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Note

THE NON-ISOTHERMAL DEVITRIFICATION OF SODIUM METAPHOSPHATE GLASS

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In previous papers [1–3] methods for evaluating the kinetic parameters of crystal growth in inorganic glasses from DTA curves were proposed by the authors. These methods were used to study the devitrification kinetics of different glass systems and the results were in good agreement with those obtained by alternative methods.

In this paper the non-isothermal devitrification of $NaPO_3$ glass has been studied in order to show that in some cases two different interpretations can be drawn from the experimental DTA results. It has been shown that the correct interpretation can be selected if SEM investigations are also carried out.

EXPERIMENTAL

The glass was prepared by melting $NH_4H_2PO_4$ and Na_2CO_3 pure reagents in a Pt crucible in an electric oven.

The melt was cast with a high cooling rate in an Fe mould. The as-quenched glass was cut to obtain samples of small bulk (suitable for the size of the sample holder of the DTA apparatus).

Differential thermal analysis (DTA) curves of ~ 90 mg specimens at different heating rates (5–20°C min^{-1}) were recorded in air. Powdered Al_2O_3 was added to improve the heat transfer between bulk samples and the sample holder. A Netzsch thermoanalyzer (Model 404M) was used for the analysis, with powdered Al_2O_3 as reference material.

Bulk samples devitrified at 400°C for 1 h were examined by scanning electron microscopy (SEM) using a Cambridge Stereoscan 100 apparatus.

RESULTS AND DISCUSSION

When a glass is heated in a DTA furnace, its heat of crystallization is evolved and an exothermic peak appears on the DTA curve.

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The extent of crystallization, α, can be related to the absolute temperature, T, by the following equation proposed by Matusita and Sakka [4]

$$-\ln(1-\alpha)=\frac{A}{\beta^{n+b}}\exp\left(-\frac{nE}{RT}\right) \tag{1}$$

where E is the activation energy for the crystal growth, β the DTA heating rate and A a constant. The Avrami parameter, n, is related to the crystal shape (rod-like, $n=1$; plate-like, $n=2$; spheres, $n=3$). If the number of nuclei does not change with heating rate, then $b=0$, and if the number of nuclei is inversely proportional to the DTA heating rate, then $b=1$.

From eqn. (1) the following two equations can be derived [1,2,5,6]

$$\ln\beta=-\frac{n}{n+b}\frac{E}{R}\frac{1}{T_\mathrm{p}}+\text{const} \tag{2}$$

$$\ln\Delta T=\frac{nE}{R}\frac{1}{T}+\text{const} \tag{3}$$

The first equation is based on the assumption that at the temperature T_p (of the DTA crystallization peak), the crystallization degree, α, reaches the same specific value independent of the heating rate [5]. The second equation is based on the assumption that in the initial part of the DTA crystallization peak, the change in temperature T has a much larger effect on the change in the ΔT deflection from the baseline compared with the change in α [6].

By plotting ln β vs. $1/T_\mathrm{p}$ (Fig. 1) and ln ΔT vs. $1/T$ (Fig. 2), two straight lines were obtained.

The values of their slopes were

$$\frac{n}{n+b}\frac{E}{R}=11\ \mathrm{K}^{-1}\ \text{and}\ \frac{nE}{R}=22\ \mathrm{K}^{-1}$$

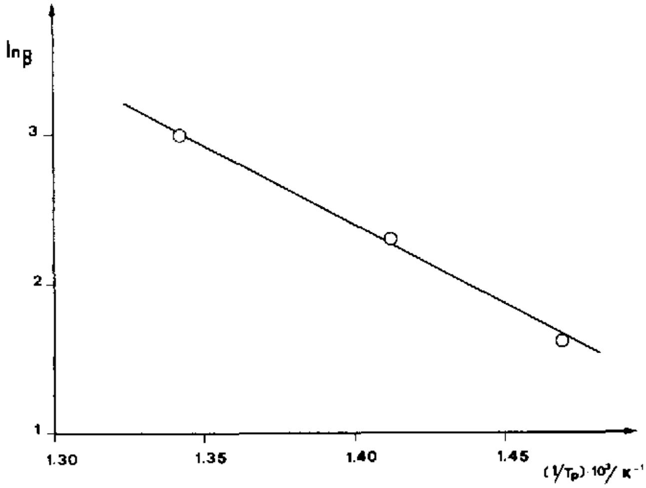

Fig. 1. Plot of ln β vs. $1/T_\mathrm{p}$.

