SILICATE GROUPINGS IN GLASSY AND CRYSTALLINE 2PbO · SiO$_2$

J. GÖTZ

Joint Laboratory for Silicate Research of the Czechoslovak Academy of Sciences and the Institute of Chemical Technology, Prague, Czechoslovakia

and

D. HOEBBEL and W. WIEKER

Central Institute of Inorganic Chemistry of the Academy of Sciences of the German Democratic Republic, Berlin-Adlershof, GDR

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The type and the amount of silicate groupings existing in glassy and crystalline 2PbO · SiO$_2$ have been determined by direct chemical methods: paper chromatography, trimethylsilylation combined with gas–liquid partition chromatography and by the molybdate method. The results obtained by these three different methods are in good agreement and demonstrate, that glassy 2PbO · SiO$_2$ and each of the three main crystalline polymorphs are characterized by its own specific silicate anion distribution: the distribution in vitreous 2PbO · SiO$_2$ is of a polyanionic nature; in T−Pb$_2$SiO$_4$ dimeric groups [Si$_2$O$_7$]$^{6-}$ prevail; M$_1$-Pb$_2$SiO$_4$ contains predominantly [Si$_4$O$_{12}$]$^{8-}$ rings and H-Pb$_2$SiO$_4$ is a typical polysilicate with chain anions [SiO$_3^{2-}$]$_n$. The results fit a structural model according to which glass is a random array of discrete polyatomic groupings; the gradual transition from the glassy state to the stablest crystalline structure is connected with degradation and polymerization of silicate anions.

1. Introduction

The question whether glasses contain structural groupings * exceeding the limits of short-range order has been the subject of study for many years. Paper chromatographic works by Westman and Murthy [2,3]**, Grunze [4], Schulz and Hinz [5] demonstrated the existence of polyphosphate ions in alkali phosphate glasses, thus con-

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* In this paper, the term silicate grouping or Si−O grouping signifies the larger identifiable silicate units [SiO$_4$]$^{4-}$, [Si$_2$O$_7$]$^{6-}$, [Si$_3$O$_{10}$]$^{8-}$, etc. which exist in crystalline silicates. Similarly as in Bockris and Lowe [1] we sometimes call them silicate anions; this does not imply ionic bonds between these units and Pb in the lead silicate studied.
** References to many other works of Dr. Westman and his group may be found in these two papers.

firming the structural concept suggested by Van Wazer [6]. Extensive structural investigations of borate melts, vitreous and crystalline borates made by Krogh-Moe [7] as well as pioneering NMR studies by Bray [8] have provided sufficient evidence that borate glasses also contain randomly oriented structural units, B—O groupings, which are not consistent with a typical random network structure according to Warren and Zachariasen [9,10].

Indirect evidence for the existence of discrete structural units in silicate melts and glasses has been obtained by various physical methods [11], but direct proof has been missing. One reason for this is the fact that silicate glasses are mostly insoluble in conventional solvents and their structural units readily undergo hydrolysis in acid solutions; this makes the use of direct chemical methods for the identification and determination of various Si—O units in these materials very difficult. However, some progress has been made recently. Wieker and Hoebbel [12] developed a method of silicate anion analysis based on paper chromatography which, due to a special procedure minimizes the possibility of polycondensation or hydrolysis. Götz and Masson [13] introduced a method of direct trimethylsilylation, which converts silicate anions into their stable trimethylsilyl derivatives and in this way eliminates undesirable side reactions. By using this method for the study of lead silicate glasses, the presence of various discrete Si—O groupings could be confirmed [14].

Having reached this stage of development, it was considered useful to apply both the paper chromatography technique and the TMS method to the quantitative study of Si—O groupings in glassy and crystalline $2PbO \cdot SiO_2$. Thus, it was hoped to eliminate certain inherent shortcomings of each individual method and to obtain a detailed answer to the two main points of the investigation: which silicate units exist in the vitreous state, and what are the main structural differences between glassy and crystalline $2PbO \cdot SiO_2$?

2. Experimental procedure and results

2.1. Sample preparation

Glassy $2PbO \cdot SiO_2$ was prepared from a batch containing pure laboratory grade Pb_3O_4 and SiO_2 (grain size $<150\ \mu m$). The amount of Pb_3O_4 was slightly increased to allow for losses caused by volatilization of PbO. After melting the batch in a covered Pt crucible for 2 h at 1000°C, the fluid melt was poured into a quenching bath of ice and water. The obtained glass was immediately dried, crushed and ground to grain size $<250\ \mu m$, remelted for 2 h at 1000°C and quenched as before, amounts of PbO and SiO_2 in the glass being determined by chemical analysis. The weight percentages were 88 · 16% PbO and 11 · 84% SiO_2, which practically corresponds to the theoretical composition $2PbO \cdot SiO_2$. All crystalline samples were prepared by heating finely ground glass (grain size $<40\ \mu m$). To prepare T-Pb_2SiO_4, the glassy $2PbO \cdot SiO_2$ was heated for 1 h at 425°C. M_1-Pb_2SiO_4 was produced by heating the

glass for 24 h at 500°C and M_2-Pb_2SiO_4 by heating for 1 h at 620°C. The high-temperature modification H-Pb_2SiO_4 was prepared by heating the glass for 24 h at 725°C. After the heat treatment, the samples were ground to obtain grain size <40 μm.

