

EXAFS ANALYSIS OF LOCAL NEIGHBOURHOOD OF Pb ATOMS IN LEAD-GERMANATE GLASSES

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Abstract: Germanate glasses containing oxides of heavy metals such as PbO, Bi₂O₃, have been studied for many years due to their interesting optical and electrical properties. We have investigated the structure of lead-germanate glasses using combined EXAFS (extended X-ray absorption fine structure) and MD (molecular dynamics) methods. We describe the local structure around lead atoms and its changes as the function of glass composition. The obtained results are compared with data provided by other authors. We have shown that combined usage of EXAFS and MD analysis (in the framework of the GNXAS approach) could be a source of detailed information on the short-range order in disordered materials.

1. INTRODUCTION

In the last decades, lead-germanate glasses, xPbO (1-x)GeO₂, have become the object of numerous studies due to their interesting physical and optical properties. Their characteristic features include a high non-linear refraction index, high infrared absorption coefficient, a high coefficient of thermal expansion, high density, and a low glass transition temperature. Lead-germanate glasses have numerous technological applications (as optical glasses or as special glasses used in the production of plate image amplifiers and scintillators).

A large number of papers on xPbO·(1-x)GeO₂ glasses concern their structure at the atomic level. Attempts are made at describing atomic-level and

medium-range orders using various experimental and theoretical (numerical) methods. However, there are many discrepancies in the literature and differing views persist on the shape and parameters of the structural unit, as follows from a brief review of the literature given below.

In 1993, S.J.L.Ribeiro *et al.* (EXAFS, IR and Raman spectroscopy) [1] observed that the structure of the nearest neighbourhood of Pb ions in lead-germanate glasses of the xPbO(1-x)GeO₂ composition, where x = 0.2, 0.25, 0.33, 0.4, 0.5, 0.53, 0.56, and 0.60 resembled that occurring in red lead oxide. Thus, its basic units were covalent PbO₄ pyramids, with 4 atoms of oxygen in the vertices of their square bases and an atom of lead in the apex. The authors noted that lead oxide's main role was that

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of a modifier of the germanium dioxide's structure. The average distance between Pb and O atoms was determined as 2.35 ± 0.05 Å.

In 1995, N.Umesaki *et al.* (ND) [2], analyzing lead-germanate glasses with lead oxide contents of $x = 0.2, 0.33,$ and 0.5 , observed six-fold coordination of Ge(IV) atoms. According to these authors, the structure of GeO_6 units resembled that of rutile, GeO_2 , while the Ge–O distance was $1.872\text{--}1.902$ Å and increased with the increasing lead oxide content in the glass. The average distance between oxygen and lead atoms equalled 2.33 Å, while that between lead atoms amounted to 3.55 Å. At the same time, PbO_4 pyramids were named as possible structural units of the lead oxide sub-lattice, with an atom of lead in the apex and four oxygen atoms in the vertices of the square base. In such a unit, two oxygen atoms were 2.21 Å from the Pb atom, while the other two remained at a distance of 2.42 Å therefrom.

In 2001, V.Sigaev *et al.* (Raman spectroscopy) [3], concluded that in lead-germanate glasses of $x=0.2, 0.28, 0.36,$ and 0.625 the shape of the structural unit of the lead oxide sub-system was independent of the glass' composition. In systems with lead contents of $x=0.2, 0.28,$ and 0.36 the neighbourhood of lead presumably resembled a tetragonal PbO_4 pyramid or a triangular PbO_3 pyramid with a Pb atom in the apex. The length of the Pb–O bonds varied considerably, its values ranging from 2.02 Å to 3.27 Å (like as in $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ crystal structure). Therefore, the pyramids tended to be very asymmetrical structural units. At the same time, the authors claimed that the local and medium-range neighbourhood of the Pb atom of lead-germanate glasses became more homogenous and ordered at the lead oxide content of $x=0.625$.

