

# THE STRUCTURE OF THE FIRST CO-ORDINATION SHELL OF Pb ATOMS IN LEAD-SILICATE GLASSES: A MOLECULAR DYNAMICS STUDY

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**Abstract:** The structure of lead-silicate glasses, although being investigated for over sixty years, remains still controversial. One of the open questions is the structure of the lead subsystem: what are the basic structural units like, and how are they interconnected. In the literature the appearance of  $[\text{PbO}_4]_n$ , or  $[\text{PbO}_3]_n$  chains is reported even in the glasses of the same stoichiometry. In order to elucidate the problem of contradicting experimental findings, extensive molecular dynamics (MD) simulations in the isobaric-isoenthalpic (NpH) ensemble of the structure of lead-silicate glasses have been performed in the whole range of glass-formation. The atoms were assumed to interact by a two-body Born-Mayer-Huggins interaction potential with full ionic charges. The potential parametrization was taken from Damodaran et al. [Phys. Chem. Glasses, 31, 212 (1990)]. The simulation box contained about 3000 atoms. For each composition an equilibrated melt at 10000 K was prepared, and then slowly ( $6 \times 10^{13}$  K/s) cooled down to 300 K, passing several equilibrium states at intermediate temperatures. The simulation results can be summarised as follows. For  $0.1 \leq x \leq 0.33$ , about  $\frac{1}{3}$  of all Pb atoms is either placed in the front of the faces of the  $\text{SiO}_4$  tetrahedra, forming  $\text{PbO}_3$  pyramids with the Pb atom in the vertices or in the middle of an almost flat triangle formed from apical oxygens of three different  $\text{SiO}_4$  tetrahedra. Another  $\frac{1}{3}$  of all Pb atoms can be qualified as vertices of rather distorted square pyramids. The remaining  $\frac{1}{3}$  of lead atoms have neighbourhoods difficult to classify. For  $x \geq 0.67$  only a few Pb atoms were identified as remaining in the front of a face of a  $\text{SiO}_4$  tetrahedron. Most of the Pb atoms are placed in the vertices of edge sharing square  $\text{PbO}_4$  pyramids. Our MD results are compared with available experimental data.

## 1. INTRODUCTION

Lead-silicate glasses find a lot of industrial applications, mainly as optical glasses [1]. As special materials, they are used in electronics and optoelectronics in production of plate image amplifiers and scintillators [2], Modified lead-silicate glasses, containing metallic Pb granules, reveal high secondary emission coefficient, and thus find application in the production of electron channel multipliers [3],

The atomic structure of the lead-silicate glasses has been investigated for sixty years, using various experimental techniques, including IR spectroscopy [4], Raman spectroscopy [4-6], NMR [5,7, 8], XPS [9], X-ray [10,11] and neutron diffraction methods [12], EXAFS and XANES [7, 8, 13]. However, until now no single commonly accepted structural model for  $x\text{PbO} (1-x)\text{SiO}_2$  glasses has been elaborated, and it is still not clear whether and how do structural parameters change with variations of  $x$ . For these reasons we performed extensive molecular dynamics (MD)

[14-17] investigations of the considered glasses. In the present contribution we concentrate on the structure of the first co-ordination shell of lead atoms.

The paper is organised as follows. Section 2 is dedicated to several rather technical points related to the simulation technique. In Section 3 we describe the results of our simulations. The numerical results are discussed and compared with the experimental ones in Section 4. Section 5 contains concluding remarks.

