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Formation of high-temperature crystalline phases in ceramic from illite clay and dolomite

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Abstract

The formation of ceramic with the prevailing cordierite/mullite in the crystalline phase is greatly dependent on the raw materials used. In the present work the cordierite and mullite (or their solid—solutions accordingly with spinels and corundum) formation processes from compositions of natural raw materials (illite clay, dolomite) with synthetic additives (MgO, $Al(OH)_3$, K_2CO_3) are studied. It is shown that the illite clay acts as a low viscosity liquid medium as well as a precursor for cordierite and mullite crystallisation in ceramics.

The phase development using XRD—analysis and the SEM is studied. Particles size distribution of staiting powder and some properties of ceramic obtained are also demonstrated. It is shown that formation of the above mentioned phases starts at temperatures 1050–1080 °C and remarkably increases at 1200 °C for mullite and at 1300 °C for cordierite.

Keywords: Traditional ceramics; Mullite; Clays; Dolomite

1. Introduction

Mullite ($3Al_2O_3{\cdot}2SiO_2$) ceramics is expected to be used as high temperatures engineering material.[1] Cordierite ($2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$) ceramics because of its low linear expansion coefficient and other features is supposed for the application as a material with a high thermo-durability, as well as multi-layered substrates which could be co-fired with good electrical coductors (gold, silver, copper).[2]

To obtain dense mullite bodies by conventional sintering methods it is necessary to fire the samples of system SiO_2–Al_2O_3 above the eutectic temperature (1587 ± 10 °C). The sintered bodies above the eutectic temperature usually contain glass as an irregular phase, which promotes the reactions and mullite development in sintering process. However, the presence of this phase in mullite ceramics degrades the mechanical properties of mullite ceramics.[3]

It is known (e.g.[1,2]) that the ceramic containing cordierite and mullite phases usually has been synthesized from a starting powder on the base of synthetic compounds—oxides, hydroxides and mineral raw materials such as kaolin, talc. Often some additives—mineralizers are used to promote the reactions or to prevent the modification changes.[3,4]

The simplest and most used method for crystallisation of these phases is thermal treatment of samples at high temperatures. In the crystallisation processes predominate solid-state reactions.[5] By the presence of liquid phase the crystallisation can be accelerated.

The role of illite clay and dolomite on the cordierite formation has been studied in our previous work.[6] It is shown that particularly the illite clay above the temperature 700 °C forms the liquid phase and promotes the cordierite formation starting from 1200 °C.

This study focuses on the preparation of mullite and cordierite containing ceramics by using the starting powder compositions formulated of illite clay and dolomite along with different synthetic additives.

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The purpose is to examine the effect of the mineral raw materials (illite clay, dolomite and quartz sand) on the formation of the both different crystalline phases—mullite and cordierite.

2. Materials and procedure

As the synthetic starting materials $Al(OH)_3$, MgO, K_2CO_3 reagents of chemical grade and two modifications of alumina—αAl_2O_3 and θ-modification—nanopowder, plasma sprayed were used. Tables 1 and 2 characterize illite clay, dolomite and quartz sand. Two kinds of illite clay (A) and (B) with the different content of carbonate minerals—calcite and dolomite, namely from point of view of chemical compositions with the different content of CaO and MgO were used. It is also essential to consider the various content of Al_2O_3 in clays used.

For mullite phase development in ceramics the starting mixture of illite clay (A) was mixed with three different Al^{3+} agents—$Al(OH)_3$, αAl_2O_3 and θ-modification of Al_2O_3 nanopowder in weight ratio: illite clay: Al^{3+} agent—1, 1.5, 2.3, 4. Five mixtures are used to form a cordierite phase, Table 3.

The starting powders were prepared by the ball-milled process for 12 h in 500 ml corundum laboratory mill with corundum balls. Particle size topographic image and distribution—of obtained powders were measured using surface imaging systems SIS an ultraobjective 404 on pico-station with a 40 μm scanning head (maximum scan range 40 μm × 40 μm lateral, 4 μm vertical). An agglomeration of the particles were prevented. There is determined that in powder dominante the spherical particles with the dominante size 0.1–0.4 μm. The powders were pressed into 25 mm disks at pressure 150 MPa and subjected to different firing schedules in air at temperatures ranged from 1000 to 1200 °C with interval 50 °C for mullite phase and at 1100, 1200 and 1300 °C for cordierite phase (heating rate in whole temperature range 5°/min). At the maximum temperature samples were held for 1 h. To characterise the sintering degree after thermal treatment bulk density of samples was measured. Phase composition of the fracture of sintered disks samples after each step of firing was analysed using XRD (model DRON-3, S.-Petersburg, with Cu Kα radiation at scanning interval from $2\theta = 10–60°$ and speed 1°/min). The morphology of the mullite phase formation was observed by the transmission EM—analysis (model MP EM—89, Tshernogolowka, Russia) at the magnification 1000 times.