2.2. X-ray identification

Finely ground samples (grain size <40 μm) were examined by the powder technique using a Geigerflex diffractometer (Rigaku Denki, Japan). CoK_α radiation filtered by Fe was employed. Fig. 1 shows diffractograms of the glass and all studied crystalline phases. Detailed evaluation of d values demonstrated that the crystalline modifications T-Pb_2SiO_4 and M_1-Pb_2SiO_4 are identical with corresponding phases studied by Billhardt [15]; diffraction lines of H-Pb_2SiO_4 sufficiently agree with those found by Argyle and Hummel [16] except for the line d = 9.54 Å, which is not listed in ref. [16].

So far, no determination of the crystal structure of the various modifications of crystalline Pb_2SiO_4 has been published. Recently, Smart and Glasser [17] investigated compound formation and phase equilibria in the system PbO–SiO₂ and reported, that of all four crystalline polymorphs only H-Pb_2SiO_4 is stable.

2.3. Quantitative determination of silicate groupings

The various silicate groupings and their respective amounts present in vitreous and crystalline 2PbO · SiO₂ were determined by paper chromatography and by direct trimethylsilylation; in two cases, additional measurements by the molybdate method were made. A detailed description of the paper chromatography technique is given in [12,18]; the TMS procedure published in [13] has been used. For details of the molybdate method, see [19].

