STRUCTURAL CHARACTERISTICS OF CORDIERITES BASED ON COMMERCIAL VERMICULITES IN RELATION TO THE NATURAL AND SYNTHETIC CORDIERITES

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The preparation and characterization of cordierites based on the commercial vermiculites obtained from the powder pre-ceramic mixtures containing talc, kaolinite and vermiculite in the composition close to the cordierite $2MgO\cdot2Al_2O_3\cdot5SiO_2$ has been reported since 2009. The aim of this paper was to characterize the structural properties of the nine synthetic cordierites sintered from the pre-ceramic mixtures containing commercial vermiculites at 1300°C, in comparison with the orthorhombic natural and synthetic hexagonal cordierites (indialites) selected from literature. The orthorhombic natural cordierites showed the elements Fe and Mn replacing Mg in an appropriate correlation F = (Fe+Mn)/(Fe+Mn+Mg) with the unit cell parameter a, and an inverse correlation with parameter c. The unit cell parameters c calculated for the nine synthetic cordierites based on vermiculites (Ver) were in good linear relation with the $F_{Ver} = (Fe/(Fe+Mg))_{oct} + (K+Na+Ca)_{int})$ per formula unit of the corresponding vermiculites in the pre-ceramic mixtures. The structural disorder of cordierites based on vermiculites was determined higher, according to the wide index W1/3 of (211) reflection varying in a narrow range $W1/3_{(211)}$ from 0.290° to 0.299° 2θ, in comparison with the $W1/3_{(211)} = 0.324°$ 2θ of the cordierites based on the alumina.

INTRODUCTION

The cordierite glass-ceramics based on MgO–SiO_2–Al_2O_3 crystalline system are widely used due to their excellent mechanical properties, low dielectric constant and low coefficient of thermal expansion. The earliest physicochemical investigation of the system MgO–Al_2O_3–SiO_2 brought information about the α form of cordierite $2MgO{:}2Al_2O_3{:}5SiO_2$ (2:2:5) and an unstable μ-cordierite modification of cordierite $MgO{:}Al_2O_3{:}3SiO_2$ (1:1:3) [1]. A natural analogue of α form was cordierite subsequently discovered in India and named indialite [2]. The crystal structure of indialite is isotypic with that of hexagonal beryl [3-5].

Cordierite aluminosilicate $Al_4Si_5O_{18}$ framework consists from tetrahedra $(Al^{3+}, Si^{4+})O_4$ and octahedra $(Mg^{2+}, Fe^{2+})O_6$ interspersed with channels that can contain larger molecules (e.g., H_2O, CO_2) or cations (e.g. Na^+, Cs^+). Mg-cordierite, $Mg_2Al_4Si_5O_{18}$, crystallizes in two polymorphic forms: the high-temperature disordered hexagonal form (space group *P6/mmc*), stable above about 1450°C and the low-temperature slightly disordered orthorhombic form (space group *Cccm*), stable below 1450°C [6-8]. In the high-temperature hexagonal structure the Al and Si atoms are distributed over two sets of tetrahedral sites (3 T1 and 6 T2 sites

per formula unit). The refined structure of indialite has a disordered distribution of 2Al and 1Al atoms over T1 sites and 2Al and 4Si disordered over T2 site [8-10]. During Al, Si ordering an opposite pair of T2 tetrahedra are occupied by the 2 Al atoms and symmetry is reduced to orthorhombic with the space group *Cccm* (Figure 1). The relationship between the hexagonal and orthorhombic unit cells (Figure 1a), which could form from the hexagonal structure, can be performed at three equivalent orientations of the orthorhombic unit cell (Figure 1b) [11].