Table 1
The characteristics of illite clay A and B

Chemical compositions, wt.% ([a])

SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O/Na_2O	Wt. loss (1000 °C)
A[a] 50.5	20.8	7.5	0.8	1.9	3.6	5.0/0.1	9.8
B[b] 49.5	13.2	6.5	0.6	8.9	4.6	3.6	13.1

Mineralogical composition wt.sh.

Illite ($K_{0.5}(H_3O)_{0.5}Al_2[(OH)_2//AlSi_2H_4O_{10})$	Quartz (SiO_2)	Calcite ($CaCO_3$) dolomite ($CaCO_3 \cdot MgCO_3$)	Goethite (αFeOOH)	Kaolinite ($Al_2[(OH)_4/Si_2O_5)$
65–70	18–20	5–10	7–8	3–7

[a] Illite clay A, Devonian geological period, Kuprava quarry, Latvia.
[b] Illite clay B, Quarternary geological period, Spartaka quarry, Latvia.

Table 2
The chemical composition of quartz sand and dolomite, wt. %

Mineral raw materials	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Wt. losses
Quartz Sand[a]	98.7	0.7	0.13	–	$\underline{TiO_2}$ 0.07	0.4
Dolomite[b]	6.1	1.1	1.1	28.7	19.0	44.1

[a] Bales quarry, Latvia.
[b] Kranciema quarry, Latvia.

Table 3
The mixtures for cordierite phase formation, wt. %

Mixtures	MgO	K_2CO_3	Al_2O_3	Mineral raw materials		
				Quartz sand	Dolomite	Illite clay (B)
0	12.0–12.5	7.1–7.5	33.5–34.0	46.0–47.0	–	–
I	11.5–12.3	6.5–7.0	30.5–31.8	42.0–43.0	4.5	4.5
II	10.3–11.2	5.8–6.2	27.2–28.5	39.0–40.5	8.2	8.2
III	8.5–9.0	5.1–5.8	24.1–24.8	33.5–34.7	14.0	14.0
IV	7.7–8.2	4.5–5.5	21.3–21.7	29.5–30.8	18.4	18.4

3. Results and discussion

Illite clay A or illite clay B with dolomite in compositions for high-temperature crystalline phases formation in ceramic is based on the fact that illite clay after decomposition at temperatures above 700 °C act as a low temperature K(Na)–Al–Si–O liquid former.[7] XRD studies (Fig. 1) have shown that during the sintering of composition (wt. ratio) illite clay A: $Al(OH)_3 = 1.5$ (I) in temperature range from 1000 to 1200 °C mullite phase starts to form from 1100 °C and maximum of mullite or mullite-corundum crystalline phase formation relates to 1150 and 1200 °C (Fig. 1). The samples sintered at 1150 and 1200 °C are dense and have the bulk density between 1.85 and 2.50 g/cm^3 and open porosity from 1.5 to 5.0%.

In the case of samples by wt. ratio illite clay: $Al(OH)_3 > 1.5$ with the increase of temperature mullite peaks decrease. By this ratio grows the open porosity and accordingly decreases a bulk density. Therefore, the experiments were further extended with lower percentages of illite clay, that is, by weight ratio illite clay/Al^{3+} agents ≤ 1.5. For this purpose three kinds of samples (I) sintered at 1200 °C with different Al^{3+} agents—$Al(OH)_3$, αAl_2O_3 and θAl_2O_3 were applied and compared.

