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Crystallization studies of cordierite originated from sol-gel precursors

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Abstract

Detailed studies of the crystallization behavior of two sol-gel derived precursors of cordierite have been made by differential scanning calorimetry (RT-1350 ºC) and *in-situ* high temperature X-ray diffraction from RT up to 1165 ºC. Powder precursors were prepared using tetraetoxysilane (TEOS), $Mg(NO_3)_2 \cdot 6H_2O$ and two different aluminum sources, Al-*sec*-butoxide (for precursor BC) and $Al(NO_3)_3 \cdot 9H_2O$ (for precursor NC). The Rietveld method was performed for quantitative phase analysis of the crystallization products and for refinement of their crystal structures. It was found that crystallization occurred at ~800 ºC for both precursors. For precursor BC crystallization involves the appearance of stuffed derivative of β-quartz (containing Mg and Al), α-cordierite, mullite and enstatite, while for precursor NC it involves the formation of stuffed derivative of β-quartz, sapphirine, mullite, α-cordierite and β-cristobalite.

Keywords: cordierite, stuffed derivatives of quartz, high temperature XRD, Rietveld structure refinement, DSC.

Introduction

Cordierite ($Mg_2Al_4Si_5O_{18}$) ceramics has a wide range of applications due to its advantageous properties like: low thermal expansion, small dielectric constant, high chemical and thermal stability [1]. It can be prepared by solid-state reactions, liquid phase sintering, glass-ceramic route and sol-gel synthesis [2-5]. The interest in preparation of ceramics by a sol-gel method has been lately increased. The method has an advantage of excellent control of material chemical composition and the possibility of reducing the temperature of ceramic processing. High surface area, high intrinsic energy and consequently the higher sinterability of the sol-gel-derived powders allow a widening of the sinter interval. However, a choice of starting materials (e.g. soluble metal salts, metal alkoxides, colloidal suspensions etc.), steps involved in sol and gel formation along with a processing time, have to be considered very carefully in the synthesis of pure high-temperature polymorph. Cordierite occurs in two polymorphic forms: in the high-temperature hexagonal form α, space group *P6/mcc*, stable above about 1450 °C [6] and in the slightly distorted and ordered orthorhombic β form, space group *Cccm.* Stable below 1450 °C. Both phases, α- and β-cordierite, structurally are related to beryl, $Be_3Al_2Si_6O_{18}$ [7]. The structure consists of six-membered rings of $(Al/Si)O_4$ tetrahedra, T_2, laying in the basal plane. The rings are stacked one above the other in the *c* direction and they are connected laterally and vertically by additional $(Al/Si)O_4$ tetrahedra, T_1, and MgO_6 octahedra. Viewed along the *c*-axis, the ring stacking produces channels parallel to the *c*-axis [8]. The high-temperature hexagonal α polymorph of cordierite is characterized by a more or less random distribution of Al and Si in the T_1 and T_2 tetrahedra. Ordering of Si and Al on the tetrahedral sites lowers the symmetry to the orthorhombic space group *Cccm* of β-cordierite [9]. However, this ordering is rather continuous process. It takes place via a sequence of intermediate structural states characterized by splitting of diffraction lines in the XRD powder pattern of the sample [6].

The crystallization sequence in the sol-gel derived powders of cordierite stoichiometry is relatively complex, involving a formation of several intermediate and metastable phases such as: μ-cordierite, spinel ($MgAl_2O_4$), sapphirine ($Mg_4Al_8Si_2O_{20}$), mullite ($Al_6Si_2O_{13}$) and others [10]. Most of these phases are well defined in literature. However, Schulz et al. [11] found that a phase denoted in literature as μ-cordierite [12] is not a cordierite allotrope at all, but a member of solid solution series constituted from β-quartz (high-quartz). While pure β-quartz is not quenchable, the incorporation of small cations (Li^+ or Mg^{2+}) into the structural channels of β-quartz can open the framework and stabilize the high-temperature structure at room temperature [13, 14]. Charge balance can be achieved by replacing a fraction of Si^{4+} cations with cations of lower valence (e.g. Al^{3+}). The resulting phases are classified as "stuffed derivatives of β-quartz" [15]. The stabilization of β-quartz at room temperature can only be achieved when the content of substituting cations exceeds a critical threshold. On the other hand, when the dopand content falls below this threshold, the silica framework will adopt the denser "stuffed derivative of α-quartz", because the impurity cation content is too low to sustain the more expanded β-quartz framework [14].

