

ON THE CONSTITUTION OF SILICATE GROUPINGS IN BINARY LEAD SILICATE GLASSES

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Direct chemical methods have been used to determine the type and the percentage of silicate groupings present in binary lead silicate glasses within the composition range $4\text{PbO} \cdot \text{SiO}_2 - \text{PbO} \cdot \text{SiO}_2$. The results obtained indicate that the constitution and the relative amounts of various silicate groupings change with the changing total amount of SiO_2 in the glass. Glasses containing small amounts of SiO_2 are characterized by the presence of few low-molecular silicate units; increasing the percentage of SiO_2 promotes the formation of higher polymerized silicate groupings. The results are discussed with regard to stoichiometry, and are consistent with Hägg's concept of glassiness.

1. Introduction

The $[\text{SiO}_4]^{4-}$ tetrahedron is the elementary building unit for both crystalline and glassy silicates. The lattice of crystalline silicates is characterized by a periodical arrangement of definite building units which include various types of silicate anions; in silicate glasses the periodicity of atoms exists only on a limited scale. "Short-range" periodicity characterizes glasses with a typical random network structure, e.g. glassy SiO_2 . In such glasses, the $[\text{SiO}_4]^{4-}$ tetrahedra are statistically distributed, so that no regions of higher order exist. However, other glasses may have less uniform distributions, resulting in the existence of Si–O groupings* of higher order. Such groupings should be expected in glasses containing significant amounts of metal oxides, which make the formation of an interconnected silicate network impossible. This has been demonstrated in a preceding paper, which described the application of newly developed chemical methods to the determination of silicate groupings in glassy and crystalline

* Our understanding of the term "grouping" has been explained in a preceding paper [1].

$2\text{PbO} \cdot \text{SiO}_2$ [1]. It was found that glassy $2\text{PbO} \cdot \text{SiO}_2$ contained a whole array of various silicate groupings, ranging from $[\text{SiO}_4]^{4-}$ over low-molecular chains and rings to polysilicate chains and two- to three-dimensional units. Evidently, the distribution of silicate groupings in glasses depends on the chemical composition. The purpose of the following investigation was to study the effect of composition changes on the constitution of Si–O groupings in binary lead silicate glasses ranging from $4\text{PbO} \cdot \text{SiO}_2$ to $\text{PbO} \cdot \text{SiO}_2$.

2. Experimental procedure

Eight binary lead silicate glasses of different composition (table 1) were prepared by rapid quenching of the corresponding melts. The obtained glasses were examined by X-ray diffraction and chemically analysed to establish the precise ratio of PbO to SiO_2 . Finally, in all the samples the present silicate groupings were determined. The detailed procedures were as follows.

2.1. Glass preparation

Glasses were prepared from batches containing pure laboratory grade PbO and SiO_2 (grain size $<150 \mu\text{m}$). To avoid reduction of PbO, very small amounts of NH_4NO_3 were added. About 50 g of the batch was melted in a covered Pt crucible for 15 min at 850°C . The liquid melt was poured into a quenching bath of ice and water and the glass was dried, crushed and ground to grain size $<250 \mu\text{m}$. The powdered glass was remelted in small amounts ($\approx 10 \text{g}$) for 5 min at 850°C and rapidly quenched by dropping the crucible with the melt directly into the quenching bath. In this way, a cooling rate of about 10^3°C/s was achieved. Microscopic examination of the glasses showed no sign of crystallization, only the glassy $4\text{PbO} \cdot \text{SiO}_2$ containing a few crystalline patches which were eliminated by hand-picking.

Table 1
Chemical composition of the glasses.

PbO (wt%)	SiO (wt%)	Molar ratio $R = \text{PbO}/\text{SiO}_2$
78.90	21.28	1.00
81.75	17.96	1.22
83.92	15.68	1.44
84.90	15.20	1.50
88.32	11.85	2.01
90.58	9.65	2.53
92.00	8.02	3.08
93.90	6.10	4.14

2.2. X-ray testing of glassiness

In addition to microscopic examination, the glassiness of the prepared samples was tested by X-ray diffraction using a Geigerflex diffractometer (Rigaku Denki, Japan). CoK_α radiation filtered by Fe was employed.

2.3. Quantitative determination of silicate groupings

Silicate groupings present in the prepared glasses were determined by simultaneous application of three chemical methods – paper chromatography, trimethylsilylation combined with gas-liquid chromatography, and the molybdate method. Details of the procedures employed were described in a recent paper [1]. The relative error of the results depended on the percentage of the determined silicate anion: with percentages $>30\%$ the error equalled $\pm 5\%$ of the result, when the percentage was smaller, the relative error increased.

3. Results and discussion

X-ray diffractograms of all prepared glasses demonstrate, in agreement with microscopic observation, that the quenched samples are true glasses with no crystalline phases present (fig. 1).

The results obtained by combined silicate anion analysis of the lead silicate glasses studied are listed in table 2. They show that glasses corresponding to the molar ratio $R = \text{PbO}/\text{SiO}_2$ ranging from 4 to 2 contain mainly monosilicate, disilicate and trisilicate anions and tetrameric rings (fig. 2). With decreasing values of R (2.50–1.50) the percentage of these low-molecular silicate anions diminishes and groupings of higher molecular weight – chain-forming polysilicates and two- to three-dimensional silicate groupings – appear*. As R declines further to 1.50–1.22, the percentages of low-molecular anions Si_1 – Si_4 , polysilicate chains and two- to three-dimensional groupings decrease, whereas phyllosilicates and higher polymerized silicate groupings arise, which cannot be quantitatively separated. For this reason the values obtained for the glassy $\text{PbO} \cdot \text{SiO}_2$ should be regarded as semiquantitative (expressed by a dashed line in fig. 2). Glasses with a molar ratio $R < 1$ cannot be studied quantitatively by the methods employed because of their low solubility in 0.1 N acids. However, qualitative results indicate that with further increase in SiO_2 the amount of phyllosilicate groupings declines and silicate formations appear, which are more highly polymerized than phyllosilicates. This general tendency towards continuous polymerization with in-

* Paper chromatograms of the lead silicate glasses studied contain a characteristic band below the spot of $[\text{Si}_4\text{O}_{12}]^{8-}$. Investigations on soluble alkali silicates [2] and silicic acid [3] show that this band corresponds to two- to three-dimensional silicate groupings which are less polymerized than phyllosilicates.

