

CLAYS, CLAY MINERALS AND CORDIERITE CERAMICS - A REVIEW

MARTA VALÁŠKOVÁ

Nanotechnology Centre, VŠB – Technical University of Ostrava,
17.listopadu 15/2172, CZ-708 33 Ostrava – Poruba, Czech Republic
T4Innovations Centre of Excellence, VŠB-Technical University of Ostrava,
17.listopadu 15, CZ-708 33 Ostrava – Poruba, Czech Republic

E-mail: marta.valaskova@vsb.cz

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The conventional methods for the synthesis of cordierite ceramics include the solid-state sintering of individual oxides of magnesium, aluminium and silicon of the corresponding chemical composition of cordierite, or sintering of the natural raw materials. Clays are used in the ceramics industries largely because of their contribution to the molding and drying properties. The most effective use of clays meets with the problems of the improvement of the working properties of clays and bodies through additions of non-plastic materials or chemicals and the influence of the clay content of ceramic bodies on their behavior during firing. Applicable nomenclatures for clays, clay minerals, ceramic raw materials, cordierite ceramics and characteristic structural properties of the cordierite and cordierite polymorphs are summarized. Selected published data confirmed the fact that identical formulation of clay mineral mixtures led to a variable mineral phases sintered in cordierite ceramics. Among the many factors, important roles play chemical and structural characteristics of individual clay minerals used in the clay mineral mixtures and methodology of processing of the green body and sintering conditions.

INTRODUCTION

Porous ceramic materials have applications in many industrial areas, such as catalyst supports for heterogeneous chemical reactions, filters, membranes, thermal insulators, and bioceramics. These applications require the porous microstructure, chemical inertia, and resistance to thermal and/or mechanical shock. Cordierite is inexpensive mineral and has been widely used for manufacturing many ceramic products. Cordierite ceramics include not only pure cordierite products, but also materials based on cordierite with various additives [1]. The low thermal expansion coefficient makes it suitable for applications such as heat exchangers, thermal shock-resistant tableware, ceramics for electric heaters, and for the fabrication of monolithic catalyst support produced by extrusion in a honeycomb shape for diesel automobiles. More effective and reliable methods for production of porous ceramics are based on the replica technique, using a foamed polymer as precursor. Incorporation of organic substances that burn off is method to obtain pores corresponding to the original organic particle size and shape. The conventional methods for the synthesis

of cordierite ceramics include the solid-state sintering of individual oxides of magnesium, aluminium and silicon of the corresponding chemical composition of cordierite, or sintering of the natural raw materials.

Theoretically, cordierite, $Mg_2Al_4Si_5O_{18}$, is composed of 13.7 % of MgO, 34.9 % of Al_2O_3 , and 51.4 % of SiO_2 . Natural raw materials kaolinite and talc, containing oxides MgO, Al_2O_3 and SiO_2 , were often used for cordierite synthesis [2-5]. Cordierites were synthesized from mixtures of clay, talc, alumina, and silica sand [6], kaolin, quartz, technical silica, or talc, kaolin, silica, and feldspar [7], from talc, fly ash, fused silica, and alumina [8]. Special compact cordierite ceramic was prepared from kaolinite and magnesium hydroxide [9] and from kaolinite and magnesium carbonate [10]. Cordierites were also sintered by partial substitution of the clay minerals in the mixture with vermiculite [11-13]. Cordierite forms by exothermic reaction at $\sim 1300^\circ C$ [14].

The work presents the characteristic structural properties of clays and clay minerals, which are potentially used for the preparation of ceramic green bodies and sintering of the ceramic material, as well as the structure of cordierite and cordierite polymorphs.

RESULTS AND DISCUSSION

Clays, clay minerals and ceramic materials

Clays and clay minerals are extensively used in a wide variety of industrial applications because of their inertness and stability, and their reactivity and catalytic activity [15].

Clays

Clays are silicates belonging to the phyllosilicate group.

Silicates are classified, based on their structure, to the six silicate groups [16]:

- *Nesosilicates* (isolated $(\text{SiO}_4)^{4-}$ tetrahedra connected only by interstitial cations);
- *Sorosilicates* (isolated $(\text{Si}_2\text{O}_7)^{6-}$ double tetrahedra);
- *Cyclosilicates* (linked tetrahedra with $(\text{Si}_x\text{O}_{3x})_{2x}$ - rings, which exist as 3-member $(\text{Si}_3\text{O}_9)^{6-}$, 4-member $(\text{Si}_4\text{O}_{12})^{8-}$ and 6-member $(\text{Si}_6\text{O}_{18})^{12-}$ rings);
- *Inosilicates* (interlocked silicate tetrahedra leading to either two-single chains of SiO_3 or $(\text{Si}_4\text{O}_{11})^{6-}$ double chains);
- *Phyllosilicates* (parallel tetrahedral sheets of silica and alumina $(\text{Si}_2\text{O}_5)^{2-}$, $(\text{AlSi}_3\text{O}_{10})^{5-}$ or $(\text{Al}_2\text{Si}_2\text{O}_{10})^{6-}$) and
- *Tectosilicates* (three-dimensional frameworks of silicate tetrahedra with formulas of SiO_2 , $(\text{AlSi}_3\text{O}_8)^{1-}$ or $(\text{Al}_2\text{Si}_2\text{O}_8)^{2-}$).

Clay is a term for naturally occurring mineral aggregates consisting mainly of the various clay minerals content and degree of purity. Clays were formed at the site of the parent rocks and were not transported by any of the various agencies such as wind and water. Primary clays (e.g. china clays) are usually found in irregular pockets with unaltered rocks remaining. These deposits are coarse grained and non-plastic as the clay was not transported by water. The formation of clay is a chemical process that is assisted by mechanical breakdown and the separation of fine particles from coarse grains [17].

