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Nucleation and crystallization studies of a basalt glass-ceramic by small-angle neutron scattering

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The nucleation and crystallization behaviour of a basalt glass-ceramic was studied by small-angle neutron scattering (SANS). The interparticle interference effects in the SANS spectra of the different nucleated samples indicate that the number density of crystallites, measured at the longest crystallization time at 710° C, saturates with the nucleation time at different values depending on the nucleation temperatures; the saturation level is higher at lower temperatures. This number density, measured at the shortest crystallization time, shows a maximum around 635° C (nucleation maximum) and it also decreases with the time of crystallization at 710° C and saturates at higher times, depending on the nucleation treatment; this is interpreted as due to the redissolution of the smaller particles as the larger ones grow. There is also competition between the nucleation and growth processes at the higher nucleation temperature. The crystallization behaviour of this glass-ceramic tends to follow an Ostwald ripening mechanism at higher crystallization times.

1. Introduction

Basalt usually forms a black homogeneous glass when cooled from the molten state; subsequent reheating above the annealing temperature results in the development of fine-grained glass-ceramics [1]. In order to control the quality of glass-ceramics, it is important to study the nucleation and crystallization behaviour of this system. Initially, X-ray diffraction (XRD) and transmission electron microscopy (TEM) measurements were carried out on samples heat-treated at 600, 650, 700, 800 and 900° C for 2, 4 and 8 h, as well as on the as-annealed glass (hereafter called the blank glass). XRD showed that there was no crystalline peaks for the blank glass, 600 and 650 samples. The peaks due to magntite appeared for the 700 sample; the strongest peak being at the *d*-spacing of 0.250 nm. For the 800 and 900 samples, there were also peaks due to pyroxene along with those of other minor phases. However, TEM showed the presence of magnetite in the 650 sample, and also in the 700 sample, while the last two samples showed the presence of a mixture of phases. The particle sizes of magnetite were estimated to range between 4.5 and 7.0 nm between 650 and 900° C (8 h only). Since the particles are small, the superparamagnetic behaviour of the magnetite particles is very interesting [2–4]. Mössbauer measurements at 4 K showed that the maximum amount of magnetite was formed at 700° C, and the evolution of the Mössbauer parameters showed that the magnetite particles have the most improved symmetry at this temperature [2, 3].

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The study of growth process immediately following nucleation is the most accessible, though indirect, method of inquiry into the nucleation process [7]. In order to determine an optimum nucleation condition for magnetite in the basalt glass-ceramics, small-angle neutron scattering (SANS) measurements were carried out dynamically at 710° C, as a function of time, on a series of samples heat-treated (nucleated) between 550 and 665° C for different times. The importance of SANS measurements for such a study has been discussed elsewhere [8]. Based on the results mentioned above, for the dynamic study of crystallization, the growth temperature was fixed at 710° C. This was also higher than the Curie temperature of the bulk magnetite (578° C), so that magnetic scattering could be neglected.

2. Experimental procedure

For this study, a basalt glass was supplied by Corning Glass Works (USA). Its composition was 52.0 SiO_2, 14.1 Al_2O_3, 12.8 Fe_2O_3, 9.3 CaO, 6.4 MgO, 3.2 Na_2O, 1.2 K_2O and 1.0 TiO_2 (wt %). The raw material was from Westfield in the holyoke Basalt flow (USA). This glass was melted twice in a platinum crucible at 1500° C for 16 h and subsequently annealed at 525° C. First, dilatometry measurement was carried out at a heating rate of 3° C min^{-1}, and the glass transition temperature (T_g) was determined to be 635° C. The samples, of dimensions 10 mm x 10 mm x 7 mm, were then heat-treated at 550, 577, 610, 634 and 665° C. Longer times (up to 32 h) were employed for lower temperatures and shorter times (up to 8 h) for higher temperatures of heat-treatment.

The SANS measurements were carried out in the spectrometer D-17 at the Institut Laue-Langevin (Grenoble); the details of this spectrometer are given elsewhere [9]. The detector distance was 2.85 m and $\lambda_0 = 1.282$ nm. Absolute small-angle cross-sections were deduced from the experimental neutron intensity, measuring the incoherent scattering on a thick vanadium sample. The sample was put in a small furnace between the incident beam and the detector, and the temperature was raised to 710° C in about 10 to 15 min. The runs were made at 10 min intervals from 10 to 120 min, except for one sample (nucleated at 577° C for 19 h) which was extended up to 360 min.

