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Characterization of the Pb Coordination Environment and Its Connectivity in Lead Silicate Glasses: Results from 2D ^{207}Pb NMR Spectroscopy

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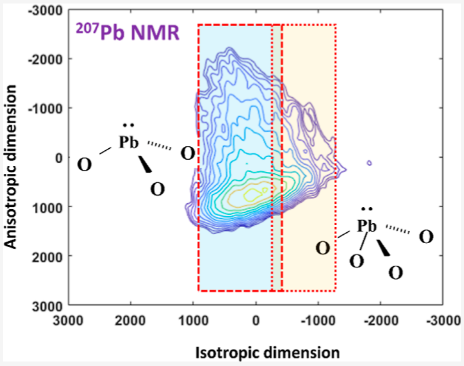
ABSTRACT: The Pb−O coordination environment in binary $(PbO)_x(SiO_2)_{100-x}$ glasses with $30 \leq x \leq 70$ is probed by using two-dimensional ^{207}Pb nuclear magnetic resonance (NMR) isotropic−anisotropic correlation spectroscopy. The isotropic ^{207}Pb NMR spectra show little composition-dependent evolution of the Pb−O nearest-neighbor coordination environment. The systematic variation of the chemical shift tensor parameters offers a unique insight into their local site symmetry and suggests the presence of pyramidal PbO_3 and PbO_4 sites with sterically active electron lone pairs and with Pb−O bond lengths ranging between 0.23 and 0.25 nm. The PbO_3/PbO_4 ratio shows a small but monotonic increase from ∼70:30 to 80:20 as the PbO content increases from 30 to 70 mol %. When taken together, the isotropic and anisotropic ^{207}Pb NMR spectra suggest that the majority of the PbO_n $(3 \leq n \leq 4)$ pyramids in these glasses are connected to the SiO_4 tetrahedra via Pb−O−Si linkages. A significant fraction of Pb−O−Pb linkages, where the oxygen is linked only to Pb atoms, appears only in glasses with PbO ≥ 60 mol %. These oxygen atoms appear to be corner-shared between the PbO_n pyramids in the structure, and no evidence for edge-sharing between these pyramids is observed in this composition range. We hypothesize that a substantial fraction of the constituent PbO_n pyramids start to participate in edge-sharing only at higher PbO contents (>70 mol %), which diminishes the glass-forming ability of the network. This work illustrates the potential of isotropic−anisotropic correlation NMR spectroscopy in structural studies involving nuclides with large chemical shift ranges and anisotropy.



1. INTRODUCTION

The addition of Pb imparts unique attributes to a glass, including a high linear and nonlinear refractive index, strong absorptivity of high-energy radiation, thus making it suitable for various electronic or photonic applications as well as for radiation shielding.[1−3] Moreover, the affinity of Pb for chalcogen elements such as S, Se, or Te has been utilized in precipitating lead chalcogenide IV−VI quantum dots in various oxide glass matrices upon heat treatment.[4−6] The addition of lead oxide (PbO) to the archetypal network-forming oxides such as SiO_2, B_2O_3, and P_2O_5 leads to bulk glass formation over an unusually wide composition range extending to rather high concentrations of PbO.[7−16] The upper limit of the PbO content for glass formation, as reported in some of these previous studies, is likely strongly dependent on alumina and/or silica contamination from the crucible material. A careful study by Feller et al.[16] of Pb-silicate glasses melted in platinum crucibles suggests a reliable upper limit of ∼83 ± 2 mol % PbO for glass formation. A fundamental understanding of this rather unusual glass-forming ability of high PbO-containing oxide liquids was sought in previous studies in the literature on the structural role of Pb in the derived glasses using a wide range of techniques, including vibrational, X-ray photoelectron, X-ray absorption, electron spin resonance, nuclear magnetic resonance (NMR) spectroscopy, and X-ray and neutron diffraction.[7,8,10−27]

Some of the most detailed structural information reported in the literature regarding the Pb−O coordination environment in oxide glasses have been obtained from X-ray and neutron diffraction studies of Pb-silicate glasses.[10−15] The majority of these structural studies have suggested that over the entire glass-forming composition range, Pb is present in PbO−SiO_2 glasses in the form of covalently bonded PbO_n $(3 \leq n \leq 4)$ pyramidal coordination environments with Pb−O distances ranging between ∼0.22 and 0.25 nm and with sterically active lone pair electrons on the Pb atoms. The most consistent results have been reported by Alderman et al.[10] in a recent combined high-resolution pulsed neutron, high-energy X-ray diffraction, and empirical potential structural refinement

