Preparation of Cordierite Ceramic from Iraqi Raw Materials

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ABSTRACT

In this study cordierite has been synthesized by solid state process at temperature range of 1050-1400 ℃ from Iraqi raw materials (kaolin clay and magnesite). The products are investigated using x-ray diffraction and scanning electron microscope techniques. The thermal properties and unit cell parameters of the prepared cordierite have been evaluated. The results revealed that thermal expansion coefficient of cordierite are more compatible with results obtained from natural cordierite. The prepared cordierite have positive expansion for a°-axis (a°-axis is increased with increasing sintering temperatures) and negative expansion for c°-axis (c°-axis is decreased with increasing sintering temperatures).

1. INTRODUCTION

Cordierite ($Mg_2Al_4SiO_5O_{18}$) is naturally occurring magnesium aluminum silicate [1]. It has a combination of properties, such as low dielectric constant, low dielectric loss, low thermal expansion, high chemical durability, low thermal conductivity and high hardness 7-7.5 (Moh's scale)[2-4]. Hence, it is used in electronic packaging especially for integrated circuit substrate, as refractory material for coating of metals, kiln furniture, sound insulating boards, catalyst support for exhaust gas purification, microwave absorbing heating elements, filters for separating solids from fluids, and electromagnetic wave absorbers[5]. There are two modes of Mg–cordierite, natural and synthetic. Natural cordierite is crystallized in two polymorphic forms; the first is an orthorhombic low temperature form, whereas the second is hexagonal high temperature form. Low cordierite is transferred to high cordierite on heating at high temperatures but, the transformation of high to low cordierite does not take place in any case. Synthetically, cordierite is crystallized in three polymorphic forms α (high temperature form), β (low temperature form), and μ (meta-stable form). They are hexagonal in symmetry and have different optical properties [6-10]. The goal of this study was to produce pure cordierite, with absence of secondary crystalline or amorphous phases.

2. EXPERIMENTAL PROCEDURE

2.1 Preparation of specimens

Cordierite has been synthesized by solid state process based on stoichiometric mixture of 71.65 wt% of kaolin and 28.35 wt% of magnesite. The chemical compositions of the kaolin and magnesite are given in Table 1.

Table 1. Chemical composition of raw materials determined by wet analysis.

Materials	SiO_2	Al_2O_3	MgO	Fe_2O_3	$(Na,K)_2O$	LOI
Kaolin	51.9	32.4	0.3	1.4	0.6	13.3
Magnesite	1.0	0.5	46.1	1.5	0.05	49.9

The starting materials were wet mixed in planetary ball mill, which runs at 400 rpm in ethanol alcohol as dispersive media for 16 hours to provide homogenous mixture. The obtained mixture was oven dried for 24 hours at 100 ℃, then finely milled using pestle and mortar. Particle size analysis was measured using laser particle size analyzer (Bettersize 2000) to give bimodal particle size of 1 μm and 10 μm as shown in Fig.1.
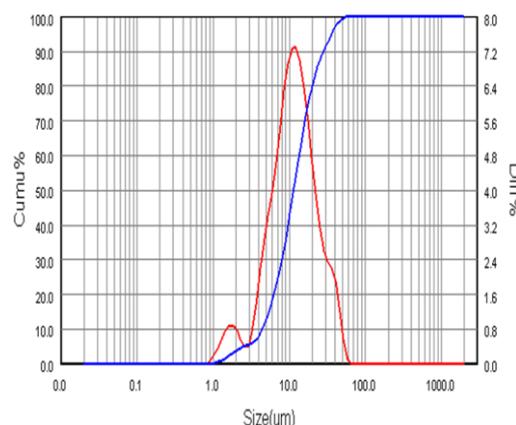

Fig.1. Particle size analysis of the mixed powder.

Subsequently, the powder mixture was compacted at 48 MPa and sintered at different temperatures of 1050, 1150, 1250, 1300 and 1400 ℃ for 2h with an average heating rate of 7 ℃/min.

2.2 Characterizations

All samples obtained from the fired batches were finely ground and scanned by x-ray diffractometer (Shimadzo, 6000) at room temperature using CuKα radiation with Ni filter. The microstructures were observed using the scanning electron microscope (VegaII XMV). All samples were finely polished and then coated with thin layer of gold by sputtering deposition technique (EMITECH k450x, UK) for conduction, and then scanned to produce images with magnification of (X20000). The linear thermal expansion coefficient (α) of sintered samples was measured at temperature range of 25-900 ℃ by dilatometer (Quickline–05).