Bentonite is term for rock whose dominant clay minerals are smectites formed through the weathering of volcanic glass [18]. Bentonite material settled in water occurs in the form of lenses in other sediments. It also occurs as a product of supergene or hydrothermal alteration of some volcanic rocks.

Smectite is a family name, which includes sodium and calcium *montmorillonites*.

Ceramic raw materials are generally classified in two groups:

- I. *Plastic ceramic raw materials* involve any clay material that when mixed with water reveals the property called plasticity. *Plasticity* was defined as a property which permits a material to be deformed under stress without rupturing and to retain the shape produced after the stress is removed [19]. Bentonites are the most plastic common clay. Many clay raw materials are not plastic. The claystones, clay shales, talc, pyrophyllite, vermiculite and coarser mica are semi-

Table 1. The common names of clays, their origin, main clay mineral constituents and their practical applications [22].

Current name	Origin	Main clay mineral constituents	Remarks to application
Ball clay	Sedimentary	Kaolinite	Highly plastic, white burning
Bentonite	Volcanic rock alteration or authigenic	Montmorillonite	
Bleaching earth	Acid-activated bentonite	Decomposed montmorillonite	
Common clay	Sedimentary or by weathering	Often illite/smectite mixed-layer minerals	General for ceramics excluding porcelain
China clay	Hydrothermal	Kaolinite	Kaolins from Cornwall plastic, white burning
Fire clay	Sedimentary	Kaolinite	Plastic, high refractoriness
Flint clay	Sedimentary with subsequent diagenesis	Kaolinite	Non-slaking, not plastic, used for refractories
Fuller's earth	Sedimentary, residual, or hydrothermal	Montmorillonite, sometimes palygorskite, sepiolite	
Primary kaolin	Residual or by hydrothermal alteration	Kaolinite	
Secondary kaolin	Authigenic sedimentary	Kaolinite	
Refractory clay	Authigenic sedimentary	Kaolinite	With low levels of iron, alkali and alkali earth cations for refractories
Laponite	Synthetic	Hectorite-type smectite,	
Nanoclay		mostly montmorillonite	Superfluous term for clays used for nanocomposites

plastic [17]. *The plastic sedimentary clays* (kaolin, clay and bentonite) for the fine ceramics industry are often substituted by the term ‘ball clays’. The term is derived from the original method of production. In open pits, the clay was cut into cubes. Subsequent handling of these cubes prior to sale led to a rounding of the corners, giving them a characteristic spherical shape. The clay deposits in South-West England were originally worked in this fashion and are the only true ‘ball clays’. Nevertheless, the term is applied more generally to plastic sedimentary clays high in kaolinite, which possess white-firing properties and high green strength [20]. Good plastic clay deposits suitable for the fine ceramic industry are rare. In general, such clays occur in isolated lenses or as seams in large, complex deposits. Clays of different plasticity exhibit significantly different properties. For example, ball clays are highly plastic, but undesirable cracks are formed when they are dried. Bentonites have a high affinity for water that it can take a week to dry a specimen. Kaolins can dry in a short time and have little shrinkage. Some plastic kaolins contain bentonite or have a mineralogy that is bordering on ball clay.

II. *Non-plastic ceramic raw materials* (containing feldspars, quartz, limestone, dolomite, magnesite, calcium phosphate and talc) when mixed with water are not plastic. A part of the non-plastic ceramic raw materials acts as a filler for reducing of high plasticity or shrinkage of the body when drying or firing.

Further detail classification depends on the material composition [21].

Common clays contain mixtures of different clay minerals such as illite/smectites, kaolinites, smectites, micas and associated minerals and have the largest usage in engineering applications. Although these clays are typically impure, they contain sufficient clay minerals for developing of plasticity and to produce adequate strength, porosity and other properties. Large amounts of smectite may develop undesirable shrinkage and drying properties. The presence of kaolinite in clays used for bricks and tiles would increase the firing temperature and a light burning colour. Common clays for production of tiles, bricks and ceramics are generally used without any processing. In some cases the largest particles are removed by simple sedimentation techniques without re-purification to obtain homogeneous ceramic bodies.

Kaolin is both a rock term and a mineral term. As a rock term, kaolin means that the rock is comprised predominantly of kaolinite and/or one of the other kaolin minerals. Kaolins and ball clays, which are kaolin clays, are both used as major ingredients in many ceramic products.

Raw kaolin contains kaolinite, white mica (muscovite and illite or mixed-layers structures of illite and smectite), quartz and residues of silicates, mostly feldspars, biotite and accessory minerals.

The *industrial kaolins* contain relatively high amounts of kaolinite (kaolins) and sometimes a small proportion of high-quality kaolin minerals. Industrial beneficiation of kaolins is necessary for separation of non-clay minerals to obtain them enriched by kaolinite. Kaolins of high-purity are main raw materials for ceramic products such as porcelain, vitreous sanitary ware and earthenware. Low-quality kaolins are also used as fillers in a wide range of ceramic products including brick, pipes and tiles. In industrial applications ‘delamination’ of kaolinite particles into single particles or smaller aggregates improves the quality of porcelain. This reaction was used by Chinese ceramists to produce very thin (‘egg-shell’) porcelain of high mechanical stability.

The common current names of clays, their origin, main clay mineral constituents and the impact of these materials on the practical applications are in Table 1 [22].

Clay minerals

Many properties of clay minerals can be derived from their crystal structures and crystal chemistry. Their structure consists of octahedral (O) or tetrahedral (T) sheets firmly arranged in structural layers. The resulting negative charge of the layers is from the metal cation substitutions in octahedra and tetrahedra, which is compensated by cations in the interlayer space.

