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THE INFLUENCE OF MINOR COMPONENTS ON THE STRUCTURAL REORGANIZATION IN GLASSFORMING MATERIALS

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Correlation of structure parameters of glasses and related crystals formed in homogeneous or heterogeneous nucleation processes by thermal treatment is discussed on the basis of DTA, TG and EGA measurements in relation to the textural patterns of the materials. For cordierite glass, crystallization of metastable disordered cordierite polymorphs is related to an exothermic heat evolution and simultaneous with a small weight loss (appr. 0.025%). By MS-EGA, evolution of water was determined during the transformation of the metastable melt to a metastable intermediate crystalline phase. Interpretation of the crystallization by comparing the available structure parameters of cordierite glasses and crystals alone is insufficient to explain the role of water in the kinetics of crystallization. Optical and electron microscopy of the primary crystallization phenomena show the metastable solid solution with low quartz-type structure. Interpretation of the crystallization behaviour in terms of conventional theory of nucleation and crystal growth is impossible.

Keywords: glassforming materials, minor components, structural reorganization

Introduction

Glass systems can be placed in one of two groups with respect to their nucleation processes:

Systems that nucleate homogeneously, i.e. formation of nuclei is a random process throughout the whole glass. Examples are Li_2O-SiO_2, Na_2O-SiO_2, $CaO{\cdot}Al_2O_3{\cdot}2SiO_2$ (anorthite glass) [1].

Systems that nucleate heterogeneously, such as Na_2O-$2SiO_2$ or $Na_2O{\cdot}Al_2O_3{\cdot}6SiO_2$ (albite glass).

Structural parameters of such glasses and crystals are usually obtained by X-ray or neutron diffraction, EXAFS, NMR or molecular dynamic simulations.

A particularly clear demonstration of the influence of structural parameters on nucleation behaviour is given by crystallization of the two feldspar glasses. In *al-*

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bite glass the more regular oxygen environment of the sodium ion is provided by the oxygen atoms of six-membered rings of $[SiO_4]$ tetrahedra which are not compatible with the four-membered rings of the crystalline albite structure. Nucleation requires reconstruction of the $[SiO_4]$ tetrahedra and crystallization is only heterogeneous. In glass of *anorthite* composition, very good correspondence with the crystalline feldspar structure is observed. During nucleation cation coordination in the glass need not be changed substantially.

However, structural similarities are not the only criteria for the type of nucleation. *Cordierite* glass ($2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$) and the stable modification of crystalline cordierite have a framework silicate structure of six-membered rings. In cordierite polymorphs the rings are stacked along the crystallographic *c*-axis. Large open channels are formed where ions such as alkalines or molecules as H_2O, CO_2 or noble gases can be fixed.

It has been shown experimentally that crystallization of stable orthorhombic low-cordierite from glass leads to the formation of metastable hexagonal high-cordierite. However, the first step in the nucleation is the formation of an intermediate, disordered cordierite modification, a metastable solid-solution with a quartz-type structure. Differences in refractive index indicate differences in the structural framework which could not be observed by structural analysis (Table 1).

Table 1 Optical properties of glasses

Phase	n (D) / $n\,\alpha$	$n\,\beta$	$n\,\gamma$	Ref.
Glass $2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$	n_c=1.551			This paper
	n_d=1.553			
	n_e=1.555			
	n_f=1.560			
	n_g=1.564			
	Δn=±0.003			
	ν_c~60			
Glass $2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$	1.550			[2]
Cordierite orthorombic	1.540	1.550	1.550	[3]
Cordierite orthorombic	1.530	1.535	1.538	[4]
Indialite hexagonal	1.534		1.539	[3]
Cordierite hexagonal	1.519		1.552	[5]

In this study we have analysed the early state of nucleation and crystal growth in a special prepared specimen of cordierite glass, in an attempt to obtain a detailed characterization of the early state of crystallization in a well-defined starting material.

Experimental procedure

The glassy material was prepared by the Institute of Inorganic Chemistry (ZIAC) Berlin. The composition of the starting material is given in Table 2.

