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Formation of Anorthite Containing Cordierite Materials through Reaction Sintering Kaolin, MgO and CaO Precursors

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Abstract:

The effect of CaO on cordierite formation from kaolin-MgO-CaO powder mixtures, milled for 5 h and reaction sintered for 2 h in the temperature range 900-1400 °C, was investigated. Phases formed in the developed materials were characterized by x-ray powder diffraction method (XRD) and Raman spectroscopy. Non-isothermal differential thermal analysis (DTA) and thermogravimetric (TG) experiments were performed from room temperature to 1400 °C, at heating rates from 20 to 40 °C/min. Activation energies were determined using Kissinger method. It was found that sintering the stoichiometric kaolin-magnesia mixture led to the nucleation and growth of monolithic cordierite; while cordierite along with anorthite were present in the other two samples where 4 or 8 wt% of CaO was added. The increase in CaO decreased cordierite formation temperature and increased the activation energy, which ranged from 445 to 619 kJ/mol for μ -cordierite and from 604 to 1335 kJ/mol for α -cordierite.

Keywords: Clays; MgO; Cordierite; Sintering; Kinetics.

1. Introduction

It is known that kaolin, a natural clay mineral composed primarily of Al₂O₃ and SiO₂, experiences many reactions and transformations where the oxides and additives react to yield mullite [1] or cordierite [2, 3] based materials. As one of the main phases of the magnesia-alumina-silica system, cordierite has values of 2.53 g/cm³, 1470 °C, and $10^{12} \Omega \text{ cm}$ for its density, melting temperature, and electrical resistivity, respectively. Additionally it has very low thermal expansion (values of α between 10^{-6} to $2 \times 10^{-6} \text{ C}^{-1}$) and conductivity. Furthermore, it possesses satisfactory mechanical characteristics and is very stable in harsh environments [4, 5]. Because of these attributes, cordierite materials are widely used in several industries [4-7]. They are candidate materials for packaging and thermal insulation

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applications [7]. Moreover, they are very suitable for making turbine heat exchanger components or supports for catalysts in the automotive industry [4-6].

Due to the unavailability of cordierite as natural material [8], it is usually prepared from diverse raw and/or waste materials using many methods [8-17]. However, reaction sintering abundant natural clay minerals and/or waste [4, 7, 18-24] remained the preferred way to produce unexpansive cordierite materials. Intentionally, additives such as nickel dioxide [25], zinc [26], phosphorous and boron oxides [27], phosphorous oxide [28], ceria [29], nickel dioxide and titania [30], barium oxide [31], magnesia [32, 33], and calcium oxide [8, 34-37] are added to ease the nucleation and growth of cordierite.

Boudchichaat *et al.* [8] developed anorthite and cordierite based materials through sintering of a glass powder, of the calcium oxide–magnesia–alumina–silica system, prepared by melting followed by quenching and crushing. Yin *et al.* [34] prepared magnesia-alumina-silica based glass ceramics by melting method using pure chemical reagents and found that certain content of CaO promotes the glass crystallization, and transfers sapphirine to α -cordierite. Also, addition of CaO in the presence [35] or absence of B₂O₃ [36] was reported to improve sintering and the formation of cordierite in glass–ceramics prepared via sol–gel method. Similar trend was observed by Guo-hua Chen [37] who investigated the influence of replacing magnesium oxide by calcium oxide on phases formed in the magnesia–alumina–silica system.

The formation of cordierite and phase transformation kinetics in cordierite materials [8, 25-31, 38-41] were characterized by differential thermal analysis [28-31, 38-39], differential scanning calorimetry [8, 39-40], and x-ray diffraction [8, 25-27]. Isothermal [25-27, 35] and non-isothermal [8, 25, 28-31, 38-41] experiments were carried out and activation energy values from 170 to 964 kJ/mol were reported [8, 2, 3, 25-31, 38-43]. Recently, the authors synthesized low-cost stoichiometric [2] and non-stoichiometric [3] cordierite ceramic materials, by reaction sintering Algerian natural clay minerals and synthetic magnesia, and studied the effect of temperature and MgO on cordierite formation. The objectives of this study are to investigate and report the influence of CaO content on the kinetics of cordierite formation from kaolin-MgO-CaO powder mixtures and explore the possibility to reduce the synthesis temperature.

2. Materials and Experimental Procedures

Two natural clay minerals named DD1 and TK kaolin were used in this work; their chemical compositions are presented in Table I. Three powder mixtures of DD1 kaolin, TK kaolin, MgO, and CaO were prepared. The first mixture contains 59, 29 and 12 wt.% of Kaolin DD1, Tamazarte kaolin TK, and MgO, respectively, to prepare monolithic cordierite sample abbreviated DTM00C. The second and third powder mixtures contained extra 4 and 8 wt.% CaO, respectively, to prepare cordierite ceramic materials named DTM04C and DTM08C. The powder mixtures were milled for 5h and sintered for 2 h between 900 and 1350 °C.

