

Thermally induced conversion of Mg²⁺ cation exchanged LTA, FAU, GIS and SOD zeolites: syntheses and characterization of γ -cordierite, a new Mg₂Al₄Si₅O₁₈ polymorph

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Abstract: The thermal behaviours of fully Mg²⁺ cation exchanged LTA, FAU (X and Y species), GIS and SOD zeolites were investigated in the temperature range from ambient to 1400 °C. The initial zeolite frameworks collapsed into amorphous intermediate substances after air heating between 800–850 °C. Prolonged annealing of these products above 850 °C induced recrystallization into sapphirine-like phases (Mg–LTA and Mg–FAU_x zeolites) and μ -cordierite (Mg–FAU_y and Mg–GIS zeolites) phases. These phases were unstable during further temperature/time treatment and between 1000–1100 °C they polymorphously transformed into γ -cordierite, a new Mg₂Al₄Si₅O₁₈ polymorph. γ -Cordierite was formed as a transformation product from the investigated zeolite precursors, except for the Mg–SOD zeolite. Structurally the γ -cordierite phase is a modulated, Mg-stuffed derivative of cristobalite with the approximate composition Mg₂Al₄Si₅O₁₈, which precedes the appearance of α -cordierite. The orthorhombic unit cell dimensions calculated from X-ray powder diffraction pattern are: $a = 16.387(7)$ Å, $b = 8.835(4)$ Å, $c = 7.853(3)$ Å. γ -Cordierite has a narrow range of temperature stability (1100–1200 °C) and during prolonged temperature/time treatment, it is polymorphously transformed to the α -cordierite phase.

Keywords: Mg²⁺ cation exchanged zeolites, thermal conversion, γ -cordierite new polymorph, phase stability.

INTRODUCTION

Due to a wide range of suitable dielectric and thermomechanical properties, earth-alkaline aluminosilicate-based ceramics have attracted a great deal of attention in recent years as alternative substrate materials to the conventionally used corundum (α -alumina). Of ceramic compounds such as: celsian and hexacelsian (BaAl₂Si₂O₈), anorthite (CaAl₂Si₂O₈), Sr-feldspar (SrAl₂Si₂O₈) and α -cordierite (Mg₂Al₄Si₅O₁₈), the last offers the best combination of all these properties.^{1,2}

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The crystal structure³ of high-temperature α -cordierite form is characterized by hexagonal symmetry and a disordered distribution of Al and Si cations in a tetrahedral framework.⁴ This form is metastable and under prolonged temperature/time annealing treatment,⁵ it is polymorphously transformed into the ordered orthorhombic β -cordierite form.^{6–8} The α -cordierite phase is conventionally prepared by melting the appropriate oxides and quenching to form a glass of the desired composition. The glass is subsequently crystallized in α -cordierite by controlled heat treatment. However, this process is usually preceded by primary crystallization of the μ -cordierite phase, which is the third $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$ polymorph in the three-component phase $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ (MAS) system.⁹ The μ -cordierite phase is a metastable Mg-stuffed derivative¹⁰ of the β -quartz structure,^{11,12} which would be topotactically transformed into the α -cordierite phase by prolonged heating, Fig. 1.

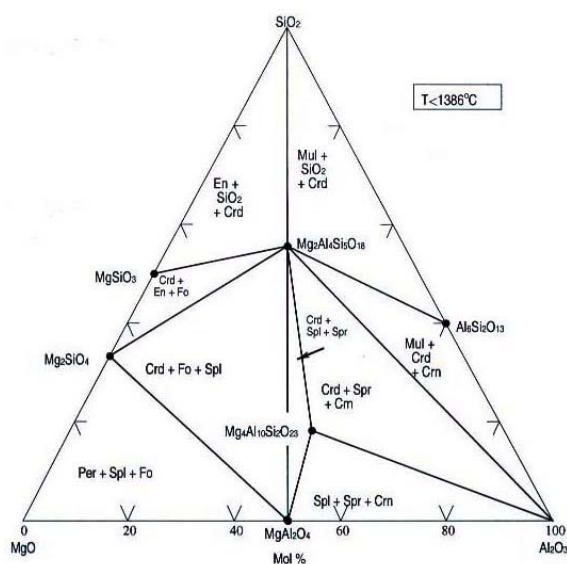


Fig. 1. Constitutional data for $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ (MAS) ternary phase system.⁹ Abbreviations: Crd – cordierite; Spl – spinel, Spr – sapphirine; Mul – mulite; En – enstatite; Fo – forsterite.

