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Crystallization of nickel-bearing stoichiometric cordierite glasses

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A complete crystalline solid solution exists between magnesium cordierite ($Mg_2Al_4Si_5O_{18}$) and nickel cordierite ($Ni_2Al_4Si_5O_{18}$). Isothermal crystallization experiments were conducted at 1 atm on stoichiometric powdered glasses in this compositional range in which high quartz crystallized and then transformed to hexagonal cordierite. When nickel is present, these three phases can be simply identified by colour changes: the glass is brown, the high quartz is red and the cordierite is yellow. The sequence of appearance of the phases is independent of the nickel content of the glass. At any given temperature, the higher the nickel content, the shorter are both the time required for crystallization of high quartz from the glass and that required for the transformation to hexagonal cordierite. This implies that the processes involved in both steps might be similar. Measurements of lattice constants of cordierite crystallization products show a linear decrease in *a* and a linear increase in *c* as a function of increasing nickel content between the magnesium and nickel end members. There is no change of the cell volume with the substitution of nickel into the structure. The increase in reaction rates caused by increasing the Ni/Mg ratio of the glass starting material may be due to the stronger network modifying effect of nickel in comparison to magnesium.

1. Introduction

Glass-ceramics based on magnesium cordierite ($Mg_2Al_4Si_5O_{18}$) have widespread applications because of their low thermal expansion, high melting point, high chemical durability and high electrical resistivity. Therefore, the examination of the crystallization behaviour with changing annealing conditions and composition is of great practical interest. Glasses of pure magnesium cordierite composition first crystallize to a metastable high quartz structure[‡] which then transforms to hexagonal cordierite. At low temperatures and long annealing times, the hexagonal cordierite transforms to the stable orthorhombic structure which is stable up to 1450 °C at 1 atm in the system $MgO–Al_2O_3–SiO_2$ [1]. The presence of NiO in this system can change the crystallization mechanism of cordierite-type glasses so that spinel forms instead of high quartz [2]. The quantitative change of crystallization behaviour of stoichiometric cordierite glasses and the chemistry of the crystalline phases (extent of Mg–Ni substitution) is, however, not known.

The general structural formula of cordierite is $XM_2[T_9O_{18}]$ with X for sites in the channels, M for sites with octahedral coordination and T for tetrahedral ones. The structure contains a network of aluminosilicate tetrahedra forming six-membered rings which are stacked to form channels parallel to the *c*-bar axis; these rings are connected by four membered rings. In this framework are polyhedra of octahedral coordination. The Al/Si distribution in the tetrahedral sites determines the structural state of cordierite [3, 4]. Natural cordierites are mostly orthorhombic and appear to have fully ordered Al/Si distribution. Reconstructing the near equilibrium physical conditions that existed during crystallization of natural cordierites, numerous experimental studies in the pure magnesium end-member system have been carried out on the structural transformation of hexagonal to orthorhombic cordierite [1, 5, 6]. However, the structural transformations of glass → high quartz and of high quartz → hexagonal cordierite are of more interest in ceramics where hexagonal cordierite is usually the final product. Infrared studies [5] and a comparison of enthalpies of vitrification [7] show that the stuffed high-quartz structure is more similar to the glass structure than hexagonal cordierite, and formation of high quartz from the glass is, therefore,

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[‡] Because of the confusing usage in literature, our nomenclature will be defined: "high quartz" is used for a stuffed hexagonal quartz structure (it is also called β-quartz or μ-cordierite); "hexagonal cordierite" gives a description of the structural state. (The same phase is also called "high cordierite", because of the high-temperature stability of this modification. At lower temperatures the orthorhombic modification is stable, which then is called "low cordierite". In ceramics literature, the hexagonal cordierite also has the name α-cordierite.)

