

Crystallization statistics. A new tool to evaluate glass homogeneity

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Abstract

We propose and test a new method to evaluate the chemical homogeneity of glasses based on statistical analyses of the volume distribution of crystals developed through thermal treatments. The method is based on the fact that each volume element of a glass piece subjected to a proper thermal treatment should exhibit a certain number of crystals, which is dictated by its chemical composition. We performed numerical simulations to interpret the experimental results obtained for some glasses, and demonstrate that this new method is adequate to determine the *degree* and *scale* of heterogeneity of glasses that display volume crystallization.

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1. Introduction

The chemical and physical differences of the starting materials used in glass production give rise to complex reactions during the first stages of melting. While some components melt, others continuously dissolve in the liquid. Moreover, due to molecular weight differences, some elements tend to sink to the bottom of the crucible while others partially volatilize. Diffusion processes are necessary to completely dissolve and homogenize the batch materials, but glass-forming melts are quite viscous, which impairs diffusion and mixing. Therefore, depending on the melting conditions (the material's particle size, temperature, time, mixing, etc.), the result is quite often a heterogeneous glass. Knowledge of the variations in the chemical composition from one volume element of the glass to another (*degree of homogeneity*) and of the characteristic length (*scale of homogeneity*) of such heterogeneities is important for a number of applications.

The standard technique to measure glass homogeneity in industries and laboratories was developed by Christiansen–

Shelybskie [1]. This technique is based on the fact that the transmission of visible light of an inhomogeneous material, for instance, a transparent glass powder immersed in a liquid, depends on the refractive index of both materials. The major advantage of this method is that it expresses the *degree* of homogeneity (σ^2) and *scale* of the heterogeneities, which is inferred by varying the size of the glass grains.

However, some works [2,3] strongly criticize this method. The problem in question involves the equations used by Christiansen–Shelybskie, which disregarded several important contributions to the transmittance losses. Hoffmann [3] compared data from the literature obtained by the Christiansen–Shelybskie method and demonstrated incoherent results. For example, the degree of homogeneity of optical glasses and ordinary bottles measured by this method was found to be of the same order of magnitude! This is clearly inconsistent, because glasses produced on a large scale cannot be as homogeneous as optical glasses, which are produced by sophisticated stirring processes.

To produce glasses of optical quality, the melt has to be stirred continuously, but on a laboratory scale, due to its simplicity, the most common homogenization process is to repeatedly melt and crush the glass. Although the use of this procedure is widespread, the number of times this

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process is repeated and the melting times are completely empirical. Most researchers use from one to five melting/crushing cycles, but rarely test the homogeneity of the resulting glass due to the practical difficulties of the Christiansen–Shelybskie method.

In this paper we propose a new method, based on a statistical analysis of the volume distribution of crystals that are developed by heat treatment above T_g , to characterize the *degree* and *scale* of the homogeneity of glasses that *crystallize in the volume*. Internal crystallization may occur spontaneously above T_g , as in the glasses described by Fokin et al. [4], or it may be induced by adding nucleating agents. We then produce glasses with different degrees of homogeneity by varying the melting temperatures and the number of melting/crushing cycles, and test the proposed method.

2. Theoretical fundamentals of the new method

The new method is based on the fact that, after a certain nucleation time t_N at a given temperature T_N , each volume element of a *homogeneous* glass has the same probability to nucleate a crystal. By the development of an appropriate thermal treatment (growth time t_G at a temperature $T_G > T_N$), crystalline nuclei may grow on an observable scale, allowing a sample cross-section to be examined by optical or electron microscopy. This procedure yields an average number of crystals N per examined field, and a corresponding standard deviation σ_N . If the condition of perfect homogeneity is met, according to Poisson's statistics, the average number of crystals and its standard deviation satisfy the condition $\sigma_N/N = 1/N^{1/2}$.

The value of N depends on the optical field area l^2 , which in turn is related to the microscope's magnification, M , through a constant k , ($l^2 = kM^2$), and on the volume density of crystals N_v . Crystals generated by two-step (nucleation and growth) heat treatments lead to an N that depends on the product of the crystal nucleation rate $I(T_N)$ and time t_N , as well as on the product of the crystal growth rate $U(T_G)$ and growth time, t_G . A thermal nuclei, i.e., nuclei that formed during glass preparation, also grow upon heating to T_G .

From geometrical considerations, the following relationship holds for the average number of spherical crystals N appearing on a surface area l^2 , after a proper heat treatment:

$$N = 2N_v l^2 U(T_G) t_G, \quad (1)$$

where $N_v = I(T_N) \times t_N$ is the volume density of crystals.