Due to the growing interest for the syntheses of α -cordierite, several publications^{13–16} and patents,^{17,18} dealing with the zeolite conversion route firstly proposed by Breck,¹⁹ appeared recently. By this method of synthesis, which include the thermal conversion of cation exchanged zeolites, all the above-mentioned compounds were also prepared.^{20–23} Moreover, several new aluminosilicate phases, such as: Ag-carnegieite,²⁴ γ -eucryptite,^{25–27} δ -eucryptite,²⁸ CsAlSiO_4 -ANA²⁹ and KAlSiO_4 -ANA³⁰ were synthesized. Therefore, the discussed zeolite conversion route could be considered as a powerful method for the investigation of aluminosilicate phase systems.

The work presented here is a continuation of previous^{21,22} studies on thermally induced phase conversions of sodium LTA, FAU, GIS, SOD³¹ and other syn-

thetic zeolites, exchanged with alkaline earth elements. In this study, interest was focused on the titled zeolites, synthesis conditions and preliminary characterization of a new $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$ phase, hitherto unrecognised in the other experiments.

EXPERIMENTAL

The initial sodium zeolites LTA (Si/Al = 1.00) and FAU (13X specie; Si/Al = 1.34 and SK-40 specie; Si/Al = 2.40; X and Y species, respectively) were manufactured by Union Carbide Co., whereas GIS (P specie; Si/Al = 1.38) and SOD (Si/Al = 1.00) zeolites were self-prepared. Near fully cation exchanged Mg^{2+} forms of these zeolites were obtained after several successive exchanges from aqueous 0.5 M solutions of $\text{MgSO}_4 \cdot \text{H}_2\text{O}$.

The chemical composition of the samples was analysed by atomic absorption spectrophotometry, using a Perkin Elmer 380 instrument.

The prepared Mg^{2+} cation exchanged forms of LTA, FAU, GIS and SOD zeolites were air-heated in a Carbolite CTF 15/75 electric furnace using a programmed temperature/time regime in the range from 700–1400 °C for 1–6 hours. Thermally induced structural conversions of the Mg^{2+} cation exchanged zeolites were followed on the calcined samples by the X-ray powder diffraction (XRPD) technique, after cooling to room temperature.

The XRPD patterns were obtained on a Phillips, PW-1710 automated diffractometer, using a Cu tube operated at 40 kV and 35 mA. The instrument was equipped with a diffracted beam curved graphite monochromator and a Xe-filled proportional counter. Diffraction data were collected in the 2θ angle range 4–70°, counting for 0.25 and 2.50 seconds at 0.02 steps. A fixed 1° divergence and 0.1 mm receiving slits were used. The trial and error indexing program Dicvol³² and a program for the refinement of the cell dimensions Lsucrip³³ were used.

Investigations of the crystal morphology of the synthesized phases were performed by scanning electron microscopy (SEM), using a Jeol 840A instrument. The investigated samples were gold sputtered in a JFC 1100 ion sputter.

RESULTS

The results of the chemical analyses of the Mg^{2+} cation exchanged zeolites are presented in Table I. It is evident from the results that near complete $\text{Mg}^{2+} \rightarrow 2\text{Na}^+$ exchange was achieved for LTA, GIS and SOD zeolites, whereas for the species of FAU zeolite, the cation exchange was incomplete.

TABLE I. Chemical analyses of the initial Mg^{2+} cation exchanged zeolites: LTA, FAU, GIS and SOD, used as precursors for thermal conversion

Initial zeolite	Si/Al Ratios	Chemical analyses
Mg-LTA	1.00	(0.988MgO-0.012Na ₂ O)·Al ₂ O ₃ ·2.00SiO ₂
Mg-FAU _(X)	1.34	(0.976MgO-0.024Na ₂ O)·Al ₂ O ₃ ·2.48SiO ₂
Mg-FAU _(Y)	2.40	(0.970MgO-0.030Na ₂ O)·Al ₂ O ₃ ·4.80SiO ₂
Mg-GIS _(P)	1.38	(0.991MgO-0.009Na ₂ O)·Al ₂ O ₃ ·2.76SiO ₂
Mg-SOD	1.00	(0.994MgO-0.006Na ₂ O)·Al ₂ O ₃ ·2.00SiO ₂