- [1] A. Hirsch, *The Chemistry of the Fullerenes*, Thieme, Stuttgart, 1994.
- [2] a) D. Gust, T. A. Moore in *Topics in Current Chemistry*, Vol. 159, *Photoinduced Electron Transfer III* (Ed.: J. Mattay), Springer, Berlin, 1991, pp. 103–151; b) M. R. Wasielewski, *Chem. Rev.* 1992, 92, 435–461; c) J. Deisenhofer, J. R. Norris, *The Photosynthetic Reaction Center*, Academic Press, San Diego, 1993; d) H. Kurreck, M. Huber, *Angew. Chem.* 1995, 107, 929–947; *Angew. Chem. Int. Ed. Engl.* 1995, 34, 849–867.
- [3] a) J. Helaja, A. Y. Tauber, Y. Abel, N. V. Tkachenko, H. Lemmetyinen, I. Kilpelläinen, P. H. Hynninen, *J. Chem. Soc. Perkin Trans. 1* 1999, 2403–2408; b) N. V. Tkachenko, L. Rantala, A. Y. Tauber, J. Helaja, P. H. Hynninen, H. Lemmetyinen, *J. Am. Chem. Soc.* 1999, 121, 9378–9387.
- [4] a) T. G. Linssen, K. Dürr, M. Hanack, A. Hirsch, *J. Chem. Soc. Chem. Commun.* 1995, 103–104; b) T. Drovetskaya, C. A. Reed, P. D. W. Boyd, *Tetrahedron Lett.* 1995, 36, 7971–7974; c) D. Kuciauskas, S. Lin, G. R. Seely, A. L. Moore, T. A. Moore, D. Gust, T. Drovetskaya, C. A. Reed, P. Boyd, *J. Phys. Chem.* 1996, 100, 15926–15932; d) E. Dietel, A. Hirsch, E. Eichhorn, A. Rieker, S. Hackbarth, B. Röder, *J. Chem. Soc. Chem. Commun.* 1998, 1981–1982; e) A. C. Tomé, R. F. Enes, J. P. C. Tomé, J. Rocha, M. G. P. M. S. Neves, J. A. S. Cavaleiro, J. Elguero, *Tetrahedron* 1998, 54, 11141–11150; f) P. Cheng, S. R. Wilson, D. I. Schuster, *J. Chem. Soc. Chem. Commun.* 1999, 89–90; g) N. Armaroli, F. Diederich, L. Echegoyen, T. Habicher, L. Flamigni, G. Marconi, J.-F. Nierengarten, *New J. Chem.* 1999, 77–84.
- [5] a) H. Imahori, Y. Sakata, *Adv. Mater.* 1997, 9, 537–546; b) D. Gust, T. A. Moore, A. L. Moore, *Res. Chem. Intermed.* 1997, 23, 621–651; c) N. Martín, L. Sánchez, B. Illescas, I. Pérez, *Chem. Rev.* 1998, 98, 2527–2547; d) F. Diederich, R. Kessinger, *Acc. Chem. Res.* 1999, 32, 537–545.
- [6] a) F.-P. Montforts, *Angew. Chem.* 1981, 93, 795–796; *Angew. Chem. Int. Ed. Engl.* 1981, 20, 778–779; b) F.-P. Montforts, U. M. Schwartz, *Liebigs Ann. Chem.* 1985, 1228–1253; c) F.-P. Montforts, B. Gerlach, F. Höper, *Chem. Rev.* 1994, 94, 327–347; d) F.-P. Montforts, M. Glasenapp-Breiling in *Progress in Heterocyclic Chemistry*, Vol. 10 (Eds.: G. W. Gribble, T. L. Gilchrist), Pergamon, Oxford, 1998, pp. 1–24.
- [7] a) F.-P. Montforts, *Angew. Chem.* 1982, 94, 208–209; *Angew. Chem. Int. Ed. Engl.* 1982, 21, 214–215; *Angew. Chem. Suppl.* 1982, 499–505; b) F.-P. Montforts, J. W. Bats, *Helv. Chim. Acta* 1987, 70, 402–411.
- [8] a) Y. Abel, E. Haake, G. Haake, W. Schmidt, D. Struve, A. Walter, F.-P. Montforts, *Helv. Chim. Acta* 1998, 81, 1978–1996; b) G. Haake, D. Struve, F.-P. Montforts, *Tetrahedron Lett.* 1994, 35, 9703–9704.

