

The effect of fuel type and calcination temperature on the structure and morphology of fabricated nano-cordierite based on gel-combustion method

Aida Rahmani and Arman Sedghi*

Materials Engineering Department, Imam Khomeini International University, Qazvin 34149-16818, Iran

The aim of this study is to evaluate the influence of fuel type and temperature on the synthesis of nano-cordierite powder by gel combustion method. Two different fuels, urea and citric acid, along with silica fume and metal nitrates, as an oxidant, are used to prepare nano-cordierite powder. Ignited samples are calcinated in different temperatures and characterized by different analytical techniques such as thermal analysis (TG-DTA), X-ray Diffractometer (XRD), Fourier transform infrared spectroscopy (FTIR) and field emission electron microscope (FE-SEM). The Debye-Scherrer formula is used to calculate the average crystallite size. Although Analysis of XRD spectrum shows that α -cordierite nano-crystalline phase is formed completely, a minor spinel impurity phase is found in the structure. The average crystallite sizes calculated by FWHM are about 47 to 87 nm. Morphology of powders are identified by FESEM analysis. While the results of implemented method show that the particle size of powders is in nano-meter range, most of them are agglomerated.

Key words: Nano-cordierite, Gel-combustion, Fuel type, Urea, Citric acid.

Introduction

Cordierite ($2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$) is one of the important ternary compounds in $\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ system [1-3]. The cordierite is characterized by three polymorphs: ① α -cordierite, of hexagonal symmetry (space group P6/mcc), is a stable high-temperature modification. It must be noted α -cordierite named indialite [2, 4, 5], ② β -cordierite, of orthorhombic structure (space group Cccm), is a stable low-temperature modification [4, 5], and ③ μ -cordierite is a metastable low-temperature modification which is a solid solution with β -quartz structure [4].

Indialite has special properties such as low thermal expansion coefficient [1, 3, 5, 6], high refractoriness [3, 4], low dielectric constant and low dielectric loss at high frequencies [1, 3, 5, 7], high thermal shock resistance [1, 3-6], high mechanical strength [3, 7], high temperature stability [1] and outstanding chemical stability. These properties make cordierite based materials as the most potential candidate for many industrials applications, such as multilayer circuit boards [2, 3, 7], catalysts support in diverse processes [1, 3, 4], filters [2, 4, 5], kiln furniture [2], thermal insulation materials [3] and fairing [8].

Main methods for synthesis of cordierite are solid-state reactions [1-3, 9], liquid phase sintering, glass-ceramic route [1-3], sol-gel synthesis [1-3, 5, 10] and mechanochemical treatments [11]. The most conventional ways to synthesis cordierite are solid-state reaction and crystallizations of

its glassy products [3, 5, 9]. However, these methods have several disadvantages such as narrow firing range. Therefore, many researches have used chemical synthesis in order to reduce synthesis and sintering temperature of α -cordierite [4]. Gel combustion is a new method for fabrication of nano sized oxide ceramic due to its remarkable advantages such as less processing duration, low processing temperature and homogeneous products [12, 13].

Ianos et al. [4] examined fabrication of cordierite by using gel combustion method and α -cordierite obtained by thermal treatment at 1300 °C for 1 hr but its fabrication parameters and samples morphology was not completely studied. In another study Sedghi et al. [14] synthesized nano-cordierite by the solution combustion technique using fuel glycine. This paper investigates the fabrication of cordierite nanopowders by gel combustion method using urea and citric acid as a fuel. It also analyzed the effect of fabrication parameters on its structure and morphologies.

Experimental

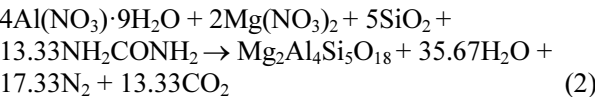
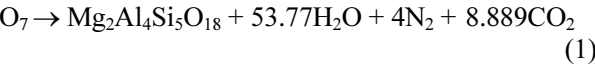
For synthesis of cordierite nano powders, analytical grades of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, silica fume (as SiO_2 source), urea ($\text{CH}_2\text{N}_2\text{O}$) and citric acid ($\text{C}_6\text{H}_8\text{O}_7$) (all of them from Scharlau company, Spain) are used as raw materials. The starting raw materials are dissolved in distilled water and reacted at the stoichiometric ratio based on the (1) and (2) which their ratios are summarized in Table 1.



