

Self-organized nano-crystallisation of BaF₂ from Na₂O/K₂O/BaF₂/Al₂O₃/SiO₂ glasses

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Abstract

In glasses with the compositions $(100 - x)(2\text{Na}_2\text{O} \cdot 16\text{K}_2\text{O} \cdot 8\text{Al}_2\text{O}_3 \cdot 74\text{SiO}_2) \cdot x\text{BaF}_2$ (with $x = 0$ to 6), the glass transition temperature decreases with increasing BaF₂-concentration. Samples with $x = 6$ were thermally treated at temperatures in the range from 500 to 600 °C for 5–160 h. This leads to the crystallisation of BaF₂. The quantity of crystalline BaF₂ increases with increasing time of thermal treatment, while the mean crystallite size remains constant within the limits of error. The glass transformation temperature of partially crystallised samples increases with increasing crystallisation time and approaches a value equal to the temperature, at which the samples were treated. This is explained by the formation of a highly viscous layer enriched in SiO₂ which is formed during crystallisation. This layer acts as a diffusion barrier and hinders further crystal growth.

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1. Introduction

Glass–ceramics containing crystals, such as alkaline earth fluorides, (Cd, Pb)F₂ or LaF₃ with crystallite sizes in the range from 5 to 50 nm are considered as materials for numerous photonic applications.^{1–6} Among these materials are glass–ceramics containing rare earth doped fluoride crystals. They are candidates for laser materials combining advantageous properties of crystals (large fluorescence life time) and of glasses (ability to draw fibres), and they can be considered, for example as fibre amplifiers. In addition, up-conversion glasses containing (Cd, Pb)F₂⁵ solid solutions doped with YbF₃^{2,4} should be mentioned. For photonic applications, the materials have to be transparent at the respective wavelength and hence, a prerequisite is that the crystallite sizes are smaller than half of the wavelength of the light used. Furthermore, the crystallite size distribution must be narrow in order to avoid light scattering and the volume concentration should be at least several percent.

In classical theories of crystallisation, the crystallisation process is usually separated in two steps, nucleation and subsequent crystal growth. The first step, nucleation, occurs at lower temper-

atures than crystal growth. Nucleation rates exhibit a maximum at temperatures some 10 °C above the glass transition temperature. In order to determine nucleation rates, a glass sample is usually brought to a temperature around ten degrees above T_g , held for a certain period of time, and then heated up to a higher temperature at which the crystal growth velocity is large enough to enable the crystals to grow to an observable size. This method was first described by Tammann⁷ and, strictly speaking, can only be applied because at nucleation temperatures, slight crystal growth also occurs. Otherwise the nuclei would dissolve again during heating^{8,9}. The latter is due to an increase of the critical nuclei with increasing temperature (see e.g. Ref.¹⁰). Thus, if a sample is held at the nucleation temperature, nuclei are formed and simultaneously start to grow. Most systems where fundamental studies on nucleation have been carried out are so called isochemical systems, i.e. systems where the crystalline phase formed possesses the same chemical composition as the glass from which it is crystallised^{11,12}. In such systems, in an ideal case, the chemical composition of the residual glassy matrix does not depend on time and hence the crystal growth velocity is also independent of time.

By contrast, glass–ceramics of technical potential are never prepared from isochemical systems, but from 7 to 15 component systems (see e.g. Refs. 13, 14^{13,14}). In these materials, the chemical composition of the residual glassy matrix changes during the

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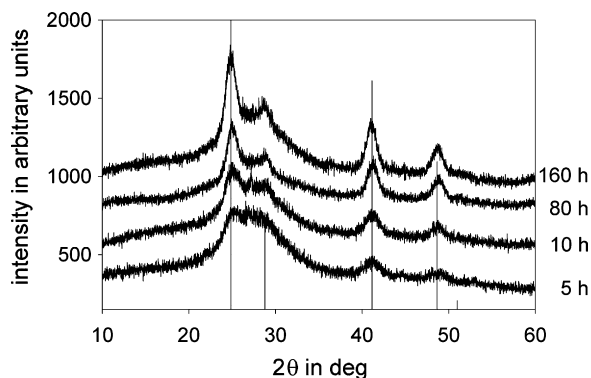


Fig. 1. XRD-patterns of a sample with 6 mol% BaF₂ heat-treated at 500 °C for different periods of time.