The structural transformations of Al,Si order-disorder were studied on the high- (hexagonal), inter-mediate- (modulated hexagonal) and low- (orthorhombic) cordierites [7, 12-14]. An intermediate crystal phases are of either the indialite or cordierite between the highest disorder and a rather high degree of order. Miyashiro [5] used a distortion index $\Delta = 2\theta_{(131)} - (2\theta_{(511)} + 2\theta_{(421)})/2$, as a measure of the degree of disorder which is defined by the X-ray diffraction (XRD) angles in the region between 2θ = 29 and 30° (CuKα radiation) for the orthorhombic peaks (131), (511) and (421) in the powder XRD patterns. Distortion indices Δ describing the state of advancement of the hexagonal to orthorhombic transition are in a range from 0.0 in hexagonal cordierite to about 0.25 in fully ordered, orthorhombic Mg-cordierite.
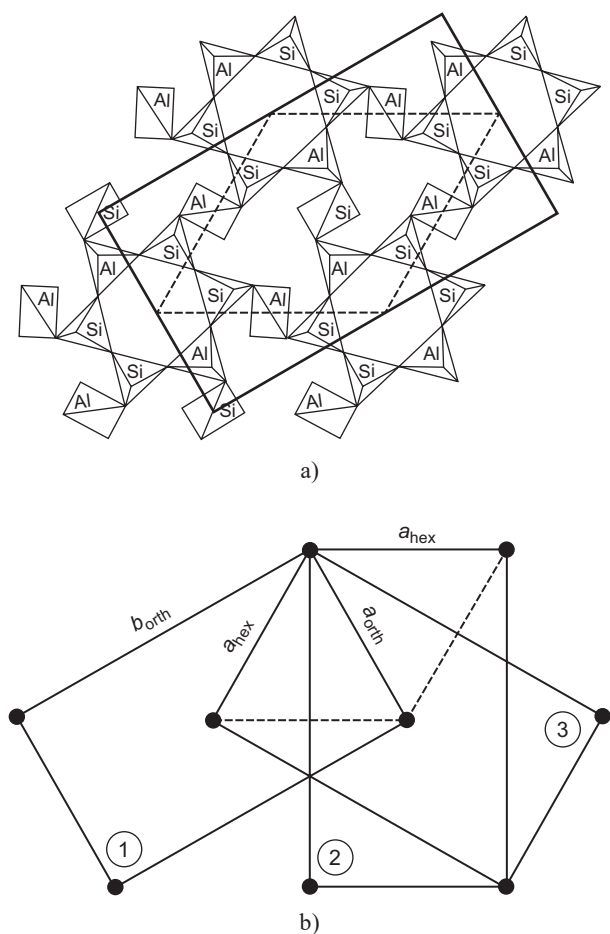
Figure 1. Geometry of the cordierite structures: a) The orthorhombic unit cell of the ordered structure (full line) and the hexagonal unit cell of the disordered cordierite structure (dashed line); b) Three equivalent orientations of the orthorhombic unit cell derived from the hexagonal unit cell [11].

Natural cordierites occur mostly as (Si,Al)-ordered orthorhombic low-cordierites with minor amounts of alkaline earth and alkali metal elements [7] and occasionally as hexagonal high-cordierites, indialites, with a less ordered (Si,Al)-arrangement [8]. Substitution of the large cations Mg^{2+} and Fe^{2+} for Al^{3+} is sustained by the decreasing average size of the octahedral cation. Tetrahedral substitution of Fe^{2+} up to 11 % in Fe,Mg-cordierites was assessed by Mössbauer spectroscopy [15].

Synthetic hexagonal cordierites were found at low temperatures in glass ceramics. The synthetic indialite was obtained from the melts at the high temperatures as the component of solid solutions of Mg-cordierite ($Mg_2Al_4Si_5O_{18}$) – Mg-beryl ($Mg_3Al_2Si_6O_{18}$) [16]. Longer annealing of this system in the low-temperature region, which occurs at about 1300°C, resulted in the breakdown of the solid solutions and the separation of cordierite in the stoichiometric composition $2MgO·2Al_2O_3·5SiO_2$. The

solid solutions of cordierite, which may be considered as metastable form at lower temperatures (1250°C) remain at very low temperatures (1050°C) unchanged for more than a year [16]. Disordered high cordierite also crystallizes as a metastable phase from all temperatures below 1455°C and be retained by quenching [17].

Most clay minerals and clays, alone or in mixtures, are used for their contribution to the working properties and drying strength of the ceramic masses [18]. Some of clays are applied more because they offer an inexpensive integral component or filler of the desired chemical composition. Natural clay materials used in preparing of ceramics include impurities of alkali oxides and alkaline earth oxides. These admixtures together with the layered structure of clay minerals facilitate structural changes in a relatively low temperature annealing.

Vermiculite is a secondary 2:1 clay mineral formed primarily alteration of micas (biotite and phlogopite). At all the major commercial deposits, natural vermiculites occur as the mixed-layer vermiculite-biotites or vermiculite-phlogopites [19-21]. The commercial vermiculites from Sta. Olalla (Huelva, Spain), Catalão (Goiás, Brasil), China and Palabora (South Africa) were examined at elevated temperatures for the thermal transformation [22]. Vermiculites containing the principal cations K^+, Na^+ and Ca^{2+} in the interlayer space transformed at 1000°C during 1 min to mica-like or mica-like phases coexisting with enstatite. Vermiculite from Sta. Olalla, containing only Mg^{2+} in the interlayer space, changed to enstatite.

Vermiculites are well-known for their water-retention properties. Porous ceramics with good water-retention properties were prepared from mixtures of ground vermiculite with allophane at 600 - 800°C [23]. The exchangeable Mg^{2+} cations in Mg-saturated vermiculite structure, $Mg_3(Si_3Al)O_{10}(OH)_2·Mg_{0.5}(H_2O)_{4.0}$, lie in a plane midway between 2:1 layers and have a plane of water molecules on each side. Each water molecule is linked by a hydrogen bond to single oxygen in the silicate layer surface and the water sheets are held together by the exchangeable cations [24]. An isomorphous substitution of metal cations with similar size and lower valence, such as $Si^{4+}–Al^{3+}$ (in tetrahedra) and $Al^{3+}–Mg^{2+}$ (in octahedra) creates a net negative charge of 2:1 layers [25]. The negative layer charge, which arises mostly from the substitution of Al^{3+} for Si^{4+} in tetrahedral sites, is between 0.6 and 0.9 eq/$(Si,Al)_4O_{10}$. 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 characteristic properties of vermiculite (e.g., the high cation exchange capacity, the ability to form complexes with organic substances, depending on the exchangeable cations and the humidity) are suitable for modifying of vermiculite precursors into the cordierite ceramics with specifics properties. During the last five years, vermiculites were prepared