The First Crystal Structure of a Germanium(II) Amide with a Germanium–Lithium Bond and Its Behavior Towards Oxygen and Water**

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Dedicated to Professor Gerhard Fritz
on the occasion of his 80th birthday

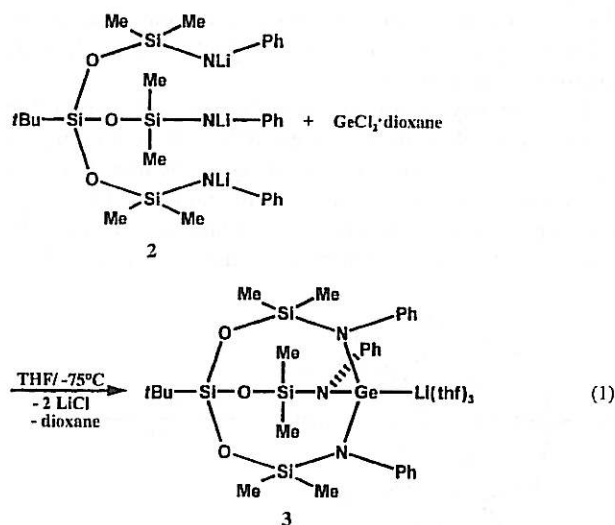
Amides of Group 4 metals that contain metal–lithium bonds are relatively rare. A few years ago, Gade et al. reported the crystal structure of a tripodal silyl amide with a

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tin(II)–lithium bond.^[1] A mixed germanium–lithium amide was also synthesized;^[2] however, the structure of this compound could not be determined by X-ray structure analysis. In recent years only a few compounds containing germanium–lithium bonds have been synthesized and characterized by X-ray crystallography.^[3–5] Very little is known about the chemistry of these compounds. We report here on the synthesis and crystal structure of a tripodal germanium(II) siloxamide with a germanium–lithium bond as well as on the reaction behavior of this bond towards water and oxygen. Interestingly, these reactions led to a simple Li/H exchange and an insertion of an oxygen atom into the germanium–lithium bond, respectively. We were able to isolate the reaction products from the hydrolysis and the oxidation and determine the structure of these compounds by X-ray crystallography.

The ligand system used was the tripodal amine *t*BuSi(OSiMe₂NHPh)₃ (**1**);^[6] its lithium salt **2**^[6] was taken as the starting material for the synthesis of the germanium(II) siloxamide **3**. Compound **2** reacted with an adduct of germanium(II) chloride and dioxane^[7] (equimolar amounts with respect to **2**) in THF at –75 °C to give the heterometallic amide **3** in good yields [Eq. (1)]. The ¹H, ¹³C, ²⁹Si, and ⁷Li NMR spectra of **3** in



solution showed only one singlet each for the dimethylsilyl groups, for the methyl groups of the *tert*-butyl group, and for the lithium atom. This indicates that in solution **3** should have, at least on a time-average, C_{3v} symmetry. The ¹H and ¹³C NMR spectra also contain signals for coordinated THF molecules.

Controlled hydrolysis of **3** in THF gave the solvent-free germanium hydride **4** in 63% yield [Eq. (2)] along with the soluble side product **1** (20–30%). The remarkably simple Li/H exchange, for which there are only a few analogies,^[8] can be explained by an attack of the oxygen atom of the water molecule on the Lewis acidic lithium atom of the Ge–Li bond. The proton transfers to the partially negatively charged germanium atom to yield **4** and lithium hydroxide. This corresponds to a change in the partial charge on the germanium atom since the proton is now regarded as a hydride. In the IR spectrum of the product the characteristic

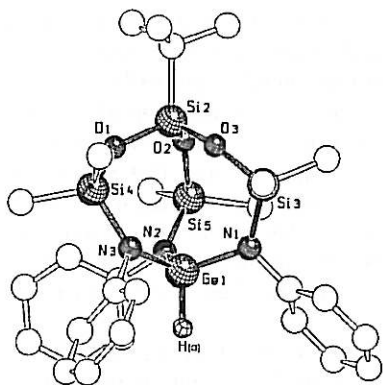


Figure 2. Crystal structure of **4**. Selected bond lengths [Å] and angles [°]: Ge1–N3 1.848(3), Ge1–N2 1.848(3), Ge1–N1 1.849(3), Ge–H(a) 1.40(3), Si3–N1 1.733(3), Si4–N3 1.738(3), Si5–N2 1.749(3), N3–Ge1–N2 110.29(13), N3–Ge1–N1 113.65(13), N2–Ge1–N1 111.59(13), N1–Ge1–H(a) 106.1(12), N2–Ge1–H(a) 109.9(13), N3–Ge1–H(a) 105.0(13). The hydrogen atoms are omitted for clarity. The unlabeled atoms are carbon atoms.

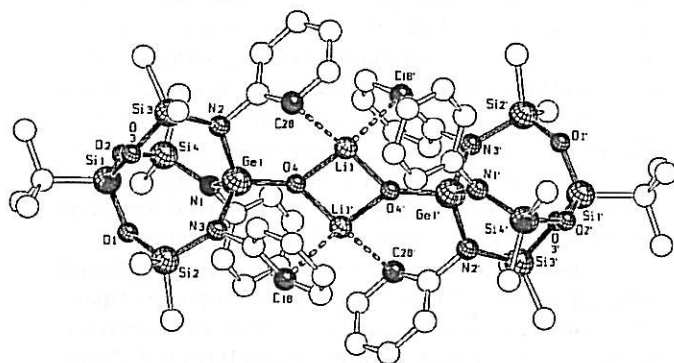


Figure 3. Crystal structure of **5**. Selected bond lengths [Å] and angles [°]: Ge1–N1 1.847(6), Ge1–N3 1.866(5), Ge1–N2 1.866(6), Ge1–O4 1.702(4), Si2–N3 1.725(5), Si3–N2 1.738(6), Si4–N1 1.729(6), Li1–O4' 1.806(15), O4–Li1 1.784(15), Li1–Li1' 2.31(3), C18–Li1' 2.61(2), C28–Li1 2.71(2); N1–Ge1–N3 109.6(2), N1–Ge1–N2 110.0(3), N3–Ge1–N2 109.6(3), Li1–O4–Li1' 80.0(7), O4–Li1–O4' 100.0(7). The hydrogen atoms are omitted for clarity. The unlabeled atoms are carbon atoms.

