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Crystal growth kinetics in cordierite and diopside glasses in wide temperature ranges

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ABSTRACT

We measured and collected literature data for the crystal growth rate, $u(T)$, of μ-cordierite ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$) and diopside ($CaO \cdot MgO \cdot 2SiO_2$) in their isochemical glass forming melts. The data cover exceptionally wide temperature ranges, i.e. 800–1350 °C for cordierite and 750–1378 °C for diopside. The maximum of $u(T)$ occurs at about 1250 °C for both systems. A smooth shoulder is observed around 970 °C for μ-cordierite. Based on measured and collected viscosity data, we fitted $u(T)$ using standard crystal growth models. For diopside, the experimental $u(T)$ fits well to the 2D surface nucleation model and also to the screw dislocation growth mechanism. However, the screw dislocation model yields parameters of more significant physical meaning. For cordierite, these two models also describe the experimental growth rates. However, the best fittings of $u(T)$ including the observed shoulder, were attained for a combined mechanism, assuming that the melt/crystal interface growing from screw dislocations is additionally roughened by superimposed 2D surface nucleation at large undercoolings, starting at a temperature around the shoulder. The good fittings indicate that viscosity can be used to assess the transport mechanism that determines crystal growth in these two systems, from the melting point T_m down to about T_g, with no sign of a breakdown of the Stokes–Einstein/Eyring equation.

1. Introduction

Crystal growth kinetics in glass forming liquids has been extensively studied and reviewed elsewhere [1–5]. For isochemical or polymorphic crystallization, the crystal growth rates have been described in terms of standard models of interface-controlled growth (see, e.g., [6–8]) such as *normal growth*, *screw dislocation growth* or *2D surface nucleated growth*. Detailed studies of crystal growth mechanisms are known for various glass forming compositions, such as SiO_2 and GeO_2 (normal growth) [9,10], $Na_2O \cdot 2SiO_2$ (screw dislocation) [11] and $K_2O \cdot 4B_2O_3$ (2D nucleated growth) [12]. However, in most studies the inferred crystal growth mechanisms are typically restricted to temperature ranges near the melting point, T_m, or somewhat above the glass transformation temperature, T_g, where crystal growth rates can be most easily measured.

In one of the first studies of crystal growth in glasses in *wide* temperature ranges, Burgner and Weinberg [13] analyzed the growth rates of internally nucleated lithium disilicate crystals in isochemical $Li_2O \cdot 2SiO_2$ glass forming melts between the glass transition temperature, T_g, and the melting point, T_m. Their analysis suggested that different governing growth mechanisms may be active for distinct temperature ranges, and that the usual phenomenological models could be applicable only for limited temperature ranges.

Meanwhile, crystal growth rate data for other two silicate glasses, cordierite and diopside, have also been measured in similarly broad temperature ranges. Thus, the extensive studies of surface nucleated, isochemical crystallization of high-quartz solid solution crystals, denominated "*μ-cordierite*" ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$), in cordierite glasses reported in Refs. [14–21] allow a similar analysis. Some of these studies were part of a cooperative effort of the *TC* 7 Committee of the International Commission on Glass [22], which's aim was to advance the understanding of surface crystallization phenomena. Herein, numerous glasses close to the stoichiometric cordierite composition were melted in different laboratories and crystal growth experiments were conducted over a long period of time covering various experimental conditions.

As another case of surface nucleated crystallization, the crystal growth rates of *diopside* ($CaO \cdot MgO \cdot 2SiO_2$) in isochemical melts have also been comprehensively studied. Thus, crystal growth rate data are known for diopside glasses between 750–1155 °C and 1277–1378 °C [14,23–27]. In addition, thermodynamic and kinetic data, such as melting enthalpy and viscosity as a function of temperature are available for both systems, which facilitate quantitative comparisons between theory and experiment.

The objective of the present work is thus to summarize all measured growth rate data for μ-cordierite and diopside crystals in

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their isochemical liquids in wide temperature ranges, then to analyze and discuss their observed temperature dependencies in terms of the classical crystal growth models. We also present a proposal using combined growth mechanisms to explain the shoulder in the crystal growth curve of μ-cordierite.

2. Experimental

2.1. Samples

2.1.1. Cordierite glasses

Most of the data for the crystal growth rates of μ-cordierite refer to glasses having the nominal composition of cordierite (in wt%): 51.3 SiO_2, 34.9 Al_2O_3 and 13.8 MgO. In this work and in Refs. [14,15,19] cordierite glasses were melted from reagent grade MgO and Al_2O_3 (both from Merck) and SiO_2 (quartz sand, Walbeck GmbH, Weferlingen) at 1590 °C in air for at least 8 h in Pt-crucibles. Meltings of 500 ml batches were carried out in conventional electric furnaces and in medium frequency inductive furnaces (4*l* batches). In the latter case, glass homogeneity was improved by stirring. Diaz-Mora et al. [20,21] used two cordierite glasses from Schott Glaswerke: one glass (B9455) had the nominal cordierite composition; another (GM30870) had 14.6 MgO, 33.2 Al_2O_3, 52.3 SiO_2 wt%. Yuritsyn et al. [16,17] used stoichiometric cordierite glasses melted from chemically pure $Al(OH)_3$, $MgCO_3$ and $SiO_2 \cdot n\text{-}H_2O$ in Pt/Rh crucibles at 1600 °C for 4 h. All compositions are summarized in Table 1.

In this work and Refs. [14,15,19], glass plates of ≈10 × 15 × 1 cm^3 were prepared by casting the melts onto steel plates and slowly cooling to room temperature from 750 °C. Wet chemical analysis of the quenched glasses showed that no oxide component deviates more than 0.8 wt% from the nominal composition. The water content determined by hot vacuum extraction and IR spectroscopy [28] for one of the glasses was 0.033 mol/l (226 wt ppm).