Table 2

	Starting material		Theoretical composition $2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$	
	weight / %	mol / %	weight / %	mol / %
SiO_2	51.7	56.14	51.36	55.55
Al_2O_3	34.6	22.1	34.86	22.22
MgO	13.3	21.5	13.78	22.22
P_2O_5	0.02	0.01		
Na_2O	0.13	0.14		
K_2O	0.03	0.02		
CaO	0.04	0.05		
Fe_2O_3	0.08	0.03		
TiO_2	0.02	0.02		

The homogeneity of the glass was checked by optical methods. It was free of visible inclusions (bubbles and crystals). The glass block was cut into disks, both parallel planes were polished to high quality, and these scratched immediately prior to heat treatment to produce fresh fracture surfaces.

The specimens were heated in a modified DTA furnace, which allowed reproducible sample positioning in relation to the thermocouple (±0.1 K). The thermocouple was regularly calibrated by ICTA reference materials. The specimens were heated in air in a Pt crucible at temperatures between 850°C and 920°C for 0.5 h up to 24 h. In order to allow comparison with data from the literature, two samples were treated at 875° and 1050°C for 40 h and 24 h. The heating rate of all specimens up to the isothermal heat treatment was 10 $\text{deg}{\cdot}\text{min}^{-1}$.

In a separate experiment, the starting material was analysed by thermobalance in combination with a MS-gas detector under high vacuum up to 1600°C at a heating rate of 10 $\text{deg}{\cdot}\text{min}^{-1}$.

After heat treatment, samples were quenched at room temperature. All were analysed with an optical microscope using polarized light and a differential phase-contrast system.

Electron micrographs were produced by a replica technique after etching the samples for 20 s with a mixture of 5% HF and 20% HNO_3. After coating the surface with a mixed layer of Pt-Ir-C, the sample was dissolved and a replica examined by TEM. Analysis of the bulk glass and crystals was carried out on a scanning electron microscope with linked microanalysis facility.

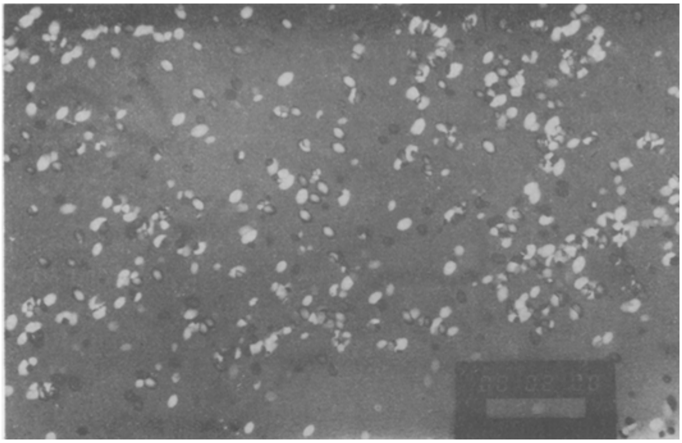

Fig. 1a Optical micrographs of the crystallization of a cordierite glass after heat treatment at 875°C and different times (bar: 200 µm, 875°C, 2 h)

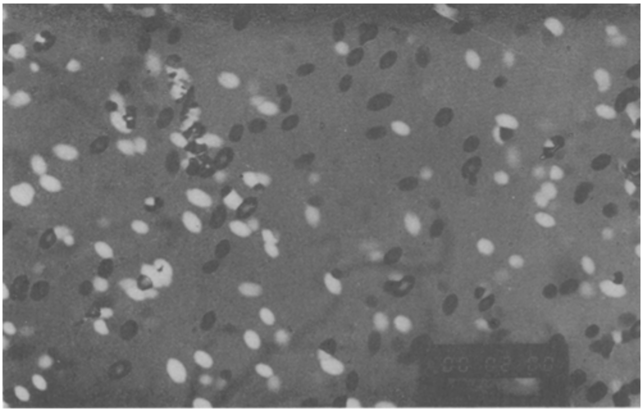

Fig. 1b (bar: 200 µm, 875°C, 3 h)

