



Crystallization Kinetics of LaF3 Nanocrystals in an Oxyfluoride Glass

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Crystallization Kinetics of LaF₃ Nanocrystals in an Oxyfluoride Glass

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Abstract

Nanocrystallization of LaF₃ in a glass of composition 55SiO₂-20Al₂O₃-15Na₂O-10LaF₃ (mol %) has been achieved by heat treatment above the glass transition temperature. A maximum crystal size of 14 nm has been attained, with the crystalline fraction and crystal size dependent on the time and temperature of thermal treatment. The effect of lanthanum fluoride crystallisation is noticeable from the microstructural and compositional changes in the glass matrix, which have been studied using several techniques, including viscosity, dilatometry, X-ray diffraction (XRD) and quantitative Rietveld refinement, transmission electron microscopy (TEM) and differential scanning calorimetry (DSC). The crystallisation mechanism is shown to occur via regions of La- and Si-phase separation in the glass, from which the fluoride crystals develop during heat treatment. The interface between the glass matrix and the crystals in the demixed ranges is enriched in network formers, mainly SiO₂, creating a viscous barrier, which inhibits further crystal growth and limits the crystal size to the nanometric range.

Keywords: Oxyfluoride glasses; Glass-ceramics; Crystallisation; Nano-crystals; LaF₃

1. Introduction

Glass-ceramics containing nanoscaled crystals are key materials for photonic applications due to their low phonon energy and optical transparency. Oxyfluoride glass matrices are of particular interest since they combine the high chemical durability associated with oxide glasses with the high solubility of rare-earth cations and transparency offered by fluoride crystals [1-6]. Lanthanum fluoride glass-ceramics are excellent candidates for photonic applications [7-12] due to their ability to host rare-earth ions in crystalline precipitates in which the phonon energy is very low. If the optically active ion is incorporated into the fluoride crystalline phase, the intensity of the characteristic laser emission is enhanced. Ideally, the crystal size should be in the range 5–100 nm, with a narrow size distribution in order to minimize scattering losses. The crystallisation of a fluoride phase is achieved by heat treatment slightly above the glass transition temperature (T_g). The base glass composition, the temperature and the time of heat treatment will influence the crystallisation process, and the resulting phase composition, crystal size, volume concentration and distribution.

Since a pre-requisite for optical applications is the high transparency of glass-ceramics, the crystallites must be nanosized and present a narrow crystal-size distribution. Knowledge of their preparation and a better understanding of the crystallization mechanism are, therefore, of considerable importance. Theories of crystallization are usually restricted to isochemical systems in which the crystalline phase has the same chemical composition as the glass matrix. However, the challenge of obtaining large volume concentrations of crystals, with sizes in the nanometric range and a narrow size distribution, can only be achieved in multicomponent systems in which the interface formed during nucleation and crystal growth is controlled. In highly viscous liquids, such as glass melts near the glass transition

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3 temperature, this leads to a locally altered chemical composition at the interface between the
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5 crystalline precipitates and their surrounding matrix. For coupled processes of viscosity and
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7 crystal growth, two cases can be distinguished: (i) the viscosity of the liquid at the interface is
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9 smaller than that of the bulk, leading to an increase in the crystal growth rate due to enhanced
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11 diffusion; (ii) the viscosity increases, such that the interface acts as a diffusional barrier which
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13 decelerates the crystal-growth velocity. With regard to this latter scenario, Rüssel [13]
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15 suggested a mechanism for the crystallisation of CaF_2 , in which crystallisation takes place
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17 starting from a homogeneous glass. The formed interface is enriched in glass formers
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19 increasing viscosity near the crystals, with the effect that a diffusional barrier forms around
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21 each crystal, which hinders further crystal growth. This mechanism was later confirmed by
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23 Bocker *et al.* [14], who described the crystallization of BaF_2 in a similar glass matrix, and
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25 Bhattacharyya *et al.* [15] who discussed the impact of such diffusion barriers on the action of
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27 nucleation agents in lithia-aluminosilicate glass ceramics. Hémono *et al.* [16,17] studied LaF_3
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29 nanocrystallisation and its characterisation by TEM in similar glasses, indicating that phase
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31 separation precedes crystallisation. The application of transmission electron microscopy for
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33 the investigation of glasses and glass-ceramics in general was recently reviewed by Höche
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35 [18]; the advantages of employing energy-filtered transmission electron microscopy (EFTEM)
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37 for the study of enrichment zones in glass ceramics is described in detail by Bhattacharyya *et*
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39 *al.* [16,19]. ^{19}F -NMR experiments of both phase-separated and non-phase-separated glasses
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41 showed that La-F or Ba-F bonds are already present in the parent glass and diffusion of
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43 fluoride takes place from the glass to the crystal when crystallisation progresses [20, 21].
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53 Knowledge of the crystallization mechanism of lanthanum fluoride nano-
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55 glassceramics is fundamental in order to design improved materials. In this paper, the process
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57 of crystallization of an oxyfluoride glass in which LaF_3 precipitates has been analysed in
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3 detail, employing dilatometry, viscometry, DSC, XRD, and TEM to study the mechanism of
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5 nanocrystallization.
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10 **2. Experimental**

11 *2.1. Glass melting, crystallisation and chemical analysis*

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17 A glass with composition $55\text{SiO}_2.20\text{Al}_2\text{O}_3.15\text{Na}_2\text{O}.10\text{LaF}_3$ (mol %) was prepared by
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19 melting reagent grade SiO_2 (Saint-Gobain, 99.6%), Al_2O_3 (Panreac, calcined for 12 h at
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21 800°C), Na_2CO_3 (Panreac, 99.5%) and LaF_3 (Panreac, 99%). Batches were firstly calcined for
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23 2 h at 1200°C and then melted during 1.5 h at 1600°C . The batches were quenched twice in
24
25 air onto a brass mould in order to obtain homogeneous transparent glasses. Glass-ceramics
26
27 were obtained by controlled crystallisation of LaF_3 on heat treatments at temperatures
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29 between $T_g + 35^\circ\text{C}$ and $T_g + 95^\circ\text{C}$ for various time lengths.
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34 Samples were analysed by X-ray Fluorescence Spectroscopy (XRF) with a Panalytical
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36 spectrometer. The content of all oxides was determined employing the melting method with
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38 $\text{Li}_2\text{B}_4\text{O}_7$; the fluorine content was analysed employing pressed pellets of powdered glass (8 g)
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40 in order to avoid volatilization.
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45 *2.2 X-ray diffraction*

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50 Phase analysis of glass-ceramics obtained after thermal treatment at 620°C for
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52 different lengths of time were conducted using powder XRD with a D-5000 Siemens
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54 diffractometer using monochromatic $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). Patterns were scanned
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56 over the angular range $20 \leq 2\theta \leq 60^\circ$ with a step size of 0.05° and a fixed counting time of 2.5
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58 s/step.
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3 Glass-ceramics obtained at 660 °C and 680 °C, from 1 to 80 h, were studied by XRD
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5 using an X'Pert PRO Panalytical diffractometer equipped with an X'Celerator detector. The
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7 patterns were collected with monochromatic Cu K α radiation over the range $10 \leq 2\theta \leq 70^\circ$
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9 with a step size of 0.0167° and a fixed counting time 200 s/step.
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12 The crystallized fraction of LaF₃ on prolonged thermal treatment (620 °C, 40 h) was
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14 estimated by quantitative Rietveld analysis of XRD data, employing a similar method to that
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16 applied to a similar glass-ceramic with nanocrystals [22] and other largely amorphous
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18 multiphase materials [23]. The glass was ground to a fine powder in an agate mortar, sieved
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20 through a 60 μm mesh then milled again with NaF (PRO-VYS, 99.9%), which was used as
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22 internal standard in a suitable quantity (3 wt.%) to approximate the peak intensity of the
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24 crystalline LaF₃. The average particle size of the NaF internal standard was determined to be
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26 11.4 μm using the laser light dispersion method with a Mastersizer S instrument (Malver
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28 Instruments Ltd.). XRD powder data for Rietveld analysis were collected over the range $10^\circ \leq$
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30 $2\theta \leq 110^\circ$ with a stepwidth of 0.02° and a fixed counting time of 4 s/step, employing a Bruker
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32 TT diffractometer equipped with a Lynx Eye detector and monochromatic Cu K α radiation.
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34 Rietveld refinement was carried out with the FULLPROF program [24] using interpolation of
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36 background points to model the amorphous contribution to the pattern.
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46 *2.3 Transmission electron microscopy*

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50 Samples of the oxy-fluoride glasses and glass-ceramics for TEM were prepared by
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52 cutting slices, plane-parallel grinding, dimpling to a residual thickness of 10 to 15 μm , and
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54 ion-beam thinning using Ar⁺ ions. Overheating of the TEM foils and the consequent
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56 introduction of artefacts was avoided by means of double-sided, ion-beam etching at small
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58 angles ($< 6^\circ$) and low etching energies (acceleration voltage, 2.5 kV; beam current < 8
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3 μA). The non-conducting sample was selectively coated with carbon prior to TEM
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5 investigation [25] in order to reduce electrostatic charging under the electron beam.
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8 TEM samples were characterised in two transmission electron microscopes.
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10 Conventional TEM imaging and diffraction was performed at an acceleration voltage of 75
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12 keV in a Hitachi H-8100 instrument (point-to-point resolution: 0.23 nm), EFTEM imaging
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14 was performed in a Zeiss EM 912 microscope ($c_s=2.7$ mm, $c_c=2.7$ mm, Köhler illumination),
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16 operating at 120 kV (LaB₆ filament) and equipped with an in-column Omega-type energy
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18 filter. Elemental maps were generated using the three-window technique [26] only for regions
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20 that obeyed Crozier's conditions [27], i.e., multiple scattering effects are negligible. The
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22 energy-window width was 10 eV for the La-N_{4,5} /Si-L_{2,3} map. Digital micrograph software
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24 (Gatan Inc., Pleasanton, CA, USA) was used for image processing.
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32 *2.4 Dilatometry and differential scanning calorimetry*