The phase transformations of so-prepared zeolite precursors as a function of temperature are presented in Figs. 2–6. The thermally induced conversion processes could be summarized as follows: The aluminosilicate frameworks of the initial Mg^{2+} cation exchanged zeolites (Figs. 2–6, curves a), became unstable with increasing temperature and commenced to collapse between 700–850 °C,

when intermediate amorphous products were formed, (Figs. 2–6, curves b). Further annealing at about 900 °C led to the recrystallization of the amorphous products into Mg-aluminosilicates: sapphirine-like compounds (Figs. 2 and 3, curves c) and μ -cordierite (Figs. 4 and 5, curves c). These Mg-aluminosilicate phases were unstable during the prolonged temperature/time heat treatment and at about 1100 °C they recrystallized by complex polymorphic transformation processes to the same new phase, named γ -cordierite (Figs. 2–5, curves d). The behaviour of the Mg-SOD zeolite precursor (Fig. 6, curve a–e) was an exception, with the final conversion leading to a spinel phase and amorphous silica (Fig. 6, curve e).

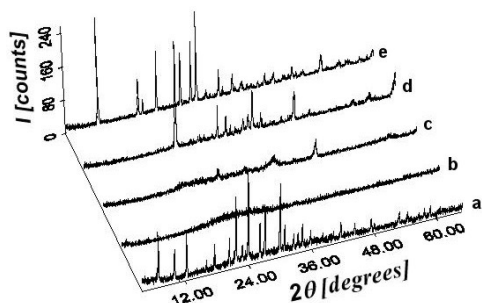


Fig. 2. XRPD Patterns of the phases synthesized in the process of thermally induced conversion of Mg^{2+} cation exchanged LTA zeolite: a) initial Mg-LTA zeolite (specie A, Si/Al = 1.00), 25 °C; b) amorphous intermediate substance, 800 °C, 1 h; c) sapphirine-like phase, 1030 °C, 2 h; d) γ -cordierite_{LTA} phase, 1100 °C, 4 h; e) α -cordierite_{LTA} phase, 1350 °C, 2 h.

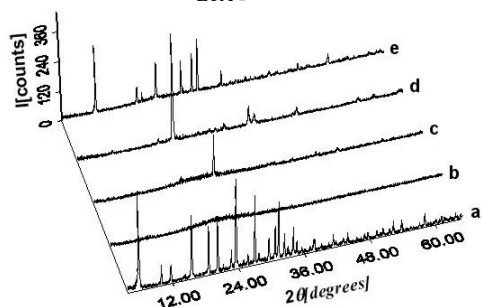


Fig. 4. XRPD Patterns of the phases synthesized in the process of thermally induced conversion of Mg^{2+} cation exchanged FAU (specie Y) zeolite: a) initial Mg-FAU_(Y) zeolite (Si/Al = 2.40), 25 °C; b) amorphous intermediate substance, 850 °C, 1 h; c) μ -cordierite_{FAU(Y)} phase, 1000 °C, 1 h; d) γ -cordierite_{FAU(Y)} phase, 1150 °C, 3 h; e) α -cordierite_{FAU(Y)} phase, 1350 °C, 2 h.

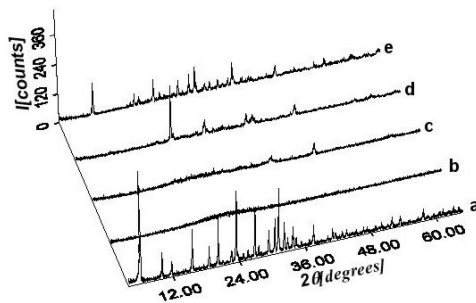


Fig. 3. XRPD Patterns of the phases synthesized in the process of thermally induced conversion of Mg^{2+} cation exchanged FAU (specie X) zeolite: a) initial Mg-FAU_(X) zeolite (Si/Al = 1.24), 25 °C; b) amorphous intermediate substance, 820 °C, 1 h; c) sapphirine-like phase, 1030 °C, 3 h; d) γ -cordierite_{FAU(X)} phase, 1100 °C, 1 h; e) α -cordierite_{FAU(X)} phase, 1350 °C, 2 h.