Another paper by L.Cerwinka *et al.* [4] (2001) (X-ray dispersion and fluorescence spectroscopy) concerns structural analysis of $x\text{PbO} \cdot (1-x)\text{GeO}_2$ glasses of $x=0.2$ and 0.36 . The authors investigated the relationship between the glasses' composition and structural parameters. They obtained a Ge–O distance in a tetrahedral GeO_4 structure of 1.72 Å and 1.88 Å for an octahedral GeO_6 structure, with tetrahedral structure seven times more numerous than octahedral ones. The nearest neighbourhood of lead ions consists of highly deformed PbO_4 units, with all oxygen atoms on one side of the lead atom and a $R_{\text{Pb-O}}$ distance between 2.38 Å and 2.43 Å.

Many authors have investigated the structure of lead oxide in connection with other oxides, e.g. $\text{SiO}_2,$ $\text{B}_2\text{O}_3,$ and $\text{Ga}_2\text{O}_3.$

In 1986, M.Imaoka, H.Hasegawa, I.Yasui (XRD) [5] analysed the structure of lead-silicate glasses of $0.5\text{PbO} \cdot 0.5\text{SiO}_2$ and $0.66\text{PbO} \cdot 0.34\text{SiO}_2$ compositions. They reported PbO_3 pyramids to be the model structural units, with Pb–O inter-atomic distances amounting to 2.25 Å and 2.45 Å. For the $0.5\text{PbO} \cdot 0.5\text{SiO}_2$ composition, they found chains of $(\text{PbO}_3)_n$ pyramids coexisting with chains of SiO_4 groups, while in the $0.66\text{PbO} \cdot 0.34\text{SiO}_2$ glass they detected isolated SiO_4 units, Si_4O_{12} rings and short $(\text{SiO}_3)_n$ chains. Moreover, according to these authors, with increased concentration of PbO, increasingly deformed SiO_4 tetrahedrons appear in the glass.

The 1993 work of A.Zahara and C.Zahara (Raman spectroscopy) [6] is devoted to structural analysis of compounds of lead oxides and boron and silicon oxides. Glasses with low PbO content were observed to contain a continuous two- and three-dimensional lattice of the boron oxide subsystem with 3-fold and 4-fold coordination of boron atoms. At the same time, rings and chains of PbO_4 units were detected in PbO-rich glasses (with x in excess of 0.27).

In 1999, Y.G.Choi *et al.* (EXAFS, XANES) [7], while analyzing the structure of $\text{PbO-Ga}_2\text{O}_3$ glasses, reported lead oxide to exist in the form of PbO_3 and PbO_4 pyramids, with a majority of lead ions found to be Pb^{2+} . The authors suggested coexistence of PbO_3 and PbO_4 pyramids, similar to that found in crystalline PbSiO_3 (alamosite structure).

The work of F.Fayon *et al.* (XAFS, NMR, 1991) [8] also argues in favour of coexistence of PbO_3 and PbO_4 pyramids in lead-silicate glasses with small distances between the Pb atom and oxygen atoms, typical for covalent bonds.

A structural analysis of the $0.5\text{PbO} \cdot 0.5\text{SiO}_2$ glass and its crystallized form is the main objective V. Mastelaro's research of 2000 (EXAFS) [9]. It confirmed the occurrence of PbO_4 units, with coordination number $N_{\text{Pb-O}} \approx 4.2$ (similar to that of pure PbO). At the same time, crystallized $0.5\text{PbO} \cdot 0.5\text{SiO}_2$ was found to have only three atoms of oxygen on the first Pb coordination shell.

As far as lead atom's neighbourhood in the above mentioned glasses is concerned, three main options can be discerned. One suggests the existence of the PbO_4 pyramid as the basic structural unit. Another claims the PbO_3 pyramid to be the basic structural unit. Yet another allows the existence of both of these units. Moreover, opinions as to the length of the Pb–O bond and its homogeneity vary widely. The shortest proposed distance is 2.02 Å, the longest being 2.43 Å (or even 3.27 Å [3]). As far as homogeneity is concerned, some researchers favour

a high degree of structural units' regularity, while others claim them to be greatly deformed.

In the present work, $x\text{PbO}\cdot(1-x)\text{GeO}_2$ glasses of $x=0.1, 0.2, 0.33,$ and 0.5 have been subjected to structural analysis using X-ray absorption spectra in EXAFS (Extended X-ray Absorption Fine Structure) range. Due to difficulties involved in this method of structural analysis of disordered systems, results of classical molecular dynamics (MD) [10–12] simulations have also been taken into account. Both methods are capable of producing exact descriptions of matter at the atomic level and are currently applied beyond analysis of crystalline materials, viz. for highly disordered systems. Combined, they have proven to be an irreplaceable tool to investigate amorphous materials such as glass, liquid metals, or even liquids, a source of medium- as well as short-range structure. Their combined use allows verification of atomic interaction potentials used in MD simulations.