*Corresponding author:
Tel : +98-2833901156
Fax: +98-2833901124
E-mail: sedghi@eng.ikiu.ac.ir

Table 1. Raw material ratios which were used for combustion reaction.

Sample No.	Sample composition (molar ratio)					Combustion Temperature
	Mg (NO ₃) ₂	Al (NO ₃) ₃	SiO ₂	C ₆ H ₈ O ₇		
1	2	4	5	—	4.444	500 C
2	2	4	5	13.33	—	500 C



The mixtures are continuously stirred on a magnetic stirrer hot plate at 70 °C until viscous gel-like liquid are formed. After this stage, in order to initiate the combustion reaction of samples 1 and 2, the capsules with the concentrated solution are placed in the electric furnace per heated at 500 °C. After the combustion reactions are finalized, the voluminous ash powders are easily crumbled and calcinated at 800 °C, 1000 °C, 1100 °C, 1200 °C, 1250 °C, 1300 °C and 1350 °C for 1hr in electrical furnace.

TG-DTA is carried out on dried gels in N₂ atmosphere up to 800 °C at 10 °C min⁻¹ heating rate by Perkin Elmer, (Pyris Diamond) Thermal analyser. The IRS of calcinated powder is recorded over Tensor 27. Phase structure of samples was studied by XRD (Philips XL30) and their crystallite size was determined by using Scherrer formula (3):

$$D = \frac{K\lambda}{\beta(2\theta)\cos\theta} \quad (3)$$

Where, λ is the wavelength (= 0.15406 nm), θ the

Bragg angle, k the constant (0.94), and D is the crystallite size. The half-width of the diffraction line β (2θ) (in radians) was calculated from 5 which in this equation, half-width was measured from main XRD peaks and instrumental broadening (β_{instr}) was calculated from XRD calibration procedure [4].

$$\beta(2\theta) = (\beta_{\text{exp}}^2 - \beta_{\text{instr}}^2)^{1/2} \quad (4)$$

The morphology of nano powders and agglomeration condition of calcinated nano-cordierite powders was characterized by FE-SEM (Hitachi 4160). Flow chart of the experimental procedure for synthesis and characterization of cordierite is shown in fig.1.

Result and Discussion

Fig. 2 and Fig. 3 show the diagram of simultaneous thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) of 1 and 2 samples dried gels, respectively. The DTA-TG curve of sample 1 (Fig. 2)

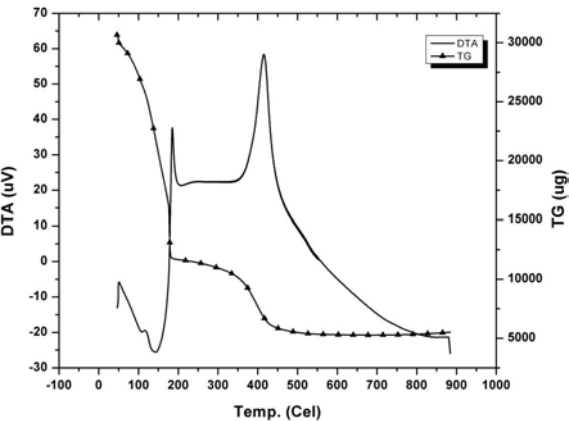


Fig. 2. TG-DTA curves of sample 1 at a heating rate of 10 °C/min.

