

Crystallization of phosphate glasses

Part 1 *Compositional effects*

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A microscopical technique has been used to determine rates of crystallization (devitrification) of some lead phosphate and potash lead phosphate glasses. The devitrification rate is viscosity dependent, and compositional effects were resolved from viscosity effects by the use of isoviscous rate plots, which were obtained by plotting the half-time of crystallization against ΔT , where ΔT is the difference between the crystallization temperature and the transformation temperature of the glass.

1. Introduction

Above the transformation range most inorganic glasses are unstable and over extended periods a crystalline phase may form in the glass melt. These crystals may be of different chemical composition from the bulk glass. The crystallization process is frequently referred to as devitrification of the glass. Whilst studies of crystal growth in silicate glasses have been reported [1], little seems to have been published on the crystallization of phosphate glasses.

A study has now been made of the crystallization of some simple glasses containing various amounts of phosphorus and lead oxides, and phosphorus, lead and potassium oxides. The structure, and hence the properties of such a glass, depend not only upon the nominal composition, but also upon the manner in which the glass was refined. This has been shown to be due to the removal of hydroxyl groups from the melt on prolonged refining of the glass with the elimination of water [2]. Thus the comparison of crystallization rates between glasses is complicated by the number of interdependent variables. The effect of composition on the crystallization of the glasses is discussed in this paper, whilst the effect of refining is described in a subsequent paper.

2. Experimental

2.1. Apparatus

Studies of the crystallization of silicate glasses necessitate the use of high temperatures (1000°C), with the attendant difficulties of working at these

temperatures. However, the lead phosphate and potash lead phosphate glasses used in these studies have low transformation temperatures, and devitrification occurs within the range 200 to 480°C. This made it possible to use a simple microscopical technique to measure the overall rate of crystallization, a method previously used for crystallization studies on organic high polymers [3]. The apparatus consists essentially of two joined hot-stages insulated from each other and held at different constant temperatures. Normally, one stage (the fusion stage) may be held above the melting point, whilst the other stage (the crystallization stage) is held at a temperature below the melting point where the rate is to be determined. The two stages are joined by a shallow channel allowing rapid transfer of the sample from the fusion to the crystallization stage. In this work the fusion stage remained at room temperature and the sample was raised to the crystallization temperature on entering the crystallization stage. The whole assembly was mounted on a polarizing microscope such that the sample was viewed when in the crystallization stage. The temperature of the crystallization stage is controlled by a Eurotherm stepless indicating controller with proportional/integral/derivative control. A thermocouple is used as a detector embedded in the metal plate of the hot-stage, and the temperature of the stage is indicated by a second thermocouple connected to a recorder; the measured temperature being calibrated using simple compounds with sharp melting points.

The crystallization process may be followed by monitoring the light transmitted by the sample, when observed between crossed polars, by means of a photoconductive cell the output of which is fed into a chart recorder to give a continuous record of light transmission. For a given sample viewed under constant conditions, the transmitted intensity is proportional to the degree of crystallinity of the sample, unless a change of birefringence of the crystals occurs. The maximum light transmission is taken to indicate the completion of primary crystallization. The half-time of crystallization $t_{1/2}$, is defined as the time taken to reach the half-height of the transmission curve, and includes the induction time (if any). The induction period is defined as the time between the sample reaching the crystallization temperature and the onset of a detectable amount of crystallinity. It should be noted that this method does not allow any estimate of the degree of crystallinity of a sample, only a measure of the time to reach equilibrium crystallinity at the crystallization temperature.

Samples were prepared by placing a small quantity of freshly ground glass between two microscope coverslips and melting with a small bunsen burner. The sample was pressed flat as soon as the (lead phosphate) glass was molten, and immediately quenched to room temperature by placing on an aluminium block. The sample was then placed in the hot-stage, which was controlled at the crystallization temperature, T_c , to an accuracy of 0.5°C . The transformation temperature of the glasses were determined by differential thermal analysis using a heating rate of $20^\circ\text{C}/\text{min}$ and a silica reference sample.