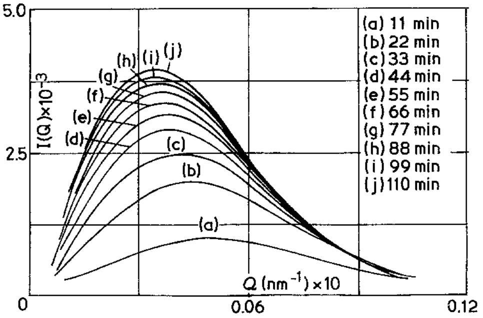

Figure 1 The SANS spectra at different crystallization times at 710° C for a sample nucleated at 634° C for 2 h.

3. Results and discussion

The general form of the scattering curves, which were obtained on a sample nucleated by a pretreatment at 634° C for 2 h, is shown in Fig. 1. The SANS intensity was almost negligible immediately after nucleation and corresponds to the zero-time curve (not shown). On heating *in situ* at 710° C, SANS intensity increases with particle growth giving sufficient scattered intensity to allow the scattering curve to be followed every few minutes. This was almost the general feature for all other samples nucleated at different temperatures. The important feature is that there is a pronounced maximum ($Q_{max} \sim 0.005$ nm at about 11 min) with the intensity falling towards zero at low Q [10]. A high density of the precipitating particles is responsible for an interference effect which produces a maximum, Q_m, in the SANS spectrum [8]. The maximum is always apparent, even for the shortest times for which the particle size is quite small, and remains stable during the growth period at higher crystallization times.

The values of Q_m are plotted against time of crystallization for the samples nucleated at 634° C for 2, 4 and 8 h in Fig. 2. It is seen that, for the 8-h sample, Q_m falls very rapidly during the early times of crystallization up to about 60 min, which is characteristic of a redissolution process of the smaller particles before the onset of growth, as discussed later. After 60 min, Q_m remains almost constant towards higher times indicating a growth process with about a constant number of crystallites. A very similar feature is noted for the other two samples treated at 634° C for 2 and 4 h, respectively.

The same plot is shown in Fig. 2 for the sample nucleated at 577° C for 19 h. It is seen that Q_m falls much more rapidly up to about 250 min

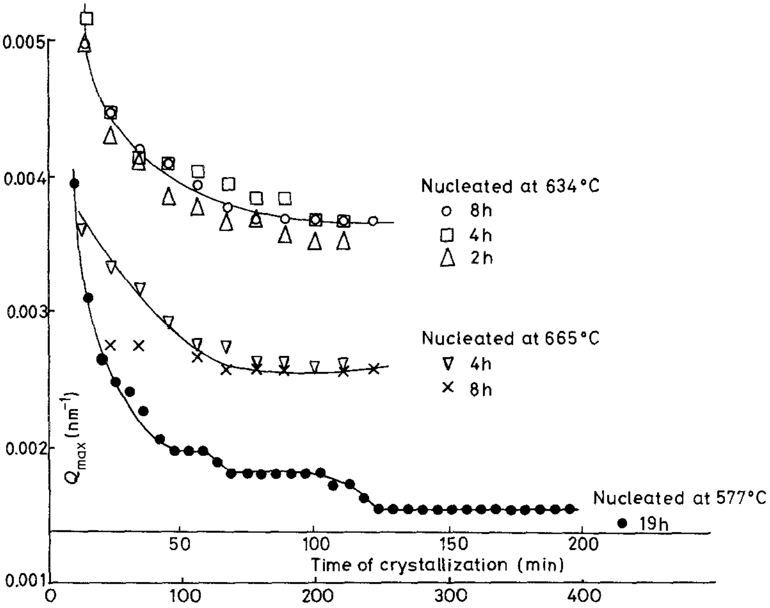

Figure 2 A plot of the values of $Q_{\max}$ against the time of crystallization for different nucleated samples; for each of the samples nucleated at 634 and 665° C (the upper time axis), a smooth line is drawn through all the points to show the trend with time.

and then saturates to a constant value towards higher time. For the sample nucleated at 665° C (4 and 8 h), Q_m does not decrease so rapidly and tends to saturate to an almost constant value before 60 min (see Fig. 2), because the growth process starts earlier. This is due to the overlap of the nucleation and growth processes at a nucleation temperature of 665° C [10].