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36 Glass transition temperatures (T_g) and coefficients of thermal expansion (CTE) were
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38 determined by dilatometry at a heating rate of 10 K/min in air using a Netzsch Gerätebau
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40 dilatometer, model 402 EP.
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43 DSC measurements were performed with a Setaram instrument (Model Setsys
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45 Evolution 16/18) using powdered Al₂O₃ as inert reference material and employing 100–150
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47 mg of glass with particle size of 1– 1.25 mm in order to reproduce bulk conditions. The DSC
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49 scans were carried out with heating rates in the range 5 – 40 K/min in order to determine the
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51 activation energy for crystallisation and the Avrami parameter, n . In addition, peak
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53 crystallisation temperatures of glass samples previously heat treated during 1 h within the
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55 temperature range, $T_g +10 - T_g+135$ °C, were monitored by heating samples through the
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3 crystallization temperature range at 10 K/min in order to identify a possible optimum
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5 nucleation temperature.
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10 *2.5 Viscosity*

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15 The viscosity of the glass was determined using the procedures of fibre elongation and
16 rotation in melted glass, employing a high-temperature Haake viscometer equipped with a ME
17 1700 sensor. The fibre-elongation method was performed in the interval $10^{12} - 10^7$ Pa.s
18 according to International Standard ISO 7884-3, using loads of 2 – 250 g, depending on the
19 viscosity. Fibres were prepared with diameter 0.6 – 0.8 mm and a length of 50 ± 2 mm with a
20 ball at each extreme, in accordance with rule DIN 52 312 part 3. The viscosity at each
21 temperature and time was determined for at least three samples using different weights. The
22 maximum error in the viscosity determination was $\log \eta \pm 0.1$. In order to study the influence
23 of crystallization on viscosity, some fibres were thermally treated at 620, 640 and 660 °C for
24 different time lengths (20 - 80 h) and the viscosity was measured at 660 °C.
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39 The rotation procedure was applied for viscosity in the range $10^3 - 10^1$ Pa.s using a
40 high-temperature rotation viscometer of the cylindrical Searle type at rotation speeds of 1–30
41 rpm for 10 min, following the International Standard ISO 7884-2. Three measurements were
42 taken at three different rotation speeds for each temperature within this range. The use of both
43 methods allows determination of the complete viscosity-temperature curve.
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51 Hot-Stage Microscopy (HSM) was performed in a Leica-EM201 microscope with
52 image analysis for determination of the viscosities in air at a heating rate of 5 K/min. The
53 samples were initially cold pressed to conformed bodies of 3 mm in both height and diameter
54 from glass powder with a particle size $< 60 \mu\text{m}$. The temperature was measured with a Pt/Rh
55 (6130) thermocouple placed under and in contact with the alumina support. The temperatures
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3 corresponding to the characteristic viscosity points, following Scholze's definition [28, 29],
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5 were obtained from photomicrographs.
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8 Indentation methods allow the viscosity to be determined at a certain temperature as a
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10 function of time. Micro-indentation measurements were performed on a vertical dilatometer
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12 (Bähr VIS 404, Hüllhorst, Germany) by force control at 10 N and using a pushing rod which
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14 was equipped with a sapphire micro-sphere of radius 0.75 mm. Samples with coplanar
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16 surfaces and height of ca. 5 mm were prepared by grinding and polishing. Viscometer runs
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18 were carried out at ambient atmosphere at 620, 660 and 680 °C for 5 h, employing a heating
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20 rate of 10 K/min. After a dwell time for thermal equilibration and structural relaxation, the
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22 weight was loaded on the pushing rod and the sphere started to penetrate the glass surface. For
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24 measurements at 620 and 660 °C, the applied weight was 500 g and for 680 °C it was 300 g. A
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26 linear variable displacement transducer continuously recorded the indentation depth of the
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28 sphere into the glass. The micropenetration viscometer was calibrated using a standard glass
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30 (G1) of PTB (Physikalisch-Technische Bundesanstalt, Germany). The certified viscosity data
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32 [30] could be reproduced with an accuracy of 0.02 (rotation) and 0.1 (micropenetration) in log
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34 units [31].
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45 **3. Results and discussion**

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48 The nominal and analysed compositions of the oxyfluoride glass are summarized in
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50 Table 1. The fluorine loss during melting in air is around 38 %, similar to that observed in
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52 another composition of the same system [22]. The glass transition temperature of the
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54 oxyfluoride glass was $585 \pm 2^\circ\text{C}$.
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58 Figure 1 shows the variation of the glass transition temperature as a function of the
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60 heat treatment time at 620 °C. T_g increases by 60 K within the first 20 h, and then remains

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3 almost constant for longer treatment times. The initial increase is explained by the depletion
4 of fluoride ions in the glass matrix due to the crystallization of LaF_3 , developing an
5 enrichment of network former ions in the residual glassy matrix, which leads to an increase in
6 T_g . For time lengths > 20 h, the crystallization process is finalized and the structure of the
7 glass matrix does not change significantly, resulting in a slight decrease in T_g . All the glass-
8 ceramics heated according to the detailed regimes were transparent.
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20 *3.1 X-ray diffraction and the crystallization process*

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24 The XRD patterns of the glass-ceramics after treatments at 620°C for time lengths
25 ranging from 1 to 80 h are shown in Fig. 2. The reflections of the crystallized fraction were
26 consistent with those of hexagonal lanthanum fluoride LaF_3 (PDF file No. 32-0483). The
27 crystallization of LaF_3 was detected after 1 h of treatment at 620°C , with the peak intensity
28 increasing with further treatment time. The size of the crystals was calculated from the (111)
29 peak of LaF_3 ($2\theta \approx 27.5^\circ$) using the Scherrer equation:
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$$41 \quad D = \frac{G\lambda}{B \cos\theta} \quad (1)$$

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46 where D is the crystal size, G is a constant whose value is 0.9, B is the corrected full width at
47 half maximum of the peak and θ is the Bragg angle. The errors were calculated by peak fitting
48 and in accordance with error theory. The crystal size increased in the measured temperature
49 range from 5 to 10 nm, as shown in Fig. 3.
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56 In order to analyse more thoroughly the crystallization mechanism as a function of
57 time and temperature of treatment, two further crystallization kinetics at 660 and 680°C were
58 carried out from 1 to 80 h. All glass-ceramics were transparent, except those obtained at 680
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3 °C for times longer than 40 h. Crystal sizes, as calculated by the Scherrer equation, increased
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5 non-linearly (Fig. 3). The time-dependence of the crystal size in Fig.3 was, therefore, fitted
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7 according to
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$$10 \quad r = Ut^p \quad (2)$$

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18 giving,

$$19 \quad \log(r) = \log(U) + p \log(t) \quad (3)$$

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27 where r is the average crystal radius, U is the growth rate, t is the dwell time, and p is the
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29 growth exponent. Figure 4 shows the time dependence of r in double logarithmic scales. The
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31 growth exponent p was found to be very small (≤ 0.17). Practically no crystal growth was
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33 detected for dwell times > 10 h, where the value of p was close to zero. As discussed in more
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35 detail later, the arrest of the crystal growth is related to the formation of a viscous SiO_2 layer
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37 around the crystals during heat treatment, which acts as diffusion barrier inhibiting crystal
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39 growth. At higher temperatures such as 680°C , it is observed that the diffusional barrier is
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41 overcome and coarsening of the crystals in the demixed areas occurs. At these temperatures,
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43 the viscosity decreases and the crystal growth rate increases, thus the diffusional barrier is less
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45 efficient for preventing crystal growth and the crystals are able to grow more. [On the other](#)
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47 [hand, the formation of agglomerates is also expected at higher temperatures with increasing](#)
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49 [annealing time, which leads to the loss of transparency in the glass-ceramics \[17\].](#)
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Quantitative Rietveld Analysis

Structural models of LaF_3 (space group, $P\bar{3}c1$) and the NaF internal standard ($Fm\bar{3}m$) were refined by Rietveld analysis based on published structural data [32, 33]. LaF_3 is known to crystallize in hexagonal platelets [34]. The effects of the crystal shape on the diffraction data were incorporated in the Rietveld refinement by allowing the independent refinement of the profile parameters of certain “special reflections” in Fullprof, e.g. (002), which are subject to broadening. The thermal vibration factors of the two phases were not refined in order to avoid correlation with the background or other parameters [35]. The observed diffraction pattern and the difference pattern between observed and calculated data on termination of Rietveld refinement are shown in Fig. 5. Final structural parameters and reliability factors indicating the quality of the refinement are listed in Table 2.

The weight fraction of LaF_3 obtained by refinement was corrected for the presence of the amorphous phase from the X-ray and real weight fractions of the NaF internal standard with the same procedure as outlined in previous works [22, 23]. The actual weight fraction of LaF_3 in the glass, after correction for the presence of the NaF standard in the refinement data, was calculated to be ~ 7.3 wt%. Absorption contrast effects (microabsorption) of phase mixtures with different linear absorption coefficients may influence the X-ray diffraction intensities and the results of the quantitative analysis. Brindley [36] classified the absorption effects in mixed powders on the basis of the value of μD where μ is the linear absorption coefficient and D is the particle size. In the present case, the LaF_3 nanocrystals and NaF internal standard may be classified as fine powders ($\mu D < 0.01$) on the basis of their weighted absorption coefficients and particle sizes such that no microabsorption correction need be applied.

3.2. TEM

A TEM micrograph of the base glass collected at 75 keV is shown in Fig. 6a, which reveals liquid-liquid phase-separation droplets enriched in elements of high atomic number (strong scattering). The droplets are fully amorphous and with an average diameter in the range 30 – 40 nm, as determined by electron diffraction (not shown).

