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Leaching of Lead and Connectivity of Plumbate Networks in Lead Silicate Glasses

Megumi Mizuno, Masahide Takahashi,*,[†],[‡] Taigo Takaishi, and Toshinobu Yoko*

Institute for Chemical Research, Kyoto University, Kyoto 611-0011, Japan

The formation of a plumbate network in binary lead silicate glasses was examined based on the leaching behavior of Pb^{2+} in lead silicate glasses over a wide composition region. The effective diffusion coefficient of Pb^{2+} at 40°C was on the order of 10^{-17} m²/s for PbO < 35 mol% glasses, and increased three orders of magnitude for 35–50 mol% PbO contents. Such a steep composition dependence is considered to be because of changes in the medium or longer range structure. That is, it is proposed that the plumbate network forms a percolative 3D network in the composition region to form diffusion paths for the lead ions. In addition, the present results indicate that the lead ion exists as a network former over the entire glass forming composition range of the binary silicate glasses.

I. Introduction

LEAD-CONTAINING glasses have been one of the special materials for human beings, being used as crystal glass tableware and ornaments for several hundreds of years. After the industrial revolution, they found a great number of applications as soldering and sealing glasses for electronic devices, and optical glasses, because of their excellent stability against devitrification, high refractive index, and low melting temperature. From the view point of environmental protection, however, the toxicity of lead compounds has now become one of the urgent issues. Many attempts to replace lead with other elements have been made, but most of them could not solve this problem as other heavy metal ions, which may have a problem similar to lead ions in nature, are still used. It is important to understand the leaching process of the lead ions from lead glasses into aqueous solutions and find ways to minimize it. Also, it may show a clue of developing substitute materials that meet the requirements of society.

Lead silicate glasses, $PbO–SiO_2$, are also interesting from the viewpoint of structural chemistry because these glasses exhibit thermal, optical, and mechanical properties different than other silicate glasses, and they form a thermally and chemically stable glass over a wide composition range. Various experimental techniques have been used to investigate the local structure of lead ions, such as IR spectroscopy,[1] Raman spectroscopy,[1–3] NMR,[2,4–6] electron spin resonance,[7] X-ray photoemission spectroscopy (XPS),[8] X-ray diffraction methods,[9–11] neutron diffraction methods,[12] extended X-ray absorption fine structure,[13] and molecular dynamics.[14]

In recent years, the present authors have reported detailed studies of lead silicate glasses over a wide composition region

mainly based on X-ray and neutron radial distribution function (RDF) analyses and XPS.[15] As a consequence, the first Pb–Pb correlation peak was clearly observed at 0.38 nm not only in the high lead region but also in the low lead region, and the Pb–Pb and Pb–O correlation lengths did not change over the entire composition range. These results indicated that the local structure around the lead atoms in the high lead glasses is also found in the low lead ones, which contradicted the network modifier model, which assumes that the Pb^{2+} ion takes a sixfold coordinated structure, previously proposed in the low lead region.[15] Therefore, based on the fact that the Pb–O coordination number was 3 in the high lead region and the Pb–Pb correlation length was about 0.38 nm, we proposed a new structural model, which states that lead atoms are linked to another lead by sharing an edge via two oxygens to form a Pb_2O_4 polyhedron unit (Fig. 1). As the formal charge of oxygen in the basic unit is the same as that in the SiO_4 tetrahedra, the unit is incorporated into the silicate network as a network former without disturbing the charge balance of the neighboring silicate network. The Pb_2O_4 unit has a large free volume around the lead atoms because of the existence of the lone electron pairs. In the high lead region, the basic units are three-dimensionally linked to each other to form the glass network.

However, it has not been clarified whether all the Pb atoms in lead silicate glasses behave as a network former. In other words, the existence of a certain amount of Pb as a network modifier cannot be ruled out. The linking manner of such basic units in the medium lead region is also interesting. Conventional spectroscopic methods mainly provide information about the short-range structure depending on its wavelength, and are not suitable for investigating the medium- and long-range structures related to the linking manner of the basic units.

In the present study, we investigated the leaching behavior of Pb^{2+} from lead silicate glasses for a wide variety of composition ranges in acidic solutions. A difference in the leaching behavior is expected to be because of the different short-, medium-, or long-range structures of the plumbate networks. A traditional leaching test is used to determine how much the harmful metal ion in tableware glasses is corroded in water or other solutions.[16,17] Here, the network connectivity of the Pb_2O_4 trigonal pyramids in lead silicate glasses was investigated based on the leaching behavior of lead ions in acidic solutions. A change in the network structure with lead content is discussed based on the diffusion of the Pb^{2+} ions.