For a set of measurements with pre-selected values of N_v , $U(T_G)$ and t_G :

$$N^{1/2} \propto l. \quad (2)$$

A σ_N/N vs. $1/N^{1/2}$ plot for a crystal distribution in a perfectly homogeneous glass obtained with different microscope magnifications should show a straight line with *slope 1* and

zero intercept. In the case of an inhomogeneous glass, however, different volume elements exhibit different nucleation probabilities, and a σ_N/N vs. $1/N^{1/2}$ plot will not display a straight line of slope 1 with zero intercept. If the plot shows a transition from homogeneous to inhomogeneous behavior for a given N value, we can use Eq. (2) to assign a typical l that characterizes the *scale* of heterogeneity.

For a given N (or l), the ratio $(\sigma_N/N)_{\text{homo}}/(\sigma_N/N)_{\text{measured}}$ is a measure of the *degree* of homogeneity. When this quotient is 1, homogeneity is maximum; values of the ratio lower than 1 indicate lower homogeneity.

Let us explain this method in more detail. If one raises the temperature of a internally crystallizing glass for some time above T_g , crystalline nuclei may grow, for example, to a few micrometers. Then, by observing a polished cross-section of the sample with an optical or electron microscope, it is possible to evaluate the number of crystals N_i present in each observed field. The field area depends on the magnification M . N is thus the average of the N_i values obtained for various optical fields with the same M .

In a homogeneous glass in the nucleation stage, before any significant crystal growth, the probability of finding a nucleus in each volume element is the same throughout the sample; in other words, the birth of one nucleus does not interfere with the appearance of another. The probability $p(N_{vi})$ of finding N_{vi} nuclei in a given sample volume is described by Poisson statistics [5], and is summarized by Eq. (3):

$$p(N_{vi}) = \frac{N_v^{N_{vi}} e^{-N_v}}{N_{vi}!} \quad (N_{vi} = 0, 1, 2, \dots, n), \quad (3)$$

where N_v is the average crystal number for that volume.

From now on, based on stereological considerations, we consider that the aforementioned analysis is also valid for a sample plane cut. In other words, N_{vi} is replaced by the number of crystals N_i counted in an optical field of the sample cut, and N_v is replaced by the average of a set of N_i 's, namely N (the average number of crystals in the glass surface in a field of size l^2).

The standard deviation of the N_i values obtained with the same magnification M is given by Eq. (4a):

$$\sigma = \sqrt{\frac{\sum_i (N_i - N)^2}{s - 1}}. \quad (4a)$$

Thus, for a number s of optical fields of size l^2 , N can be determined, enabling one to calculate the standard deviation of the distribution with Eq. (4a).

If the glass is chemically homogeneous, then Eq. (4a) can be written as [5]

$$\sigma = \sqrt{N}. \quad (4b)$$

For each magnification M , a corresponding (σ, N) pair is obtained for a perfectly homogeneous glass. A plot of the

(σ, N) pairs obtained for different M should plot as a straight line with slope 1 and zero intercept. We have chosen a plot of the type σ/N vs. $1/N^{1/2}$, which yields the same function, to normalize for different glasses and to let the x -axis vary from optical to electron microscopy scale from left to right.

We thus propose a statistical test to evaluate glass homogeneity by plotting σ/N vs. $1/N^{1/2}$ using experimental crystal densities measured in cross-sections of any previously heat-treated glass sample. A random behavior (line with slope = 1 and 0 intercept in a σ/N vs. $1/N^{1/2}$ plot) is expected for magnifications M for which the optical fields are significantly larger than the typical heterogeneity scale. Deviations from the Poisson statistics are likely to be found when the optical field is smaller than the heterogeneity scale, since different fields correspond to different glass compositions.

One can now distinguish three different magnification levels for sampling a *heterogeneous* glass:

1. *Low magnifications*: each optical field covers a large area and the sample is homogeneous in that large scale. Thus, the experimental points in a σ/N vs. $1/N^{1/2}$ plot will draw a straight line with slope 1 and 0 intercept;
2. *Medium magnifications*: the chosen field distinguishes areas with different crystal densities and the experimental points will appear above the straight line;
3. *Very high magnifications* (for example, SEM or AFM): the small field does not distinguish areas with different crystal densities, the number of crystals typically varies between 0 and 1 in each field, and the experimental σ/N points appear below the straight line. This can be explained as follows: σ is a measure of the distribution frequency width. However, when the magnification is sufficiently large, only two N_i values are possible: 0 (no crystals in the field) and 1 (1 crystal in the field) and this does not characterize a Poisson distribution; hence, the experimental σ is *underestimated*.

Magnifications can be considered low, medium or very high according to the scale of heterogeneity. Depending on the experimental conditions, all the above possibilities or a particular one can be observed. Since the crystal nucleation and growth kinetics strongly depend on the glass chemical composition and, consequently, on its chemical homogeneity, different volume elements of a heterogeneous glass present different nucleation probabilities. Thus, for a heterogeneous glass, a measure of crystallization statistics plotted as σ/N vs. $1/N^{1/2}$ will not be a straight line with inclination 1 and 0 intercept.