TG/DTA experiments were performed from room temperature to 1400 °C. The samples were heated at 20, 30, 40, and 50 °C/min using LABSYS EVO DTA/DSC-TG SETARAM equipment. In order to characterize the phases formed in the samples, a diffractometer MRD, PANalytical (ISM) with CuK α radiation of a wavelength 0.15418 nm, and a BRUKER SENTERRA Raman spectroscopy apparatus were used. Activation energies were determined from DTA results [2-3].

The Kissinger method as explained presented in reference [3] was “used to calculate the non-isothermal activation energy (E_A) for the formation of cordierite according to equation” 1.

$$\ln\left(\frac{\varphi}{T_p^2}\right) = -\frac{E_A}{RT_p} + C_1 \quad (1)$$

“where φ [$^{\circ}\text{C min}^{-1}$] is the heating rate, E_A [kJ mol^{-1}] is the energy of formation, T_p [$^{\circ}\text{C}$] is the absolute peak temperature in DTA curves, and R is the gas constant”.

Tab. I Composition of the two natural clay minerals (wt.%).

Kaolin	Al ₂ O ₃	SiO ₂	Na ₂ O	SO ₃	K ₂ O	MgO	CaO	MnO	Fe ₂ O ₃	TiO ₂	LOI
KT	19.29	69.86	0.13	0.03	2.67	0.4	0.4	-	0.72	0.4	6.31
DD1	39.13	45.30	0.04	-	0.21	0.05	0.15	0.02	0.07	-	14

3. Results and Discussion

Typical TG/DTG and DTA resulting curves for DTM08C sample, which was heated to 1300 $^{\circ}\text{C}$ at 20 $^{\circ}\text{C}/\text{min}$, are presented in Figure 1 (a) and (b), respectively. The DTA curve shows the presence of three endothermic peaks at 125, 445 and 560 $^{\circ}\text{C}$ besides five exothermic peaks at 963, 1002, 1140, 1232, and 1262 $^{\circ}\text{C}$. Three mass losses are observed on the TG curve. The first 4 wt% mass loss (57–300 $^{\circ}\text{C}$) results from the loss of adsorbed water and matches the endothermic peaks at 125 and 122 $^{\circ}\text{C}$ seen on the DTG and DTA curves, respectively. The second 5 wt% mass loss (300–500 $^{\circ}\text{C}$) is characteristic of the dehydration of magnesium hydroxide and calcium hydroxide and corresponds to endothermic peaks at 445 and 452 $^{\circ}\text{C}$ present on the DTG and DTA curves, respectively. The third 11 wt% mass loss (500–700 $^{\circ}\text{C}$) is related to change of the dehydroxylated kaolinite to metakaolinite and matches the endothermic peaks at 560 and 568 $^{\circ}\text{C}$ seen in the DTG and DTA curves, respectively. As for the exothermic peaks, the first and second peak at 963 and 1002 $^{\circ}\text{C}$ are associated with spinel and anorthite formation, respectively. The third peak at 1140 $^{\circ}\text{C}$ is related to the formation of cristobalite, mullite, and sapphirine phases. The fourth and fifth peak at 1232 and 1262 $^{\circ}\text{C}$ are characteristic of the μ and α cordierite, respectively. DTA curves of DTM00C, DTM04C and DTM08C powders heated between 800 and 1400 $^{\circ}\text{C}$ at a heating rate of 20 $^{\circ}\text{C}/\text{min}$, are shown in Figure 2. From these DTA results, one can conclude that exception the formation of the anorthite phase in DTM00C and DTM04C samples, the same phases were present in all samples. This eventually yielded cordierite single phase in DTM00C sample, and cordierite along with anorthite in and DTM04C and DT08M samples.

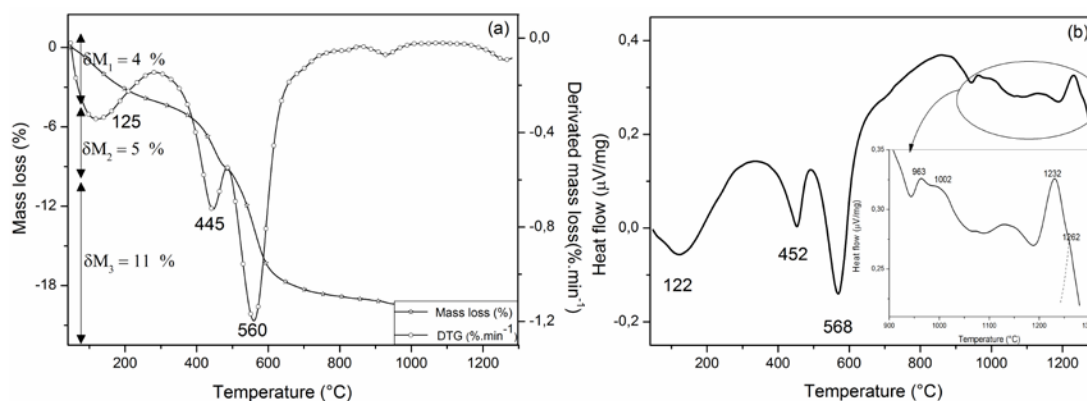


Fig. 1. TG, DTG (a) and DTA (b) curves for DTM08C powder heated at 20 $^{\circ}\text{C}/\text{min}$.