The paper chromatograms of the glassy and crystalline 2PbO · SiO₂ obtained by elution solvent L I [12] are given in fig. 2. Chromatogram A represents the glass; it shows a very intensive spot in the mono-, di-, trisilicate position, a weak spot in the cyclotetrasilicate position and a diffuse band. By applying elution solvent L II it is possible to separate the upper spot into two, representing monosilicate anions $[SiO_4]^{4-}$ and the sum of $[Si_2O_7]^{6-}$ and $[Si_3O_{10}]^{8-}$, respectively. From a recently published study on condensation reactions of monosilicic acid [20] it follows that that part of the above-mentioned diffuse band which lies below the $[SiO_4]^{4-}$ position is due to a whole array of probably 2–3-dimensional silicate polyanions of various sizes. Polyanions of relatively lower molecular weight are located in the upper region of the band, which reaches from the monosilicate position to beyond the spot of $[Si_4O_{12}]^{8-}$; higher condensed silicate polyanions run as far as the tricycloheptasilicate anion $[Si_7O_{19}]^{10-}$. Evidently, these higher condensed species are not present in the glassy 2PbO · SiO₂, yet the low-molecular 2–3-dimensional units are indicated by the diffuse band below the monosilicate position. In chroma-
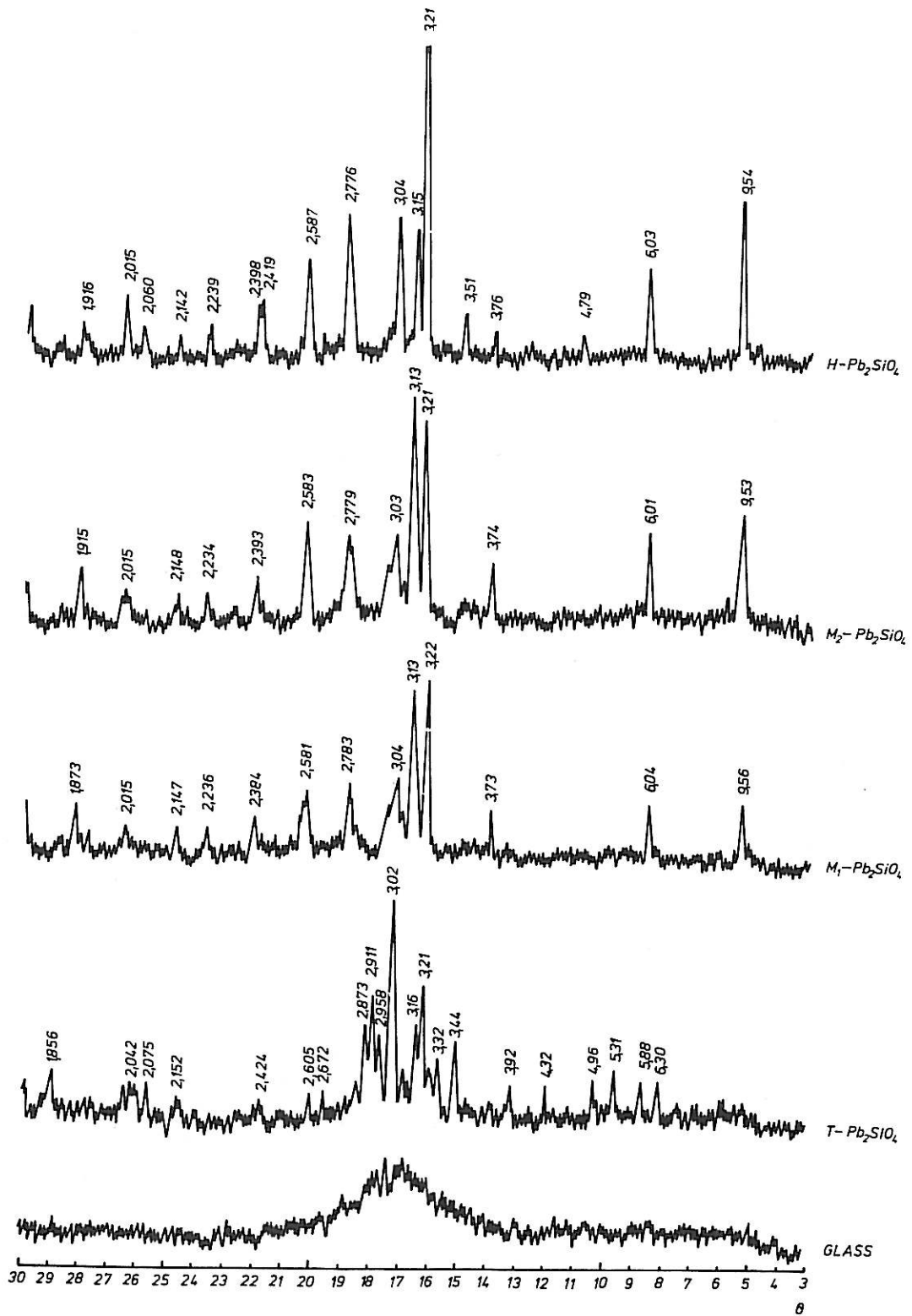
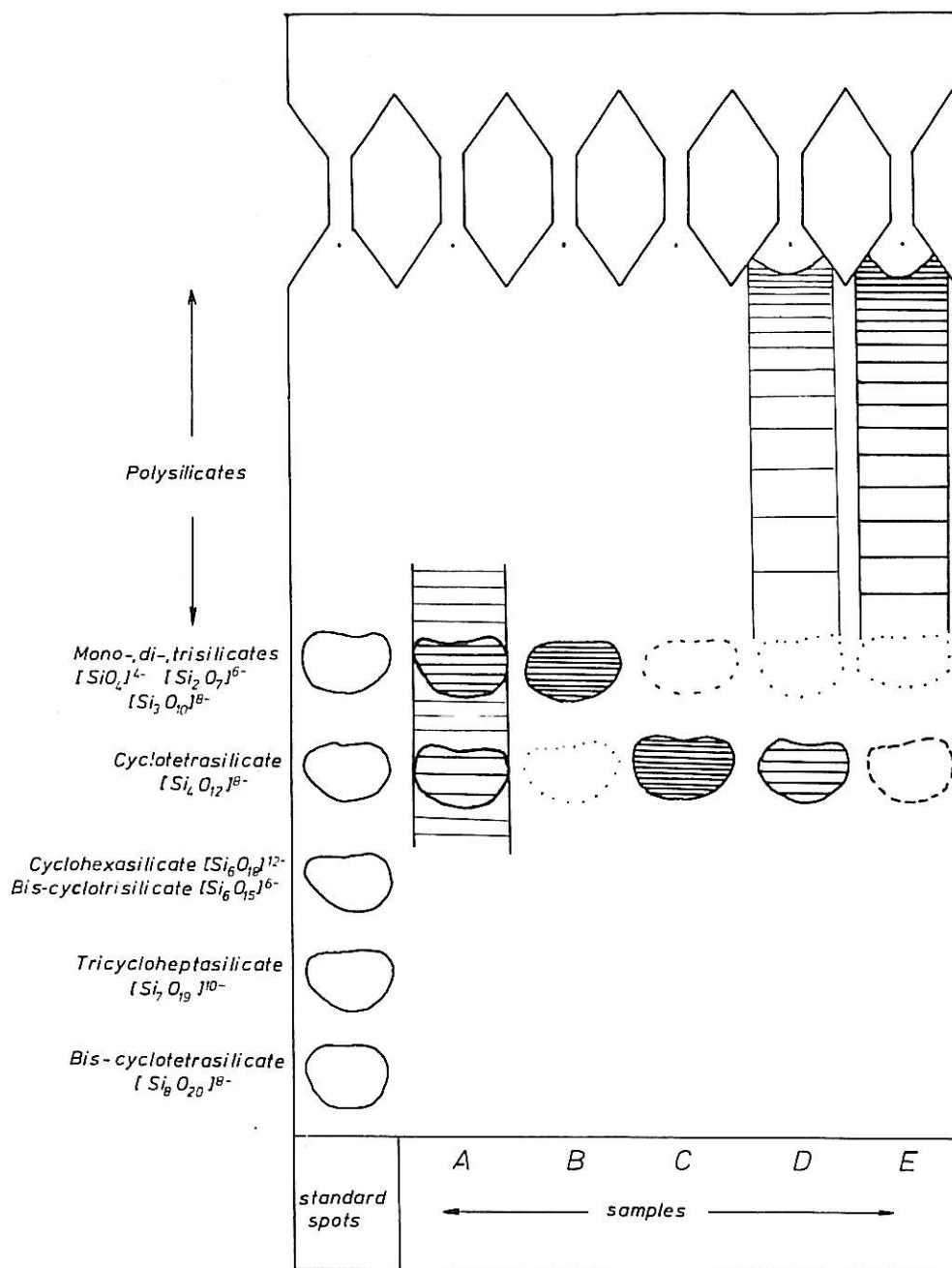Fig. 1. Diffractograms of vitreous and crystalline 2PbO · SiO₂.

