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THE INFLUENCE OF THE COOLING RATE OF A $2PbO \cdot SiO_2$ MELT ON THE CONSTITUTION OF SILICATE ANIONS

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The kinetics of crystallization in a $2Pbo \cdot SiO_2$ melt have been investigated. A TTT-diagram was constructed, which describes the kinetic parameters for the formation of crystalline phases in the system. By means of silicate anion analysis the relationship between the cooling rates of the melt and the structure of silicate units in solid $2PbO \cdot SiO_2$ has been studied. Substantial differences in the thermal treatment of the melt lead to alterations of the silicate anion constitution, which cause changes in the crystallization behavior of glassy $2PbO \cdot SiO_2$.

1. Introduction

Kinetic studies of crystallization in undercooled melts of glass forming silicates demonstrate the decisive role of the applied cooling rate: by rapid quenching glass is obtained, low cooling rates promote the formation of crystals. Various models have been developed to describe glass formation [1] or the growth of crystals from the melt [2], but none of them considers the structural changes of silicate groupings occurring during these processes. Recently direct chemical methods were employed to investigate the constitution of silicate anions in glassy and crystalline $2PbO \cdot SiO_2$ [3]. It was found that glassy $2PbO \cdot SiO_2$ contained various different silicate anions, while in the crystalline modifications one type of silicate anions prevailed. The composition $2PbO \cdot SiO_2$ melts congruently, both solid and liquid phases are of the same composition. For the latter reason it was used for the present study, which was undertaken to investigate the effect of the cooling rate of the $2PbO \cdot SiO_2$ melt on the constitution of silicate anions in the solid phase.

2. Experimental

As starting material glassy $2PbO \cdot SiO_2$ was used, its preparation had been described earlier [3]. About 0.66 g of finely powdered glass (grain size <40 μm) were weighed into a Pb crucible (volume 0.3 ml) of a Netzsch thermoanalyzer (model 429 STA, Netzsch Gerätebau Selb, FRG). As reference substance α-Al_2O_3 was used. The sample carrier with both the covered sample and reference crucibles was introduced into a preheated furnace, the temperature of which was kept at 850°C. Thermal exposure for 15 min at this temperature was found to be sufficient to achieve thermal equilibrium within the molten silicate. Afterwards the temperature of the melt was lowered according to the respective cooling rates, using the automatic temperature regulation of the STA equipment. In this way it was possible to measure the actual temperature of the melt during the whole cooling process and to record DTA signals caused by enthalpy changes within the sample. All DTA measurements were made in air using the highest available sensitivity of 0.05 mV. Preliminary tests had shown that during the crystallization of the melt within the temperature range 850°C–T_g always only one DTA signal appeared. It was of exothermic character and indicated the crystallization of $2PbO \cdot SiO_2$ from the melt. Therefore, in all experiments the DTA measurements of the melt were carried out from 850°C downwards to the exothermic maximum. As soon as the whole peak was recorded, the temperature was kept constant for another 15 min. Then the sample carrier was withdrawn from the furnace and the DTA recording was switched off (fig. 1).

The solid product obtained was ground to pass through a 40 μm sieve and studied by two methods of silicate anion analysis–paper chromatography [4] and the

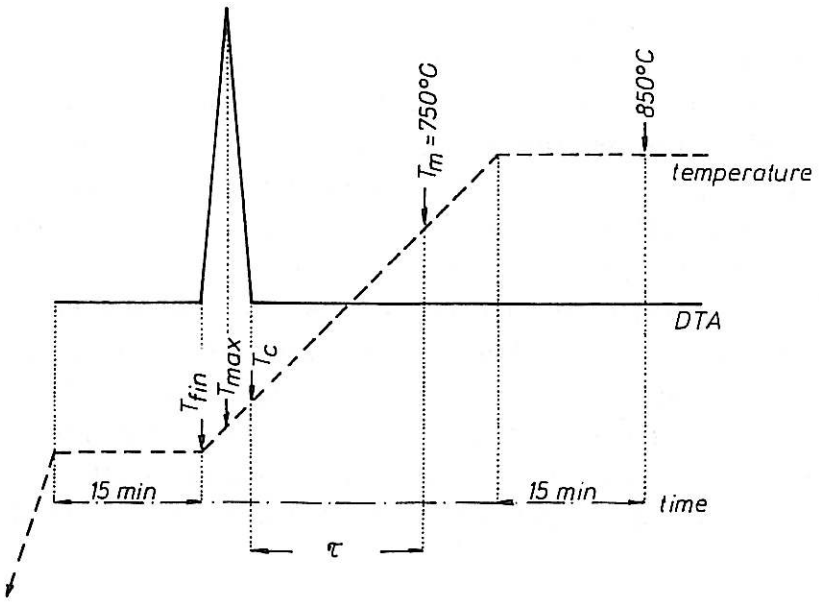

Fig. 1. DTA parameters of the cooling procedure.

molybdate method. The molybdate method measures the rate of formation of molybdatosilicic acid. As this rate depends on the average molecular weight of the silicate anions it is possible to use the method to distinguish between silicate anions of different average molecular weight [5]. Paper chromatography allows the determination of various types of silicate anions. Their quantitative determination was in some cases impaired by the appearance of strong bands caused by higher molecular 2–3 dimensional silicate anions. These bands overlapped spot positions and increased the relative error, which was found to be ±5% when the respective silicate anion amounted to more than 50% of the total Si in the sample, but increased gradually with decreasing percentage of the respective silicate anions. If the concentration of the silicate anion was only 5–10% of the total Si, the relative error grew to ±35%.

3. Results and discussion

The solidification of the $2PbO \cdot SiO_2$ melt was investigated using different cooling rates. Their actual values Φ as well as the corresponding DTA characteristics T_c, T_{max}, T_{fin} and τ (fig. 1) are listed in table 1.