The plots of the stabilized Q_m values as a function of nucleation conditions showed that the number density of particles (directly proportional to Q_m) increases with nucleation time, but in the case of treatments at 634 and 665° C saturation occurred after a few hours. The particle density at saturation was higher for the lower temperature of nucleation [10]. This behaviour has already been observed in a previous study on cordierite glass-ceramic [8]. The higher value of stabilized Q_m (at higher nucleation time) for lower nucleation temperatures, coupled with the observation that the time taken to reach saturation at the growth temperature (i.e. at 710° C) is longer for the samples treated at lower nucleation temperatures, suggests that there is competition between the nucleation and growth processes even at the nucleation temperatures, particularly noticeable for the 665° C treatment, as mentioned above (see also Fig. 2).

From the scattering curves three parameters were calculated:

(1) from the position of the maximum (Q_m) a rough estimate of the mean distance between the precipitates is obtained ($\bar{l} \simeq 2\pi/Q_m$);

(2) hence, the relative number density of the particles (i.e. the total number of particles per unit volume of the sample) is also obtained ($N \simeq (\bar{l})^{-3}$)

(3) the size of the particles is obtained from the Guinier plots on the higher Q side of the maximum. Within the limit of validity $QR_G \leqslant 1.2$, the scattering function $\overline{SQ}$ is related to the radius of gyration R_G according to $\overline{SQ} = \exp\,(-Q^2/R_G^{2/3})$ and $R_G = \sqrt{(3/5)}R_S$, where R_S is the radius of the "spherical" particle.

It has been mentioned before that a high density of precipitating particles is responsible for an interference effect, which produces a maximum (Q_m) in the SANS spectrum. From this Q_m, a characteristic wavelength $\bar{l}$ of density fluctuations has been calculated, which can be interpreted as the mean distance between the precipitates, and hence a relative density of precipitates is obtained. However, as pointed out by Guinier [11], this is only an approximate evaluation. For comparison purposes between the different samples, this relative number density can still be used as a parameter; this also gives an order of magnitude of the number of particles [10].

The parameter $\bar{l}$ is not plotted here, because it shows the same behaviour as Q_m. Parameters N and R_G are plotted against crystallization time in Figs 3 and 7 for the samples nucleated at 634° C for 2, 4 and 8 h. It is seen from Fig. 3 that N decreases rapidly up to 30 min, which can be considered due to the larger nuclei eating the smaller ones before growth starts, i.e. a redissolution process for the smaller particles as the larger ones continue to grow. After 30 min, N does not change significantly up to about 60 min, and then it approaches a constant value when there is a growth of stable nuclei. For the sample nucleated at 665° C, this change is less remarkable (see Fig. 3), because the saturation arrives at a lower time due to an earlier growth process. This is obviously due to the shorter time necessary for the attainment of stable nuclei (for the growth process) owing to the higher nucleation temperature.

The above behaviour can be described according to the following model. The importance of two-stage heat-treatment for the study of nucleation of glass-ceramics has been emphasized by James [7], who made two assumptions:

(1) after nucleation the glass contains an assembly of nuclei, some of which will have grown into small crystals, the large majority of which do not redissolve on heating to the second stage;

(2) the nucleation rate at the growth temperature is negligible.

If assumption 1 is correct, then varying the growth temperature should not radically change the number of crystals observed after a given nucleation heat-treatment. As a test, the sample nucleated at 577° C for 19 h was treated at three growth temperatures (i.e. at 680, 710 and 740° C). The values of N as a function of crystallization time at three different temperatures are shown in Fig. 4. Indeed, it is seen that N varies significantly at these temperatures invalidating assumption 1. For assumption 2, it was found that the as-annealed glass (blank glass) showed a high level of nucleation at the growth temperature, as mentioned later; this invalidates assumption 2. Therefore, in order to explain our results the situation is schematically represented in Fig. 5.

According to classic theory, the size of the critical nucleus increases with rising temperature. Consequently, a cluster of critical size at the lower nucleation temperature will not constitute a critical size at the higher growth temperature and will redissolve, because it is not thermodynamically stable. However, during the nucleation heat-treatment many of the nuclei that reach critical size will continue to grow and will attain a size larger than the corresponding critical size at the growth temperature, which will make them stable and enable them to grow to larger particles at this temperature at higher time. Therefore, the number of particles after a longer growth treatment would not be a good estimate of the number of nuclei formed at the lower nucleation temperature, because of the redissolution of many of the nuclei which were present in the original nucleated sample.