II. Experimental Procedure

Lead silicate glasses of $xPbO–(100−x)SiO_2$ ($x = 25, 33, 40, 45, 50, 66,$ and 70 mol%) were prepared. A mixture of reagent grade PbO (Nacalai Tesque, Kyoto, Japan) and SiO_2 (Wako, Osaka, Japan) was melted in a Pt–Rh crucible and then quenched in ice water. The obtained glasses were crushed into pieces using an alumina mortar and pestle. The sample powders with an average diameter of 138 μm were immersed in 0.1N HNO_3 solution at 40°C for a given time. The diameter was estimated by a laser scattering technique (LA-300; Horiba, Kyoto, Japan) and direct
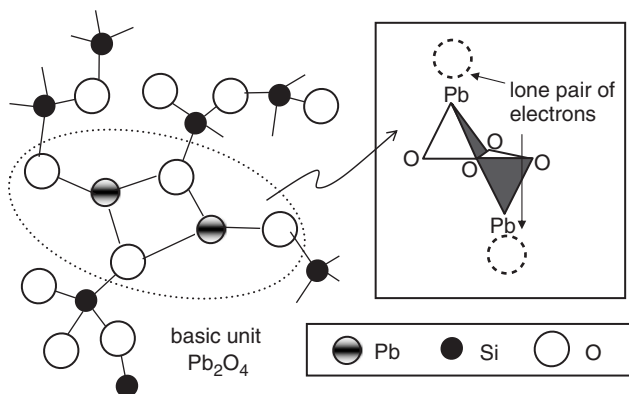
Fig. 1. Structural model of lead silicate glass in the low lead region.

observations with an optical microscope (BX51; Olympus, Tokyo, Japan). The ratio of the total surface area (S) to the solution volume (V) was fixed at $S/V = 91.2$ m^{-1} by assuming each glass particle is spherical. The Pb^{2+} concentration in the leaching solution was measured by inductively coupled plasma atomic emission spectrometry (ICP-AES, ICAP-500; Jarrel Ash, Tokyo, Japan). Moreover, we also examined the samples before and after leaching by means of XPS using Mg$K\alpha$ radiation as the X-ray source (ESCA-850; Shimadzu, Kyoto, Japan), ^{29}Si CP/MAS NMR (CMX400; JEOL, Tokyo, Japan), and an optical microscope.

III. Diffusion Coefficient

When lead silicate glass is soaked in an aqueous solution, lead ion leaching is known to proceed by different mechanisms;[18–21] the ionic diffusion by ion exchange (Pb^{2+}(glass)$\leftrightarrow$2H$^+$(aqueous solution)) and the dissolution of the glass matrix. In addition, the formation of gel layer on the glass surface[22] and the activity change

in the leaching solution,[23] which possibly take place depending on the experimental conditions, may affect the leaching behavior.

In the present experimental conditions, it can be assumed that the leaching solution was dilute enough, the diffusion layer thickness was much thinner than the particle radius, and glass dissolution could be negligible during the initial stage of the leaching experiments. Therefore, the lead concentration in the glass at a distance y from the glass–solution interface is given by Fick's second law

$$\left(\frac{\partial c^g}{\partial t}\right)_y = \frac{\partial}{\partial y}\left[D\left(\frac{\partial c^g}{\partial y}\right)_t\right] \tag{1}$$

where D is the diffusion coefficient, and c^g the lead concentration in the diffusion layer in the glass. From Eq. (1), the concentration of lead ion in the solution, c^s, is obtained,[18,24]

$$c^s = \frac{S}{V}c_0^g a - \frac{S}{V}\int_0^a c^g\,dy \tag{2}$$

where c_0^g is the lead concentration of the initial glass, a the thickness of the diffusion layer, S the total area of the sample powder, and V the solution volume. c^s can then be solved using Eqs. (1) and (2) as

$$c^s = 2\frac{S}{V}c_0^g\left(\frac{Dt}{\pi}\right)^{1/2} \tag{3}$$

In the present study, the time dependence of c^s was fitted by Eq. (3) to obtain the D values.

