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Degassing of a cordierite glass melt during nucleation and crystallization[1]

K. Heide[a,*], E. Hartmann[a], Th. Stelzner[a], R. Müller[b]

[a] *Friedrich-Schiller-Universität Jena, Institut für Geowissenschaften, Lehrstuhl für Mineralogie, Burgweg 11, 07749 Jena, Germany*
[b] *Bundesanstalt für Materialforschung und -prüfung (BAM); Zweigstelle Adlershof, Rudower Chaussee 5, 12489 Berlin, Germany*

Abstract

The crystallization of coarse cordierite glass particles (0.4–0.63 mm in diameter) was studied by means of evolved gas analysis during constant heating. It was observed that crystallization is accompanied by complex degassing phenomena of H_2O, CO, CO_2, O_2 and Ar. The evolution process gradually appears at temperatures above the glass transition temperature. At higher temperatures two distinct degassing maxima are evident which can be attributed to the formation of the primary high-quartz solid-solution phase ("μ-cordierite") and its subsequent transformation into the hexagonal high-temperature polymorph of cordierite ("indialite"). In respect of these two crystallization steps, characteristic differences in the evolution behaviour between (a) CO and (b) H_2O, CO_2, O_2 and Ar are detectable. The results are discussed in relation to the different chemical properties and the "porosity" of both crystalline structures.

Keywords: Cordierite glass; Evolved gas; Glass crystallization; Glass nucleation; High-temperature mass spectrometry; Indialite; Vacuum effusion

1. Introduction

The incorporation of fluids and gases such as H_2O, CO_2 and N_2 in Mg-cordierite is a well-known phenomenon in natural and synthetic crystals. Recently, Le Breton and Schreyer [1] have studied the incorporation of CO_2 in cordierite and its dependence on pressure, temperature and time. An unexpected non-linear behaviour of the time

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* Corresponding author.

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dependence of CO_2-incorporation was observed. As an explanation of this behaviour an oscillation of the stabilizing and destabilizing effect of CO_2-incorporation into the c-parallel channels of the cordierite structure, which are formed from $(Si^{iv}, Al^{iv})_6O_{18}$ rings, was discussed.

Although, at present, the petrogenetic relevance of such behaviour is indistinct, this phenomenon gives a hint of the importance of minor (volatile) compounds on the formation of synthetic cordierite from glasses. Up to now, the incorporation of volatiles in glass-forming melts was investigated mainly by spectroscopic experiments [2]. In a more recent paper [3], the degassing behaviour of cordierite glasses was studied by means of thermogravimetric and MS investigations. In Ref. [3] was first described a mass loss of up to about 0.025 wt% originating mainly as a result of the degassing of water, which occurs in the temperature range of crystallization.

In the present study, a new device was used for evolved gas analysis. This device enables more sensitive study of the weak degassing phenomena that were found in Refs. [3] and [4] to be related to the surface-induced crystallization of cordierite glasses. Attention was focused on the surface-induced primary crystallization of high-quartz solid-solution ("*μ-cordierite*") and its transformation to the hexagonal high-temperature polymorph of cordierite ("*indialite*") [5].

2. Experimental

2.1. Samples

Cordierite glass samples were prepared by melting reagent grade raw materials in the stoichiometric proportions for cordierite. Batches were heated in air at 1590°C for 16 h. After forming a more or less homogeneous melt, the glass was fritted in water and remelted for 8 h at 1590°C. Glass plates of about 10 × 15 × 1.5 cm were prepared by casting onto steel plates. Finally, the glass plates were slowly cooled from 750°C to room temperature in a special furnace within 24 h. The results of chemical analysis are given in Table 1.

The homogeneity of the glass was checked by use of optical data. The glass was free from visible bubbles and crystals. The index of refraction was determined as $n_C = 1.551 \pm 0.003$ at $T = 20°C$.