The average size of the phase-separation droplets did not change significantly after annealing for 40 h at 620 °C (Fig. 6b). However, the shape of the droplets became less spherical as a result of the formation of LaF₃ crystallites (cf. XRD results presented in Section 3.1). The crystallites are of smaller diameter than the droplets such that up to four crystallites can coexist within a droplet. As is the case for glasses with different fractions of lanthanum and silicon [16], TEM and EDX analyses indicate that the phase-separation droplets contain not only lanthanum and fluorine but also silicon and oxygen, in addition to traces of aluminium. It may be assumed, therefore, that on annealing the growth of the LaF₃ crystallites within the droplets is limited to some extent by an excess of silicon. On termination of the crystallization process, several LaF₃ nanocrystals of ca. 9 nm in diameter are formed, which are trapped in a volume determined by the size of the preceding liquid-liquid phase-separation droplets. The remaining volume of this former droplet is filled with the excess of Si, Al and O, as has been observed previously in a 40SiO₂.30 Al₂O₃.18 Na₂O.12 LaF₃ (mol %) glass [16]. In order to verify this hypothesis, energy filtered TEM was employed. A silicon elemental map was obtained with the three-windows technique [26] using images from two pre-edge windows centred at 77 eV and 87 eV, and one post-edge window centred at 109 eV. The calculated spatial resolution of this image is ≈ 3 nm using $cc = 2.7$ mm [37]. Since the Si-*L*_{2,3} and La-*N*_{4,5} edges are very close to each other, the latter cannot be excluded as having an effect on the intensity distribution in the Si map; the existence of La is supported by an

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3 EFTEM simulation presented previously for the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{LaF}_3$ system [22]. In
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5 order to confirm the presence of La in the nanocrystals, it would have been instructive to
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7 acquire a La elemental map using the La- $M_{4,5}$ edge at 832 eV as, in this case, there is no
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9 superimposed contribution from Si ; however, this was not possible due to the high sensitivity
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11 of the specimen to the electron beam and the unfavorable signal-to-noise ratio.
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15 There is a difference in the manner in which the silica-enriched region is formed
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17 around the crystals in phase-separated and non-phase-separated glasses. In a non-phase-
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19 separated parent glass, such as the CaF_2 - or BaF_2 -containing glasses studied by Rüssel [13,
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21 14], fluorides precipitate from a homogeneous glass. The silica enrichment around the formed
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23 crystals induces an increase of viscosity which limits further crystal growth. For a phase-
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25 separated parent glass like the title composition, droplets are present, which, in the present
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27 case, are rich in lanthanum and silicon. Further thermal treatment of the glass results in the
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29 growth of LaF_3 crystals inside the droplets, while silicon redistributes itself around the
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31 crystals forming a shell, which then inhibits further crystal growth. Nevertheless, as
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33 mentioned in the introduction, in both types of glass, La-F bonds (presumably in the phase-
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35 separated droplets) or Ba-F bonds are already present in the parent glasses, and F diffusion
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37 from the glass matrix to the crystal has been demonstrated in both cases.[20, 21].
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51 The DSC results at different heating rates are shown in Fig. 7. The glass transition
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53 temperature is identified as the point of intersection of the two tangents of the depression in
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55 the baseline of the curves. The crystallization peak corresponds to LaF_3 crystallization. Table
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57 3 lists the T_g and the temperature of the crystallisation peak, T_p , at different heating rates.
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60 Determination of the Avrami exponent was performed using Avrami's law

$$x = 1 - \exp[-(kt)^n] \quad (4)$$

where x is the volume fraction crystallised after time t , and n is the Avrami exponent. The apparent reaction rate, k , is usually assigned an Arrhenius temperature dependence

$$k = k_0 \exp(-E/RT) \quad (5)$$

where E is the activation energy describing the overall crystallisation process.

Rearranging eq. (5):

$$\ln[-\ln(1-x)] = n \ln k + n \ln t \quad (6)$$

The crystallized volume x may be calculated from the ratio of the partial area at a certain temperature to the total area of the exothermic crystallization peak. The values of n are, thus, directly determined by plotting $\ln[-\ln(1-x)]$ versus $\ln t$. It should be noted that eq. (4) strictly applies to isothermal conditions. However, the relation is commonly modified to describe non-isothermal crystallization for which experimental studies are easier to conduct. Yinnon and Uhlmann [38] have summarized several different treatments for non-isothermal conditions based on eqs. (4) and (6) assuming a constant heating rate Q . On this basis, plotting $\ln[-\ln(1-x)]$ versus $\ln Q$ at a fixed temperature yields n from the Ozawa equation (7):

$$\left. \frac{d[\ln[-\ln(1-x)]]}{d[\ln Q]} \right|_T = -n \quad (7)$$

Values of n were calculated according to eq. (7) from the plot shown in Fig. 8 for a quantity of x associated with the temperature range 660 – 680 °C. Table 4 summarizes the Avrami parameters determined from figure 8a, with an average value of $n \approx 1$.

To determine the apparent activation energy for crystallization, the data obtained using different heating rates in figure 7 can be analyzed assuming two alternative scenarios: (1) that crystal growth occurs at a fixed number of nuclei; (2) that further nuclei are formed during the DSC measurement.

In the first situation, either the Kissinger , Takhor or Augis-Bennett (KTAB) equations can be applied, respectively given as

$$\ln(Q/T_p^2) = -E/RT_p + A \quad (8)$$

$$\frac{d[\ln Q]}{d[1/T_p]} = \frac{E}{R} \quad (9)$$

and

$$\frac{d[\ln(Q/(T_p - T_0))]}{d[1/T_p]} = \frac{E}{R} \quad (10)$$

where T_p is the temperature of the maximum of the crystallization peak in K, Q is the heating rate, T_0 is the temperature at the beginning of the experiment in K, R is the gas constant, E is the activation energy of the overall crystallization process, including nucleation and crystal-growth phenomena and A is a constant. Figure 9a shows the plots obtained using these equations, of which the Kissinger relation (eq. (8)) is the most representative.

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3 For the second scenario, where further nuclei are formed during the DSC
4 measurement, the Matusita equation (11) may be applied:
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$$\ln(Q^n / T_p^2) = -mE / RT_p + A \quad (11)$$

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15 where m represents the dimensionality of crystal growth and determines which equation is
16 correct in each case: If $m = n$, crystallization occurs at a fixed number of nuclei and the
17 Kissinger equation can be applied, whereas if $m = n-1$, nucleation occurs during the DSC
18 experiment and the Matusita relation is more appropriate.
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25 In the present work, E/n was first obtained from the Marseglia equation (12):
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$$\ln(Q/T_p) = -(E/nRT_p) \quad (12)$$

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35 The value of n obtained from the Ozawa equation allows the activation energy E to be
36 calculated from a plot of the Marseglia relation (Figure 9b), from which m can also be
37 determined.
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42 The activation energies obtained from the various relations are summarized in Table 4.
43 The E value determined from the KTAB-equation (eq. (10)) approaches 338 kJ/mol,
44 equivalent to that determined from the Marseglia equation (eq. (12)). The value of m , 0.85,
45 approaches a value of 1, and is very similar to that obtained for n (0.99). According to Donald
46 [39] such values of m and n can correspond to a bulk crystallization mechanism with a
47 constant number of nuclei (i.e. a well nucleated sample in which the number of nuclei is
48 independent of the heating rate). Crystal growth occurs in two dimensions with a crystal size
49 growth rate $\sim \sqrt{t}$ (diffusion controlled), as expected for LaF₃ nanoplates [34]. For this type of
50 mechanism, where $m \approx n \approx 1$, adoption of the Kissinger equation (eq.(10)) is correct.
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3 DSC scans collected at 10 K/min of the glasses treated at different nucleation
4 temperatures for one hour are shown in Fig. 10. If effective nucleation takes place during
5 thermal treatment, a decrease in the crystallization peak should be observed with respect to
6 the untreated glass. However, the crystallization peaks appear at higher temperatures and are
7 of lower area on increasing the nucleation temperature. This is due to the fact that, during
8 thermal treatment for 1 hour, crystallization originates from the previously formed nuclei and
9 no additional nuclei are formed. Even for the glass treated at higher nucleation temperatures,
10 670 – 720 °C, no crystallization peak is observed because all the glass has already been
11 crystallized during the thermal treatment. This observation is consistent with the
12 crystallization mechanism proposed from the values of the m and n parameters, which
13 involves crystallization originating from a constant number of nuclei located at the La- and F-
14 rich phase-separation droplets in the base glass, as shown in the TEM analysis of the samples
15 [11].
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3.4. Viscosity

41 The viscosity-temperature curve using the isokom temperature T_{12} (for which the
42 Newtonian viscosity is 10^{12} Pa.s) as scaling parameter of the glass is shown in Fig. 11. The
43 viscosity was determined from points obtained by different methods: T_g (measured by DSC)
44 corresponds to a viscosity of $\log \eta = 12.0$ Pa.s, the three highest viscosity points were
45 obtained by the fibre-elongation method ($\log \eta = 12-7$ Pa.s), and four intermediate points were
46 determined on the basis of photographs from hot-stage microscopy (HSM). The last method
47 [29] defines some fixed viscosity points as follows: first shrinkage ($\log \eta = 7.9$), maximum
48 shrinkage ($\log \eta = 6.9$), half ball ($\log \eta = 3.5$) and flow ($\log \eta = 2.1$). The rotation method was
49 also used for $\log \eta < 3$ Pa s. The temperature dependence of viscosity was fitted using the
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empirical Vogel-Fulcher-Tammann (VFT) [40-42] and Avramov-Milchev (AM) [43] equations, employing exclusively the rotation-viscometry and T_g data in order to ensure the absence of immiscibility and crystallization effects, which are expected to be insignificant at temperatures up to glass transition and above the liquidus.