## 2. SIMULATION TECHNIQUE

The molecular dynamics (MD) simulations have been performed in the (NpH) ensemble, using the MDSIM program [18], which bases on the classical Andersen algorithm [19]. The atoms were assumed to interact by a two-body forces: the Born-Mayer repulsive forces, and Coulomb forces due to full ionic charges, calculated with the aid of the standard Ewald technique. The potential parametrization was taken from [20]. All the systems discussed in the present work were initially prepared in a well equilibrated molten state at 10000 K, and then slowly cooled down to 300 K, passing equilibrium states at 8000 K, 6000 K, 5000 K, 4000 K, 3000 K, 2500 K, 2000 K, 1500 K, 1000 K, 600 K. At each temperature the system was being equilibrated during 30000 fs time steps, and sampled during other 10000 fs time steps. The simulations have been performed in the whole range of glass-formation, *i.e.* for  $0.0 \leq x \leq 0.9$  [17], In dependence of the glass stoichiometry, the number of atoms within the simulation box ranged from 1600 to 3250 (Table I), resulting in box edge lengths from about 20 to 30 Å. The structural information on

Table I. Numbers of atoms used in the simulations of  $x$  PbO (1 -  $x$ ) SiO<sub>2</sub> glasses

<b>x</b>	<b>Pb</b>	<b>Si</b>	<b>O</b>
0.10	100	900	1900
0.20	200	800	1800
0.25	200	600	1400
0.33	200	400	1000
0.40	500	750	2000
0.45	540	660	1860
0.50	500	500	1500
0.67	800	400	1600
0.80	800	200	1200
0.90	900	100	1100

short-range correlations was obtained in a conventional way, mainly from radial and angular distribution functions. The connectivity of basic structural units was studied by means of cation-anion ring analysis, performed using a new highly efficient redundancy aware algorithm [21,22].

## 3. SIMULATION RESULTS

Figure 1 shows radial distribution functions (RDFs) related to the Pb structural unit for  $x$ PbO (1- $x$ )SiO<sub>2</sub> glasses,  $0.0 \leq x \leq 0.9$ . The peak profile in the RDF,  $g(r)$ , is given by:

$$g(r) = \frac{Np(r)}{4\pi\rho r^2},$$

where  $N$  is the co-ordination number,  $p$  is the density. The bond-length probability density,  $p(r)$ , can be described using a  $\Gamma$ -like distribution [23]. Its general expression, valid for  $(r-R) \beta > -2\sigma$ , has a form:

$$p(r) = \frac{2}{\sigma \cdot |\beta| \cdot \Gamma\left(\frac{4}{\beta^2}\right)} \cdot \left(\frac{4}{\beta^2} + \frac{2 \cdot (r-R)}{\sigma \cdot \beta}\right)^{\frac{4}{\beta^2}-1} \cdot \exp\left[-\left(\frac{4}{\beta^2} + \frac{2 \cdot (r-R)}{\sigma \cdot \beta}\right)\right], \quad (1)$$

where  $R$  is the average distance,  $\sigma^2$  is the Debye-Waller disorder factor describing both the structural and vibrational disorder,  $\beta$  is the asymmetry parameter and  $\Gamma(x)$  is the Euler's gamma function calculated for  $x = 4/\beta^2$ . Table II contains the parameters of the first Pb-O RDF peak: the MD extracted most probable Pb-O distance  $R_o$  (position of the maximum of the first RDF peak), and  $R$ ,  $\sigma$ ,  $\beta$ ,  $N$  from (1). The last column of the table contains recent EXAFS data on pure crystalline PbO, quoted after [13]. Table III, constructed in a similar way, refers to the O-O RDF.

As one can see from Figure 1, the first RDF peak of the Pb-O correlation is rather sharp, with its maximum (the most probable distance  $R_o$ ) at about 2.3 Å. For high PbO concentrations,  $0.67 \leq x \leq 0.9$ , the average Pb-O distance,  $R$ , is in our MD-simulated glasses close to the corresponding value in pure PbO (Table II). However, for lower lead oxide contents ( $x \leq 0.33$ ) the approximation of this peak with (1) gives the average Pb-O distance in the range from 2.40 to 2.45 Å, which is clearly higher than the Pb-O distance in pure PbO.