The physical and chemical properties of a particular clay mineral are dependent on its structure and composition. Clay minerals are characterized by certain properties [22]:

- A layer structure with one dimension in the nanometer range: the thickness of the 1:1 (T-O) layer is about 0.7 nm, and the 2:1 (T-O-T) layer is about 1 nm (Figure 1),
- The external basal (planar) and edge surfaces as well as internal (interlayer) surfaces,
- Modification of the external, and often also the internal surfaces,
- Plasticity, and
- Hardening on drying or firing, (but not all) clay minerals.

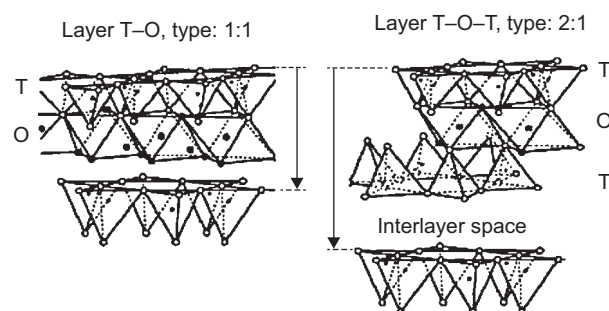


Figure 1. Schema of tetrahedral (T) and octahedral (O) sheets in the 1:1 and 2:1 layers occurring in clay minerals. The basic structural unit is indicated by the arrow.

Classification of the clay minerals was proposed by Grim [23], which is a basis for outlining the nomenclature and differences between the various clay minerals. Currently recommended classifications of clay minerals according to the Joint nomenclature committees (JNCs) of the Association Internationale pour l'Etude des Argiles (AIPEA) and the Clay Minerals Society (CMS) is performed in Handbook of Clay Science [22].

In the current nomenclature [24, 25], the term clay refers to a "naturally occurring material composed primarily of fine-grained materials, including crystalline and amorphous oxides and hydroxides of various metals, which are generally plastic at appropriate water contents and will harden when dried or fired". The term clay mineral refers to a certain group of lamellar or layered crystalline silicate minerals (phyllosilicates).

The current classification of clay minerals is according to the recommendations of Nomenclature Committees Relevant to Clay Mineralogy (AIPEA) [24]:

Smectites are swelling and disordered minerals occurring in nature as the main component of bentonites. The term smectite is used for planar dioctahedral and trioctahedral 2:1 clay minerals with a negative layer charge between 0.2 and 0.6 per formula unit which contain hydrated exchangeable cations. Smectite 2:1 layer unit is formed by one alumina octahedral sheet sandwiched between two silica tetrahedral sheets (Figure 1). The ion substitution or the site vacancies at the tetrahedral and/or octahedral sheets gives rise to a negatively charged surface. Minerals of the smectite group have high specific surface area and ability of cation exchange capacity. Hydrated exchangeable cations between the layers in the interlayer space compensate the negative charge and may be easily exchanged by other metal cations. *Montmorillonites* are defined as dioctahedral smectites.

Vermiculites are planar dioctahedral and trioctahedral 2:1 clay minerals (phyllosilicates) with a negative layer charge between 0.6 and 0.9 per formula unit and hydrated exchangeable cations in the interlayer space. Vermiculites originate from alteration of mica-type minerals and, less commonly, from amphiboles and chlorites [26]. Reichenbach and Bayer [27] prepared Mg-vermiculite from phlogopite flakes. Therefore, natural vermiculites are not all pure Mg-vermiculite members but the mixed-layer phyllosilicates, such as biotite-vermiculite, phlogopite-vermiculite or vermiculite-chlorite. Several observations suggest that vermiculitization is not the final stage of alteration. A continuous process of mica-vermiculite-smectite alteration results in vermiculites that show a smectite charge. The excess layer charge is compensated by the hydrated exchangeable cations such as Mg^{2+} , Ca^{2+} , Na^{+} and K^{+} that occupy the interlayer space [25].

Ceramic materials

Ceramic material was defined by Committee on Definition of the Term "Ceramics" as the arts and sciences of making products and articles (a) chiefly or entirely from "earthy" raw materials, that is, from the so-called non-metallic excepting fuels and ores of metals, and (b) with a high temperature treatment involved, either in their manufacturing or in service [28]. According to the Concise Encyclopedia of Advanced Ceramic Materials [29], the ceramic materials have to contain at least 30 % of crystallized phases in volume. A mean pore size of the porous ceramic is defined as a pore diameter corresponding to 50 % of the total pore volume having the pore diameter of 10 nm-100 μm in the pore size distribution. Ceramic processes during sintering occur at temperatures higher than 800°C.

Ceramic materials are classified from various aspects and are very often evaluated according to their use and according to their chemical and mineralogical composition. Another classification of ceramics is to the traditional ceramics (which include clay products, silicate glass and cement) and advanced ceramics (based on the carbides, pure oxides, nitrides, non-silicate glasses and many others).

Traditional ceramics. The common raw materials used for most of the ceramic products are: Ball clay, china clay, feldspars, silica, dolomite, talc and calcite. Each raw material contributes a certain property such as surface area, particle size and distribution, particle shape, density, dry strength, plasticity, shrinkage, etc. to the ceramic body. Therefore, preparation of powder materials is a major procedure in the ceramic industry. Powder has to be prepared to meet required particle size, particle shape, and other requirements for a particular industry. Milling is done to get the desired particle size. Unlike in the advanced ceramics industry the purity of ceramic powder is not an issue in traditional ceramics.

Advanced ceramics are special type of ceramics used mainly for electrical, electronic, optical, and magnetic applications. This sector is different from traditional ceramics due to the fact that ceramic powder preparation is quite important. Advanced production techniques such as sol-gel processing and liquid-gas reactions are employed to assure that the produced ceramic powders possess sufficient purity.