Fig. 2. Paper chromatograms of vitreous and crystalline 2PbO · SiO$_2$.

togram A the short band above the $[SiO_4]^{4-}$ position is, according to our present knowledge, caused by low-molecular silicate chains composed of n' structural units, where n' has a value between 4 and that of polysilicate ($4 < n' < n_{poly}$).

Thus, it has been established that the vitreous 2PbO · SiO$_2$ contains $[SiO_4]^{4-}$, $[Si_2O_7]^{6-}$, $[Si_3O_{10}]^{8-}$ and $[Si_4O_{12}]^{8-}$, low-molecular polysilicate chains and 2—3-dimensional polyanions. Quantitative determination of these anionic groupings was made according to [18]; final weight percentages representing the average of five parallel measurements are listed in column A of table 1.

Table 1
Results of silicate anion analysis.

Indicated silicate anions	Glass A[a]	B[b]	C[c]	T-Pb$_2$SiO$_4$ A	B	C	M$_1$-Pb$_2$SiO$_4$ A	B	C	M$_2$-Pb$_2$SiO$_4$ A	C	H-Pb$_2$SiO$_4$ A	C
[SiO$_4$]$^{4-}$	10	14	10	18	13	18	{11	5	5	{8	4[d]	{4	4[d]
[Si$_2$O$_7$]$^{6-}$	{37	21	21	{63	51	·58		3	3		4[d]		–
[Si$_3$O$_{10}$]$^{8-}$		16	16		4	5		3	3		–	–	–
[Si$_4$O$_{12}$]$^{8-}$	14	10	14	10	23	10	89	89	89	57	57	16	16
low-molecular polysilicate	28	–	28	9	–	·9	–	–	–	–	–	–	–
polysilicate	–	–	–	–	–	–	–	–	–	35	35	80	80
2–3-dimensional units	11	–	11	–	–	–	–	–	–	–	–	–	–

