# Cordierite ($2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$) synthesis by unconventional methods

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**Abstract**

*The cordierite was synthesized by two unconventional methods: 1) the method which uses hydrosilicate precursors and 2) the method which uses organic precursors. Comparison of these synthesis methods with the classical one is the main subject of the presented paper. The influence of $Li_2O$ on the cordierite phase formation was investigated too. The results have suggested that the method which uses hydrosilicate precursors provides the $SiO_2$ linkage as magnesium metasilicate, but is not adequate for the cordierite synthesis. Only in the presence of $Li_2O$ considerably amount of the μ-cordierite modification was formed, confirming the mineralizing effect of this oxide. In addition, the results have clearly demonstrated that the method which uses organic precursors is suitable for the cordierite synthesis. Thus, even without mineralizer it can be used for the preparation of the almost pure α-cordierite at 1200°C. Because of that this method was used to obtain pigments with cordierite structure, in which $Al^{3+}$ was partially substituted with $Cr^{3+}$ (pink pale colour), and $Mg^{2+}$ was partially substituted with $Co^{2+}$ (blue colour).*

*Keywords: cordierite, synthesis, $Li_2O$ mineralizer, pigments*

## I. Introduction

The cordierite is a magnesium/aluminium aluminosilicate [1] with the crystallo-chemichal formula $Mg_2{}^{[4]}Al_3{}^{[6]}(Si_5Al^{[4]}O_{18})$ and a complex structure having six tetrahedral units: five of $[SiO_2]$ and one of $[AlO_4]$. Binding of the tetrahedral units is ensured by the $[AlO_6]$ octahedral and $[MgO_4]$ tetrahedral. The cordierite has several polymorphic modifications. A low temperature modification, β-$Mg_2Al_4Si_5O_{18}$, crystallizes in the orthorhombic system and a high temperature modification, α-$Mg_2Al_4Si_5O_{18}$ named indialite, crystallizes in the hexagonal system [2]. Existence of a metastable modification, μ-$Mg_2Al_4Si_5O_{18}$, was also mentioned in literature [2]. The μ-$Mg_2Al_4Si_5O_{18}$ modification crystallizes in the hexagonal system and could be obtained by crystallization of some glasses at 900°C for 200 hours.

The cordierite has important properties such are: low electrical conductivity, very low thermal expansion coefficient, relatively high hardness (7÷7.5 on Mohs scale) and high chemical inertness. Because of these properties, the cordierite represents a valuable mineralogical constituent in some electrotechnical porcelains, thermally stable ceramic masses or supports for catalysts. An interesting field of application is also synthesis of thermoresistant pigments by including some chromophore ions ($Co^{2+}$, $Cr^{3+}$) in the cordierite crystalline network [3–5].

The literature data underlines the difficulty of cordierite synthesis. Using the classical method, based on annealing of mechanical mixed raw materials, temperatures over 1250°C [6] and frequently up to 1350°C [3,4] are needed. The valuable properties of cordierite and problems with the classical method are reasons for development of different unconventional synthesis methods [5–14].

One very attractive unconventional synthesis method (the method which uses hydrosilicate precursors) is based on the precipitation reaction taking place between a sodium silicate solution and solutions of some soluble salts of alkaline-earth metals [15–18]. Silicates of the respective metals are formed by annealing of the obtained precipitates at temperatures over 800°C and represent a source of linked $SiO_2$, being able to react further with the $Al_2O_3$, $Cr_2O_3$ etc. Thus, the reduced reactivity of $SiO_2$, introduced as quartz or even as silica gel

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(which transforms in cristobalite during annealing), can be in large measure avoided. This results in decrease of the formation temperature of some complex oxide compounds ($CaO{\cdot}Al_2O_3{\cdot}2SiO_2$, $3CaO{\cdot}Cr_2O_3{\cdot}3SiO_2$, $CaO{\cdot}SnO_2{\cdot}SiO_2$) for 200-300°C in respect to the classical method.