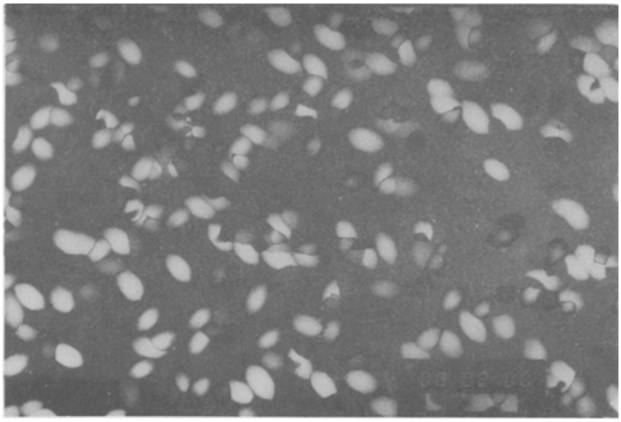

Fig. 1c (bar: 100 μm, 875°C, 3 h)

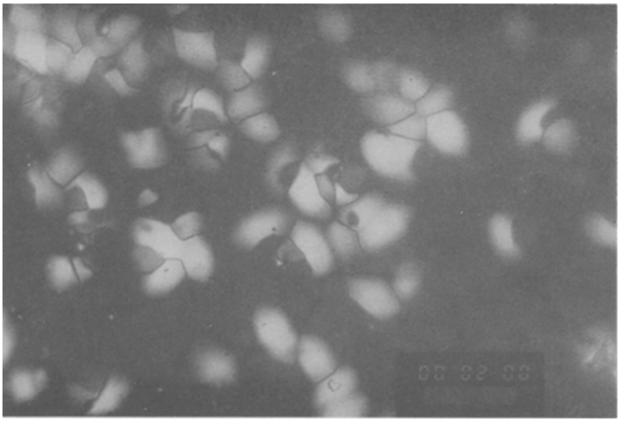

Fig. 1d (bar: 50 μm, 875°C, 3 h)

Results

Initial heating trials showed that nucleation occurred between 860°C and 900°C. As can be seen in the micrographs from a run of experiments at 875°C (Fig. 1a–d), formation of (pseudo) hexagonal crystals is dominant in this range. Orientation of the dislike crystals parallel to the surface and perpendicular to the (pseudo) hexagonal *c*-axis was observed; the birefringence was low and elongation positive in the direction of the *c*-axis. The refractive index was similar to that of the matrix glass.

As shown in the micrographs, *shapes* of the crystals change depending on heating time. However no changes in *number* of crystals were observed (Fig.2), indicating that the number of nucleii were constant within a particular temperature range.

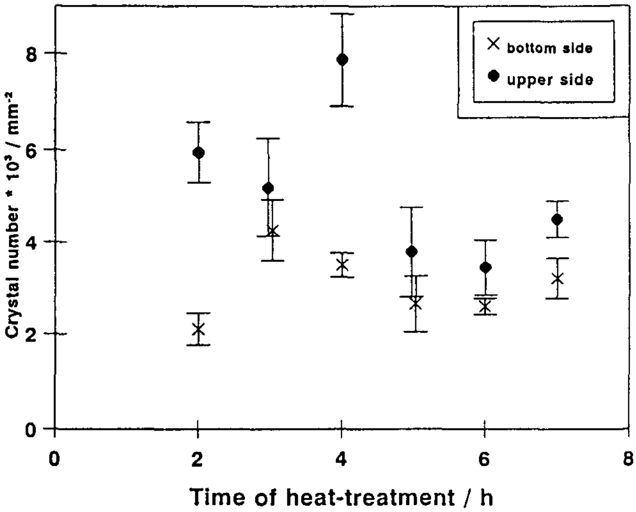

Fig. 2 Number of (pseudo)-hexagonal crystals on the surface of the cordierite glass as a function of heat treatment