According to the VFT equation

$$\log \eta = A_1 + \frac{B_1}{T - C_1} \quad (13)$$

the parameters were fitted as $A_1 = -5.7 \pm 0.07$, $B_1 = 11713 \pm 1720$ and $C_1 = 197 \pm 13$ (Pa.s,

K). On employing the AM relation

$$\log \eta = A_2 + B_2 \left(\frac{T_g}{T} \right)^{C_2} \quad (14)$$

the fitting parameters were determined as $A_2 = -4.3 \pm 0.86$, $B_2 = 16.35 \pm 0.93$ and $C_2 = 1.4 \pm 0.1$ (Pa.s, K).

A physically based viscosity model involving the temperature dependence of configurational entropy has recently been introduced by Mauro-Yue-Ellison-Gupta-Allen (MYEGA) [44]:

$$\log \eta = A_3 + \frac{B_3}{T} \exp\left(\frac{C_3}{T}\right) \quad (15)$$

Fitting of this relation gives $A_3 = -5.6 \pm 0.8$, $B_3 = 11186 \pm 1749$ and $C_3 = 256 \pm 96$ (Pa.s, K).

Figure 11 shows that Eqs. 13-15 fitted the data equally. Transformation kinetics in the

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3 temperature range from T_g to the liquidus seem not to influence viscosity for the short period
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5 of heat treatment used for hot-stage microscopy.
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8 In order to classify the energetic character of liquids, Angell [45] introduced kinetic
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10 fragility expressed by the steepness index m at the glass transition
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$$m = \left. \frac{d(\log \eta)}{d\left(\frac{T_g}{T}\right)} \right|_{T=T_g} \quad (16)$$

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25 This relation provides a measure of the deviation from Arrhenian temperature dependence.
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27 From Angell's plot (Fig. 11), it is apparent that the viscosity of the examined oxyfluoride
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29 glass ($m = 22$) lies between two extremes referred to as "strong" (e.g. tetrahedral networks
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31 such as SiO_2 and GeO_2 , $m \approx 17$) and "fragile" (e.g. nitrate melt, $m \approx 100$).
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35 The fibre-elongation method was used in order to analyze the effects of liquid-liquid
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37 phase separation and subsequent crystallization of lanthanum fluoride on viscosity. Fibres
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39 were thermally pre-treated for prolonged time lengths, i.e. at 620 °C for 20 and 80 h, 640 °C
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41 for 20 h and 660° C for 20 h, subsequent to viscosity measurement at 660 °C. Effective
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43 viscosity increased by up to one order of magnitude with both dwell temperature and dwell
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45 time of the pre-treatment (Fig. 12). Time-dependent viscosity measurements were also
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47 performed by micro-indentation. The increase in viscosity with dwells at 620, 660 and 680 °C
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49 for 1.5 to 7 h is shown in Fig. 13. Assuming a linear increase in the logarithm of the effective
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51 viscosity with crystal volume fraction for dilute systems [46] and a constant number of
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53 crystals, the slope of a straight line through the data is given by $3p$. Values of p were
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55 determined as 0.22 (620 °C), 0.18 (660 °C) and 0.16 (680 °C), which are close to those
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57 determined from the increase in crystal size (eq. (1) and Fig. 4). A relative viscosity value up
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3 to 15 (Fig. 12) for a crystallized volume fraction of around 7.3 % (neglecting small changes in
4 density of the two liquids) indicates that the increase in effective viscosity is attributable to a
5 factor other than suspended crystals. A relative viscosity up to 2 has been determined for
6 spherical and plate-like, micro-sized crystals in silicate melts, where the crystal phase and the
7 glass matrix had the same chemical composition or crystals act as quasi inert filler [47]. The
8 large value of the relative viscosity shown in Fig. 12 is, thus, assumed to reflect liquid-liquid
9 phase separation, which probably changes the chemical composition of the matrix melt
10 towards one of higher flow resistance. Demixing of a network modifier-rich glass
11 composition (lanthanum fluoride) will initially lead to soft amorphous inclusions, which will
12 gradually become more rigid as crystallization proceeds in the demixed droplets. However,
13 we assume that the effects of changes in melt composition on effective viscosity are much
14 greater than those of dispersed soft/rigid inclusions. The strong increase in glass transition, as
15 determined by dilatometry (Fig. 1), provides supporting evidence for this hypothesis since
16 glass transition mainly reflects the change in thermal expansion of the continuous matrix
17 phase, as also observed in CaF_2 and BaF_2 compositions [13, 14].
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41 4. Conclusions

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43 Transparent LaF_3 -oxyfluoride glass-ceramics with LaF_3 nano-crystals up to 14 nm in
44 diameter were obtained from thermal treatments of $55\text{SiO}_2.20\text{Al}_2\text{O}_3.15\text{Na}_2\text{O}.10\text{LaF}_3$ (mol %) glass
45 at temperatures from $T_g + 35$ to $T_g + 95$ °C. Changes in the microstructure due to phase
46 separation and subsequent fluoride crystallization, with a crystalline mass fraction up to 7.3
47 wt.%, were made evident by several techniques.
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55 The glass transition temperature increased with treatment time at 620 °C, indicating
56 enrichment in network formers in the glassy matrix and subsequent fluorine crystallisation.
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58 The limited variation of crystal size on treatment from 1 to 80 h at 620, 660 and 680 °C
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3 indicated a low crystal growth velocity which decreased close to zero with the time of
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5 treatment. TEM and EDXS analyses indicate that the phase-separation droplets contain not
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7 only lanthanum and fluorine but also silicon and oxygen, in addition to traces of aluminium. It
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9 may be assumed, therefore, that, on annealing, the growth of the LaF_3 crystallites within the
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11 droplets is limited to some extent by an excess of silicon. On termination of the crystallization
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13 process, several LaF_3 nanocrystals are formed, which are trapped in a volume determined by
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15 the size of the preceding liquid-liquid phase-separation droplets. The remaining volume of
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17 this former droplet is filled with the excess of Si, Al and O. Diffusional barriers and the
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19 confinement to the demixed ranges in which fluoride crystallizes are assumed to freeze the
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21 crystal growth at crystal sizes smaller than demixed droplets. The change in composition in
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23 the glass matrix due to demixing, subsequent crystal growth and the minimal effect of
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25 suspended volume fraction were confirmed by an increase in viscosity of up to an order of
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27 magnitude with temperature and time of treatment at 620 °C. The reason for the increase in
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29 viscosity has been demonstrated to be the same as that reported previously for CaF_2 and BaF_2
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31 compositions in which crystallisation from a homogeneous glass takes place. The presence of
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33 nuclei in the base glass was confirmed by calculation of the Avrami parameter n from DSC
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35 data, which indicated bulk crystallization from a well-nucleated sample via a two-dimensional
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37 growth mechanism (nanoplates). Moreover, DSC curves performed at different nucleation
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39 temperatures revealed that crystallization takes place from preexisting active sites. The
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41 broadened profiles of certain reflections in the XRD data of the glass-ceramic provided
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43 supporting evidence for the growth of nanoplate-shaped crystals.
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Figure captions

Figure 1: Variation of the glass transition temperature as a function of dwell time at 620°C.

The dashed line is a visual guide only.

Figure 2: XRD patterns of glass samples treated at 620 °C during (a) 0h, (b) 1 h, (c) 3 h, (d) 30 h, (e) 40 h and (f) 80 h.

Figure 3: Variation of the crystal size of the glass-ceramics as a function of the time of heat treatment at 620, 660 and 680 °C as calculated on the basis of the (1 1 1) diffraction peak at 27.5° (2 θ).

Figure 4: Time-dependent progress of the average crystal radius in double logarithmic scales. The lines provide best fits (Eq. 3) to the data. Numbers indicate growth index p .

Figure 5: Observed and difference X-ray powder diffraction profiles of glass-ceramic treated at 620 °C for 40 h with 3 wt.% NaF as internal standard (reflections marked with asterisks).

Figure 6 : Zero-loss filtered bright-field TEM image of (a) the glass sample ,(b) the glass-ceramic obtained at 620 °C for 40 h and (c) the corresponding La- $N_{4,5}$ /(Si- $L_{2,3}$) map.

Figure 7: DSC curves of the glass recorded from 5 to 40 K/min.

Figure 8: Ozawa plot constructed from DSC data from 660 to 680 °C for the determination of the Avrami exponent n .

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6 Figure 9: (a) ■ Kissinger, □ Takhor and ● Augis-Bennett plots constructed from the DSC
7 data; (b) Marseglia and Matusita plots. Q is the heating rate and T_P is the DSC crystallisation
8 peak.
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15 Figure 10: DSC curves of the glass with nucleation temperatures from 595 to 720°C recorded
16 at a rate of 10 K/min.
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22 Figure 11: Viscosity-temperature curve of the glass obtained from T_g point, hot-stage
23 microscopy (HSM), fibre elongation and rotation methods. Curves were fitted according to
24 the Vogel-Fulcher-Tamman (VFT), Avramov-Milchev (AM) and Mauro-Yue-Ellison-Gupta-
25 Allen (MYEGA) equations.
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34 Figure 12. Viscosity of the treated fibres as a function of temperature and time of treatment,
35 measured at 660 °C.
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41 Figure 13: Viscosity as a function of isothermal dwelling at 620, 660 and 680 °C measured by
42 micro-indentation. Straight lines of slope $3p$ give the best linear fit to the data.
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Table 1: Nominal and analyzed compositions (in mol %) of base glass

Glass Components	Nominal (mol %)	Analysed (mol %)
SiO ₂	55	55.10
Al ₂ O ₃	20	20.39
Na ₂ O	15	14.77
LaF ₃	10	6.51
La ₂ O ₃	0	3.23
F ⁻ (wt %)	6.92	4.30

Table 2. Structure refinement data for LaF₃ nanocrystals

Space group $P\bar{3}c1$; $a = 7.1926(3)$ Å, $c = 7.3716(7)$ Å; $R_p = 2.17$; $R_{wp} = 2.93$; $\chi^2 = 2.74$

Atom	Site	x/a	y/b	c/z	occupancy
La(1)	6f	0.6535(5)	0	$\frac{1}{4}$	1.0
F(1)	12g	0.332(8)	-0.001(5)	0.096(2)	1.0
F(2)	4d	$\frac{1}{3}$	$\frac{2}{3}$	0.133(2)	1.0
F(3)	2a	0	0	$\frac{1}{4}$	1.0

- * Thermal vibration factors were constrained to $B_{iso} = 1.0$

Table 3: T_g and T_p values at different heating rates obtained from the DSC curves in Fig.7

Q (K/min)	T_g ($^{\circ}\text{C}$) ± 2	
	T_g (Dilatometry) = 585 $^{\circ}\text{C}$	T_p ($^{\circ}\text{C}$) ± 2
5	581	667
10	590	679
15	590	687
20	591	693
30	592	703
40	598	714

Table 4: The Avrami exponent of Ozawa's equation obtained from Fig. 7 and activation energies as determined from various relations.