Cooling the melt at rates between 0.1°C min^{-1} and 13.8°C min^{-1} always leads to only one exothermic crystallization peak. The melt cooled at 65°C min^{-1} is essentially glassy; only a few crystalline spots are found on the surface of the solid sample. This is confirmed by IR absorption measurements, which indicates that the absorption band at 650 cm^{-1}, a characteristic for crystalline $2PbO \cdot SiO_2$, appears only as a slight dent in the spectrum of the sample cooled at 65°C min^{-1} (fig. 2).

The results listed in table 1 were evaluated with regard to the kinetics of crystallization and glass formation respectively. By using the temperatures T_c character-

Table 1
Cooling rates Φ and crystallization data of the melt

Φ (°C min^{-1})	log Φ	T_c (°C)	T_{max} (°C)	T_{fin} (°C)	τ (min)
0.1	–1.0	665	665	665	850
0.2	–0.7	665	665	665	425
0.5	–0.3	670	665	663	160
1.0	0.0	665	660	657	85
1.8	0.26	662	655	645	48.9
4.5	0.65	670	650	620	17.8
9.2	0.96	657	630	570	10.1
13.8	1.14	650	625	560	7.2
65.0	1.81	no measurable peak			
~70 × 10^3	4.85	no DTA recording			

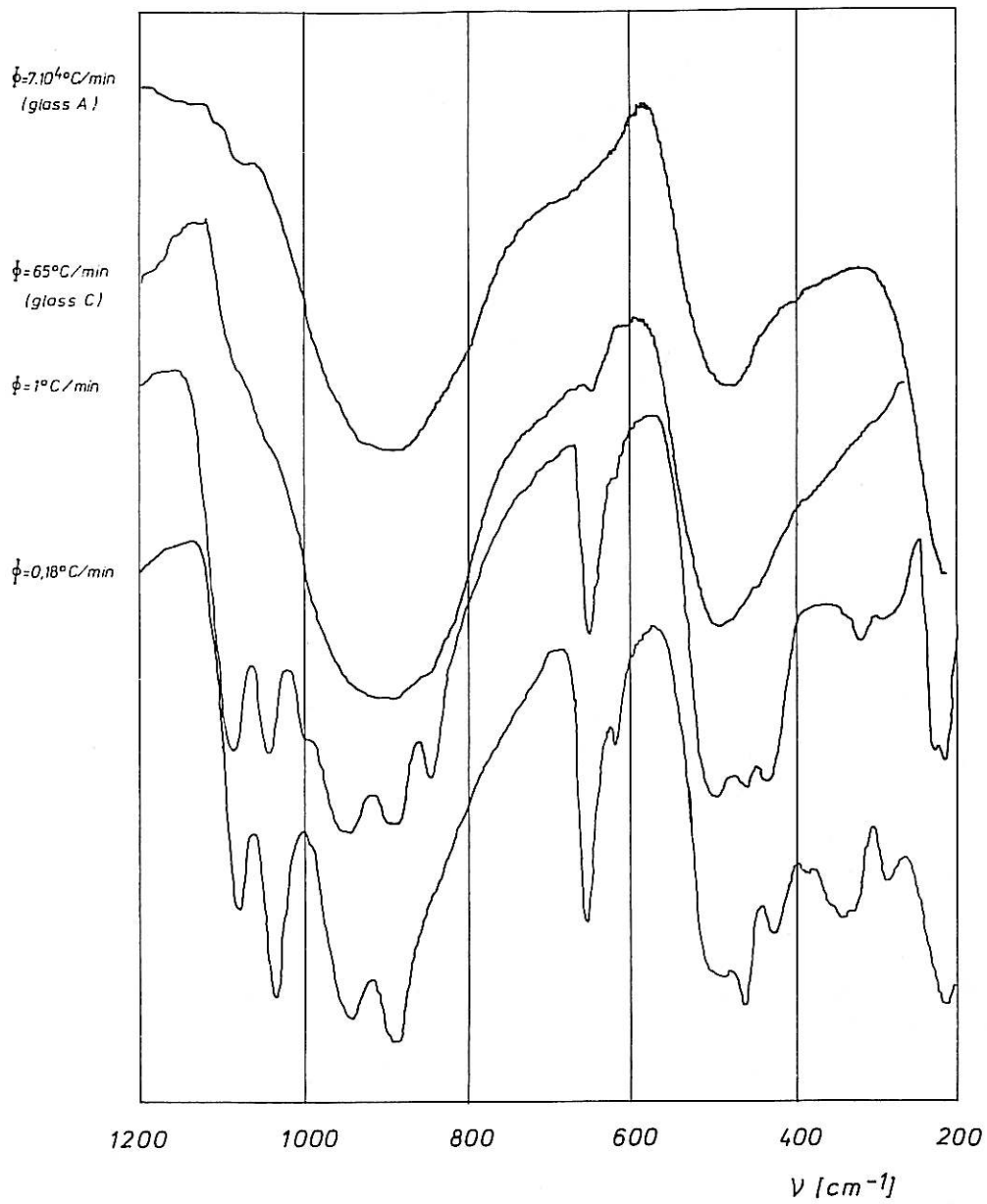

Fig. 2. Infrared absorption spectra of samples cooled at different cooling rates (KBr method).

izing the onset of crystallization and the corresponding times τ for both the crystallization from the $2PbO \cdot SiO_2$ melt (table 1) and crystallization of the solid glassy $2PbO \cdot SiO_2$ (table 2) a time–temperature–transformation (TTT) diagram of the given system was constructed (fig. 3). DTA curves measured at cooling rates faster than 13.8°C min^{-1} allowed no reliable determination of T_c, therefore it was necessary to obtain the nose of the TTT diagram by employing other methods. As the sample solidified at the cooling rate $\Phi = 65$°C min^{-1} showed only very slight traces of surface crystallization, the nose of the TTT diagram was arbitrarily constructed in the point K which lies on the curve of $\Phi = 65$°C min^{-1}. Its position at

Table 2
Heating rates Φ and crystallization data of the solid glass [a]

Φ (°C min^{-1})	log Φ	T_{c_1} (°C)	T_{max_1} (°C)	τ (min)
2.2	0.34	393	400	207
5.0	0.70	394	410	87
10.4	1.02	400	428	36.5
22.2	1.35	415	440	25.0

[a] Evaluated from DTA measurements made in connection with [6].

