>49.01</td>
<td>0.05</td>
<td>5.90</td>
<td>9.16</td>
<td>24.56</td>
<td>5.61</td>
<td>0.17</td>
<td>0.01</td>
<td>0.01</td>
<td>4.81</td>
</tr>
<tr>
<td>Kaolin</td>
<td>44.56</td>
<td>1.98</td>
<td>37.34</td>
<td>1.12</td>
<td>0.39</td>
<td>0.09</td>
<td>0.10</td>
<td>0.02</td>
<td>0.08</td>
<td>14.10</td>
</tr>
</tbody>
</table>

Table 2. Chemical composition of the C5 and C6 batches.

<table>
<thead>
<tr>
<th>Raw Material</th>
<th>SiO₂</th>
<th>TiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>MgO</th>
<th>CaO</th>
<th>Mg/Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>C5</td>
<td>48.75</td>
<td>1.12</td>
<td>26.21</td>
<td>5.63</td>
<td>13.17</td>
<td>4.48</td>
<td>0.21</td>
</tr>
<tr>
<td>C6</td>
<td>49.45</td>
<td>1.05</td>
<td>26.93</td>
<td>5.49</td>
<td>13.38</td>
<td>3.05</td>
<td>0.15</td>
</tr>
</tbody>
</table>

3. Results and Discussion

3.1. Characterization of sintered glass and ceramic

The developed crystalline phases after sintering process, between 1000 and 1300 °C, of glasses (GC5 and GC6) and ceramics (CS5 and CS6) are identified in Figure 1 and 2. Cordierite (Al₆Mg₂Si₅O₁₈, COD card # 96-900-6272) is the main crystalline phase in both samples, however, spinel (Al₁₈Mg₀₂₀₉₈O₄₆, COD card # 96-900-2072) and cristobalite (SiO₂, COD card # 96-900-8231) were crystallized in the sintered GC5 and GC6 glasses at 1100 °C / 2h and 1200 °C /2h. In both CS5 and CS6 ceramic samples sintered between 1000 °C / 2h and 1300 °C /2h, protoenstatite (MgSiO₃, COD # 96-154-8551 and mullite (Al₂.₅₅O₆.₇₁SiO₇.₅₇, COD card # 96-900-1568) were developed too. The early sintering of ceramic CS5 and CS6 samples at 1000 °C / 2h and 1100 °C temperatures led to the crystallization of mullite with cristobalite, protoenstatite and spinel. Increasing the temperature up to 1200 °C/2h endorsed the crystallization of cordierite as the main phase with little protoenstatite, spinel and cristobalite. At 1300 °C/2h, cordierite was crystallized with spinel in both CS5 and CS6 ceramic samples (Fig 2). Lately, Valášková et. al., prepared ceramic containing cordierite/indialite, enstatite and non-crystalline phases from kaolin, quartz, and...
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muscovite were sintered with vermiculite (Mg,Fe\textsuperscript{2+},Al)\textsubscript{3} (Al,SiO\textsubscript{3})O\textsubscript{10}(OH)\textsubscript{2}.4(H\textsubscript{2}O) [17]. We can imagine the results of sintering between 1000 and 1300 °C temperatures as follow:

**Equation (1):**
\[
\text{Al}_2\text{O}_3(\text{SiO}_2)(\text{H}_2\text{O}) + \text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2 \\
\text{Kaolinite} + \text{Talc} \rightarrow \text{Brown glass} \quad \text{Amorphous silica}
\]

**Equation (2):** Glass \(\sim 1100 \degree C/2h\) → Cristobalite – Cordierite – Spinel

**Equation (3):** Glass \(\sim 1200 \degree C/2h\) → Cordierite – Cristobalite – Spinel

**Equation (4):**
\[
\text{Al}_2\text{O}_3(\text{SiO}_2)(\text{H}_2\text{O}) + \text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2 \\
\text{Kaolinite} + \text{Talc} \rightarrow \text{MgSiO}_3 + \text{Al}_2\text{O}_3.\text{SiO}_2 + \text{SiO}_2
\]

**Equation (5):**
\[
\text{SiO}_2 \sim 1100–1200 \degree C/2h \\
\text{Amorphous silica} \rightarrow \text{SiO}_2
\]

**Equation (6):**
\[
3(\text{MgO}.\text{SiO}_2) + 3\text{Al}_2\text{O}_3.2\text{SiO}_2 \\
\text{Enstatite} + \text{Mullite} \rightarrow 2\text{MgO}.2\text{Al}_2\text{O}_3.5\text{SiO}_2 + \text{MgO}.\text{Al}_2\text{O}_3
\]

**Equation (7):**
\[
3(\text{MgO}.\text{SiO}_2) + \text{MgO}.\text{Al}_2\text{O}_3 + 2\text{SiO}_2 \\
\text{Enstatite} + \text{Spinel} \rightarrow 2\text{MgO}.2\text{Al}_2\text{O}_3.5\text{SiO}_2
\]

The microstructure of GC5, GC6, CS5 and CS6 samples sintered at 1200 °C/2h were scanned by SEM (Fig. 3, 4). Scattered pores were spread in both GC5 and GC6 samples which was bigger in GC6 (~ 10 %) than in GC5 (~ 5 %) (Fig. 3). The microstructure of GC5 showed rounded to subrounded cluster of nanosize particles (50-100 nanometer) which are clear through spread pores whereas in case of GC6 ceramic euhedral crystals of both cordierite (hexagonal) and cristobalite (cubic) in sub-micron size in residual glassy matrix (Fig. 3). The sintered ceramic CS5 and CS6 samples showed scattered pores (~ 3 and ~ 5 % respectively) in matrix of fused residual glass (Fig. 4). The cordierite with spinel and cristobalite in CS5 sample was modified into rod-like particles whose width between 100 and 200 nanometer. However, in the CS6 sintered sample the microstructure shows clear cordierite crystals of hexagon marking spread in glassy matrix (Fig. 4).

