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# Kinetic Studies of the Crystallization of Vitreous Beryllium Fluoride

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The kinetics of the crystallization of vitreous beryllium fluoride were studied using the quantitative X-ray diffraction and calorimetric methods. Analysis of the data using the Johnson-Mehl-Avrami equation shows that the crystallization proceeds through spherulitic growth. The activation energy of 222 kJ $\text{mol}^{-1}$ was obtained from the temperature dependence of the crystallization rate using a modified Johnson-Mehl-Avrami equation.

Investigations of the crystallization of beryllium fluoride from various fluoroberyllate glasses have been reported by many workers. However, no quantitative analysis of the crystallization of the pure vitreous beryllium fluoride has been performed. Several years ago, Batsanova *et al.* made a rough estimate of the rate of crystallization of pure vitreous beryllium fluoride at three temperatures.[1] The crystallization data, however, could not be analyzed because the data were very scarce; their main objective was to study the structure of the glasses.

Recently, enthalpy increments of the crystalline, liquid, and vitreous beryllium fluoride were measured between 456 and 1083 K by the normal drop method and by the transposed-temperature drop method in our laboratory.[2,3] In the transposed-temperature drop calorimetry, it was observed that the vitreous phase turned into the crystalline phase between 623 and 800 K. Qualitatively, the rate of crystallization at about 730 K was faster than those below and above that temperature. We measured the rate of crystallization by a calorimetric method using the enthalpy data as well as an X-ray diffraction method, and studied the kinetics of crystallization in detail using the Johnson-Mehl-Avrami equation.

## Experimental

*Materials.* The beryllium fluoride used for this study was prepared from a commercial beryllium fluoride (Mitsuwa Kagaku Co., Ltd.) which was approximately 99.5 moles per cent pure. The sample was further purified by vacuum distillation at about 1070 K. Beryllium fluoride vapor was condensed onto the inner wall of a platinum crucible of about 800 K. Further analysis was not carried out for the purified beryllium fluoride. The vitreous sample was prepared by heating the sample in a sealed platinum container at 903 K and by then dropping it into the silver crucible at room temperature for rapid cooling. These vitreous samples were then submitted to the X-ray diffraction method and the calorimetric measurements.

*Calorimetric Method.* The calorimeter used for this study was a high-temperature calorimeter of the Calvet type which has been described previously.[4] The assembly of the apparatus is identical to that used previously in the normal drop method. However, the calorimeter was maintained at 730 or 760 K, and coarse silver powder was used instead of liquid mercury to aid heat conduction in the calorimeter cells. Although the electric furnace above the calorimeter had two different constant-temperature zones, only one of them was used for the present study. The vitreous sample (1.5 to 2.5 g) was loaded into a platinum container 8 mm in diameter, 45 mm in height, and 0.2 mm thick (2 to 2.5 g) and the top of the container was sealed by arc-welding in a glove box filled with nitrogen. The method of the quantitative determination of crystallization by the calorimeter is as follows. First, a vitreous sample of $n$ moles is inserted into the furnace and maintained at a certain temperature, $T_1$, for the time $t$ and then partially crystallized by the mole fraction, $X$. Then the sample is dropped into the calorimeter at another temperature, $T_0$, and crystallized completely in it. In this case, the measured heat, $Q$, contains both enthalpy increments, $\{H(T_1)-H(T_0)\}$, and the heat of crystallization,

$\{H(\text{gl},\ T_0)-H(\text{c},\ T_0)\}$;

$$Q = nX\{H(\text{c},\ T_1)-H(\text{c},\ T_0)\}+n(1-X)\{H(\text{gl},\ T_1)-H(\text{gl},\ T_0)\}+n(1-X)\{H(\text{gl},\ T_0)-H(\text{c},\ T_0)\} \tag{1}$$

This equation can be rewritten in this form;

$$X=\frac{\{H(\text{gl},\ T_1)-H(\text{gl},\ T_0)\}+\{H(\text{gl},\ T_0)-H(\text{c},\ T_0)\}-Q/n}{\{H(\text{gl},\ T_1)-H(\text{gl},\ T_0)\}+\{H(\text{gl},\ T_0)-H(\text{c},\ T_0)\}-\{H(\text{c},\ T_1)-H(\text{c},\ T_0)\}} \tag{2}$$

Thus, the mole fraction of the crystalline phase, $X$, can be determined by means of the measured heat, $Q$, and the enthalpy data obtained previously. The temperatures used for measuring the crystallization rate ranged from 626 to 821 K.