coordinated to two oxygen atoms, they also weakly interact with the π electrons of the phenyl groups (shortest Li–C bond lengths: 2.61(2), 2.71(2) Å), so that they have distorted tetrahedral coordination. The shortening of the Ge–O bond (1.702(4) Å) is remarkable: This bond is not only 0.25 Å shorter than the sum of the covalent radii of germanium and oxygen, but it is also shorter than typical Ge–O single bonds.^[13, 26–29] This is apparently caused by the high electronegativity of the “charged” oxygen atom. As in **4**, the oxidation state of Ge^{IV} in **5** is responsible for the shorter Ge–N bonds (av 1.860(6) Å) and larger N–Ge–N angles (av 109.73(3)°) than in **3**. Our results are remarkable in that there is a simple change of charge on the germanium atom in **3** as a consequence of the lithium–hydrogen exchange (**4**) and a simple insertion of oxygen into a bond between two electro-positive elements (**5**).

Experimental Section

3: To a solution of **2** (0.60 g, 1 mmol) in THF (20 mL) at -75°C was added $\text{GeCl}_2 \cdot \text{dioxane}$ (0.23 g, 1 mmol) in THF (5 mL). The mixture was stirred

for 2 h at $\approx 25^\circ\text{C}$, concentrated under vacuum, taken up in diethyl ether, and filtered. Slow concentration of the filtrate under reduced pressure resulted in precipitation of colorless prisms of **3**. Yield: 0.70 g (80%). $^1\text{H NMR}$ (200.13 MHz, C_6D_6): $\delta = 0.63$ (s, 18H; $\text{OSi}(\text{CH}_3)_2\text{N}$), 1.30 (s, 9H; $\text{SiC}(\text{CH}_3)_3$), 1.32 (m, 12H; THF), 3.25 (m, 12H; THF); $^{13}\text{C NMR}$ (50.3 MHz, C_6D_6): $\delta = 3.95$ (s, 6C; $\text{OSi}(\text{CH}_3)_2\text{N}$), 16.96 (s, 1C; $\text{SiC}(\text{CH}_3)_3$), 26.65 (s, 3C; $\text{SiC}(\text{CH}_3)_3$), 25.51 (s, 6C; THF), 68.35 (s, 6C; THF), 118.48, 126.31, 128.10, 154.65 (4s; arene C); $^{29}\text{Si NMR}$ (39.7 MHz, C_6D_6): $\delta = -8.96$ (s, 3Si; $\text{OSi}(\text{CH}_3)_2\text{N}$), -56.05 (s, 1Si; $\text{SiC}(\text{CH}_3)_3$); $^7\text{Li NMR}$ (77.7 MHz, C_6D_6): $\delta = -3.57$ (s, 1Li; GeLi); correct elemental analysis; cryoscopy: calcd 876.85, found 890.

4: To **2** (0.65 g, 1.08 mmol) in THF (20 mL) at -75°C was added dropwise $\text{GeCl}_2 \cdot \text{dioxane}$ (0.25 g, 1.08 mmol) in THF (5 mL). After stirring for 2 h at about 25°C , the mixture was cooled with ice and a 1M solution of water in dioxane (1 mL) was slowly added. The mixture was stirred for 2 h at about 25°C . The solvent was evaporated to give a solid residue, which was taken up in hexane (20 mL). The LiCl precipitate was filtered off, and the filtrate was slowly concentrated under reduced pressure until colorless parallelepipeds of **4** began to precipitate. Yield: 0.44 g (63%). $^1\text{H NMR}$ (200.13 MHz, C_6D_6): $\delta = 0.40$ (s, 18H; $\text{OSi}(\text{CH}_3)_2\text{N}$), 1.18 (s, 9H; $\text{SiC}(\text{CH}_3)_3$), 5.66 (s, 1H; GeH); $^{13}\text{C NMR}$ (50.3 MHz, C_6D_6): $\delta = 2.37$ (s, 6C; $\text{OSi}(\text{CH}_3)_2\text{N}$), 16.59 (s, 1C; $\text{SiC}(\text{CH}_3)_3$), 25.92 (s, 3C; $\text{SiC}(\text{CH}_3)_3$), 123.86, 128.20, 129.34, 147.34 (4s; arene C); $^{29}\text{Si NMR}$ (39.7 MHz, C_6D_6): $\delta = -4.64$ (s, 3Si; $\text{OSi}(\text{CH}_3)_2\text{N}$), -56.91 (s, 1Si; $\text{SiC}(\text{CH}_3)_3$); IR (NaCl, hexane): $\tilde{\nu} = 2105.3\text{ cm}^{-1}$; correct elemental analysis; cryoscopy: calcd 654.60, found 660.