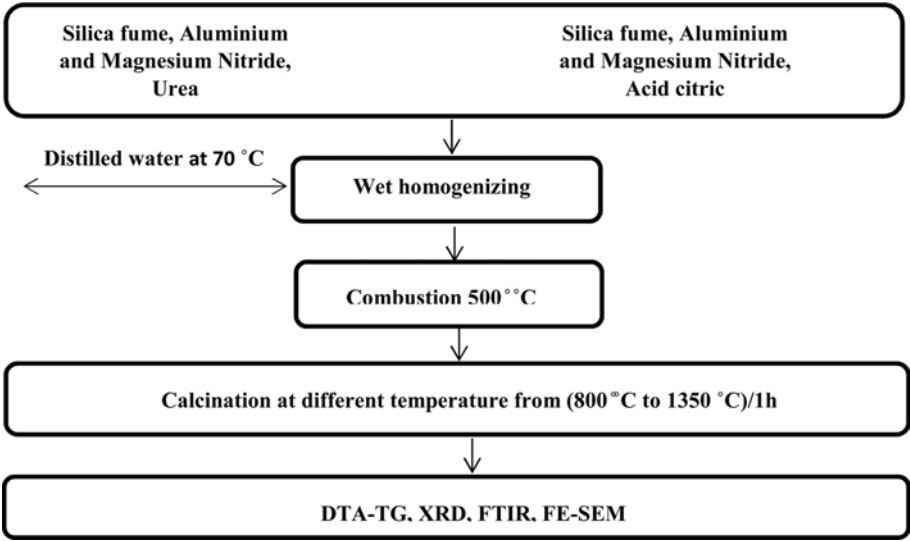


Fig. 1. Flowchart of the experimental procedure for synthesis and characterization of sample.

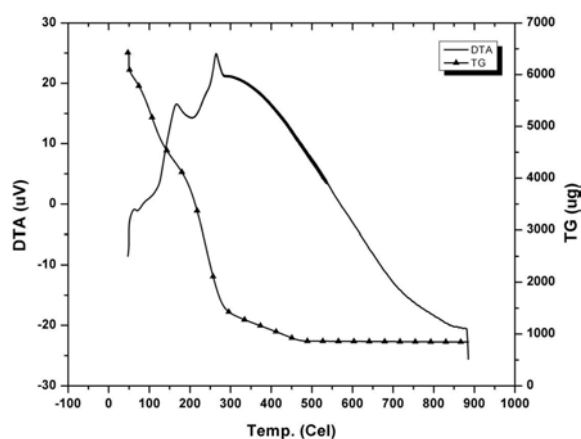


Fig. 3. TG-DTA curves of sample 2 at a heating rate of 10 °C/min.

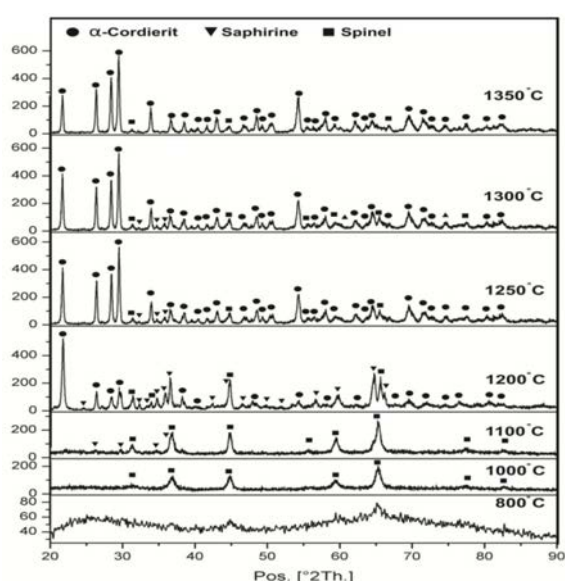


Fig. 4. XRD curves of sample 1.

reveals that the first endothermic peak happens at around 140 °C, corresponding to 35% weight loss, which is attributed to absorbed water evaporation and the aluminum nitrate and citric acid decomposition. According to TGA curve a gradual weight loss is detected from 60 °C to 172.5 °C. Two present exothermic peaks on the DTA curve suggest that combustion process performs at two stages. The first exothermic peak appears at about 187 °C, leading to 18% weight loss from the combustion reaction of aluminum nitrate and citric acid, which stimulates the redox reaction of magnesium nitrate and citric acid (410 °C).

As shown in Fig. 3, the endothermic peak is appeared around 73 °C which due to the evaporation absorption water and the aluminum nitrate and urea decomposition. TGA curve suggests that the total weight loss is 5%. It is obvious that the two exothermic peak appearances on the DTA plot are associated with a two-stage combustion process. The first exothermic peak, related to the combustion reaction aluminum nitrate and urea is

appeared at about 174 °C, leading to a weight loss of 10%. The second obvious exothermic peak, corresponding to the redox reaction of magnesium nitrate and urea is revealed at about 296 °C, leading to maximum 15% weight loss. Based on Fig. 3, the endothermic peak is appeared at around 73 °C which seems to be associated with the absorbed water release and aluminum nitrate and urea decomposition. Based on DTA curve, it is possible to find out that there is a two-stage combustion process. This is similar to our findings based on Fig. 2. The first obvious exothermic peak, may be related to combustion reaction of aluminum nitrate and urea at about 174 °C, leading to 10% weight loss. The second obvious exothermic peak, corresponding to the redox reaction of magnesium nitrate and urea is performed at about 296 °C, leading 15% weight loss.