into the powder mixtures as: (1) The cation exchanged zirconium-vermiculite precursor of zircon ($ZrSiO_4$) in dense cordierite-$ZrSiO_4$ ceramics [26, 27], (2) The carrier of an anchored ceria (CeO_2) nanoparticles precipitated on the negative surface for the cordierite/steatite/CeO_2 photocatalysts [28], and (3) Organovermiculite pore-forming additive to the porous cordierite ceramics [29].

The aim of the work is to compare the structural data of the cordierites based on vermiculite prepared from the powder mixtures containing commercial vermiculites in the stoichiometric oxides composition close to the cordierite composition $2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$ with the data of the published selected natural and synthetic cordierites.

EXPERIMENTAL

The clay minerals kaolinite, Ka, (from LB Minerals, s.r.o., Czech Republic), talc KT5, Tc, (from Koltex Color, s.r.o., Czech Republic) and commercial vermiculites (Grena, s.r.o., Czech Republic) were used for preparation of the pre-ceramic cordierite mixtures. Five natural vermiculite samples prepared by milling and then sieving to the particles size fraction less than 0.40 μm were denoted as Ver-L, Ver-B, Ver-S, Ver-P and Ver-C.

Ver-L from the Letovice crystalline complex in the eastern part of the Bohemian Massif (Czech Republic) is a product of transformation of Mg-chlorites in metamorphosed basalts, as well as gabbroic and ultrabasic bodies.

Ver-B from Belitsa, northwestern region of Bulgaria, was found in calc-alkaline rocks, biotite-hornblende granodiorites and tonalities, that apparently has resulted from the action of rain water on the biotite and phlogopite [30].

Ver-S from the Paraiba region of Brazil occurs in the Santa Luzia mine mainly within zones of complex mafic, ultramafic and carbonatite after transformation of phlogopite and biotite [31].

Ver-P from Palabora mine in the Limpopo province of South Africa occurring in the phlogopite- and apatite-rich pyroxenites is a product of hydration of phlogopite into vermiculite. This vermiculite was described as mixed-layer vermiculite-phlogopite, with the content of vermiculite less than 50 % [32].

Ver-C from the Qieganbulak apatite-vermiculite deposit in Xinjiang Yuli Xinlong (China) is the weathering product of phlogopite from a basic-ultrabasic complex [33].

The chemical composition of commercial vermiculites (Table 1) was determined using the X-ray fluorescence spectrometer Spectro X-lab [26-29]. The

Table 1. Chemical analysis of commercial vermiculites, kaolinite and talc and cations in structural formulae of vermiculites.

Oxides	Ver-L	Ver-B	Ver-P	Ver-S	Ver-C	Ka	Tc
SiO_2	32.00	41.15	41.25	43.34	40.16	46.13	60.22
TiO_2	0.50	0.41	1.03	0.85	1.07	0.19	0.00
Al_2O_3	14.51	9.98	8.75	10.83	12.40	37.28	0.60
Fe_2O_3	7.91	5.36	5.06	6.14	4.31	0.77	0.19
FeO	0.26	0.79	1.25	0.46	0.47	0.00	0.00
CaO	0.18	1.46	2.43	1.30	2.16	0.32	0.73
MgO	22.25	23.22	23,48	23.23	23.88	0.43	31.55
MnO	0.11	0.05	0.06	0.10	0.04	0.00	0.00
Na_2O	0.02	0.19	0.15	0.35	0.46	0.00	0.00
K2O	0.06	0.48	4.81	1.82	3.55	0.65	0.01
LOI	21.56	16.70	11.47	11.40	10.98	14.14	6.24
Total	99.36	99.79	99.74	99.82	99.48	99.91	99.54

Ions p.f.u*	Ver-L	Ver-B	Ver-P	Ver-S	Ver-C
Si	2.65	3.15	3.10	3.14	2.95
Al^{IV}	1.35	0.85	0.78	0.86	1.05
Fe	–	–	0.12	–	–
Al^{VI}	0.06	0.05	–	0.06	0.03
Fe^{3+}	0.49	0.31	0.23	0.33	0.24
Fe^{2+}	0.02	0.05	0.08	0.04	0.03
Mg	2.40	2.57	2.64	2.52	2.64
Ti	0.03	0.02	0.05	0.05	0.06
K	0.01	0.05	0.45	0.15	0.33
Na	0.01	0.02	0.02	0.02	0.05
Ca	0.02	0.12	0.10	0.10	0.16
Mg	0.34	0.07	–	–	–