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favoured for kinetic reasons. As in the cordierite structure, the tetrahedral framework of high quartz forms six-membered rings which, however, are twisted in a manner different from that in cordierite. In the stuffed high-quartz structure, aluminium probably substitutes for silicon in the tetrahedra, whereas magnesium can be located (stuffed) in the channels of the six-membered rings [8, 9]. Therefore, an effect on the phase sequence and crystallization times might be anticipated from changes made in the glass structure. The addition of transition elements to the glass is especially of interest because these elements can be network-formers or network-modifiers.

The objective of the present work was to determine the influence of the substitution of nickel for magnesium on the thermal stability, phase-growth sequence and structural transformations of powdered glasses with the stoichiometric cordierite composition.

2. Experimental procedure

Mixtures of pure oxide starting materials of stoichiometric cordierite compositions (Table I) were used to prepare glasses by melting them twice in a platinum crucible at 1580 °C for 1 h in air. Glasses of the pure nickel end-member cordierite compositions were melted at 1620 °C because at lower temperatures even quenching the melt into water yielded mullite, the primary crystalline phase for pure cordierite [1]. The glasses were homogenized by grinding them in an agate mortar and then remelting. To avoid contamination a new crucible was used for each composition. Loss of nickel from the sample to the platinum crucible was considered to be negligible because all experiments were performed in air where essentially all of the nickel exists as NiO.

Stoichiometric cordierite compositions with the substitution of nickel for magnesium in the octahedral site are given in atomic ratios: $F_{Ni} = Ni/(Ni + Mg)$. For crystallization experiments, 100 mg glass ($F_{Ni} = 0.00$ or $F_{Ni} = 0.50$) was crushed and ground in an agate mortar. In each experiment, these two powders were annealed simultaneously in a platinum boat. Annealing temperatures were 880, 980 and 1200 °C and durations of runs varied from 5 min to 3 days. To determine the influence of the humidity on the crystallization of magnesium cordierite, experiments were performed at 880 °C in air, in steam and under vacuum.

To generate steam, clean nitrogen was bubbled through water which was held at 83 °C with a constant temperature control. The vapour pressure of water at this temperature corresponds to 400 mm Hg, which is about 53% water in the steam experiments carried out at 1 atm. (For comparison, at room temperature the vapour pressure of water is about 20 mm Hg, i.e. about 3% water under equilibrium conditions.) With a flow of 100 ml min^{-1}, the water-bearing nitrogen was passed over the sample in the furnace, to study the influence of humidity on the crystallization.

The phase content and the phase-sequence were determined using X-ray powder diffraction, while the grain size and colour of the samples were observed with an optical transmission microscope. The mean refractive index of the sample, $\bar{n}$, was measured by immersing the samples into oils of different refractive index n.

To determine the growth-phase sequence of the different crystalline phases, the intensities of the reflections (1 0 1) from high quartz and (1 0 0) and (2 1 1) from hexagonal cordierite were compared. To avoid changes because of different sample weights, the same sample holder with 50 (± 2) mg powdered sample, was used for all X-ray diffraction measurements. For calibration of the highest intensities of high quartz and hexagonal cordierite, glass of magnesium cordierite composition was crystallized. The highest observed intensity of high quartz is about three times larger (12 000 counts) than that of hexagonal cordierite (4 000 counts), therefore the change of the intensities are plotted in diagrams with the corresponding scales given. The reproducibility of the intensities measurements was checked by running cubic tungsten powder and crystallized hexagonal cordierite several times. Whereas the tungsten powder was on a plastic tape which guarantees the same amount and the same orientation of the sample, the same amount of cordierite powder was reloaded in the holder each time. The variation of the intensities of tungsten powder gives the accuracy of the diffractometer (≈15%). The intensities of the cordierite reflections varied in the range of ± 20%, which is also the uncertainty of the quantity of crystals present. The relative intensities of the cordierite changed with different amounts of the same

TABLE I Glass compositions (wt. %)