The aim of the method proposed here is therefore to quantify chemical heterogeneity in the glass volume, but crystallization statistics are normally obtained by counting crystals on polished cross-sections. Hence, the method relies on the property that a spatially random distribution of crystals generates a random distribution of crystals on a flat polished sample cross-section.

3. Computational test of the method

We performed a computational simulation that emulated surface cuts of homogeneous samples having randomly distributed crystals (Fig. 1) and surface cuts of inhomogeneous samples including striae having a high crystal density (Figs. 2 and 3). Using 500 randomly positioned windows for each magnification (corresponding to 100, 250 and 500 \times in an optical microscope, and to 1000 and 1500 \times in a SEM), the number of points per field, N_i , was computed and the average value N and its corresponding σ_N were calculated.

Fig. 4 shows that, in the computer-generated homogeneous specimen, σ/N vs. $1/N^{1/2}$ points lie on a straight line of slope 1 and 0 intercept, while deviations are exhibited by

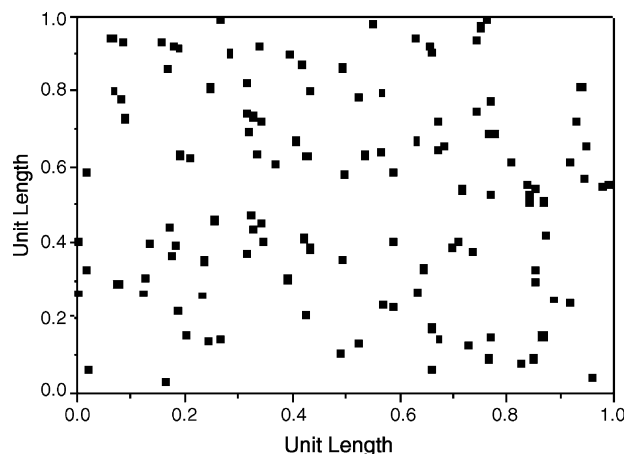


Fig. 1. Computational simulation of a 1 mm cross-section surface with randomly distributed points. The surface density of points is 120 crystals/mm².

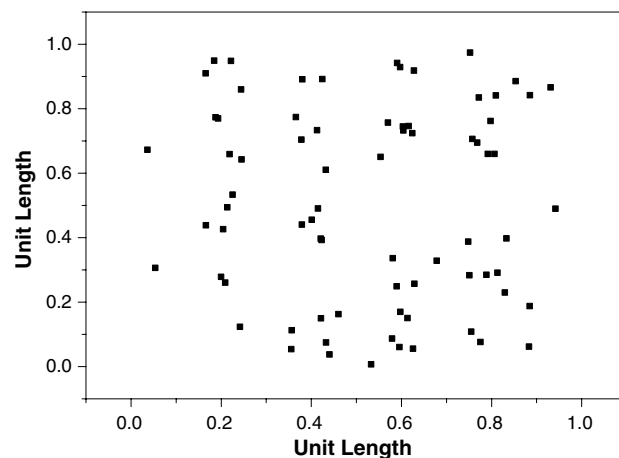


Fig. 2. Simulated sample cross-section of 1 \times 1 mm² with vertical striae of high crystal density of 100 μ m width centered at $x = 0.2, 0.4, 0.6$ and 0.8 . The matrix density is 120 crystals/mm² and the striae density is 300 crystals/mm².

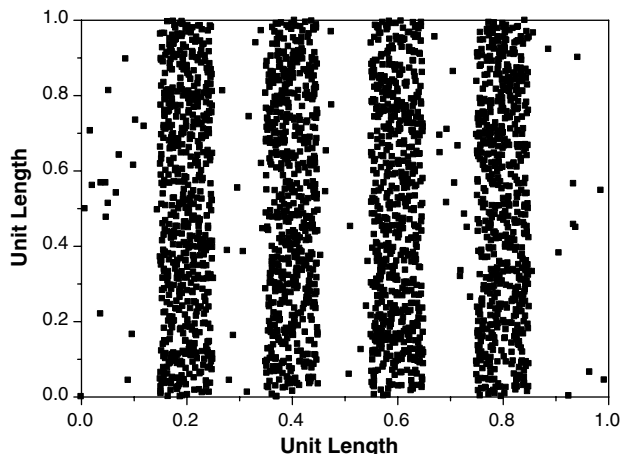


Fig. 3. Simulation of 1 mm length of vertical striae 100 μm width centered at $x = 0.2, 0.4, 0.6$ and 0.8 . The matrix density is 120 crystals/ mm^2 and the striae density is 6120 crystals/ mm^2 .