Avrami parameter n			Activation Energy E_a (kJ/mol)			
T ($^{\circ}\text{C}$)	n	R^2	$\ln Q$	$\ln (Q/T_p^2)$	$\ln (Q/(T_p-T_0))$	$\ln (Q^n/T_p^2)$
			<i>Takhor</i> ($R^2 = 0.992$)	<i>Kissinger</i> ($R^2 = 0.9943$)	<i>Augis-Bennett</i> ($R^2 = 0.990$)	<i>Marseglia</i> ($R^2 = 0.990$)
660	1.12	0.998	348 ± 23	330 ± 24	335 ± 24	338 ± 23
670	0.87	0.9996				
675	0.80	0.9993				
680	0.75	0.998				

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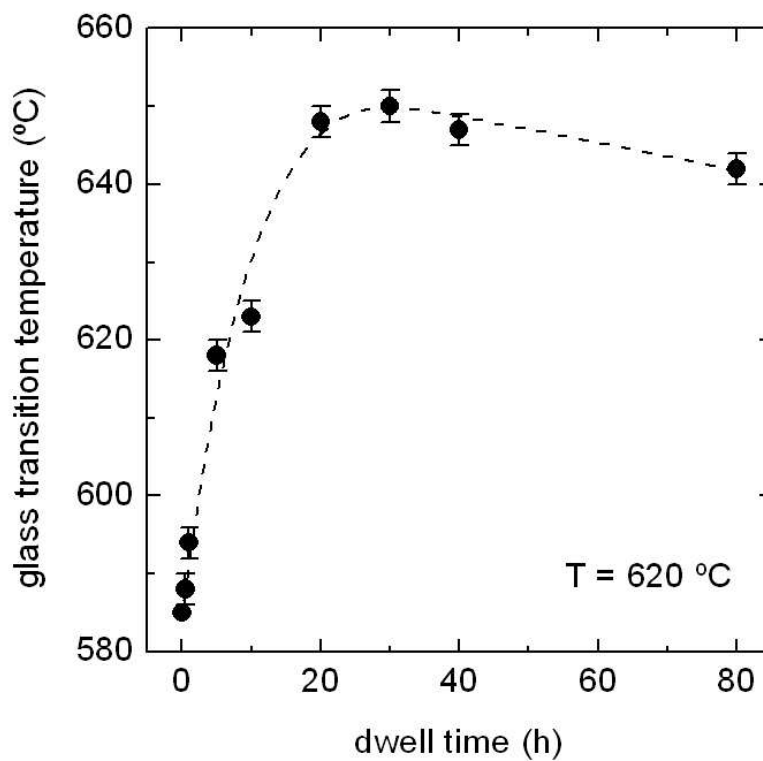


Figure 1: Variation of the glass transition temperature as a function of dwell time at 620°C. The dashed line is a visual guide only.
220x203mm (100 x 100 DPI)

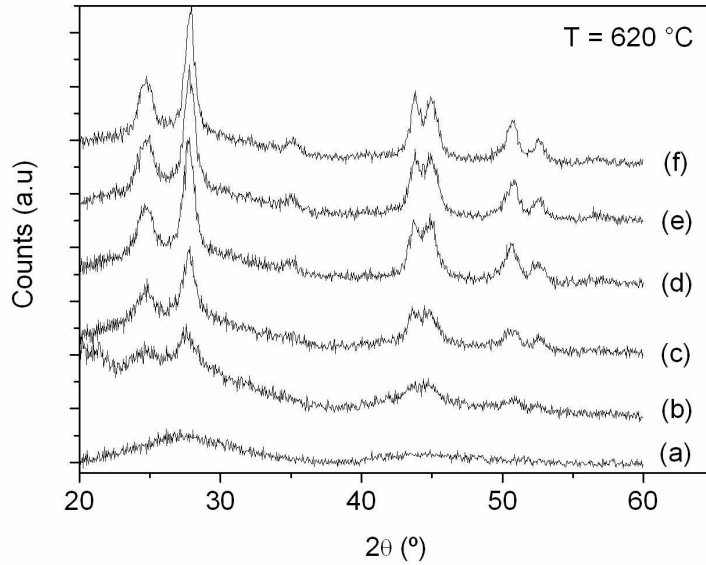


Figure 2: XRD patterns of glass samples treated at 620 °C during (a) 0h, (b) 1 h, (c) 3 h, (d) 30 h, (e) 40 h and (f) 80 h.
290x203mm (150 x 150 DPI)

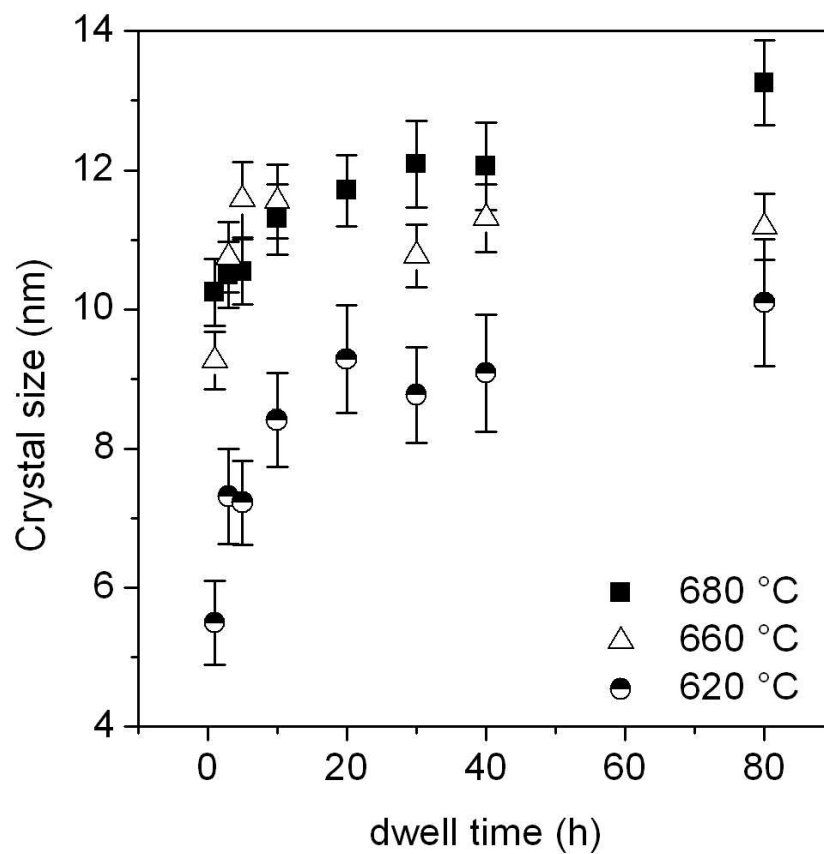


Figure 3: Variation of the crystal size of the glass-ceramics as a function of the time of heat treatment at 620, 660 and 680 °C as calculated on the basis of the (1 1 1) diffraction peak at 27.5° (2θ).

197x203mm (150 x 150 DPI)

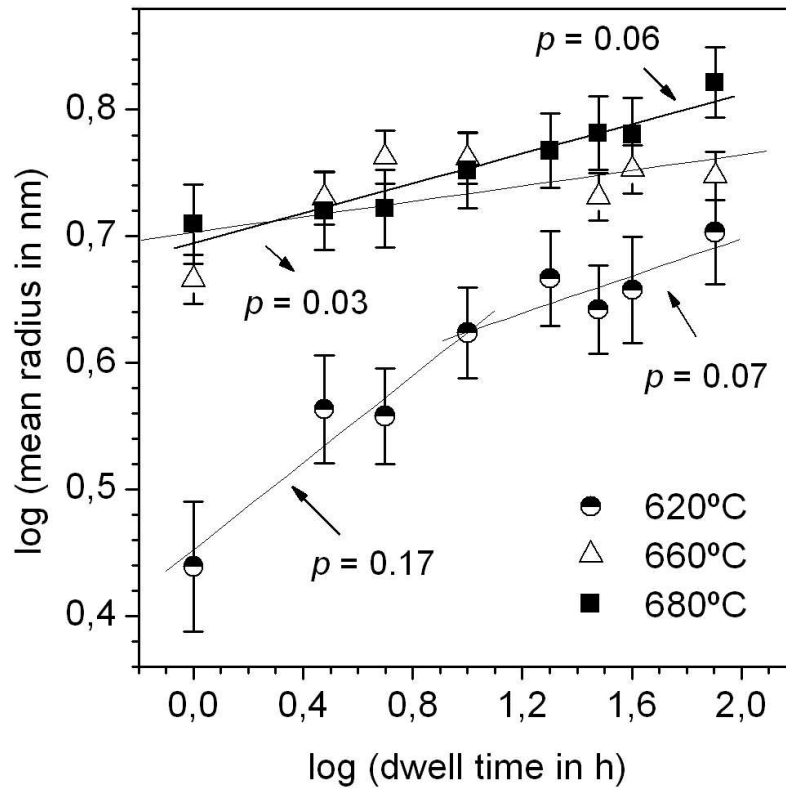


Figure 4: Time-dependent progress of the average crystal radius in double logarithmic scales. The lines provide best fits (Eq. 3) to the data. Numbers indicate growth index p .
206x183mm (150 x 150 DPI)