Identification of the crystalline phase was attempted by finely grinding a devitrified sample and placing the powder in a thin walled glass tube. An X-ray powder diffraction picture of this sample was obtained using a Unicam S25 X-ray camera mounted on a Philips generator. The exposure was taken using Ni filtered $\text{CuK}\alpha$ radiation and Ilford Industrial G X-ray film. The sample was rotated during exposure to ensure the necessary randomization of the crystallites to produce uniform diffraction rings. The diffraction patterns obtained were compared with those listed for known compounds in the ASTM data files (a standard compilation of known structures and compounds).

Melt viscosity measurements were performed on selected glasses over a range of temperatures (260 to 350°C) using a Weissenberg rheogonio-

meter operating in oscillatory shear mode.

2.2. Materials examined

Crystallization studies were made on two series of glasses. The first consisted of three glasses containing 60 P_2O_5 , 40 PbO ; 65 P_2O_5 , 35 PbO ; and 70 P_2O_5 , 30 PbO mol % phosphorus pentoxide-lead oxide respectively, and the second series comprised glasses containing 60 mol % phosphorus pentoxide and various proportions of lead oxide and potassium oxide totalling 40 mol %. Both series were prepared by premixing the required proportions of materials and furnacing at approximately 700°C for 45 min.

Subsequently, a third series of glasses was investigated. This series consisted of four glasses containing 70 mol % phosphorus pentoxide, with lead oxide and potassium oxide in varying proportions totalling 30 mol %. These glasses were prepared by a modified procedure in which the constituents were mixed in the required proportions and subjected to a premelt treatment at 450°C for 4 h before furnacing for 1 h at 700°C . Special care is, therefore, necessary in making comparisons between the different series.

The transformation temperatures obtained showed a scatter of values about a curve relating T_g to composition. As the degree of condensation of these glasses is a function of refining time, comparatively large fluctuations in T_g could arise from small variations in such a short refining time. Samples chosen for crystallization studies had, where possible, T_g 's falling on or close to the average curve, in an attempt to eliminate atypical glasses that might show spurious crystallization rates arising from different degrees of condensation.

The compositions of the glasses investigated are listed in Table I, together with the transformation temperatures (T_g) and melt viscosity data for some glasses.

3. Results

3.1. Morphology of the crystalline phase

The morphology of the crystalline aggregates formed in the low softening point glasses bears some resemblance to the spherulitic texture frequently observed in polymers and some simple organic compounds. Needle-shaped crystals form in aggregates, often growing radially from a central nucleus to form a spiky spherulite, or needle-shaped aggregates grow in a few directions only from the central nuclei and cross

TABLE I

Glass composition (mol %)			T_g ($^{\circ}\text{C}$)	T_{10^5} ($^{\circ}\text{C}$) T at $= 10^5 \text{ N sec m}^{-2}$	$T_{10^5} - T_g$ ($^{\circ}\text{C}$)
P_2O_5	PbO	K_2O			
70	30	—	145		
65	35	—	164		
60	40	—	220	340	120
60	30	10	201		
60	25	15	200	303	103
60	18	22	187	282	95
60	10	30	173	279	106
60	5	35	170		
60	—	40	158	257	99
70	30	—	133		
70	20	10	142		
70	10	20	176		
70	—	30	113		

neighbouring growths to form a criss-cross pattern. Unlike polymeric spherulites, which grow until impingement with neighbours prevents further growth, the crystalline aggregates in the glasses frequently terminate before reaching a neighbouring growth; presumably because of a dearth of suitable molecules at the growing interface, either due to the difficulty in transporting more there, or because all the available crystallizable units have been used. It is not surprising that the growth habit of the crystal phase should vary from glass to glass although this change in habit does not necessarily imply a change in chemical structure of the crystalline phase. A typical crystalline aggregate is shown in Fig. 1 resembling the so-called "wheat-sheaf" aggregate observed in polymers, which is considered to be a spherulite precursor.