The present work aims at a detailed structural analysis of unmodified glasses of the above-mentioned composition range, focused on the lead ion's local neighbourhood. The paper is organized as follows. Section 2 covers technical issues: the EXAFS measurements and simulation methods are described. Experimental results of XAFS spectra measurements at the Pb L_3 -edge, EXAFS analysis, and Pb-O pair distribution functions obtained for selected lead-germanate glasses from MD simulations are presented and discussed in Section 3. Section 4 contains our concluding remarks.

2. TECHNICAL ISSUES

In this Section we describe the experimental and computational methods used (Subsections 2.1 and 2.2, respectively).

2.1. EXAFS measurements

$x\text{PbO}\cdot(1-x)\text{GeO}_2$ glasses were prepared as follows: PbO and GeO_2 powders mixed in proportions relevant to the compound's stoichiometry were placed in a platinum crucible and annealed in an electric furnace. The system was heated for 3–4 h from room temperature (RT) to the melting point, which ranged from 1400K for $x=0.5$ to 1600K for $x=0.1$. The compounds were kept at the melting point for a few minutes and stirred mechanically to safeguard the system's homogeneity. Subsequently, they were abruptly cooled by being poured over a brass plate. Glasses obtained in this way were free from ceramic inclusions and uniform in colour. The material's

amorphousness was indicated by the lack of peaks in X-ray diffraction patterns. The glasses were finely milled (to grain diameter of ca $1\ \mu\text{m}$) and the powder so obtained was used to prepare pellets for XAFS measurements. 16 mg of powder was carefully mixed with some 180–200 mg BN and pressed, thus obtaining homogenous pellets 12 mm in diameter, ca 2–3 mm thick.

The spectra of lead-germanate glasses at the Pb L_3 edge were recorded at the BM29 beam-line of the European Synchrotron Radiation Facility, Grenoble, using a double-crystal monochromator equipped with $\text{Si}(311)$ crystals. Room temperature measurements were performed in the 12600–14000 eV energy range (the Pb L_3 -edge energy being 13035 eV). The sampling procedure was chosen to yield high quality data for both pre- and post-edge background analyses used to normalize the spectra. More details on the experimental setup can be found in [13,14].

The experimental data were analysed with an advanced technique using theoretical calculations of the X-ray absorption cross-section in the framework of the GNXAS method [15–17]. The method is based on a comparison in the energy space between the experimental signal and the theoretical one, in an attempt to optimise the relevant structural parameter values.

As a simple Gaussian shape of the short-range peak of a pPDF (partial Pair Distribution Function) is usually insufficient to describe accurately the short-range ordering of highly disordered systems, the bond length probability density $p(r)$ was modelled using a Γ -like distribution [18]:

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

defined for $(r-R)\beta > -2\sigma$. In Eq. (1) Γ is the Euler Gamma function, while N_c is the coordination number, R – the average inter-atomic distance, σ – the standard deviation of distance, β – the skewness parameter.

The width of the pair distribution function broadens and the peaks usually overlap in highly disordered systems. It is then difficult to distinguish particular coordination shells. In that case, one should

Table 1. Parameters obtained during decomposition of the Pb–O pair distribution function in $x\text{PbO}(1-x)\text{GeO}_2$ glasses with $x=0.1, 0.2, 0.33,$ and 0.5 through MD simulation based on a double-oxygen-shell model, yellow PbO.