Figure 2 shows that the peak temperature (T_p) at which α -cordierite forms decreased with the increase in CaO from 0 wt% (sample DTM00C) to 8 wt% (sample DTM08C). This agrees with the results of Yin *et. al.* [34] who prepared magnesia-alumina-silica based glass ceramics by melting method using pure chemical reagents and found that, at certain content, CaO promotes the glass crystallization, and transfers sapphirine to α -cordierite. In addition, it supports the fact that addition of CaO in the presence [35] or absence [36] of B_2O_3 improves sintering and the formation of cordierite in glass-ceramics prepared via sol-gel method. Similar trend was observed by Guo-hua Chen [37] who partially replaced MgO by CaO in the magnesia-alumina-silica system.

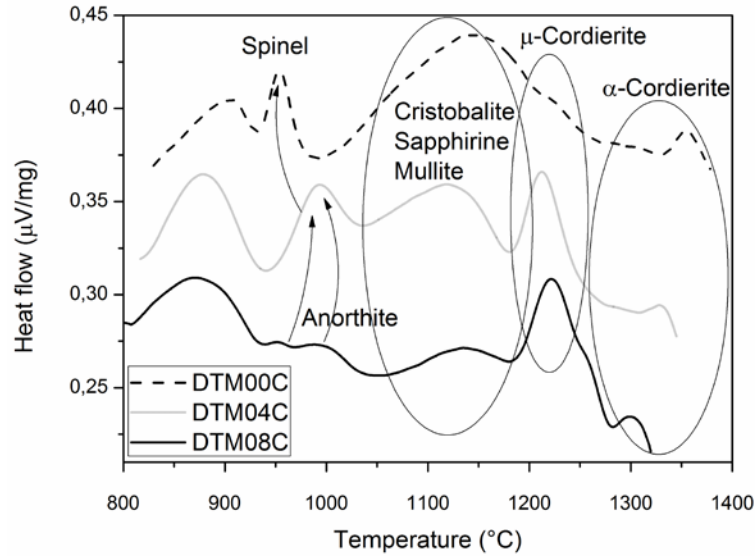


Fig. 2. DTA curves of DTM00C, DTM04C and DTM08C powders heated between 800 and 1400 °C at a heating rate of 20 °C/min.

Figure 3 shows DTA curves of DTM00C and DTM08C powders heated between 900 and 1400 °C at 20, 30, 40, and 50 °C/min. The shift of the peak temperature positions towards higher temperatures, with the increase in the heating rate, can be clearly noticed on Figure 3.

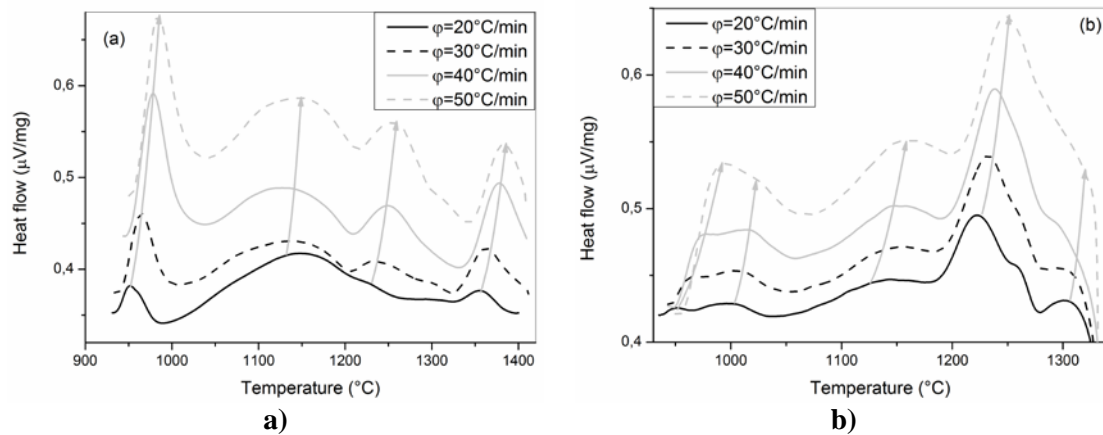


Fig. 3. DTA curves of DTM00C (a) and DTM08C (b) at four different heating rates in the 900-1400 °C temperature range.

