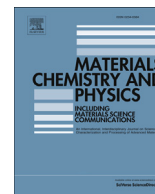




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# The effect of niobium- and tantalum oxide on nucleation and growth kinetics in lithium disilicate glasses

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## HIGHLIGHTS

- $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$  glasses were doped with up to 2 mol%  $\text{Nb}_2\text{O}_5$  or  $\text{Ta}_2\text{O}_5$ .
- The dopants decrease the nucleation rates and increase the induction times.
- The crystal growth velocities are drastically decreased by the additives.
- The crystals grow in form of several lamellae similar to spherulitic growth.
- A possible explanation for the effect of the nucleation inhibitors is given.

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## ABSTRACT

Stoichiometric lithium disilicate glasses were doped with up to 2 mol%  $\text{Nb}_2\text{O}_5$  or  $\text{Ta}_2\text{O}_5$ . The additives led to an increase in viscosities and to a change in the crystallization behavior. The steady-state nucleation rates, the induction times and the crystal growth velocities were studied as a function of the temperature using in situ optical hot stage microscopy. While the nucleation rates decrease by up to three orders of magnitude, the induction times significantly increase. The effect of nucleation inhibition is not solely based on higher viscosities. It is assumed that the glasses consist of  $\text{SiO}_4$  tetrahedra and  $\text{MO}_6$  ( $M = \text{Nb}, \text{Ta}$ ) octahedra and hence, with increasing additive concentration, the structural similarities between glass and lithium disilicate crystal decrease leading to smaller nucleation rates. Moreover, the crystal growth velocities decrease drastically. Optical micrographs indicate a lamellar growth proceeding from the crystal center. During growth, the lithium disilicate crystals get a constriction in their center leading to a dumbbell-like shape.

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## 1. Introduction

The nucleation and crystallization behavior of stoichiometric lithium disilicate glass ( $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ ) has intensively been studied in the past decades as this glass is one of the model systems for homogeneous nucleation where detailed thermodynamic and kinetic data are available [1–8].

Moreover, in a so called isochemical system the crystalline phase has the same chemical composition as the parent glass. Crystalline lithium disilicate melts incongruently at 1033 °C [9] and according to several authors an orthorhombic high-temperature phase is stable above 936 °C while below this temperature a monoclinic phase is found [1]. However, de Jong et al. only found an

orthorhombic lithium disilicate (space group Ccc2) with the lattice parameters of  $a = 5.807 \text{ \AA}$ ,  $b = 14.582 \text{ \AA}$  and  $c = 4.773 \text{ \AA}$  [10]. This phyllosilicate consists of corrugated sheets of  $(\text{Si}_2\text{O}_5)^{2-}$  parallel to the (010) plane which are linked by the lithium ions [11]. In the stoichiometric glass, lithium disilicate crystals with the shape of a prolate ellipsoid were observed as well as nearly spherical cross sections at 450–660 °C, i.e. the ellipsoids under a view angle perpendicular to the major axis [6,12,13]. The spherical ones consist of crystalline fibers radiating from the crystal center [12]. After long thermal treatments at temperatures, where crystal growth occurs, new branches formed on some crystals [12] which was supposed to be due to a twinning mechanism resulting from growth faults or defects [14]. At higher temperatures (from 750 °C to the melting temperature), a spherulitic crystal morphology was detected [15]. A change in the crystal morphology from ellipsoidal to spherical has also been reported from lithium disilicate crystallization from

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zirconia doped glasses [16]. The crystal growth velocities of stoichiometric lithium disilicate glass were determined by measuring the crystal size or the thickness of the surface crystallized layer after one-step heat treatments in a wide temperature range from 440 °C to  $T_m$  [6,7,12,15,17–21]. Recently, the effect of small concentrations of additives such as  $Al_2O_3$ ,  $La_2O_3$ ,  $TiO_2$  or  $ZrO_2$  on the crystal growth velocities was reported [13,16]. The addition leads, with the exception of  $TiO_2$ , to a remarkable deceleration of crystal growth in the temperature range from 590 to 660 °C and is in the case of  $Al_2O_3$  and  $La_2O_3$  likely due to a concentration gradient formed by an enrichment of the added oxides at the crystallization front [13]. The decrease of the crystal growth velocities in the zirconia-doped glasses might be explained by higher viscosities [16]. In the literature it was shown that the viscosity increase in a diffusion layer around nanocrystallites may cause a decrease in the diffusion coefficient which may act as a barrier leading to a suppression of crystal growth [22,23] in a larger extent than it might be caused by a simple diffusion gradient. Moreover, the decrease in crystal growth velocities can be also caused by concentration gradients which are formed by shoving away some components during crystallization [24–26]. Recently, the effect of minor concentrations of additives on nucleation rates and induction times was reported [13,16]. The addition of small concentrations of some components, such as  $ZrO_2$  or  $La_2O_3$  results in a drastic decrease of the nucleation rates and to a notable increase in induction times.

This paper describes the addition of  $Nb_2O_5$  and  $Ta_2O_5$  to a stoichiometric lithium disilicate glass and their effect on the nucleation and crystal growth. The determined nucleation rates and growth velocities are furthermore related to the glass viscosities at the respective temperatures. The crystallization processes are studied by in situ hot stage laser scanning microscopy.