3.2. Crystallization rates

Plots of the half-time of crystallization (devitrification) $t_{\frac{1}{2}}$ versus the crystallization temperature (T_c) for the first two series are shown in Figs. 2, 5 and 6. An alternative presentation of the data is to plot the half-time, $t_{\frac{1}{2}}$ versus ΔT , where ΔT is defined as the difference between the crystallization temperature, T_c , and the transformation temperature T_g , (i.e. $\Delta T = T_c - T_g$). This is shown in Figs. 3, 7 and 8 and it will be shown later that these plots are approximately "isoviscous". Melt viscosity data are shown in Fig. 4; most samples showing the expected dependence of viscosity (η) on temperature (an approximately linear relationship of $\log_{10} \eta$ to melt temperature), and that furthermore, the

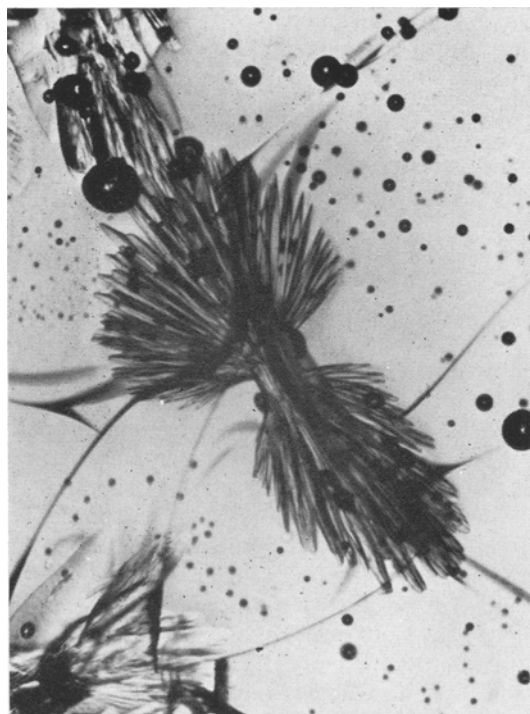


Figure 1 Photomicrograph of crystalline aggregate in a lead phosphate glass ($\times 135$).

viscosity data fall within a narrow temperature band when plotted against ΔT . The temperature at which the glasses have a viscosity of $10 \text{ N}^5 \text{ sec m}^{-2}$ (T_{10^5}), and the temperature $T_{10^5} - T_g$ are shown in Table I.

The third series of glasses containing 70 mol % P_2O_5 , and varying proportions of lead oxide and

TABLE II

Glass composition (mol %)			Crystalline phase
P ₂ O ₅	PbO	K ₂ O	
60	40	—	Some unidentified lines but predominantly lead metaphosphate, Pb ₂ (PO ₃) ₄
60	30	10	As above
60	25	15	As above
60	18	22	As above
60	10	30	Predominantly potassium metaphosphate with minor phase of lead metaphosphate
60	—	40	Some unidentified lines but predominantly potassium metaphosphate, KPO ₃

potassium oxide totalling 30 mol %, did not devitrify in the time scale of the experiment.

3.3. Identification of the crystalline phase

As described previously, X-ray diffraction powder pictures of partially crystalline glasses were obtained. Special care was necessary with glasses containing significant quantities of lead due to the high absorption of X-rays. Small amounts of samples were used to obtain the diffraction patterns, but some of the rings were uneven due to the small amounts of sample which prevented proper (powder) averaging. This difficulty, together with the high level of background scatter, prevented a satisfactory assessment of the relative intensity of the diffraction rings. Samples containing small amounts of lead and more potassium were more tractable, showing few spots and a lower background scatter, thus allowing a better assessment of the relative intensities of the diffraction rings in the pattern.

Identification of the crystalline phase was made by comparing the powder patterns obtained from the devitrified glasses with ASTM data on known compounds likely to occur in the devitrified glass. The glasses were devitrified by maintaining them at 300°C in an oven for a period of several weeks. Glasses thus examined and the crystalline phase identified are given in Table II.

4. Discussion

These glasses are produced by a polycondensation reaction involving the removal of hydroxyl groups from the phosphate chain and for a given nominal composition, the degree of condensation is dependent upon the furnacing cycle used. Marked (30°C) increases in the transformation temperature (T_g) of some glasses have been

obtained with increasing furnacing time, and have been attributed to the elimination of hydroxyl groups, and the resultant increases in the degree of cross-linking [2].