Figure 4 shows plots of $\ln(\phi/T_p^2)$ versus $(1/T_p)$ for the formation of α -cordierite and μ -cordierite, at different heating rates, in DTM00C, DTM04C, and DTM08C samples. The α -cordierite and μ -cordierite formation energy values, calculated using Kissinger method, from non-isothermal DTA measurements are presented in figure 4. The obtained values for DTM00C sample were equal to 445 and 604 kJ mol⁻¹, respectively. The same energies were 632 and 1152 kJ mol⁻¹ for DTM04C sample, and 619 and 1335 kJ mol⁻¹ for DTM08C sample.

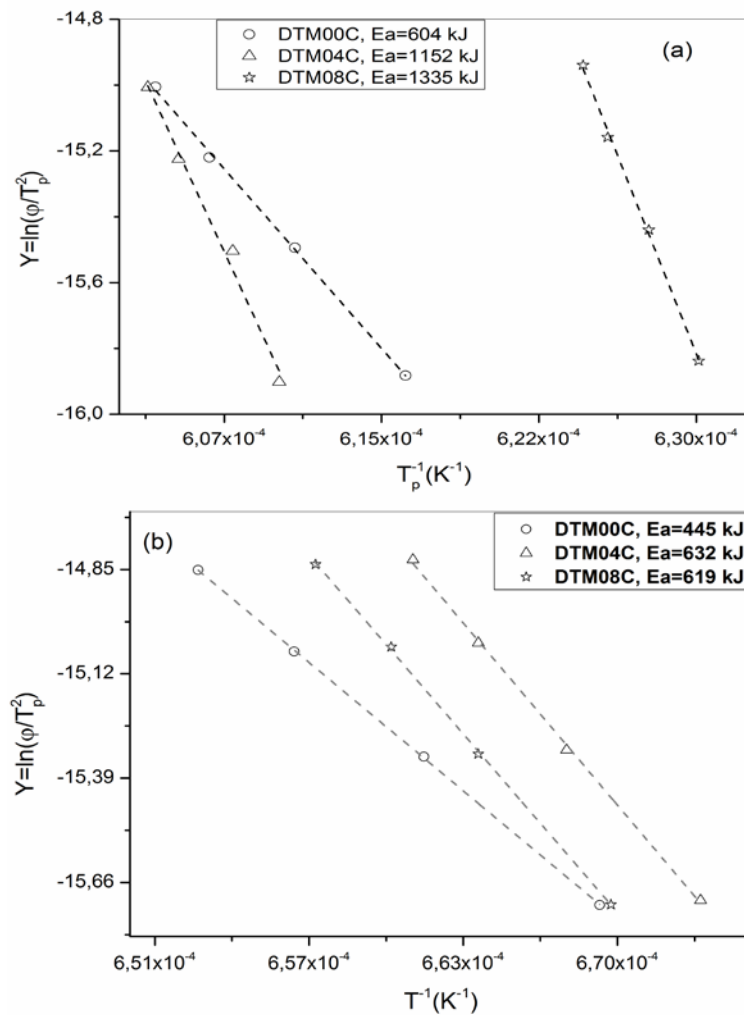


Fig. 4. Plot of $\ln(\phi/T_p^2)$ versus $(1/T_p)$ of (a) α -cordierite formation and (b) μ -cordierite formation at different heating rates for DTM00C, DTM04C, and DTM08C powders.

The activation energies for the formation of μ and α cordierite as function of CaO content (wt%) are shown in figure 5. The activation energy for μ -cordierite and α -cordierite increased with CaO addition. The increase in CaO content from 00 to 08 wt% increased the value of activation energy from 445 to 619 kJ mol⁻¹ for μ -cordierite and from 604 to 1335 kJ mol⁻¹ for α -cordierite. These activation energy values fall within the range reported in the literature by researchers who synthesized cordierite from different materials and evaluated cordierite energy formation from non-isothermal DTA or DSC measurements [8, 29-31, 38-41]. Boudchichaat *al.* [8] obtained anorthite and cordierite rich materials through sintering of a glass powder, of the calcium oxide–magnesia–alumina–silica system, prepared by melting followed by quenching and crushing. The author reported a value of 450 kJ/mol for the activation energy of crystallization. Donald [39] obtained cordierite from mixtures of