Ceramic materials used as technical ceramics or advanced ceramics in technical applications must satisfy high demands in terms of their properties. The property such as wear and heat resistance, temperature and corrosion resistance all the way to biocompatibility and food compatibility make it possible to use technical ceramics in a variety of applications in the automotive industry, electronics, medical technology, energy and environment and in general equipment and mechanical engineering.

Technical ceramics generally include: Silicate ceramics, oxide ceramics, non-oxide ceramics and

piezoceramics.

Silicate ceramics are the oldest type of ceramic materials for technical applications [30].

Sintering is a process of densification the ceramic powder (green body) at the temperature below melting point. Sintering occurs by diffusion of atoms through the microstructure. The three conventional methods are generally used for the synthesis of cordierite ceramics: (1) solid-state sintering, (2) sol-gel procedures and (3) glass crystallization. The firing behavior of clay green body at a given temperature is determined by its mineral composition, particle size distribution, firing atmosphere, and by the amount and kind of accessory minerals present or added. Heating of clays at 700–800°C at pyroplastic condition is a second plastic stage. The pyroplastic properties are determined by the relative amounts of liquid and solid phases, and the viscosity of the liquid phase [31]. The temperature, time and furnace atmosphere are the most important factors involved during sintering. The high sintering temperatures and long sintering times required for the consolidation of ceramic powders often result in grain coarsening and decomposition of the ceramic. Therefore an additive that forms a small amount of liquid-phase between the grains at the sintering temperature are used. More details about sintering nanocrystalline ceramic powders using the various technologies for producing nanosized ceramic powders can be found in literature [32].

The clay minerals kaolinite, talc and vermiculite at the elevated temperatures dehydrate and dehydroxylate and at higher temperatures transform to the new crystalline phases. *Kaolinite dehydration* starts from 20 to 200°C. *Dehydroxylation* and structural changes take place in three stages:

- I. 450–700°C. Structural change to the metakaolinite:
 $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + 2\text{H}_2\text{O}$
- II. 930–980°C. Recrystallization of $\gamma\text{-Al}_2\text{O}_3$ and meta-kaolinite to Si-Al spinel.
- III. 1200–1250°C. Crystallization of mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) and cristobalite (SiO_2).

Talc dehydroxylate at temperature from 800 to the 900°C and transforms to the enstatite and cristobalite:
 $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH}) \rightarrow 3\text{MgSiO}_3 + \text{SiO}_2 + \text{H}_2\text{O}$.

Vermiculite shows stepwise *dehydration* at the temperature gradually raised. The existence of a definite hydration states was characterized by maximal intensities of basal spacing (002) observed at individual temperatures on the values $d(002)$: 1.441 nm (20°C), 1.429 nm (55–58°C), 1.376 nm (65–67°C), 1.165 nm (84–162°C), 1.151 nm (162°C), 1.002 nm (201–225°C), 0.926 nm (700°C), which correspond to the changed number of sheets of interlayer water molecules per interlayer Mg^{2+} : 9.61, 8.98, 8.16, 3.84, 3.21, 1.04, 0.00, respectively. *Dehydroxylation of vermiculite* occurs in the temperature range from 700 to 1000°C. At about 830°C vermiculite structure crystallizes to the enstatite [27].

Vermiculites exfoliate after flash-heating to temperatures of about 870–900°C, or up to 1500°C and after quick cooling. Its volume increases to more than 20 times the original value, giving rise to a very porous, lightweight material. *Exfoliation* is attributed to the action of steam, which develops explosively between the layers, pushing them apart, while layer dehydroxylation (at the high prevailing temperatures) is restrained by rapid cooling. The degree of exfoliation depends upon the particle size. The smaller the particles, the easier it is for interlayer water to escape, and the less extensive is the exfoliation. Vermiculites containing mica or interstratified mica/vermiculite exfoliate more intense than pure vermiculite [33].

Cordierite ceramics

Cordierite ceramics are term for not only pure cordierite products, but also materials based on cordierite with various additives [1]. Cordierite has a very low expansion coefficient of about $2.5 \times 10^{-6} \cdot ^\circ\text{C}^{-1}$ and a high resistance against repeated cycles of heating and cooling. Therefore, cordierite is used as a refractory material in electrical heaters, electrical resistant porcelain and heating apparatuses employed in the chemical industry, as well as a carrier having a catalyst for purifying the exhaust gas of automobiles.

Cordierite

Cordierite ($\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$) is magnesium aluminium silicate with a tetrahedral framework structure. According to the classification of silicates [16, 34], cordierite belongs to the class of silicates and subclass of cyclosilicates. Cordierites containing the hexagonal and orthorhombic magnesium/aluminosilicate frameworks consist of tetrahedral units $[(\text{Si}/\text{Al})\text{O}_4]$, forming Si_6O_{18} six-membered rings (Figure 2). The rings are stacked one above the other and successively rotated about 30° relatively to each other. These rings are linked together laterally and vertically by tetrahedra and $[\text{MgO}_6]$ octahedra. The ring stacking produces large hexagonal channels parallel to the c-axis, in which various cations or small molecular units can be inserted.

The crystal structure of cordierite was investigated by Rankin and Merwin [35], Takane and Takeuchi [36], Byström [37], Gibbs [38], Cohen et al. [39], Meagher and Gibbs [40], and Schwartz et al. [41]. Many studies reported changes of the tetrahedral Si/Al ordering and transition to the ordered form [41–48].