Glasses in the two original series were prepared using furnacing times of approximately 45 min at 700°C, which probably accounts for the scatter in T_g values observed for some batches, as small variations in furnacing times could result in appreciable changes in T_g . The observed changes in T_g with furnacing time would appear to vary not only on a time-temperature basis, but also with the batch scale, the changes occurring more rapidly for small batches. Those samples used for crystallization studies were chosen because they exhibited transformation temperatures falling on, or close to, the average curve relating T_g to composition. This procedure was adopted in order to exclude batches showing spurious crystallization rates due to polycondensation effects, but in view of the complex behaviour of a number of inter-related variables, it is not possible to state categorically that this is so. Accordingly, comparison of crystallization rates between glasses must be made with some caution. The presentation of data in the form ($t_{\frac{1}{2}}$ versus ΔT) is an attempt to resolve effects due to viscosity phenomena from those arising from compositional changes, within a series of glasses. Mention has been made previously of melt viscosity data falling within a narrow band of temperature dependence when plotted against ΔT . Similarly, plotting the half-time of crystallization $t_{\frac{1}{2}}$ versus ΔT should give an approximately "isoviscous" family of curves.

It is known that an important factor determining the crystallization rate is the melt viscosity of the glass at the crystallization temperature. Thus, providing the melt viscosities of the glasses

concerned show similar temperature dependence, the relative position of the devitrification curve along the ΔT axis may be regarded as an assessment of the inherent resistance of that composition to devitrification. That is, a particular formulation displays greater resistance for high values of ΔT , although in an absolute temperature sense it may devitrify at lower temperatures than another glass whose curve falls at lower ΔT . In view of the previous discussion, this is probably a considerable oversimplification of the facts, but the available data will be interpreted using this approach in an attempt to form a coherent picture.

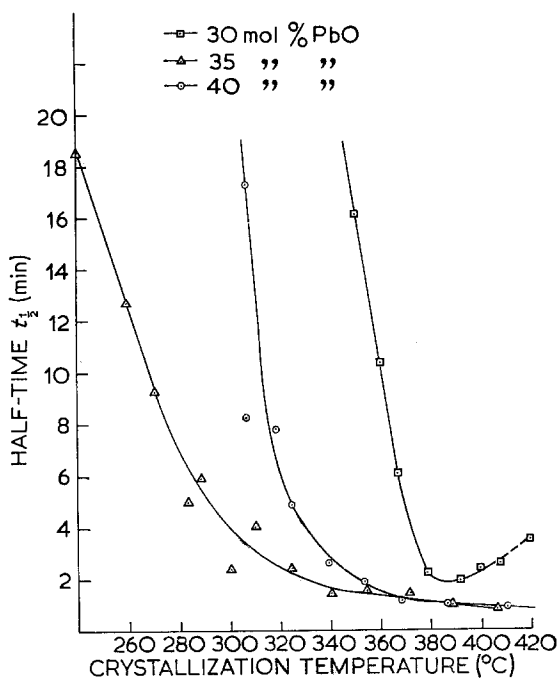


Figure 2 Plots of half-time of crystallization $t_{1/2}$, against crystallization temperature T_c , for lead phosphate glasses.

4.1. Series 1, glasses with varying proportions of P_2O_5 -PbO

The rate curves for the first series (varying proportions of P_2O_5 and PbO) are shown in Figs. 2 and 3. Fig. 2 gives plots of $t_{1/2}$ versus T_c and shows that the 40 mol % PbO glass lies between the two glasses containing 35 and 30 mol % PbO respectively. When the data is plotted against $\Delta T (= T_c - T_g)$ as in Fig. 3, the relative positions of the curves are changed.

However, the viscosity of the 40 mol % sample

is greater than the other glasses, and falls outside the range of values observed for the other glasses when plotted against ΔT (see Fig. 4). Thus a further temperature correction is made to the crystallization data for this sample in order to compare results under equi-viscous conditions. The correction made is a subtraction of 22°C from ΔT for each point (22°C being the shift necessary to bring the viscosity curve for the 40 mol % sample into approximate coincidence with the curves for other glasses).