Another important unconventional synthesis method is based on the formation of a complex organic Al/Mg precursor (the aluminium and magnesium glyoxylate) [18–28]. The complex organic precursor is obtained by the oxidation of 1,2-ethanediol with aluminium and magnesium nitrates according to the following reactions:

$$Al(NO_3)_3 + H_2O \rightarrow Al(OH)(NO_3)_2 + HNO_3$$

$$6C_2H_4(OH)_2 + 4Al(OH)(NO_3)_2 + 2Mg(NO_3)_2 \xrightarrow{xH_2O} \xrightarrow{xH_2O} Al_4Mg_2(OH)_4(C_2H_2O_4)_6 \cdot xH_2O + 12NO + 12H_2O$$

$$NO_{(g)} + 1/2O_{2(g)} \rightarrow NO_{2(g)}$$

In order to obtain the cordierite phase, the complex organic Al/Mg precursor is synthesized in the presence of $SiO_2$. The advantage of the method is again considerably lower synthesis temperature.

In this work, two unconventional methods were employed for the cordierite synthesis: 1) the method which uses hydrosilicate precursors and 2) the method which uses organic precursors. In addition, comparison of these synthesis methods with the classical one is also presented. Finally, the possibility of preparing some thermoresistant pigments with cordierite structure was investigated too.

## II. Experimental

Three synthesis methods, one classical and two unconventional, were employed for synthesis of different cordierite samples (Tables 1–3). Due to difficulties regarding the cordierite formation two set of experiments were done, one without and another with $Li_2O$ (introduced as $Li_2CO_3$).

*Classical method*

The samples P.1 (without $Li_2O$) and P.1.1 (with $Li_2O$) were prepared with the classical method (Table 1) starting from $MgCO_3$ (Reactivul Bucureşti, Romania), aluminium hydroxide (ALOR ORADEA, Romania) and quartz with 99.2 % $SiO_2$ (Mindo-Dorohoi, Romania). After dosing, the mixture was wetly homogenized, dried in stove, milled and then annealed at different temperatures in porcelain crucibles.

*Method which uses hydrosilicate precursors*

The cordierite ($2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$) was also synthesized by the precipitation reaction between the precursors containing Mg, Si and Al cations (Table 2). $MgSO_4{\times}7H_2O$ (Reactivul Bucureşti, Romania) and $Na_2O{\cdot}2.5SiO_2$ granules (Loba Feinchemie) were used as source of MgO and $SiO_2$, respectively, whereas $Al(OH)_3$, *Al-hydroxide* (ALOR-ORADEA, Romania) or $(NH_4)Al(SO_4)_2{\times}12H_2O$, *alum* (Reactivul Bucureşti, Romania) as source of $Al_2O_3$. Magnesium sulphate was dissolved in warm water (50°C) and mixed with aluminium hydroxide to form a suspension. The sodium silicate was also dissolved in warm water (50°C) and then slowly added to the previously prepared suspension. The precipitation reaction took place practically instantaneous:

$$2MgSO_4 + 2(Na_2O \cdot 2.5SiO_2) \xrightarrow[-2Na_2SO_4]{+4Al(OH)_3\ suspension} \xrightarrow[-2Na_2SO_4]{+4Al(OH)_3\ suspension} 2MgO \cdot 5SiO_2 \cdot xH_2O + 4Al(OH)_3$$

$$\xrightarrow{t°C} 2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$$

The resulted suspension was heated 30 minutes, and the prepared particles, with notation P.2 (without $Li_2O$) and P.2.1 (with $Li_2O$), were separated from a liquid phase by filtration. The cordierite samples P.3 (without $Li_2O$) and P.3.1 (with $Li_2O$) were prepared on the similar way, however, $(NH_4)Al(SO_4)_2{\times}12H_2O$ was used as $Al_2O_3$ source instead of $Al(OH)_3$. The obtained particles were washed, dried and finally annealed at different temperatures in porcelain crucibles.