550°C is in agreement with the shape of the experimentally determined part of the TTT diagram; it is based on the assumption that the degree of crystallinity in the sample solidified at 65°C min^{-1} corresponds to the crystallinity at temperature T_c in kinetic DTA measurements.

From fig. 3 the kinetic conditions which lead to the crystallization of solid glassy 2PbO · SiO_2 or of the 2PbO · SiO_2 melt can de determined. Only within the area limited by the TTT curve can crystalline 2PbO · SiO_2 exist, beyond it the composition is either an undercooled melt or glassy. The temperature T_g of glassy 2PbO · SiO_2 was found to be 340°C [6]. Crystallization of the glass starts at 393°C, if the heating rate is about 2°C min^{-1}. Within the interval 340–393°C the structural units of the glass become mobile, this mobility leading eventually to the appearance of the first low-temperature crystalline phase T-2PbO · SiO_2. As shown

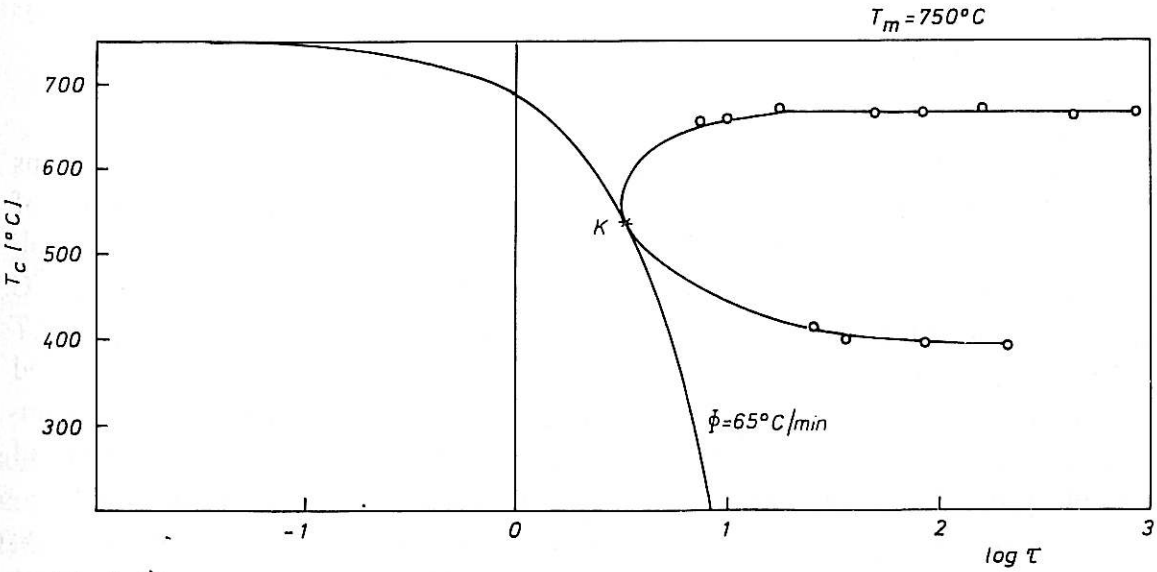

Fig. 3. Time–temperature–transformation (T-T-T) curve of the composition 2PbO · SiO_2.