a) Results of quantitative paper chromatography in wt% Si of the solid sample as various anions.
b) Corrected TMS results.
c) Final results in wt% Si of the solid sample as indicated anions.
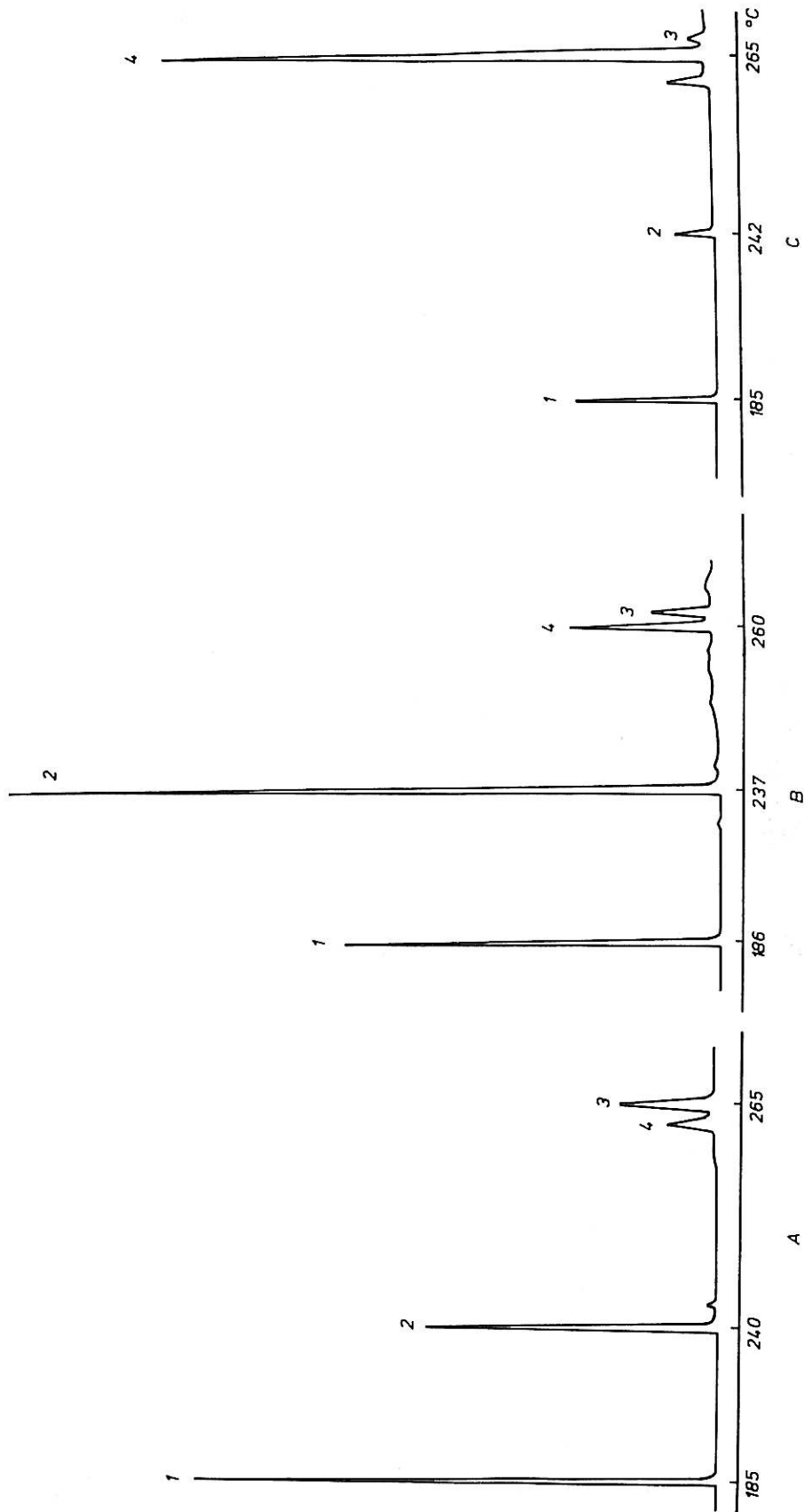d) Based on peak ratios of TMS chromatograms.

Fig. 3. Chromatograms obtained by the TMS method. (A) glassy 2PbO · SiO₂, (B) T-Pb₂SiO₄, (C) M₁-Pb₂SiO₄.

Crystalline T-Pb_2SiO_4 (fig. 2, chromatogram B) contains silicate anions which are indicated by a spot in the mono-, di-, trisilicate position. After resolving the spot by elution solvent L II, quantitative determinations were made, according to which 18 wt% Si of the crystalline sample is present as $[SiO_4]^{4-}$ anions and 63 wt% Si as disilicate (trisilicate) anions. Besides, minor amounts of $[Si_4O_{12}]^{8-}$ rings and low-molecular polysilicate anions were found.

The main spot in the chromatogram of M_1-Pb_2SiO_4 (chromatogram C, fig. 2) is due to $[Si_4O_{12}]^{8-}$; M_2-Pb_2SiO_4 (chromatogram D) contains tetrameric rings and polysilicates. The high-temperature modification H-Pb_2SiO_4 chromatogram E, fig. 2) shows an intensive polysilicate band and a weak spot in the $[Si_4O_{12}]^{8-}$ position. The weight percentages of total Si present in the form of various silicate anions in these solid samples are given in column A of table 1.