Glass $F_{Ni} = Ni/(Ni + Mg)$	MgO[1]	NiO[2]	Al_2O_3[3]	SiO_2[4]	Mol weight corresponding to 1 mol cordierite
$F_{Ni} = 0.00$	13.78	–	34.86	51.36	585
0.05	13.02	1.27	34.65	51.06	588
0.30	9.32	7.40	33.67	49.61	606
0.50	6.51	12.06	32.92	48.51	619
1.00	–	22.85	31.19	45.96	654

[1] $MgCO_3$: Alfa Products, Batch No. 593750 A.
[2] NiO: Alfa Products Ni (II) oxide puratomic 99.9998% metals basis.
[3] γ-Al_2O_3: Sumitomo Chemicals, fine powder (particle size < 0.1 µm).
[4] SiO_2: CAB-O-SIL, scintillation grade No. 13107, Kodak.

sample, which could be partly explained by orientation of grains in the powder. Therefore, the intensities of two reflections of hexagonal cordierite at $2\theta \approx 10°$ (1 0 0) and $2\theta \approx 29°$ (2 1 1) were used to determine the amount of crystalline cordierite.

For the determination of lattice constants, silicon powder was added to the samples as an internal standard. The lattice constants were calculated with the program "INDLSQ" [10] for a hexagonal cell (SG: P6/mcc).

3. Results and discussion

3.1. Phase content and phase characterization

The sequences of phase development were the same for both compositions ($F_{Ni} = 0.00$, 0.50) at 880 and 980 °C. After high quartz crystallized from the glass, it transformed to hexagonal cordierite. No orthorhombic modification of cordierite was observed in the X-ray powder diffraction.

At 1200 °C, no high quartz could be formed in either composition; whereas the nickel-free composition yielded hexagonal cordierite as a single phase product, the composition $F_{Ni} = 0.50$ yielded mullite, spinel and an SiO_2 modification besides cordierite. With increasing annealing time the amount of spinel increases, whereas the cordierite content decreases. This indicates that cordierite is no longer stable. As with cobalt-containing cordierite ($F_{Co} = 0.50$) [11], the nickel-containing cordierite ($F_{Ni} = 0.50$) seems to have lower thermal stability than pure magnesium cordierite.

At 980 °C, compositions with $F_{Ni} = 0.05$, 0.50 and 1.00 after 1 h yielded hexagonal cordierite as a single-phase product, which indicates that Ni^{2+} can fully substitute for magnesium in the octahedral sites in cordierite. The change of the X-ray powder diffraction patterns with increasing nickel content is shown in Fig. 1. The change of the intensities is similar to the variations observed for Fe^{2+} substitution in cordierite [12].

As shown by X-ray diffraction patterns corresponding to the different phases, the colour of the nickel-containing compositions changed from brown for the glass to red for high quartz and to yellow greenish for hexagonal cordierite (Fig. 2). The spinel-containing powders are blue. The colour change makes it easy to observe the transformation from high quartz to hexagonal cordierite on a macroscopic and microscopic scale. The transformation from glass to high quartz starts from the surface and propagates into the core and is accompanied by a colour change from brown to red. After the glass fully crystallizes to high quartz, it has red particles of relative large grain size. For our crystallization experiments, all the samples were ground in an agate mortar to a particle size of 5–20 µm for all runs. For optical measurements, larger particles of about 100–150 µm were examined. The transformation of high-quartz particles into hexagonal cordierite also propagates from the surface into the core, and is indicated by a colour change from red to yellow. This colour change is accompanied by a reduction in dispersion and of crystal grain size (≈ 1 µm). It was not possible to prepare large single crystals; only polycrystalline samples were available for observation. With longer annealing time of the samples, the amount of the smaller yellow particles increases until only the cores of very large particles (150–200 µm) contain red high quartz. In these samples, all smaller particles are completely transformed. This observation indicates that the amount of crystalline cordierite, which is detectable in the X-ray powder diffraction, will be influenced by the particle size at the beginning of the annealing of the glass. The smaller the particle size, the shorter will be the crystallization time needed for the whole powder sample to transform completely. To understand further the colour changes resulting from the different phase transformations, more thermodynamic and spectroscopic studies are planned.