*Method which uses organic precursors*

The aqueous solution of magnesium and aluminium nitrates and 1,2-ethandiol was heated in a water bath at approximately 80°C. During the exothermal reaction, elimination of $NO_2$ took place and the complex organic Al/Mg precursor (the aluminium and magnesium glyoxylate) was prepared. In order to obtain the cordierite, the reaction was preceded in the presence of $SiO_2$. Aerosil (Degussa, Germany), as reactive form of $SiO_2$, was dispersed in the solution containing 1,2-ethandiol,

**Table 1. Composition of the samples synthesized by classical method**

| Sample No. | Molar ratio MgO | $Al_2O_3$ | $SiO_2$ | Mineralizer $Li_2O$ [wt.%] |
|---|---|---|---|---|
| P.1 | 2 | 2 | 5 | - |
| P.1.1 | 2 | 2 | 5 | 2 |

**Table 2. Composition of the samples synthesized from hydrosilicate precursors**

| Sample No. | Molar ratio MgO | $Al_2O_3$ | $SiO_2$ | Mineralizer $Li_2O$ wt.%] |
|---|---|---|---|---|
| P.2 | 2 | 2(hydroxide) | 5 | - |
| P.2.1 | 2 | 2(hydroxide) | 5 | 2 |
| P.3 | 2 | 2(alum) | 5 | - |
| P.3.1 | 2 | 2(alum) | 5 | 2 |

**Table 3. Composition of the samples synthesized from organic precursors**

| Sample No. | Molar ratio MgO | $Al_2O_3$ | $SiO_2$ | $Cr_2O_3$ | CoO | Mineralizer $Li_2O$ [wt.%] |
|---|---|---|---|---|---|---|
| P.4 | 2 | 2 | 5 | - | - | - |
| P.4.1 | 2 | 2 | 5 | - | - | 2 |
| P.5 | 2 | 1.90 | 5 | 0.10 | - | - |
| P.5.1 | 2 | 1.90 | 5 | 0.10 | - | 2 |
| P.6 | 1.6 | 2 | 5 | - | 0.4 | - |
| P.6.1 | 1.6 | 2 | 5 | - | 0.4 | 2 |

magnesium and aluminium nitrates. The obtained solid phase (the samples P.4 and P.4.1, see Table 3) was dried and then annealed at different temperatures in porcelains crucibles.

*Preparation of thermoresistant pigments*

In order to obtain pigments with cordierite structure, partial substitution of $Al^{3+}$ with $Cr^{3+}$ (the samples P.5 and P.5.1) and $Mg^{2+}$ with $Co^{2+}$ (the samples P.6 and P.6.1) was performed (Table 3). For this purpose sample preparation was done with the method which uses organic precursors, as it is suitable for synthesis of the cordierite having complex composition.

*Characterization*

The phase composition of samples annealed at different temperatures, between 800°C and 1200°C, was ascertained by X-ray diffraction, using a DRON 3 diffractometer with $Cu_{K\alpha}$ radiation.

The colourimetric characterization of the obtained pigments has been made by diffuse reflectance spectrophotometry, using a SPEKOL 10 (Carl-Zeiss-Jena) spectrophotometer.

## III. Results and Discussion

XRD patterns of the samples annealed at 1200°C are presented in Figs. 1–4. It can be seen that the phase compositions of annealed samples is strongly influenced by synthesis method and presence of $Li_2O$.

In the sample P.1, synthesized using the classical method without $Li_2O$, even at 1200°C the cordierite is not formed. The only reaction product identified on the XRD pattern is a small proportion of the spinel, $MgO{\cdot}Al_2O_3$, phase (Fig. 1). On the other side, the sample P.1.1, prepared with the same method and 2 wt.% $Li_2O$, consists of μ-cordierite as the main phase, and the spinel, quartz and $Li_2O{\cdot}Al_2O_3{\cdot}6SiO_2$ phases (Fig. 1). This confirms very strong influence of $Li_2O$ addition on the phase composition of annealed product. The similar ionic radius of $Li^+$ and $Mg^{2+}$, but a pronounced fondant action of $Li_2O$ could justified the mineralizing effect of this oxide on the μ-cordierite formation. The sample P.1.1 with $Li_2O$ showed higher degree of shrinkage and improved sinterability, most probably due to presence of a liquid phase at the annealing temperature. These conditions are favorable for the formation of the μ-cordierite modification.