Fig. 3 shows a progressive shift of the rate curves to greater values of ΔT with increasing phosphorus oxide contents, suggesting a corresponding increase in the inherent devitrification resistance.

4.2. Series 2, glasses containing 60 mol % P_2O_5 -40 mol % (PbO + K_2O)

The second series comprised those glasses containing 60 mol % P_2O_5 and varying proportions of lead oxide and potassium oxide totalling 40 mol %. Plots of half-time, $t_{1/2}$, versus crystallization temperature, T_c , are given in Figs. 5 and 6, and $t_{1/2}$ versus ΔT in Figs. 7 and 8. Here also the glass containing 40-0 mol % PbO- K_2O (the 60-40 P_2O_5 -PbO glass of the first series) shows atypical viscosity behaviour (Fig. 4) and the rate curve falls partially to the right of the next member in the series (30-10, PbO- K_2O), when plotted against the crystallization temperature, T_c (see Fig. 5), whilst the next curve (25-15, PbO- K_2O) falls at much higher temperatures. The rate curve for this latter sample shows $t_{1/2}$ passing through a minimum at approximately 465°C , before rising rapidly at higher temperatures. This is in marked contrast to the previous two samples where the crystallization rate is almost constant over a wide temperature range. A similar correction to that described earlier was applied to the data for the 40-0, PbO- K_2O sample, before plotting $t_{1/2}$ against ΔT for these samples (Fig. 7). This shows a relative shift of the 40-0, PbO- K_2O curve with respect to the 35-5, PbO- K_2O plot, with the former curve now falling to the left of the latter. The displacement to higher temperatures, and the sharp curvature of the 25-15 PbO- K_2O plot, indicates the greater resistance to devitrification of this composition.

Fig. 6 shows plots of half-time, $t_{1/2}$ versus T_c for the other end of the compositional scale, i.e. glasses containing 0-40 and 5-35 mol % PbO- K_2O respectively (and the same 25-15, PbO- K_2O glass plotted in Fig. 5). The rate curve for the

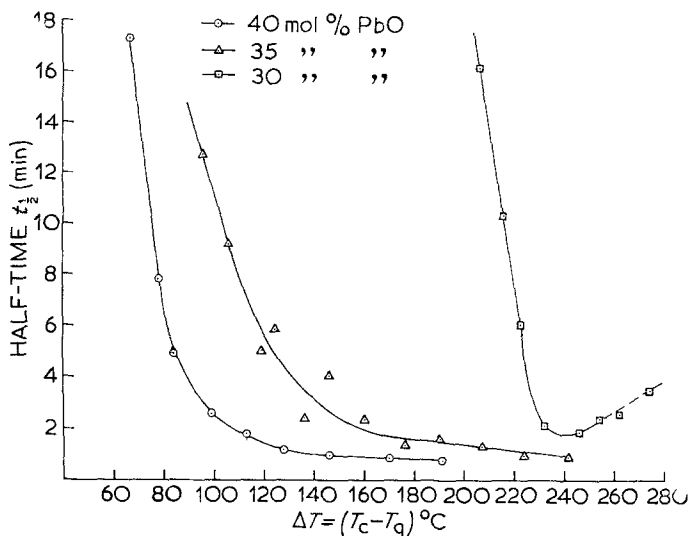


Figure 3 Plots of $t_{1/2}$ against ΔT (where $\Delta T = T_c - T_g$) for lead phosphate glasses.