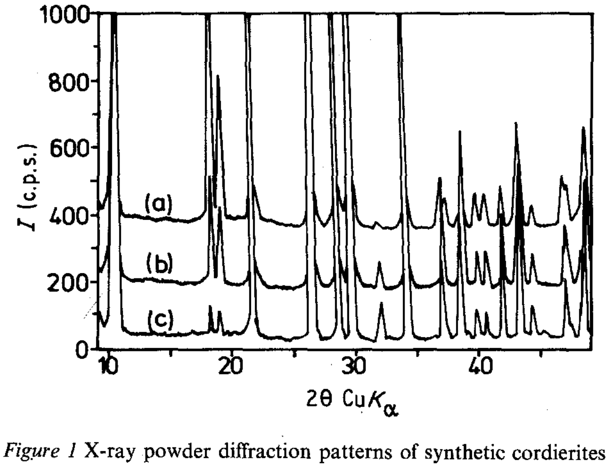

Figure 1 X-ray powder diffraction patterns of synthetic cordierites with the compositions: F_{Ni} = (a) 0.00, (b) 0.50, (c) 1.00.

The measured increase of the mean refractive index is in good agreement with the calculated data from the Gladstone–Dale relation [13], using the measured cell volume. With increasing nickel-content the lattice constant *a* decreases, whereas *c* increases with no change of the cell volume (Fig. 3).

The change of the lattice constants can be explained structurally by a slight size decrease of the octahedron in the hexagonal cordierite, due to the substitution of the smaller nickel for magnesium in this site which results in a decrease of *a*. The rotation of the six-membered rings in the crystallographic *c*-axes is connected with the octahedra [14], therefore the smaller size of the octahedra is responsible for less rotation of these rings which results in an increase of *c*.

3.2 Crystallization behaviour

Crystal growth in a powdered sample was measured by means of the intensity variations of the strongest X-ray reflections of the growing phases. We define the crystallization time, t_{cr}, as that when half of the intensity of the fully crystallized phase is reached or the phase transformation is completed. The amount of high quartz present increases and is seen to reach a maximum, after which the transformation into hexagonal cordierite starts (Figs 4, 5). Independent of the composition of the glass, the crystallization time decreases with increasing temperature. The observed crystallization behaviour at 980 °C in air for pure