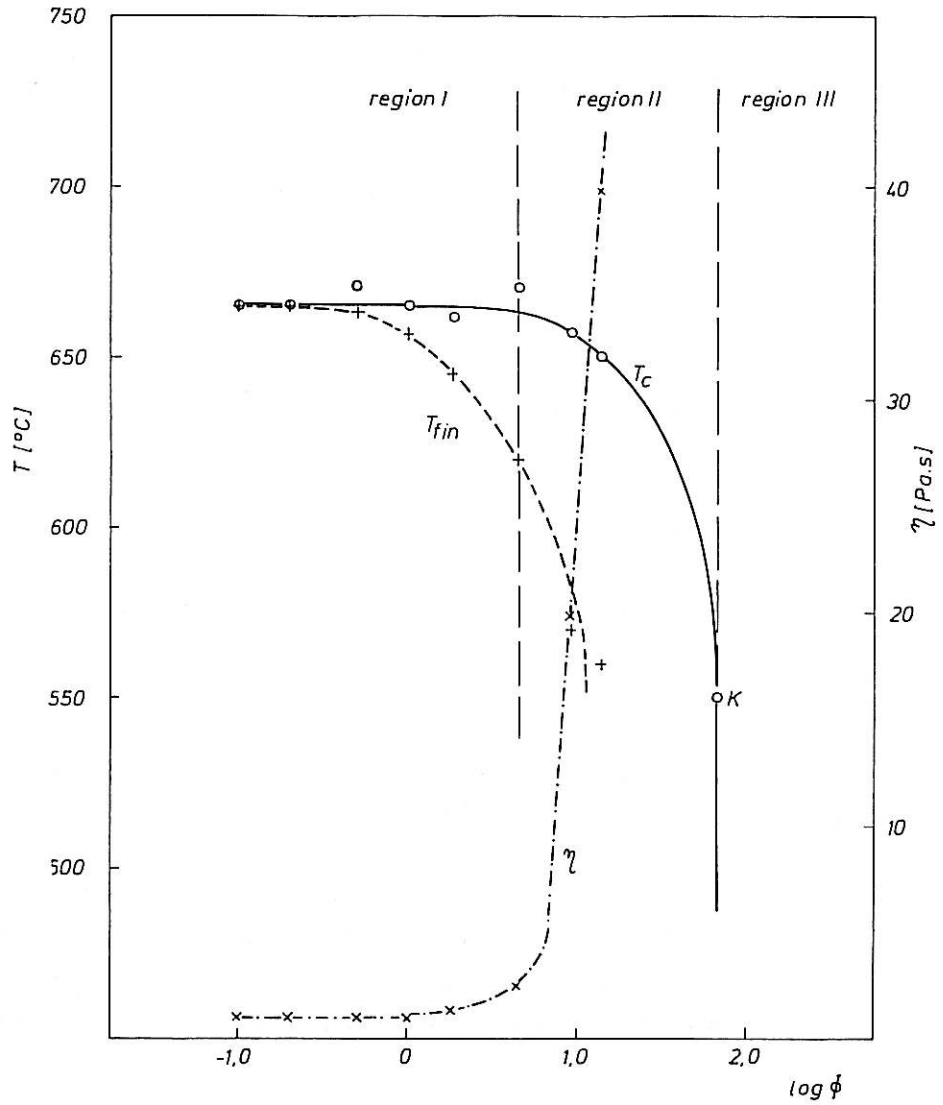

Fig. 4. Dependence of T_c and T_{fin} on the cooling rate Φ. (Curve η depicts viscosities of the melt at T_{fin}).

elsewhere [3], this crystallization is due to the formation of mainly dimeric anions $[Si_2O_7]^{6-}$. Large undercooling $\Delta T = T_m - T_c$ characterizes the crystallization of the $2PbO \cdot SiO_2$ melt. Fig. 4 depicts the dependence of temperature T_c on the cooling rate Φ of the melt. It is obvious that for the lowest cooling rates up to 4.5°C min^{-1} the value of T_c remains constant at about 670°C (region I). In this region ΔT is 80°C and does not change with changing Φ. If the cooling rate is increased beyond 4.5°C min^{-1}, then T_c becomes dependent on Φ (region II). This dependence declines with increasing Φ and reaches point K, which represents the limit of crystallization. Beyond K, in region III, cooling of the melt produces only glasses.

The growth of crystals from the melt causes exothermic changes of enthalpy, which occur within the temperature interval $T_c - T_{fin}$ (fig. 1). In fig. 4, the area

Table 3
Viscosities of glass melts at the temperature T_{fin}

Φ (°C min^{-1})	T_{fin} (°C)	η [a] (Pa s)
0.1	665	1.00
0.2	665	1.00
0.5	663	1.00
1.0	657	1.00
1.8	645	1.26
4.5	620	2.51
9.2	570	19.95
13.8	560	39.81

a) Viscosity values were obtained from the temperature dependence of viscosity of 2 PbO · SiO_2 given in [7] and are expressed in SI units (1 Pa s = 10 P).

limited by the curves T_c and T_{fin} represents the temperatures of crystal growth. This area is narrow if the cooling rates are very low: it broadens with increasing Φ. However, the growth of crystals in melts cooled at higher cooling rates is more and more hindered by the increased viscosity of the melt. Viscosity values corresponding to the respective temperatures T_{fin} of the 2PbO · SiO_2 melt are listed in table 3, the dependence of viscosity on the cooling rate Φ is included in fig. 4. From this graph it is evident that whereas in region I the crystals grow at constant viscosities of about 1 Pa s, the viscosities in region II rise sharply and reach a value of 40 Pa s at $\Phi = 13.8$°C min^{-1}. This tendency continues and as Φ approaches the critical cooling rate 65°C min^{-1} more and more melt solidifies as glass. Finally, in region III the melt does not crystallize, it forms only glasses. Accordingly, the three different regions marked in fig. 4 may be characterized as follows:

region I	$\Phi < 0.65°$ min^{-1},	solidification products crystalline ;
region II	$0.65 \leqslant \Phi \leqslant 65$°C min^{-1},	solidification products crystalline and glassy ;
region III	$\Phi > 65$°C min^{-1},	solidification products glassy .

The influence of the cooling rate on the condensation of silicate anions in the solidified melt was studied by the molybdate method, which provides information about changes in the average molecular weight of silicate anions in the given system. The obtained dependences are plotted in fig. 5 together with the molybdate curves of two calibration standards representing monosilicate anions $[SiO_4]^{4-}$ and chain-