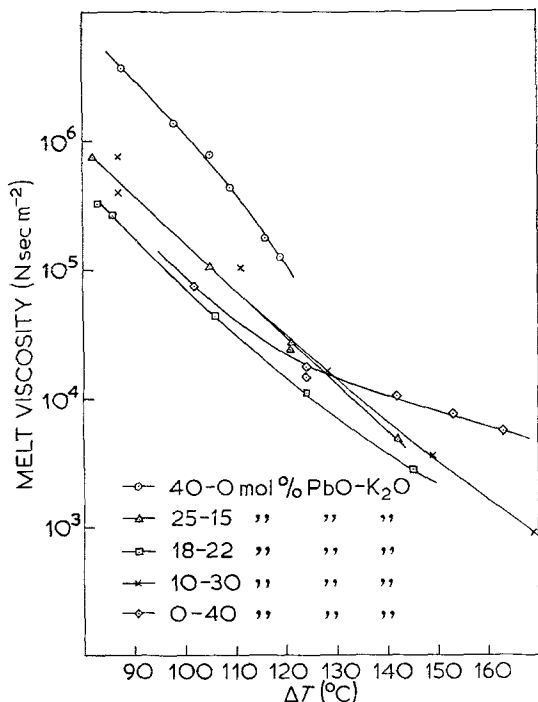


Figure 4 Plots of $\log_{10} \eta$ against ΔT .

5-35, PbO-K₂O glass falls to the right of that for the 0-40 PbO-K₂O composition. Both show essentially constant values of $t_{1/2}$ over a wide

temperature range (330 to 400 °C), but the former curve shows a slight increase in $t_{1/2}$ at higher temperatures (420 °C). The plot for the 25-15 PbO-K₂O sample falls at much higher temperatures.

Fig. 8 gives plots of $t_{1/2}$ versus ΔT for these glasses. These show a small relative shift, bringing all three curves slightly closer together, with the 25-15 PbO-K₂O sample remaining at much higher temperatures. However, the dramatic changes observed in the devitrification rate of glasses within the compositional range 30-10 mol % to 25-15 mol % PbO-K₂O respectively, are not apparent from these figures. A glass containing 10-30 mol % PbO-K₂O showed a minimum in half-time of 20 min at 420 °C (off scale in Fig. 6), whilst another of composition 18-22 mol % PbO-K₂O did not crystallize within the time scale of the experiment. Reference to Fig. 4 and Table I shows that the melt viscosities of these two formulations fall within the normal temperature range. Therefore, the large change in the rate of crystallization cannot be attributed to atypical viscosity behaviour.

It may be anticipated that a change in the bond network (such as an increase in cross-link density) will result in an increase in the melt viscosity. The absence of such differences in viscosity suggests that the change in crystallization rate is not attributable to differences in bond networks.