Gas—liquid partition chromatograms of glassy $2PbO \cdot SiO_2$, T-Pb_2SiO_4, and M_1-Pb_2SiO_4 obtained by the method of direct trimethylsilylation and subsequent GLC separation are depicted in fig. 3. In each chromatogram, peak 1 indicates $[(CH_3)_3 Si]_4 SiO_4$, the TMS derivative of $[SiO_4]^{4-}$ anions, peak 2 corresponds to the TMS derivative of $[Si_2O_7]^{6-}$, peak 3 to the trimethylsilylated anion $[Si_3O_8]^{10-}$ and peak 4 represents the TMS derivative of $[Si_4O_{12}]^{8-}$. A very small peak following peak 2 in the chromatogram of glassy $2PbO \cdot SiO_2$ is believed to be the TMS derivative of the cyclic anion $[Si_3O_9]^{6-}$; the minor peak preceding peak 4 in M_1-Pb_2SiO_4 is due to incompletely trimethylsilylated $[Si_4O_{12}]^{8-}$ rings. Area percentages resulting from integrator measurements of individual peak areas are given in table 2, column A. These percentages refer to TMS derivatives; the values of wt% Si present as various silicate anions have been determined by internal calibration [13] and are listed in column B of table 2.

Comparison of corresponding measurements on identical lead silicate samples by both methods revealed that the TMS chromatograms contained no peaks of low-molecular polysilicates, polysilicates and 2—3-dimensional polyanions, the presence of which had been indicated by paper chromatography. A similar observation was made

Table 2
Results of TMS analysis.

	Glass		T-Pb_2SiO_4		M_1-Pb_2SiO_4	
	$A^{a)}$	$B^{b)}$	A	B	A	B
$[SiO_4]^{4-}$	41	24	26	14	10	5
$[Si_2O_7]^{6-}$	31	34	56	56	4	3
$[Si_3O_{10}]^{8-}$	18	26	4	4	3	3
$[Si_4O_{12}]^{8-}$	10	16	14	26	83	89

a) Area% of TMS derivatives.
b) Wt% Si as various anions.

by Lentz [21], who used the TMS technique to analyze silicate structures in hydrated Portland cement paste. The reason for this is found in the low volatility of high-molecular TMS derivatives; these very large non-volatile species are not detected by gas—liquid chromatography. Thus, direct comparison of paper chromatography and TMS results is possible only by introducing "corrected" TMS results, which are obtained by multiplying the results of TMS analysis (table 2, column B) by the factor

$$f = (Si_1 + Si_2 + Si_3 + Si_4)/100 ,$$

where Si_1, Si_2, Si_3 and Si_4 are the weight percentages of the $[SiO_4]^{4-}$, $[Si_2O_7]^{6-}$, $[Si_3O_{10}]^{8-}$ and $[Si_4O_{12}]^{8-}$ anions, respectively, obtained from quantitative paper chromatography and listed in column A of table 1. These corrected values respect the presence of certain high condensed Si—O groupings, undetected by TMS analysis, the quantity of which has been established by paper chromatography. The corrected TMS values are listed in column B of table 1.

The agreement between quantitative paper chromatography and corrected TMS results is in most cases very good. This provides a basis for the use of corrected TMS results to establish mutual relations between $[Si_2O_7]^{6-}$ and $[Si_3O_{10}]^{8-}$, which are not separated by elution solvent L II in paper chromatography. These relations were projected into the final results listed in column C of table 1; these results have been used for all further evaluations.
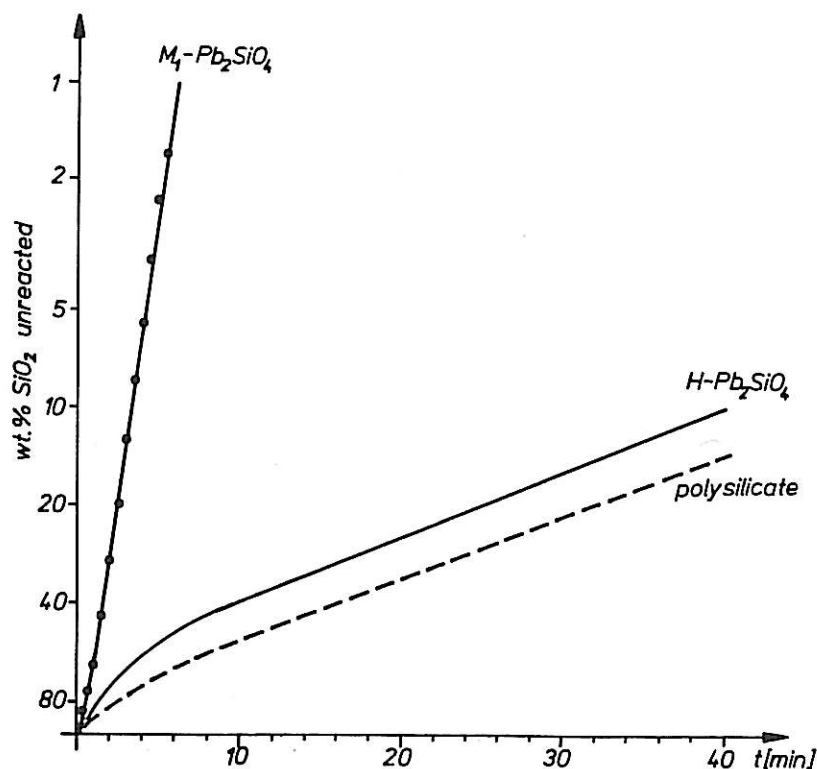

Fig. 4. Molybdate reaction dependences for M_1-Pb_2SiO_4 and H-Pb_2SiO_4. The dots represent the experimental results obtained by measuring M_1-Pb_2SiO_4; the straight line corresponds to the test substance.