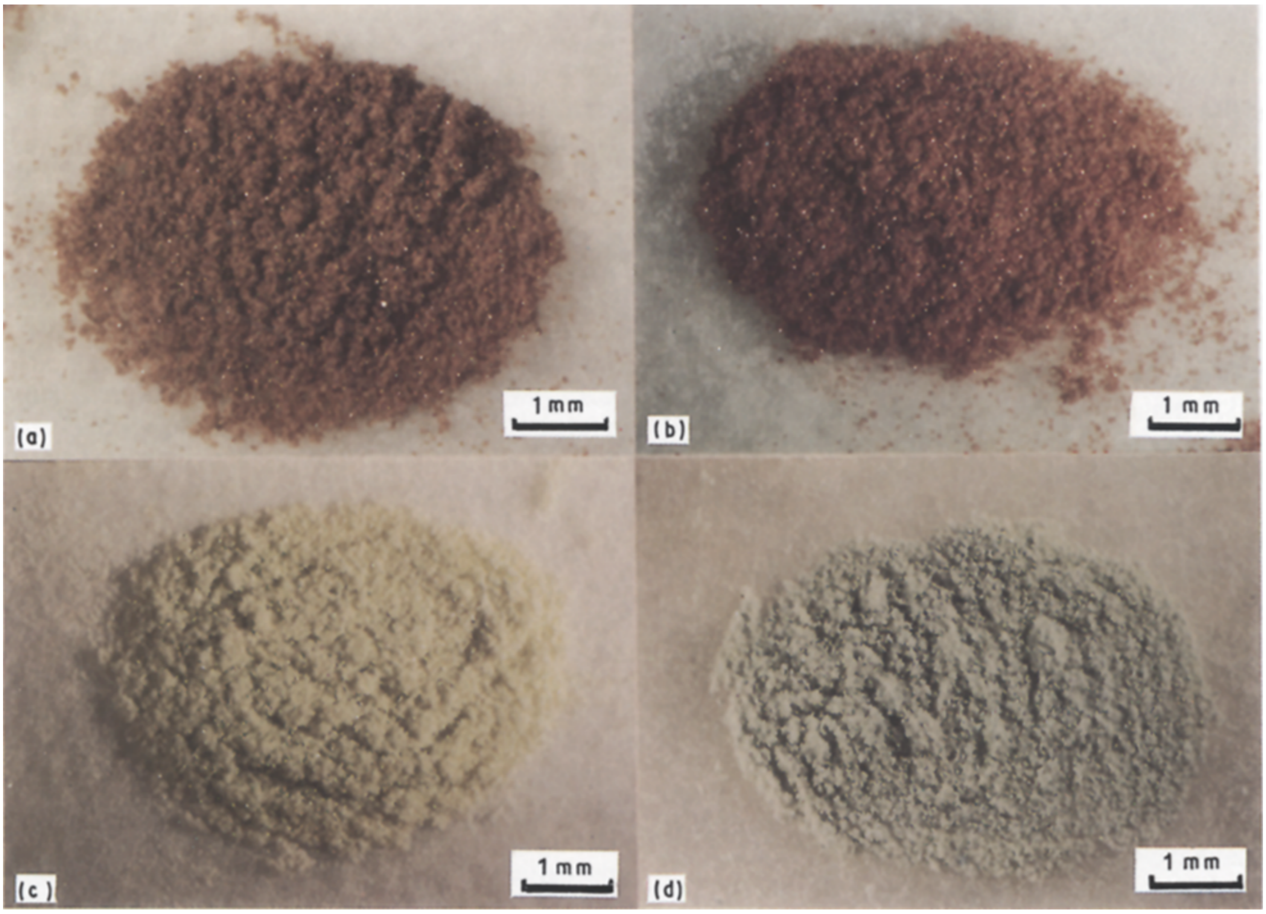

Figure 2 Samples viewed as grained powders prepared by annealing glass of the composition $F_{Ni} = 0.50$. (a) Glass, (b) high quartz made by annealing the glass at 915 °C for 60 h, (c) hexagonal cordierite as a crystallization product after annealing at 980 °C for 66 h, (d) hexagonal cordierite with minor amounts of spinel and quartz annealed at 1200 °C for 1 h.

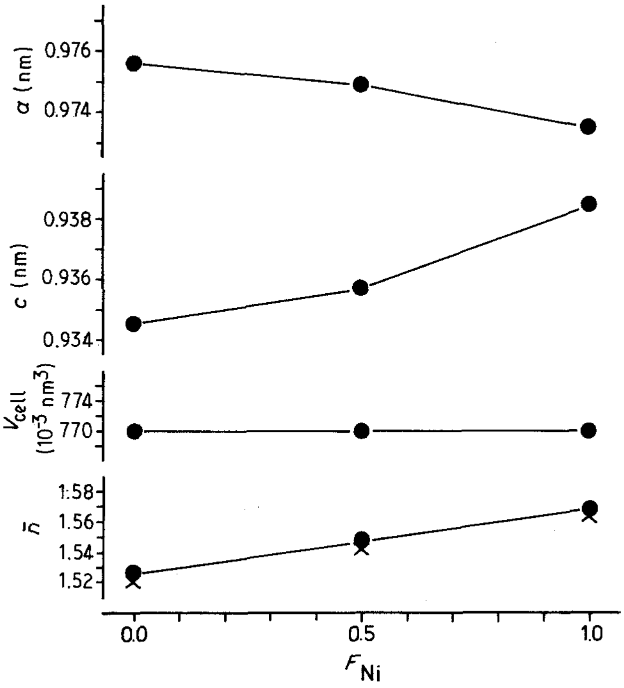

Figure 3 Lattice parameters and mean refractive index of synthetic hexagonal cordierite: (●) measured data, (x) calculated data.