Now, let us say that T_1 is the temperature of nucleation (T_N) and T_3 is the temperature of crystallization (T_C). Therefore, according to Fig. 5, at T_N the total number of nuclei (N^*) with $r \geqslant r_1^*$ is stable. If we increase the temperature to T_C and make the particles grow, then the number of nuclei (N_1^*) with $r_1^* < r < r_3^*$ are

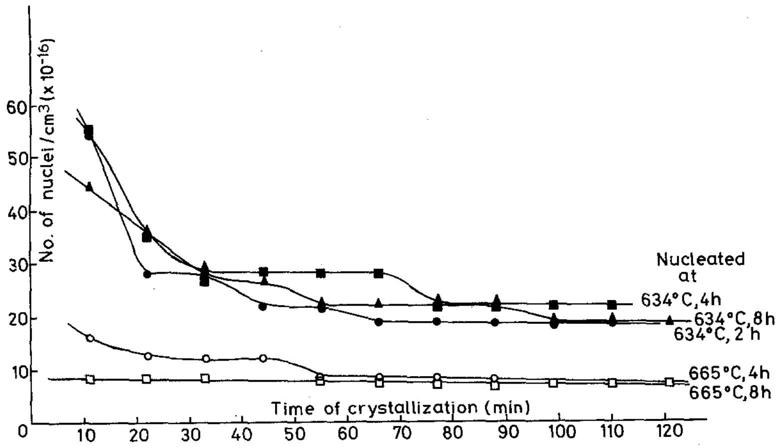

Figure 3 Variation of the number of nuclei with crystallization time for different nucleated samples.

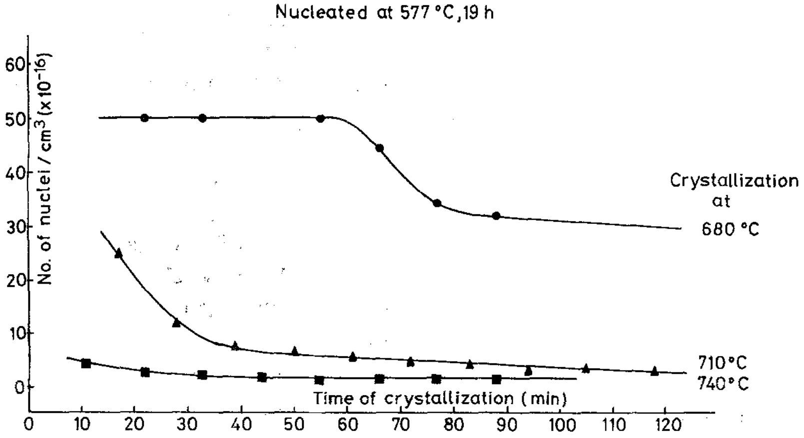

Figure 4 The number of nuclei as a function of time of crystallization for the sample nucleated at 577° C for 19 h at three different growth temperatures.

not stable, but the number of nuclei (N_2^*), which are stable at T_C, will grow at this temperature with $r \geqslant r_3^*$. This means that at T_C (i.e. at 710° C), $N^* = N_1^* + N_2^*$ as $t \to 0$, but as $t \to \infty$, $N^* = N_2^*$, because N_1^* number of nuclei have redissolved during the initial time of crystallization at T_C [12].

It should be mentioned that the nucleation rate of magnetite will depend on the level of supersaturation at the nucleation temperature, which is related to the amount of iron remaining dissolved in the glass matrix. As precipitation occurs the level of supersatuation will decrease with time and hence the nucleation rate will itself decrease and gradually approach zero. Thus the number of nuclei N should reach a constant maximum or saturation value, as observed in our case. Thereafter, Ostwald ripening effects may slowly take over. Thus N should reach a maximum simply due to all the available magnetite being eventually precipitated so that no new nuclei can be formed.

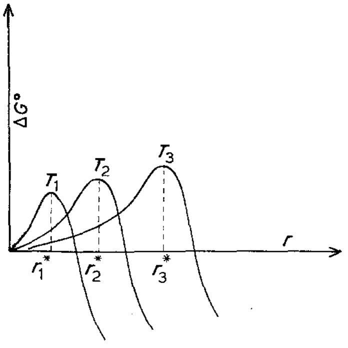

Figure 5 A schematic diagram of the free energy as a function of the radius of the nuclei at three different temperatures.

However, the saturation number of nuclei reached at a given temperature will depend on the rapidity of the overall precipitation process which is governed by the nucleation and growth rates, and so will vary strongly with temperature. Hence, use of a two-stage heat-treatment might have resulted in the redissolution of the magnetite particles into the glass with the disapperance of some particles and partial dissolution of others. The process proposed in this paper is "at least as probable" as the process of redissolution of subcritical nuclei at the growth temperature. However, in practice, the situation might be more complex than this model, considering the complex nature of the basalt glass [13].