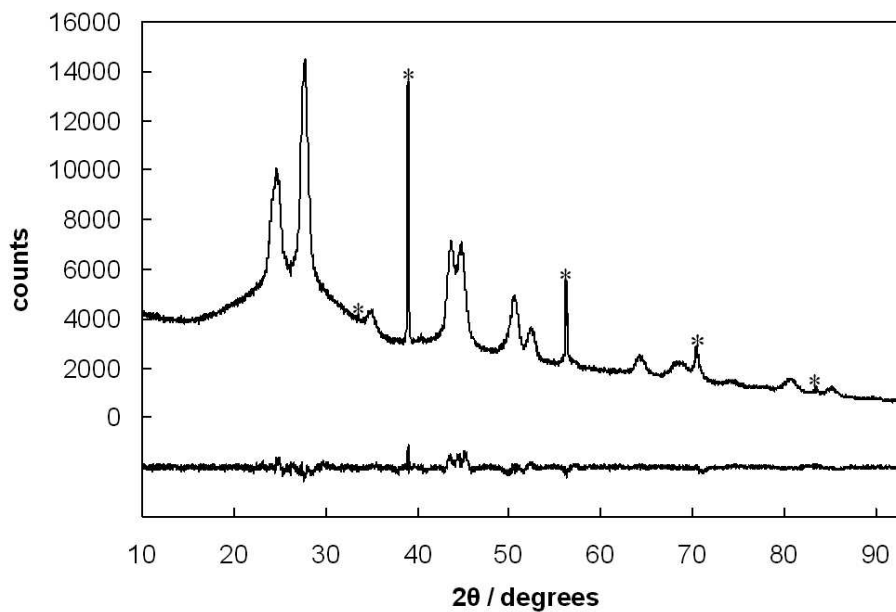


Figure 5: Observed and difference X-ray powder diffraction profiles of glass-ceramic treated at 620 °C for 40 h with 3 wt.% NaF as internal standard (reflections marked with asterisks).
380x246mm (72 x 72 DPI)

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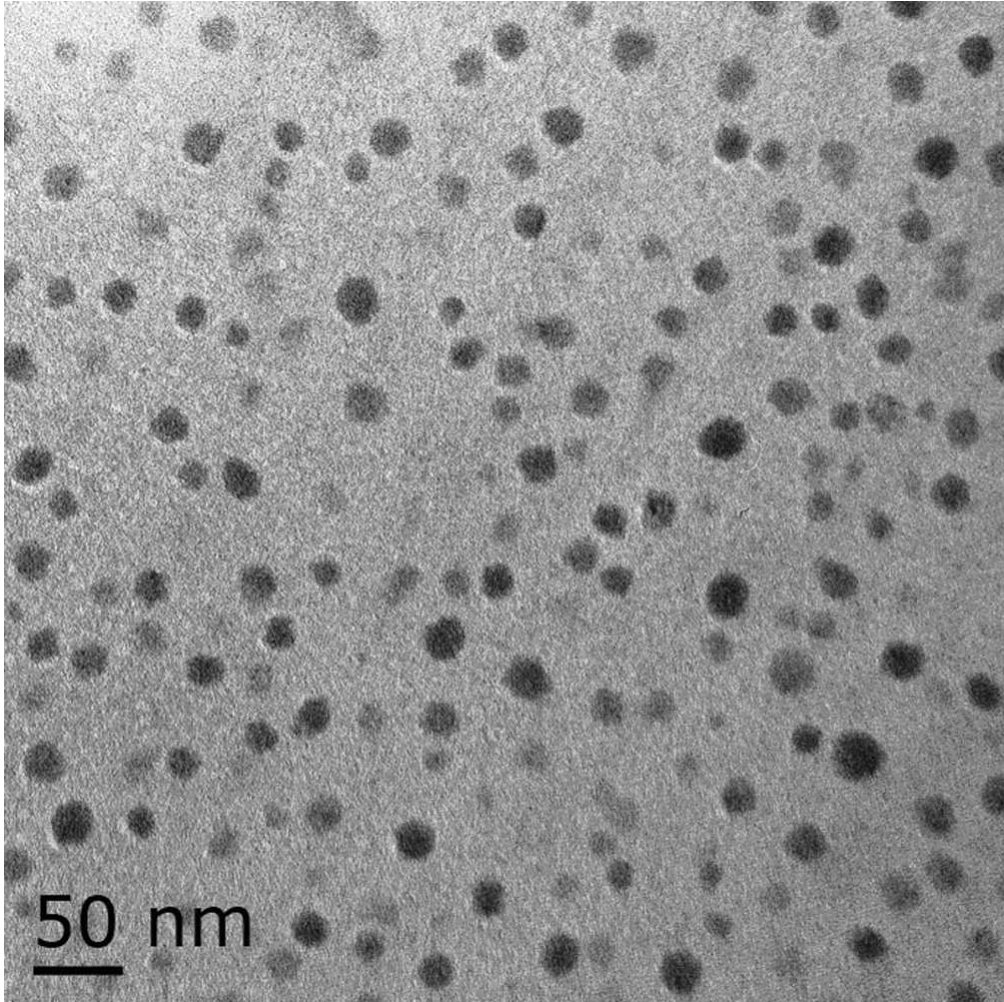


Figure 6a

Figure 6 : Zero-loss filtered bright-field TEM image of (a) the glass sample ,(b) the glass-ceramic obtained at 620 °C for 40 h and (c) the corresponding La-N4,5 /(Si-L2,3) map.
264x264mm (96 x 96 DPI)

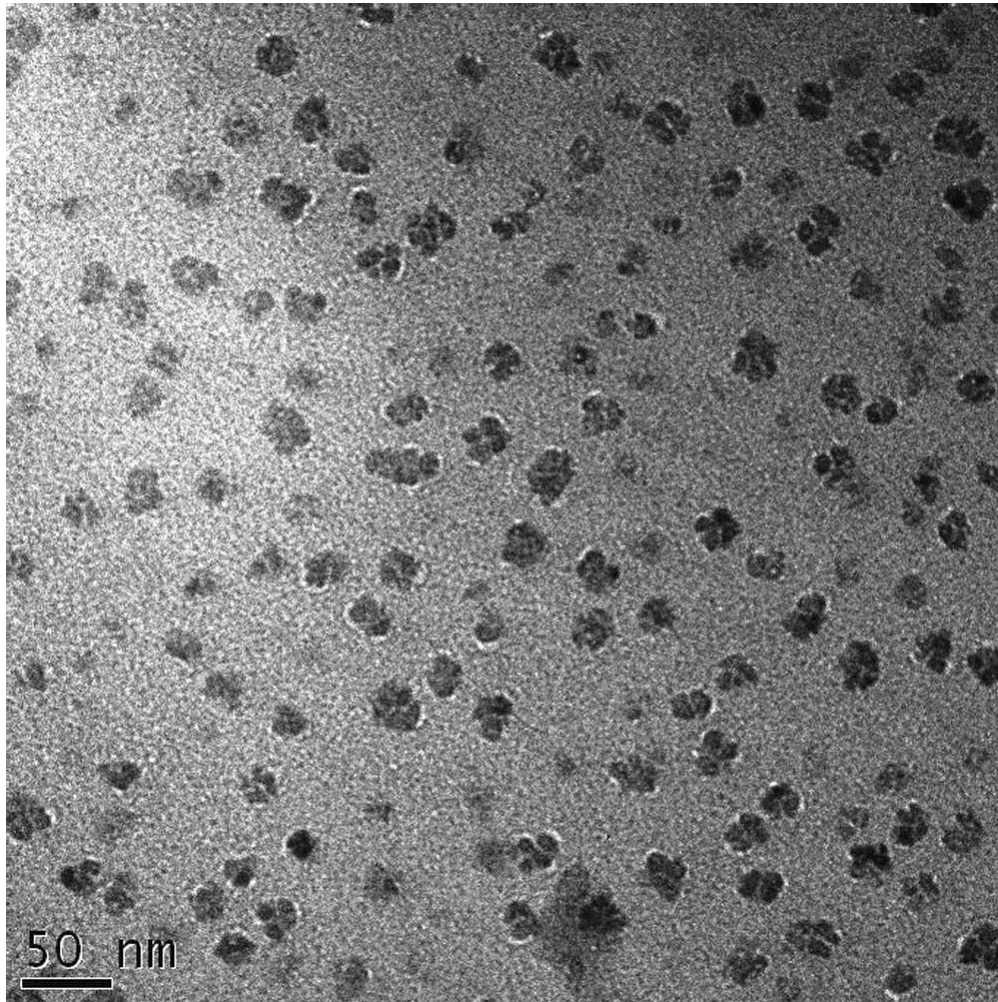


Figure 6b

Figure 6 : Zero-loss filtered bright-field TEM image of (a) the glass sample ,(b) the glass-ceramic obtained at 620 °C for 40 h and (c) the corresponding La-N4,5 /(Si-L2,3) map.
264x264mm (96 x 96 DPI)