DTA results suggest that the combustion process of citric acid and urea is completed at two-stage, whereas Sedghi et al. [14] reported combustion reaction of glycine occurs at 225 °C and hence the combustion process of dried gel is a one-stage process. In comparison to citric acid and urea, the combustion reaction of glycine is most exothermic and also causes more heat release during combustion. In another study, Sedghi et al. [16] studied synthesis of titanium oxide nano powder by gel-combustion method with glycine, citric acid and urea fuels. Their DTA results show that the combustion process of citric acid and urea completed at one-stage which is different from our findings. This suggests that raw materials and type of fuel directly affect combustion reaction.

Figs. 5 and 6 show the X-ray diffraction pattern of calcinated powder of sample 1 and 2 after calcination in different temperatures, respectively. According to Fig. 5, after calcination at 800 °C no crystalline peaks are observed at sample 1. Crystallization of powder is improved at 1000 °C and Spinel is formed as first crystalline phase after calcination at 1000 °C. When the calcination temperature rises to 1100 °C, intermediate sapphirine phase is appeared. The peak intensities of spinel increase at this temperature. The peaks related to α -cordierite are shown after 1200 °C calcination. Also the sapphirine peaks increase after 1200 °C thermal treatment. By increasing temperature up to 1250 °C, amount of α -cordierite phase increases on the other side, the peak intensities for spinel and sapphirine decrease. At 1300 °C, specific changes are not seen. When the sample was calcinated at 1350 °C, the major phase identified is α -cordierite. The sapphirine phase also disappeared at this temperature. Based on above observation, it seems that a small amount of spinel remains at 1350 °C.

The XRD patterns of samples 1 and 2 (Figs. 5 and 6) exhibit a similar pattern. The only difference is the peaks intensity; the peaks of sample 2 are more intense. According to Figs 5 and 6, α -cordierite could not be formed directly from the combustion reaction. It is particularly

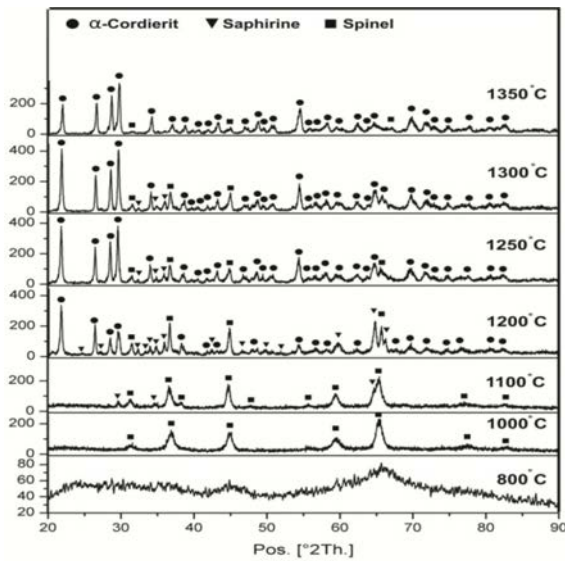


Fig. 5. XRD curves of sample 2.

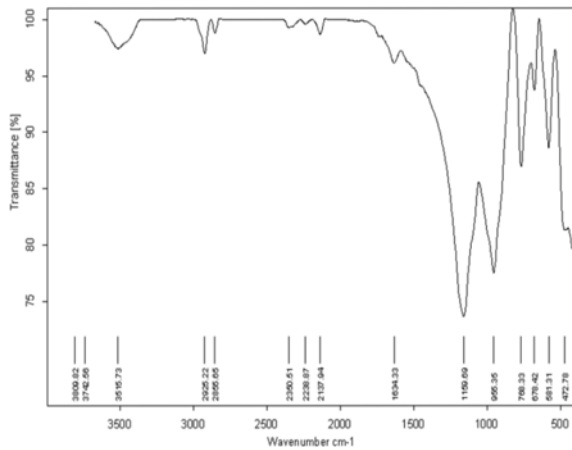


Fig. 6. FTIR spectra of sample 1 at 1350 °C.

related to two facts; first, SiO_2 acts as an inert substance in combustion reaction behavior. Second, the reaction duration is short and/or the combustion temperature is insufficient. Then, formation of α -cordierite is occurred after additional thermal treatments of combustion products [4, 14]