x	$R_{0,1}$ [Å]	R_1 [Å]	σ_1^2 [Å ²]	β_1	N_1	$R_{0,2}$ [Å]	R_2 [Å]	σ_2^2 [Å ²]	β_2	N_2
0.1	2.20	2.26	0.013	0.9	1.83	2.45	2.57	0.039	1.0	1.44
0.2	2.25	2.28	0.011	0.6	1.91	2.42	2.55	0.030	1.1	1.51
0.33	2.26	2.30	0.010	0.4	2.11	2.42	2.53	0.025	1.0	1.54
0.5	2.30	2.32	0.007	0.2	2.11	2.43	2.54	0.020	1.0	1.94

decompose the $g(r)$ function into one or more short-distance peaks, $g_i(r)$, and a long-range tail, $g_l(r)$:

$$g(r) = g_l(r) + g_i(r) = \sum_i g_i(r) + g_l(r). \quad (2)$$

With the structural parameters of the first coordination shell, or sub-shells describing a complex neighbourhood, we can obtain the shape of the first peak of the pPDF function. This is possible even for amorphous systems, but always subject to the accuracy of the $g_i(r)$ distribution overlapping with the first peak, which contains information on medium-range ordering. This is why it is so important for EXAFS analysis of disordered systems to allow for the influence of $g_l(r)$ on the shape of the first peak, as well as for the entire $g(r)$ distribution. The GNXAS method is capable of such allowance, but a pPDF function obtained by any other method (e.g. from Molecular Dynamics simulations) is necessary.

2.2. Molecular dynamics simulations

Our MD simulations (e.g. [11, 12]) were performed for lead-germanate glasses of $x\text{PbO} \cdot (1-x)\text{GeO}_2$ composition, $x=0.1, 0.2, 0.33,$ and 0.5 , in the constant volume regime (NVE ensemble), using the *mdsim* code [19]. The atoms were assumed to interact by the two-body Born-Mayer potential, containing the Born-Mayer repulsive contribution, $A_{ij} \exp[(\sigma_{ij}-r)/b_{ij}]$, with parameterisation based on [20, 21], and Coulomb interactions (with full ionic charges). Periodic boundary conditions along the xyz directions were used. The simulation box contained about 3000 particles.

The samples were initially prepared in a well-equilibrated molten state at 10000K, then cooled down to 300K at the average rate of $2 \cdot 10^{13}$ K/s, passing several equilibrium states. Equilibrated systems were sampled during 10000 fs time steps.

For the purposes of EXAFS analysis performed on the basis of the GNXAS approach, the pPDFs obtained from the simulations have been decomposed into a short-range peak of well-defined shape and a long-range tail. Tables 1 and 2 presented in the next section show results obtained for two different local structure models of Pb ions in a lead oxide subsystem.

3. RESULTS AND DISCUSSION

Results of structural analysis obtained by the above mentioned research method are presented in this Section. The analysis has been focused on short-range ordering around Pb ions of the considered structures of unmodified lead-germanate glasses of various PbO contents ($x\text{PbO} \cdot (1-x)\text{GeO}_2$, $0.10 \leq x \leq 0.50$). Fig. 1 shows normalized absorption spectra in the XANES range measured at the Pb L_3 -edge.

As our analysis of the spectra's shape near the absorption edge shows no significant differences among the various compositions of the examined material, they were analysed in the EXAFS range.

Table 2. Parameters obtained during decomposition of Pb–O pair distribution function in $x\text{PbO} \cdot (1-x)\text{GeO}_2$ glasses with $x=0.1, 0.2, 0.33,$ and 0.5 through MD simulation based on a single-oxygen-shell model, red PbO.

X	R_0 [Å]	R [Å]	β^2 [Å ²]	β	N
0.1	2.22	2.35	0.034	1.2	2.79
0.2	2.28	2.37	0.028	0.9	3.25
0.33	2.30	2.36	0.019	0.6	3.95
0.5	2.34	2.38	0.013	0.5	3.73

In our analysis, because the GNXAS method has shown a high flexibility in modelling atomic backgrounds due to the possibility of accounting for multi-electron excitation channels, the $(2p_{3/2} 5p)$, $(2p_{3/2} 4f)$, and $(2p_{3/2} 4d)$ double-electron excitation channels have been considered. The importance of including of these double-electron excitation channels into the model absorption signal of the Pb L_3 -edge has been discussed in [22].

As the present paper aims at determining the structure of lead ions' neighbourhood in $x\text{PbO} \cdot (1-x)\text{GeO}_2$ glasses, two polymorphous forms of lead oxide were selected as model structures to calculate the EXAFS signal [23,24]: yellow and red PbO. The double- and the single-shell models were applied accordingly during decomposition of the pPDF functions obtained through MD simulation.