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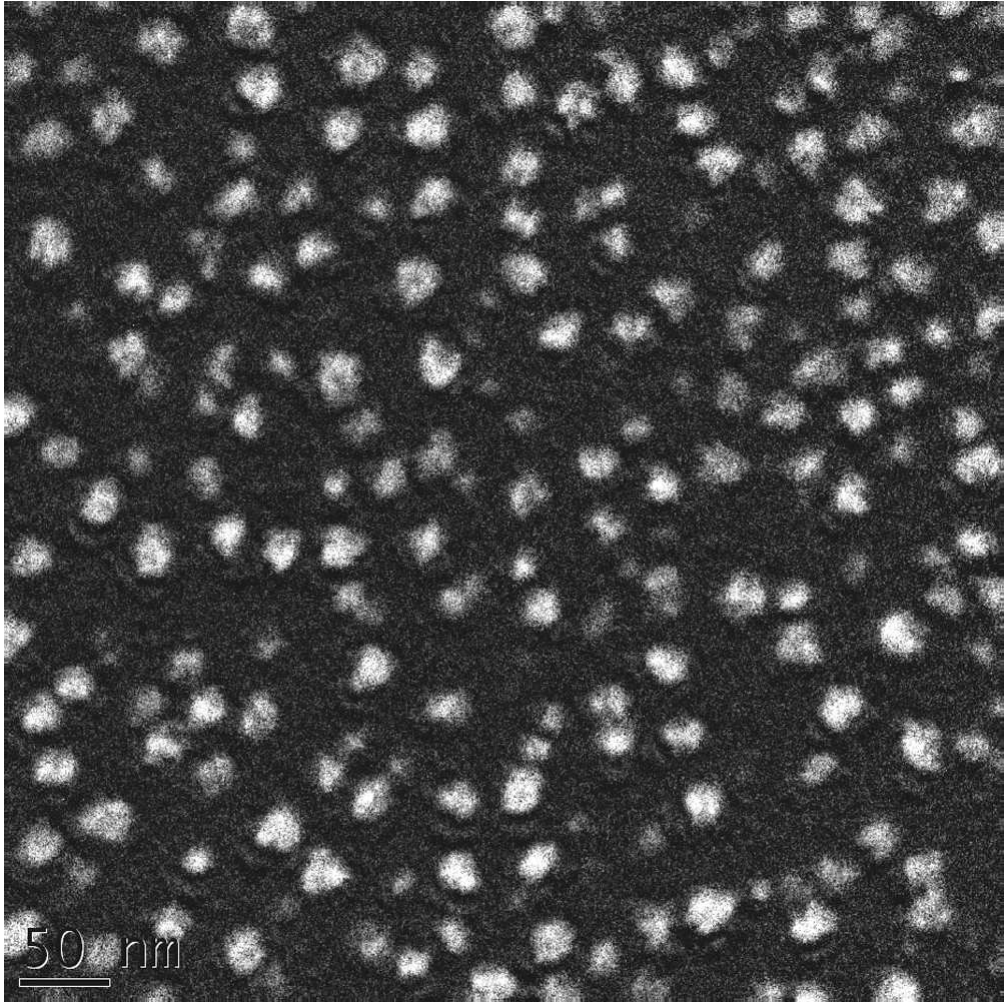


Figure 6c
Figure 6 : Zero-loss filtered bright-field TEM image of (a) the glass sample ,(b) the glass-ceramic obtained at 620 °C for 40 h and (c) the corresponding La-N4,5 /(Si-L2,3) map.
264x264mm (96 x 96 DPI)

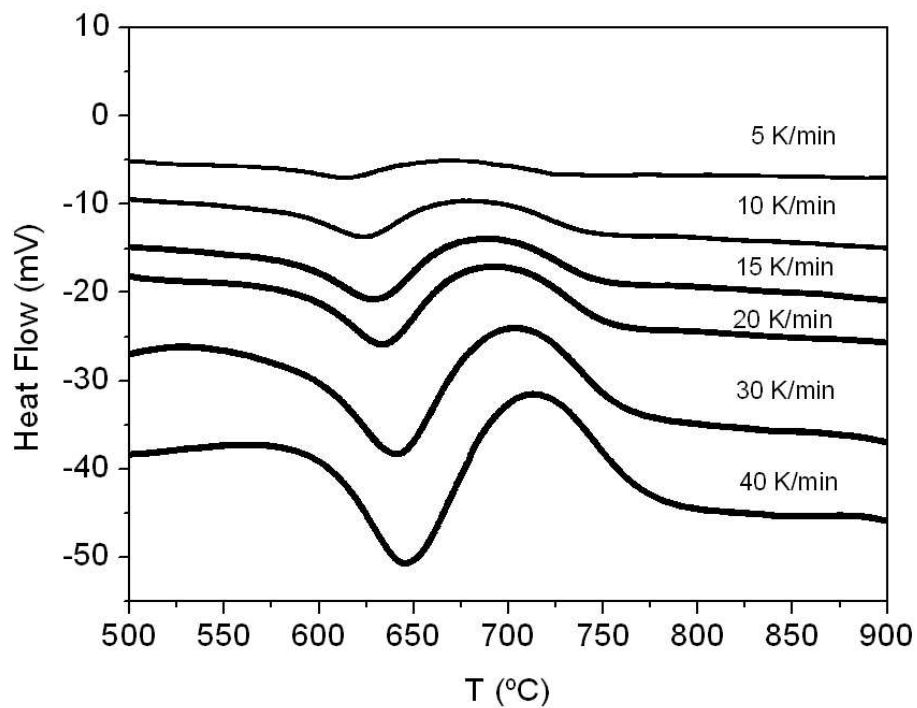


Figure 7: DSC curves of the glass recorded from 5 to 40 K/min.
329x246mm (72 x 72 DPI)

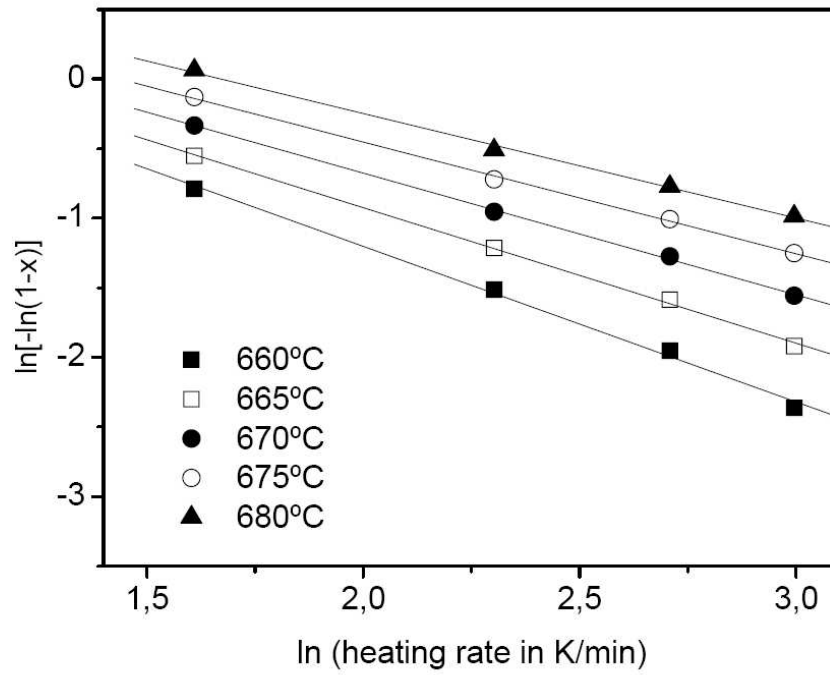


Figure 8: Ozawa plot constructed from DSC data from 660 to 680 °C for the determination of the Avrami exponent n .
346x252mm (72 x 72 DPI)

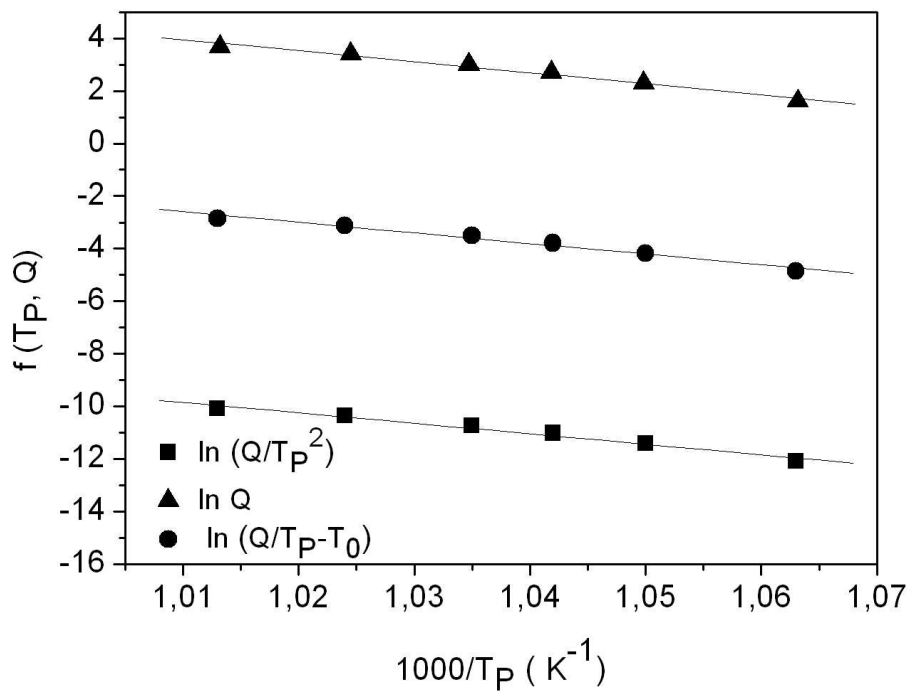


Figure 9a

Figure 9: (a) ■ Kissinger, □ Takhor and ● Augis-Bennett plots constructed from the DSC data; (b) Marseglia and Matusita plots. Q is the heating rate and TP is the DSC crystallisation peak.