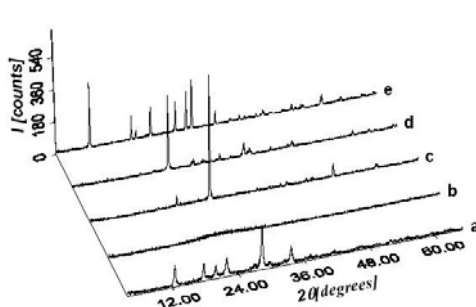


Fig. 5. XRPD Patterns of the phases synthesized in the process of thermally induced conversion of Mg^{2+} cation exchanged GIS (specie P) zeolite: a) initial Mg-GIS_(P) zeolite (Si/Al = 1.38), 25 °C; b) amorphous intermediate substance, 820 °C, 1 h; c) μ -cordierite_{GIS} phase, 900 °C, 1 h; d) γ -cordierite_{GIS} phase, 1100 °C, 3 h; e) α -cordierite_{GIS} phase, 1350 °C, 2 h.

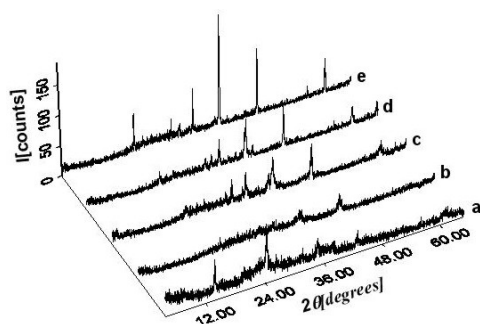


Fig. 6. XRPD Patterns of phases synthesized in the process of thermally induced conversion of Mg^{2+} cation exchanged SOD zeolite: a) initial Mg-SOD zeolite ($\text{Si}/\text{Al} = 1.00$), 25 °C; b) amorphous intermediate substance and low crystallized spinel, 850 °C, 1 h; c) amorphous intermediate substance and low crystallized spinel, 1000 °C, 1 h; d) well crystallized spinel and amorphous substance, 1200 °C, 2 h; e) excellently crystallized spinel and amorphous substance, 1350 °C, 2 h.

An example of the XRPD patterns for the novel γ -cordierite phase synthesized from Mg-GIS zeolite precursor is presented in Table II, whereas the unit cell dimensions are given in Table III. This newly synthesized Mg-aluminosilicate phase has a narrow interval of temperature stability (around 100–150 °C, Fig. 7a and 7b), after which prolonged heating induced its conversion to α -cordierite (Figs. 2–5, curves e, and Fig. 8b) in all cases investigated. The final products synthesized at around 1350 °C, except for the quantitatively dominant α -cordierite phase, contained some traces of spinel, mullite and quartz phases.

TABLE II. XRPD Data for γ -cordierite_{GIS(P)} polymorph synthesized by thermal decomposition of Mg-GIS_(P) zeolite at 1100 °C for 4 hours

I/I_0 , %	h	k	l	$d_{\text{obs}} / \text{Å}$	$d_{\text{calc}} / \text{Å}$
100	4	0	0	4.1013	4.0968
1	2	1	2	3.2846	3.2866
3	3	0	2	3.1928	3.1882
3	3	1	2	3.0020	2.9989
	4	2	0	–	3.0039
1	2	3	0	2.7742	2.7714
1	4	1	2	2.6969	2.6992
2	6	0	1	2.5808	2.5796
13	0	1	3	2.5122	2.5097
5	3	3	1	2.4606	2.4616
2	0	3	2	2.3560	2.3559
3	3	4	0	2.0484	2.0477
	8	0	0	–	2.0484
1	1	1	4	1.9029	1.9034
	2	3	3	–	1.9029
1	3	3	3	1.8417	1.8419
1	4	0	4	1.7704	1.7704
3	1	3	4	1.6258	1.6254
2	9	3	0	1.5491	1.5487
1	7	4	2	1.4864	1.4869
3	0	6	1	1.4471	1.4473
	4	1	5	–	1.4467
5	7	2	4	1.4232	1.4239