A crystal chemical formula of cordierite in orthorhombic symmetry (space group *Cccm*) (Figure 2) can be written based on the assignment of Cohen et al. [39] at follows: $(\text{M})_2(\text{T}_2\text{3})_2(\text{T}_2\text{1})_2(\text{T}_2\text{6})_2(\text{T}_1\text{6})(\text{T}_1\text{1})_2\text{O}_{18}$, where *M* represents an octahedrally coordinated metal ion (Mg^{2+} , Fe^{2+} or Mn^{2+}) and *T* represents a tetrahedral position (Figure 2a). Tetrahedra T_2 build six-membered

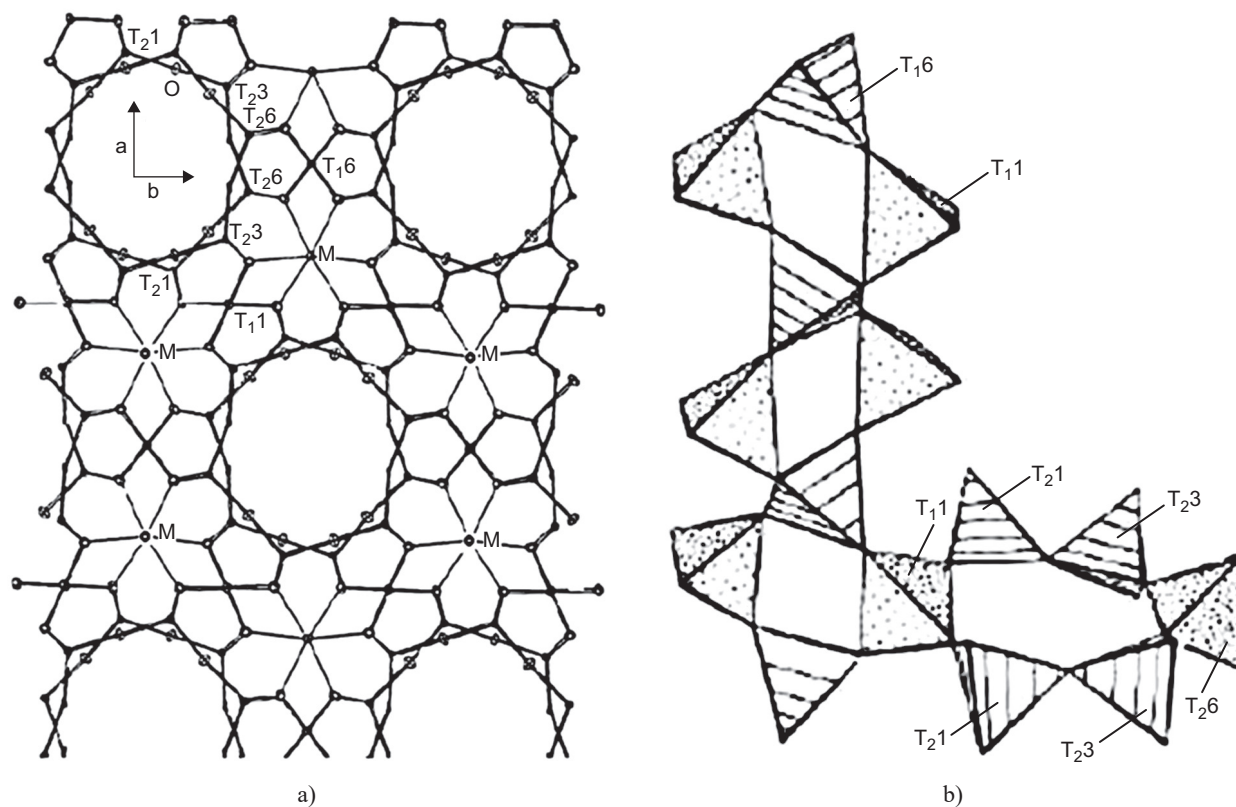


Figure 2. Schema of the structure of orthorhombic low-cordierite viewed down c: a) T₁₁ and T₂₆ represent tetrahedral Al atoms, T₁₆, T₂₁ and T₂₃ represent tetrahedral Si atoms. The octahedral atoms M are Mg and Fe; b) An isolated six-membered tetrahedral ring attached to a single chain of four-membered rings running parallel to c axis [38, 52].