*X-Ray Diffraction Method.* The further quantitative determination of the crystallization was done by means of X-ray diffraction analysis, using the powder method. Use was made of a Tokyo Shibaura Electric ADG-102 or ADG-301 diffractometer furnished with a fine focus copper tube, a nickel filter, and a SU-021E or SU-321 high-temperature sample holder attached to a goniometer, GD-2 or GD-3. The vitreous sample was grounded to 200 mesh in an agate mortar. Then the powder sample (0.1 g) was pressed on a platinum plate under a pressure of 8 MPa. The platinum plate with the sample was put on the heater in a high-temperature sample holder. Before heating, the sample was evacuated at 373 K for a day to evaporate the adsorbed water. Then the sample was heated at various constant temperatures. It took 5 min for the sample to attain thermal equilibrium in each heating. The integrated intensity of the strongest diffraction peak (101) at 27.5 degrees in $2\theta$ was counted every two minutes. After these measurements, the sample was rapidly cooled to room temperature and then again heated at 730 K (optimum temperature of crystallization) for one hour in order to crystallize it completely. Then the sample was brought to the original temperature, and the intensity of the diffraction peak of this 100-per-cent-crystallized sample was counted in order to confirm the normalization. During these processes, the sample on the platinum plate was left as it had been in the high-temperature sample holder *in vacuo*. Mechanical mixtures of vitreous and crystalline powder of various compositions were prepared for the calibration experiment. The intensity of diffraction was proportional to the composition of the crystalline part within ±5 per cent. The temperatures for measurement ranged from 630 to 750 K.

## Results and Discussion

The volume fraction of the crystallized part obtained by both the X-ray diffraction and calorimetric methods is shown at various temperatures as functions of the time in Fig. 1. The crystallization starts almost without induction time at each temperature and proceeds rapidly up to the 0.9-volume fraction, after which it proceeds very slowly. Although the temperature range covered is different in each method, the crystallization rate shows a maximum around 720 K and decays both below and above that temperature. The temperature ranges which the two experiments covered were different because (1) the calorimetry mainly covered higher-temperature ranges, since the scatter of the data is large at low temperatures, and so the time consumption for every experimental point became formidable and (2) the X-ray diffraction method covered low-temperature ranges since, because of the temperature inertia of the sample furnace, the crystallization during the heating period (especially around 720 K with a maximum crystallization rate) was too much to be neglected compared with that in time intervals at the aimed-for temperature higher than 720 K.

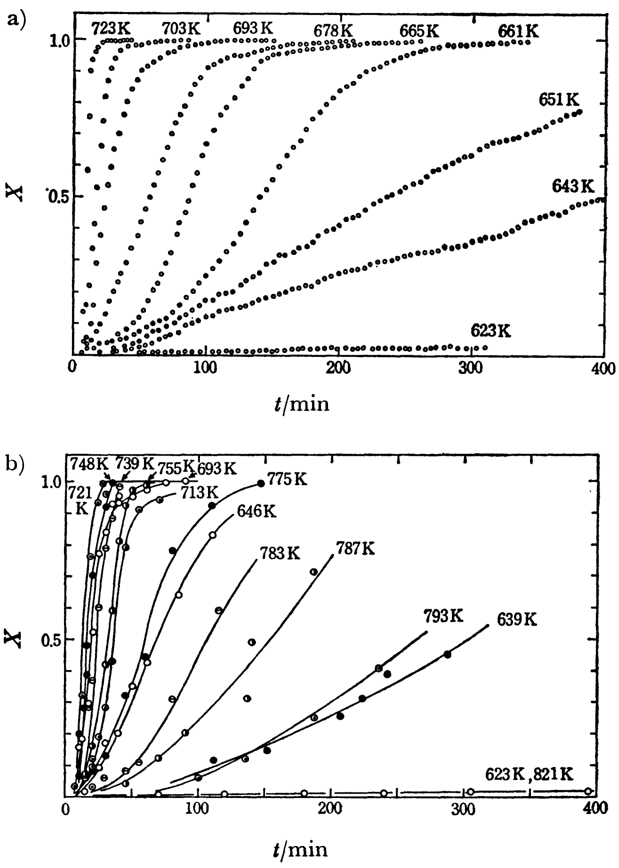

Fig. 1. a) Variation of crystallinity with time by the X-ray diffraction.

b) Variation of crystallinity with time by the calorimetric method.