2.1.2. Diopside glasses

The diopside glasses reported by several authors [14,23–27,29–34] and that used in the present study were melted in air in Pt crucibles. In this work and Ref. [14], glass plates of ≈10 × 15 × 1 cm^3 were splat cooled onto steel plates and slowly cooled to room temperature from 740 °C. Briggs and Carruthers [23] made an X-ray fluorescence analysis confirming that the composition of their glass was very close to the nominal composition, and was free of iron, titanium and alkali metal oxides, but had 0.25 mol% Al_2O_3. Nascimento et al. [25] used the ICP technique for chemical analysis, which showed that his glass composition deviates less than 1 wt% from the diopside stoichiometry. Reinsch [14] used a diopside glass with addition of 1 wt% Al_2O_3. Chemical analysis of this glass (19.7 MgO, 25.8 CaO, 54.5 SiO_2, 1 Al_2O_3 wt%) showed that no oxide component deviate more than 1 wt% from the nominal composition. The water content measured by hot vacuum extraction was 0.12 mol/l (758 wt ppm) [28]. Zanotto [27] used also a diopside glass with 1 wt% Al_2O_3. Kirkpatrick et al. [24] analyzed their glass with an electron microprobe, indicating a composition of 19.1 MgO, 26.4 CaO, 56.2 SiO_2 wt%, thus having only a minor discrepancy from the nominal diopside composition. Unfortunately, however, impurity and water contents were not always reported, but all these glasses have small departures from the stoichiometric diopside (18.61 MgO, 25.9 CaO, 55.49 SiO_2 wt%). All compositions are summarized in Table 1.

Table 1
Composition of all glasses used for crystal growth measurements in wt%

Cordierite glasses	SiO_2	MgO	Al_2O_3	Impurities
Cordierite	51.3	13.8	34.9	
This work and [13,14,18]	51.3 ± 0.8	13.8 ± 0.8	34.9 ± 0.8	
Yuritsin [15,16]	51.85	12.82	34.62	0.39 CaO/0.33 Na_2O
Diaz-Mora [19,20]	52.3	14.6	33.2	
Diopside glasses	SiO_2	MgO	CaO	Al_2O_3
Diopside	55.49	18.61	25.9	
This work and Reinsch [13]	54.55	19.72	25.80	1.02
Nascimento [24]	55.5 ± 1	18.6 ± 1	25.9 ± 1	
Briggs [22]	55.49	18.61	25.9	0.25 mol%
Zanotto [26]	54.96	18.4	25.64	1
Kirkpatrick [23]	56.2	19.1	26.4	

2.2. Measurements

2.2.1. Viscosity

In the present work, the viscosities of cordierite and diopside melts were determined by complementary methods. T_g was determined by a horizontal dilatometer (heating rate 5 K/min, Netzsch 402 E). Beam bending viscometry (heating rate 5 K/min, BAM) was used for the range $\log_{10}(\eta/(\text{Pa s})) = 12.3 - 9$ and for $\log_{10}(\eta/(\text{Pa s})) < 5$ ($T > 1000$ °C) rotational viscometry (BAM, measuring head Haake VT550) was applied.

The viscosity of the cordierite melt was also measured by Giess and Knickerbocker [35] at 900 and 920 °C with a parallel plate viscometer. Yuritsyn et al. obtained T_g data by means of dilatometry [16]. The viscosity of the diopside melt was measured by Licko and Danek [29] in an oscillating viscometer using a platinum–rhodium crucible and a cylinder with conical end. Nascimento et al. [25], Kozu and Kani [30] and McCaffery et al. [31] used a rotation viscometer. Sipp et al. [33] measured η by a compression method. Taniguchi [34] applied the counterbalanced method with Pt body and crucible, and the fiber elongation method. And finally, Neuville and Richet [32] did not disclose the technique used in their work.

2.2.2. Crystal growth rate

2.2.2.1. *μ-Cordierite.* Crystal growth rate measurements were performed using bulk pieces of glass (≈5 × 5 × 5 mm^3) with fractured, polished, or SiC ground surfaces in the present study as well as in Refs. [14–21]. Most of the thermal treatments were performed in air with ≈20% relative humidity (dew point ≈8.5 °C). The influence of the ambient water vapor pressure was checked by crystal growth experiments in argon/air atmospheres of different humidity [14,36] (dew point = −60 to 25 °C). Different techniques were used to measure the crystal growth rates of μ-cordierite at low and high temperatures. Below 830 °C we measured the growth of pre-existing crystals by electron or optical microscopy (increase of the maximum radius of selected surface crystals). Between 830 and 920 °C the maximum radius of crystals grown during one-step crystallization treatments were measured. Above 1000 °C we measured the thickness of the crystalline surface layer. Between 900 and 1050 °C both methods were used.

Isothermal treatments at 830–1100 °C were carried out in a conventional laboratory furnace. The samples were driven into the hot furnace using a platinum thermocouple as the sample holder. In other cases, annealing steps were made in a quartz glass tube furnace under controlled ambient conditions within a steel glove box. The accuracy of temperature measurement was ±10 K. Short time thermal treatments at high temperatures (1100–1350 °C) were performed in a specially designed vertical corundum tube furnace. The thermocouple and the platinum specimen holder were quickly moved along the tube axis where a linear gradient of 20 K/cm between 300 and 1500 °C was maintained. Due to the small heat capacities of small samples and the platinum holder, very high heating rates, up to about 1200 K/min, at least in the vicinity of the glass surface were attained. An empty sample holder