alumina, silica, and magnesia; he reported activation energies between 532 and 574 for μ -cordierite and between 399 and 426 kJ/mol for α -cordierite. Kim and Lee [29] obtained average energy values of 653 and 418 kJ/mol for cordierite developed from the crystallization of ceria free and ceria containing glasses, respectively. This indicates that the addition of ceria decreased cordierite energy formation [29]. Cordierite formation from titania doped magnesia-alumina-silica glass was investigated by Goel and co-workers [41]. They achieved formation energy values of 340 and 498 kJ/mol for μ -cordierite and α -cordierite, respectively. Hu and Tsai [31] reported energy value of 366 kJ/mol and values between 290 and 487 kJ/mol for the formation of cordierite in barium dioxide free and barium dioxide containing samples, respectively. The authors concluded that crystallization of α -cordierite might be suppressed by the addition of small amount of barium dioxide. Additionally, they observed that energy for cordierite formation first increased and then decreased gradually with the increase in BaO content. Activation energy for the crystallization of cordierite from diphasic gels was found to be equal to 467 kJ/mol [38]. Song and co-researchers [40] obtained cordierite through the crystallization of potassium and feldspar and reported values from 230.77 to 279.81 kJ/mol for the activation energy of formation of α -cordierite. However, in the presence of leucite these values increased to 348.85-374.33 kJ/mol. Activation energy values for the formation of μ -cordierite and α -cordierite in NiO-added glass samples [30] were equal to 300 and 500 kJ/mol, respectively. Başaran and co-workers used industrial waste to prepare cordierite materials and obtained energy values of 410 kJ/mol [42] for cordierite formed in the titania doped magnesia–alumina–silica glass; and values of 336, 218, and 170 kJ/mol [43] for cordierite formed in the same system when Bi₂O₃ was added at 2.5, 5, and 10 wt.%, respectively. This clearly shows that co-doping with TiO₂ and Bi₂O₃ decreased the activation energy for cordierite formation in the magnesia–alumina–silica glass.

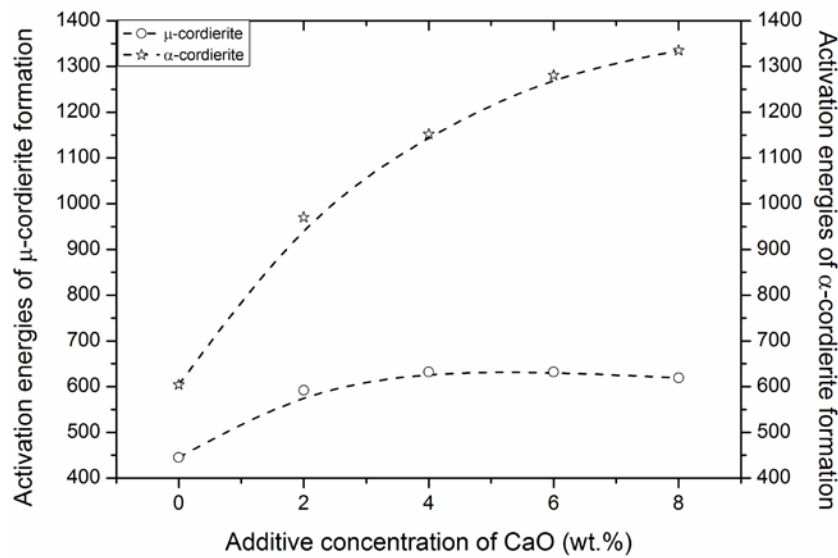


Fig. 5. Influence of CaO content on the activation energy of cordierite formation.

X-ray diffraction spectra of DTM00C, DTM04C, and DTM08C samples sintered at 950, 1050, 1150, and 1250 °C for 2 h, and the corresponding weight fraction of phases are shown in figure 6 and 7 respectively. For DTM00C sample, quartz, spinel, and mullite phases were present at 1050 °C. The sapphirine phase formed and the spinel phase disappeared upon the increase in temperature to 1050 °C, and a further increase to 1150 °C resulted in the formation of cristobalite phase, which coexisted with sapphirine phase. At 1250 °C, only α -cordierite was detected. Similar phases formed in DTM04C and DTM08C samples along with anorthite phase. In addition, μ -cordierite appeared in these samples at 1150 °C and

transformed to α -cordierite at 1250 °C. This is in agreement with DTA results, which showed the presence α -cordierite at 1262 °C.