course of the nucleation and crystallisation process, and hence the crystal growth velocity also changes with time. This effect has recently been described for an Na₂O/CaO/B₂O₃/Fe₂O_{3-x} glass,¹⁵ from which Fe₃O₄ with crystallite sizes in the nanometer-range can be precipitated in a large volume concentration. Another system, where the same effect has been reported was the Na₂O/K₂O/CaO/CaF₂/Al₂O₃/SiO₂-system.¹⁶ Here, crystallisation of a high volume concentration of CaF₂ was observed. In this case, the mean crystallite size was around 10 nm. The conclusion in both cases was that the formation of a highly viscous layer around the growing crystals decelerates crystal growth and hence acts as a diffusion barrier, which then hinders further crystal growth.

This paper presents a study on the crystallisation of BaF₂ from a glass in the system Na₂O/K₂O/BaF₂/Al₂O₃/SiO₂.

2. Experimental

Glasses with the composition (100 - x)(2Na₂O·16K₂O·8Al₂O₃·74SiO₂)xBaF₂ (with x=0 to 6) were melted from reagent grade Na₂CO₃, K₂CO₃, BaF₂, Al(OH)₃ and SiO₂ (quartz) in batches of 200 g in a platinum crucible at 1590 °C, held for 1.5 h. The melts were cast on a copper block and placed in a furnace preheated to 450 °C. Then the furnace was switched off and the samples were allowed to cool.

The samples were thermally treated at temperatures in the range from 500 to 600 °C. Glasses and thermally treated samples were cut into pieces 4 mm × 9 mm × 18 mm and studied by dilatometry (Netzsch 402 E). From powdered thermally treated samples, XRD-patterns were recorded using an X-ray diffractometer Siemens D 5000.

Some thermally treated samples were studied by transmission electron microscopy (TEM) using a Hitachi H 8100 with an acceleration voltage of 200 kV.

3. Results

The melted glasses were X-ray amorphous and visually transparent. Fig. 1 shows XRD-patterns of samples with 6 mol% BaF₂ thermally treated at 500 °C for different periods of time.

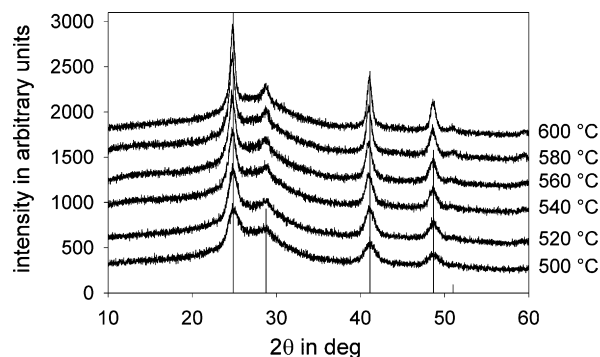


Fig. 2. XRD-patterns of samples with 6 mol% BaF₂ heat-treated at various temperatures for 20 h.

In these patterns strongly broadened XRD-lines attributable to crystalline cubic BaF₂ (JCPDS Nr. 4-452) are observed. The intensities of the lines increase with increasing time of thermal treatment. In Fig. 2, XRD-patterns of samples with 6 mol% BaF₂ thermally treated for 20 h at various temperatures are shown. All the patterns show lines at the same 2θ-values, which are all attributable to BaF₂. The intensities of the lines increases with increasing temperature and the lines get slightly narrower. The line broadening is well pronounced. In Fig. 3, the mean crystallite sizes of the BaF₂ phase calculated by Scherrer equation¹⁷ (see Eq. (1)) is shown as a function of the time, the samples with 6 mol% BaF₂ were thermally treated at temperatures of 500 and 560 °C. Here, it was assumed that XRD-line broadening is not affected by stresses.

$$d = \frac{G\lambda}{B \cos \theta} \quad (1)$$

with $G=0.899$ for a cubic system, λ = wavelength of the X-ray radiation (Cu K α = 0.154 nm) and B = full width at half maximum (FWHM) and θ = Bragg angle of the XRD-peak.

