

**EXPERIMENTAL TEST OF THE GENERAL THEORY OF TRANSFORMATION KINETICS:  
Homogeneous nucleation in a BaO · 2SiO<sub>2</sub> glass**

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The isothermal crystallization of a BaO · 2SiO<sub>2</sub> glass at 745 and 760 °C was studied by X-ray diffraction (XRD) and optical microscopy (OM). Two main observations were made. First, there is a large discrepancy between the experimental crystallinity determined by OM and XRD. The latter is initially equal to the former and gradually drops until a constant value of 64% is reached. This can be explained if one realizes that the spherulites are not entirely crystalline, some residual glassy phase remaining inside them. Second, the experimental and calculated (by the JMA equation) crystallinity versus time curves are displaced on the time axis. Explanations are given for the discrepancy.

The Johnson–Mehl–Avrami theory of transformation kinetics has been assumed to be valid and is intensively used by materials scientists to infer the various mechanisms by which phase transformations occur. However, no rigorous experimental proof for the theory has been given yet. It is the purpose of this letter to describe an attempt carried out in 1982 [1] to experimentally test this theory [2–4]. The general theory and its applications to glass crystallization will be reviewed in ref. [5]. For the limiting case of three-dimensional growth with constant nucleation ( $I$ ) and growth ( $U$ ) rates, the volume fraction of crystallized material ( $\alpha$ ) is given by

$$\alpha = 1 - \exp\left[-\frac{\pi}{3} U^3 I t^4\right], \quad (1)$$

where  $t$  is the time of isothermal treatment.

In the case of constant growth rate from a fixed number of nuclei,  $\bar{N}$ , eq. (1) is modified to give

$$\alpha = 1 - \exp\left[-\frac{4}{3}\pi\bar{N}U^3t^3\right]. \quad (2)$$

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Therefore, by measuring the crystal nucleation and growth rates at a certain temperature it is possible to calculate the volume fraction transformed with time and to compare it with experimentally determined values. The agreement between calculated and experimental values could prove the theory.

The BaO · 2SiO<sub>2</sub> glass was chosen because it exhibits volume nucleation of crystals having spherical geometry [6–9]. Two glasses were prepared: 33.3A (43.4 SiO<sub>2</sub>, 56.1 BaO, 0.3 SrO and 0.2 wt% of other impurities) and 33.2B (43.5 SiO<sub>2</sub>, 56.0 BaO, 0.3 SrO and 0.2 wt% of other impurities). The other impurities were mainly Na<sub>2</sub>O and Fe<sub>2</sub>O<sub>3</sub>. The crystal nucleation and growth rates of glass 33.3A were measured at 745 and 760 °C by the technique described in ref. [1]. The results are summarized in table 1.

The nucleation rates were constant from the beginning [1] but the growth rate curves exhibited large induction periods  $t_0$ , i.e. 16 500 and 5400 s at 745 and 760 °C, respectively. These induction times have been fully discussed in ref. [6]. Figure 1 shows the growth curves for glass 33.3A.

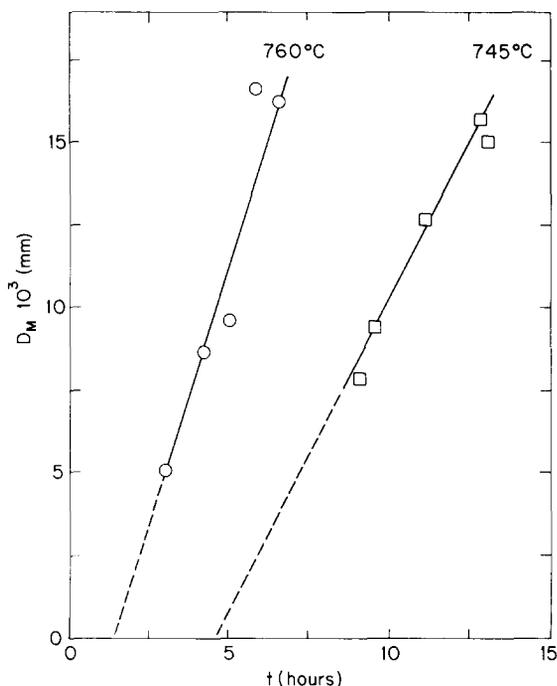


Fig. 1. Diameters of the largest spherulites in glass 33.3A at 745 and 760 °C.

Figure 2 shows the volume fraction of crystallized material for glass 33.3A measured by optical microscopy, and for glass 33.2B, measured by two techniques described in ref. [1], optical microscopy and X-ray diffraction. This figure also shows the theoretical curves obtained by substituting  $(t - t_0)$  for  $t$  in eqs. (1) and (2). Curve A was obtained by means of eq. (1) and reflects the situation where both  $I$  and  $U$  are constant at 760 °C. It must be realized, however, that appreciable growth of the nuclei only occurs after a certain induction period,  $t_0$ , and a large number of nuclei  $\ast \bar{N}$  was already formed when crystal growth begins. Assuming that nucleation is negligible after the growth process starts, the crystallinity values can be calculated by eq. (2) and are plotted as curve B. The actual transformed fraction is given by a combination of curves A and B and lies in between them.