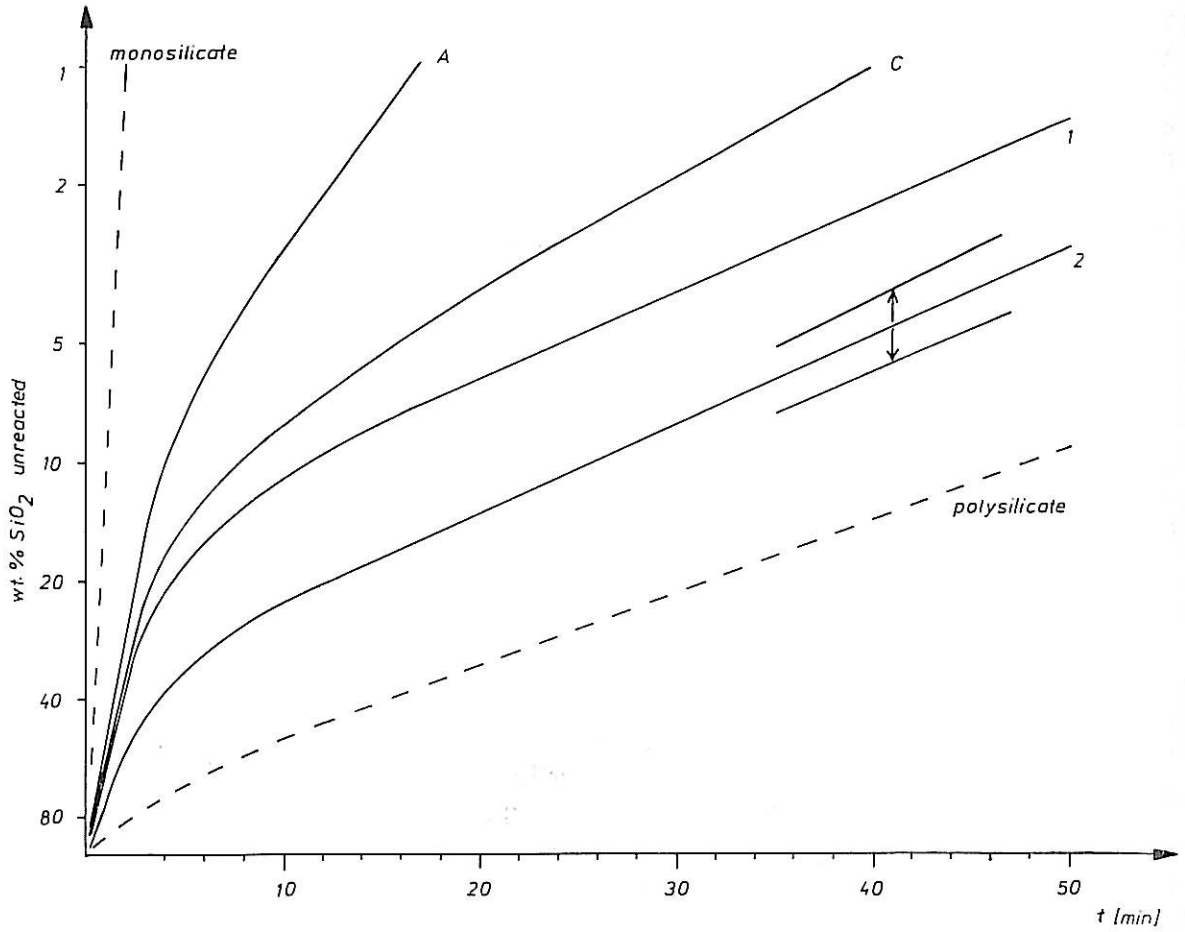

Fig. 5. Molybdate curves of various glassy and crystalline samples. Glass A – cooling rate $\Phi \sim 70 \times 10^3$ °C min^{-1}. Glass C – cooling rate $\Phi = 65$°C min^{-1}; Curve 1 – cooling rate $\Phi = 13.5$°C min^{-1}. Curve 2 – cooling rates 0.1–4.5°C min^{-1}.

like polysilicate anions $[SiO_3^{2-}]_\infty$ respectively. The differences in the final linear ascent of the corresponding molybdate curves demonstrate that a low cooling rate of the melt promotes the formation of higher molecular silicate anions and vice versa: the faster the melt is cooled the lower the number of silicate units that condense into higher molecular units. The differences in the molybdate curves of specimens solidified at 65, 13.5 and 0.1–4.5°C min^{-1} respectively correspond to the increasing amounts of the crystalline phase in these samples. There are only very small differences between the molybdate curves of melts cooled at rates between 0.1 and 4.5°C min^{-1}, which agrees with the conclusions drawn from fig. 4.

Table 4 contains the results of silicate anion analysis carried out by paper chromatography. It shows that the silicate anions in the crystalline samples obtained from the melt at cooling rates within the range 0.1–4.5°C min^{-1} are composed of both tetrameric rings $[Si_4O_{12}]^{8-}$ and polysilicate chains $[SiO_3^{2-}]_\infty$. The reason for this has to be sought in the fact that the $2PbO \cdot SiO_2$ melt cooled at the above men-

Table 4
Silicate anions in melts solidified at different cooling rates Φ (in wt.% of the total amount of Si in the solid sample)

Φ (°C min^{-1})	Solid [a]	$\Sigma(Si_1 + Si_2 + Si_3)$	$[Si_4O_{12}^{8-}]$	Higher condensed silicates (polysilicates and 2–3 dimens. units)
0.1	(A)	traces	60	40 [b]
0.2	(A)	<10	50	45 [b]
0.5	(A)	<10	45	50 [b]
1.0	(A)	<10	45	50 [b]
1.8	(A)	<10	46	46 [b]
4.5	(A)	<10	44	48 [b]
9.2	(B)	10	40	50 [b]
13.8	(B)	20	40	40 [b]
65.0	(C)	45	19	36 [b]
~70 × 10^3	(D)	47	14	39

[a] The notation in this column is as follows: (A) crystalline; (B) predominantly crystalline; (C) glassy with traces of surface crystals; (D) entirely glassy.
[b] Predominantly polysilicate chains.

tioned rates crystallizes at temperatures between 665 and 630°C; in a previous paper it was shown that at these temperatures both anions $[Si_4O_{12}^{8-}]$ and $[SiO_3^{2-}]_\infty$ are stable [3].