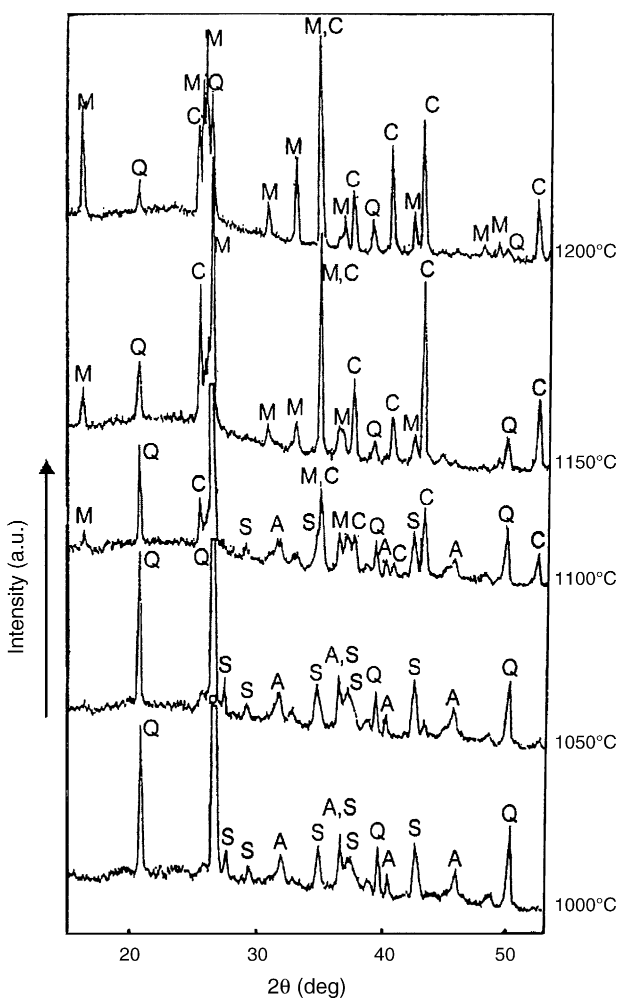

Fig. 1. XRD patterns of mullite formation of sample (I) after annealing at different temperatures: S, spinels; A, anorthite;. M, mullite; C, corundum; Q, quartz.

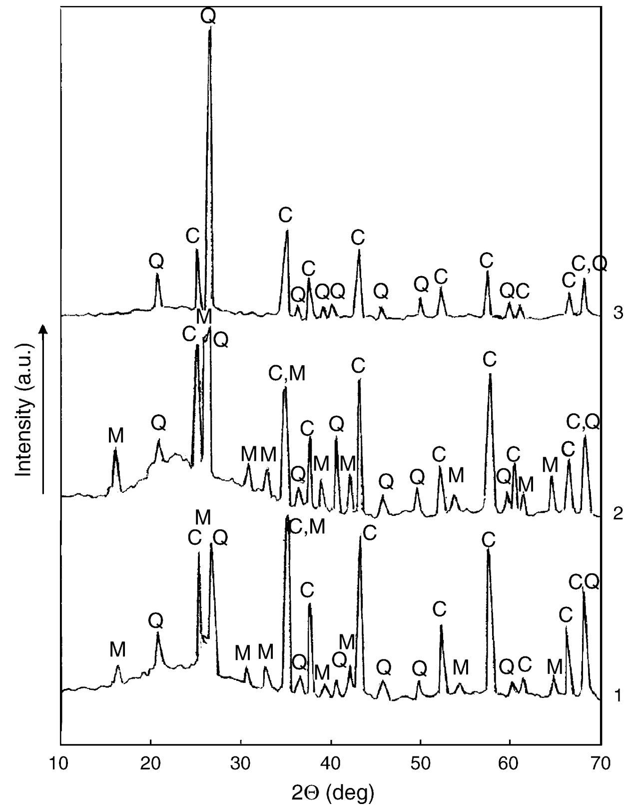

Fig. 2. XRD patterns of mullite formation at 1200 ° for samples (I) by using as Al^{3+} agents: 1, αAl_2O_3; 2, $Al(OH)_3$; 3; θAl_2O_3 nanopowder: M, mullite; C, corundum; Q, quartz.

Comparative XRD—analysis results (Fig. 2) show that mullite peaks are reduced by using the αAl_2O_3 reagents and get lost by using θAl_2O_3. In the last case as crystalline phases there are formed the corundum and quartz. The mullite formation is enhanced only by $Al(OH)_3$ which decomposes at temperature ~500–550 °C to form an active γAl_2O_3 form.

In regard to the dependence on different content of clay A on morphology of the samples (wt. ratio) illite clay: $Al(OH)_3 = 1$, 1.5, 2.3, 4, sintered at temperature 1200 °C is stated that the shape and size of mullite crystalls with the increasing of illite clay become weaker, Fig. 3. For sample illite clay: $Al(OH)_3 = 4$ the morphology becomes amorphous, develop closed pores and mullite crystallization is suppressed, Fig. 3d.

XRD patterns of samples 0, I, II, III, IV for cordierite phase formation sintered at 1300 °C shows (Fig. 4) that intensity of cordierite peaks decreases and disappears when mineral raw material additives (dolomite and illite clay) in starting mixture exceed 40 wt.%. That amount of dolomite and clay promote the formation of forsterite and anorthite phases.