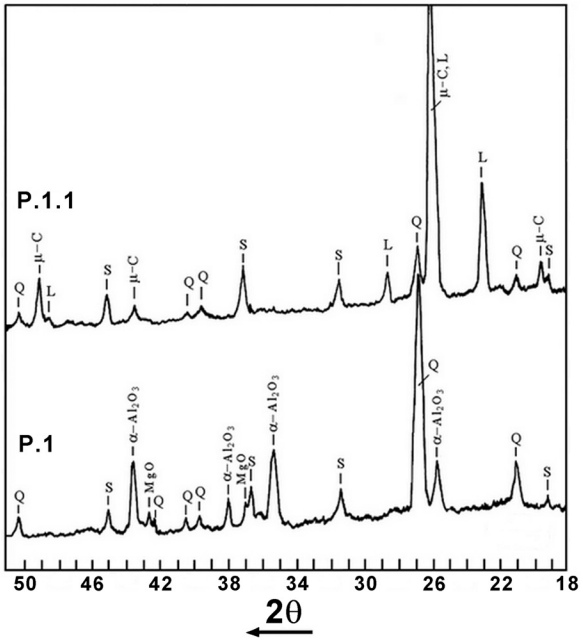


**Figure1. The XRD patterns of the samples P.1 and P.1.1 annealed at 1200°C ($MgO{\cdot}Al_2O_3$ (S), μ-cordierite (μ-C), quartz (Q), lithium aluminosilicate (L))**

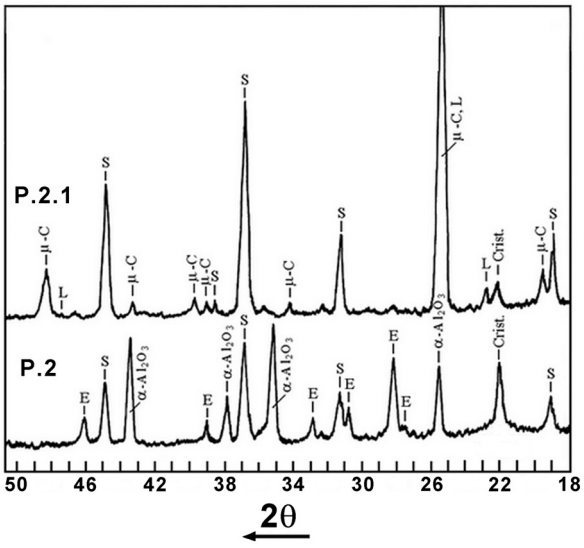


**Figure2. The XRD patterns of the samples P.2 and P.2.1 annealed at 1200°C (μ-cordierite (μ-C), $MgO{\cdot}Al_2O_3$ (S), cristobalit (Cris.), enstatite (E)).**

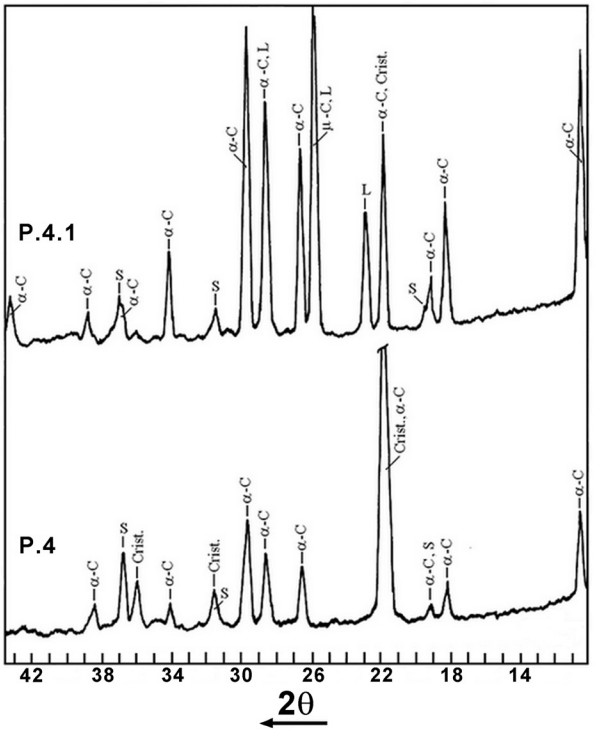


**Figure 3. The XRD patterns of the samples P.4 and P.4.1 annealed at 1200°C (α-cordierite (α-C), μ-cordierite (μ-C), $MgO{\cdot}Al_2O_3$ (S), cristobalit (Cris.), lithium aluminosilicate (L))**