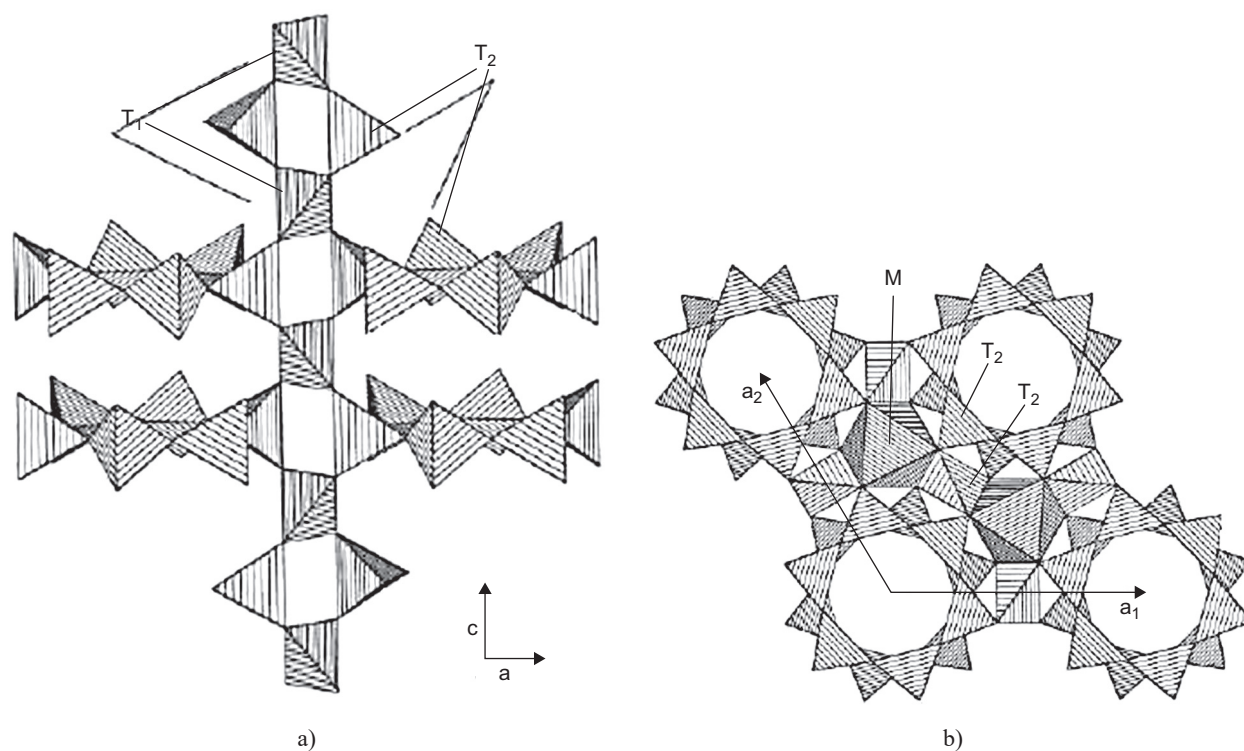


Figure 3. Schema of the arrangement of polyhedra in hexagonal high-cordierite (indialite): a) tetrahedral six-membered rings and chains, b) projection parallel [001] showing octahedra (M) attached to a single chain of four-membered rings parallel to c axis [49].

rings and T_1 tetrahedra cross-link these units to form a framework (Figure 2b). Tetrahedra T_{11} and T_{16} are occupied by Al, whereas all others are occupied by Si. Such a preferred (Si/Al) distribution gives rise to orthorhombic symmetry. Structures of the high cordierites have disordered arrangement in hexagonal symmetry (space group $P6/mcc$) (Figure 3).

Variation in the chemical composition is related to the isomorphous substitution by Fe^{2+} and Mn^{2+} in octahedra, occupied predominantly by Mg^{2+} . The microporous structure allows mobile alkali (Na^+ , K^+) and alkaline-earth (Ca^{2+}) cations, as well as water molecules for migration through the channels [49].

The polymorphism of cordierite and investigation of glass-ceramic formation are routinely studied in the $MgO-Al_2O_3-SiO_2$ system (Figure 4). Schreyer and Schairer [42] investigated the central part of the cordierite system and revised the polymorphism, structural transformations and nomenclature.

The first workers of the system $MgO-Al_2O_3-SiO_2$ distinguished in a ternary compound $2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$ differently refractive indices of μ - and α -forms [35]. Karkhanavala and Hummel [50] defined β -cordierite as the stable low-temperature phase with a cordierite structure synthesized hydrothermally below $830^\circ C$ [51] from a composition close to $2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$ below $830^\circ C$. According to the X-ray investigations, both the synthetic α - and β -cordierites show hexagonal symmetry, in comparison with the orthorhombic natural cordierites. In the temperature range from 830 to $1050^\circ C$ when heated in air, the β - and μ -cordierites readily converted to the stable α -form.

Cordierite from fused sediments of the Bokaro coalfield in India was found identical with the synthetic α -form. Miyashiro [53] used for a new mineral species of hexagonal symmetry (the space group $P6/mcc$) the term “indialite” and the term “cordierites” for orthorhombic forms.

Meagher and Gibbs [40] in a structure of the natural hexagonal polymorph indialite found that the Si/Al distribution involved over the T_1 sites disordered two Al and one Si atoms and over the T_2 sites disordered two Al and four Si atoms. The investigators also found that the α -cordierite was formed by the devitrification of glass at temperatures in the range 1050 to $1450^\circ C$, while the μ -cordierite was formed using heat treatments of long duration at temperatures from 800 to $900^\circ C$ range.

Detailed studies of different natural cordierites by several workers indicated that the low temperature orthorhombic form is cordierite stable below $1450^\circ C$ and the high temperature hexagonal form is disordered indialite stable above $1450^\circ C$ [44, 54]. Indialite below $1450^\circ C$ transformed slowly to β phase [55].

The classification of cordierites and indialites and the stable and metastable polymorphs as well as the nomenclature were based on X-ray diffraction criteria and distortion index (Δ) developed by Miyashiro [53]:

$\Delta = 2\theta_D - (2\theta_A + 2\theta_B/2)$, where $2\theta_D$, $2\theta_A$, and $2\theta_B$ are the Bragg angles (in degrees) of peaks A, B, and D on a cordierite powder diffraction pattern for copper $K\alpha_1$ radiation. A selected diffraction lines A, B, and D were for hkl indexes (511), (421), and (131), respectively [56].

The value of Δ ranges from 0.0 in hexagonal cordierite to about 0.25 in fully ordered, orthorhombic Mg-cordierite. The structural change $P6/mcc \rightarrow Cccm$ has been considered to be first order with a first order discontinuity of $\Delta \sim 0.25$, associated with the distortion [44].