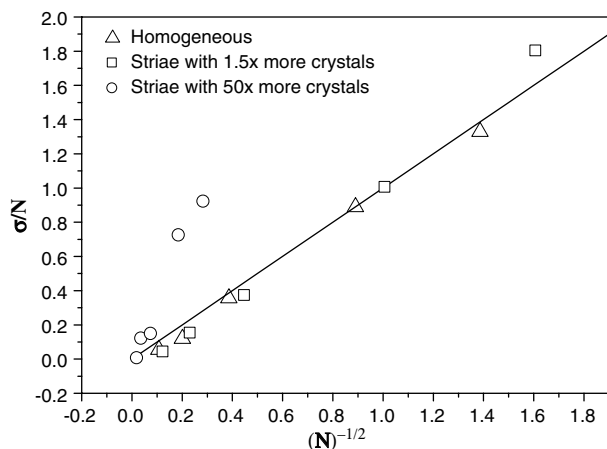


Fig. 4. Statistical analysis performed on computer-simulated crystal distributions corresponding to a homogeneous matrix and two inhomogeneous matrices with vertical striae having different crystal densities. The straight line (slope 1 and 0 intercept) corresponds to the (σ, N) pairs obtained for a perfectly homogeneous glass.

some data corresponding to heterogeneous samples. The data corresponding to the sample in Fig. 3 with slight inhomogeneity deviates at a larger N than those of the sample having striae of higher crystal density. However, an analysis of the inhomogeneity size using Eq. (2) reveals the same *scale* of inhomogeneity for both. Moreover, the $(\sigma_N/N)_{\text{homo}}/(\sigma_N/N)_{\text{measured}}$ ratios are different for the two samples, indicating a clear difference in the *degree* of heterogeneities. The same procedure was then used to analyze the experimental data for real glasses.

4. Experimental procedure

To experimentally test the proposed method, two glass systems were evaluated: a glass with composition 23.26Na₂O–

23.26CaO–47.38SiO₂–6P₂O₅ (mol%), which will be dubbed *SSP6*, and a 45Li₂O–20Nb₂O₅–35SiO₂ (mol%) glass, which will be denominated *LNS*. These glasses were chosen because they display internal crystallization easily and have volatile elements that can lead to significant degrees of heterogeneity.

We prepared the *SSP6* glasses by melting appropriate quantities of SiO₂ (crushed Brazilian quartz) with analytical grade Na₂CO₃ (Mallinckrodt), CaCO₃ (Mallinckrodt) and Na₂HPO₄ (Mallinckrodt). After weighing these reagents, they were mixed in a planetary mill for 1 h. Melting was carried out in Pt crucibles in an electric furnace at 1350 °C for several hours. To obtain glasses with different degrees of homogeneity, we varied the number of melting/crushing cycles. At first, we melted 100 g of glass for 1 h and poured it on a steel plate. Some of this glass was separated and a second part was broken up into 2 mm pieces, melted for another hour and poured onto a steel plate. We repeated this procedure and a third part was melted for another hour. All these glasses were then subjected to nucleation treatments for 8, 10, 12, 16 and 20 h at 570 °C and subsequently to a ‘development’ treatment at 720 °C for 10 or 20 min to allow for crystal growth. Glasses containing extra OH[−] were also evaluated. After polishing with CeO₂ to an optical degree, measurements of N_i (number of crystals/unit area) were conducted with an optical microscope at 100, 250 and 500 \times (it is important to stress that the analyzed sample surfaces were, in fact, cross-sections of the crystallized volume). The same samples were also prepared for SEM analysis and the measurements of N_i were carried out at 1000 and 1500 \times .

The *LNS* glasses were melted by the conventional method, using Li₂CO₃ (Synth, PA), Nb₂O₅ (CBMM, optical grade) and SiO₂ (crushed Brazilian quartz). After these chemicals were carefully weighed, they were mixed in a planetary mill for 30 min. Melting was carried out in Pt crucibles for 2 h in an electric furnace at 1250 °C. At first, we melted 100 g of glass for 1 h and poured it onto a steel plate. The glass was re-melted three times at 1250 °C for 30 min (A) and then divided into three parts. One part was further divided into parts which were melted at 1150 °C for 1 h (B) and 2 h (C and D), at 1300 °C for 2 h (E) and at 1200 °C for 2 h (F). The second part was melted at 1200 °C for 1 h (G) and, finally, the third part was melted at 1300 °C for 1 h (H). Fig. 5 shows a schematic diagram of the melting procedure.