There seems to be a connection between the observed large undercooling of the $2PbO \cdot SiO_2$ melt ($\Delta T \sim 80$°C) and the mechanism of the formation of polysilicate anions $[SiO_3^{2-}]_\infty$ in the melt. As shown in a crystallization study of glassy $2PbO \cdot SiO_2$ [3], in this system the anions $[SiO_3^{2-}]_\infty$ are the stablest silicate anions at temperatures slightly below T_m. They form during the heat-treatment from tetrameric rings $[Si_4O_{12}^{8-}]$, which are stable at lower temperatures. If we assume that the formation of $[SiO_3^{2-}]_\infty$ chains in the undercooled melt proceeds also via $[Si_4O_{12}^{8-}]$, it is possible to understand why anions $[SiO_3^{2-}]_\infty$ form rapidly only at lower temperatures (larger undercooling) where sufficient $[Si_4O_{12}^{8-}]$ rings are present. The relationship between the cooling or heating rates Φ and the constitution of silicate anions in the crystalline $2PbO \cdot SiO_2$ is schematically depicted in fig. 6, which represents a somewhat modified TTΦ diagram. It contains the estimated areas of stability of the various crystalline polymorphs, T, M and H which gradually develop during the heat-treatment of glassy $2PbO \cdot SiO_2$ (left half) and the regions I and II which correspond to the formation of fully [I] or partly [II] crystalline $2PbO \cdot SiO_2$ from the undercooled melt (right half). Melts cooled at 65°C min^{-1} or quenched at a rate of about 70 × 10^3°C min^{-1} solidify as glasses, which are characterized by a distribution

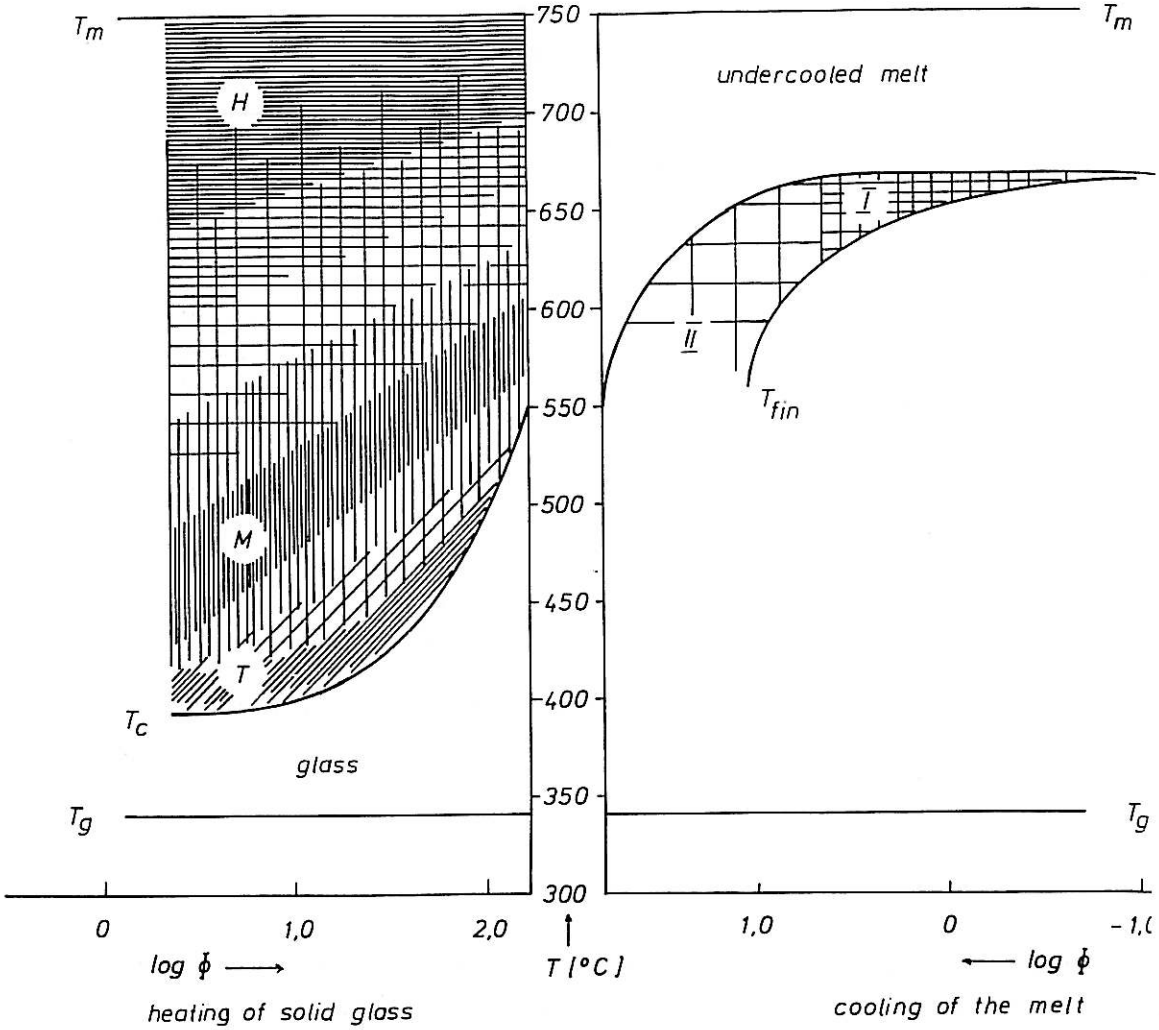

Fig. 6. Areas of stability of crystalline polymorphs T-, M- and H-2PbO · SiO_2 plotted agains the cooling or heating rate respectively.

of different silicate anions including many low molecular species. Comparison of th respective molybdate curves C and A in fig. 5 * shows that the average molecula weight of silicate anions in the quenched glass A is lower than in glass C which wa cooled at 65°C min^{-1}. This was confirmed by additional parallel paper chromatog raphic measurements of samples A and C which indicated a higher amount of poly silicate anions in glass C. To investigate this phenomenon more in detail, three san ples of the studied melt were cooled from 850°C at a rate of 0.1°C min^{-1} and kep for 24 h at 690°C, or for 48 h at 700°C, or 96 h at 730°C, respectively. After th heat-treatment the melts were brought instantly to room temperature by withdraw ing the DTA sample carrier from the furnace. Differential thermograms wer