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(EPSR) modeling study of PbO−SiO_2 glasses with 35 to 80 mol % PbO. The neutron radial distribution functions (RDF) obtained in this study indicate that over the entire composition range, the Pb atoms are bonded to ∼2.3 to 2.6 O atoms at a distance ranging between 0.223 and 0.228 nm and to ∼0.8 to 1.2 O atoms at a longer distance of ∼0.242 to 0.251 nm. It may be noted here that diffraction by itself may not always lead to an unambiguous estimation of the speciation for an atom with multiple coordination environments or the coordination number for an environment characterized by a relatively broad range of nearest-neighbor distances. Besides, although diffraction yields a specific coordination number, the associated coordination geometry needs to be determined using either structural modeling of the diffraction data or other spectroscopic techniques such as NMR. Such issues are apparent in the assignment of peaks at 0.226 and 0.266 nm in the X-ray RDF of PbO−SiO_2 glasses by Neuville and co-workers to Pb in tetrahedral and octahedral environments, respectively.[27] Takaishi et al.,[11] on the other hand, indicated that the peak near ∼0.265 nm is likely associated with the O−O correlation of SiO_4 tetrahedra. These authors, in their combined X-ray and neutron diffraction study of PbO−SiO_2 glasses with 25 mol % ≤ PbO ≤ 89 mol %, claimed that all Pb-silicate glasses were characterized by Pb atoms in a trigonal pyramidal PbO_3 environment with Pb−O distances ranging between 0.23 and 0.24 nm. However, they also observed a correlation at ∼0.28 nm to be present in the X-ray RDF of glasses with ≤50 mol % PbO and assigned it to a longer Pb−O correlation but ignored the possibility of contributions from Pb−Pb and/or Pb−Si correlation at such long distances. A similar situation led Kohara et al.[14] to deduce a primarily fourfold coordination for Pb atoms in Pb silicate glasses with Pb−O coordination numbers ranging between 3 and 5, although it was not clear whether such long Pb−O distances of 0.27−0.28 nm represented any bonding interaction in these glasses.

Previous ^{29}Si and ^{17}O NMR spectroscopic studies have shown that, similar to the addition of typical network-modifier cations such as alkalis and alkaline-earths to SiO_2, the addition of PbO results in the formation of nonbridging oxygen (NBO) atoms.[16,19] At the same time, these studies have shown that Pb^{2+} also behaves rather differently from other monovalent or divalent modifier cations such as alkalis and alkaline-earths in terms of its effect on the Si Q^n speciation, where n indicates the number of bridging oxygen (BO) atoms per SiO_4 tetrahedron and oxygen speciation. For example, the addition of PbO to SiO_2 strongly favors Q-species disproportionation according to the reaction: $Q^n \rightarrow Q^{n+1} + Q^{n-1}$, with the equilibrium constant for this reaction being an order of magnitude larger than that characteristic of the alkali silicates.[16,17] Moreover, PbO also promotes the disproportionation reaction 6 NBO → FO + BO, where BO represents the BO shared between two Si atoms and FO is the free oxide ion shared solely by Pb atoms in Pb−O−Pb linkages.[19] It may be noted that the formation of FO becomes inevitable in liquids/glasses with modifier-rich compositions such that the O/(Si,P) ratio exceeds 4. This was shown to be indeed the case for alkali and alkaline-earth ions.[28,29] However, Pb proves to be an exception where ^{29}Si and ^{17}O NMR as well as Raman spectroscopic results suggest the formation of FO in glasses with as low as ∼60 mol % PbO, i.e., with an O/Si ratio of 3.5.[19] This propensity for the formation of FO is also observed in crystalline Pb silicates such as $Pb_3Si_2O_7$ and Pb_2SiO_4, which are characterized by overpolymerized Q^2 species coexisting with Pb-FO-Pb free oxide ions.[18]

The NMR spectroscopy of the ^{207}Pb nuclide presents its own problems in the determination of the Pb−O coordination. Despite being a spin-1/2 nuclide with moderate sensitivity and decent natural abundance (∼22%), the solid-state NMR spectroscopy of ^{207}Pb remains rather challenging, especially in glasses and other disordered materials. This difficulty primarily arises from the large chemical shift range of ^{207}Pb (∼8000 ppm), resulting from the large number of electrons and their high polarizability, which gives rise to NMR line shapes in glasses that are broadened to an extreme by a combination of chemical shift distribution and chemical shift anisotropy (CSA).[10,17,20,30] Both sources of broadening can contribute on the order of a few thousands of parts per million to the ^{207}Pb NMR line width in glassy materials. As a result, it has remained difficult to obtain high-resolution ^{207}Pb NMR spectra of glasses with 1D NMR to determine the isotropic shift and the associated CSA to conclusively establish the Pb−O coordination number and the geometry of the coordination environment. It may be noted here that while the isotropic chemical shift δ_{iso} of a nuclide is characteristic of its coordination environment, the CSA carries important complementary information related to the symmetry of its local electronic and, therefore, of its bonding environment.