5: Compound **3** (0.9 g, 1.03 mmol) was dissolved in benzene (20 mL) and dry oxygen was bubbled through the solution for approximately 10 s at about 25°C . The mixture was stirred for 30 min. The solvent was evaporated to give a yellow solid which was recrystallized from hexane to afford **5** as colorless, cuboid rods with a total yield of 0.51 g (73%). $^1\text{H NMR}$ (200.13 MHz, C_6D_6): $\delta = 0.38$ (s, 36H; $\text{OSi}(\text{CH}_3)_2\text{N}$), 1.20 (s, 18H; $\text{SiC}(\text{CH}_3)_3$); $^{13}\text{C NMR}$ (50.3 MHz, C_6D_6): $\delta = 2.57$ (s, 12C; $\text{OSi}(\text{CH}_3)_2\text{N}$), 16.65 (s, 2C; $\text{SiC}(\text{CH}_3)_3$), 26.04 (s, 6C; $\text{SiC}(\text{CH}_3)_3$), 123.31, 128.77, 129.95, 148.26 (4s; arene C); $^{29}\text{Si NMR}$ (39.7 MHz, C_6D_6): $\delta = -6.37$ (s, 6Si; $\text{OSi}(\text{CH}_3)_2\text{N}$), -55.85 (s, 2Si; $\text{SiC}(\text{CH}_3)_3$); $^7\text{Li NMR}$ (77.71 MHz, C_6D_6): $\delta = -4.99$ (s, 2Li; GeOLi); correct elemental analysis; cryoscopy: calcd 1353.07, found 1340.

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- [1] K. W. Hellmann, L. H. Gade, O. Gevert, P. Steinert, *Inorg. Chem.* **1995**, *34*, 4069–4078.
- [2] M. Contel, K. W. Hellmann, L. H. Gade, I. J. Scowen, M. McPartlin, M. Laguna, *Inorg. Chem.* **1996**, *35*, 3713–3715.
- [3] R. West, H. Sohn, D. R. Powell, T. Müller, Y. Apeloig, *Angew. Chem.* **1996**, *108*, 1095; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1002–1004.
- [4] S. Freitag, R. Herbst-Irmer, L. Lameyer, D. Stalke, *Organometallics* **1996**, *15*, 2839–2841.
- [5] J. H. Hong, Y. Pan, P. Boudjouk, *Angew. Chem.* **1996**, *108*, 213–216; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 186–188.
- [6] M. Veith, O. Schütt, V. Huch, *Z. Anorg. Allg. Chem.* **1999**, *625*, 1155–1164.
- [7] T. Fjeldberg, A. Haaland, B. E. R. Schilling, M. F. Lappert, A. J. Thorne, *J. Chem. Soc. Dalton Trans.* **1986**, 1551–1556.
- [8] A. G. Brook, F. Abdesaken, H. Söllradl, *J. Organomet. Chem.* **1986**, *299*, 9–13.
- [9] M. Veith, A. Detemple, V. Huch, *Chem. Ber.* **1991**, *124*, 1135–1141.
- [10] F. Cosledan, A. Castel, P. Rivière, J. Satgé, M. Veith, V. Huch, *Organometallics* **1998**, *17*, 2222–2227.
- [11] H. Schmidbaur, J. Rott, G. Reber, G. Müller, *Z. Naturforsch. B* **1988**, *43*, 727–732.
- [12] K. M. Baines, J. A. Cooke, J. J. Vittal, *J. Chem. Soc. Chem. Commun.* **1992**, 1484–1485.
- [13] M. F. Lappert, S. J. Miles, J. L. Atwood, M. J. Zaworotko, A. J. Carty, *J. Organomet. Chem.* **1981**, *212*, C4–C6.
- [14] O. Schütt, Dissertation, Universität des Saarlandes, **1999**.
- [15] Crystal structure analysis: diffractometer: Stoe IPDS (**3**), Stoe AED 2 (**4**, **5**). **3**: Monoclinic, $C2/c$, $a = 19.401(4)$, $b = 15.434(3)$, $c = 34.151(7)$ Å, $\beta = 98.31(3)^\circ$, $V = 10119(4)$ Å³, $Z = 8$, 5535 “observed”