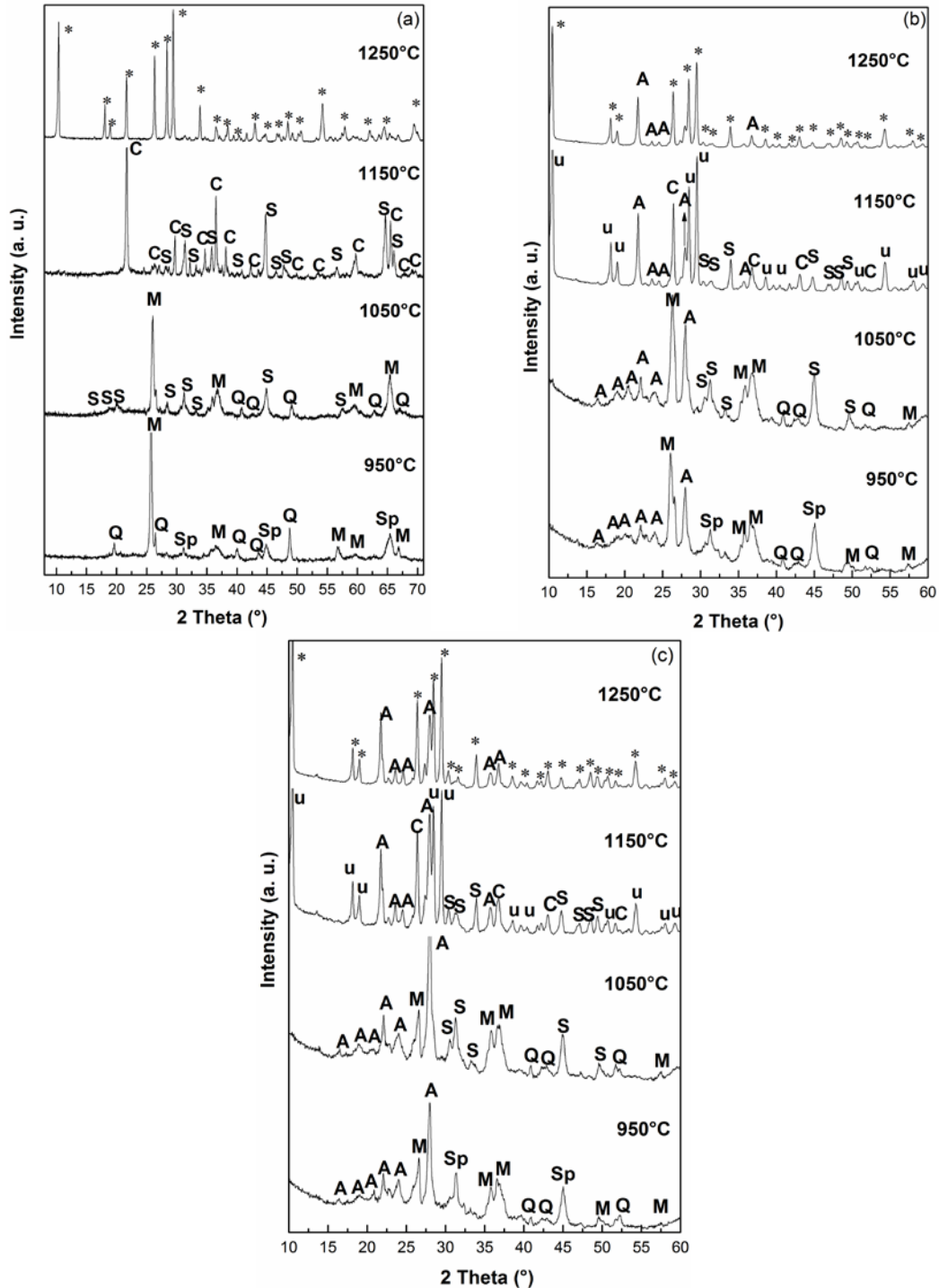


Fig.6. XRD patterns of DTM00C (a), DTM04C (b) and DTM08C (c) powders treated at different temperatures for 2 h. Q: quartz, Sp: spinel, M: mullite, S: sapphirine, A: anorthite, C: cristobalite, μ : μ - cordierite and *: α - cordierite).