* 10 structural oxygens plus two OH and a total negative charge of 22 per formula unit

samples were mixed with the wax and pressed into the form of pellets. The concentration of Na^+, K^+, Mg^{2+} and the total content of the Fe^{2+} and Fe^{3+} was also determined using the atomic emission spectrometer JY 24 with inductively coupled plasma (ICP-AES) after total sample dissolution in HCl and HF and acid mixture ($H_3PO_4 + H_2SO_4 + H_3BO_3$). The content of Fe^{2+} was determined using titration with 0.1 M solution of $K_2Cr_2O_7$ after sample decomposition in HCl and HF in a CO_2 atmosphere, according to the Czech standard CSN 722041 Part 11. The loss on ignition was determined by heating of samples in muffle furnace at 1000°C. The chemical composition of vermiculites was recalculated into structural formulae using a basis of 10 structural oxygens plus two OH and a total negative charge of 22 per formula unit, p.f.u (Table 1).

The X-ray powder diffraction (XRD) patterns of cordierite ceramic samples were recorded in the 5 – 80° 2θ range with a scanning rate of 2°·min⁻¹ using the X-ray diffractometer Ultima IV Rigaku (Rigaku, Japan), operated at 40 kV and 40 mA with CuKα radiation (reflection mode, scintillation counter). The unit cell parameters of cordierites were calculated by a least squares refinement program [34] using the interlayer d-values and assigned h k l indices.

Cordierites based on the vermiculite in mixtures

A basic clay mixture for sintering cordierite, which is often used in scientific research and industry, is composed of talc ($Mg_3Si_4O_{10}$)($OH)_2$, kaolinite ($Si_2Al_2O_5$)($OH)_4$ and alumina (Al_2O_3). Vermiculite from Czech Republic (named Ver-L) was added to the basic clay mineral mixtures in an amount from 13 to 50 wt. %

Table 2. Structures of selected natural and synthetic cordierites according to literature.

No.	Host rock, Locality [Reference]	Formula
Orthorhombic natural cordierites (space group Cccm)		
	The Bergell region in the Central Alps [36]	
1.	Inclusion in tonalite	$(Mg_{1.86}Fe_{0.14}) Al_{4.03}Si_{4.98}O_{18}$
2.	Pelitic zone	$(Mg_{1.79}Fe_{0.19}) Al_{4.02}Si_{5.00}O_{18}$
3.	Cordierite-garnet-biotite-gneiss	$(Mg_{1.72}Fe_{0.27}) Al_{4.00}Si_{5.00}O_{18}$
4.	Cordierite-K feldspar-biotite gneiss	$(Mg_{1.36}Fe_{0.64}) Al_{4.03}Si_{4.98}O_{18}$
5.	Inclusion zone in Bergell granite	$(Mg_{1.19}Fe_{0.73}) Al_{4.03}Si_{5.01}O_{18}$
6.	Contact of Bergell granite	$(Mg_{1.11}Fe_{0.80}) Al_{4.01}Si_{5.03}O_{18}$
	Tuscany, Italy [9]	
7.	"Torniella" cordierite from a rhyolite	$(Mg_{1.12}Fe_{0.82}Mn_{0.02}) Al_{4.02}Si_{4.99}O_{18}$
8.	San Vincenzo Cordierite from a rhyodacite	$(Mg_{0.95}Fe_{1.09}Mn_{0.03}) Al_{3.91}Si_{5.03}O_{18}$
9.	"Lipari" nodule. Cordierite from rhyodacite	$(Mg_{0.90}Fe_{1.12}Mn_{0.03}) Al_{4.00}Si_{5.00}O_{18}$
10.	"Lipari" crystal. Cordierite from rhyodacite.	$(Mg_{1.17}Fe_{0.86}Mn_{0.02}) Al_{3.96}Si_{5.00}O_{18}$
	Other natural cordierites [37]	
11.	White Well, Western Australia	$(Mg_{1.88}Fe_{0.09}Na_{0.05}) Al_{3.96}Si_{4.94}O_{18}$
12.	Casper, Wyoming	$(Mg_{1.76}Fe_{0.23}Na_{0.04}) Al_{4.00}Si_{5.00}O_{18}$
13.	SN2229 from metapelite, Labrador	$(Mg_{1.67}Fe_{0.32}Mn_{0.02}Na_{0.02}) Al_{4.00}Si_{5.00}O_{18}$
14.	Guilford from pegmatite vein	$(Mg_{1.55}Fe_{0.45}Mn_{0.02}Na_{0.07}) Al_{4.00}Si_{5.00}O_{18}$
15.	Pielosca, Finland	$(Mg_{1.46}Fe_{0.55}Mn_{0.01}Na_{0.03}) Al_{4.00}Si_{5.00}O_{18}$
16.	Haddam, Connecticut	$(Mg_{1.34}Fe_{0.58}Mn_{0.02}Na_{0.27}) Al_{4.00}Si_{5.00}O_{18}$
17.	Ghost Lake, Canada	$(Mg_{1.21}Fe_{0.77}Na_{0.03}) Al_{4.00}Si_{5.00}O_{18}$
18.	SN72123, Labrador	$(Mg_{0.86}Fe_{1.12}Na_{0.02}) Al_{4.00}Si_{5.00}O_{18}$
19.	Sugama, Japan	$(Mg_{0.49}Fe_{1.17}Mn_{0.20}Na_{0.33}) Al_{4.00}Si_{5.00}O_{18}$
20.	Dolni Bory, Czechoslovakia	$(Mg_{0.19}Fe_{1.61}Mn_{0.08}Na_{0.20}) Al_{4.00}Si_{5.00}O_{18}$
Hexagonal cordierites(space group P6/mcc)		
	Natural indialites	
21.	Indialite from xenolithic rocks, Italy [38]	$(K_{0.17}Mg_{1.94}Fe_{0.06}Ca_{0.04}) Al_{4.25}Si_{4.75}O_{18}$
22.	Indialite from coal seam, India [8]	$(Mg_{1.40}Fe_{0.66}) Al_{4.11}Si_{4.89}O_{18}$
23.	Indialite from cordierite gneisses, India [39]	$(Mg_{1.38}Fe_{0.63}Mn_{0.05}Ca_{0.25}) Al_{4.72}Si_{4.19}O_{18}$
	Synthetic cordierites	
24.	Cordierite from the gel [40]	$Mg_{2.00}Al_{4.00}Si_{5.00}O_{18}$
25.	Cordierite from glass [41]	$Mg_{2.00}Al_{4.00}Si_{5.00}O_{18}$
26.	Cordierite from glass [42]	$Mg_{2.00}Al_{4.00}Si_{5.00}O_{18}$