Previous systematic ^{207}Pb MAS NMR studies of crystalline Pb-oxides have indicated that an ionic Pb−O environment in oxides with long (0.26−0.28 nm) Pb−O bonds and relatively large Pb−O coordination numbers (≥6) are characterized by significantly lower chemical shift and CSA, compared to those that are characteristic of covalently bonded PbO_3 and PbO_4 pyramidal environments with relatively short (0.22−0.24 nm) Pb−O bonds.[30] This intriguing correlation between the Pb−O bonding environment and the ^{207}Pb chemical shift and CSA suggests that 2D ^{207}Pb isotropic−anisotropic correlation NMR spectroscopy may greatly enhance our current understanding of the Pb−O bonding environment and its compositional variation in oxide glasses.[31] Here, we present 2D ^{207}Pb isotropic−anisotropic correlation NMR spectra of select Pb-silicate glasses with PbO concentrations ranging between 30 and 70 mol % to separate the effects of the chemical shift distribution from that of the CSA. These spectra conclusively demonstrate the presence of a broad distribution of covalently bonded pyramidal Pb−O coordination environments with coordination numbers of 3 and 4 in silicate glasses. The structural implications of Pb coordination chemistry are discussed in terms of the stability of the resulting network.

2. MATERIALS AND METHODS

2.1. Sample Synthesis and Thermophysical Characterization. A series of $(PbO)_x(SiO_2)_{100-x}$ glasses with $x = 30$, 40, 50, 60, and 70 were prepared in 10−20 g quantity by a conventional melt-quenching method. Appropriate mixtures of SiO_2 (99.995%, Alfa Aesar) and Pb_3O_4 (99.9%, Sigma-Aldrich) were taken in a platinum crucible and melted in air for 10−15 min at temperatures ranging from 1000 °C for the composition with the highest PbO content to 1500 °C for the one with the lowest PbO content. Melts of composition $x = 30$ and 40 were quenched by dipping the bottom of the crucible in water, while those with higher PbO contents were poured on a graphite plate and splat-quenched by pressing with a steel block.

The glass transition temperature T_g of these glasses was measured using differential scanning calorimetry (DSC;

Netzsch STA 449 F3 Jupiter). For each glass composition, approximately 20 to 30 mg of sample was taken in a platinum crucible. The samples were heated at 10 K/min under a nitrogen atmosphere to 50 K above glass transition to erase any thermal history, cooled down to 543 K, and then reheated at the same rate. The T_g is taken as the onset of the endothermic glass transition signal during reheating. The estimated error in T_g is within ±2 K. The density of these glasses was measured using a gas expansion pycnometer (Micromeritics AccuPyc II 1340) at 293 K using helium (6N purity) as the displacement gas. For each measurement, approximately 1 g of the glass sample was loaded into a 1 cm^3 cup. All reported density values are averages of 10 consecutive measurements of each sample. The T_g and density of these glasses are shown in Figure 1 and are found to be in good agreement with those reported in previous studies in the literature.[8,10] However, we do note that the densities of our high-PbO glasses with ≥60 mol % PbO are on the low side compared to the values reported in the literature,[8,10] which could indicate some loss of PbO via evaporation during glass melting, leading to slightly silica-rich compositions compared to the nominal.