The Johnson-Mehl-Avrami (J-M-A) equation has been developed to describe the kinetics of processes where nucleation and growth occur together.[5,6] Application of the J-M-A expression enables one to predict the volume fraction of a new phase that will form as a function of time, if suitable information about the nucleation and growth rates is available or if they can be assumed:

$$X = 1 - \exp\left\{-\int_{t'=0}^{t'=t} gIG^n(t-t')^n \mathrm{d}t'\right\} \tag{3}$$

Eq. (3) is the general form of the J-M-A equation: $g$ is a shape factor; $I$, the nucleation rate; $G$, the growth rate; $t'$, the time at which a given particle is nucleated; $n$, an integer which depends on the dimensionality of the growth mechanism, and $X$, the volume fraction of the new phase. In deriving this equation, the growth rate was assumed to be independent of the time. Eq. (3) may be integrated only by making specific assumptions about the variation in $I$ with the time. If $I$ is assumed to be independent of the time, Eq. (4) is obtained by integrating Eq. (3):

$$X = 1 - \exp\{-gIG^n t^{n+1}/(n+1)\} \tag{4}$$

If the nucleation rate, $I$, is assumed to be a rapidly decreasing function of the time—if, that is, the nucleation is completed at an early stage in the reaction, $I$ may be replaced by the number of nuclei, $N_0$;

$$X = 1 - \exp(-gN_0G^n t^n/n) \tag{5}$$

For the present system, the latter assumption seems to be suitable since it has been found in our laboratory that, even at the same temperature, the crystallization rate of the "quenched glass," which has been quenched to room temperature before it is brought to the growth temperature, is very much greater than that of the "non-quenched glass" prepared by cooling a molten sample directly to the temperature of the growth experiment. This implies that the numbers of nuclei in the unit volumes of both the glasses are quite different at the beginning of the reaction. Thus, the nucleation in the quenched glass seems to have finished in an early stage of the reaction. Leadbetter and Whycherley also observed that the quenched glass of beryllium fluoride contained a number of small bubbles lined with a white powder which was identified with the quartz form of beryllium fluoride by means of X-ray diffraction.[7] When $gN_0G^n/n$ in Eq. (5) is set equal to $k_c$, defined as a crystallization rate constant, one obtains Eq. (6), which is the same form as the so-called Kolmogorow-Avrami equation:[8]

$$X = 1 - \exp(-k_c t^n) \tag{6}$$

By taking the double logarithm of both sides of Eq. (6), one gets the following equation:

$$\ln\ln\left(\frac{1}{1-X}\right) = n\ln t + \ln k_c \tag{7}$$

If the left-hand side of Eq. (7) is plotted against ln $t$, one may know the growth morphology of the transforming phase from the slope of the line, $n$. The curves