TABLE III. Unit cell dimensions of γ -cordierite_{GIS(P)} phase and some cristobalite stuffed derivatives

Compound	$a / \text{Å}$	$b / \text{Å}$	$c / \text{Å}$	$\alpha / ^\circ$	$\beta / ^\circ$	$\gamma / ^\circ$
γ -Cordierite _{GIS(P)}	16.387(7)	8.835(4)	7.853(3)	90.00	90.00	90.00
Ag-Carnegieite ²⁴	5.023(3)	5.074(3)	16.982(9)	98.30	81.62	119.20
Carnegieite ⁴⁷	10.261(1)	14.030(2)	5.1566(6)	90.00	90.00	90.00
γ -Eucryptite ²⁶	8.299(1)	5.0365(8)	8.263(1)	90.00	107.42	90.00

Due to the complexity of the system and the overlapping of the synthesized phases, the results of temperature/time transformation (TTT) processes are presented schematically in Figs. 7a and 7b. An analysis of the XRPD, SEM and TTT results, lead to the conclusion that the α -cordierite phase was obtained by different and complex transformation routes, whereas the γ -cordierite phase always proceeded to α -cordierite.

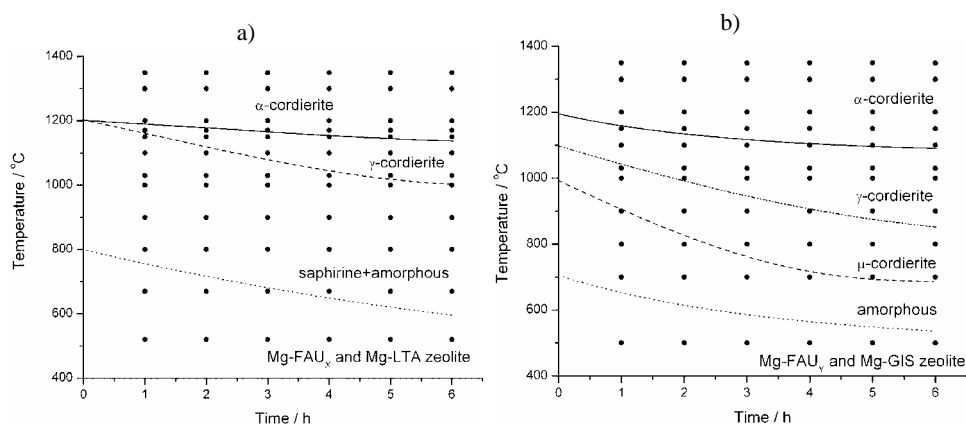


Fig. 7. A time-temperature-transformation (TTT) diagram for the cordierite polymorphs synthesized in the process of the thermally induced conversion of synthetic: a) Mg-LTA (Si/Al = 1.00) and Mg-FAU_(X) (Si/Al = 1.24) zeolites; b) Mg-FAU_(Y) (Si/Al = 2.40) and Mg-GIS_(P) (Si/Al = 1.38) zeolites.

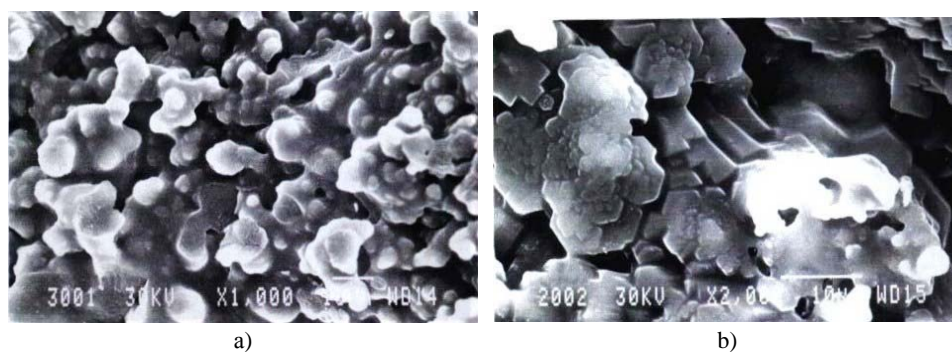


Fig. 8. Selected characteristic SEM morphologies of cordierite polymorphs synthesized in the process of thermally induced conversion of Mg-GIS_(P) zeolite: a) γ -cordierite_{GIS(P)} phase morphology (rounded grains), 1100 °C, 3 h; b) α -cordierite_{GIS(P)} phase morphology (hexagonal crystals), 1350 °C, 2 h.