In the case of yellow lead oxide (two oxygen shells with coordination of 2 have radii differing by some 0.3 Å), decomposition of the first peak of all the considered lead-germanate glass compositions was obtained by superposition of two functions, $g_1(r)$ and $g_2(r)$, Γ -like in shape (see Eq. (1)). The results of such decompositions are shown in Table 1.

In the case of the model structure of red lead oxide, the shape of the first peak was described with a single Γ -like function (Eq. (1)). The resulting best-fit parameters are listed in Table 2.

It is clearly seen, that in MD-simulated glasses the asymmetry of Pb–O distribution decreases and the average coordination number increases with the increasing lead oxide concentration. It should also be noted, that the single-shell model is sufficient to describe the nearest neighbourhood of the Pb atom of glasses with the lower PbO concentrations, i.e. for $x \leq 0.33$. For glasses of higher lead oxide content, e.g. $x=0.5$, the single-shell model apparently fails to render fully the shape of the first peak of the pair distribution function. On the other hand, a double-oxygen-shell model yields a very good rendering of the shape of the first peak of the Pb–O distribution function for all glass compositions.

Parameters so obtained, describing the local structure in the neighbourhood of Pb ions with an isolated $g_1(r)$ contribution, were used in EXAFS analysis, the results of which are presented in the following paragraphs.

3.1. EXAFS analysis: yellow PbO model

Structural analysis was carried out for the yellow PbO model, wherein the signal was modelled with two two-body contributions, $\gamma_1^{(2)}$ and $\gamma_2^{(2)}$, originat-

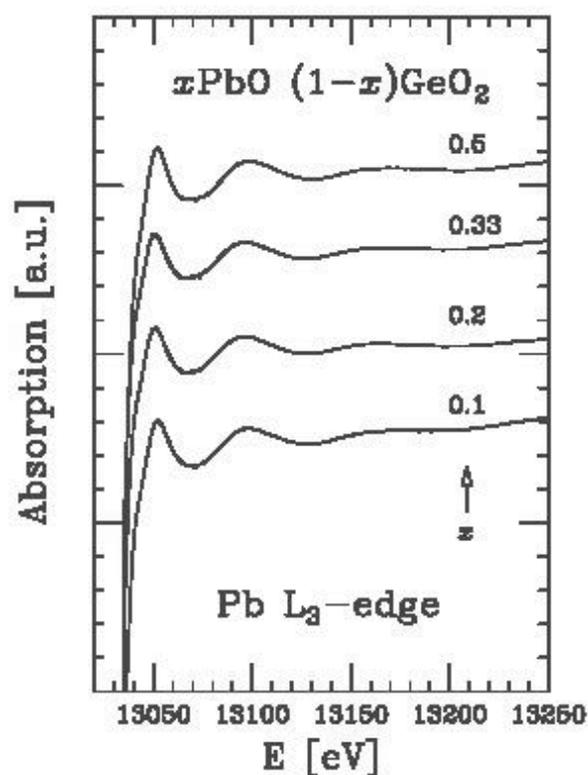


Fig. 1. Comparison of X-ray absorption spectra in the XANES range for $x\text{PbO} \cdot (1-x)\text{GeO}_2$ glasses with $x=0.1, 0.2, 0.33$, and 0.5 , Pb L_3 -edge.

ing from two oxygen coordination shells and a contribution from the long-range tail, γ_{tail} of the Pb–O distribution. The results of the GNXAS analysis show that the first coordination shell is located at the mean distance $R_1 \approx 2.30 \pm 0.01$ Å with invariant number of oxygen atoms $N_1 \approx 2.0 \pm 0.2$, while the second coordination shell is located at the mean distance $R_2 \approx 2.50$ Å with the number of oxygen atoms assuming values of N_2 from 1.2 to 2.0 with the increasing x . The disorder parameters suggest increased ordering in both shells with the increasing lead oxide contents.

Nevertheless, the most probable Pb–O distances of the first and the second coordination shells are always about 0.07 Å greater and 0.08 Å lower, respectively, then appropriated distances in yellow lead oxide and the quality of model signals matching the experiment is unsatisfactory and every improvement effort has lead to parameters losing their physical meaning or some of the contributing signals being eliminated.