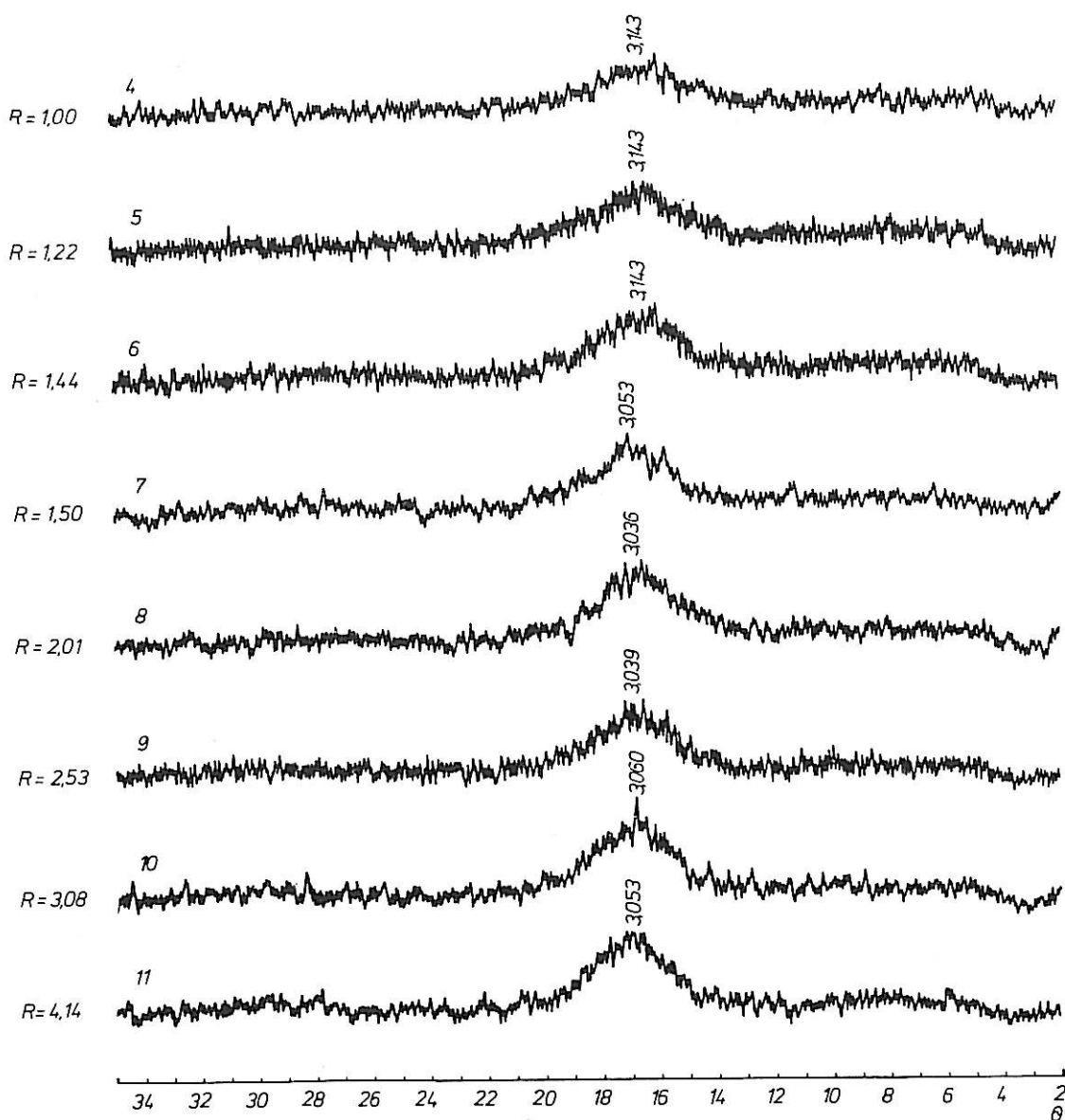


Fig. 1. X-ray diffractograms of lead silicate glasses with various molar ratios $R = \text{PbO}/\text{SiO}_2$.

creasing percentage of SiO_2 leads finally to the three-dimensional, high-molecular silica network occurring in glassy SiO_2 .

Obviously, in all the studied glasses the existing silicate groupings are more polymerized than required by stoichiometry, if one assumes that lead is present as Pb^{2+} cations (table 3). Were the Si and Pb atoms statistically distributed, then glasses with high percentages of PbO should contain only $[\text{SiO}_4]^{4-}$ anions and free PbO according to



However, X-ray analysis shows no free crystalline PbO; and the existence of glassy PbO has not been reported in the literature [4]. The agreement between stoichiome-

Table 2
Results of silicate anion analysis expressed in wt% Si of the total amount of Si in glasses studied.

Silicate anions present	Glasses with molar ratio <i>R</i>							
	4.14	3.08	2.53	2.01	1.50	1.44	1.22	1.00
[SiO ₄] ⁴⁻	43	31	15	10	8	9	6	—
[Si ₂ O ₇] ⁶⁻	38	33	33	21	11	8	7	—
[Si ₃ O ₁₀] ⁸⁻	14	13	16	16	8	7	7	—
[Si ₄ O ₁₂] ⁸⁻	5	23	24	14	11	8	7	—
polysilicate chains [SiO ₃] _{<i>n</i>} ²⁻	—	—	—	28	28	36	15	—
two- to three-dimensional silicate units	—	—	12	11	20	19	15	—
phyllosilicates and higher molecular silicates	—	—	—	—	14	13	43	about 85