The crystallite size after thermal treatment at 500 °C for 5 h is around 4.5 nm. It increases up to 6.5 nm after thermal treatment for 80 h and possesses the same size (within the limits of error) after thermal treatment for 160 h. The crystallite sizes after thermal treatment at 560 °C are larger. After 10 h, they are

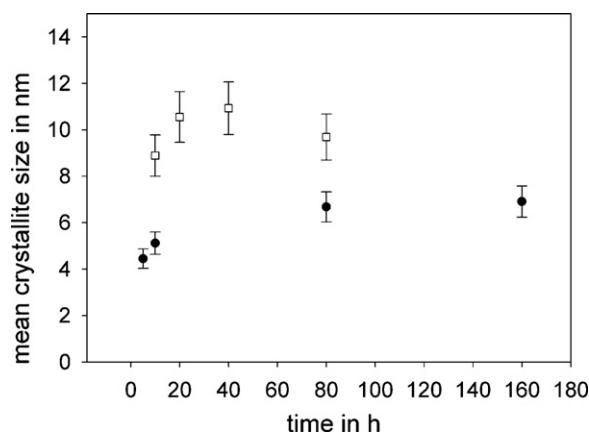


Fig. 3. Mean crystallite sizes calculated by Scherrer equation from XRD-line broadening as a function of the time of the samples with 6 mol% BaF₂ were heat-treated at (●) 500 °C and (□) 560 °C.

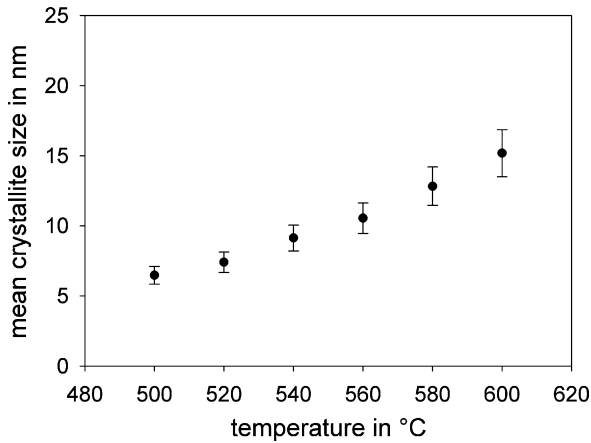


Fig. 4. Mean crystallite sizes calculated by Scherrer equation from XRD-line broadening as a function of the temperature of the samples with 6 mol% BaF₂ were treated for 20 h.

approximately 9 nm, a value which remains constant within the limits of error up to 80 h of thermal treatment.

Fig. 4 presents the as calculated mean crystallite size as a function of temperature of the samples with 6 mol% BaF₂ thermally treated for 20 h. While the sample tempered at 500 °C shows a crystallite size of around 6 nm that of the same sample tempered at 600 °C is as large as 15 nm. In the whole temperature range studied, a steady increase of the crystallite size with the temperature of thermal treatment is observed.

The tempered samples were studied by dilatometry in order to determine the glass transition temperature of the residual glassy phase. In Fig. 5, the determined glass transition temperatures of samples with 6 mol% BaF₂ thermally treated at a temperature of 500 °C are shown as a function of the time of thermal treatment. After 5 h, the glass transition temperature is 467 °C, after 10 h, a value of 474 °C is reached. Increasing the times of thermal treatment to 80 and 160 h, both result in a glass transition temperature of 493 °C.

Fig. 6 shows the quantity of BaF₂, illustrated by the area of the peak at $2\theta = 41^\circ$ as well as the densities of the samples tempered at 500 °C both as a function of the time of thermal treatment. The quantity of BaF₂ formed steadily increases with time, also

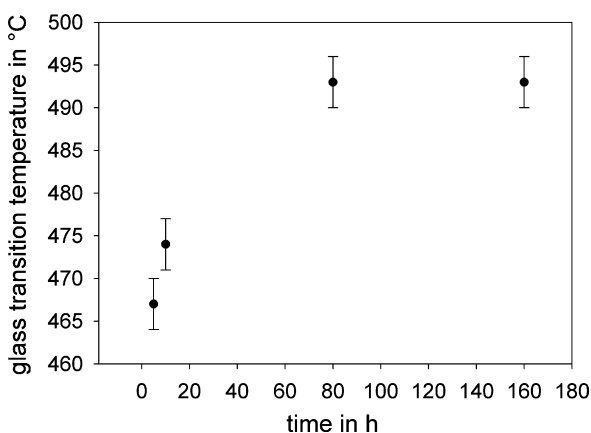


Fig. 5. The glass transition temperature, T_g , of samples with 6 mol% BaF₂ as a function of time of the thermal treatment at 500 °C.