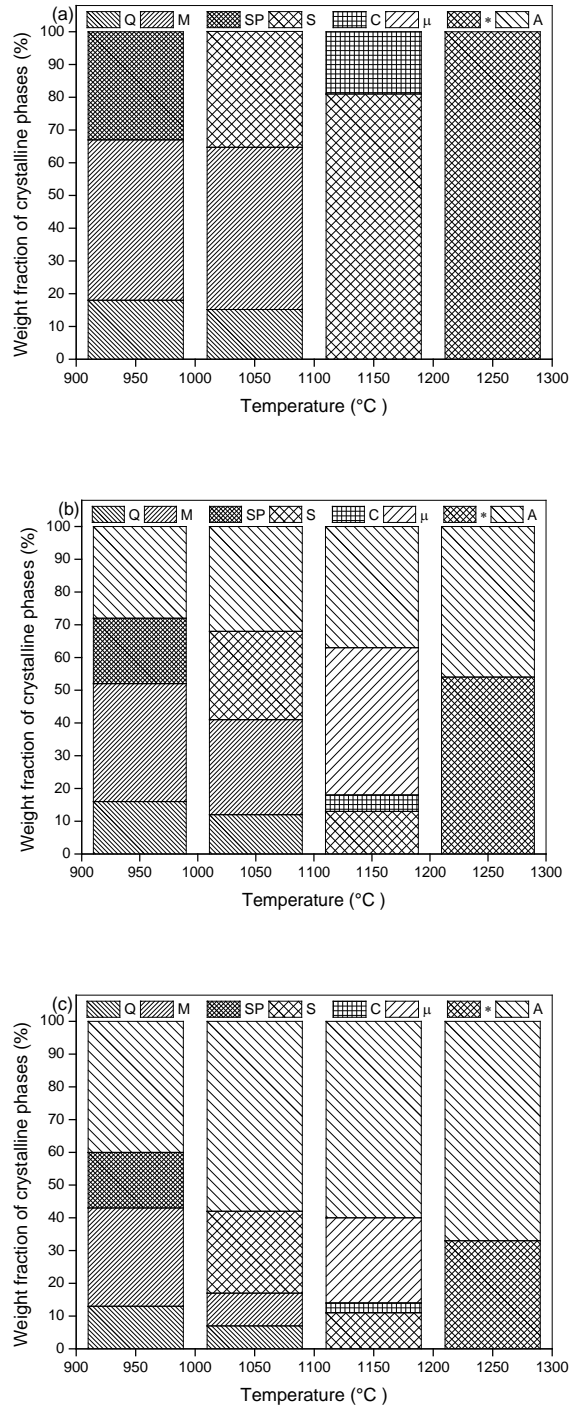


Fig. 7. Weight fraction of phases present in (a) DT00C, (b) DT04C, and (c) DT08C samples sintered at different temperature for 2 h (Sp: spinel, Q: quartz, M: Mullite, S: Sapphirine, A: anorthite, μ : μ -Cordierite, *: α -Cordierite).

Figure 8 shows Raman spectra of the powders treated at different temperatures for 2 h. The formed phases and their associated peak positions are presented in Table II. It can be clearly noticed that the same phases formed, at each temperature, in all samples exception that anorthite appeared only in samples containing CaO. The cordierite phase started to form at

1150 °C in all samples. At 1250 °C, it existed as a single phase in DTM00C sample; however, it was present along with anorthite in DTM04C and DT08M samples. The Raman results are in agreement with the DTA and XRD results discussed above. Anorthite was reported to form as major crystalline phase in cordierite/anorthite composites [44] prepared from a mixture of sugar beat filter cake and talc carbonate. In other works, researchers reported the crystallization of anorthite in calcium oxide–magnesia–alumina–silica glass ceramics obtained from waste material and $(\text{CaMg}(\text{CO}_3)_2)$ [45] or CaCO_3 [46]. This clearly indicates that phases formed in cordierite materials do depend on the synthesis method, starting raw materials, and the addition of additives and/or sintering aids.