IV. Results and Discussion

(1) Lead Leaching of Lead Silicate Glasses

Figure 2(a) shows the time dependence of the extracted Pb^{2+} ion concentration in the solution, which obviously increases with the increasing PbO compositions in the xPbO–(100–x)SiO$_2$ glass. The extracted Pb^{2+} concentration varies in proportion to $t^{1/2}$ for glasses of $x = 33$–40. On the other hand, it does not obey the
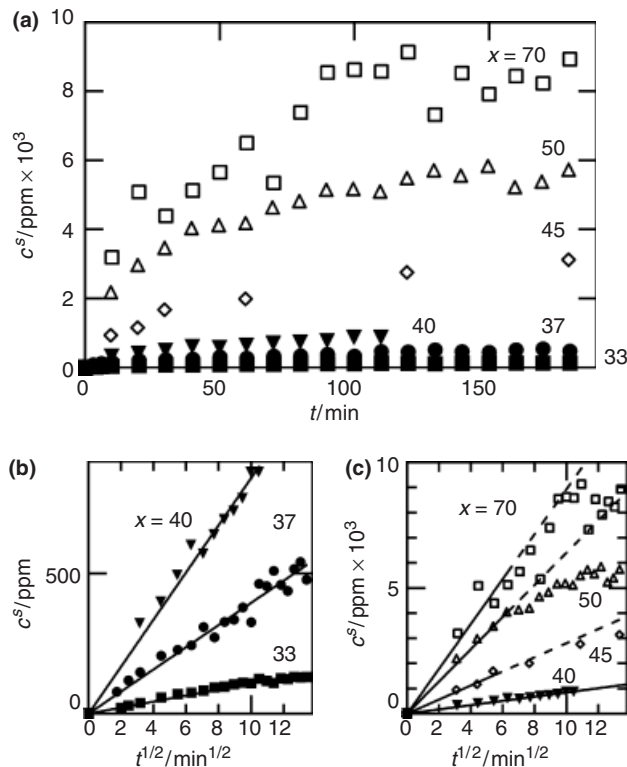

Fig. 2. Time dependence of the extracted Pb^{2+} concentration in the supernatant liquid, c^s,: (a) at $x = 33$–70, (b) at $x = 33$–40, (c) at $x = 40$–70. (b) and (c) are shown as a function of $t^{1/2}$.
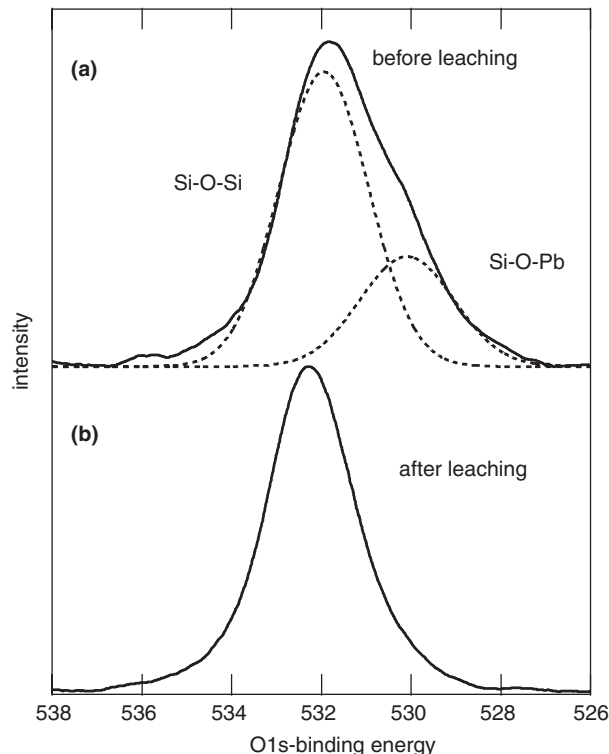