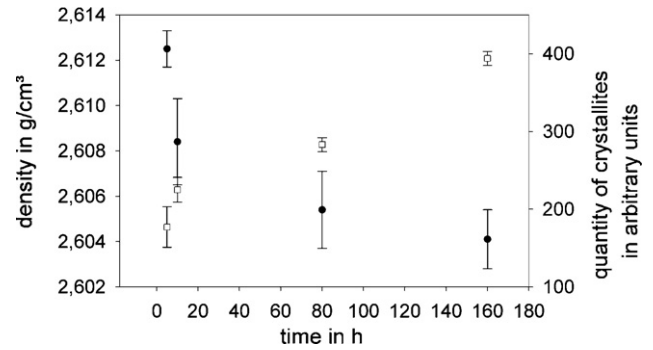


Fig. 6. Quantity of BaF₂ formed (□) (area under the XRD-peak at $2\theta = 41^\circ$) and the density of the samples with 6 mol% BaF₂ (●) as a function of the time of thermal treatment at 500 °C.

from 80 to 160 h, a notable increase is observed. The density drops strongly within the first 10 h of thermal treatment. Within the time from 80 to 160 h, the decrease observed is within the limits of error.

In Fig. 7, a TEM-micrograph of a sample with 6 mol% BaF₂ is shown. The BaF₂ crystals (with dark appearance) can clearly be distinguished from the glassy matrix. The sizes of the crystals are in the range from 12 to 18 nm.

Fig. 8 shows the glass transition temperatures of samples with the compositions $(100-x)(2\text{Na}_2\text{O}\cdot 16\text{K}_2\text{O}\cdot 8\text{Al}_2\text{O}_3\cdot 74\text{SiO}_2)\cdot x\text{BaF}_2$ with $x=0$ to 6. These values have been determined by dilatometry. While the glass without BaF₂ possesses a glass transition temperature of 588 °C, after addition of 1 mol% BaF₂, the glass transition temperature is 523 °C which further drops to 479 °C for a glass with 6 mol% BaF₂.

4. Discussion

As shown in Figs. 1 and 2, the XRD-lines are notably broadened. In principle this may be caused by two effects. The first

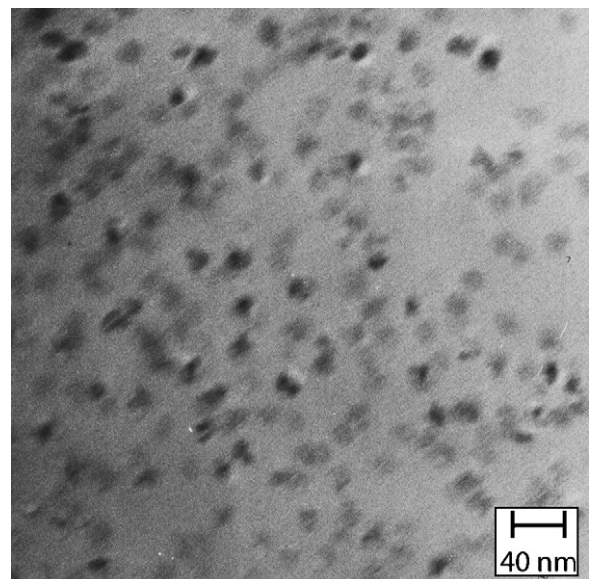


Fig. 7. TEM-micrographs of a sample with 6 mol% BaF₂ thermally treated at 560 °C for 20 h.