with the simultaneous adjustment of the other incorporated minerals, while maintaining close to cordierite composition $2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$ [26, 35]. Cordierites named here as X1-X4 were prepared from the powder mixtures containing variable representation of talc, kaolinite, alumina and vermiculite (in mass %) as follows:

X1: talc (40), kaolinite (47), alumina, Al_2O_3 (13) [35].

X2: talc (30), kaolinite (45), vermiculite (12) and alumina (13) [35].

X3: talc (20), kaolinite (50), vermiculite (30) [26].

X4: kaolinite (50), vermiculite (50) [26].

Mixtures were homogenized, milled for 20 min in ball mill and sintered at 1300°C for 1 hour, and then the cooling for ca. 10 hours.

Cordierites based on the different vermiculites in mixtures

Cordierites based on vermiculites, samples named here L, B, S, P and C, were sintered from the powder cordierite mixture containing talc (40 mass %), kaolinite (47 mass %) and vermiculite (13 mass %) instead of alumina [21]. Vermiculites (Ver) from different commercial deposits were applied always in the same quantity.

The average crystal chemistry formulas of vermiculites (Table 1) show a variable substitution of Fe^{3+} and Fe^{2+} in octahedra and Na^+, K^+ and Ca^{2+} in the interlayer space and indicate deviation from the pure Mg-vermiculite. According to the XRD analysis, diffraction patterns of Ver-B and Ver-L were very similar to the Mg-vermiculites. Other Ver-S, Ver-P and Ver-C were mixed layered mica-vermiculites.

Structures of cordierites based on vermiculites can be compared with the selected from literature data about 26 natural orthorhombic and synthetic hexagonal cordierites, containing similar elements in the structure as studied vermiculites (Table 2).

The six crystals of cordierites from metamorphic rocks of the Bergel Alps are Nos. 1 to 6 with Fe/(Fe+Mg) ranging from 0.07 to 0.42 (p.f.u) [36]. The single crystals of cordierites Nos. 7 to 10 from volcanic rocks of Tuscany and Lipary (Italy) were analyzed in the structure of Fe-rich cordierites [9]. Cordierites natural grains Nos. 11 to 20 were selected from various host rocks in the range of the atomic ratio of elements (Fe + Mn)/(Fe + Mn + Mg) from 0.046 to 0.898 (p.f.u) [37]. The representatives of natural hexagonal cordierites are three indialites: No. 21, occurring in xenolithic rocks of Somma-Vesuvius volcano (Italy) with significant content of potassium [38], No. 22 from coal seams at Bokaro (India) [8], and No. 23 from the metamorphic cordierite-sillimanite rock complexes [39]. The synthetic hexagonal cordierites prepared from

the cordierite glasses using sol-gel process are: No. 24 [40], No. 25 [41] and No. 26 [42].

RESULTS AND DISCUSSION

The previous studies showed that the substitution Fe^{2+} and Mn^{2+} for Mg^{2+} caused the increase of the octahedral volume of cordierite [43]. The increased content of Fe influenced the channels to move apart and rotate and move closer together within each channel resulting in decrease of the unit cell parameter c [36].