Fig. 3. O-1s-binding energy of low lead glass of $x = 25$: (a) before leaching (solid line, measured; dotted lines, deconvoluted) and (b) after leaching for 3 h.
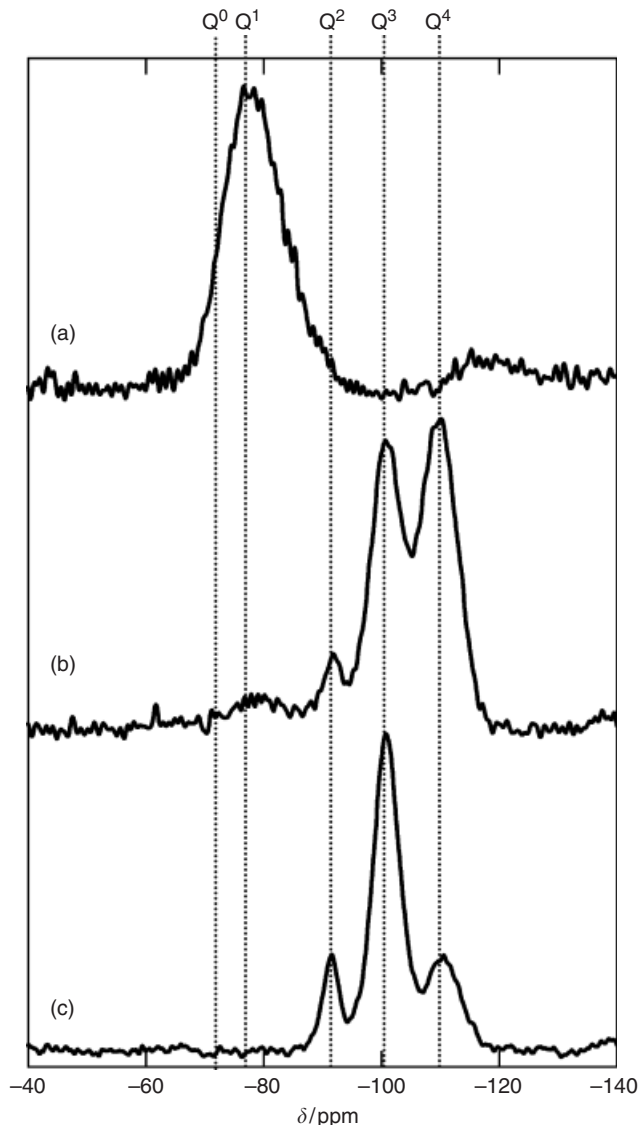
Fig. 4. ^{29}Si NMR spectra of $x = 70$ glass: ^{29}Si MAS NMR (a) before and (b) after leaching for 3 h, and (c) ^{29}Si CP/MAS NMR after leaching for 3 h.

Fig. 5. ^{29}Si MAS NMR spectra of $x = 33$ glass: (a) before and (b) after leaching for 3 h.

square root law for glasses of $x > 40$. Therefore, we classify our glass samples into two types, $x = 33$–40 in the low lead region and $x = 45$–70 in the high lead region for convenience.

Figure 2(b) shows the square root time dependence of the extracted lead ion concentration for the low lead silicate glasses, which show a linear relation passing through the origin, indicating that the rate-determining step of Pb leaching is the diffusion process. The O-1s XPS spectra of the samples $x = 25$ before and after 3 h of leaching are shown in Fig. 3. The profiles of the O-1s core electron spectra changed after 3 h of leaching. Two peaks were found in the O-1s spectra before leaching, which are ascribed to the bridging oxygens in Si–O–Si (532 eV) and the non-bridging oxygens in Pb–O–Si or Pb–O–Pb (530 eV). On the other hand, only one peak was observed after leaching and its spectral profile was almost the same as that of the higher energy component present before leaching. In other words, the bridging oxygens remain unchanged and the non-bridging oxygens bonded to the lead disappeared from the glass surface after leaching for 3 h. This indicates that the lead leaching out of the present glasses takes place via ion diffusion. For the samples in which all the lead ions were removed from the surface by ion-exchange, it has been recognized that the Pb leaching follows only one diffusion process. If several lead leaching processes proceed at the same time, the slope of the line should change
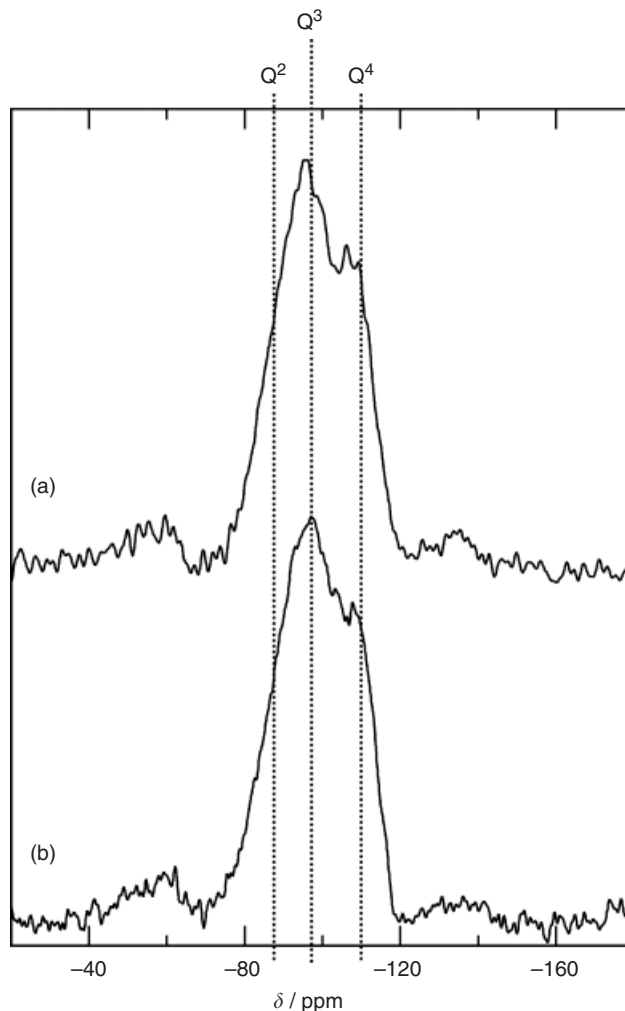
somewhere or the line should not pass through the origin. Therefore, we can say that the local environment of lead ions is very similar to each other in the low lead region.