The physical properties, open porosity and bulk density of sintered cordierite samples from mixtures I–IV are examined in temperatures from 1080 to 1300 °C; results of sintered at 1300 °C samples are summarized in Table 4.

The crystalline phase development from mixture II at three various temperatures in range from 1100 to 1300 °C demonstrates that the cordierite phase starts to form at 1200 °C and intensity of cordierite peaks remarkably increases at 1300 °C (Fig. 5).

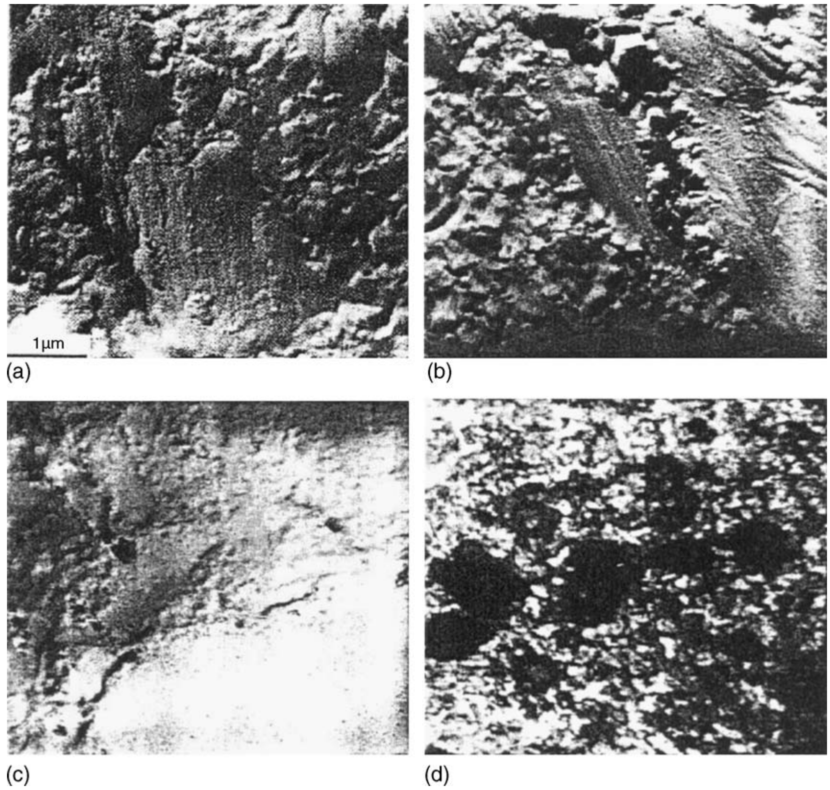

Fig. 3. TEM of sintered at temperature 1200 °C mullite compositions (wt. ratio): a, illite clay A: $Al(OH)_3$ = 1; b, 1.5; c, 2.3; d, 4.

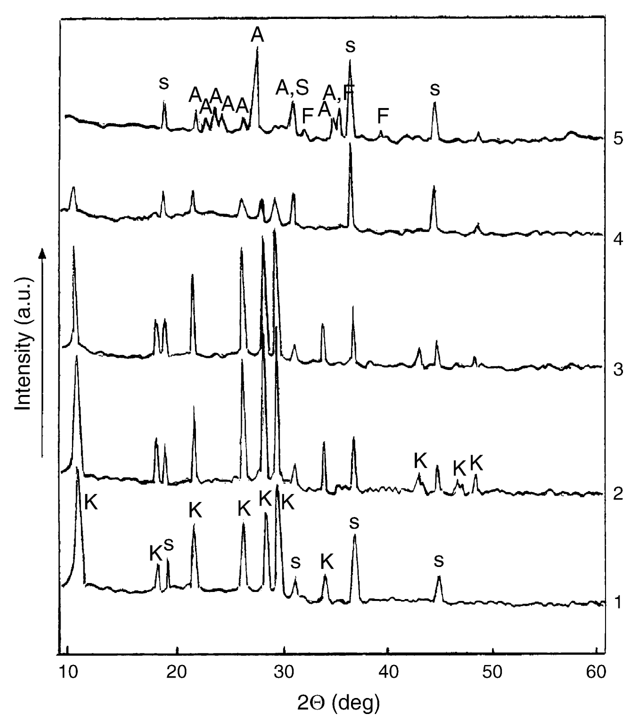

Fig. 4. XRD patterns of the sintered at 1300 °C cordierite samples from mixtures 0–IV by increasing amount of dolomite/illite clay: 1, 0: 2, I; 3, II; 4, III; 5, IV: K, cordierite $Mg_2Al_3[AlSi_5O_{18}]$, S, spinel Mg, $Fe[Al_2O_4]$, F, forsterite $Mg_2[SiO_4]$, A, anorthite $Ca[Al_2Si_2O_8]$.