3. Results and Discussions

3.1 X-Ray Diffraction (XRD)

Fig.2 shows the XRD patterns of the crystallization behavior of powder sintered at different temperatures. It has been experimentally found that the high temperature cordierite (α-cordierite) appears as the main phase with quartz phase in the earlier stages of sintering, in particular, at temperature less than 1050 ℃ with small amount of spinel. The increasing of sintering temperature to 1150°C causes gradually growing in cordierite phase and in the same time, there is declined for silica and spinel phases. The upgrade of the sintering temperatures up to 1400 ℃ induces the oxides components of the raw materials to react better and produce the unique α-cordierite.
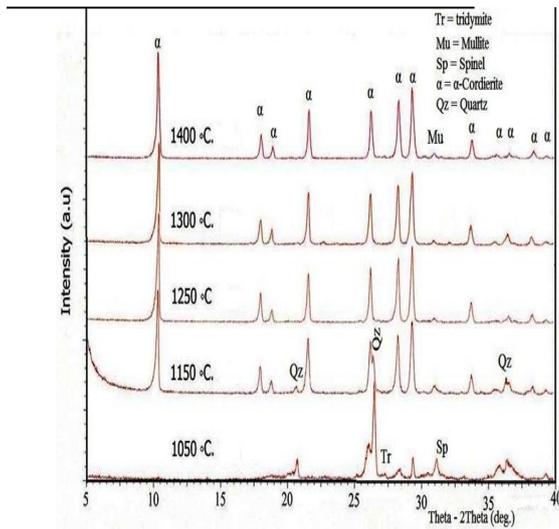

Fig.2 XRD patterns of the cordierite sintered at different temperatures.

3.2 SEM Micrographs

The microstructure of sintered cordierite is demonstrated in Fig.3. The image (a) represents the densification manner of specimens fired at 1300 ℃. This image shows good coalescence of grains which represents α–cordierite and reflects a dense structure. There are homogenous large grains with very high densification were observed, and no appearance of pores which indicates the occurrence of the proper reaction between the raw materials to form the required product of high temperature cordierite. Image (b) depicts the microstructure of specimen sintered at 1400 ℃. This image shows good coalescence for its content of the phase α–cordierite. As a result of this, different properties will be improved when compared with that sintered at lower temperature.
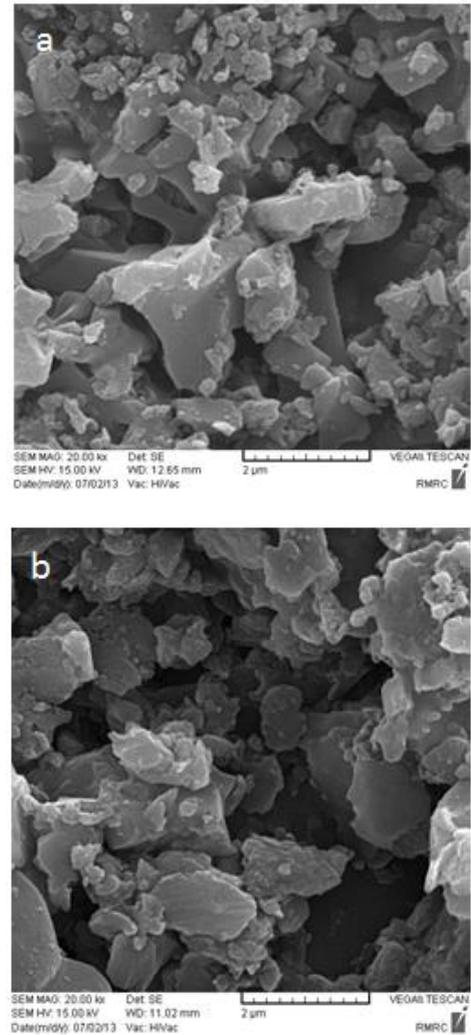

Fig.3 SEM for cordierite specimens fired at (a) 1300ºC and (b) 1400 ºC.