The extracted lead ion concentration for the high lead glass samples are plotted versus the square root of time as shown in Fig. 2(c). The time dependence of the Pb^{2+} concentration obeyed the square root law only during the early stage ($t < 40$ min) and then gradually deviated downward from the square root law with the increasing leaching time. Such a decline in the diffusion rate is generally thought to be caused by the formation of a diffusion barrier, for example, a silica gel layer, at the surface, the reduction of the lead concentration in the bulk glass, or the saturation of specific ions in the leaching solution. Concerning the lead ion concentration in the present leaching solution, it was undoubtedly dilute enough and the diffusion layer was limited only at the surface of the glass particles.

^{29}Si MAS and CP/MAS NMR spectra of the $x = 70$ and 33 glasses are shown in Figs. 4 and 5, respectively. Figure 4(a) clearly shows that before leaching the main peak was principally composed of the Q^1 unit for the $x = 70$ glass. (Q^n ($n = 0$–4), n indicates the number of bridging oxygens per silicon.) After leaching (Fig. 4(b)), the Q^1 peak significantly decreased, but also the Q^4, Q^3, and Q^2 peaks appeared. As shown in Fig. 4(c), the Q^4, Q^3, and Q^2 units were observed in the ^{29}Si CP/MAS spectra after leaching. The CP/MAS spectra provided information for only the local vicinity of the OH group, that is, the dissolved Si–OH. This means that the SiO_2-rich gel layer formed not only at the surface but also in the bulk glasses. The formation of the gel layer was observed in all the samples of $x > 45$. Therefore, it
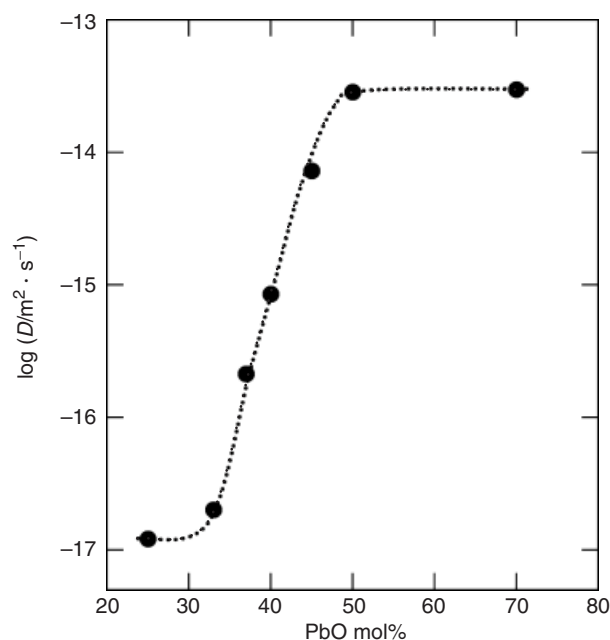
Table I. Diffusion Coefficient of Pb^{2+} in $xPbO$–$(100-x)SiO_2$ Glasses ($x = 25$–70) Measured at $40°C$ in $0.1N$ HNO_3