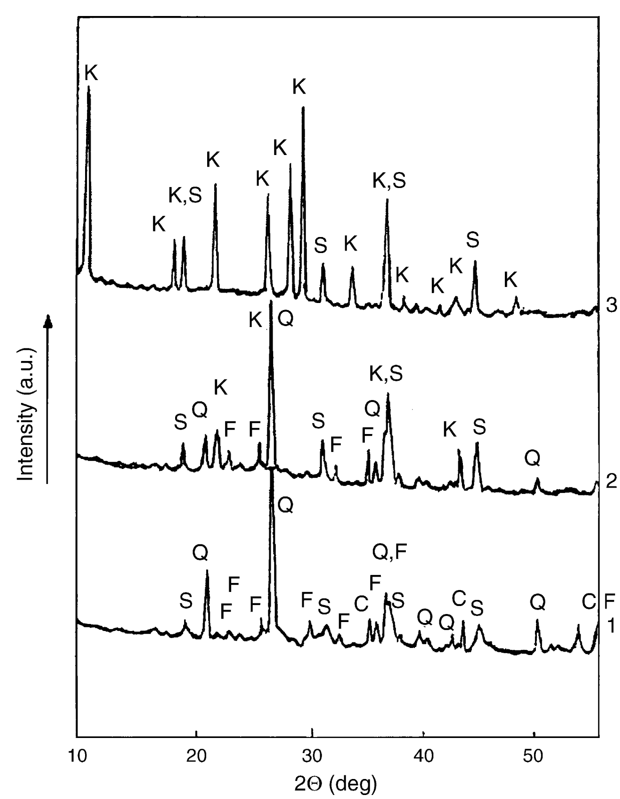

Fig. 5. XRD patterns of the sintered at different temperatures cordierite samples of compsition II: 1, 1100; 2, 1200; 3, 1300 °C: K-cordierite (Mg, $Fe^{2+}Al_3)_2[AlSi_5O_{18}]$, S, spinel Mg, Fe_2O_4, F, forsterite $(Mg,Fe)_2[SiO_4]$, Q, quartz SiO_2, C, corundum αAl_2O_3.

Table 4
The open porosity and bulk density in dependence on mineral raw materials additives of cordierite ceramic sintered at 1300 °C

Samples	Bulk density (g/cm^3)	Open porosity (%)
I	2.75	2.50
II	2.65	4.80
III	2.50	4.75[a]
IV	2.35	1.80[a]

[a] There appear the closed pores.

According the sequence of crystalline phases formation from point of view of symmetry order[8] and XRD-analysis results, e.g. for sample II it can be proposed that the sequence of cordierite phase formation in dependence on temperature is as follows: after decomposition of illite clay at temperatures ~700 °C and dolomite at 800–900 °C there forms a liquid phase and start to form the crystalline phase. This process schematicaly can be demonstrated as follows:

$$\begin{aligned} & MgO(+Al_2O_3 + Fe_2O_3 + SiO_2) \\ & \rightarrow Mg(Fe_2O_4)(\text{spinels}) + SiO_2 \\ & \rightarrow Mg_2[Si_2O_6] + (Mg, Fe)_2[SiO_4](\text{enstatite and forsterite}) \\ & \rightarrow (Mg, Fe^{2+}Al_3)_2[AlSi_5O_{18}]\text{-cordierite.} \end{aligned}$$

4. Conclusions

The process of mullite or cordierite crystalline phases formation in ceramic from compositions mineral raw materials (illite clay and dolomite) and synthetic additives—$Al(OH)_3$, Al_2O_3, K_2CO_3, MgO have been studied. For mullite phase formation three kinds of Al^{3+} agents along with the illite clay are used and compared. According the XRD results at the temperature 1200 °C the tendency towards formation of mullite increases by using $Al(OH)_3$ which decomposes at temperature 550 °C to form an active γAl_2O_3.

It is shown that illite clay at temperature above 700 °C and dolomite at 900 °C decompose forming a liquid phase which favours the reactions and development of mullite phase at temperatures above 1100 °C and cordierite above 1200 °C.

Experimental results also confirm that the development of intended cordierite phases in particular is promoted by the presence of illite clay and dolomite either of which does not exceed 14 wt.%.

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