Sedghi et al. [14] reported that the α -cordierite is formed through the reaction of intermediate phases such as spinel, cristobalite, sapphirine, enstatite, alumina and sillimanite. Based on this hypothesis, first, spinel is formed and then it is converted to sapphirine through the chemical reactions with cristobalite. In the samples 1 and 2, cristobalite probably is formed at the temperature between 1000 °C and 1100 °C. Formation of α -cordierite during thermal treatment of powders has already been reported. Sembiring and Manurung [17] used rice husk silica, as a raw material, for the cordierite synthesis; the X-ray diffraction patterns of their samples reveal that α -cordierite is formed through reaction of cristobalite, corundum, spinel and periclase intermediate phases at

Table 2. Average crystallite size of sample 1 and 2 at different calcination temperature.

Calcination Temperature [°C]	Average Crystallite Size [nm] Sample 1	Average Crystallite Size [nm] Sample 2
800	—	—
1000	—	—
1100	—	—
1200	47	56
1250	56	71
1300	74	76
1350	78	87

1500 °C. Robert Ianos et al. [4] studied solution combustion synthesis of α -cordierite. They show that in the sample prepared by using triethylenetetramine, after calcination at 1300 °C, α -cordierite is main phase. However, they further show that in the sample prepared by using urea and monoethanolamine fuel mixture the major phase identified is α -cordierite along traces of spinel and cristobalite. J.R. Gonzalez-Velasco in [9] shows that cordierite monolithic honeycomb is prepared successfully by solid state reaction of precursor oxides, cordierite synthesized at 1400 °C for 40 minutes and a small trace of spinel and α -alumina. Sedghi et al. [14] reported 1250 °C as the synthesis temperature of cordierite. In our study the synthesis temperature of cordierite is occurred at 1350 °C, which is different from the temperature reported in other studies [4, 5, 17]. It is important to note that using glycine as fuel could bring down the formation temperature of α -cordierite by about 100 °C, compared to using urea and citric acid.

The X-ray diffraction patterns do not expose any sign of μ -cordierite. This result is similar to some previous reports [4, 14, 18], though B. Tang et al. [5] and A.F Affendi [19] have revealed the presence of μ -cordierite phase when nanopowders formed from water-based sol-gel. Table 2 summarizes the average crystallite size of calcinated nano cordierite powders of sample 1 and 2 at various calcination temperatures, respectively. The evaluation of crystallite size is determined based on Scherrer equation. The main diffraction peaks of (100), (211) and (202) planes are selected to measure the crystallite size. The cordierite crystallites show wide size range from 47 to 87 nm which may be due to their crystallite growth orientation. It is obvious that the size and the number of the grains of the nanocrystallite powders increase at higher calcinated temperatures. In a recent paper by A. Cheraghi and R. Malekfar [20], the size of the crystallites is calculated by Debye-Scherrer and includes a range of 27 to 120 nm. Sedghi et al. [14] in their paper reports the average crystallite size as about 61 nm.

The FTIR pattern of samples 1 and 2 synthesized and thermally treated at optimum temperatures for 1hr are

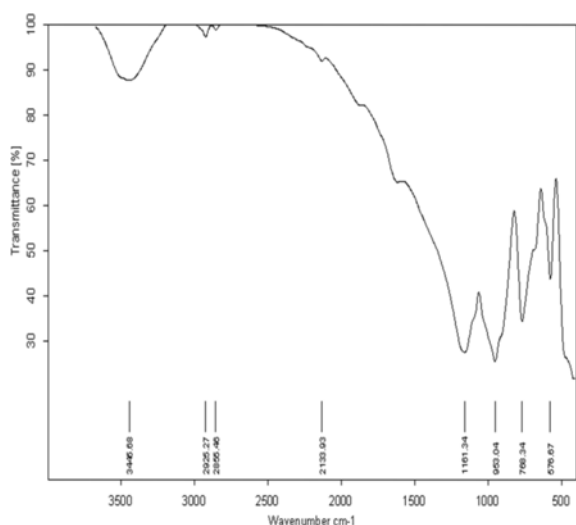


Fig. 7. FTIR spectra of sample 2 at 1350 °C.