The linear regression analyses of the natural orthorhombic cordierite samples Nos. 1-20 showed an appropriate correlation (Figure 2) between parameter a (Figure 2a) and an inverse correlation between parameter c (Figure 2b) and the corresponding Fe and Mg ratio F = (Fe+Mn)/(Fe+Mn+Mg).

The XRD patterns of the synthetic cordierites based on vermiculite samples are very similar (Figure 3). The maxima positions 2θ (°) of reflections and assigned

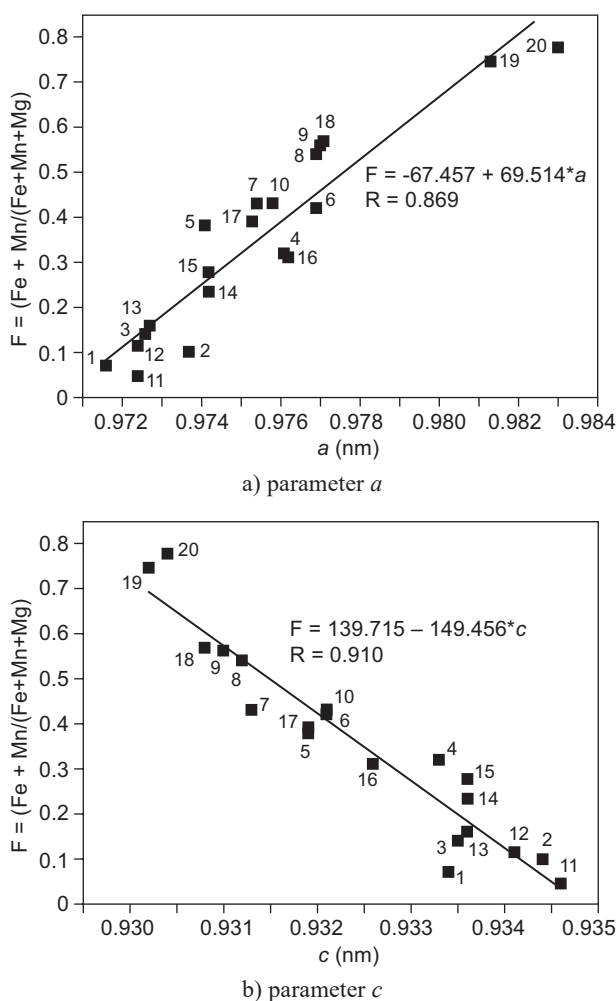a) parameter a

b) parameter c

Figure 2. The orthorhombic unit cell parameters vs. atomic ratio F = (Fe+Mn)/(Fe+Mn+Mg) (p.f.u.) in the natural cordierites Nos. 1-20 (Table 2): a) parameter a; b) parameter c.

indexes (hkl)$_{hex}$ in the hexagonal symmetry (Figure 3a) were used to calculate the unit cell parameters (Figure 4).