* In figs. 5 and 7 curves A, B and C signify glassy samples, whereas samples corresponding t curves 1, 2, 3 and 4 are crystalline.

recorded during the whole procedure, no crystallization peak appeared. The obtained solid samples were investigated by X-ray diffraction and IR absorption methods and found to be entirely glassy. Measurements of these three glasses by the molybdate method indicated that the average molecular weight of their silicate anions is practically identical. In fig. 7 the molybdate curve of one of these glasses (B) is compared with glass A quenched at 70×10^3 °C min^{-1} and with crystalline $2PbO \cdot SiO_2$ obtained either from the melt by cooling at 1°C min^{-1} (curve 3) or from solid $2PbO \cdot SiO_2$ glass by heating for 15 min at 700°C (curve 4). Glass B (48 h at 700°C) as well as glass C in fig. 5 contains higher molecular silicate anions than glass A. Paper chromatographic investigations indicate increased amounts of polysilicate anions $[SiO_3^{2-}]_\infty$ in both glasses B and C. The presence of higher molecular silicate units in glass B is due to the prolonged heat-treatment at 700°C, which facilitated the gradual conversion of the relatively few unstable $[Si_4O_{12}^{8-}]$ rings present into stable polysilicate chains. The condensation of silicate anions in glass C is caused by the lower cooling rate Φ. This proves that glasses of the same chemi-

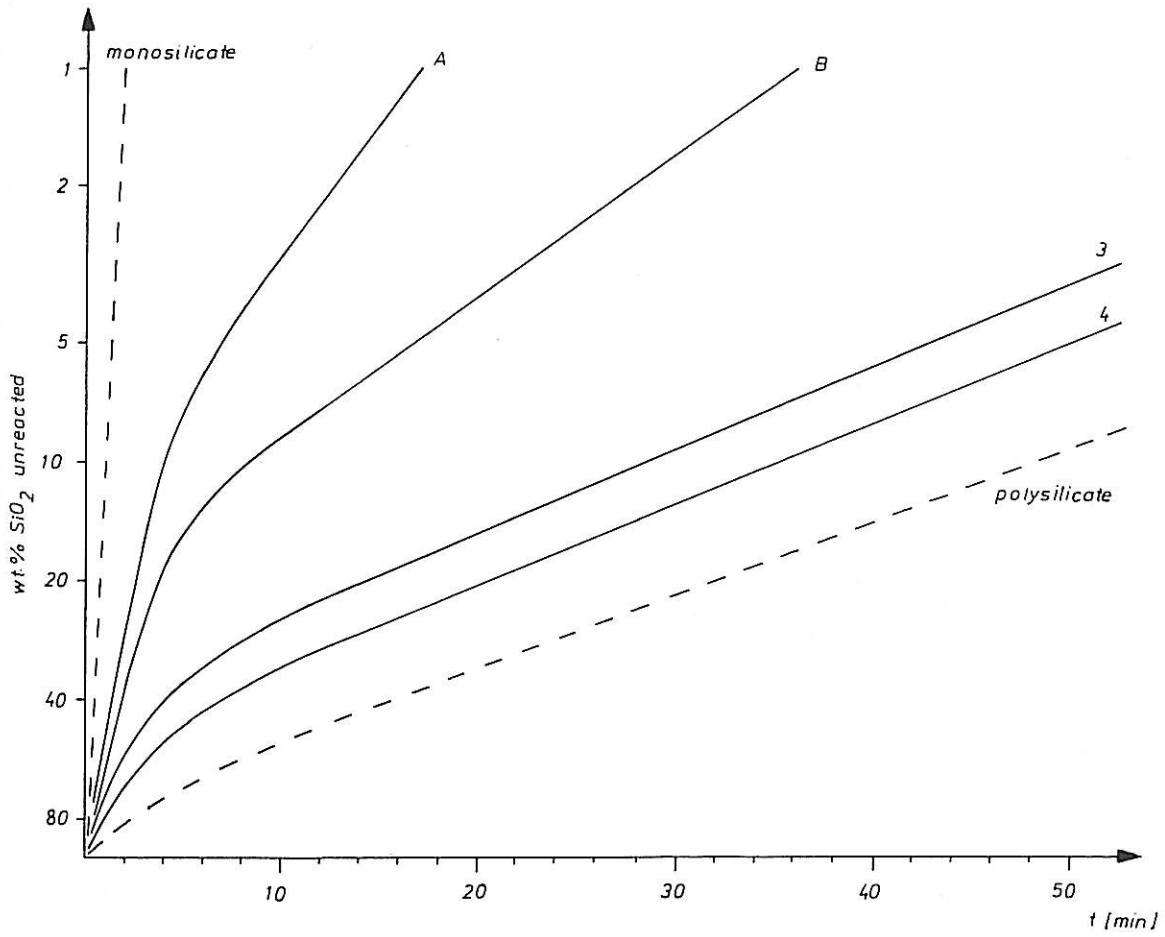

Fig. 7. Molybdate curve of glassy and crystalline $2PbO \cdot SiO_2$. Glass A – cooling rate $\Phi \sim 70 \times 10^3$ °C min^{-1}; Glass B – melt heat-treated for 48 h at 700°C. Curve 3 – cooling rate $\Phi = 1.0$°C min^{-1}. Curve 4 – solid glass heated for 15 min at 700°C.

cal composition differ in the constitution of their silicate anions, provided the thermal history of the glasses is sufficiently different. This finding contradicts the results of Smart and Glasser published in a very recent work [8], in which they discovered no evidence that annealing or quenching significantly affected the silicate anion distribution of any given glass. This discrepancy is not surprizing. Smart and Glasser used for the determination of silicate anions the method of direct trimethylsilylation according to [9]. In one of our previous papers [3] it was shown that this method permits the quantitative analysis of low molecular silicate anions, but it fails to detect higher molecular silicate units.