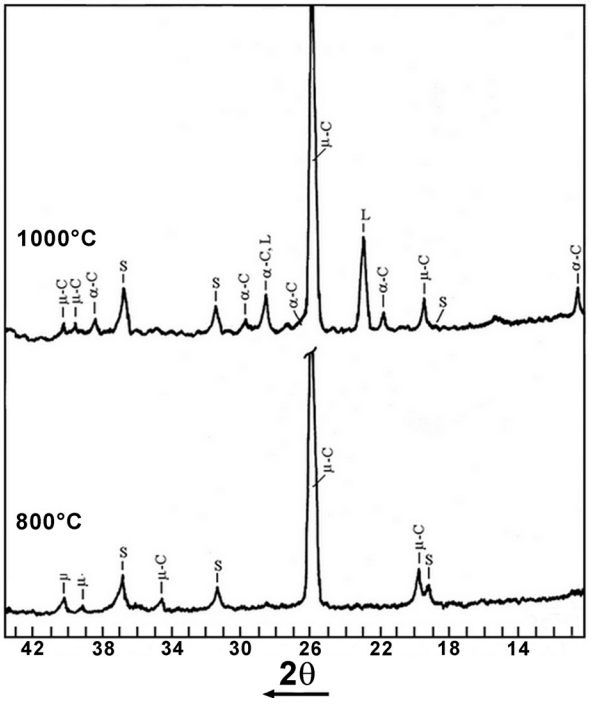


**Figure 4. The XRD patterns of the sample P.4.1 annealed at 800°C and 1000°C (α-cordierite (α-C), μ-cordierite (μ-C), $MgO{\cdot}Al_2O_3$ (S), lithium aluminosilicate (L))**

XRD pattern of the sample P.2, prepared from hydrosilicate precursors and without $Li_2O$ (Fig. 2), confirmed that the cordierite phase was not formed at 1200°C. The similar result was obtained for the sample P.3, when $(NH_4)Al(SO_4)_2{\times}12H_2O$ (as a source of $Al_2O_3$ with increased reactivity) instead of $Al(OH)_3$ was used. The presence of the spinel $MgO{\cdot}Al_2O_3$, enstatite ($MgO{\cdot}SiO_2$), α-$Al_2O_3$ and cristobalite phases indicate that the reaction between enstatite and $Al_2O_3$, with $SiO_2$ liberation and the spinel formation was performed at these conditions. The formation of magnesium metasilicate (enstatite), in the method which uses hydrosilicate precursors, was also confirmed in literature [15–18]. The above results suggest that this method, providing the $SiO_2$ linkage as magnesium metasilicate, is not adequate for the cordierite synthesis. This is in accordance with the thermodynamic data [6], affirming the necessity to have the spinel $MgO{\cdot}Al_2O_3$ phase as the previous phase, which could subsequently react with $SiO_2$ and form the cordierite. XRD pattern of the sample P.2.1 (with 2 wt.% $Li_2O$) annealed at 1200°C is presented in Fig. 2. It can be seen that in the presence of $Li_2O$ considerably amount of the μ-cordierite modification was formed, confirming again the mineralizing effect of this oxide. There is a high portion of the spinel and small amount of lithium aluminosilicate and cristobalite phases.

In the sample P.4, prepared from the organic precursor based on the aluminium and magnesium glyoxylate and Aerosil ($SiO_2$), almost pure cordierite phase was obtained at 1200°C, even when the mineralizer was not added (Fig. 3). This could be explained with the facts that the method which uses organic precursor enables the formation of the $MgO{\cdot}Al_2O_3$ phase already at temperatures lower than 800°C and favors reaction of the formed spinel with $SiO_2$ at somewhat higher temperature. The influence of $Li_2O$ addition (the sample P.4.1, Fig. 3) is not pronounced such in the P.1 and P.2 samples, but it enables preparation the sample with higher proportion of the α-cordierite, but also small amount of the μ-cordierite, lithium aluminosilicate and the untransformed spinel and cristobalite phases. The temperature influence on the phase evolution was studied too. Thus, XRD patterns of the sample P.4.1 annealed at 800 and 1000°C are presented in Fig. 4. It can be seen that already at 800°C the μ-cordierite is present as main phase and at 1000°C the α-cordierite and lithium aluminosilicate have appeared.