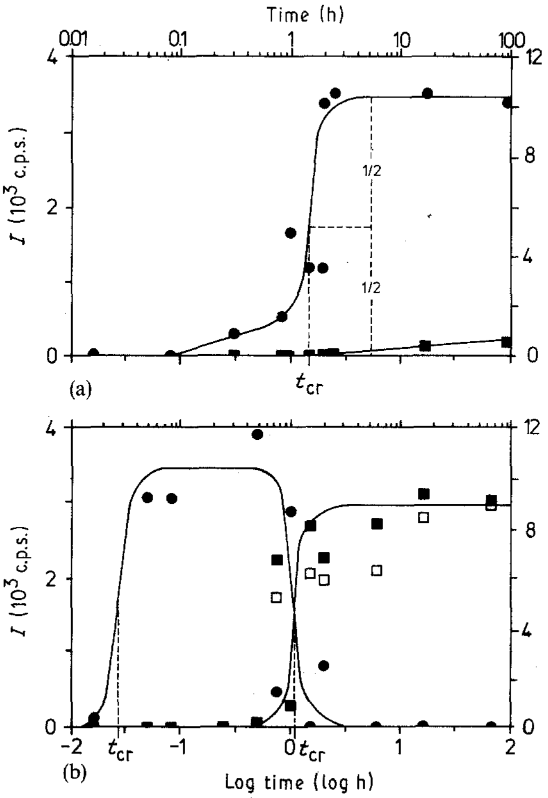

Figure 4 X-ray powder diffraction data and crystallization time, t_{cr}, for divitrification products of magnesium cordierite glass as a function of heating time. The intensities for high quartz (1 0 1) (●) are given on the left-hand scale; and for hexagonal cordierite (1 0 0) (□) and (2 1 1) (■) on the right hand scale. (a) 880 °C, (b) 980 °C.

magnesium cordierite is in good agreement with data in the literature [5].

To investigate the influence of water on the crystallization of high quartz from the glass, experiments with various amounts of water vapour were carried out at 880 °C with pure magnesium cordierite. The presence of water vapour slightly decreases the crystallization time t_{cr} of high quartz from 4 h in a vacuum to 1 h in air to 0.5 h in water vapour. This could be explained by the formation of hydroxyl groups which disrupt and weaken the glass structure and thereby facilitate its rearrangement in the crystalline lattice [15]. We carried out all the experiments in air to have comparable results. In contrast to the minor influence of water, the nickel content in the glass significantly lowers the crystallization times of high quartz and cordierite (Figs 4, 5). This is shown in a time–temperature–transformation (TTT) diagram for pure magnesium cordierite $F_{Ni} = 0.00$ (Fig. 6a) and nickel-containing cordierite $F_{Ni} = 0.50$ (Fig. 6b). Transformation I (glass → high quartz) could be described as a change in the long-range order of the tetrahedral framework and a diffusion of magnesium into the channels of high quartz [5]. The rearrangement and twisting of the six-membered tetrahedral rings and the diffusion of magnesium into the octahedral sites in the cordierite structure controls transformation II. Transformation III, the hexagonal → orthorhombic transformation of cordierite, can be characterized by a diffusion of elements between different tetrahedra in the rings with no change of the cation in the octahedral site except a distortion of the octahedron [1, 6]. The line for transformation III in Fig. 6a was taken from the literature [6]; our X-ray powder diffraction experiments showed no orthorhombic cordierite. At 1200 °C the nickel-bearing hexagonal cordierite decomposed into spinel and quartz, similar to Co^{2+} [11] the Ni^{2+} substitution for magnesium lowers the thermal stability. Transformations I and II were shifted to lower temperatures and shorter times with nickel substitution in cordierite.