2.2. Degassing measurements

Degassing experiments were performed using dynamic high-temperature mass spectrometry consisting of an effusion–vaporisation crucible interfaced with a quadrupole mass spectrometer (see Ref. [4] for more technical details). A schematic diagram of the equipment is presented in Fig. 1.

The starting material was prepared by grinding cordierite glass (30.0 mg, particle size 0.4–0.63 mm); this was loaded in a high-purity Al_2O_3 crucible. All samples were then heated at a constant heating rate (10 K min^{-1}) to 1400°C under vacuum of 10^{-6} mbar. The partial pressure of volatiles was measured by means of the mass spectrometer,

Table 1
Chemical composition of prepared cordierite glass (wt%)

Oxide	Wet chemical analysis data of glass	Theoretical composition of cordierite
SiO_2	51.4	51.36
Al_2O_3	34.5	34.86
MgO	13.3	13.78
P_2O_5	0.02	–
NaO	0.13	–
K_2O	0.03	–
CaO	0.04	–
Fe_2O_3	0.08	–
TiO_2	0.02	–

which was operated in scan–bargraph mode. The total pressure was measured simultaneously by means of a pressure gauge. Both results enable semi-quantitative characterization of the volatiles. Limited by the background, the sensitivity for volatiles was different : $H_2O < H_2 < CO_2 < O_2 < CO < N_2 <$ hydrocarbons $<$ Ar.

In contrast to other vacuum effusion mass spectrometric techniques, the volatiles are immediately ionized and analysed by the mass spectrometer. Highly non-equilibrium conditions are realised which are far from Knudsen conditions. A free vaporization process without back reactions between gas and the melt or condensed phases and without collisions between released volatiles can be maintained. Hence, the identification of primary fluid species escaping from the specimen is possible with high sensitivity.

3. Results

A typical degassing curve is shown in Fig. 2. During constant heating of the cordierite glass particles at 10 K min^{-1}, degassing phenomena gradually appear above the glass transition temperature. At higher temperatures two distinct degassing maxima are evident; these can be attributed to the formation of μ-cordierite and indialite [3,4]. This effect indicates that the overall crystallization process of cordierite glass is related to the liberation of volatiles.

Confirming previous results [3,4] mainly water is evolved in the temperature range of nucleation and growth of both crystalline phases. The quantity of evolved water was determined independently by TGA. A total amount of released water of about 0.025 wt% was found in the temperature range between 600 and 1000°C.

The water release in the crystallization range is also connected with a degassing of other compounds. The quantities of evolved H_2, CO, CO_2, O_2 and Ar are shown in relation to the partial pressure of water in selected temperature ranges (Fig. 2 and Table 2: A, B, C, D, E, F).

There are characteristic differences in the degassing phenomena which are related to the formation of metastable μ-cordierite and indialite. As the most striking difference,