These glasses were heated at 650 °C to allow crystal growth from a thermal nuclei. We then polished several samples with CeO₂ and counted the number of crystals N_i in each optical field with an optical microscope, using 50, 100, 200, 320 and 500 \times magnification. Only sample (D) – which was melted at 1150 °C for 2 h – was nucleated at 555 °C during 24 h and annealed at 650 °C for 30 min for crystal growth. This sample was analyzed by SEM at 5000 \times magnification.

The use of different optical magnifications allowed us to clearly detect heterogeneities and to identify on which *scale* they were significant. After obtaining the experimental N_i ,

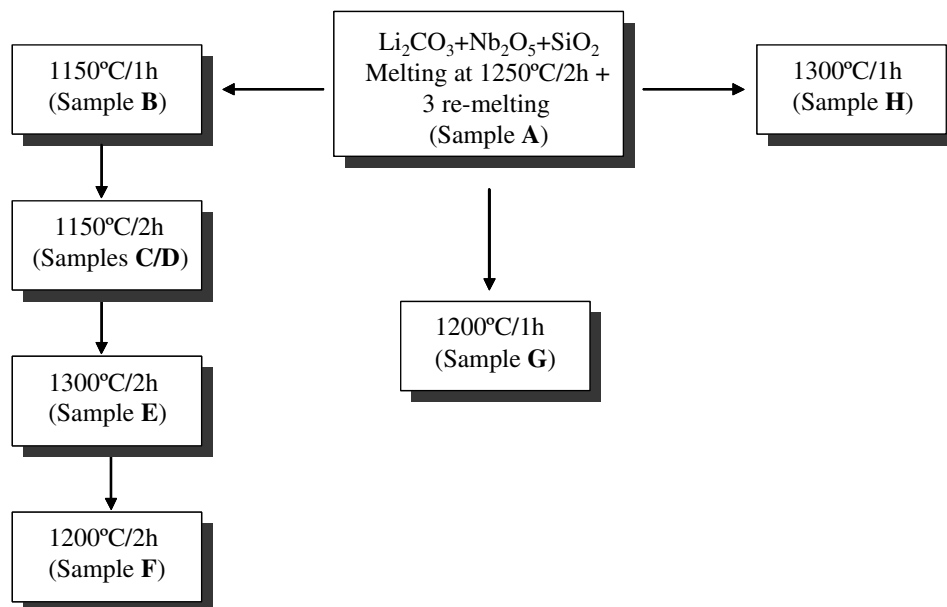


Fig. 5. Re-melting schedule of the LNS glasses.

we calculated the corresponding N and σ and plotted them as σ/N vs. $1/N^{1/2}$ to analyze the adherence of these experimental data to Poisson's statistics.

5. Results

5.1. SSP6 glasses

We adopted the legends 0 M, 1 M and 2 M for glasses melted for 1 h, crushed and melted once more, and crushed and melted twice, respectively. We adopted this procedure expecting to vary the degree and scale of chemical heterogeneity. All these glasses were heat-treated simultaneously, in the same furnace, to minimize temperature variations.

The degree of crushing before melting is also important for homogenization. However, for this system, the particles were only crushed into coarse sizes of about 2 mm; therefore, and thus homogeneity had to be achieved by atomic diffusion during melting.

Fig. 6 shows the results for samples 0 M, 1 M and 2 M annealed at 570 °C for 10 h, as well as the results of a simulation with a matrix having a crystal density similar to the experimentally evaluated glass (120 crystals/mm²).

Fig. 6 shows that the experimental data are close to the simulated results, and that, in this particular case, further crushing/melting does not significantly influence the glass homogeneity on a scanning electron microscope scale. We carried out the same test for other groups of samples, with results similar to those presented in Fig. 6. Therefore, subsequent melting is not necessary to homogenize the SSP6 glass, which has a low viscosity. This is an important conclusion, since re-melting increases the time and cost, can lead to the uptake of impurities and the loss of some components of high vapor pressure, such as P and Na.

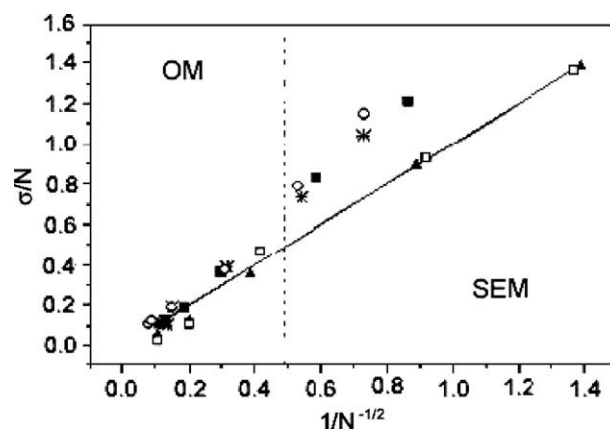


Fig. 6. Poisson test. Experimental data for 0 M (*), 1 M (O), 2 M (■) glasses annealed at 570 °C for 10 h – compared with the calculated data for a homogeneous matrix having the same crystal density: (□) simulation with the same number of windows utilized in the experiments, (▲) simulation with 500 windows. Optical microscopy (OM); scanning electron microscopy (SEM). The straight line (slope 1 and 0 intercept) corresponds to the (σ, N) pair obtained for a perfectly homogeneous glass.