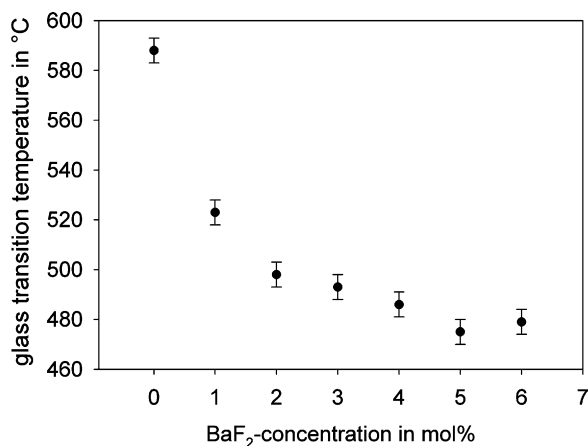


Fig. 8. The glass transition temperature, T_g (●) as a function of the BaF₂-concentration of glasses with the mol% composition $(100-x)(2\text{Na}_2\text{O}\cdot 16\text{K}_2\text{O}\cdot 8\text{Al}_2\text{O}_3\cdot 74\text{SiO}_2)\cdot x\text{BaF}_2$.

are small crystallites, the second is an inhomogeneous stress distribution in the crystals. Stresses in glass–ceramics are predominantly due to phase transitions during cooling or to a mismatch in the thermal expansion coefficients of the glassy matrix and the crystalline inclusions. In the present case, phase transitions can be excluded. In the case inclusions possess almost spherical shape; the stresses can be calculated by the Eshelby equation.¹⁸ While the stresses outside the inclusion decay with $(r/R)^{1/3}$, where r is the radius of the inclusion and R is the distance from the center of the inclusion ($r < R$), the stresses inside the inclusion are isostatic. Hence, they do neither depend upon the size of the crystals, nor do they vary inside the crystal. Thus, this type of stresses may give rise to a slight shift of the XRD-lines; however, they may not cause XRD-line broadening. Hence, small crystallites should be the only reason for XRD-line broadening and it is justified to apply Scherrer equation.

As shown in Fig. 3, within the limits of error, the mean crystallite sizes calculated do not depend upon the time of thermal treatment. Hence, in the regarded time scale from 5 to 160 h, crystal growth is not observed. Since, however, the critical diameter of a nucleus should be in the 1–3 nm range, the crystals must have grown earlier. As shown in Fig. 6, at 500 °C the quantity of crystals formed increases steadily within the whole period of time regarded (160 h). Hence nucleation and subsequent crystal growth continuously occurs within that time scale. Within a relatively short time (<5 h), the crystals grow to their final size.

As shown in Fig. 8, the glass transition temperature determined by dilatometry decreases with increasing BaF₂-concentration in the glass. Hence, during crystallisation of BaF₂, the glass transition temperature of the residual glass matrix increases due to a decrease of the BaF₂-concentration. This can also be observed in Fig. 5, during the course of the crystallisation process, the glass transition temperature increases until a value is reached which is equal to the temperature the sample was thermally treated. The increase in the glass transition temperature with increasing time (see Fig. 5) of thermal treatment runs parallel to the quantity of crystalline BaF₂ formed (see Fig. 6). In principle, this is approximately the same behaviour as

already reported from the crystallisation of CaF₂ from glasses in the system Na₂O/K₂O/CaO/CaF₂/Al₂O₃/SiO₂.¹⁶ In that system, the CaF₂ crystallites possessed a mean size of 9.5 ± 1 nm after thermal treatment at temperatures in the range from 520 to 560 °C which was kept for different periods of time (1–40 h). The CaF₂ crystals did not grow with time and their size did not depend on temperature.

By contrast, in the system under investigation, the temperature supplied had a certain effect on the crystallite size as shown in Fig. 4. The crystals formed at 500 °C possessed a mean crystallite size of around 6 nm which steadily increased to a value of around 15 nm at 600 °C. It should be noted that this effect is clearly significant; however, it is also comparably small.