The hexagonal indialite called *high-cordierite* is the modification stable at the highest temperatures for many bulk compositions. The form with the largest Δ value (the greatest deviation from hexagonal symmetry)

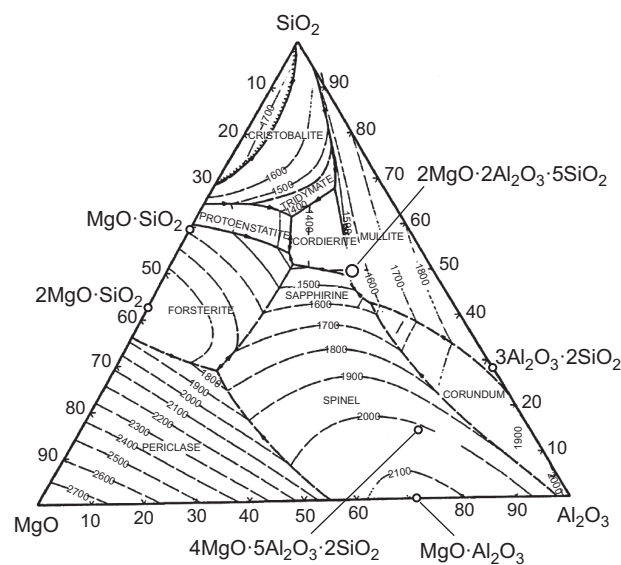


Figure 4. Phase Equilibrium Diagram $MgO-Al_2O_3-SiO_2$ [42]. (o) Stoichiometric composition of cordierite.

is called *low-cordierite*. Cordierites with $0 < \Delta < 0.20^\circ$ are called *intermediate/state cordierites* [42].

Insertions of alkaline cations within the large channels stabilize the high temperature hexagonal cordierite form [57]. In the intermediate states, the one Al- and five Si-cations in the ring are ordered in low cordierite, disordered in high cordierite and of intermediate order.

Cordierites displayed a wide range of Fe-Mg substitution. Substitution of Fe^{2+} in the octahedral and channel sites was identified by optical and Mössbauer spectra [58]. A proposed migration of Fe^{3+} from the six-membered tetrahedral rings to the walls of the channel cavities and of cations (mainly Na^+) from the rings into the cavities is primarily responsible for changes in the distortion index. The presence of structural iron in Fe-cordierite structures causes flattening of the octahedra [52, 59, 60]. In comparison with Mg-cordierite, their cell parameter c was found smaller and parameters a and b were larger. The unit cell parameters of the refined structures of Mg, Fe, Mn-cordierites are selected in Table 2.

Table 2. Structural characteristics of the selected Mg-cordierites substituted by Fe and Mn in orthorhombic symmetry (space group *Cccm*).

Crystal chemical formula	The unit cell parameters (nm)			References
	<i>a</i>	<i>b</i>	<i>c</i>	
Mg ₂ Al ₄ Si ₅ O ₁₈	1.7047	0.9731	0.9346	Schwartz et al. [41]
Mg _{1.86} Fe _{0.14} Al ₄ Si ₅ O ₁₈	1.7044	0.9716	0.9334	Wallace and Wenk [59]
Mg _{1.79} Fe _{0.19} Al ₄ Si ₅ O ₁₈	1.7089	0.9737	0.9344	Wallace and Wenk [59]
Mg _{1.72} Fe _{0.27} Al ₄ Si ₅ O ₁₈	1.7088	0.9726	0.9335	Wallace and Wenk [59]
Mg _{1.91} Fe _{0.09} Al ₄ Si ₅ O ₁₈	1.7113	0.9741	0.9358	Hochella et al. [52]
Mg _{1.12} Fe _{0.82} Mn _{0.02} Al ₄ Si ₅ O ₁₈	1.7163	0.9754	0.9313	Armbruster [60]
Mg _{0.60} Fe _{1.36} Mn _{0.03} Al ₄ Si ₅ O ₁₈	1.7201	0.9790	0.9301	Armbruster [60]

Clay mixtures of cordierite composition

Swelling behavior, adsorption properties, colloidal and rheological phenomena of clay minerals allow their ease modification. New materials are created by modification of 2:1 clay minerals by different ways, especially using ion exchange with inorganic cations and cationic complexes, ion exchange with organic cations, grafting of organic compounds, reaction with acids, dehydroxylation and calcination, and delamination of smectite clay minerals.

Ito et al. in 1984 [61] have patented process for sintering of a cordierite ceramic product from the clay formulation of kaolin, talc and aluminum oxide having a cordierite composition. The resulting cordierite ceramic showed a very low rate of contraction, a low thermal expansion coefficient and an isotropic crystalline orientation. Raw materials into green body should be selected

to form a nominal composition consisting of (in percent by weight) about 11.5 to about 16.5 MgO, about 33.0 to about 41.0 Al₂O₃, and about 46.5 to about 53 SiO₂, and then will be dried and fired at a sufficient temperature for a sufficient time to form the cordierite body [61].

Chemical reaction describing the formation of cordierite from the mixture of clay minerals: talc (3MgO·4SiO₂·H₂O), kaolinite (Al₂O₃·2SiO₂·2H₂O), and gibbsite (Al(OH)₃) can be written as follows [1]: 4(3MgO·4SiO₂·H₂O) + 7(Al₂O₃·2SiO₂·2H₂O) + 10Al(OH)₃ → 6(2MgO·2Al₂O₃·5SiO₂) + 33H₂O.

Standard cordierite based on kaolin, talc, and alumina has a narrow sintering interval of 10-20°C, which makes the products highly sensitive to baking. Cordierite sintering is observed at the temperatures close to cordierite melting temperature. At lower temperatures, cordierite synthesis and sintering do not occur practically, while the increase of temperature results in glazing phase [3].

Table 3. Mineral phases in clay mixtures and cordierites sintered at 1300°C.