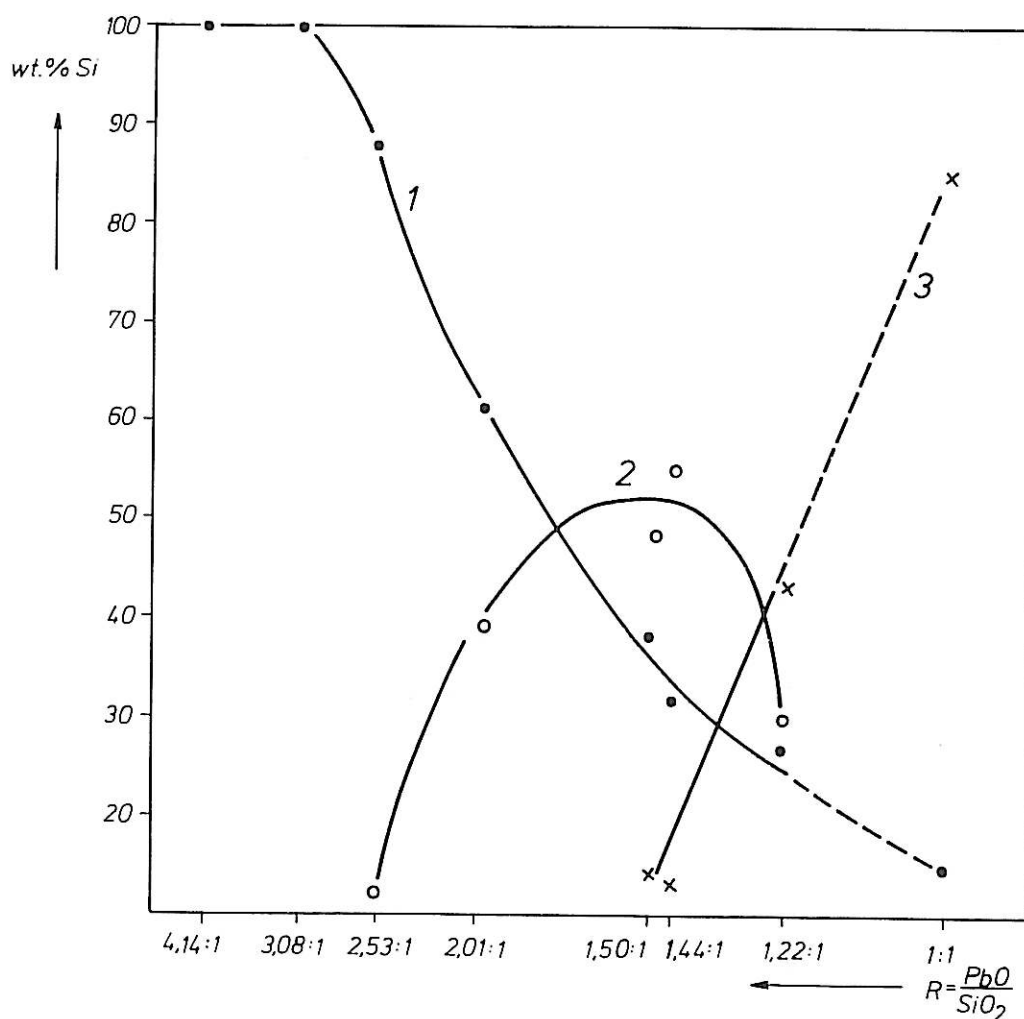


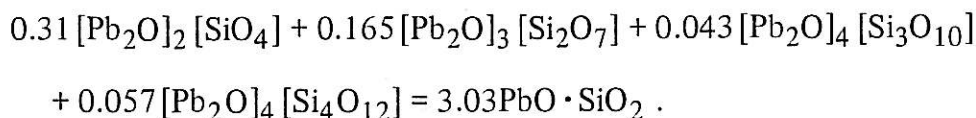
Fig. 2. Influence of molar ratio *R* on the prevailing type of silicate groupings in binary lead silicate glasses. Curve 1 low-molecular silicates (Si₁–Si₄); curve 2 polysilicates and two- to three-dimensional silicate units; curve 3 phyllosilicates and higher polymerized silicates. (The wt% Si refers to the total amount of Si in the glasses.)

Table 3

Comparison of theoretical and real polymerization rates of silicate units in binary lead silicate glasses.

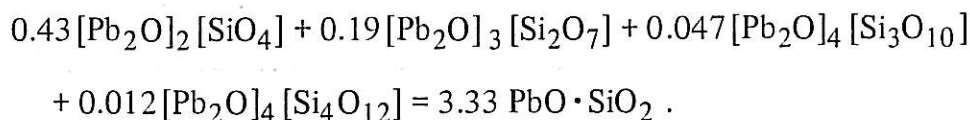
Molar ratio of the glass <i>R</i>	Silicate units calculated from stoichiometry assuming that lead is present as		Main silicate units found by analysis
	cations Pb^{2+}	cations $[\text{Pb}_2\text{O}]^{2+}$	
4.14	$[\text{SiO}_4]^{4-} + \text{free PbO}$	$[\text{SiO}_4]^{4-}$	$[\text{SiO}_4]^{4-}$
3.08	$[\text{SiO}_4]^{4-} + \text{free PbO}$	$[\text{Si}_2\text{O}_7]^{6-}$	$[\text{Si}_2\text{O}_7]^{6-}$
2.01	$[\text{SiO}_4]^{4-}$	$[(\text{SiO}_3)^{2-}]_n$ (polysilicates or rings)	polysilicates and rings $[\text{Si}_4\text{O}_{12}]^{8-}$
1.50	$[\text{Si}_2\text{O}_7]^{6-}$	double-chain polysilicates	polysilicates
1.00	polysilicates or rings	phyllosilicates $[(\text{Si}_2\text{O}_5)^{2-}]_n$	phyllosilicates

tric composition and experimentally found distribution of silicate anions in the glasses is better, if one assumes the existence of polymeric $-\text{Pb}-\text{O}-\text{Pb}-$ groupings, which are known to form the structure of tetragonal and orthorhombic PbO . This assumption is supported by results obtained by Mydlar et al. [5] in an X-ray diffraction study of lead silicate glasses. Expressing the $-\text{Pb}-\text{O}-\text{Pb}-$ groupings in glassy $3\text{PbO} \cdot \text{SiO}_2$ for stoichiometric purposes as cations $[\text{Pb}-\text{O}-\text{Pb}]^{2+}$, it is possible to calculate the stoichiometric composition of the glass from the silicate anion distribution listed in table 2:



The calculated value $3.03\text{PbO} \cdot \text{SiO}_2$ agrees excellently with the analytically determined composition $3.08\text{PbO} \cdot \text{SiO}_2$. This does not mean that in the given glass only cations $[\text{Pb}_2\text{O}]^{2+}$ exist; one should rather expect a distribution of various lead-oxygen groupings, characterized by an average polymerization rate corresponding to $[\text{Pb}-\text{O}-\text{Pb}]^{2+}$ cations.