3.2. EXAFS analysis: red PbO model

Structural analysis was also carried out for the red PbO, wherein the signal was a sum of the short-range contribution of Pb–O configuration, $\gamma_{\text{Pb-O}}^{(2)}$, the long-range tail contribution, $\gamma_{\text{tail}}^{(2)}$ of Pb–O distribution. Additionally, because of the high sensitivity of the measured EXAFS signal, the contribution of Pb–Pb distribution, $\gamma_{\text{Pb-Pb}}^{(2)}$, has also been taken into account (see, as an example, signals presented in Fig. 2). The results of this analysis, for all considered glasses, are shown in Fig. 3 and Table 3.

Eight structural parameters have been obtained from analysis of the spectra: R_1 , σ_1^2 , β_1 , N_1 (for the Pb–O distribution) and R_2 , σ_2^2 , β_2 , N_2 (for the Pb–Pb distribution). Measurement errors for the first coordination shell are: 0.01 Å for the mean $R_{\text{Pb-O}}$ distance, about 10% for the disorder parameter, σ^2 , and the coordination number, N , and 20% for the asymmetry parameter, β . At the same time, the uncertainty of parameter determination for the second coordination shell is much greater (see the sharp decline in the $\gamma_{\text{Pb-Pb}}^{(2)}$ signal intensity in Fig. 2).

The parameters shown in Table 3 suggest that the lead oxide content does not change fundamentally the mean and the most probable Pb–O distances, which amounts to $2.37 \pm 0.01 \text{ \AA}$ and $2.29 \pm 0.01 \text{ \AA}$, respectively. The number of the photoabsorber's nearest oxygen neighbours is $N=4.0$ for all the compositions. This means, that PbO_4 groups are the main structural units at the lead oxide sub-lattice, but the high values of σ^2 and β parameters suggest that they are significantly deformed.

Comparing these data with the literature, the structural parameters obtained through GNXAS analysis remain in good agreement with the results presented in [1] and [2]. However, while the authors of [1] are also of the opinion that the single-shell model is sufficient for a description of the local oxygen neighbourhood of Pb ions, the views presented in [2] are entirely different. The authors carefully distinguish two lengths of the Pb–O bond. At the same time, the authors of [4] claim that the distortion of PbO_4 units is too great for one to ascertain anything other than the variation range of $R_{\text{Pb-O}}$, and propose values exceeding 2.30 Å by about 0.1 Å.

Moreover, considering the results of GNXAS analysis for $x \geq 0.2$ glasses, especially the high disorder values combined with coordination numbers in the range of 3.4 to 4.2, occurrence of PbO_3 groups together with the dominant PbO_4 groups cannot be ruled out (as already suggested by the results presented in [3]). However, the Pb–O distances pro-

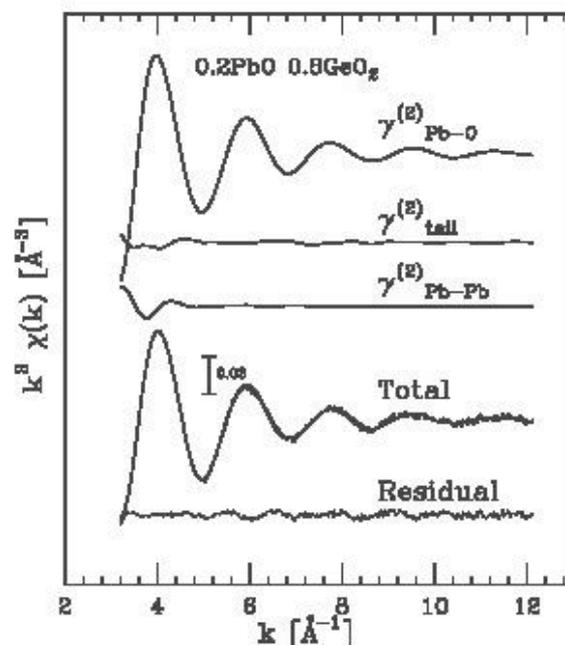


Fig. 2. Results of GNXAS analysis in 0.2PbO·0.8 GeO₂ glass. Three upper curves are components of the model signal. The thick line is the model, the thin one is the experimental result.