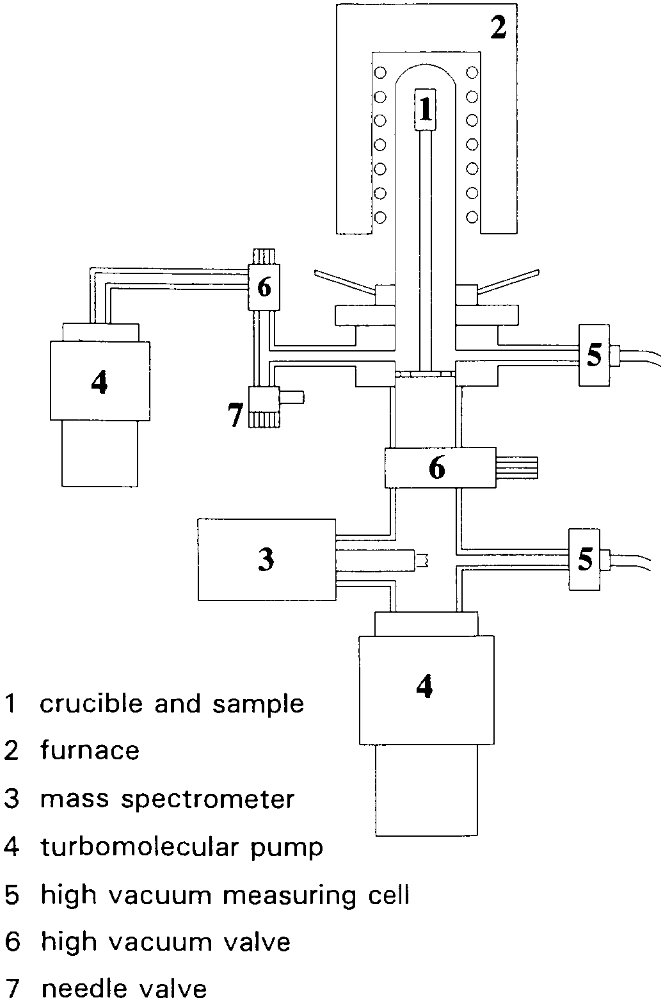

Fig. 1. Equipment used for the vacuum extraction of gases from cordierite glass.

the degassing phenomenon is more intense during the crystallization of indialite than during the μ-cordierite crystallization. Although this effect is most pronounced for the released water, quite similar behaviour is evident for H_2, CO_2, O_2 and Ar where the degassing of CO_2 seems to be correlated with water degassing. On the other hand, however, a quite similar amount of CO is evolved during both crystallization steps causing different ratios of the amounts of released CO and H_2O. The CO/H_2O ratios during the crystallization of μ-cordierite and indialite are 3.4 and 0.2, respectively.