DISCUSSION

The results obtained from the thermal investigation of Mg^{2+} cation exchanged zeolites confirmed the known transformation route to more densely packed structures *via* an amorphous²² intermediary substance. Unlike the direct conversion of zeolite,^{34,35} the amorphous synthesis route could be roughly divided into three different stages.

The initial step of the transformation correspond to changes in the frameworks of the Mg^{2+} cation exchanged zeolites, which occurs in the temperature range between ambient and temperatures where their collapse commences. These changes are generally connected with dehydration processes on the zeolite frameworks. All the investigated initial Mg^{2+} cation exchanged zeolites (Figs. 2–6, curves a) passed through this stage before the collapse of their frameworks.

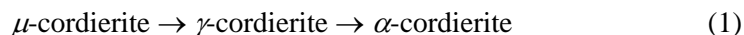
Immediately after the collapse of their frameworks, the second step of the transformations commences. This is characterized by the formation of amorphous substances which retain such properties during the following 100–150 °C temperature rise (Figs. 2–5, curves b). The amorphous matter obtained after the collapse of the Mg–GIS zeolite is an exception, having amorphous characteristics in the range between 450–850 °C. Here it is important to emphasize that the so-prepared intermediate substances are dimensionally probably nanostructured,²² *i.e.*, they consist of the relicts of different tetrahedral secondary building units,³¹ which were the elements of the preceding zeolite frameworks. Although we do not have direct experimental evidence for the structural evolution of these amorphous matters in the above-mentioned temperature ranges, this could be deduced by comparing the initial zeolite structures with framework topologies with phases which recrystallized from the amorphous substances during prolonged heating. Moreover, it seems that the amorphous substances formed from the investigated Mg-zeolites as precursors possess some preferred characteristics not observed in the corresponding glasses obtained by classical melting/devitrification routes. As a proof for the validity of this assumption, the syntheses of Ag–carnegieite,²⁴ γ -eucryptite^{25,26} and kaliophilite,³⁰ a new aluminosilicates prepared only by discussed method, can be cited. Another argument for the structural evolution of the amorphous intermediate substances lies in the particular segregation at the end of second stage, resulting in the recrystallization of the two-phase mixture. Such examples were observed earlier for Li–LTA,²⁵ Cs–LTA²⁹ and Ca–LTA²² zeolite precursors, *i.e.*, their thermal conversions. Recently published results on $\text{BaAl}_2\text{Si}_2\text{O}_8$ ³⁶ and NaAlSiO_4 ³⁷ amorphous precursors prepared from LTA zeolites by the discussed route, confirmed the pest assumptions concerning its special characteristics.

The recrystallization of the intermediate amorphous substance simultaneously indicates the processes connected to the final step of the thermally induced conversion of the zeolites. This stage is mostly characterized by the crystalli-

zation of newly formed phase(s) and its polymorphous transformation to a more stable phase, because of prolonged heating. However, during this step of the transformations, characterized by high temperature/time conditions, solid state reactions are probable and phase formation processes could not be excluded.

In the case of Mg^{2+} cation exchanged zeolite precursors, the final step commences with the recrystallization of the intermediate amorphous substances into sapphirine-like (Figs. 2 and 3, curves c) and μ -cordierite phases (Figs. 4 and 5, curves c), respectively. It is easily to conclude from Table I and Figs. 7a and 7b, that the recrystallization of the intermediate amorphous substance is dependent on the Si/Al ratio. When this ratio is closer to unity (Mg-LTA; zeolite A and Mg-FAU; zeolite X) the TTT processes proceeded in the formation of a sapphirine-like (Fig. 7a) phase whereas the siliceous samples (Mg-FAU; zeolite Y and Mg-GIS; zeolite P) gave the μ -cordierite phase (Fig. 7b). The extension "like" is used due to the confusion concerning the sapphirine composition and its structural relation³⁸ to spinel, clinopyroxene and α -cordierite phases. Sapphirine is ideally $Mg_4Al_8Si_2O_{20}$, *i.e.*, clearly different from the stoichiometry of α -cordierite, but these phases are neighbours in the MAS phase system, separated by a common border (Fig. 1). Therefore, it seems probably that the sapphirine-like phases obtained in the present experiments have compositions closer to α -cordierite than to sapphirine. The polymorphous inversion between sapphirine-like and α -cordierite phases over an intermediate γ -cordierite phase was observed for the first time, confirming also their compositional similarities.