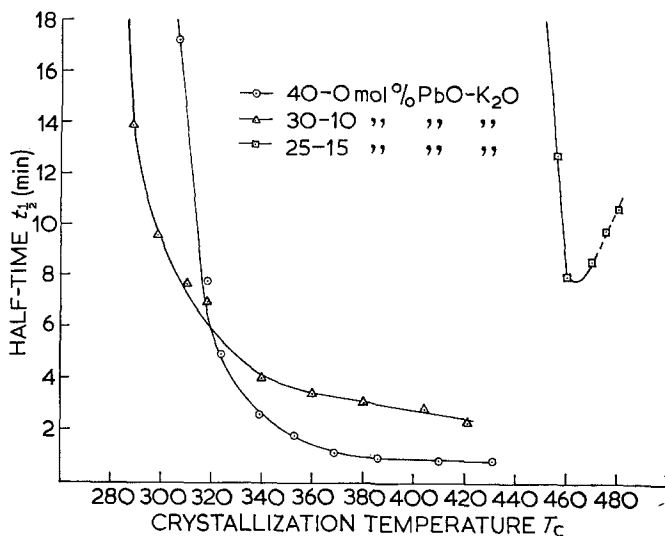


Fig. 5

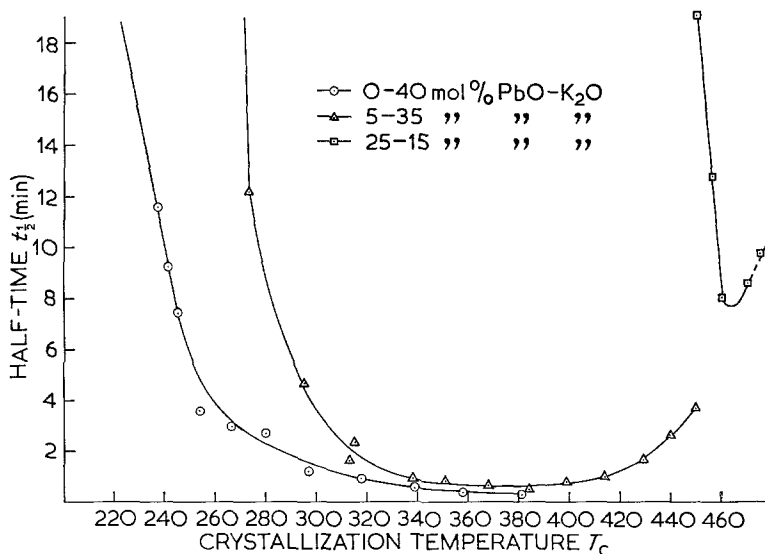


Fig. 6

Figure 5 } Plots of $t_{1/2}$ against T_c for some potash lead phosphate glasses.
 Figure 6 }

4.3. Series 3, glasses containing 70 mol % P_2O_5 -30 mol % (PbO + K_2O)

The compositions of the four samples comprising this series are given in Table I. All four samples failed to crystallize in the time scale of the experiment. At first sight the sample of composition 70-30 mol % P_2O_5 -PbO, should be comparable with the sample of the same composition in

series 1. However, the two samples were subjected to different refining cycles; series 1 being furnace for 45 min at 700°C, whilst the latter series received a premelt treatment of 4 h at 450°C before furnace for 1 h at 700°C. Apparently the observed differences in crystallization rates are caused by differences in molecular structure between the two glasses due to the different refining cycles.

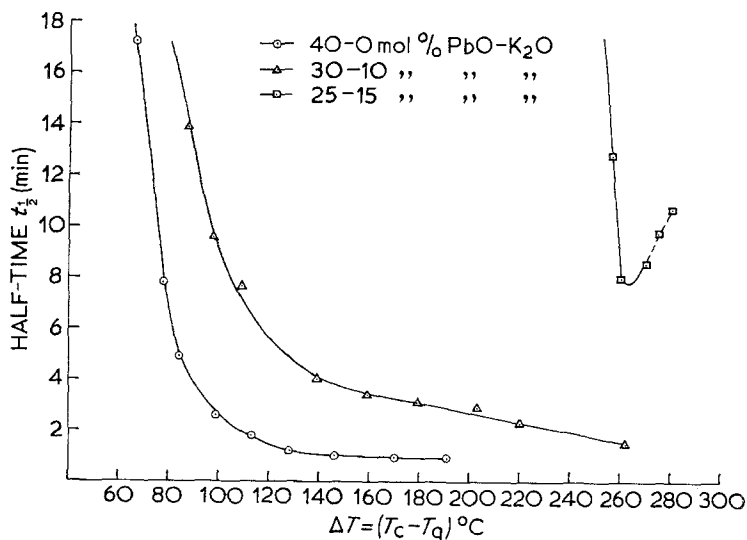


Fig. 7

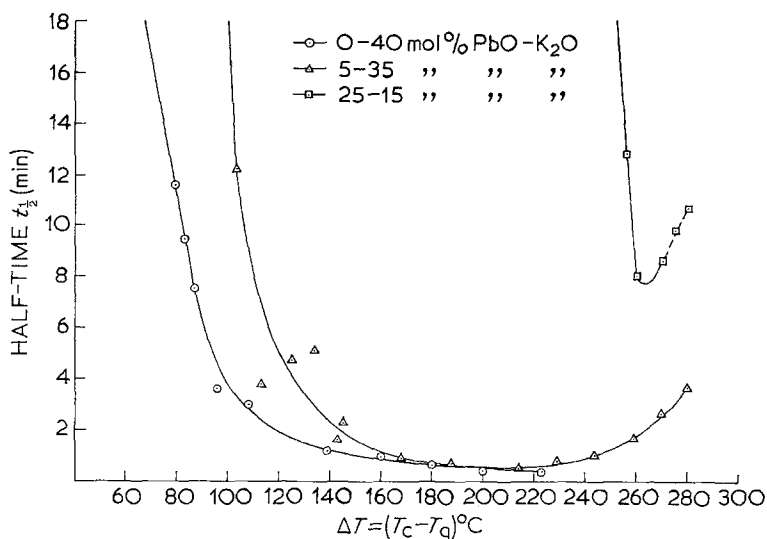


Fig. 8

Figure 7 } Plots of $t_{1/2}$ against ΔT for some potash lead phosphate glasses.
Figure 8 }