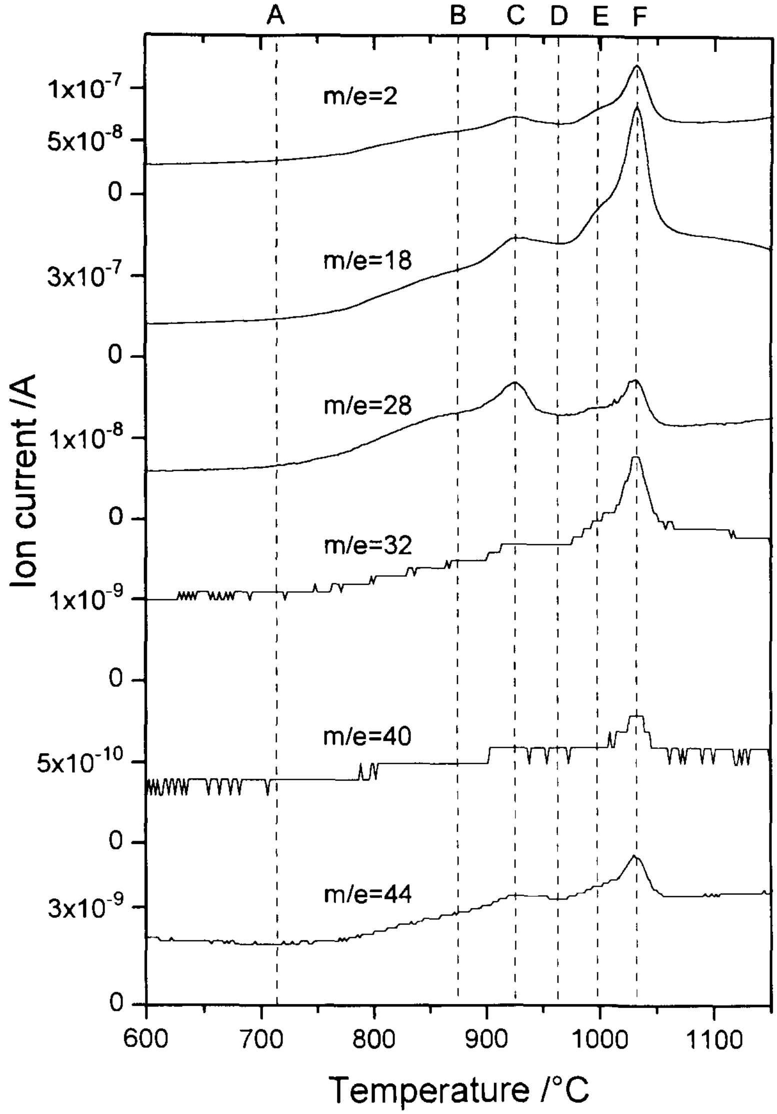

Fig. 2. The gas release profiles upon heating cordierite glass in the vacuum furnace.

4. Discussion

4.1. Degassing and nucleation

As illustrated by Fig. 2, degassing phenomena are detectable at temperatures below the onset temperature of the overall crystallization of μ-cordierite. This effect indicates

Table 2
Ratio of ion currents, $(X)/(m/e\,18)(100)$, $(X = 2, 28, 32, 40, 44)$ during the crystallization of the cordierite phase

m/e	Differences between ion currents in the temperature ranges A, B, C, D, E and F (see Fig. 2)					
	C − A	C − B	E − D	F − D	F − E	F − A
2	13.5	11.4	11.3	11.1	11.0	11.5
18	100	100	100	100	100	100
28	3.4	3.2	0.6	0.9	1.0	1.3
32	0.2	0.2	0.2	0.2	0.2	0.3
40	0.07	0.1	0.0	0.0	0.06	0.06
44	0.5	0.5	0.3	0.1	0.2	0.3

that surface-induced nucleation of μ-cordierite is accompanied by degassing phenomena.

Thus, despite those well known active surface nucleation sites like solid foreign particles (i.e. milling impurities), cracks and scratches [5], other active surface nucleation sites might be formed as a result of degassing phenomena. At the very least, this mechanism could dominate the residual surface nucleation density, $N^{\mu} < 10^{-7}\ \mu\text{m}^{-2}\ \text{min}^{-1}$ [5], at almost pristine cordierite glass surfaces fractured and thermally treated in vacuum. The interpretation of such a nucleating mechanism is difficult in case of a random distribution of volatiles in the framework. However, although it is difficult to prove directly, clustering of the different species can be assumed. On the other hand, even the strong nucleating activity of cracks or solid particles might be correlated with degassing phenomena.

4.2. *Degassing and crystallization*

(1) The slightly increased degassing phenomena of H_2O, O_2, CO_2 and Ar, during the second crystallization step (μ-cordierite → indialite, see Fig. 2), can be caused by (a) differently enhanced mobility of volatile species during the two-phase transformation steps or (b) by differences between the solubility of volatiles in μ-cordierite and indialite.

Considering the remarkably similar Raman spectra of glass and μ-cordierite [6], one can reasonably assume more similarities in atomic structure between glass and μ-cordierite than between μ-cordierite and indialite. Accordingly, the mean refraction index determined for μ-cordierite by the Becke–Line does not substantially differ from that of the glass ($n = 1.55$) whereas the refraction data of the hexagonal indialite phase are considerably lower ($n_o = 1.534$ and $n_e = 1.539$ [7]. Finally, the density of cordierite glass (2.6 g cm^{-3} [8]) is very close to that of μ-cordierite (2.59 g cm^{-3} [8]) whereas that of indialite is significantly lower (2.49 g cm^{-3} [8]). Altogether, a more thorough-going structural rebuilding can be expected for the μ-cordierite → indialite transformation than for the crystallization of μ-cordierite from the melt. This effect may serve as a possible explanation of the more intense degassing phenomena observed during the overall crystallization of indialite. Furthermore, one should keep in mind that the increased temperature of the second crystallization step may also cause increased mobility of volatiles. Although these arguments indicate the discussed degassing phenomenon to be mainly related to mobility effects, further experimental studies should be tackled concerning to the physical and chemical solubility of volatiles in cordierite glass, μ-cordierite and indialite.