The reflection region between 2θ = 29 and 30° is characteristic for an intermediate crystalline phases between indialite highest disorder and cordierite high degree of order and calculation of distortion index *Δ* [44]. Cordierites based on vermiculite showed here one single peak with the wide and asymmetrical profile (Figure 3b). For the sake of lucidity, in this region are indicated: the position of (211)$_{hex}$ peak at 29.5° 2θ calculated from the refinement structural data [41] and the positions of (511)$_{orth}$ at 29.36° 2θ, (421)$_{orth}$ at 29.45° 2θ and (131)$_{orth}$ at 29.62° according to the structural data [42]. Putnis and Bish [45] characterized according to the no splitting peak (211) on the XRD pattern and characteristic orthorhombic waves in TEM the intermediate modulated cordierite microstructure. Authors studied using the combination of XRD, TEM and IR techniques the mineral phases
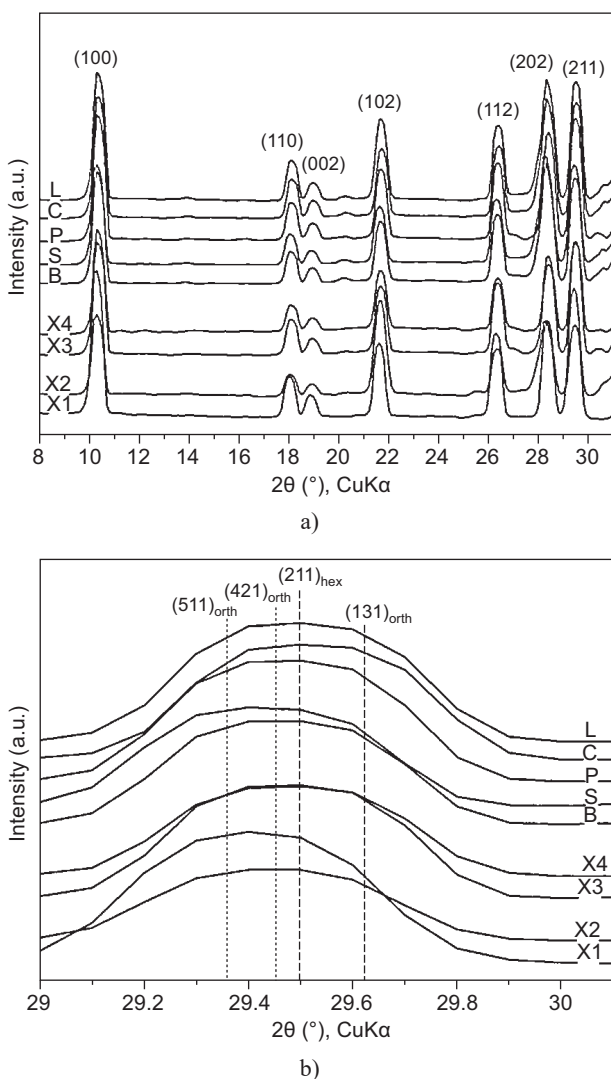
crystallizing from the stoichiometric Mg-cordierite glass by annealing at temperatures between 1050°C and 1445°C for periods from 30 seconds to 1000 hours. The first crystallization product was hexagonal cordierite which on annealing transformed to orthorhombic cordierite. After 3 hours of annealing, the onset of a modulated cordierite micro-structure was observed. Cordierites based on vermiculites were obtained from the sintering pre-ceramic mixtures at similar conditions (1 hour at 1300°C and the cooling for ca. 10 hours) [26, 35] and crystallization of modulated microstructures can be anticipated. According to the XRD patterns, the no splitting (211)$_{hex}$ peak and wide profiles of cordierite based on vermiculite samples (Figure 3b) may mask low-intensive orthorhombic peaks. Owing to the unidentifiable in the XRD patterns orthorhombic reflections, which signalize slight inclination from the hexagonal symmetry in the modulated cordierite structures, deviation from hexagonal symmetry by the distortion index Δ cannot be determined.
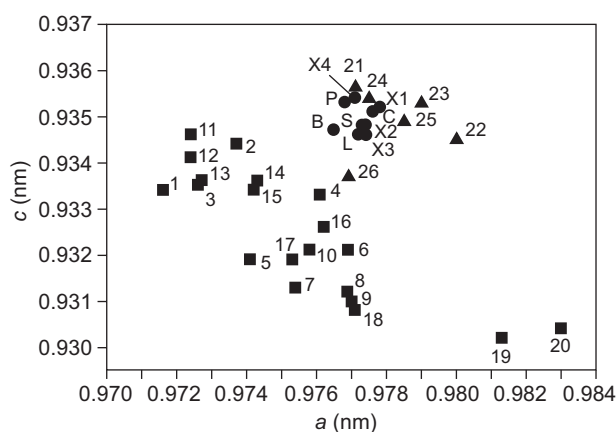

Figure 4. The unit cell parameters *a* vs. *c* for cordierites: Natural orthorhombic (Nos. 1-20); Natural hexagonal (Nos. 21, 22 and 23); Synthetic hexagonal (Nos. 24, 25 and 26); Synthetic hexagonal L, B, S, P and C based on vermiculites Ver-L, Ver-B, Ver-S, Ver-P and Ver-C in mixtures; Synthetic hexagonal X1, X2, X3 and X4 based on the mixtures of different formulation containing vermiculite.

a)

b)

Figure 3. The XRD powder patterns of cordierite based on vermiculite samples: a) The reflections with assigned (hkl)$_{hex}$ indices; b) The indicated peak positions of (211)$_{hex}$ and (511)$_{orth}$, (421)$_{orth}$ and (131)$_{orth}$ in the range 2θ from 29 to 30°.

Graphical presentation of the unit cell parameters *a* vs *c* calculated for cordierites based on vermiculite and 26 published for natural and synthetic cordierites allows their comparison (Figure 4).

Cordierites L, B, S, P and C prepared from mixtures containing different vermiculites Ver-L, Ver-B, Ver-S, Ver-P and Ver-C, respectively, have a slightly lower cell edges *c* and *a* than hexagonal natural and synthetic indialites Nos. 21-25. In the case of vermiculites used in the pre-ceramic mixtures, the substituting elements in octahedra (Fe and Mg)$_{(oct)}$ and interlayer space (Na, K, and Ca)$_{(int)}$ are released during the sintering into the melt and can take part in the crystallization of cordierites based on vermiculites. As has been estab-

lished by several authors, the alkali ions K^+ and Na^+ can enter into the structural channels of cordierite [46]; Ion K^+ is too large to be accommodated in the four- and six-coordinated sites and can be located within the cordierite large channels parallel the c axis [7]; Partial incorporation of Na^+ in the center of the six-member ring of oxygen atoms causes the rings to predominantly compress along the b-axis [47].