238x194mm (150 x 150 DPI)

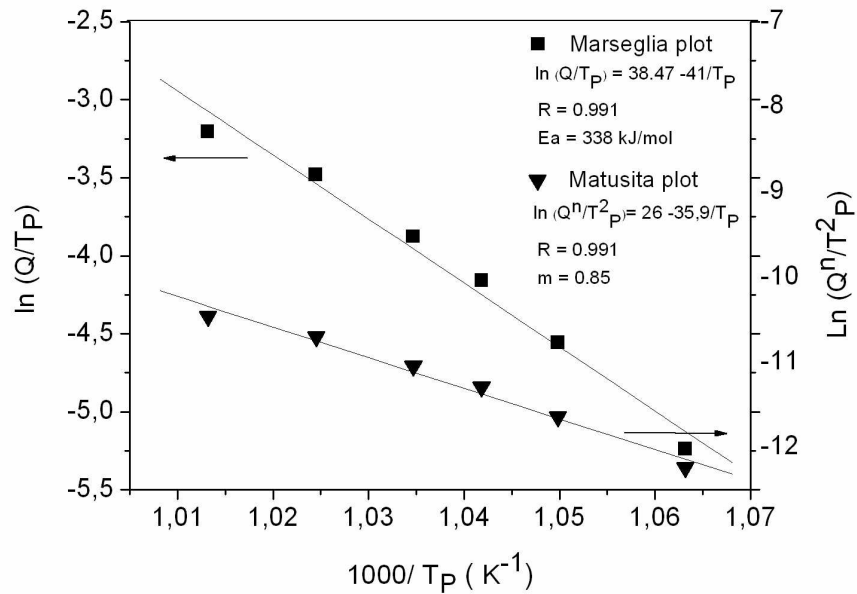


Figure 9b

Figure 9: (a) ■ Kissinger, □ Takhor and • Augis-Bennett plots constructed from the DSC data; (b) Marseglia and Matusita plots. Q is the heating rate and TP is the DSC crystallisation peak.
283x203mm (150 x 150 DPI)

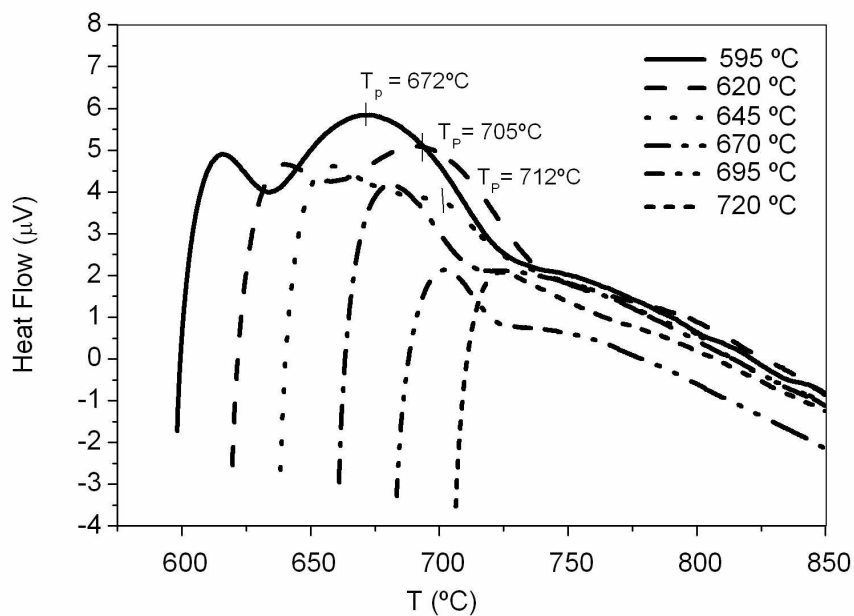


Figure 10: DSC curves of the glass with nucleation temperatures from 595 to 720 $^{\circ}\text{C}$ recorded at a rate of 10 K/min.
296x209mm (150 x 150 DPI)

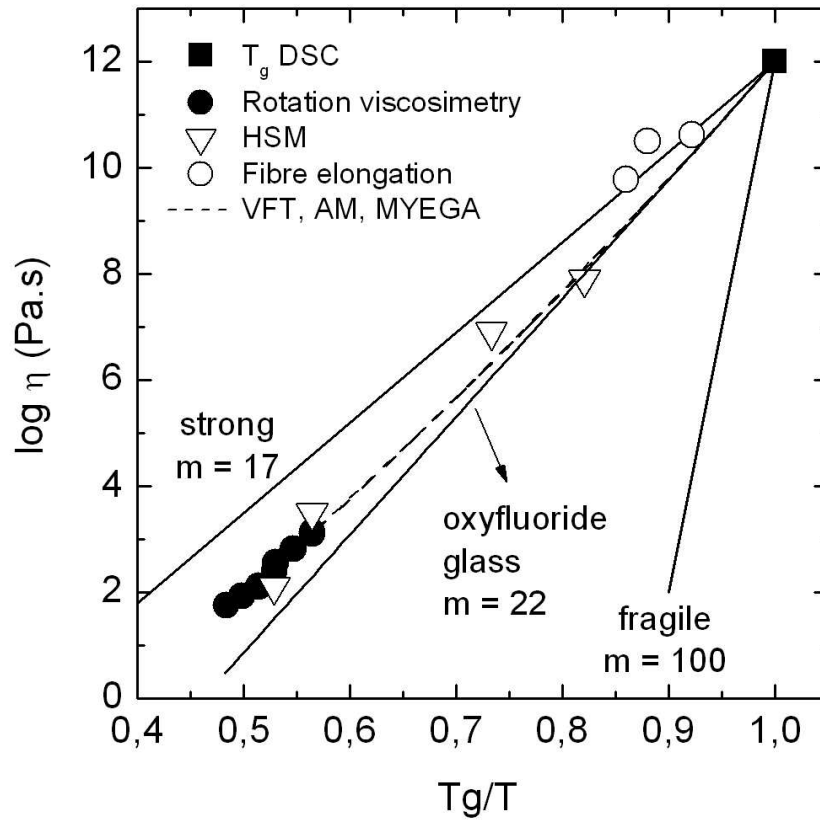


Figure 11: Viscosity-temperature curve of the glass obtained from T_g point, hot-stage microscopy (HSM), fibre elongation and rotation methods. Curves were fitted according to the Vogel-Fulcher-Tamman (VFT), Avramov-Milchev (AM) and Mauro-Yue-Ellison-Gupta-Allen (MYEGA) equations.
201x199mm (150 x 150 DPI)

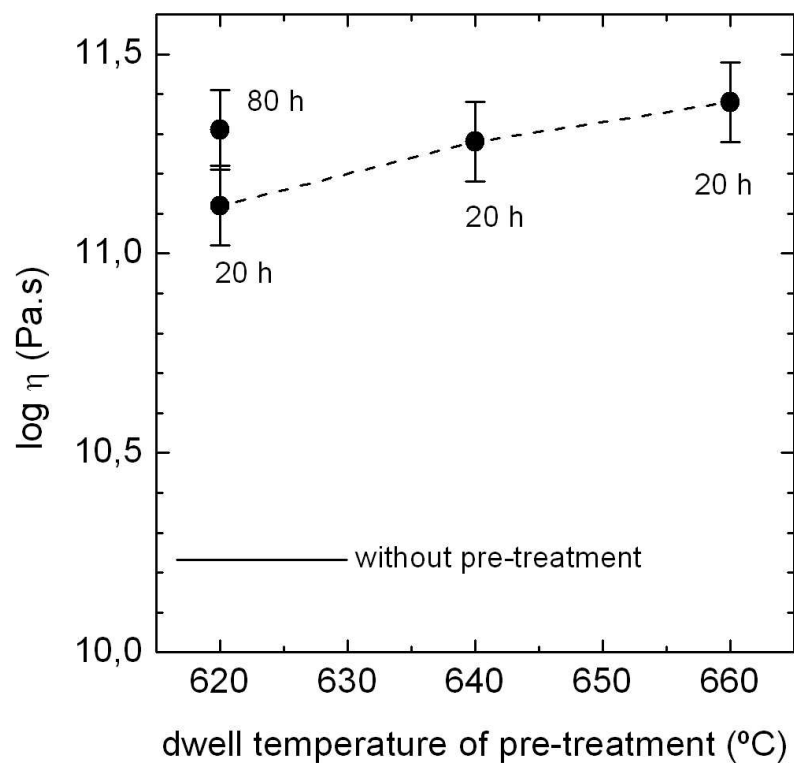


Figure 12. Viscosity of the treated fibres as a function of temperature and time of treatment, measured at 660 $^{\circ}\text{C}$.

215x203mm (150 x 150 DPI)



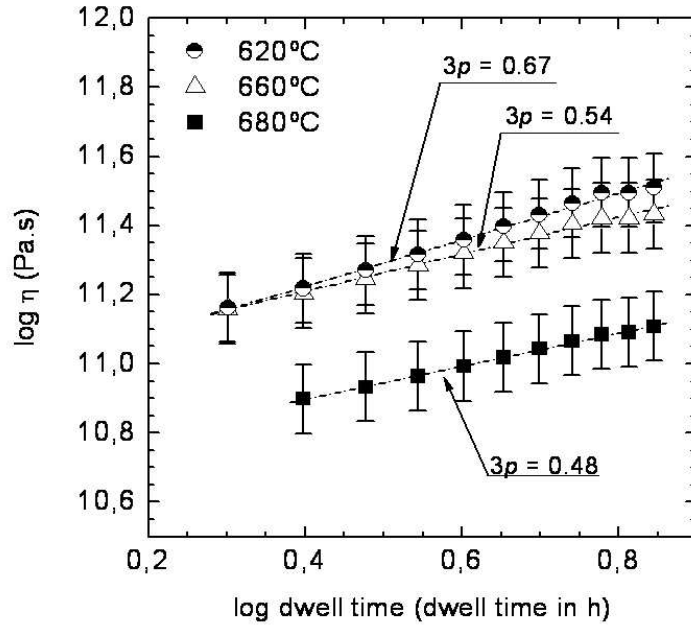


Figure 13: Viscosity as a function of isothermal dwelling at 620, 660 and 680 °C measured by micro-indentation. Straight lines of slope $3p$ give the best linear fit to the data.
254x190mm (96 x 96 DPI)