Fig. 7 shows the results of N/l^2 for the three types of samples. There were no significant changes in N/l^2 over time.

The value of N would have been different had there been losses of P and Na. Due to the match between the actual and expected values of N (considering the experimental error), we conclude that, if any losses did occur, they were negligible.

To evaluate an actual heterogeneous glass, similar measurements were conducted with a SSP6 glass melted in a humid atmosphere. This glass was quite heterogeneous, as is visually shown by its crystallization pattern (Fig. 8). The crystallization statistics results are plotted in Fig. 9.

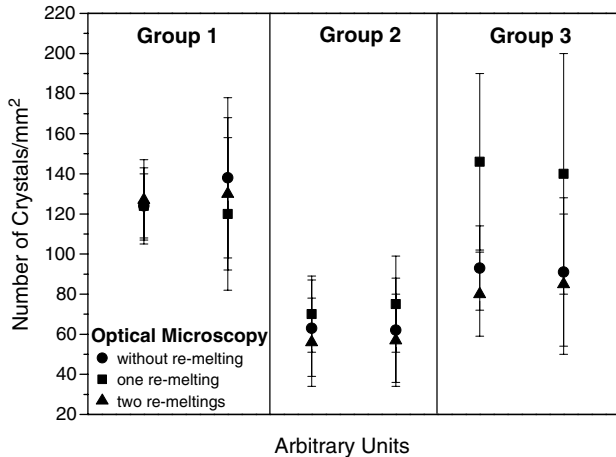


Fig. 7. Values of N/l^2 for glasses with different melting times. Group 1: glasses annealed for crystal growth at 570 °C for 10 h; group 2: glasses annealed at 570 °C for 8 h; group 3: glasses annealed at 570 °C for 16 h. (●) Without re-melting; (■) one re-melting; (▲) two re-meltings.

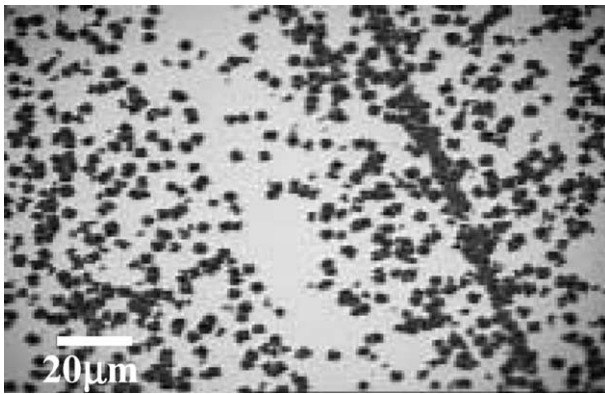


Fig. 8. Reflected light micrograph of SSP6 glass melted in a humid atmosphere, annealed at 695 °C for 40 min.

The visually observed heterogeneity in Fig. 8 led to a deviation from the expected homogeneous behavior (straight line in Fig. 9).

5.2. LNS glasses

These glasses were identified from A to H, as shown in Fig. 5. All the samples were annealed at 650 °C for the same time to allow for crystal growth, but sample D was first nucleated at 555 °C for 24 h and then annealed at 650 °C for 30 min for crystal growth.

Fig. 10 shows the experimental results obtained for samples A to H. Sample D was also crystallized for observation by SEM (magnification = 5000×). Each point corresponds to a given magnification in the optical microscope and to 5000× for sample D. The straight line represents the function $\sigma/N = 1/N^{1/2}$ for a homogeneous system. The closer the points are to the straight line, the more homogeneous

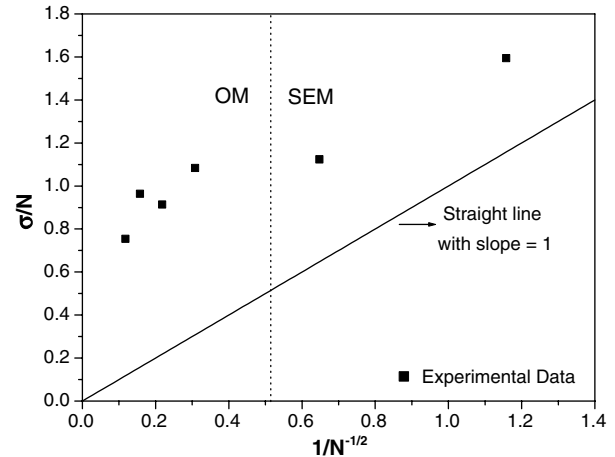


Fig. 9. Analysis of crystallization statistics of SSP6 glass melted in a humid atmosphere.

the glass is for the evaluated magnification. The standard deviation of σ/N was estimated from a set of four values obtained for the same sample B, with 200× magnification, and is approximately 5% of the average σ/N value. The error in $1/N^{1/2}$ is about 10%. The equivalent set of data from which the error was estimated is encircled in Fig. 10(B).