It should be noted that there appear to be problems in applying a two-stage heat-treatment to the basalt glass. The two-stage method has been successfully applied to similar systems such as lithium disilicate where the crystal and the liquid phases have the same composition, and the growth temperatures used were not too high; although not apparently applicable to the more complex basalt glass, this method is still valid in other systems [7]. For the basalt glass, the two-stage heat-treatment was used to develop and then grow nuclei large enough to give a SANS spectrum [8, 10].

Now, if we assume that the number of nuclei remains almost constant between the respective nucleation temperatures (e.g. 610° C) and the growth temperature (i.e. 710° C), the value of N from the first run (i.e. at 11 min) can be taken as equivalent to the number of nuclei in the original nucleated sample. The values of N_t (where $t = 11$ min) are almost equal to N^* $(= N_1^* +$

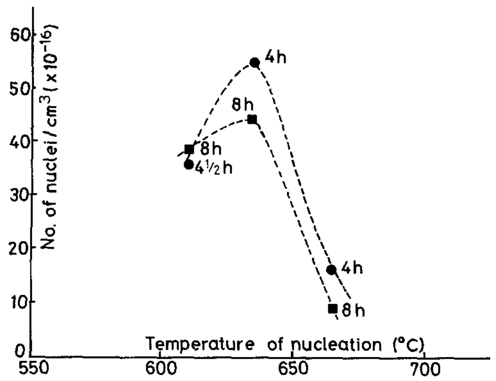

Figure 6 A plot of the number of nuclei against the temperature of nucleation.

$N_2^*)_{t\to 0}$. The values of N_t are plotted against nucleation temperature in Fig. 6. It is seen that the number of nuclei goes through a maximum at around 634° C, showing this to be the optimum temperature of nucleation.

The Guinier radius of the particles is plotted against time of crystallization in Fig. 7 for different samples. It is seen that, for the sample treated at 634° C for 2 h, R_G increases quite rapidly up to about 30 min, then it slowly increases up to about 60 min, showing the termination of the redissolution process of the smaller particles; finally, after 60 min, R_G reaches an almost constant value towards higher time indicating a ripening process. For the sample nucleated at 665° C (for 4 and 8 h), this change is less remarkable due to an earlier growth process, or rather due to an earlier termination of the redissolution process, owing to the higher nucleation temperature, rendering the attainment of the stable nuclei for the growth process at T_C easier.

In order to examine the growth process, a sample nucleated at 577° C for 19 h was crystallized at three different temperatures (i.e. at 680, 710 and 740° C). The plots of the cube of the diameter ($D^3 = 8R_S^3$) of the particles are shown against the crystallization time in Fig. 8*. It is seen that at 680° C the growth rate is very slow; the number of particles remains constant up to 60 min. This curve also shows that the redissolution of the smaller particles is almost negligible, because of the lower growth temperature [12]. At 710° C, the particle diameter increases rapidly up to about 80 min, and then it increases slowly but linearly with time, which indicates a ripening process.

At 740° C, the rapid increase of the particle diameter is up to 40 min only, and then it shows a linear behaviour towards higher time. It also shows that the redissolution process terminates earlier due to the higher growth temperature. In the linear region, the growth rate shows an increase between 710 and 740° C, which indicates that the crystallization of magnetite in the basalt glass is a thermally activated process.

It should be noted that, in the basalt glass, depending on temperature, there is an equilibrium (limiting) volume fraction of magnetite of less than 10%. Ostwald ripening only becomes predominant when the volume fraction is close to this limiting value. However, in some glass systems, e.g. the simpler system of lithium disilicate, Ostwald ripening would occur for crystallinities approaching 100%, and hence would be negligible for the low crystal volume fractions applicable in most of the nucleation studies of that system [7]. In practice "impingement" of crystals could occur at much lower crystallinities, rather than