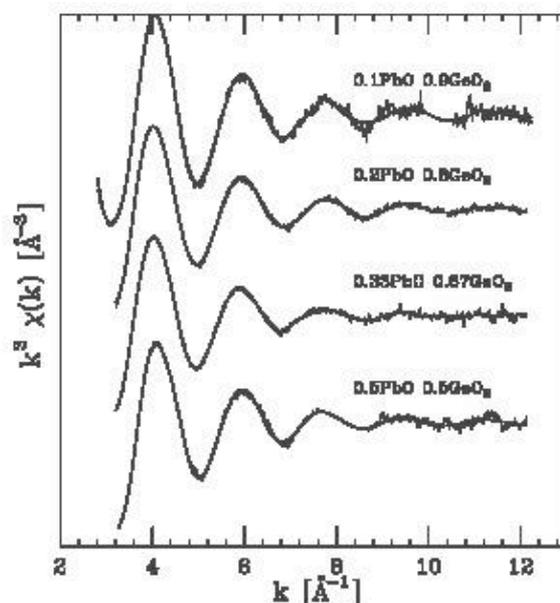
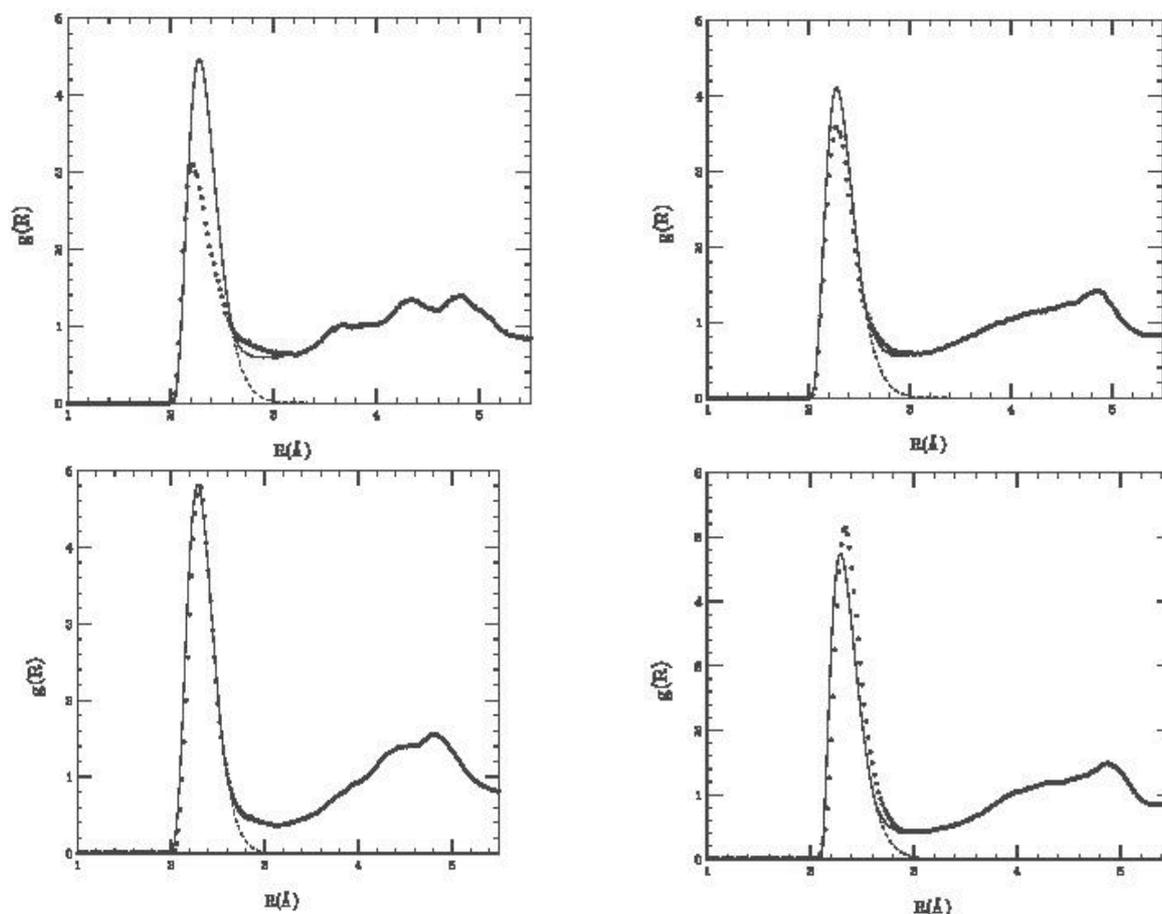


Fig. 3. Results of the analysis of $x\text{PbO} \cdot (1-x)\text{GeO}_2$ glasses spectra, $0.10 \leq x \leq 0.50$, based on the red PbO model, obtained by the GNXAS method. The thick line is the model, the thin one is the experimental result.

posed in [3] (especially their considerable broadening) have not been corroborated by the present results.