Sample D (subjected to double annealing) was specially crystallized to increase the crystal number density when compared with all the other samples. This enabled us to measure from 0 to 5 crystals in the observed SEM field with 5000× magnification. Due to its large number of crystals, N value is high. Thus, the points referring to 100, 200, 320 and 500× are situated at lower $N^{-1/2}$ values than the other samples observed under the same magnifications.

Samples A and G clearly possess heterogeneous regions. This behavior was correctly detected by the proposed method, as reflected by the higher deviation obtained from the straight line (see Fig. 10(A) and (G)). The analysis corresponding to the remaining glasses shows that they are homogeneous within the experimental error.

6. Discussion

Our tests of crystallization statistics to infer glass homogeneity through σ/N vs. $1/N^{1/2}$ plots resulted in straight lines with slope 1 and 0 intercept, for *simulated* cross-sections of *homogeneous* glasses. In addition, as we expected, when *simulated heterogeneities* were introduced, the plots deviated from their previously homogeneous behavior. The deviation depends on the scale and degree of homogeneity.

After a minimum melting time, sequential grinding and re-melting have no effect on the homogeneity of the low viscosity glass SSP6, which is homogeneous on an optical scale, but is inhomogeneous on a SEM scale. However, an SSP6 glass having a high OH content exhibits heterogeneity at both optical and SEM levels.