Two main observations can be made: (1) There is a large discrepancy between the experimental crystallinity determined by optical microscopy and

$\ast \bar{N} = I \cdot t_0 \approx 10^6 \text{ mm}^{-3}$  at 760 °C.

Table 1  
Experimental nucleation and growth rates of glass 33.3A

	745 °C	760 °C
$I \text{ (m}^{-3} \text{ s}^{-1}\text{)}$	$4.61 \times 10^{11}$	$2.22 \times 10^{11}$
$U \text{ (m s}^{-1}\text{)}$	$3.24 \times 10^{-11}$	$4.63 \times 10^{-10}$

X-ray diffraction. The latter is initially equal to the former and gradually drops until a constant value of approximately 64% crystallinity is reached. This can be explained if one realizes that the spherulites are not entirely crystalline, some residual, uncrystallized, glass remaining inside them [6]. Results similar to those obtained by XRD here, have also been found for the spherulitic crystallization of polymers. For instance, Schultz [10] has shown that bulk polyethylene crystallizes very slowly after a volume fraction of about 60% crystallinity is reached. It is interesting that the maximum degree of crystallinity of the

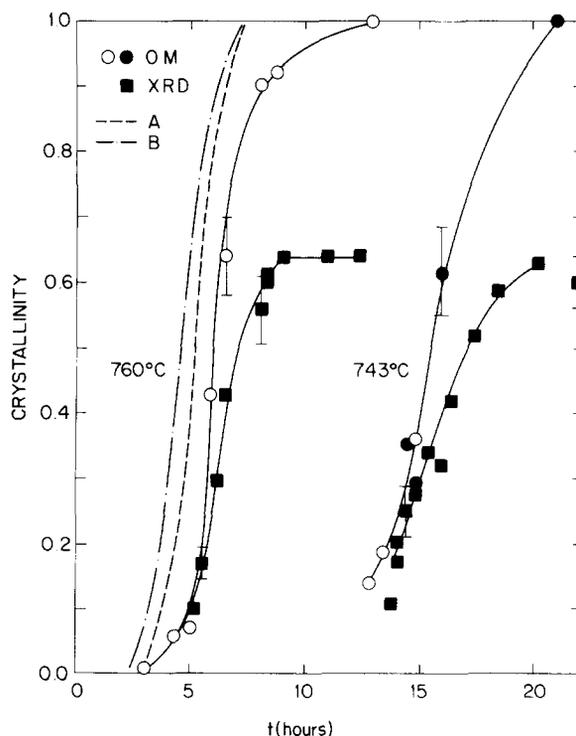


Fig. 2. Crystallinity as a function of heat treatment time. ○: Glass 33.3A, optical microscopy; ●: Glass 33.3B, optical microscopy; ■: Glass 33.3B, X-ray diffraction; - - - - -: Curve A, calculated by eq. (1); - · - · -: Curve B, calculated by eq. (2).

BS<sub>2</sub> glass, as measured by XRD at 745 and 760 °C, indicates that each spherulite is only 64% crystalline. (2) Figure 2 shows that the calculated and experimental curves at 760 °C are displaced on the time axis. At 745 °C, the theoretical curves (not shown for clarity) nearly coincide with the experimental curves for 760 °C, being a long way from the measured curves for the 745 °C treatment.

There are a number of reasons for the lack of agreement. The form of eqs. (1) and (2) shows clearly that very accurate experimental values of the shape factor, nucleation rate, and especially growth rate, are needed if comparison between theory and experiment is to be made. As discussed previously [1], however, the shape of the spherulites is irregular (nearly 'star-like') in the BS<sub>2</sub> glasses. Further complications arise because the spherulites are only about 64% crystalline and the first phase to nucleate (as small spheres) is the high-temperature form of barium disilicate (h-BS<sub>2</sub>), the stable low temperature form (l-BS<sub>2</sub>) nucleating on the spheres and growing as needles or 'spikes' [6]. Also the growth rates of the two forms of barium disilicate are quite different. The result is that spherulites grow very slowly in the early stages but after a certain period of time, when the spikes appear, the crystallinity develops much more rapidly. Finally, the slight composition shift of the parent glass from BaO · 2SiO<sub>2</sub> can have a large influence on the crystallization kinetics, especially in the latter stage, as was discussed

in ref. [5]. All these factors make a reliable test of the JMA equation very difficult in this system.

It is suggested, therefore, that another glass system be chosen with the following requirements: (1) the shape of the crystals can be clearly defined and determined; (2) crystal nucleation and growth in the volume of the glass predominates over surface nucleation and growth; (3) both nucleation and growth rates are constant with time; and (4) the stable phase precipitates in the supercooled liquid and is 100% crystalline.

Under these circumstances the JMA could be compared accurately with experiment. A more suitable system, Na<sub>2</sub>O · 2CaO · 3SiO<sub>2</sub>, was studied in ref. [5].

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