These results have clearly demonstrated that the method which uses organic precursors is suitable for the cordierite synthesis. Thus, even without mineralizer it can be used for the preparation of the almost pure α-cordierite at 1200°C. Because of that this method was used to obtain pigments with cordierite structure. In the samples P.5 and P.5.1 $Al^{3+}$ was partially substituted with the choromophore cation $Cr^{3+}$, whereas in the samples P.6 and

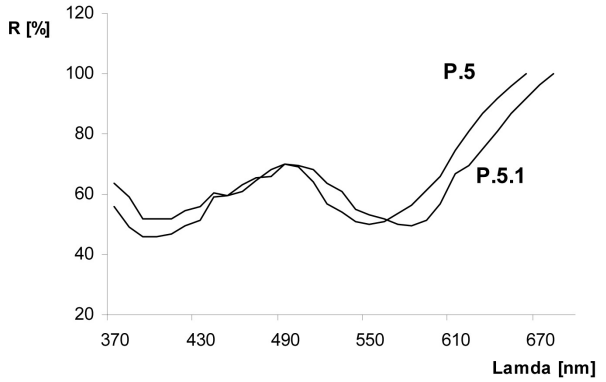


**Figure 5. The diffuse reflectance spectra of the samples P.5 and P.5.1**

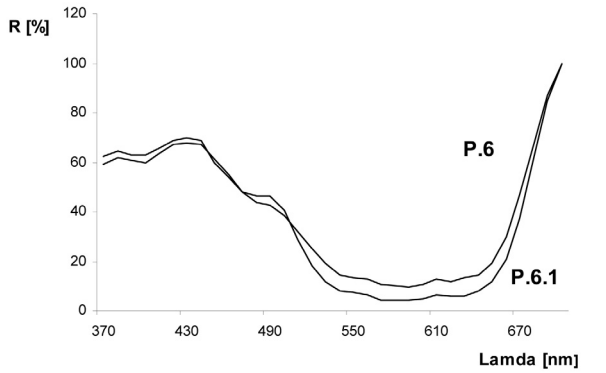


**Figure 6. The diffuse reflectance spectra of the samples P.6 and P.6.1**

P.6.1 $Mg^{2+}$ was partially substituted with $Co^{2+}$. The phase composition of these samples annealed at 1200°C is very similar to that observed for the samples P.4 and P.4.1. The diffuse reflectance spectra of the samples P.5/P.5.1 and P.6/P.6.1 annealed at 1200°C are presented in Figs. 5 and 6, respectively. It can be seen that partial substitution of $Al^{3+}$ with $Cr^{3+}$ (pink-pale colour) produces the diffuse reflectance curves specific for $Cr^{3+}$ hexacoordinated materials (with two absorption bands: at 400 nm and 550 nm). On the other side, partial substitution of $Mg^{2+}$ with $Co^{2+}$ (blue colour) produces the diffuse reflectance curves specific for $Co^{2+}$ tetracoordinated materials (large absorption bands between 530 and 660 nm). This all confirmed that the method which uses organic precursors can be successfully used for the preparation of different pigments with cordierite structure

## IV. Conclusions

Using the classical method, only in the presence of 2 wt.% $Li_2O$ as mineralizer the μ-cordierite modification was obtained.

The method which uses hydrosilicate precursors provides the $SiO_2$ linkage as magnesium metasilicate but was not adequate for the cordierite synthesis. Only in the presence of $Li_2O$ considerably amount of the μ-cordierite modification was formed, confirming the mineralizing effect of this oxide.

The method which uses organic precursors in the presence of $SiO_2$ was suitable for the cordierite synthesis. Almost pure cordierite phase was obtained at 1200°C even without mineralizer. In the presence of 2 wt.% $Li_2O$, μ-cordierite was formed already at 800°C.

The method which uses organic precursors can be used for the preparation of different pigments with cordierite structure. Pink pale colour pigments resulted by the partial substitution of $Al^{3+}$ with $Cr^{3+}$ and blue colour pigments resulted by the partial substitution of $Mg^{2+}$ with $Co^{2+}$.

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