3.3 Crystallographic Studies

Thermal expansion coefficient and unit cell parameters aº-axis, cº-axis, c/a ratio and unit cell volume have been studies for samples sintered at different temperatures. Generally, the thermal expansion coefficient of cordierite prepared from raw materials is increased in its value with increasing the temperature from 50 ℃ up to 900 ℃ (Fig.4). But the specimens which have sintered at higher temperatures (1250, 1300 and 1400 ℃) showed the lowest values of thermal expansion coefficient in comparison with those specimens sintered at lower temperatures (1050 and 1150 ℃). Thermal expansion coefficient of high sintering temperatures was about 0.02×10^{-6}/℃ at 200 ℃ and increased linearly to reach its highest value of about 1.78×10^{-6}/ ℃ at 900 ℃.
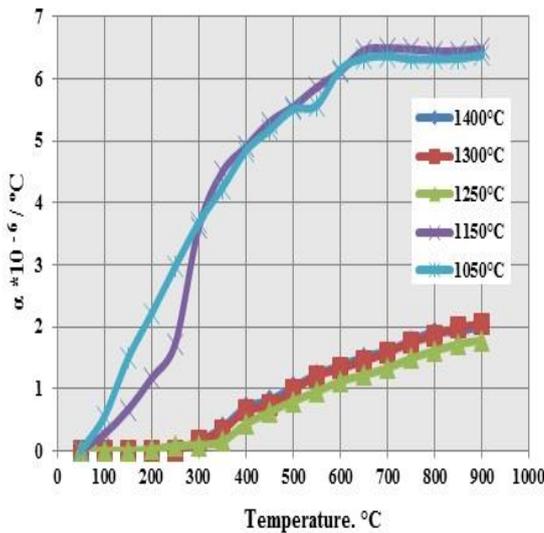
Fig.4 Thermal expansion coefficient of the batches as a function of sintering temperatures.

These values as compared with other batches are related to the formation of high temperature cordierite at 1250 ℃ which appears as a major phase associated with traces amounts of mullite as shown in Fig.2. The axial thermal expansion coefficient of cordierite is positive in the plane of hexagonal rings, and negative perpendicular to this plane. This means that cordierite has positive a°-axis expansion, but c°-axis acquires noticeable contraction. Fig.5 shows this fact where a°-axis of α-cordierite is increased with increasing sintering temperature, whereas c°-axis is decreased with increasing sintering temperatures.
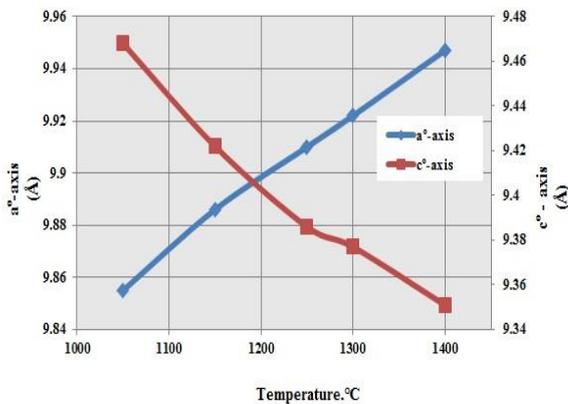

Fig.5 Variation of a° and c°-axes of cordierite with temperatures.

Fig.6 shows the relation between unit cell volume of α-cordierite which is prepared from raw materials and sintering temperatures. It is evident that the relation between unit cell volume of α-cordierite and sintering temperatures is incremental behavior. Where, the sintering process of prepared cordierite shows that the unit cell volume (796.35Å) for the specimens fired at 1050 °C are somewhat larger than its usual value (≈ 770 Å) [11]. In addition, the unit cell volume continuous in growth with increasing the sintering temperature up to 1400 °C. At the early stage of firing, cordierite was associated with other phases like spinel, and mullite which are acted as a tied block to grow of α-cordierite phase. Whereas, the higher sintering temperatures showed absence of phases accompanied with α-cordierite, and hence

becomes free in growth of its unit cell volume. It is noteworthy that the unit cell volume of prepared cordierite is greater than that of natural one, because there is an active reaction among the oxides components of cordierite in raw materials.
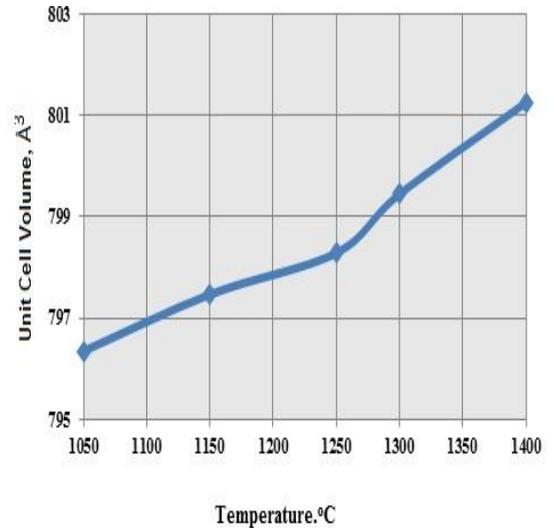

Fig.6 Unit cell volume of cordierite as a function of sintering temperatures.