x	D (m^2/s)
25	1.21×10^{-17}
33	2.01×10^{-17}
37	2.13×10^{-16}
40	8.53×10^{-16}
45	7.25×10^{-15}
50	2.85×10^{-14}
70	2.98×10^{-14}

is concluded that the decline in the leaching behavior is caused by the gel formation. On the other hand, Fig. 5 shows the ^{29}Si MAS NMR spectra of the low lead glass ($x = 33$) before and after leaching. As both spectra were very close to each other in shape and composed of the Q^4, Q^3, and Q^2 peaks, and it is clear that no gel layer was formed in the low lead region.

(2) Plumbate Network Formation in Lead Silicate Glasses

The meaningful diffusion step is, therefore, restricted to the early time period in the high lead region. In such cases, the diffusion coefficient D was determined, e.g., for the first 40 min for the $x \geq 45$ glass. The obtained diffusion coefficients D are shown in Table I and Fig. 6. The D value was as low as 10^{-17} m^2/s in the low PbO region, but sigmoidally increased to 10^{-15}–10^{-14} m^2/s in the medium composition region ($x = 35$–50). In this composition region, it has been reported by the latest X-RDF analysis that the short range structure of the lead silicate glass does not change with the composition.[15] We can say that the structural change deduced from the present leaching test originates from the change in the manner of the network connectivity. The Pb_2O_4 unit, which is the proposed local structure in Takaishi *et al.*,[15] is connected to each other to form the Pb^{2+} diffusion paths in the glasses beyond the medium lead compositions, resulting in a drastic increase in D. That is, in the low PbO region, the basic Pb_2O_4 units exist in the silicate framework. In other words, the silicate network surrounding a Pb_2O_4 unit as a diffusion barrier, giving rise to a very small D, was observed. When the lead content increases, the distance between these units becomes shorter, resulting in an increase in mobility. In the region of $x = 35$–50, the units start to be connected to each other and

form Pb^{2+} diffusion paths and the diffusion coefficient increased by several orders of magnitude because of the percolation transitions of the PbO networking. The diffusion paths become wider in the higher PbO region, providing even higher diffusion coefficients.

These results again prove that Pb_2O_4 units are embedded in the silicate framework even in the low PbO glasses, not as a network modifier, but as a network former. In Fig. 7, we propose the medium- and long-range model structures. In the low lead region, lead mainly exists at only one kind of site. The RDF data showed that Pb behaves as a network former even in this region. Therefore, it can be concluded that there is almost

Fig. 6. Diffusion coefficient of Pb^{2+} in $xPbO$–$(100-x)SiO_2$ glasses ($x = 25$–70) measured at $40°C$ in $0.1N$ HNO_3.
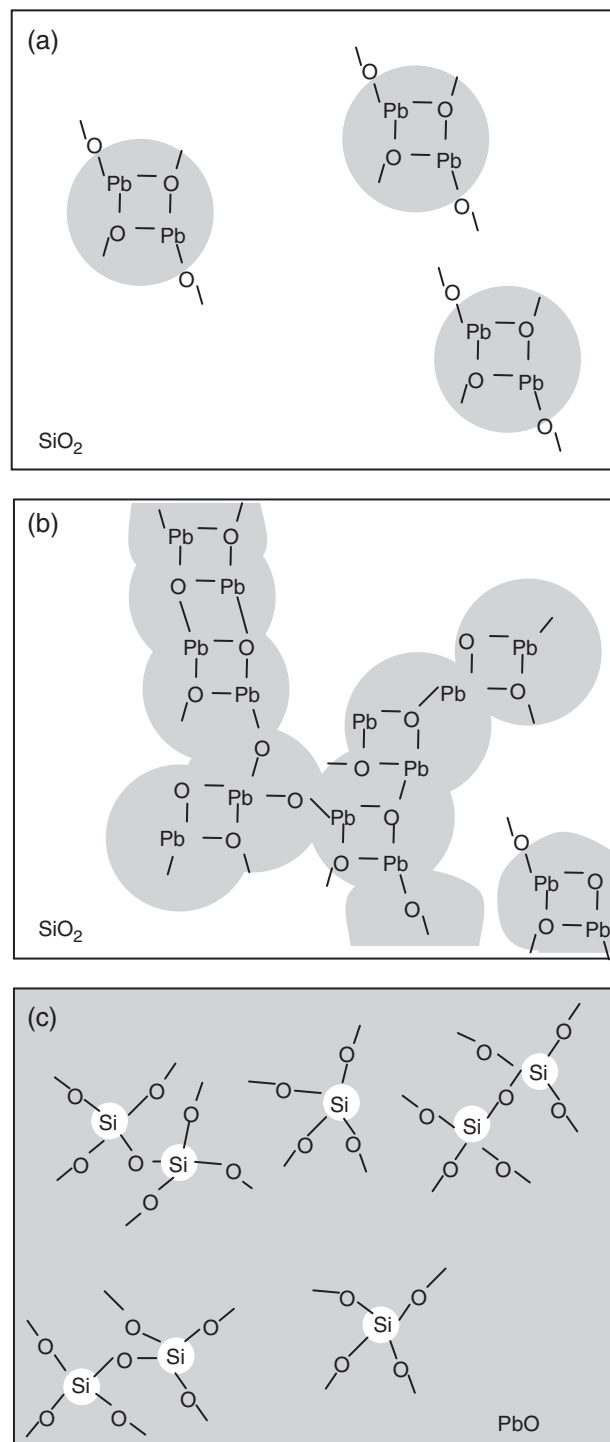
Fig. 7. The structural model of lead silicate glasses: (a) the low lead region, $x < 35$, (b) the medium lead region, $35 < x < 50$, and (c) the high lead region, $x > 50$.