(2) In contrast with H_2O, O_2, CO_2 and Ar, no increased CO degassing intensity was observed during the second crystallization step μ-cordierite → indialite (Fig. 2).

The exceptional role of CO degassing is difficult to understand in terms of crystal structures and the different size of the volatile molecules. It is well known that the open tetrahedral T_9O_{18} framework structure of cordierite can host various volatile species. This is because the cordierite structure is an "open branched framework" [9] where stacks of six-membered rings ($Al_2Si_4O_{18}$), additionally cross-linked by further (Al; Si) tetrahedra, form large open channels in the crystallographic *c*-direction (see Fig. 3). Because of their large inner diameter of about 280 pm, these channels provide favoured occupation sites for volatile molecules. Thus, it was shown in previous papers (reviewed

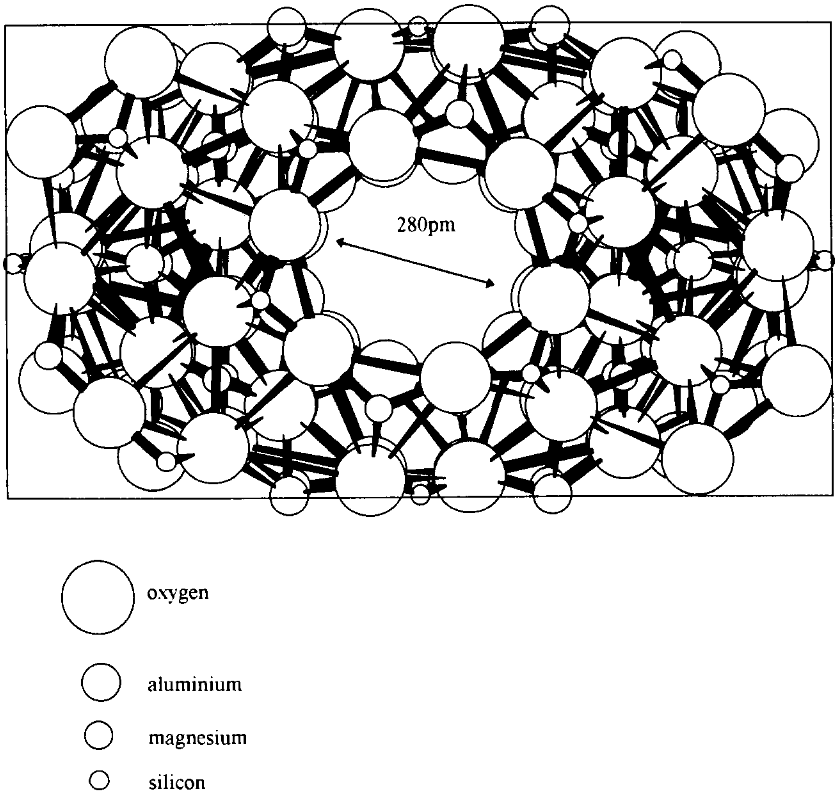

Fig. 3. Model of cordierite structure showing the molecular tunnel.

in Ref. [10]) that even large-sized molecules such as CO_2 (520 × 340 pm) and Ar (174 pm) can be introduced into the cordierite channels and that therefore the same is also to be expected for carbon monoxide.

However, it was shown in Ref. [10] that, in contrast to H_2O, CO_2 and Ar, CO could not be substantially introduced into the cordierite structure. This phenomenon was explained by a catalysing effect of the cordierite to produce CO_2 by the reaction $2CO \rightarrow CO_2 + C$. This catalytic reaction might be related to the reduced CO/H_2O ratio during the indialite crystallization step.

The presented results underline the potential of volatiles in the nucleation and crystallization kinetic of glasses. More detailed experimental investigations are necessary to quantify these phenomena.

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