The initial crystallization of μ -cordierite from siliceous amorphous substances originating from Mg-FAU_(Y) and Mg-GIS_(P) zeolites is not surprising. It has been known for a long time that μ -cordierite precedes the crystallization of the α -cordierite phase in the MAS system, especially in the case of preheated glasses^{11,12}. The fact that metastable μ -cordierite is the first crystallization product is in keeping with many such transformations. Metastable phases generally nucleate more readily than the equilibrium product, a fact that has been confirmed in many investigations of the MAS system.³⁹⁻⁴³ However, the present results obtained for Mg-FAU_(Y) and Mg-GIS_(P) zeolite shows that the polymorphous transformation μ -cordierite \rightarrow α -cordierite has an alternative route *via* the intermediate γ -cordierite phase according to scheme (1):



which was recognized for the first time in this study.

The synthesized sapphirine-like and μ -cordierite phase are unstable during prolonged heating. Therefore, at appropriate temperatures, these phases will polymorphously transform into the same phase, namely γ -cordierite, as discussed previously (Figs. 2-5, curves d and Figs. 7a and 7b). The XRPD pattern for γ -cordierite, Table II, could not be identified within the Mg-aluminosilicate phases deposited in the JCPDS file. However, the observed γ -cordierite patterns are si-

milar to low-cristobalite (file card No. 39-1425). The powder patterns of the synthesized γ -cordierites (Fig. 9, curves a–d) are also very similar to carnegieite,^{44,45} γ -eucryptite²⁶ and Ag–carnegieite²⁴ (Fig. 9, curves e–g) patterns. Structurally these phases belong to the stuffed^{10,46} derivatives of cristobalite. These were obtained by the same zeolite preparation route, as was the γ -cordierite phase. Moreover, the temperature induced structural inversions known for silica polymorphs^{10,46} have counterpart behaviours in the case of silica stuffed derivative pairs such as: γ -eucryptite \rightarrow β -eucryptite,^{25,26} α -eucryptite \rightarrow β -eucryptite²⁷ and low-carnegieite \rightarrow nepheline \rightarrow high-carnegieite.^{44–48} According to this discussion and the reconstructive polymorphous inversion observed in μ -cordierite \rightarrow γ -cordierite in the cases of Mg–FAU(γ) and Mg–GIS(ρ) zeolite, it is believed that the synthesized γ -cordierite is structurally a Mg-stuffed derivative of cristobalite. The minor differences in the calculated unit cell dimensions of the synthesized γ -cordierites suggest their probable non-stoichiometric composition inherited from parent zeolite, *i.e.*, sapphirine or μ -cordierite phases. From the crystallochemical aspect, the γ -cordierite phase is in terms of stoichiometry very similar to Mg₂Al₄Si₅O₁₈, *i.e.*, α -cordierite. According to preceding discussion, it is obvious that the γ -cordierite phase is situated in the MAS phase diagram, Fig. 1, in the field of α -cordierite in the border regions towards the sapphirine and tridymite/cristobalite (Mg-stuffed aluminosilicate derivatives) regions, due to their complex conversion relationships. Thus, the composition of γ -cordierite corresponds closely to those known for μ -cordierite^{12,13} and α -cordierite phases. Finally, it should be emphasized that the results presented for the γ -cordierite phase are rather preliminary. Due to the strong susceptibility to modulation of its crystal lattice, the XRPD structure determinations as well as other investigations on pure γ -cordierite are in progress and will be published separately.