Additional verification of the results given in table 1 can be obtained by the molybdate method according to [19], which measures the formation speed of β-molybdatosilicic acid; this speed is characteristic for the type of silicate anion. As stated in [12], the application of this method for the determination of silicate anions is meaningful only when one or maximally two different silicate anion types are present. Therefore, the molybdate method was applied to the crystalline samples M$_1$-Pb$_2$SiO$_4$ and H-Pb$_2$SiO$_4$, in which one silicate anion type prevails. Fig. 4 shows the reaction speeds of M$_1$-Pb$_2$SiO$_4$ and H-Pb$_2$SiO$_4$ as compared with test substances. The reaction speed of M$_1$-Pb$_2$SiO$_4$ is identical with that of K$_4$H$_4$Si$_4$O$_{12}$ used as a test substance, thus confirming the results of paper chromatography and TMS analysis. The molybdate curve of H-Pb$_2$SiO$_4$ runs parallel to the curve of polysilicate [Li$_2$SiO$_3$]$_n$ used as a test substance; this means that the silicate groupings in H-Pb$_2$SiO$_4$ are mainly polysilicate anions with almost the same degree of condensation as in [Li$_2$SiO$_3$]$_n$. Both dependences are not identical because H-Pb$_2$SiO$_4$ contains low-molecular silicate anions [SiO$_4$]$^{4-}$ and [Si$_4$O$_{12}$]$^{8-}$.

3. Discussion

The results of silicate anion analysis listed in table 1 provide interesting information about the existence of defined Si–O groupings in vitreous and crystalline 2PbO·SiO$_2$. The main differences between the glass and the crystalline polymorphs are clearly demonstrated by distribution diagrams, which illustrate the data of table 1 in a more expressive form (fig. 5).

It demonstrates that the distribution of Si–O groupings in the glass is of a "polydisperse" nature: the glass is characterized by the presence of a whole variety of very different silicate units, where no single type prevails. The first crystalline modification T-Pb$_2$SiO$_4$ contains mostly dimeric groupings [Si$_2$O$_7$]$^{6-}$. Their
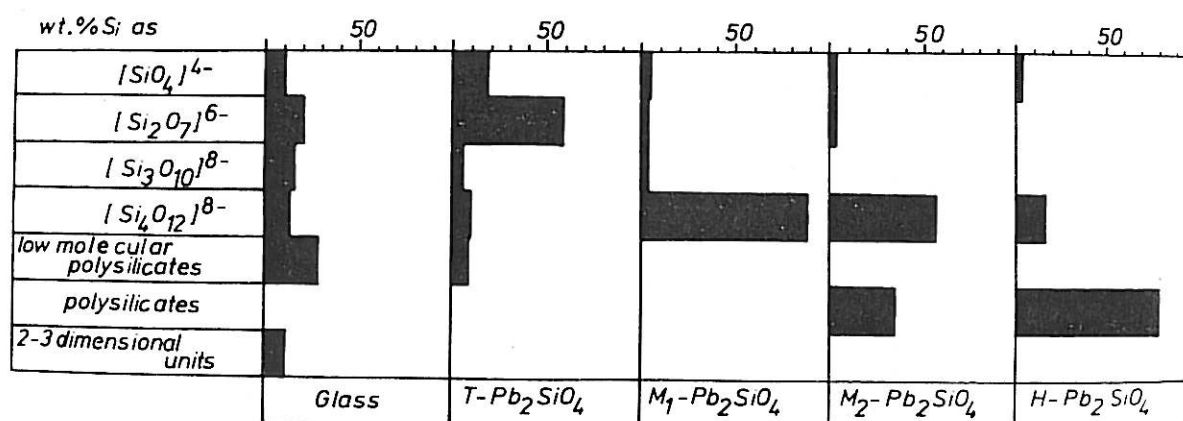

Fig. 5. Wt% Si of the solid samples detected as various Si–O groupings.