4.4. Identification of the crystalline phase in series 2

The identification of the crystalline phase (see Table II) shows that the compound lead metaphosphate, $Pb_2(PO_3)_4$, predominates, at least over the composition range 40-0 to 18-22 parts of $PbO-K_2O$. It was not possible to positively confirm the presence of a potassium compound minor phase due to the poor quality

of the powder patterns. It is of interest to note that whilst the composition containing 18-22 $PbO-K_2O$ did not crystallize in the time scale of the rate experiments, a sample did crystallize on prolonged heating in an oven, although crystals remained small as there was some line broadening of the diffraction pattern.

The sample containing 0-40 mol % $PbO-K_2O$ showed a crystalline phase identified as being

predominantly potassium metaphosphate, KPO_3 . The 30-10 mol % $PbO-K_2O$ sample showed a similar powder pattern, but in addition, the three strongest lines of the lead metaphosphate pattern were present. The crystalline phase was tentatively identified as potassium metaphosphate, with a minor lead metaphosphate component.

The available evidence suggests that the lead crystalline phase is not altered in form by the presence of potassium in the glass. Even if a potassium phosphate phase co-exists in the devitrified glass, the lead phase remains as lead metaphosphate. Thus, the observed changes in crystallization rates with composition do not appear explicable in terms of surface energy considerations for differing crystalline phases. Another possible explanation is that the potassium component acts as a diluent, thus slowing the rate of crystallization. Such a prediction is complicated by the crystallization of the potassium component itself, whilst the concentrations present seem unlikely to be sufficient to produce an effect of the observed magnitude.

The series of glass compositions appears to behave in an "eutectic" manner. That is, at the extremes of the compositional range the devitrification rate is rapid, but decreases towards the middle of the range. A "metastable" condition is attained at equal molar contents of lead and potassium oxides, where the crystallization rate is not measurable in the time scale of the microscopical experiments (although devitrification did occur on prolonged heating in an oven).

5. Conclusions

Although crystallization rates are viscosity dependent, compositional effects may be resolved from those due to viscosity differences by using "isoviscous plots" of the half-time of crystallization against temperature. Plots of melt viscosity data \log_{10} viscosity against ΔT , (where

ΔT is the difference between the melt temperature and the transformation temperature) show an approximately linear temperature dependence of viscosity, with the plots for different compositions falling within a narrow temperature band. Thus plotting the half-time of crystallization against ΔT (where ΔT is now the difference between the crystallization temperature and the transformation temperature) allows comparison between rate curves for glasses of different composition at similar viscosities.

Plots of half-time, $t_{1/2}$, against ΔT show a marked compositional dependence. The position of the rate curve on the ΔT temperature axis is a measure of the relative devitrification resistance of a formulation, irrespective of the actual crystallization temperature. For the series containing different proportions of P_2O_5 - PbO (series 1), the devitrification resistance increases with P_2O_5 content. For the series based on 60 mol % P_2O_5 and various proportions of $PbO-K_2O$ totalling 40 mol % (series 2), the crystallization rate shows an "eutectic" behaviour, attaining a metastable composition in the region 60-20-20 mol % P_2O_5 - $PbO-K_2O$. Unfortunately a series based on 70 mol % P_2O_5 with varying amounts of PbO and K_2O totalling 30 mol %, failed to devitrify, thus preventing confirmation of this trend in other compositions.

The devitrification behaviour of any particular formulation, being viscosity dependent, varies with refining time in a manner shown elsewhere [4].

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