Fig.7 depicts the relation between α-cordierite parameters (a° and c°) axes with the firing temperatures. The c/a ratio is less than unity which characterized the α-form as compared to μ-cordierite which has c/a ratio greater than unity. The increasing in firing temperatures causes an increment in a°-axis of cordierite phase and at the same time; c°-axis of cordierite will be reduced. So, c/a ratio will be decreased with increasing the sintering temperature from 1050 to 1400 ℃ [12].
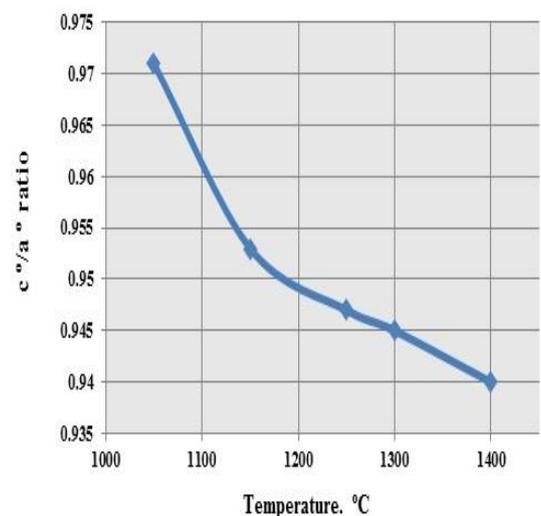

Fig.7 Crystal structure axes of cordierite as a function of sintering temperatures.

4. CONCLUSIONS

Kaolin clay and magnesite raw materials are very suitable to produce the cordierite phase. Cordierite was formed at long firing temperatures namely 1150 ℃ to 1400 ℃. Thermal expansion coefficient of cordierite which is sintered at 1400℃ was 2.02×10^{-6} ℃$^{-1}$. Unit cell parameters (a°-axis and c°-axis) varied inversely. When a°- axis increased, decreasing in c°-axis is occurred with progress of sintering temperatures. Unit cell volume increased with increasing the sintering temperatures whereas, c/a ratio decreased with increasing the temperatures.

ACKNOWLEDGEMENTS

REFERENCES

[1] Sung, Y., "The effect of additives on the crystallization and sintering of 2MgO–2Al$_2$O$_3$–5SiO$_2$ glass–ceramics". J. Mater. Sci. 31 (1996) 5421– 5427.

[2] Rodney, I., Irwin, M., and Paul, H., 1977, "Method of preparing crack free monolithic polycrystalline cordierite substrates". U.S. Patent: 4,001,028.

[3] Karkhanavala, M., and Hummel, F., 1953, "The Polymorphism of Cordierite". J. Am. Ceram. Soc. v. 36, No. 12, pp. 389-392.

[4] Blodgett, A., and Barbour, R., 1982, "Thermal conduction module, A high-performance multilayer ceramic package". IBM J. Res. Devel., pp 30-36.

[5] McMillan, 1985, "Development of the alpha-cordierite phase in glass-ceramics for use in electronic devices". Soc. Glass Tech., v. 6, No. 26, pp. 286-292.

[6] Cybulski, A; and Moulijn, A., 2005 "Structured Catalysts and Reactors" (2nd edition). CRC Press. pp.35.

[7] Miyashiro, A., Iiyama, T., 1954, "A preliminary note on a new mineral, indialite, polymorphic with cordierite". Proc. JPN. Acad., v. 30, pp 746-751.

[8] Choa, Y., Sekino, T., Adachi, T., Niihara, K., 2002. "Pressure less sintering and characterization of cordierite / ZrO$_2$ composites". Mater Res Innovations; 6(3):105–11.

[9] Suzuki, K., and Saito, H., (1988), "Mechanical properties of alkoxy-drived cordierite ceramics". J. Mater. Sci., 23, pp 1534-1538.

[10] Blodgett, A. J. and Barbour, D. R., (1982), "Thermal conduction module, a high-performance multilayer ceramic package". IBM J. Res. Devel., 26, pp 30-36.

[11] MacDowell, J., and Beall, G., 1990, "Cordierite – ceramics for microelectronic packaging. In Ceramic Transactions". J. Am. Ceram 8.

[12] Imer, K., Yener, D., Cinar, M., and Tas, C., 1996, "Synthesis of SiO$_2$, Enstatite and cordierite from isopropanol and ethanol solutions" 3rd ceramic congress, proceedings book, v. 2, pp 48-58, Istanbul, Turkey.

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