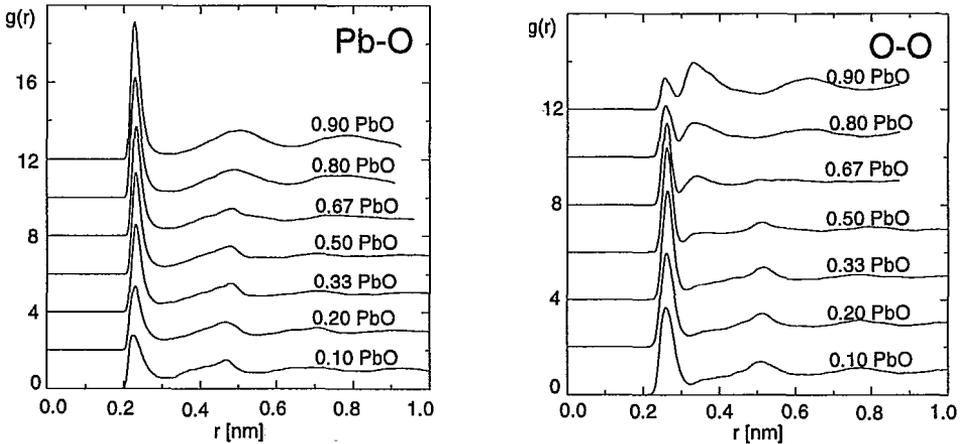


Fig. 1. Radial distribution functions relevant to the first neighbourhood of the Pb atom

Parameter  $\sigma$  decreases with increasing PbO concentration from 0.24 Å for  $x = 0.1$  to 0.13 Å for  $x = 0.9$ ; the latter value of  $\sigma$  is equal to the one reported recently in [13]. The peak asymmetry

degree,  $\beta$ , is very high at low PbO concentrations, and decreases systematically with increasing  $x$  from 1.22 for  $x = 0.1$  to 0.56 for  $x = 0.9$ . Note, that  $\beta$  for pure PbO (0.42) is close to its value in the  $x = 0.9$ .

The average co-ordination number, read formally in the RDF minimum between two first peaks, for the Pb-O pair is somewhat higher than four for  $x < 0.5$ , and close to five for higher PbO concentrations. However, the integration of the T-like peak (1) gives more reliable estimation, since the contribution from the second peak is automatically eliminated. The co-ordination numbers,  $N$ , determined in such a way are shown in Table II.  $N$  equals to 3.6 for  $0.1 \leq x \leq 0.25$ , to 4.0 for  $0.33 \leq x \leq 0.50$ , and to 4.3 for  $x \geq 0.67$  (in crystalline PbO the Pb atoms have exactly four oxygen first neighbours).

Table II. The parameters of the first Pb-O RDF peak vs. PbO concentration  
(see text for explanation of the row labels)

$x$	0.10	0.20	0.33	0.50	0.67	0.80	0.90	1.00
$R_O$ [Å]	2.26	2.30	2.30	2.30	2.30	2.28	2.28	2.32 <sup>1)</sup>
$R$ [Å]	2.45	2.41	2.40	2.39	2.38	2.38	2.38	2.32 <sup>2)</sup>
$\sigma$ [Å]	0.24	0.17	0.14	0.14	0.13	0.13	0.13	0.13 <sup>2)</sup>
$\beta$	1.22	0.92	0.69	0.64	0.65	0.59	0.56	0.42 <sup>2)</sup>
$N$	3.6	3.6	4.0	4.0	4.3	4.3	4.3	4.0 <sup>2)</sup>

1) after [24]; 2) after [13]

Table III. The parameters of the first O-O RDF peak vs. PbO concentration  
(see text for explanation of the row labels)

$x$	0.10	0.20	0.33	0.50	0.67	0.80	0.90	1.00
$R_O$ [Å]	2.60	2.60	2.64	2.62	2.62	2.58	2.56	2.81 <sup>1)</sup>
$R$ [Å]	2.68	2.67	2.66	2.65	2.64	2.67	2.78	-
$\sigma$ [Å]	0.15	0.16	0.12	0.11	0.10	0.15	0.21	-
$\beta$	0.33	0.29	0.12	0.13	0.17	0.58	0.65	-
$N$	5.8	5.4	4.9	4.1	3.0	2.2	2.0	-

1) after [24]

Detailed analysis of the first co-ordination shell around the Pb atom leads to the following conclusions:

1) for low PbO concentrations,  $x \leq 0.33$ , about one third of all Pb atoms is placed either in the front of the faces of the  $\text{SiO}_4$  tetrahedra, forming  $\text{PbO}_3$  pyramids with the Pb atom in the vertices (Figure 2A) or in the middle of an almost flat triangle formed from apical oxygens of three different  $\text{SiO}_4$  tetrahedra (Figure 2B). Assuming that the average Pb-O distance (2.42 Å) corresponds to the length of the pyramid edge, and the average O-O distance (2.67 Å) to the edge length of the basal triangle, the O-Pb-O and Pb-O-O angles should be equal to  $66^\circ$ , and  $57^\circ$ ,

respectively. In fact, the maxima of the corresponding angular distribution functions appear close to these values. In the case of the  $\text{PbO}_3$  triangles, the O-O distances contribute to the O-O RDF non-zero values between the first two peaks. Another one third of the Pb atoms can be qualified as vertices of rather distorted square pyramids. The remaining Pb atoms have more complicated neighbourhoods, which can not be rigorously classified mainly because of insufficient statistics; 2) For higher PbO concentrations,  $x \geq 0.67$ , only a few Pb atoms were identified as remaining in the front of a face of a  $\text{SiO}_4$  tetrahedron. About 65% of the Pb atoms is placed in the vertex of a square  $\text{PbO}_4$  pyramid (Figure 2C). In this concentration range the average Pb-O distance equals to 2.38 Å. Assuming that the second RDF peak of the O-O correlations (3.32 Å) corresponds to the edge of the oxygen basal plane of the pyramid, the O-Pb-O and Pb-O-O angles should be equal to  $87^\circ$ , and  $46^\circ$ , respectively. Such angles dominate in the corresponding angular distribution functions. The angular distribution function for the O-O-O triple, calculated for the O-O distances limited to the radii close to 3.32 Å has a peak at  $90^\circ$ , which confirms the conclusion that the  $\text{PbO}_4$  group is with a good approximation a square pyramid.