In the glasses under investigation, nucleation of BaF₂ and subsequent crystal growth can be described as follows: while BaF₂ is formed, the melt near the crystal formed is depleted in barium and fluoride and hence is enriched in the other glass components. As shown in Fig. 8, this leads to an increase in viscosity of the respective composition. Thus, during the course of the nucleation process and subsequent crystal growth, a layer enriched in silica and alumina is formed around the growing crystal. For a given narrow variation of a glass composition, the diffusivity of glass melt components should be proportional to the reciprocal viscosity. While the diffusivity of glass melt components decreases with time in a layer around the crystals, the crystal growth velocity should decrease strongly with time. Hence, the layer formed should act as a diffusion barrier. Near the forming crystals, the glass is depleted in barium and fluoride, and hence, further nucleation cannot occur. However, in between the crystals, nucleation continues. During further thermal treatment, nucleation should occur in all regions of the sample whose chemical composition is correlated to transition temperatures below that temperature where the sample is being treated. In summary, this process continues until nucleation and crystal growth completely stops. This should occur when the viscosity of the whole residual glass melt possesses a value of approximately 10^{13} dPas, i. e. if the glass possesses a chemical composition whose attributed transition temperature is equal to the temperature supplied during the thermal treatment. Then further nucleation is negligible and the crystallisation process becomes frozen in. At a given temperature of thermal treatment, T_g should hence approach that temperature and, the volume concentration of crystalline BaF₂ should approach a constant value which is attributed to this transition temperature. This concentration should increase with increasing temperature. The crystallisation of BaF₂ from the melt composition is considered as an example of a self-organized process. Both, the volume concentration of crystalline BaF₂ and the size of the formed crystals are controlled by the kinetics. In comparison to the crystallisation of CaF₂ from glasses in the system Na₂O/K₂O/CaO/CaF₂/Al₂O₃/SiO₂, the crystal size depends on the crystallisation temperature. It should be noted that this effect is not large. While increasing the temperature from 500 to 600 °C, the crystal size increases from around 6 to 15 nm. As reported in Refs. 19,20,^{19,20} also in the case of the CaF₂-containing system, the glass transition temperature decreased when adding the fluoride component to the glass batch.¹⁶ While adding 12.5 mol% CaF₂, T_g decreased

(within the limits of error) linearly from around 558 to 498 °C. In the case of the system under investigation, the effect of BaF₂ is even more pronounced: the addition of 6 mol% BaF₂ leads to a decrease of T_g from 588 to 479 °C. However, in contrast to the Na₂O/K₂O/CaO/CaF₂/Al₂O₃/SiO₂-system, this decrease is not at all linear. Introducing 1% BaF₂ into the glass results in a decrease in T_g from 588 to 523 while a further increase to 2 mol% leads to a decrease to 498 °C. A further increase in the BaF₂-concentration leads to only a minor effect. This means that starting from a BaF₂-concentration of 6 mol%, the crystallisation of 4 mol% BaF₂ results in an increase in T_g of 19 K, which is clearly smaller than in the case of CaF₂-crystallisation. This may explain the effect of temperature upon the crystallite size which in the case of the BaF₂ is more pronounced than in the case of the CaF₂-crystallisation.

In contrast to isochemical systems, in non-isochemical systems, the crystal growth velocities should always depend on time, since the chemical composition near the crystals changes during nucleation and crystal growth. In principle, two cases are to be considered: (i) the crystal formed is enriched in glass components which act as network modifiers. Then, as in the present case, the viscosity near the crystal increases and hence the crystal growth velocity decreases with time. In the second case (ii) a component which acts as network former crystallises. Then near a crystal, the glassy phase is enriched in network modifiers. This leads to a decrease in viscosity near the crystal which should result in an increase in the crystal growth velocity. It should be noted, that this should also happen in “non-ideal isochemical” systems, since all glasses contain as an additional component a significant quantity of water. This water acts as network modifier. During nucleation and crystal growth, water is not incorporated in the crystal and is enriched in the glassy phase near the crystal.

The crystallisation of components which act as network modifiers should generally be favorable to obtain high volume concentrations of crystallites with sizes in the nanometer-range. In crystalline fluorides such as BaF₂ or CaF₂ rare earth metals can be incorporated into the lattice. This might be advantageous for the preparation of laser materials, such as glasses with YbF₃-doped fluoride crystals embedded in a glassy matrix.

5. Conclusions

From melts in the system Na₂O/K₂O/BaF₂/Al₂O₃/SiO₂, crystalline BaF₂ was precipitated by thermal treatment of the respective glasses. The mean crystallite sizes of BaF₂ were in the range from 6 to 15 nm and increased with time of thermal treatment. Increasing the temperature from 500 to 600 °C resulted in an increase of the crystallite size from 6 to 15 nm. Since the crystallisation of BaF₂ leads to an increase in the viscosity near the crystals, a diffusion barrier around each crystal is formed. This barrier hinders further crystal growth. In between the crystals nucleation proceeds until the whole residual glassy phase

has a viscosity of 10¹³ dPas. Then nucleation and crystallisation are totally frozen in. The process is controlled by kinetics and an example for a self-organization process.

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