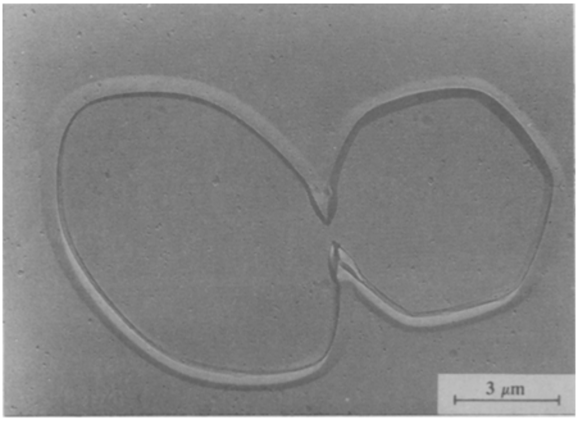

Fig. 3 Two different crystallographic orientations of the (pseudo)-hexagonal crystals at the surface of glass samples with erosion phenomena (860°C, 2 h). TEM micrograph

Textural patterns were unusual. Whereas the volume of crystals increased, crystal shapes indicated marked corrosion with increase in heating time (Fig. 3) and eventually a puzzle-like texture covered the surface (Fig. 4). After a 20 h heat treatment a new pattern formed on the surface (Fig. 5). No cordierite was identified by X-ray diffraction, products showing only the quartz-type structure of the metastable solid solution.

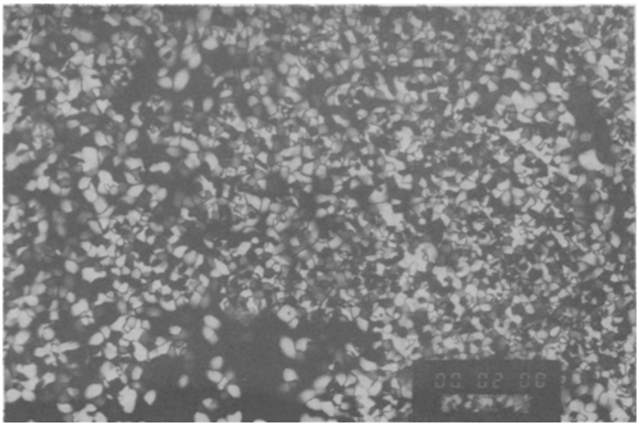

Fig. 4 The 'puzzle'-structure of (pseudo)-hexagonal crystals on the surface of cordierite glass (scale: 200 μm, 875°C, 7 h)

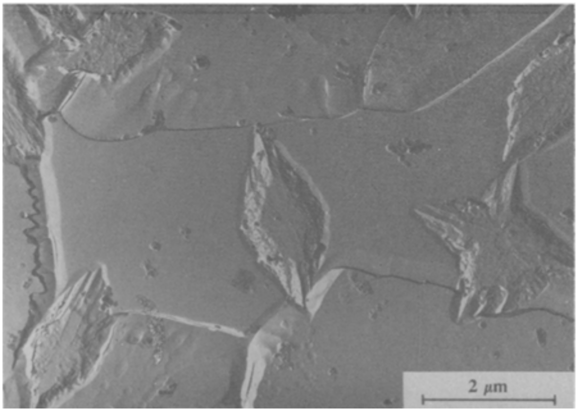

Fig. 5 (Pseudo)-orthorhombic crystals and (pseudo)-hexagonal crystals on the surface of cordierite glass after heat treatment (900°C, 2 h), TEM micrograph

No qualitative differences were observed between polished and fractured surfaces, but between the two polished planes the density of crystals is quite different. Independent of the formation of (pseudo)-hexagonal phases a second phase with a (pseudo)-rhombic habit was observed at 875°C. The refractive index was lower than that of the matrix glass and a distinct surface relief is observed (Fig. 6). Structural characterization of this new phase is a subject for further research.