The present paper reports the investigation of crystallization behavior of two different sol-gel derived powders with cordierite stoichiometry by means of differential scanning calorimetry (DSC) with thermogravimetry analysis (TGA) in the temperature range 20-1350 °C and by X-ray powder diffraction (XRD) in the range 20-1165 °C. The samples were prepared using tetraetoxysilane (TEOS), $Mg(NO_3)_2 \cdot 6H_2O$ and two different aluminum sources, either Al-sec-butoxide or $Al(NO_3)_3 \cdot 9H_2O$. Phases present in the samples that had been treated at 985 and 1165 °C were precisely defined by the Rietveld structure refinement.

Experimental

Preparation of samples

Gels with cordierite stoichiometry were prepared from tetraetoxysilane (TEOS), magnesium nitrate hexahydrate ($Mg(NO_3)_2 \cdot 6H_2O$) and either from aluminum-*sec*-butoxide, complexed with acetylacetylacetonate to reduce the hydrolysis rate, or aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$). The procedure schedule is shown in Fig. 1.

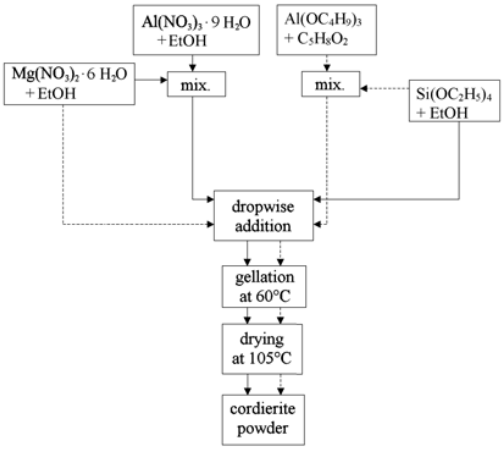

Fig.1. Flow chart for preparation of amorphous powders with cordierite composition.

The sample prepared from Al-*sec*-butoxide was designated as BC and that from $Al(NO_3)_3 \cdot 9H_2O$ as NC. The gels were dried at 105 °C for 72 h and subsequently heat-treated at 700 °C for 4 h to remove organics and volatiles prior to further analysis.

Methods

Differential scanning calorimetry (DSC) and thermogravimetry analysis (TGA) were performed on a Netzsch STA 409 Simultaneous Thermal Analyzer operating in DSC mode. Pt pans and corundum as a standard were used.

The powder samples BC and NC were characterized by using a Philips MPD 1880 diffractometer with monochromatized Cu$K\alpha$ radiation. From room temperature (RT) to 1165 °C diffraction patterns were taken using a high-temperature attachment (Paar HTK 10) in which a heating strip (sample holder) has a certain prestress, set with a setting screw through an angle lever, as to compensate the thermal expansion of the heated strip. The samples were heated to the desired temperature at the rate of 10 °C/min in a vacuum of 0.1 Pa and stabilized for 15 min before the measurements. The temperature of the sample was measured by a Pt/10%RhPt thermocouple. The XRD measurements were performed in the 2θ range from 5 to 70° in steps of 0.02 °2θ with a fixed counting time of 2 s per step. After performing the XRD measurements at 985 °C, as well after 1165 °C, the samples were cooled to RT in a closed high-temperature attachment with a cooling rate of 70 °C/min, and diffraction patterns were scanned again. That scans were taken in 2θ range from 5 to 100 °2θ, with a counting time of 8 s per step. They were used for the Rietveld structure refinement [16] of the examined samples by means of the program X′Pert HighScore Plus [17].

Results and discussion

The DSC and TGA results for the samples BC and NC from RT up to 1350 °C are shown in Fig. 2.