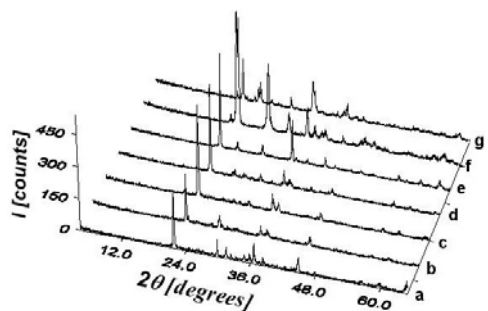


Fig. 9. XRPD Patterns of various cristobalite stuffed derivative phases synthesized by the thermally induced conversion route: a) γ -cordierite_{LTA} phase, 1100 °C, 4 h; b) γ -cordierite_{FAU(X)} phase, 1100 °C, 1 h; c) γ -cordierite_{FAU(Y)} phase, 1150 °C, 3 h; d) γ -cordierite_{GIS} phase, 1100 °C, 3 h; e) low-carnegieite phase;⁴⁵ f) γ -eucryptite phase;²⁶ g) Ag–carnegieite phase.²⁴

The synthesized γ -cordierite phases are characterized by a narrow temperature/time stability range (Figs. 7a and 7b). With further annealing, the metastable γ -cordierite phases polymorphously convert, by reconstructive transformation, to more stable α -cordierite phases (Figs. 2–5, curves e and Fig. 8). Their frameworks are characterized by Si/Al disorder, which was tested by measuring the

$\Delta 2\theta$ distortion indices⁴⁹ and ²⁷ Si-MAS-NMR spectroscopy⁸, the results of which will also be published separately.

CONCLUSIONS

The employment of the XRPD and SEM techniques, enabled the time/temperature induced structural changes and complex solid state conversion of different Mg²⁺ cation exchanged zeolites, *i.e.*, LTA, FAU, GIS and SOD structural types, to be followed. Detailed phase analysis revealed very complex conversion processes (polymorphous transformations and reactions in the solid state), which finally led to the formation of α -cordierite phases. All the investigated Mg-zeolite transformation processes were characterized by the formation of the same, structurally metastable Mg-stuffed derivative of cristobalite, with the approximate composition Mg₂Al₄Si₅O₁₈. Due to its close polymorphous relationships with the known cristobalite structure and the μ - and α -cordierite phases, the re-recognized Mg-stuffed derivative phase is named γ -cordierite.

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ИЗВОД

ТЕРМАЛНО ИНДУКОВАНА КОНВЕРЗИЈА Mg²⁺ КАТЈОНСКИ ИЗМЕЊЕНИХ ЗЕОЛИТА ТИПА LTA, FAU, GIS И SOD; СИНТЕЗА И КАРАКТЕРИЗАЦИЈА γ -КОРДИЈЕРИТА НОВОГ Mg₂Al₄Si₅O₁₈ ПОЛИМОРФА

РАДОВАН ДИМИТРИЈЕВИЋ¹ И ВЕРА ДОНДУР²

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Термално индукована фазна конверзија Mg²⁺ катјонски измењених форми синтетичких зеолиита типа: LTA, FAU (X и Y форма), GIS и SOD, испитивана је у температурном интервалу од 25–1400 °C. Полазне зеолиитске алумосиликатне мреже стабилне су до око 700 °C, када започиње њихово рушење у аморфну супстанцу. Овај процес завршен је између 800 и 850 °C. Продужено загревање ових продуката изнад 850 °C, индукује рекристализацију аморфних продуката у фазу сличну сафирину (Mg-LTA и Mg-FAU_(X) зеолиити) и μ -кордијерит (Mg-FAU_(Y) и Mg-GIS зеолиити). Рекристалисане фазе су нестабилне у току продуженог третмана температура/време, и између 1000 и 1100 °C, долази до њихове структурне трансформације у γ -кордијерит, нови кордијеритски полиморф. Са структурног аспекта γ -кордијерит представља попуњени дериватив кристобалита приближног састава Mg₂Al₄Si₅O₁₈ за који је из Ро-дифракционих мерења одређена ромбична јединична ћелија: $a = 16.387(7)$ Å, $b = 8.835(4)$ Å, $c = 7.853(3)$ Å. γ -Кордијерит има узан опсег температурне стабилности (1100–1200 °C) и у продуженом третману температура/време структурно се трансформише у α -кордијерит, у свим испитиваним случајевима осим Mg-SOD зеолиита, када се као крајњи продукт трансформације добија оксид спинел.

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