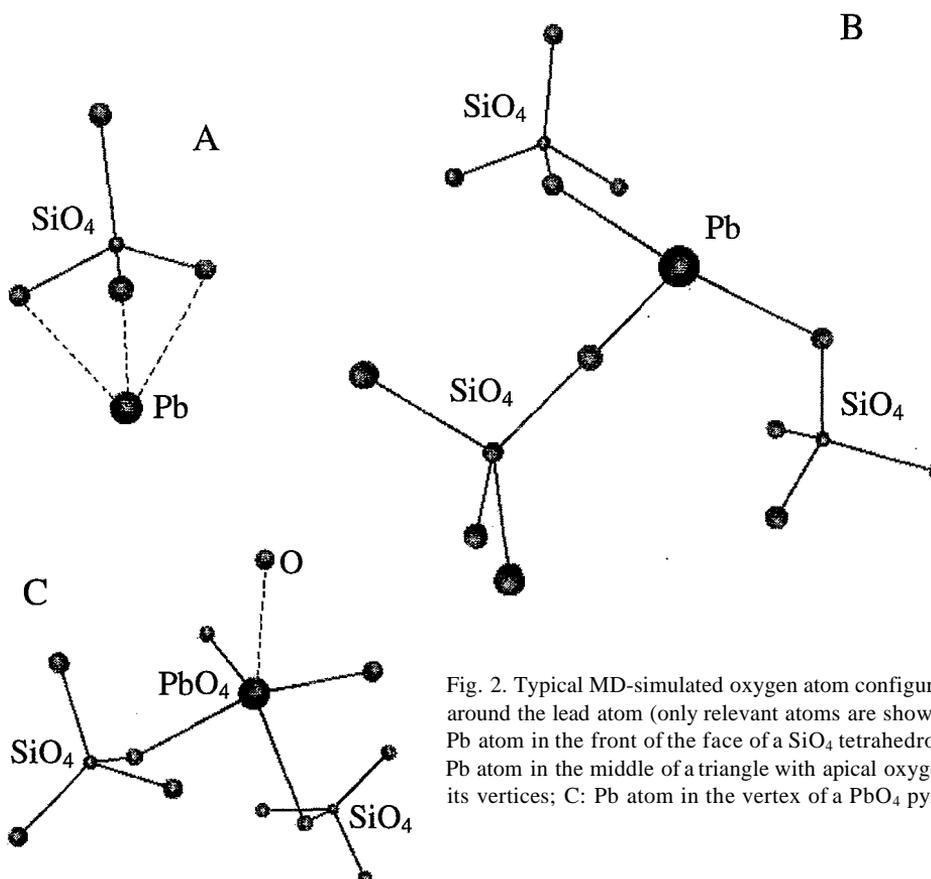


Fig. 2. Typical MD-simulated oxygen atom configurations around the lead atom (only relevant atoms are shown). A: Pb atom in the front of the face of a  $\text{SiO}_4$  tetrahedron; B: Pb atom in the middle of a triangle with apical oxygens in its vertices; C: Pb atom in the vertex of a  $\text{PbO}_4$  pyramid

The adjacency of the Pb structural units is difficult to perceive from radial, and angular distribution functions only. In order to get some insight into the units mutual positions, a ring analysis has been performed. In particular, the Pb-O-Pb-O ring statistics was calculated. A closed chain of bonded atoms, consisting of  $N$  cations and  $N$  anions is called an  $N$ -member ring. Pb and O atoms were considered bonded if their distance was less than 3.0 Å (approximately the position of the first minimum of the Pb-O radial distribution function). For  $x < 0.25$  the Pb-O adjacency graph splits into many small subgraphs, representing isolated short O-Pb-O-... linear chains or structures containing single short Pb-O rings. For  $x \geq 0.25$  the set of linearly independent rings consists predominantly of 2-member rings. From the analysis of the angle distributions along 2-member Pb-O rings results that the  $\text{PbO}_4$  units share their O-O edges.

#### 4. DISCUSSION

Let us remind in short the previously published results of other authors, and compare with our data.

##### *Distribution of the Pb-O distances*

Crystalline red PbO is built from parallel layers of edge sharing square pyramids  $\text{PbO}_4$ , and the Pb-O distance equals to 2.32 Å [24], This value falls in-between the two characteristic parameters we have used,  $R_o$  and  $R$ , which equal to 2.30 Å, and 2.39 Å, respectively. Our value of the Pb-O distance agrees with the data reported for lead-silicate glasses in [8, 10, 11, 13,25] (Table IV). The  $\sigma$  parameters of the first Pb-O RDF peak are also close to those determined experimentally in [13] in the range  $0.3 \leq x \leq 0.7$  ( $\sigma \approx 0.16$  Å independently of the glass composition). The values of the skewness parameter  $\beta$  reported in [13] equal to 1.0, 1.2, and 1.3 for  $x = 0.3, 0.5$ , and  $0.7$ , respectively, so they are significantly higher than the values obtained in the present simulations. However, an overall agreement between MD-simulated first Pb-O RDF peak, and the corresponding peak extracted from the EXAFS data is rather good, Figure 3.

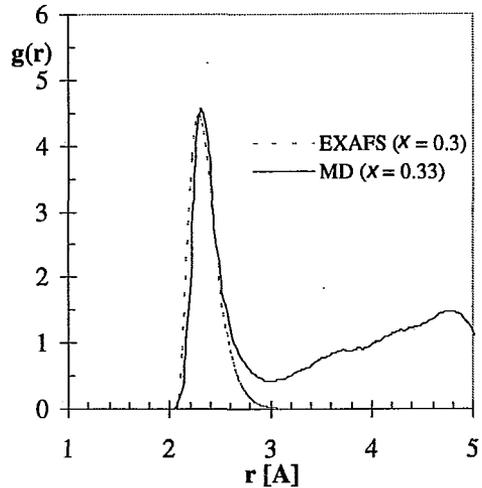
Table IV. Comparison between various experimental data on Pb-O distance in lead-silicate glasses