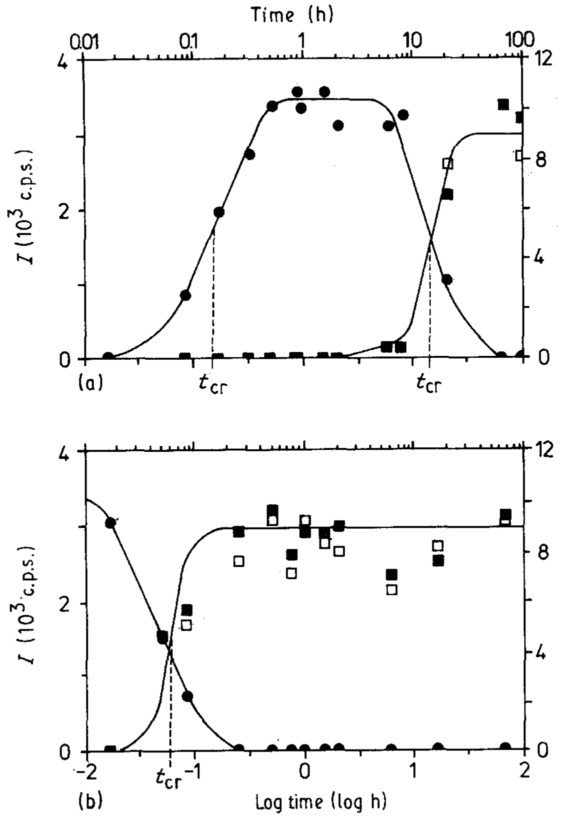

Figure 5 X-ray powder diffraction data for divitrification products of cordierite glass $F_{Ni} = 0.50$ (a) at 880 °C, and (b) at 980 °C, as a function of heating time, with symbols as in Fig. 4.