no lead existing as a network modifier, but the basic Pb_2O_4 unit is embedded in the silicate network. These characteristic compositional dependencies of the diffusion coefficient do not appear in the other thermal or mechanical properties. This is, to the best of our knowledge, the first report to show a large change in the thermal diffusion coefficient of the Pb^{2+} ion which is because of the change in the medium and long range structures of the plumbate network in lead silicate glasses.

V.　Conclusion

Based on the leaching behavior of lead ions in silicate glasses, we obtained several new insights into the short-, medium-, and long-range structures of the lead silicate glasses. In the low lead silicate glasses ($x < 35$), isolated plumbate units exist in the silicate network. The extraction of lead from the glass is then effectively depressed. In the high lead silicate glasses ($x > 50$), the lead atoms construct a glass network. In the medium lead silicate glasses ($x = 35–50$), a unique structure exists as 3D percolative plumbate. In the low lead region, the existence of only one kind of lead is revealed by only one diffusion process. Therefore, it is concluded that lead acts only as a network former and no network modifier exists even in the low lead region. The absence of non-bridging oxygen in the lead silicate glasses over the entire composition causes the high potential of glass formation irrespective of the composition.

References

[1]C. A. Worrell and T. Henshall, "Vibrational Spectroscopic Studies of Some Lead Silicate Glasses," *J. Non-Cryst. Solids*, **29** [3] 283–99 (1978).

[2]H. Verweij and W. L. Konijnendijk, "Structural Units in K_2O–PbO–SiO_2 Glasses by Raman Spectroscopy," *J. Am. Ceram. Soc.*, **59** [11–12] 517–21 (1976).

[3]A.-M. Zahra and C. Y. Zahra, "DSC and Raman Studies of Lead Borate and Lead Silicate Glasses," *J. Non-Cryst. Solids*, **155** [1] 45–55 (1993).

[4]F. Fayon, C. Bessada, D. Massiot, I. Farnan, and J. P. Coutures, "^{29}Si and ^{207}Pb NMR Study of Local Order in Lead Silicate Glasses," *J. Non-Cryst. Solids*, **232–234**, 403–8 (1998).

[5]F. Fayon, C. Landron, K. Sakurai, C. Bessada, and D. Massiot, "Pb^{2+} Environment in Lead Silicate Glasses Probed by Pb-L_{III} Edge XAFS and ^{207}Pb NMR," *J. Non-Cryst. Solids*, **243** [1] 39–44 (1999).

[6]T. Yoko, K. Tadanaga, F. Miyaji, and S. Sakka, "A ^{207}Pb MAS-NMR Study of Pb-Containing Glasses," *J. Non-Cryst. Solids*, **150** [1–3] 192–6 (1992).