Table 3. Pb–O (with index 1) and Pb–Pb (with index 2) distribution parameters obtained through EXAFS analysis based on the red lead oxide structural model.

x	$R_{0,1}$ [Å]	R_1 [Å]	σ_1^2 [Å ²]	β_1	N_1	$R_{0,2}$ [Å]	R_2 [Å]	σ_2^2 [Å ²]	β_2	N_2
0.1	2.28(1)	2.37(1)	0.027(3)	0.9(3)	4.1(4)	3.73	3.83	0.076	0.5	7.32
0.2	2.28(1)	2.37(1)	0.028(3)	0.9(3)	3.8(4)	3.71	3.83	0.091	0.5	6.81
0.33	2.29(1)	2.37(1)	0.026(3)	0.8(2)	3.9(4)	3.71	3.83	0.099	0.5	8.89
0.5	2.30(1)	2.39(1)	0.027(3)	1.1(3)	3.7(4)	3.68	3.82	0.100	0.6	9.73

**Figure 4.** Reconstruction of Pb–O distribution based on parameters obtained through EXAFS analysis (continuous line) based on model structure of red lead oxide and comparison with relevant pair distribution functions obtained through MD simulations (dots).

At the same time, the mean Pb–Pb distance is also compositionally independent, and amounts to $R_{\text{Pb-Pb}} \approx 3.83$ Å (the mean length of the Pb–Pb bond in lead oxide, some 0.3 Å more than given in [2]), whereas the number of the photoabsorber's nearest lead neighbours increases from about 7.0 to about 10.0 with increasing PbO contents. However, the considerable broadening of the Pb–Pb distribution (ca 0.3 Å) prevents us from drawing unequivocal conclusion on length alterations in the lead ox-

ide subsystems of the considered glasses. Only a high value of N with low content of PbO, $x \leq 0.2$, may suggest that a separation of phases occurs in the examined systems (the lead oxide sub-lattice does not interweave the germanium oxide one).

The shape of two-body Pb–O distribution functions was reconstructed on the basis of the structural parameters obtained through EXAFS analysis and they were compared with the MD simulation results (see Fig. 4).

It follows from structural parameter values (cf. Tables 2 and 3) that some discrepancies in the most probable Pb–O distances appear. σ^2 and β parameters of EXAFS analysis suggest a constant content, but in MD-extracted data they decrease with an increase of x . Coordination numbers also tend to vary.

Nevertheless, the shapes of the first peak of two-body Pb–O distribution functions obtained by the two methods are similar, especially for $x=0.2$ and 0.33 . Extreme compositions, such as $x=0.1$ and 0.5 , differ mainly in the peak's intensity, but exhibit similar fine features of their sides' shape (steepness of distribution, transition to $g_i(r)$).

4. CONCLUSIONS

EXAFS analysis on the base of GNXAS approach indicates, that the structure of local neighbourhood of Pb ions in lead-germanate glasses can be described as follows.

– The mean and most probable length of the Pb–O bond is practically invariant in the function of glass composition.

– PbO_4 groups are the basic structural units, with a pronounced domination of PbO_4 units at low PbO contents and additional occurrence of PbO_3 groups for $x \geq 0.2$.

– Structural units are highly irregular: $\sigma^2 \approx 0.03 \text{ \AA}^2$, $\beta \approx 1.0$.

– The local neighbourhood of Pb ions is similar to that of red PbO rather than yellow, a single-shell model with four atoms of oxygen at the distance of $R_{0,\text{Pb-O}} = 2.30 \text{ \AA}$.

The sensitivity of the measured EXAFS signal has been sufficient to allow values of the structural parameters of Pb–Pb distribution to be estimated.

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