increase — 37% compared with the glass — is apparently connected with a simultaneous 30% decrease in low-molecular polysilicates and 2—3-dimensional units and a lower content of trimeric chains $[Si_3O_{10}]^{8-}$. This shift in the distribution curve is due to the heat treatment which causes thermal vibrations leading to fragmentation of the largest units. In this way, dimeric anions $[Si_2O_7]^{6-}$ are formed either from monomeric fragments or directly from higher units. M_1-Pb_2SiO_4 contains mainly tetrameric rings $[Si_4O_{12}]^{8-}$. As it crystallizes from the glass via T-Pb_2SiO_4, the conversion T-Pb_2SiO_4 → M_1-Pb_2SiO_4 may be schematically viewed as polymerization

$$[Si_2O_7]^{6-} + [Si_2O_7]^{6-} \rightsquigarrow [Si_4O_{12}]^{8-} . \tag{1}$$
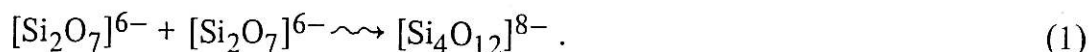
Eq. (1) expresses only one of the possible reaction mechanisms; other ways of ring formation may exist. The detailed mechanism of this polymerization is probably complicated and includes fragmentation of low-molecular polysilicates and various polymerization steps. It should be noticed that the prevalence of $[Si_4O_{12}]^{8-}$ groupings in the medium-temperature modification was reported some time ago; our present measurements confirm that result [14].

There are two ways to formulate M_1-Pb_2SiO_4 in accordance with stoichiometry: either we assume the formation of free PbO due to

$$4[2PbO \cdot SiO_2] \rightarrow Pb_4[Si_4O_{12}] + 4PbO \tag{2}$$

or we postulate the existence of [—Pb—O—Pb—] groupings and write

$$4[2PbO \cdot SiO_2] = [Pb_2O]_4[Si_4O_{12}] . \tag{3}$$

X-ray measurements by the Guinier method detected neither PbO, Pb, PbO_2 nor Pb_3O_4; therefore we suggest the formula $[Pb_2O]_4[Si_4O_{12}]$, which is in agreement with the increased oxygen coordination of Pb atoms found by several authors [22,23].

The second medium-temperature modification M_2-Pb_2SiO_4 is an intermediate between M_1-Pb_2SiO_4 and the high-temperature phase H-Pb_2SiO_4. The latter is characterized by the prevalence of high-molecular chains $[SiO_3^{2-}]_n$. These chains are formed by a very complex reaction involving fragmentation of tetrameric rings and linear polymerization of fragments. The experimental conditions for the preparation of H-Pb_2SiO_4 were chosen in accordance with Argyle and Hummel [16]; the results of silicate anion analysis indicate that more intensive heat treatment would be needed to convert all remaining tetrameric rings into polysilicate chains. Our experience shows that prolonged heat treatment alone (96 h at 725—730°C) does not significantly increase the amount of $[SiO_3^{2-}]_n$ anions in H-Pb_2SiO_4; very probably higher temperatures close to T_L would be needed. This has been confirmed by a very recent paper published after the conclusion of our own experimental work [17].

X-ray diffraction studies established that only H-Pb_2SiO_4 is a stable crystalline modification; T-Pb_2SiO_4, M_1-Pb_2SiO_4 and M_2-Pb_2SiO_4 are metastable [17]. This is understandable if the prevailing type of Si—O groupings characterizing the individual crystalline phases is taken into consideration: the dimeric anions predominant in T-Pb_2SiO_4 are metastable because they easily turn into tetrameric rings. At higher

temperatures these $[Si_4O_{12}]^{8-}$ rings decompose and convert into true polysilicate chains, which are the stablest Si—O grouping in the given system; they disrupt only on melting.

Unfortunately, at present there is no direct way to determine the type of Si—O groupings in the melt. However. for orientation the distribution diagram of the vitreous $2PbO·SiO_2$ may be used, because this glass was prepared by rapid quenching of the melt. The diagram confirms the splitting of long polysilicate chains during the melting procedure. The melt evidently contains a whole variety of discrete Si—O groupings, including monomeric anions $[SiO_4]^{4-}$, short and longer linear chains, rings and 2—3-dimensional groupings. The equilibrium distribution of these units in a given melt depends on temperature; it alters in accordance with melting history.

As to the structure of glassy $2PbO·SiO_2$, our results demonstrate that this glass contains discrete Si—O groupings of various constitutions and sizes; some of them definitely exceed the limits of short-range order. These findings are consistent with a structural concept derived by Bray [8] from NMR measurements of this very system, according to which the glassy $2PbO·SiO_2$ is composed of "a random array of ordered and recognizable structural groupings". We conclude that the discrete Si—O groupings present in the glass are formed by complex polymerization and depolymerization reactions in the melt; their variety is not limited to the types of Si—O groupings existing in the network of crystalline lead silicates of the same composition.

Acknowledgement

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