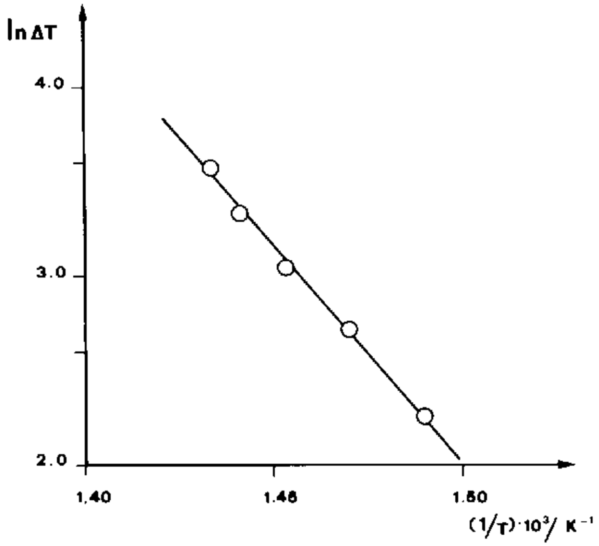

Fig. 2. Plot of ln ΔT vs. $1/T$.

These results can be interpreted in two different ways

$E = 44$ kcal mol^{-1} and $n = 1$ (rod-like crystals) if $b = 1$

$E = 22$ kcal mol^{-1} and $n = 2$ (plate-like crystals) if $b = 0$

To select the right interpretation, bulk samples of glass devitrified at 400°C for 1 h were examined by SEM. The shape of the crystals shown in Fig. 3 makes the first interpretation unacceptable. Moreover, the value of the activation energy for crystal growth ($E = 22$ kcal mol^{-1}) is very close to that obtained by Westman and Krishna Murty [7] using a two-dimensional paper

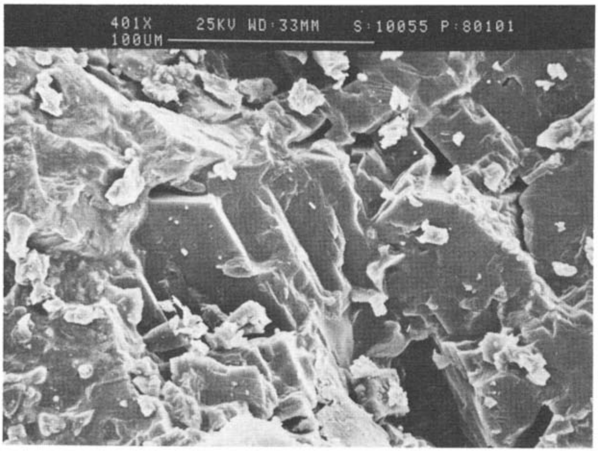

Fig. 3. SEM micrograph (400×) of a bulk sample of devitrified $NaPO_3$ glass.

chromatography method ($E = 20$ kcal mol^{-1}). The value $n = 2$ can be explained assuming that successive layers of equal thickness form on the growing crystal and that it is necessary to complete one shell before the next shell begins to form [8].

CONCLUSIONS

From the experimental results the following conclusions can be drawn:

(a) for devitrification of the $NaPO_3$ glass, DTA methods are unable to evaluate the crystallization mechanism and the value of activation energy of crystal growth if another technique is not used to select the correct interpretation of the experimental results;

(b) in the glass examined the crystals grow from nuclei whose numbers are independent of the heating rate;

(c) the activation energy of the crystal growth is $E = 22$ kcal mol^{-1} and the Avrami exponent is $n = 2$.

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