Clay mixtures composition	Minerals in cordierite ceramics	References
Kaolin, talc	Cordierite, enstatite, spinel	Trumbulovic et al. [3]
Kaolin, talc, gibbsite	Cordierite, mullite	Gusev et al. [1]
Kaolin, talc, gibbsite	Cordierite, mullite	Tamborenea et al. [63]
Kaolin, talc, alumina	Cordierite, alumina, spinel	Pavlikov et al. [64]
Kaolin, talc, alumina	Cordierite, enstatite, forsterite, quartz	Gökçe et al. [65]
Kaolin, talc, alumina	Cordierite, enstatite, corundum	Valášková et al. [12]
Kaolin, talc, alumina, silica	Indialite, protoenstatite, corundum	González-Velasco et al. [66]
Kaolin, talc, alumina, silica	Cordierite, spinel	Bruno et al. [67]
Ball clay, talc, alumina, siliceous sand	Cordierite, cristobalite, quartz	Alves et al. [6]
Kaolin, talc, MgO	Cordierite	Yamuna et al. [68]
Kaolin, talc, MgO	Cordierite, spinel, forsterite	Valášková, Simha Martynková [11]
Kaolin, talc, MgO	Cordierite, cristobalite, enstatite	Pavlikov et al. [64]
Kaolin, Mg(OH) ₂	Cordierite, spinel	Kobayashi et al. [9]
Kaolin, magnesite (raw)	Cordierite	Al-Harbi et al. [70]
Talc, diatomite, alumina	Indialite	Goren et al. [5]
Talc, pyrophyllite, alumina	Cordierite, alumina, cristobalite	Pavlikov et al. [64]
Sepiolite (raw)	Cordierite	Zhou et al. [62]
Kaolin, talc, vermiculite, gibbsite	Cordierite, enstatite, corundum, spinel	Valášková and Simha Martynková [11]
Kaolin, talc, vermiculite, alumina	Cordierite, enstatite, corundum	Valášková and Simha Martynková [13]
Kaolin, talc, vermiculite	Cordierite, enstatite	Valášková and Simha Martynková [13]
Kaolin, vermiculite	Cordierite	Valášková and Simha Martynková [13]

Clay mixtures of cordierite composition were clay minerals kaolin and talc [3]. Other cordierites were synthesized from the mixtures of kaolin clay, talc, alumina [64, 65] or gibbsite [1, 63]. The compact cordierites were sintered from magnesium hydroxide [9]) or magnesium oxide [11, 64, 68]. Pure cordierites (indialite) were sintered from talc, diatomite (fine-grained, highly siliceous sedimentary rock) and alumina [5] or a raw sepiolite [62]. Cordierite/steatite ceramics was sintered from kaolinite, talc, vermiculite and alumina or gibbsite [11, 13]. Cordierite ceramics were prepared to be used as automotive catalysts that promote purifying exhaust gas [68-70].

Selected published data on the preparation of cordierite ceramics in Table 3 show that although identical formulation of clay mineral mixtures were used for sintering, a qualitative representation of minerals in cordierites was variable. This is due to many factors. An important role play chemical and structural characteristics of individual clay minerals used in the clay mineral mixtures, methodology of processing of the green body and then sintering conditions of ceramics. For example gibbsite increases formation of mullite in cordierite, which decomposes at temperature 550°C to the γ -Al₂O₃ [71].

Glassy phases in ceramics sometimes result from silica-rich impurities or they can also be added during processing route in order to obtain ceramic specific physical or mechanical properties. The cordierite glass is inherently isotropic and begins to crystallize at about 1000°C. Cordierite-forming clay formulation is influenced by the isotropic cordierite glass and converts into crystalline cordierite at about 1370°C. The expansion coefficient of such cordierite ceramic product is lowered and its thermal stress is low, even if repeated cycles of rapid heating and cooling are applied. The cordierite glass ceramics has also an increased density and therefore the mechanical strength increased as a whole.

Sintering additives are generally used to stimulate sintering and to modify the microstructure and properties of ceramics.

The MgO:Al₂O₃:SiO₂ ratio in MgO–Al₂O₃–SiO₂ glasses strongly affects the crystallization of μ - and α -cordierite. The formation of μ -cordierite is suppressed, and the crystallization of α - form is enhanced in glasses richer in MgO and SiO₂ relative to stoichiometric cordierite. The alkali-containing compound can be, for example, a natural or synthetic colloidal clay, smectite, palygorskite, sepiolite, or ball clay. The limitation of alkali metals, sodium and potassium, present in the compositions is to a maximum of Na₂O and K₂O about 0.14 % by weight for maintaining good heat shock characteristics in ceramic [72]. Many additives of oxides such as Li₂O, Na₂O, CaO, B₂O₃, P₂O₅, Fe₂O₃, ZnO, V₂O₅, TiO₂ and ZrO₂ have been tested for their positive effect on the increase of the thermal expansion coefficient [10,

73-77]. Similarly, the combined effect of magnesium borate additive and grinding caused decreasing of sintering temperature of cordierite down to 1000°C [78]. The addition of CaO and ZnO in the MgO–Al₂O₃–SiO₂ glass-ceramic system allow to produce dense glass-ceramic at low temperature (~ 1000°C), and of low dielectric constant [79]. Densification process depends also on initial MgO:Al₂O₃ ratio or the presence of the TiO₂ or MgO additives [80, 81].

Rare earth oxides can stimulate the sintering of cordierite ceramics by forming a liquid phase prior to the transformation of cordierite. Shi et al. [82-85] studied the effect of additives of CeO₂ on removing the transitional phases in the sintering process to obtain ceramic with low thermal expansion coefficient and relatively high content of cordierite. The rare earth Eu³⁺ – doped cordierite was studied for the luminescence properties [86].

CONCLUSIONS

The nomenclature and characteristic structural properties of clays, clay minerals talc, kaolin, vermiculite, ceramic raw materials, cordierite ceramics, cordierite and cordierite polymorphs were summarized.

Mineral phases in clay mixtures and cordierites sintered at 1300°C were compared.

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