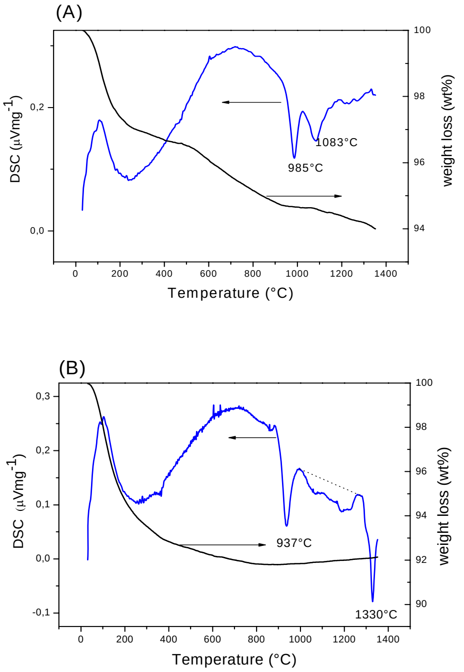

Fig. 2. Simultaneous differential scanning calorimetry (DSC) and thermogravimetrical analysis of sol-gel prepared samples dried at 105°C and heat-treated at 700°C for 4 hours. (A) sample BC (Al-sec-butoxide precursor),(B)- sample NC ($Al(NO_3)_3 \cdot 9H_2O$ precursor).

According to these results the powders BC and NC have different crystallization sequences. Two exothermic peaks at 985 and 1083 °C are seen in the scan of BC sample (Fig. 2A), while the peaks with maxima at 937 and 1330 °C are seen for NC sample (Fig. 2B). The positions of two exothermic peaks for sample BC are similar to some results reported by Einarsrud et al. for crystallization of gels (from alkoxides) in the system MgO-Al_2O_3-SiO_2 [10] who reported appearance of μ-cordierite and α-cordierite. They noticed very different range for crystallization of these crystal phases, and stressed out that the crystallization range depended on treatment of gels performed before heating (washing, drying). Even the crystallization pathway could be changed by those pre-treatments. The position of the second exothermic peak for sample NC does not fit in the known literature data for α-cordierite crystallization.

The XRD measurements showed a completely amorphous structure up to ~800 °C for both samples

BC and NC. Changes in XRD patterns of the samples caused by the heat treatment are shown in Fig. 3.

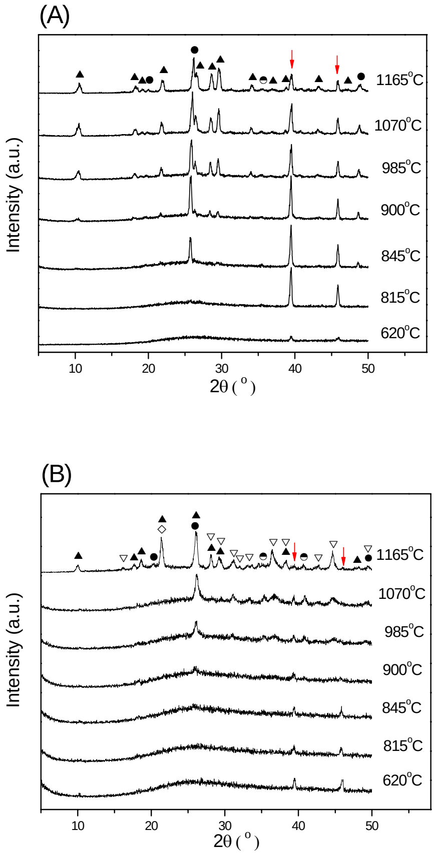

Figure 3. XRD patterns of samples BC and NC for a series of annealing temperatures. ▲: α-cordierite, ◇:β-cristobalite, ▽:sapphirine, ●:β-Q_s, ◓: mullite.

Phase identification in Fig. 3. followed from the results of the Rietveld refinement. Crystalline phases were initially identified according to the data existing in the ICDD Powder Diffraction File PDF-2 [18]: card no. 14-249 for μ-cordierite ($Mg_2Al_4Si_5O_{18}$), card 84-1222 for α-cordierite ($Mg_2Al_4Si_5O_{18}$), card no. 15-776 for mullite ($Al_6Si_2O_{13}$), card 84-653 for enstatite ($MgSiO_3$), card no. 19-750 for sapphirine ($Mg_4Al_8Si_2O_{20}$),card 46-1045 for α-quartz (SiO_2) and card 82-1403 for β-cristobalite (SiO_2). Characterization of the diffraction patterns was not straightforward because many diffraction lines were overlapped and the positions of diffraction lines for the phases μ-cordierite, α-cordierite and α-quartz were slightly moved compared to their Bragg positions (2θ) contained in the ICDD. Moreover, these displacements were not equal for the samples BC and NC at the same selected temperature. To solve the problem of phase identification the Rietveld refinement was performed, using the room-temperature XRD patterns of samples BC and NC that were scaned after the in-situ XRD measurements at 985 and 1165 °C. Starting structural models for the phases were taken from the Inorganic Crystal Structure Database (ICSD) as follows: card no. 202175 for α-cordierite, card no. 66452 for mullite, card no. 24464 for enstatite, card no. 34185 for sapphorine, card no. for α-quartz and card no. 75483 for β-cristobalite, respectively.