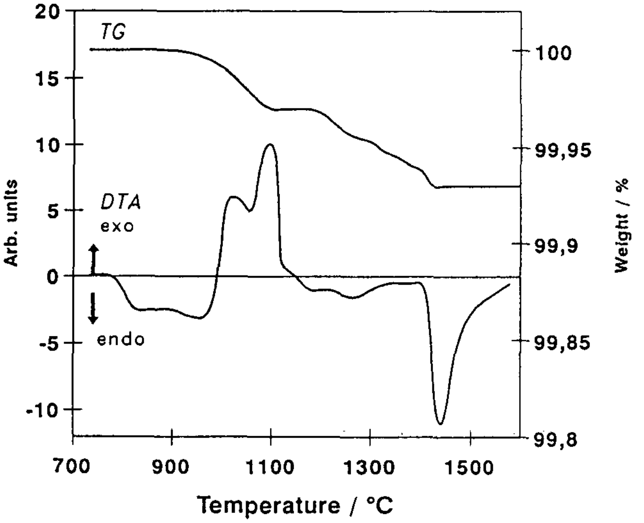

Fig. 6 DTA-TG-curve of cordierite glass

No differences in composition of crystalline phases and the glasses was observed (Table 3).

Table 3 EPMA analysis of the different phases on the surface of a cordierite glass (mol%)

	Glass	Quartz-type cryst.	Orthorhombic cryst.	Wet chem.	Theor. value
Si	16.9	17.1	17.1	17.4	17.2
Al	13.7	14.0	13.9	13.7	13.8
Mg	7.5	6.8	7.0	6.7	6.9
O	61.9	62.0	62.0	62.1	62.1
Other elements				0.1	

DTA curves of the cordierite glass show an endothermic effect in the range of 800°–900°C, characteristic for the glass transition range. Two exothermic effects with maxima at 1010° and 1090°C represent crystallisation of the metastable melt. X-ray analysis indicated that the first maximum of the DTA curve results from the crystallization of a quartz-type solid solution structure and the second maximum from the formation of indialite, the high-temperature polymorph of cordierite. The melting point of the high-temperature phase can be determined by the endotherm reaction at 1445°C; this is in good agreement with literature data.

An unusual effect was observed on the TG curve. In the crystallization range, a two-stage mass loss occurs. By MS, the first mass loss (0.025%) was shown to be due to woter, the second (0.045%) to be due to H_2O and CO_2.

Discussion

Comparison of textural patterns based on detailed TEM and optical micrographs show that formation of primary crystals after heat treatment of a cordierite glass is a nucleation process on the surface. Homogeneous nucleation in the bulk does not occur whilst the structural parameters of the glass (and melt) and that of cordierite are in a near relationship. The textural patterns also highlight problems in determination of kinetics in the case of cordierite glass crystallization. An Avrami-fit is possible with an acceptable correlation, but what do the calculated kinetic parameters actually represent? Formation of the stable cordierite phase is independent of this initial nucleation. Paramorphs are not detectable in the crystal patterns. The detection of a small water evolution during formation of the metastable quartz-type structure emphasizes the complexity of the nucleation process.

It is possible that minor components in the bulk sample are more important for the phase transformation than the structural parameters of the bulk sample. Loss of volatiles from the bulk structure could be a release process in the formation of nuclei. Concentration and degassing behaviour of volatiles in solids are factors in phase transition kinetics, which require more attention.

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Zusammenfassung — Auf der Grundlage von DTA-, TG- und EGA-Messungen wurde in Bezugnahme auf die Texturmodelle die Korrelation der Strukturparameter von Gläsern und der entsprechenden, durch Hitzebehandlung in homogenen oder inhomogenen Keimbildungsprozessen geformten Kristalle besprochen. Bei Kordieritglas ist die Kristallisierung des metastabilen, ungeordneten, polymorphen Kordierits mit einer exothermen Wärmeentwicklung und einem simultanen geringfügigen Gewichtsverlust (etwa 0.025%) verbunden. Während der Umwandlung der metastabilen Schmelze in eine metastabile, kristalline Zwischenphase wurde mittels MS-EGA die Freisetzung von Wasser ermittelt. Die Interpretation der Kristallisierung anhand eines Vergleiches der zugänglichen Strukturparameter von Kordierit-Gläsern mit denen der Kristalle allein reicht nicht aus, um die Rolle des Wassers in der Kristallisationskinetik zu erklären. Optische und Elektronenmikroskopie der primären Kristallisierungserscheinungen zeigen überraschenderweise metastabile Mischkristalle mit Quarz-Struktur. Eine Interpretation des Kristallisationsverhaltens mit Hilfe der üblichen Theorie von Keimbildung und Keimwachstum ist unmöglich.