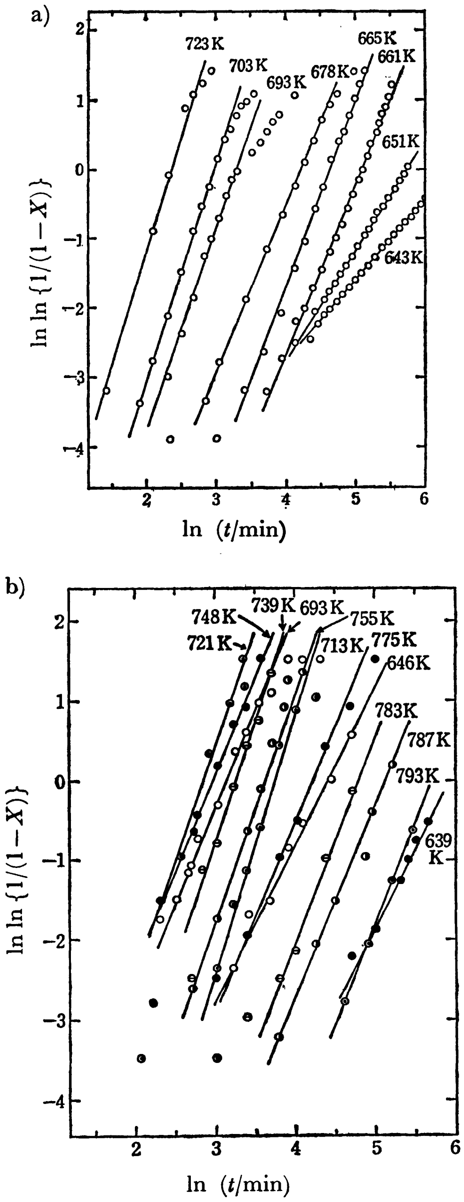

Fig. 2. a) Variation of ln ln $(1/(1-X))$ with ln $t$ by the X-ray diffraction.
b) Variation of ln ln $(1/(1-X))$ with ln $t$ by the calorimetric method.

Table 1. Experimental slopes, $n$, in Eq. (6) and the time required for samples to reach 0.5-volume fraction, $t_{X=0.5}$.

| $T$/K | $n$ | $t_{X=0.5}$/min |
|---|---|---|
| | X-ray diffraction | |
| 723 | 3.2 | 10 |
| 703 | 3.1 | 16 |
| 693 | 3.0 | 23 |
| 678 | 2.5 | 56 |
| 665 | 2.7 | 88 |
| 661 | 2.5 | 142 |
| 651 | 1.7 | 236 |
| 643 | 1.1 | 390 |
| | calorimetric method | |
| 793 | 2.5 | 265 |
| 787 | 2.4 | 155 |
| 783 | 2.6 | 105 |
| 775 | 2.4 | 60 |
| 755 | 2.8 | 32 |
| 748 | 2.6 | 15 |
| 739 | 3.1 | 22 |
| 721 | 2.9 | 13 |
| 713 | 3.1 | 37 |
| 693 | 2.5 | 20 |
| 646 | 1.9 | 69 |
| 639 | 2.1 | 304 |

are shown in Fig. 2. The values of the initial slopes of the curves before impingement occurs are presented in Table 1. Within the limits of experimental error, the values for the sample above 660 K are approximately 3, as is to be expected if the crystal growth during these periods is spherulitic in nature and if all the nuclei have been constituted at the beginning of the transformation. Below 660 K, the values of the slopes of the lines decrease to 2 or 1. Therefore, the growth mechanisms seem to be different from each other above and below this temperature, although much more information will be necessary before any conclusion can be drawn. A phenomenon similar to this was observed in the crystallization study of vitreous selenium.[9] Crystallization study by means of an electron micrograph or a photomicrograph is desirable to determine the more exact growth morphology of vitreous beryllium fluoride.

The crystallization rate constant was determined from the plots of Eq. (7) using the values of $n$ and $t_{X=0.5}$, which is referred to the time of $X=0.5$. As has been mentioned above, $k_c$ was defined as $gN_0G^n/n$. Therefore,

$$\ln k_c(T) = \ln (gN_0(T)/n) + n \ln G(T) \tag{8}$$

As Strnad and Douglas noticed, it is implicitly assumed that the nuclei formed during the low-temperature treatment are not redissolved on heating to the growth temperature and, further, that the growth temperature must be chosen so that the nucleation rate at the growth temperature is negligible.[10]
Thus,

$$N_0(T) = \text{constant.}$$

Then, as the first term on the right-hand side of Eq. (8) is independent of the temperature, one gets Eq. (9) when the temperature of 693 K is taken as the standard temperature:

$$\begin{aligned}\ln G'_{\text{exp}}(T) &\equiv \ln \{G(T)/G(693\text{ K})\}\\ &= 1/n \ln\{k_c(T)/k_c(693\text{ K})\}\end{aligned} \tag{9}$$

where $G'_{\text{exp}}(T)$ is defined as the relative growth rate. The logarithm of $G'_{\text{exp}}(T)$ is plotted against $1/T$ in Fig. 3.