There is no specific crystal data for μ-cordierite in the ICSD database, so the structural model of stuffed derivative of β-quartz, ICSD card no. 24898 (by Schulz et al. [11]) was used to model μ-cordierite phase. The Rietveld refinement confirmed the presence of that phase in both samples BC and NC, heat treated at 985 as well at 1165 °C, and showed that its chemical composition in the examined samples can be given by the formula $Mg_yAl_{2y}Si_{3-2y}O_6$, where y being in the range from 0.60 to 0.48. This result supports the presence of stuffed derivative of β-quartz (our notation β-Q_S) in samples BC and NC rather than μ-cordierite. Rietveld refinement for the phase with structural model of α-quartz showed the unit-cell parameter a greater for 1.32%, c parameter 0.81% smaller and volume 1.41% greater than that of pure α-quartz, respectively. This may suggest that this phase is likely a stuffed derivative of α-quartz described by Beall [14] (our notation α-Q_S). It was not possible to determine the chemical composition of this phase because the appropriate structural model (which would include Mg^{2+} and Al^{3+} in the structure) does not exist in literature.

Graphical results of the Rietveld refinement for samples BC and NC heat treated at 1165 °C in vacuum, and cooled to RT afterwards, are shown in Fig. 4.

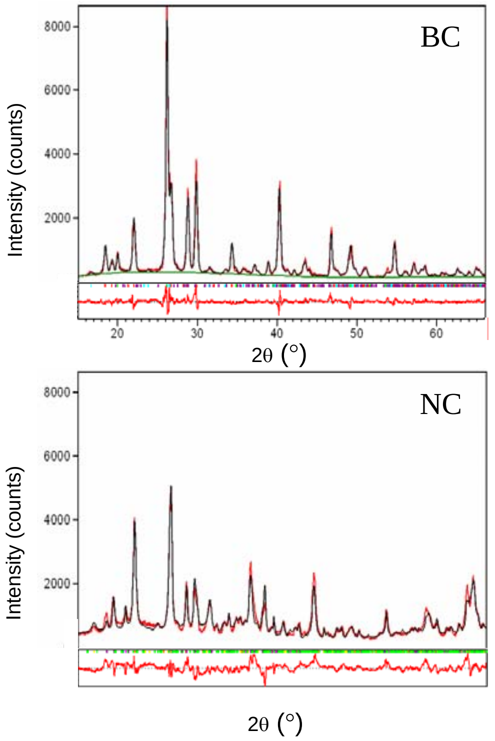

Figure 4. Result of the Rietveld refinement for samples BC and NC heat treated in vacuum at 1165 ºC and cooled to RT.

Table 1. Quantitative phase composition, given in wt%, of samples BC and NC heat treated at 985 and 1165 ºC and cooled to RT, as obtained by Rietveld refinement.

Phase	BC		NC	
	985 °C	1165 °C	985 °C	1165 °C
β-Q$_S$*	46.7(7)	34.4(3)	7.8(4)	3.9(2)
α-cordierite	44.6(5)	52.3(8)		16.7(3)
mullite	5.3(4)	9.6(5)	29.1(8)	13.7(5)
enstatite	3.4(3)	3.7(3)		
sapphirine			63.1(1)	52.0(6)
α-Q$_S$**				7.4(2)
β-cristobalite				6.3(2)

$*$ Stuffed derivative of β-quartz

$**$ Stuffed derivative of α-quartz

Table 2. Refined unit-cell parameters at RT for the phases β-Q$_S$, α-Q$_S$ and α-cordierite in samples BC and NC that were heat treated at 985 and 1165 ºC and cooled to RT.