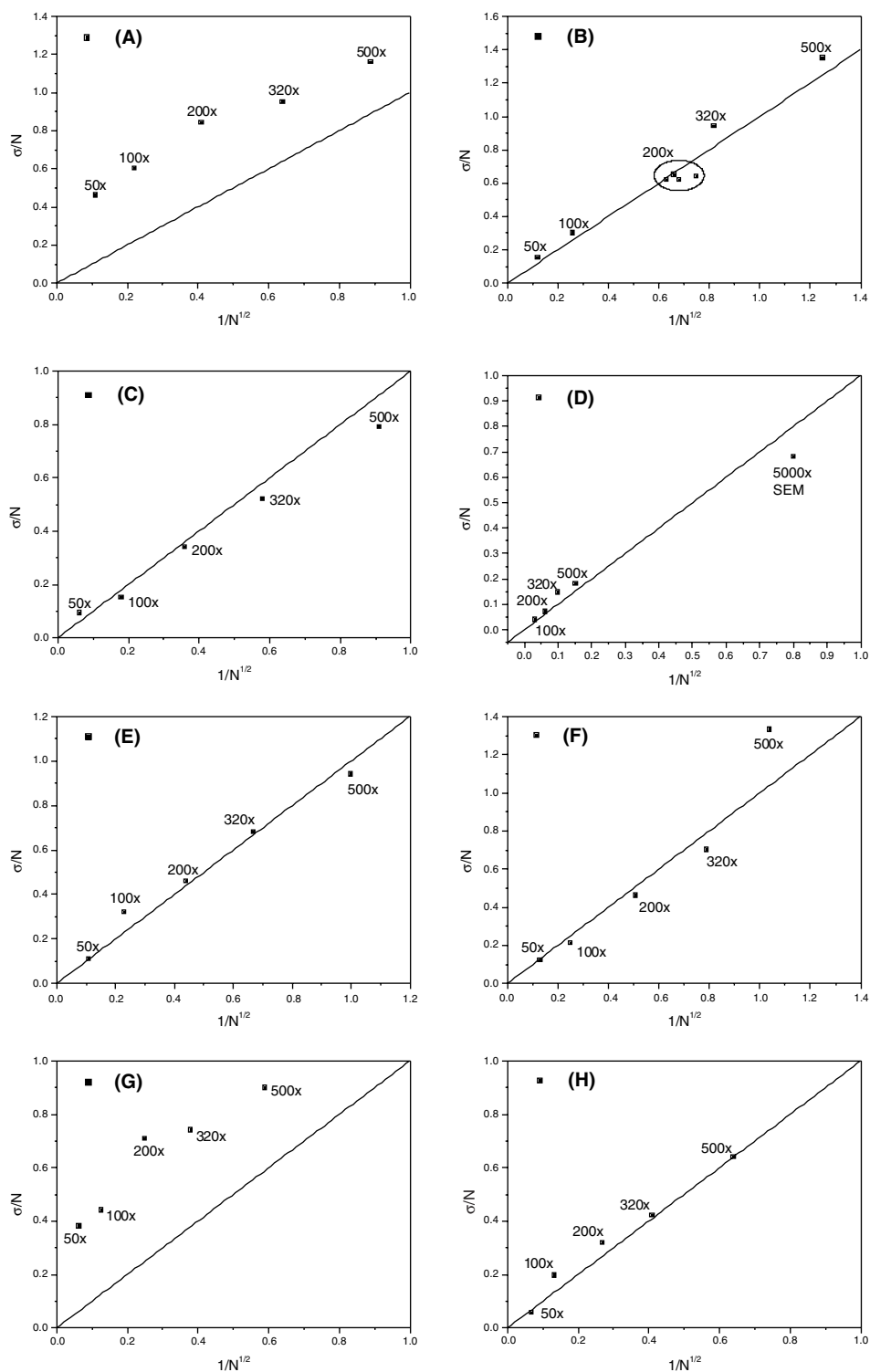


Fig. 10. Statistical test for the LNS glass. The straight line (slope 1 and 0 intercept) corresponds to the (σ, N) pair obtained for a perfectly homogeneous glass.

LNS glasses exhibit a richer variety of behaviors. Fig. 11 shows glasses that became either homogeneous (D) or heterogeneous (G). Overlapping the statistical results for glasses A, B and H (from Fig. 10) indicates that the large scale inhomogeneities found in glass A were eliminated when we prepared glasses B or H through a fourth re-melt-

ing at a different temperature. Moreover, the density of crystals at, for example, 50 \times , varied drastically from glass to glass. This variation could be due to homogenization, or else to different redox conditions of the Nb ions in the melt. But the similarity of statistical behaviors of B and H glasses was naturally due to homogenization. This new

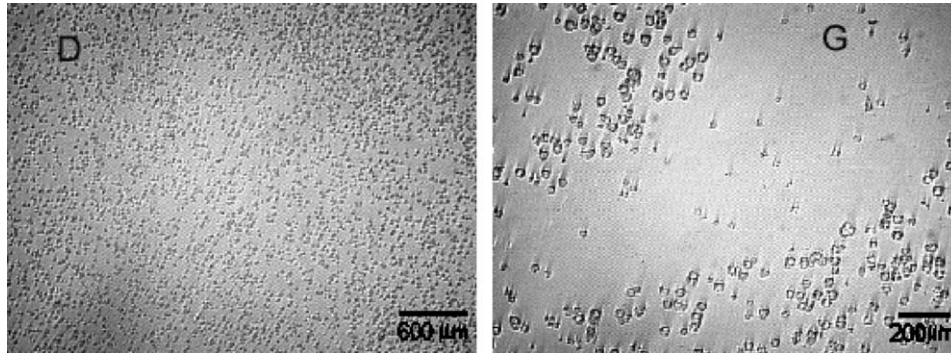


Fig. 11. Micrographs of glass samples D – homogeneous and G – heterogeneous.

method of evaluating chemical heterogeneity offers two advantages: it indicates the presence of heterogeneity and allows one to obtain information about their typical scale and degree.

7. Conclusions

We propose a new method to infer the degree and scale of heterogeneity in glasses that crystallize in the volume on laboratory time scales. The method is based on statistical analyses of the crystal distribution in sample cuts, and characterizes glass homogeneity through σ/N vs. $1/N^{1/2}$ plots. These plots are straight lines with slope = 1 and intercept = 0 for perfectly homogeneous glasses, but deviate from linearity when the glass is heterogeneous. The value of N at which the system deviates from a homogeneous sample indicates the size of the heterogeneity and the quantity $(\sigma_N/N)_{\text{homo}}/(\sigma_N/N)_{\text{measured}}$ gives information about the degree of heterogeneity. Experimental determi-

nations of crystallization statistics in several partially crystallized glasses using this new methodology have demonstrated its usefulness.

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References

- [1] K. Högerl, G.H. Frischat, *Glastech. Ber. Glass Sci. Technol.* 67 (6) (1994) 145.
- [2] H.J. Hoffmann, R. Steinhart, *Glastech. Ber. Glass Sci. Technol.* 71 (11) (1998) 319.
- [3] H.J. Hoffmann, *Glastech. Ber. Glass Sci. Technol.* 72 (4) (1999) 99.
- [4] V.M. Fokin, E.D. Zanotto, J.W.P. Schmelzer, *J. Non-Cryst. Solids* 321 (1–2) (2003) 52.
- [5] A.M. Mood, *Introduction to the Theory of Statistics*, McGraw-Hill, New York, 1974.