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However, cordierite nanocomposite was prepared from kaolin, talc and alumina with vermiculite and zirconium [18]. Also, nano-cordierite particles were prepared from sintered kaolin, talc and vermiculite doped with CeO$_2$ [19].

In general, sintering of GC5 and CS5 samples gave nano size rounded- or rod- crystals either free or in clusters in glassy matrix. In contrast, sintering of GC6 and CS6 samples gave clear euhedral to subhedral tetragonal to hexagonal crystals in submicron scale.

The EDX microanalysis of some clear crystals and grain are given in Table 3. Figure 5 shows the results of the microanalysis compared to the developed phases.

Fig. 3. SEM micrographs of GC5 and GC6 samples sintered at 1200°C/2h.

Fig. 4. SEM micrographs of CS5 and CS6 samples sintered at 1200 °C/2h.

Fig. 5. EDX microanalysis of GC5, GC6, CS5 and CS6 sintered at 1200 °C/2h.
3.2. Physical Properties of sintered glasses and ceramics

Linear shrinkage (L.S.), bulk density (Db), apparent porosity (Pa) and water absorption (Wa) are the basic parameter to evaluate densification of the prepared ceramics as shown in Table 4. In the sintered ceramic samples, the linear shrinkage and bulk density increase with the sintering temperature from 1000 to 1200 °C which may be attributed to the development of liquid phase filling some pores in ceramic samples or partial melting in sintered glasses [20]. In the later consequence, densification continues to rise due to crystallization of cordierite content through decreasing the ratio of cristobalite and spinel, which accelerates the diffusion of substance that contribute to the densification.

In ceramics and glass-ceramics, the coefficient of thermal expansion CTE is the factor of the crystalline phases and residual glass [19]. For crystalline samples, the value of CTE of the sintered ceramic were 6.38 and -0.73 × 10^{-6} °C^{-1} (in the range of 24- 500 and 700 °C) whereas the values were between 1.63 and -2.93 × 10^{-6} °C^{-1} (in the range of 24- 500 and 700 °C) in case of sintered glasses (Table 5). The aforementioned work mentioned that the CTE value of crystalline cordierite ceramic was 1.60 and 3.38 × 10^{-6} °C^{-1} [11, 13] and was 25 × 10^{-7} and 4.39 × 10^{-6} °C^{-1} for the glass-ceramics [22–25]. Also, cordierite glass-ceramics have CTE of 25.00 × 10^{-7} and 4.39 × 10^{-6} °C^{-1} [22 – 25]. On the other hand, low and negative CTE of ceramic containing cordierite was obtained and the authors ascribed that to change in the c-axis of the crystal structure of cordierite [26 – 27]. Earlier, cordierite associated with little amount of other phases has CTE value ~ 3.38 × 10^{-6} °C^{-1}, and in case of increasing the MgO ratio [i.e. increase of magnesium silicate phase], CTE value developed to 2.82 × 10^{-6} °C^{-1} and 2.32 × 10^{-6} °C^{-1} with sapphire phase [28]. In the bulk cordierite ceramic, the authors attributed the change in CTE value to the formation of multi-crystalline phases with cordierite such as quartz and cristobalite which causes micro-cracking due to the changes in the CTE of the developed crystalline phases with cordierite [29]. Lately, the porous sintered 2MgO·2Al2O3·2B2O3·5SiO2 glass gave low – ve CTE [30].

In the present work, low and – ve CTE cordierite containing sintered ceramic or glass may be due to either the change in c-axis or the cracks either due to change in CTE of the developed phases or the developed pores [30]. In general, the CTE was higher in sintered ceramic compared to those in the sintered glasses which may be due to the presence of remnants particles of minerals coexist with cordierite which may have high CTE [28]. On the other hand, the low CTE in the sintered glasses containing cordierite with little cristobalite, spinel, enstatite and mullite, was...
associated with internal porosity where GC6 has the higher porosity accompanying with negative CTE value (Table 5). The microhardness values of the present sintered ceramic and glass samples were between 468 and 577 Kg/mm² (Table 5). Although the pre-literature gave high value of the cordierite hardness, in the range of 513 – 963 kg/mm² [28, 31], whereas in the present samples the low values of microhardness may be due to the presence of cracks due to the internal pores in the samples.

4. Conclusion
Cordierite ceramic was prepared through ceramic and melt quench routes. Cordierite, spinel, mullite, enstatite and cristobalite developed in both samples through sintering process. The microstructure of the sintered glasses displayed rounded to subrounded cluster in nano-size particles which are clear through spread pores and euhedral crystals of both hexagonal cordierite and tetragonal cristobalite in sub-micron size in residual glassy matrix. In the sintered ceramic scattered pores in matrix of fused residual glass and cordierite with spinel and cristobalite was modified as rod-like particles their width in nanometer appears through pore, however, their microstructure shows clear cordierite crystals with hexagon marking spread in glassy matrix too. Density and porosity of the sintered ceramic are between 1.96 and 2.43 g/cm³ and between 29.34 and 5.46 % respectively, whereas as density and porosity of sintered glasses are between 1.90 and 2.35 g/cm³ and between 36.20 and 3.30 % respectively. Low and negative CTE were obtained in the sintered glasses (between ~ 24 × 10⁻⁶ °C⁻¹ (in the range ~ 24 -500 and 700 °C)). The microhardness values for all sintered samples are between 468 and 577 Kg/mm².

6. Acknowledgment
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7. References
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