Sample		BC		NC	
T (°C)		985	1165	985	1165
R_{wp} (%)		10.21	11.53	6.68	14.21
β-Q$_S$*	y	0.60	0.51	0.50	0.48
	a (Å)	5.2022(6)	5.2001(6)	5.14(2)	5.056(8)
	c (Å)	5.3331(9)	5.334(1)	5.36(3)	5.36(1)
	V (Å^3)	125.11(2)	124.90(2)	122.7(1)	118.7(9)
α-Q$_S$**	a (Å)				4.978(2)
	c (Å)				5.361(4)
	V (Å^3)				115.04(2)
α-cordierite	a (Å)	9.7610(7)	9.7633(6)		9.780(3)
	c (Å)	9.3539(8)	9.3519(9)		9.314(2)
	V (Å^3)	771.80(1)	772.08(1)		771.48(2)

Quantitative compositions of the samples BC and NC treated at 985 and 1165 °C and cooled to RT obtained by the Rietveld refinement are shown in Table 1. It should be mentioned here that the sample NC treated at 985 and 1165 °C contained also an amorphous phase, but it is not included in Table 1 which lists the crystalline phases only. The sum of weight fractions of crystalline phases in each sample is normalized to 100%. Refined unit-cell parameters for stuffed derivatives of β-quartz (β-Q$_S$), stuffed derivatives of α-quartz (α-Q$_S$), and for α-cordierite are listed in Table 2. Unit-cell parameters for mullite, enstatite, sapphirine and β-cristobalite were the same in all samples (at RT).

On the basis of Rietveld refinement results, the crystallization of samples BC and NC in vacuum in the temperature range from RT to 1165 °C (Fig. 3) can be described as follows. From RT up to ~800 °C both samples heated in vacuum remained amorphous. The crystallization process of sample BC involves the appearance of the stuffed derivative of β-quartz (β-Q$_S$), with a partial substitution of Si by Al and Mg entering the structural channels of β-quartz. At 985 °C the phase β-Q$_S$ and α-cordierite occurs as major phases, but enstatite and mullite as minor components are also present. With temperature increase the amount of α-cordierite increases on account of β-Q$_S$. In the case of sample NC the crystallization process goes through formation of small amount of β-Q$_S$ (at ~840 °C), followed by crystallization of sapphirine and mullite (at ~900 °C), which are the dominant phases at 985 °C (Table 1). Further heat treatment results in appearance of α-cordierite at ~1000 °C followed by β-cristobalite at higher temperature. Phase α-cordierite is formed on account of sapphirine and β-Q$_S$.

It should be pointed out that no XRD scan taken *in situ* at high temperature (Fig. 3) contained the lines of α-Q$_S$ phase. When samples BC and NC were cooled to RT after heat treatment at 985 and 1165 °C, only the room temperature XRD pattern of sample NC previously heated at 1165 °C contained the lines of the α-Q$_S$ phase (Table 1). That means that only for the sample NC at 1165 °C the amount of dopands (Mg, Al) in β-Q$_S$ phase falled below the stability threshold, so in cooling process of that sample a part of β-Q$_S$ transformed to α-Q$_S$.

The XRD study of crystallization of cordierite precursors BC and NC have different crystallization sequences as indicated by DSC. Furthermore, on the basis of the results of Rietveld refinement, the first exothermic peaks for these samples (at 985 °C for BC; at 937 °C for NC) are connected with crystallization of β-Q$_S$ rather than with μ-cordierite.

Conclusion

1. The first crystalline phase that appeared in the crystallization of cordierite precursors fits well with the crystal structure model for stuffed derivative of β-quartz proposed by Schulz et al.

2. The critical threshold for the transformation of stuffed derivative of β-quartz into stuffed derivative of α-quartz during the cooling process depends on the source of aluminum precursor.

3. If Al-*sec*-butoxide is used as a source of aluminum, β-Q_S (with higher concentration threshold) is a dominant phase that transforms into α-cordierite. On the contrary, if $Al(NO_3)_3 \cdot 9H_2O$ is used as the source of aluminum, the dominant components for α-cordierite formation are sapphirine and mullite. Stuffed derivative of β-quartz with small amounts of dopands is formed, and at cooling it transforms into stuffed derivative of α-quartz.

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