On the other hand, Hillig and Turnbull proposed a semi-empirical equation for the growth rate.[11] Further, Ainslie *et al.* reduced this equation to Eq. (10) for vitreous silica using the Stokes-Einstein relation and other simple approximations:[12]

$$G(T) = f\Delta h(T_m - T)/(3\pi a_0^2 \eta T_m) \tag{10}$$

where $f$ is the fraction of crystal surface sites to which

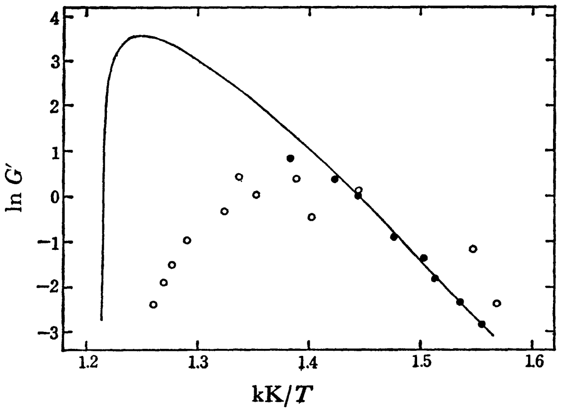

Fig. 3. Temperature dependence of relative growth rate.
——: Calculated from Eq. (11), ○: by calorimetric method, ●: by X-ray diffraction.

molecules can be attached in the growth process, $\Delta h$ is the heat of fusion per molecule, $T_m$ is the melting temperature, $a_0$ is the jump distance, and $\eta$ is the viscosity. As a matter of fact, Wagstaff found from his experimental data for vitreous silica that the crystal-growth rate could be represented by an equation of the same type as Eq. (10).[13] This temperature dependence of the growth rate can be applied to vitreous beryllium fluoride since it is very similar to vitreous silica in structure and in thermodynamic properties, especially the entropy of fusion. The viscosity of beryllium fluoride was measured over 10 orders of magnitude; it was found that it could be represented by an Arrhenius-type equation.[14,15] Using this temperature equation for $\eta$ in Eq. (10), one obtains the relative growth rate, $G'_{\text{theor}}(T)$:

$$\ln G'_{\text{theor}}(T) \equiv \ln\{G(T)/G(693\text{ K})\}$$
$$= -Q_\eta/RT + \ln(T_m - T) + 35.074 \qquad (11)$$

where $R$ is the gas constant and where $Q_\eta$ is the activation energy for the viscous flow, 230±12 kJ mol$^{-1}$.[15] The logarithm of $G'_{\text{theor}}(T)$ is also shown in Fig. 3. The two curves are consistent in the points that both have a maximum and behave similarly at both ends (especially at the lower temperatures). However, the temperature of the maximum is different by about 80 K and the behavior of decreasing after the maximum is dissimilar on the high-temperature side. Considering the consistency of the low-temperature side, it seems reasonable that the discrepancy cited above is attributable to the assumption of a constant $N_0$. It is interesting to note that the discrepancy can be eliminated if the nuclei partly redissolve on heating above 720 K and that the ratio of the number of the nuclei diminished to $10^{-1}$, $10^{-3}$ and $10^{-6}$ at 730 K, 760 K, and 795 K respectively compared with that of 693 K.

Further, if the temperature dependence of the growth rate reported by Ainslie *et al.*, Eq. (10), is substituted into Eq. (5), one gets:

$$X = 1 - \exp\{(-gN_0t^n/n)[A(T_m - T)\exp(-Q_\eta/RT)]^n\} \qquad (12)$$

where $A$ is equal to $f\Delta h/(3\pi a_0^2 T_m C)$; here $C$ is a pre-exponential factor in the viscosity expression. At a constant degree of crystallization, $\alpha$, one obtains Eq. (13) by rearranging the terms of Eq. (12) and by taking the logarithms of both sides:

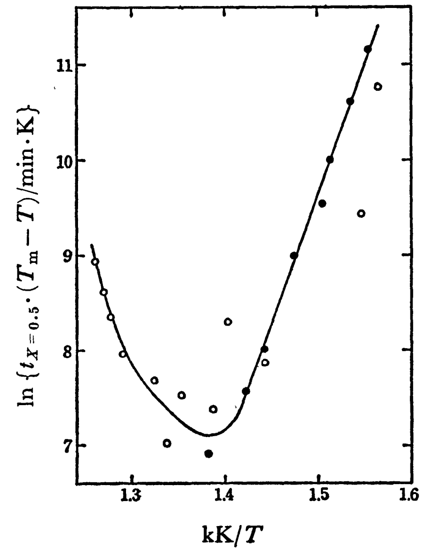

Fig. 4. Temperature dependence of $\ln\{(T_m - T)\cdot t_{X=0.5}\}$.
○: By calorimetric method, ●: by X-ray diffraction.

$$\ln\{t_{X=\alpha}\cdot(T_m - T)\}$$
$$= Q_\eta/RT - \frac{\ln(A^nN_0g/n)/\ln\left(\frac{1}{1-\alpha}\right)}{n} \qquad (13)$$

If the logarithm of the temperature difference, $(T_m - T)$, multiplied by the time needed to form a given volume fraction of the crystalline phase is plotted against $1/T$, when $N_0(T)$ is independent of the temperature, a straight line should be obtained with a slope of $Q_\eta/R$. The logarithm, $\ln\{t_{X=0.5}(T_m - T)\}$, is plotted as a function of $1/T$ in Fig. 4. We thus obtained, instead of a straight line, a curve which has a minimum value at about 720 K. However, a linearity holds true below 720 K. The activation energy for the viscous flow is evaluated from the slope of the straight line. The activation energies were obtained also when the temperature dependence of the times of $X=0.4$ and the 0.6-volume fraction were analyzed. The activation energy was estimated to be 222±4 kJ mol$^{-1}$ as the mean value from the slopes of the lines of $X=0.4$, 0.5 and 0.6. This value is in excellent agreement with that obtained by the viscosity measurement, 230±12 kJ mol$^{-1}$. Above 720 K, depending on the crystallization temperature, some of the nuclei seem to redissolve on heating and seem not to contribute to the growth. This will correspond to the "deactivation of the crystallization centers" described in Dzhalilov's paper.[9]

## References

1) L. R. Batsanova, G. S. Yurev, and V. P. Doronina, *Zh. Strukt. Khim.*, **9**, 79 (1968).
2) S. Tamura and T. Yokokawa, This Bulletin, **48**,

2542 (1975).

3) S. Tamura, T. Yokokawa, and K. Niwa, *J. Chem. Thermodynamics*, **7**, 633 (1975).

4) T. Maekawa, T. Yokokawa, and K. Niwa, *ibid.*, **3**, 143 (1971).

5) W. A. Johnson and R. F. Mehl, *Trans. AIME*, **135**, 416 (1939).

6) M. Avrami, *J. Chem. Phys.*, **7**, 1103 (1939).

7) A. J. Leadbetter and K. E. Wycherley, *Phys. Chem. Glasses*, **12**, 41 (1971).

8) A. N. Kolomogorov, *Izv. Akad. Nauk SSSR, Ser. Mat.*, **3**, 355 (1937).

9) S. U. Dzhalilov, *Russ. J. Phys. Chem.*, **39**, 1376 (1965).

10) Z. Strnad and R. W. Douglas, *Phys. Chem. Glasses*, **14**, 33 (1973).

11) W. B. Hilling and D. Turnbull, *J. Chem. Phys.*, **24**, 914 (1956).

12) N. G. Ainslie, C. R. Morelock, and D. Turnbull, "Symposium on Nucleation and Crystallization in Glasses and Melts," ed. by M. K. Reser, G. Smith, and H. Insley, The American Ceramic Society (1962), p. 97.

13) E. E. Wagstaff, *J. Amer. Ceramic Soc.*, **52**, 650 (1969).

14) C. T. Moynihan and S. Cantor, *J. Chem. Phys.*, **48**, 115 (1968).

15) S. V. Nemilov, *Fiz. Tverd. Tela*, **6**, 1375 (1964).