Chemistry of various vermiculites, according to the atomic ratios $F_{Ver} = (Fe/(Fe+Mg)_{oct} + (K+Na+Ca)_{int})$ per formula unit (p.f.u.), has small effect on the unit cell parameter c in cordierites based on vermiculites (Figure 5). The c values in cordierites L, B, S, P and C were in the range from 0.9346(7) nm to 0.9353(9) nm in a good linear relation with the F_{Ver} calculated from 0.21 to 0.69 for corresponding vermiculites Ver-L, Ver-B, Ver-S, Ver-P, and Ver-C, respectively, in the pre-ceramic mixtures (Figure 5a). The maximal difference 0.0007 nm in parameter c was between the cordierites L and P and is within the standard deviations calculated for each parameter c.

A more sensitive than distortion index Δ was designed the width index $W1/3$, assayed at the one third of the maximum intensity of peak located near 29.5° 2θ for CuKα [48]. Authors [48] recommended the use of the index $W1/3$ as a relative parameter for comparison of samples of known composition and thermal procedure. Cordierite based on vermiculite samples L, B, S, P, C, X3 and X4 showed a narrow range $W1/3_{(211)}$ from 0.290° to 0.299° 2θ. Exceeding of the range to the $W1/3_{(211)} = 0.322$ and 0.324° was determined at samples X1 and X2, respectively, sintered from the mixtures containing also alumina (Figure 5b). According to the width index $W1/3_{(211)}$ can be assumed that order-disorder of cordierites based on vermiculites is modulated highly disordered hexagonal and different from modulated structures of cordierites based on alumina.

CONCLUSIONS

Structural ordering of the 9 synthetic cordierites based on the commercial vermiculites was studied based on the X-ray powder diffraction data and compared with the literary 26 natural orthorhombic and synthetic hexagonal cordierites.

The slightly smaller than published hexagonal unit cell parameters of cordierites based on vermiculites were linearly dependent on the atomic ratio $F_{Ver} = (Fe/(Fe+Mg)_{oct} + (K+Na+Ca)_{int})$ per formula unit (p.f.u.) of the corresponding vermiculites in the pre-ceramic mixtures.

Chemistry of various vermiculites, according to the atomic ratios $F_{Ver} = (Fe/(Fe+Mg)_{oct} + (K+Na+Ca)_{int})$ per formula unit (p.f.u.), has small effect on the unit cell parameter c in cordierites based on vermiculites. The maximal difference 0.0007 nm in parameter c was within the standard deviations calculated for each parameter c.

The width index $W1/3$ determined from (211) peak allowed separation of highly disordered hexagonal cordierites based on vermiculites from modulated structures of cordierites based on alumina.
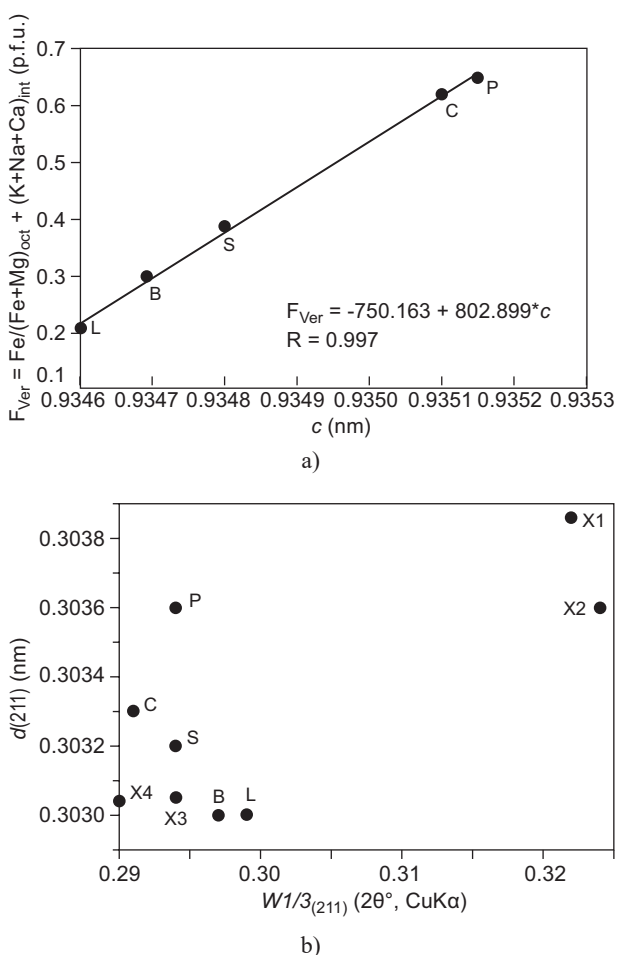
Acknowledgment

Figure 5. Structural relation in cordierites based on vermiculites: a) The unit cell parameters c in cordierites L, B, S, C, and P as a function of the atomic ratio $F_{Ver} = Fe/(Fe+Mg)_{oct} + (K+Na+Ca)_{int}$ (p.f.u.) in vermiculites Ver-L, Ver-B, Ver-S, Ver-C and Ver-P; b) The width index $W1/3_{(211)}$ vs. interlayer value $d_{(211)}$ in cordierites.

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