The influence of thermal history on the properties of glasses is a generally recognized fact, which has been demonstrated by several experimental works [10]. Our results provide the link between thermal history and the constitution of silicate anions, which so far has been missing. In this connection it was of interest to compare the thermal behavior of both structurally different glasses A and B. For this

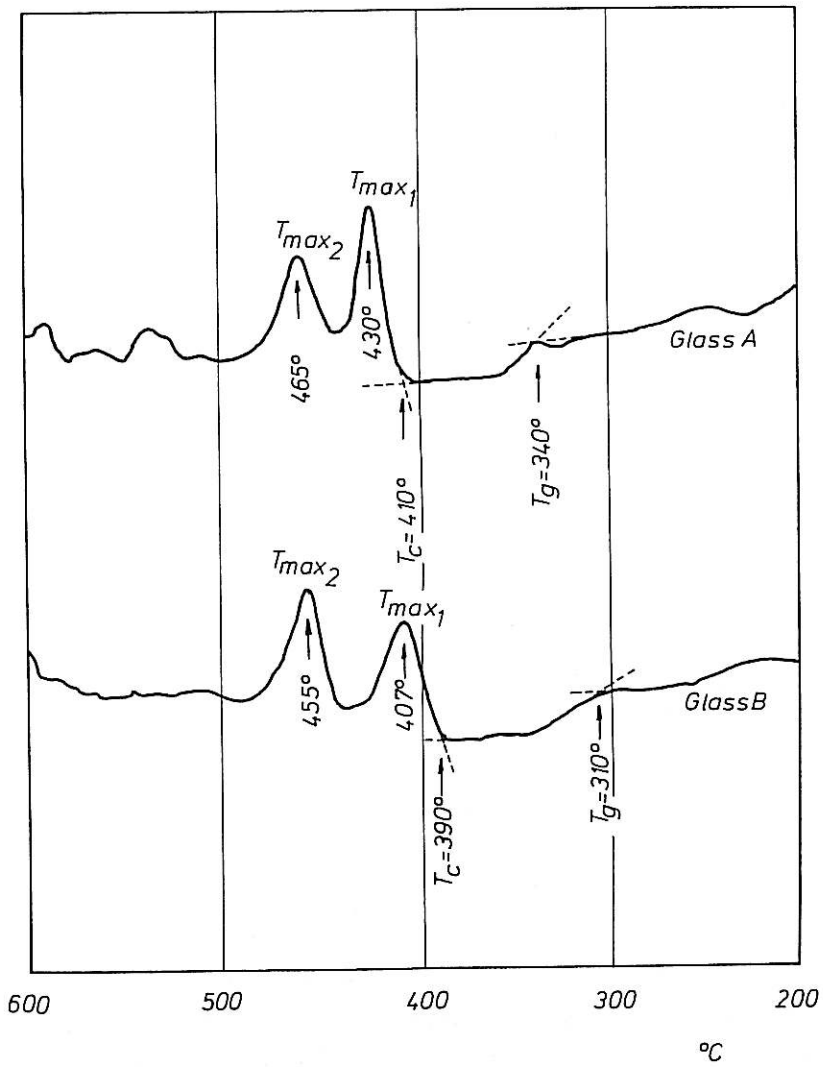

Fig. 8. Differential thermograms of glasses A and B measured under identical conditions.

purpose, comparative DTA measurements were made under entirely identical conditions. The results are depicted in fig. 8. Glass B containing a higher percentage of polysilicate anions crystallizes more readily than glass A. The decreased crystallization stability of glass B is expressed by lower values of T_c, T_{max_1} and T_{max_2} respectively.

All the results so far discussed point to the fact that the rate of structural rearrangement of silicate anions in the undercooled $2PbO \cdot SiO_2$ melt determines the silicate anion constitution and consequently the character of the solid product obtained. If the melt is quenched, the rapid quenching procedure provides no time for any significant redistribution of silicate units. As a result, the solid product is glassy, characterized by a polyanionic distribution of silicate anions with a relatively high amount of low molecular silicate units. But given the necessary conditions (temperature and time), silicate anions rearrange in the undercooled melt and form higher molecular silicate units. If this rearrangement is relatively slow, then the solid product is still glassy, yet it contains a higher amount of polysilicate chains. Very intensive rearrangement of silicate anions in the undercooled $2PbO \cdot SiO_2$ melt leads to the formation of a crystalline solid, which is characterized by the presence of both tetrameric rings $[Si_4O_{12}^{8-}]$ and polysilicate chains $[SiO_3^{2-}]_\infty$ and thus represents a mixture of the polymorphs M-$2PbO \cdot SiO_2$ and H-$2PbO \cdot SiO_2$ according to [3].

4. Summary

The kinetics of crystallization in a $2PbO \cdot SiO_2$ melt have been investigated. A TTT-diagram based on DTA measurements was constructed, which describes the kinetic conditions for the formation of crystalline phases in the given system. The minimum undercooling of the $2PbO \cdot SiO_2$ melt is 80°C. By means of silicate anion analysis it was possible to identify the connection between cooling rates of the melt and the constitution of silicate units in the obtained solid and to suggest a structural explanation for the large undercooling of the $2PbO \cdot SiO_2$ melt. Glasses of the same chemical composition differ in the constitution of their silicate anions, if the thermal history of these glasses is sufficiently different. Glassy $2PbO \cdot SiO_2$ with higher molecular silicate units crystallizes more easily than the same glass containing more low molecular silicate anions. The obtained results enable us to understand the kinetic processes of glass formation and crystallization on a more structural basis. They also offer a first insight into the complex relationship between thermal history, silicate anion constitution and properties of glasses.

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