Similar calculations of the $\text{PbO} : \text{SiO}_2$ ratio of glassy $4\text{PbO} \cdot \text{SiO}_2$ based on the assumption of $[\text{Pb}_2\text{O}]^{2+}$ cations yield lower values of *R*:



The analytically determined value for this glass is $R = 4.14$. Evidently, the difference of 0.81 mol PbO cannot be explained by analytical error. One possible explanation would be the existence of free glassy PbO which, in view of the data available in the literature [4], is not likely. Thus, it seems justified to conclude that the lead-oxygen

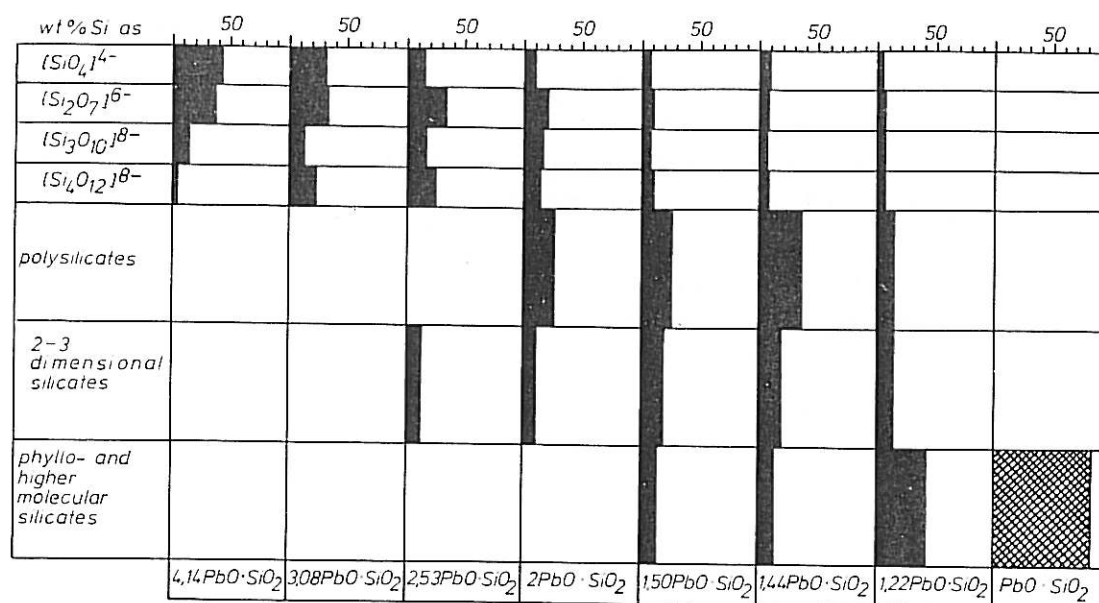


Fig. 3. Distribution diagram of silicate groupings present in binary lead silicate glasses.

groupings in glassy $4\text{PbO} \cdot \text{SiO}_2$ are on the average more highly polymerized than in glassy $3\text{PbO} \cdot \text{SiO}_2$.

Stoichiometric calculations for compositions containing more SiO_2 are less exact, because these glasses contain silicate groupings of unknown constitution, e.g. the above-mentioned two- to three-dimensional silicate units. Nevertheless, all stoichiometric considerations support a general concept according to which lead silicate glasses containing high amounts of PbO are characterized by the existence of both silicate and lead-oxygen groupings of different size. The type and relative amount of all groupings occurring are expressed by distribution curves which depend on the composition of the given glass.

Figure 3 depicts the distribution of silicate groupings in the glasses studied. It is evident, that all glasses contain several different silicate groupings*. This confirms the conclusion of our preceding work [1], which indicated, that a "polyanionic" distribution of silicate anions is characteristic for the glassy state. The polyanionic character of silicate distributions in the glasses studied is enhanced by the fact that the categories termed "polysilicates", "two- to three-dimensional silicate groupings", "phyllosilicates and higher molecular silicate groupings" each represent a whole variety of similar, but not identical silicate groupings which cannot be separated by the methods employed. The distribution diagram (fig. 3) tries to distinguish these polyanionic categories from the monoanionic ones $[\text{SiO}_4]^{4-}$, $[\text{Si}_2\text{O}_7]^{6-}$, $[\text{Si}_3\text{O}_{10}]^{8-}$ and $[\text{Si}_4\text{O}_{12}]^{8-}$ by broader horizontal columns.

* It should be noted that the existence of defined silicate groupings in the glasses studied does not imply that the internal symmetry of the respective silicate groupings in glassy and crystalline silicates is necessarily identical.

Figure 3 demonstrates that glassiness in the composition range $4\text{PbO} \cdot \text{SiO}_2$ – $\text{PbO} \cdot \text{SiO}_2$ is connected with the presence of various different silicate units in the respective lead silicates. The composition $4.14\text{PbO} \cdot \text{SiO}_2$ contains the smallest amount of silicate groupings; these groupings are short and of similar shape, and easily build regular crystalline lattices. The tendency to form glasses is lower than in systems containing higher amounts of SiO_2 , where very many silicate groupings of different size and shape are present. These findings agree with a general view expressed by Hägg [6] and confirmed later by the works of Van Wazer [7] and Westman [8] on phosphate glasses, according to which the presence of many different structural groupings in the system hinders crystallization and promotes the formation of glasses.

References

- [1] J. Götz, D. Hoebbel and W. Wieker, *J. Non-Crystalline Solids* 20 (1976) 413.
- [2] G. Engelhardt, D. Zeigan, H. Jancke, D. Hoebbel and W. Wieker, *Z. anorg. allg. Chem.* 418 (1975) 17.
- [3] D. Hoebbel and W. Wieker, *Z. anorg. allg. Chem.* 400 (1973) 148.
- [4] H. Rawson, *Inorganic glass forming systems* (Academic Press, London–New York, 1976).
- [5] F. Mydlar and N. Kreidl, *Phys. Chem. Glasses* 11 (1970) 196.
- [6] G. Hägg, *J. Chem. Phys.* 3 (1935) 42.
- [7] J. Van Wazer, *J. Am. Chem. Soc.* 72 (1950) 644.
- [8] A.E. Westman, *J. Am. Ceram. Soc.* 37 (1954) 420.