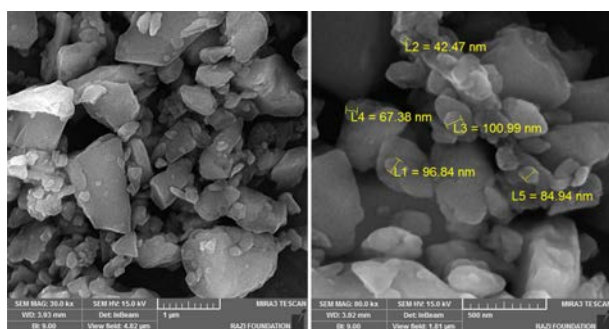


Fig. 8. Nanostructure of sample 1 at temperature of 1350 °C by FE-SEM.

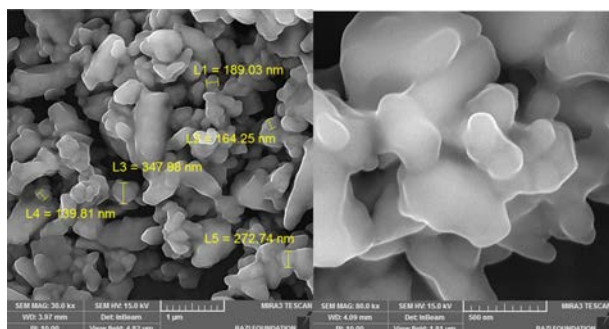


Fig. 9. Nanostructure of sample 2 at temperature of 1350 °C by FE-SEM.

illustrated in Figs. 8 and 9. The characterization of FTIR spectra are also shown in Tables 3 and 4. Radev et al. [21] reported a band centered at $\sim 590 \text{ cm}^{-1}$ corresponds to MgO_6 octahedra, a band at $\sim 920 \text{ cm}^{-1}$ corresponds to the AlO_4 tetrahedra, a band at $\sim 1160 \text{ cm}^{-1}$ corresponds to the presence of SiO_4 tetrahedra in α -cordierite. They also reported presence of bands in μ -cordierite. In other study, Cheraghi and Malekfar [20] reported a band at $\sim 1085 \text{ cm}^{-1}$ corresponding to SiO_4 tetrahedra and also a band at $\sim 512 \text{ cm}^{-1}$ corresponding to AlO_6 in μ -cordierite. In our study, according to the results of XRD patterns, no absorption peak related to μ -

Table 3. FTIR spectral results for the sample 1, synthesized at 1350°C/1hr calcinations temperature.

Wave Num. (cm^{-1})	Phase Type	Structural Type	Bond Type
677	Spinel	SiO_4	Stretching
768	α -cordierite	SiO_4	Stretching
953	α -cordierite	AlO_4	Stretching
1161	α -cordierite	SiO_4	Stretching Antisymm

Table 4. FTIR spectral results for the sample 2, synthesized at 1350 °C/1 h calcinations temperature.

Wave num. (cm^{-1})	Phase Type	Structural Type	Bond Type
577	α -cordierite	MgO_6	Stretching
672	Spinel	SiO_4	Stretching
769	α -cordierite	SiO_4	Stretching
957	α -cordierite	AlO_4	Stretching
1161	α -cordierite	SiO_4	Stretching Antisymm

cordierite are shown. The results of FTIR analysis confirmed the results of XRD patterns.

Nanostructure of samples with different types of fuel is shown in Fig. 10 and Fig. 11. The results show that the particle size of powders is in nano meter ranges. In contrast to fuel citric acid, crystallites size is smaller in prepared powder by using urea. Sedghi et al. [14] and Tang et al. [5] prepare α -cordierite phase with particle size of less than $2 \mu\text{m}$, using water-based sol-gel method. In another study, S.Wang et al. [7] synthesized nano cordierite powder by sol-emulsion-gel method. Our results have confirmed that this method is feasible for fabrication of nano cordierite.

Conclusions

The following results were obtained:

- 1) α -cordierite nano powder has been fabricated successfully by gel combustion method with citric acid and urea as fuel, and based on FESEM results, the particle size of powders was in nanometer ranges.
- 2) Based on TG-DTA results, it can be concluded that combustion process of citric acid and urea was a two-stage process and take place at about (187-410) °C and (174-296) °C, respectively. However, α -cordierite nano powder was formed after further thermal treatment.
- 3) The average crystallite size of all sample was about (47-87) nm at the optimum temperature.

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