Glass composition	Pb-O distance [Å]
$x = 0.33, 0.5, 0.67$	2.30 ( $R_o$ ), 2.39 ( $R$ ) (a)
$x = 0.5$	2.2, 2.53, 2.8 (b)
$x = 0.5, 0.66$	2.25, 2.45 (c)
$x = 0.67$	2.35 (d)
$x = 0.31, 0.5, 0.66$	2.22, 2.4 2.42 (e)
$x = 0.3, 0.5, 0.7$	2.28 ( $R_o$ ), 2.38 ( $R$ ) (f)

(a) - this work; (b) - [25]; (c) - [11];

(d) - [10]; (e) - [8]; (f) - [13]

Fig. 3. The first Pb-O RDF peak profiles of 0.3 PbO 0.7 SiO<sub>2</sub> glass determined by GNXAS analysis reported in [13] (dotted line) and obtained in the present simulations (solid line)



#### *Pb structural unit*

Many authors report a four-fold oxygen co-ordination of Pb atoms in the considered glasses, particularly for higher PbO contents. According to [10,25,26], in the 0.7PbO 0.3SiO<sub>2</sub> glass one can find zigzag chains of square PbO<sub>4</sub> pyramids, interconnected by SiO<sub>4</sub> tetrahedra or PbO<sub>6</sub> octahedra. Recent EXAFS measurements have conformed the appearance of PbO<sub>4</sub> pyramids for  $x = 0.3, 0.5,$  and  $0.7$  [13]. According to [8], for  $0.31 \leq x \leq 0.66$ , the Pb atoms have two oxygen neighbours at the distance of 2.22 Å, and two other oxygen neighbours at the distance of  $2.4 \text{ Å} \div 2.42 \text{ Å}$ , slightly increasing with increasing  $x$ . The increasing  $x$  results also in increasing dispersion of the Pb-O distances. According to [27], for crystalline PbSiO<sub>3</sub> ( $x = 0.5$ ) the Pb atoms are co-ordinated by three oxygen atoms placed at the distance of  $2.2 \div 2.3 \text{ Å}$ , and 66% of all the lead atoms have in their neighbourhood an additional fourth oxygen atom at the distance of  $2.45 \div 2.6 \text{ Å}$ .

On the other hand, according to the model of Imaoka and co-workers (1986), for  $0.33 \leq x \leq 0.66$  the lead oxide subsystem appears in the form of [PbO<sub>3</sub>]<sub>n</sub> chains mixed with SiO<sub>4</sub> tetrahedra chains [11], so the oxygen co-ordination of Pb atoms equals to 3. The predictions of the Imaoka model have been confirmed by neutron diffraction measurements of Yamada and co-workers [12].

Our MD simulations do not agree with Imaoka model [11]. Although the PbO<sub>3</sub> units have been detected in our MD-simulated structures (particularly at rather low PbO concentrations), they can not be treated as the only, or even the dominating fundamental structural elements. Instead, the suggestions that the PbO<sub>4</sub> square pyramids dominate in the considered glasses [4, 10, 28] have been fully confirmed. The coexistence of the PbO<sub>3</sub> and PbO<sub>4</sub> units takes place in the simulated structures at lower PbO concentrations, as suggested by Fayon and co-workers [7].

## 5. CONCLUSIONS

According to our simulation results, the most probable Pb-O distance is independent of the glass composition and agrees with the corresponding experimental data. The square pyramid

PbO<sub>4</sub> is a dominant structural unit in all the considered glasses (in agreement with [4, 10, 28, 7], and in contradistinction to [11,12]). Thus, the simulation results confirm the experimental data of some authors, and contradict the data of other authors. It should be underlined, that we do not claim, that the latter group of authors is wrong. All we can state is, that the results of the MD simulations performed with the particular interaction parameters we have used give the results described in this paper. Further elucidation of the structure of the lead-silicate glasses still requires both experimental, and numerical work. Since the glass structure depends strongly on the preparation procedures, more complete experimental research in well defined and controlled conditions should be undertaken. On the other hand, more realistic, three body interaction potentials should be elaborated in the future and used in MD simulations.

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