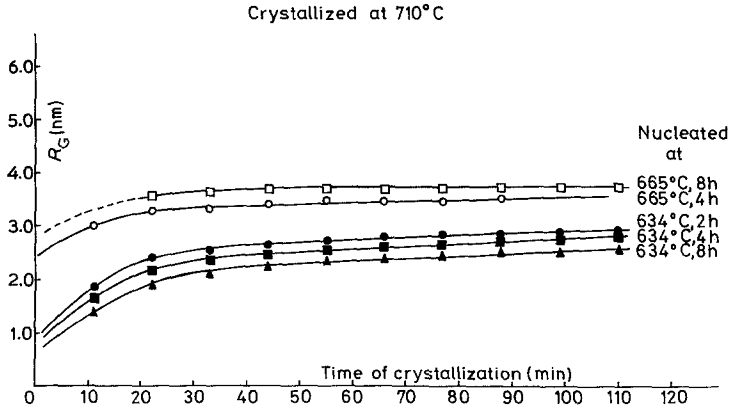

Figure 7 The Guinier radius as a function of crystallization time for different nucleated samples.

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*It should be noted that a similar plot of V (= $(4\pi/3)R_S^3$ against t_c could also be shown to indicate the ripening process.

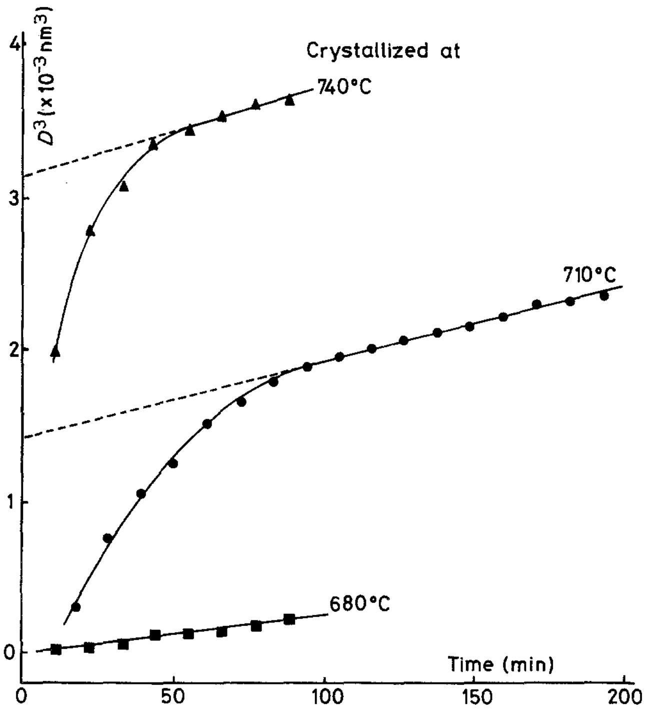

Figure 8 A plot of the cube of diameter of the crystallites against the time of crystallization at three different growth temperatures.

Ostwald ripening. Therefore, it should be borne in mind that Ostwald ripening is only important in certain circumstances [13].

As mentioned earlier, the blank glass when studied at 710° C showed sufficient scattered intensity with a maximum even at 11 min. The particle radius (R_S) varied between 3.77 and 6.13 nm between 11 and 120 min. This shows that the as-annealed glass itself was already nucleated with a high density of nuclei ($N = 19.0 \times 10^{16}$ at 11 min); this could have occurred either during quenching or during annealing. No measurement could be performed on this glass either at room temperature or at the annealing temperature (i.e. at 525° C) to determine the number and size of the nuclei in the original sample; this could not be done because of the contribution of the magnetic scattering together with that of nuclear scattering. However, Mössbauer measurements on this glass at 4 K showed that there is a short-range magnetic ordering of the Fe atoms of dimension 1.2 nm [2–5]. It is thought that this might have affected the overall nucleation and crystallization behaviour of this basalt glass.

4. Conclusion

The SANS spectra of a basalt glass-ceramic show a pronounced maximum (Q_m) due to an interparticle interference effect, and this maximum decreases with crystallization time (at 710° C) and remains stable during the growth period at higher times depending on the nucleation treatment. This indicates that the stabilized number density of crystallites saturates at different values with nucleation time; the saturation level is higher for the lower temperatures of nucleation. The number density at the shortest crystallization time is taken as equivalent to that in the different nucleated samples and this shows a maximum at 635° C (nucleation maximum). For any given nucleated sample, the number density decreases with the crystallization time at 710° C and saturates at higher time. This is interpreted as due to the redissolution of the smaller nuclei as the larger ones (stable nuclei) grow. The crystallization behaviour of this glass-ceramic tends to follow an Ostwald ripening mechanism at higher crystallization times. It has also been observed that the as-annealed glass itself already contained a high density of nuclei, which is thought to have affected the overall nucleation and crystallization behaviour of this basalt glass-ceramic.

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