[7]H. Hosono, H. Kawazoe, and T. Kanazawa, "Coordination of Pb^{2+} in Oxide Glasses Determined by ESR and Properties of Binary Lead Glasses," *Yogyo Kyokai Shi*, **90** [9] 544–51 (1982).

[8]P. W. Wang and L. Zhang, "Structural Role of Lead in Lead Silicate Glasses Derived from XPS Spectra," *J. Non-Cryst. Solids*, **194** [1–2] 129–34 (1996).

[9]M. F. Mydlar, N. J. Kreidl, J. K. Hendren, and G. T. Clayton, "X-ray Diffraction Study of Lead Silicate Glasses," *Phys. Chem. Glasses*, **11** [6] 196–204 (1970).

[10]H. Morikawa, Y. Takagi, and H. Ohno, "Structure Analysis of $2PbO \cdot SiO_2$ Glass," *J. Non-Cryst. Solids*, **53** [1–2] 173–82 (1982).

[11]M. Imaoka, H. Hasegawa, and I. Yasui, "X-ray Diffraction Analysis on the Structure of the Glasses in the System PbO–SiO_2," *J. Non-Cryst. Solids*, **85** [3] 393–412 (1986).

[12]K. Yamada, A. Matsumoto, N. Niimura, T. Fukunaga, N. Hayashi, and N. Watanabe, "Short Range Structural Analysis of Lead Silicate Glasses by Pulsed Neutron Total Scattering," *J. Phys. Soc. Jpn.*, **55** [3] 831–7 (1986).

[13]J. Rybicki, A. Rybicka, A. Witkowska, G. Bergmanski, A. D. Cicco, M. Minicucci, and G. Mancini, "The Structure of Lead-silicate Glasses: Molecular Dynamics and EXAFS Studies," *J. Phys. Condens. Mater.*, **13** [43] 9781–97 (2001).

[14]K. V. Damodaran, B. G. Rao, and K. J. Rao, "A Molecular Dynamics Study of a $PbO.SiO_2$ Glass and Melt," *Phys. Chem. Glasses*, **31** [6] 212–6 (1990).

[15]T. Takaishi, M. Takahashi, J. Jin, T. Uchino, and T. Yoko, "Structural Study on PbO–SiO_2 Glasses by X-Ray and Neutron Diffraction and ^{29}Si MAS NMR Measurements," *J. Am. Ceram. Soc.*, **88** [6] 1591–6 (2005).

[16]R. L. Lehman, S. C. Yoon, M. G. McLaren, and H. T. Smyth, "Mechanism of Modifier Release from Lead-Containing Glasses in Acid Solution," *Am. Ceram. Soc. Bull.*, **57** [9] 802–5 (1978).

[17]A. Abou El-Azm and A. L. Hussein, "Chemical Durability of Glasses Containing High Proportions of Lead Oxide in Relation to Their Structure," *J. Chem. UAR*, **5** [1] 1–20 (1962).

[18]R. H. Dremus, "Chemical Durability of Glass"; pp. 41–67 in *Treatise on Materials Science and Technology. Glass II*, Vol. 17, Edited by M. Tomozawa and R. H. Doremus. Academic Press, NY, 1979.

[19]Z. Boksay, G. Bouquet, and S. Dobos, "Diffusion Processes in the Surface Layer of Glass," *Phys. Chem. Glasses.*, **8** [4] 140–4 (1967).

[20]S. Wood and J. R. Blachere, "Corrosion of Lead Glasses in Acid Media: I, Leaching Kinetics," *J. Am. Ceram. Soc.*, **61** [7–8] 287–92 (1978).

[21]B. Grambow and R. Müller, "First-order Dissolution Rate Law and the Role of Surface Layers in Glass Performance Assessment," *J. Nucl. Mater.*, **298** [1–2] 112–24 (2001).

[22]D. M. Sanders and L. L. Hench, "Mechanisms of Glass Corrosion," *J. Am. Ceram. Soc.*, **56** [7] 373–7 (1973).

[23]A. Helebrant and B. Tošnerová, "A Mathematical Model Used to Compare Glass Durability Tests Under Different Flow Conditions," *Glass Technol.*, **30** [6] 220–3 (1989).

[24]A. Helebrant and I. Pekárková, "Kinetics of Glass Corrosion in Acid Solutions," *Ber. Bunsenges. Phys. Chem.*, **100** [9] 1519–22 (1996).　　　□