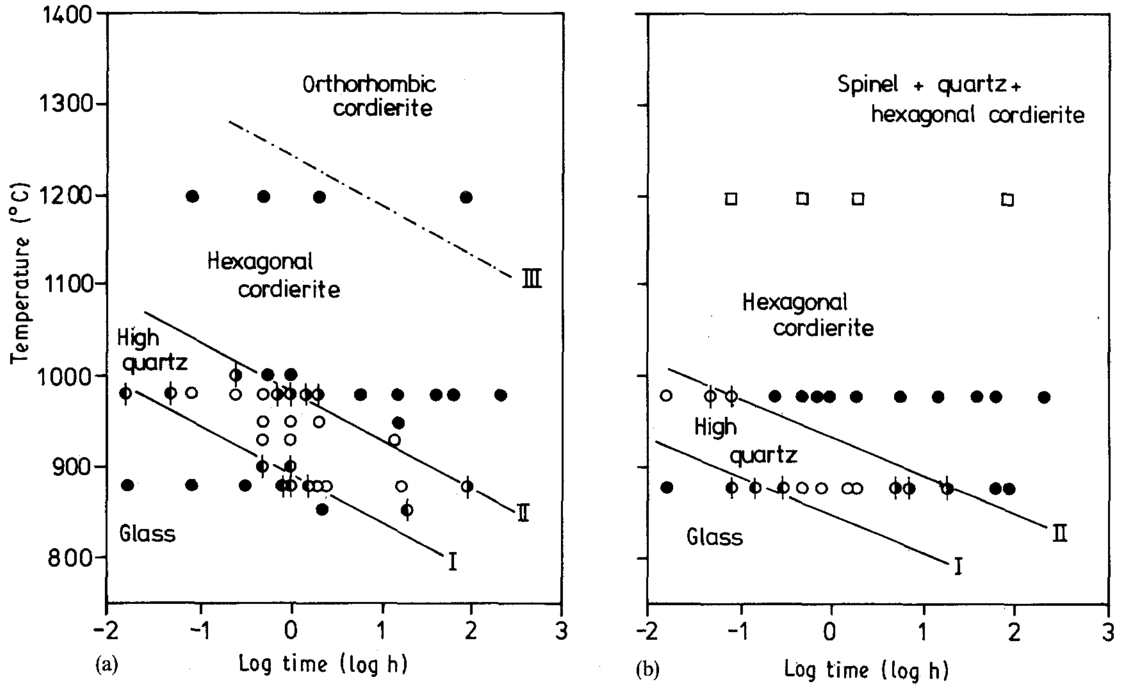

Figure 6 A time–temperature–transformation diagram for transformations of glasses of stoichiometric magnesium cordierite: (a) $F_{Ni} = 0.00$ and (b) $F_{Ni} = 0.50$. (Transformation I, glass → high quartz; II, high quartz → hexagonal cordierite; III, hexagonal cordierite → orthorhombic cordierite.) The line for transformation III was taken from Putnis and Bish [6]. Runs examined were by X-ray powder diffraction. Single phases: (●) glass (○) high quartz, (●) hexagonal cordierite. Mixed phases: (◐) glass and high quartz, (◑) high quartz and hexagonal cordierite. The lines for transformations I and II were drawn with the determined crystallization times at 880 and 980 °C (Figs 4 and 5). (□) Spinel and quartz as an additional phase for the nickel-containing composition.

The difference in the crystallization behaviour between nickel-free and magnesium-bearing cordierite glasses cannot be explained by the different sizes of the cations, because Ni^{2+} ($r = 0.069$ nm) is very similar in size to Mg^{2+} (0.072 nm). There is, however, a difference in the electron configurations and the kind of bonding to oxygen. From its crystal-field stabilization energy, Ni^{2+} would be expected to show a preference for the octahedral site. This destabilizes the nickel-bearing glass relative to the crystal more than for magnesium cordierite compositions, because magnesium shows neither tetrahedral nor octahedral site preference [16]. The field strength of the non-framework cation, nickel, plays a significant role in influencing structure and viscosity. The partial covalent bonding of the transition element nickel to the silicate groups can enhance the rearrangement of the glass structure for crystallization. Therefore, a decrease in the viscosity of the glass is necessary to explain a faster crystallization of nickel containing glasses.

Rather than determine the viscosity of glass samples directly, we made use of thermal expansion measurements to determine the glass transition temperature, T_g, which is correlated with the viscosity, η, [17]. The glass transition temperature decreases from 840 °C for magnesium cordierite to 822 °C for the composition $F_{Ni} = 0.30$. A decrease in T_g with increasing nickel content of a glass with an SiO_2-richer bulk composition has also been reported [2]. This change in T_g corresponds to a decrease of η. The decrease in the crystallization times can be explained by a decrease in the viscosity caused by the addition of the transition element, nickel. The strong influence of changes in the viscosity on kinetics of crystallization is well known [18]. Further experiments are being performed to gain a better understanding of the mechanisms and the structural changes of these transformations.

4. Conclusions

1. Complete solid solution exists between $Mg_2Al_4Si_5O_{18}$ and $Ni_2Al_4Si_5O_{18}$.

2. The crystallization sequence for magnesium cordierite and Mg–Ni cordierite is the same. After high quartz is fully crystallized from the glass, it transforms to hexagonal cordierite. No orthorhombic cordierite was observed in the X-ray powder diffraction patterns of samples treated under our experimental conditions.

3. The presence of nickel shifts transformations I (glass → high quartz) and II (high quartz → hexagonal cordierite) to lower times and temperatures, i.e., nickel accelerates the transformations. Substitutions of NiO for MgO in glass-ceramics with the cordierite composition, lower the crystallization times, and lower the thermal stability of cordierite.

4. The change in colour from a brown glass to red high quartz and yellow cordierite is most probably caused by a coordination change of Ni^{2+} during the transformations and is a useful phenomenon in phase analysis.

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