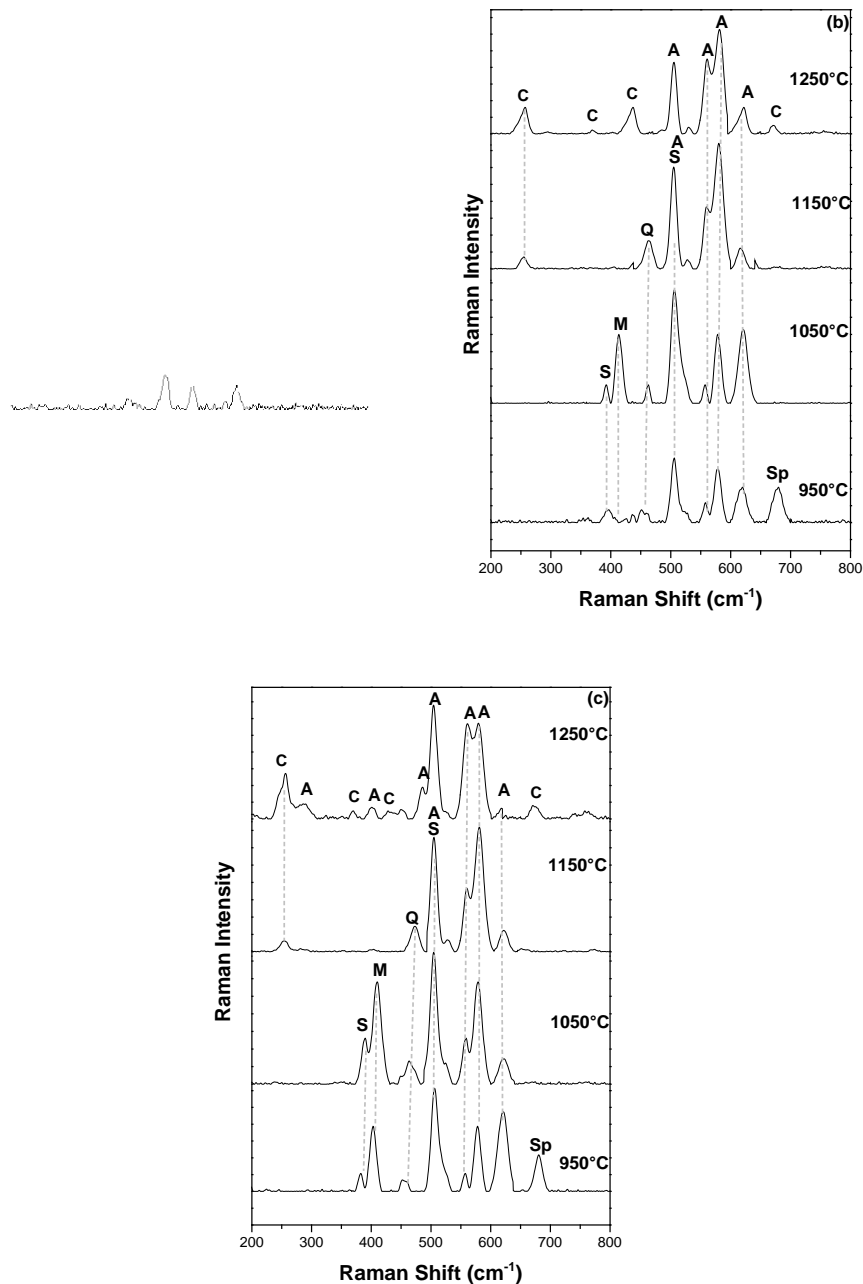


Fig. 8. Raman spectra of DT00C(a), DT04C(b), and DT08C(c) powders treated at different temperatures for 2 h. (Sp: spinel, Q: quartz, M: Mullite, S: Sapphirine, A: anorthite C: Cordierite).

Tab. II Phases formed at different temperatures (°C) and their peak positions (cm⁻¹).

Samples		950	1050	1150	1250
DT00C	Q: 463	Q: 463	C: 253, 292, 370,	C: 253, 292, 370,356,	
	Sp: 680	M: 406	435, 565 670	435, 487, 565, 670	
	M: 406	S: 393, 580, 507	Q: 463		
	S: 393,580, 507		S: 507		
DT04C	Q: 463	Q: 463	Q: 463	C: 253, 370, 435, 670	
	Sp: 680	M: 406	C: 253	A: 503, 553, 590, 620	
	M: 406	S: 393, 507	S: 507		
	S: 393, 507	A: 503, 553, 590, 620	A: 503, 553, 590, 620		
	A: 503, 553, 590, 620				
DT08C	Q: 463	Q: 463	Q: 463	C: 253, 370, 435, 670	
	Sp: 680	M: 406	C: 253	A: 281, 400, 484, 503,	
	M: 406	S: 393, 507	S: 507	553, 590, 620	
	S: 393, 507	A: 503, 553, 590, 620	A: 503, 553, 590, 620		
	A: 503, 553, 590, 620				

In this work, monolithic cordierite and anorthite containing cordierite materials were developed by solid-state sintering method [47, 48]. These ceramic materials might have potential industrial applications. This is possible because on the one hand, monolithic cordierite is characterized by not only its low thermal expansion, dielectrical constant and electrical conductivity, but also its chemical stability and acceptable strength [44, 49]. On the other hand, anorthite, which results from the addition of CaO, has similar attributes in addition to good wear resistance [44, 50]. Moreover, cordierite has higher strength than anorthite. Cordierite material properties are known to depend on the level of densification [51] as well as the amount and attributes of the different formed phases. The mechanical and physical properties of the developed anorthite containing cordierite materials will be characterized and reported in future work.

4. Conclusion

This work revealed the possibility to develop monolithic cordierite or anorthite containing cordierite materials from kaolin, MgO, and CaO precursors. The influence of CaO content on the formation of cordierite was studied by XRD, DTA, TG, and dilatometry methods. Sintering the stoichiometric kaolin-magnesia mixture led to the nucleation and growth of monolithic cordierite; while cordierite along with anorthite were present in the other two samples where 4 or 8 wt% of CaO was added. The increase in CaO decreased cordierite formation temperature and increased the activation energy, which ranged from 445 to 619 kJ/mol for μ -cordierite and from 604 to 1335 kJ/mol for α -cordierite.

5. References

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Сажетак: Испитиван је утицај СаО на формирање кордијерита из смеше прахова каолин-МgO-СаО, млевеног 5 h и синтерованог 2 h у температурском интервалу 900-1400 °C. Формиране фазе у добијеним материјалима су карактерисане XRD методом и Раман спектроскопијом. DTA-TG експерименти су рађени од собне до 1400 °C, са брзинама загревања од 20 до 40 °C/min. Енергије активације су одређене Кисинџеровом методом. Синтеровање стохиометријске смеше каолин-магнезијум води до нуклеације и раста монолитне кордијеритне фазе, док су кордијерит и анортит присутни у друга два узорка са додатком 4 одн. 8 wt% СаО. Пораст концентрације СаО утиче на снижавање температуре синтеровања кордијерита и пораста енергије активације, која варира од 445-619 kJ/mol за μ-кордијерит до 604-1335 kJ/mol за α-кордијерит.

Кључне речи: глина, MgO, кордијерит, синтеровање, кинетика.