## 2. Materials and methods

### 2.1. Glass preparation

Glasses with the compositions  $x M_2O_5 \cdot (100 - x)Li_2Si_2O_5$  ( $x = 1$  and 2 mol%,  $M = Nb$  or  $Ta$ ) were prepared from the raw materials  $SiO_2$  (Sipur A1, Bremthaler Quarzitwerke),  $Li_2CO_3$  (Polskie Odczynniki Chemiczne Gliwice),  $Nb_2O_5$  (Ventron) and  $Ta_2O_5$  (Alfa Aesar). While the base glass is denoted by A, the glasses with  $x$  mol %  $Nb_2O_5$  and  $Ta_2O_5$  are named  $Nbx$  and  $Tax$ , respectively. Batches for 200 g glass were melted in a platinum crucible in an inductively heated furnace at temperatures in the range from 1450 to 1510 °C which were kept for 0.5–1 h. Afterward the glass melts were stirred for up to 1.5 h using a frequency of 40–60  $min^{-1}$  and soaked for 15 min. In order to avoid crystallization during cooling, two glass blocks were cast on a copper and brass block. Then the glass blocks were transferred to a cooling furnace preheated to 475–490 °C and the furnace was switched off in order to allow the glass to cool and to release stresses. The lithium evaporation during melting is insignificant as described in Ref. [13]. Furthermore, the effect of the cooling procedure does not noticeably affect the number of nuclei which was checked by pouring a glass melt on a thermocouple placed in the middle of a glass block and observing the temperature during cooling [13]. The analyzed glasses were homogeneous, stria-, bubble- and crystal-free and were stored in a desiccator using  $P_2O_5$  as drying agent.

### 2.2. Thermal analyses

The glass transition and crystallization temperatures were determined by differential thermal analyses (DTA) using a Shimadzu DTA 50. In order to minimize the effect of surface crystallization, bulk samples were analyzed. For this purpose, 60 mg glass

powder was filled in a DTA platinum crucible, remelted above the liquidus temperature for 5 min and cooled in air. The remelting process was performed instead of breaking off a small piece of glass in order to get a better thermal contact. During the DTA-measurements, the samples were heated with 10 K/min to 1100 °C, kept for 30 min and then cooled down with 10 K/min to room temperature. Subsequently baseline corrections were performed.

The glass transition temperatures were verified by dilatometry. Here cylindrical samples with 8 mm diameter were heated with 5 K/min in a Netzsch DIL 402 PC.

### 2.3. X-ray diffraction

For the determination of the occurring crystal phases, X-ray diffraction (XRD) was performed using a Siemens D 5000 diffractometer. The glass samples were annealed at the crystallization peak temperature ascertained by DTA for 2 h and then powdered. The XRD patterns were recorded using  $Cu K\alpha$  radiation in a  $2\theta$ -range from 10 to 60° and a step width of 0.02°. The XRD-patterns were analyzed using the software DIFFRAC.EVA from BRUKER.

### 2.4. Viscosity measurements

The viscosity measurements were carried out with a rotation viscometer Bähr VIS 403 ( $10^{1.3}$  to  $10^3$  dPa s, rotation speed 250  $min^{-1}$ , cooling rate 5 K/min) as well as with a beam bending viscometer Bähr VIS 401 ( $10^9$  to  $10^{12.5}$  dPa s, heating rate 10 K/min). For beam bending viscometry, glass bars with the dimensions  $5 \times 5 \times 50$  and  $5 \times 4 \times 50$   $mm^3$  were prepared. The glass Advantex® from 3B-the fiberglass company was used as calibration substance. The viscosity/temperature dependencies were fitted using the Vogel–Fulcher–Tammann equation (VFT-equation):

$$\log \eta = B + \frac{C}{T - T_0} \quad (1)$$

### 2.5. Determination of the nucleation rates and crystal growth velocities

For the determination of the nucleation rates and crystal growth velocities, glass disks with a diameter of 5 mm and 0.5 mm thickness were prepared and their surfaces were ground and polished using abrasive slurries of shrinking grain size. A laser scanning microscope (LSM) AxioImager Z1m PASCAL5 (Carl Zeiss GmbH) equipped with a heating stage Linkam HS1500 was used for the measurements. A detailed explanation of the nucleation and growth experiments can be found in Ref. [13]. This method enables the acquisition of images with certain volume information by stacking the samples in z-direction. Then counting the crystals ( $N$ ) in an area  $F$  ( $N$  – crystal number in an area,  $z$  – z-stack range,  $n$  – refractive index) in these images yields the crystal number per volume unit  $N_V$ .

$$N_V = \frac{N}{F \cdot z \cdot n} \quad (2)$$

The crystal growth velocities of ellipsoidal crystals were calculated in analogy to Ref. [6]. Therefore, the major and minor axes,  $a$  and  $b$ , respectively, were measured during a one-stage heat treatment in order to calculate the mean crystal radius ( $P$  – perimeter):

$$r = \frac{P}{2\pi} = \frac{1}{2} [1.5(a + b) - (a \cdot b)^{\frac{1}{2}}] \quad (3)$$

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