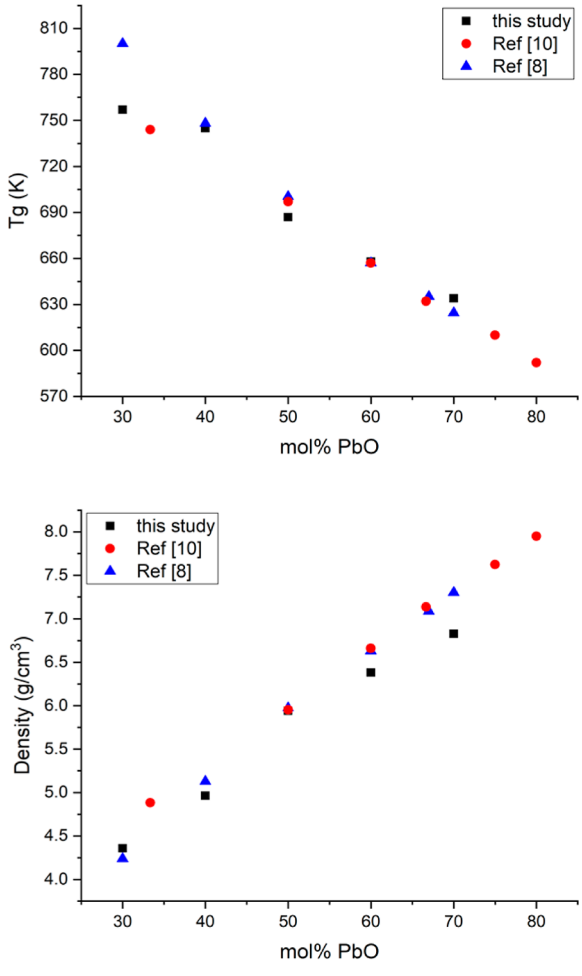

Figure 1. Glass transition temperature (top) and density (bottom) of $(PbO)_x(SiO_2)_{100-x}$ glasses measured in the present study (black squares) and reported in ref 10 (red circles) and in ref 8 (blue triangles).

2.2. 2D ^{207}Pb MATPASS Isotropic−Anisotropic Correlation NMR Spectroscopy.

The projection magic-angle-turning phase-adjusted spinning sideband/Carr−Purcell−Meiboom−Gill (*pj*MATPASS/CPMG) NMR spectroscopy is employed in the present study to separate the isotropic and anisotropic ^{207}Pb NMR spectra in two different dimensions.[32,33] The 2D ^{207}Pb *pj*MATPASS/CPMG NMR spectra were acquired at the National High Magnetic Field Laboratory (NHMFL, Tallahassee, Florida) using a Bruker AVANCE NEO console operating at a ^{207}Pb Larmor frequency of 125.5 MHz (B_0 = 14.1 T, $\nu_0(^1H)$ = 600 MHz) and a low-*E* 3.2 mm triple-resonance MAS probe. Crushed glass samples were packed into 3.2 mm ZrO_2 rotors and spun at 16 kHz. Short $\pi/2$-pulses of 1.75 μs with *rf* fields of 143 kHz were used throughout the pulse sequence to ensure uniform excitation of the full spectral range and even for the CPMG echo-train acquisition to enhance sensitivity.[34] The method of States et al.[35] for hypercomplex data acquisition was applied to the CPMG pulse phase and the receiver phase simultaneously. The 2D acquisition consisted of 64 hypercomplex t_1 increments, each with 72 transients, 260 CPMG echoes per transient, and a 9 s recycle delay, for a total experimental duration of 23 h per spectrum. The 2D spectra were obtained by summing the CPMG echoes and shearing to an isotropic/anisotropic representation in the direct/indirect dimensions during processing, as detailed by Hung et al.[32,34] The ^{207}Pb chemical shifts were referenced to neat $Pb(CH_3)_4$ with δ_{iso} = 0 ppm by using the ^{17}O signal of H_2O and the frequency ratios listed for ^{17}O and ^{207}Pb in the IUPAC recommendations.[36]

3. RESULTS AND DISCUSSION

3.1. Short-Range Order: Pb−O Coordination Environment.

The 2D ^{207}Pb MATPASS NMR spectra of the $(PbO)_x(SiO_2)_{100-x}$ glasses with $30 \leq x \leq 70$ display remarkable similarity (Figure 2), indicating the lack of any major composition-dependent evolution of the Pb−O nearest-neighbor coordination environment in this composition range. The isotropic projections of these ^{207}Pb MATPASS NMR spectra, which are free from any CSA-induced broadening effects, are shown in Figure 3. Again, these isotropic spectra show rather similar line shapes and full width at half-maximum (fwhm), with the latter being remarkably lower (∼1200−1250 ppm) than the typical fwhm of the static ^{207}Pb NMR spectra (∼3000 ppm) reported in previous studies.[17] However, as expected, the average ^{207}Pb NMR chemical shift and its compositional variation in these isotropic and static spectra are observed to be in good agreement (Figure 3). The marked narrowing of the isotropic spectra implies large CSA-induced broadening of the static ^{207}Pb NMR line shapes in these glasses, which along with the average isotropic chemical shift δ_{iso} that ranges between ∼100 and 500 ppm (Figure 3), are characteristic of covalently bonded PbO_n ($3 \leq n \leq 4$) pyramidal environments.[30] In a previous study of the correlation between the structure of various crystalline Pb-containing oxides and their ^{207}Pb NMR parameters, Fayon et al.[30] obtained a linear correlation between the ^{207}Pb δ_{iso} and the mean Pb−O bond length *d* (nm) that is given by the expression

$$\delta_{iso}\ (\text{ppm}) = 20854 - 86689.5d\ (\text{nm}) \tag{1}$$

The ^{207}Pb NMR isotropic spectral line shapes in Figure 3 cover (base-to-base) a range of δ_{iso} between −1000 and 1000 ppm, which yield from eq 1 a corresponding range of 0.23−0.25 nm for the Pb−O bond distances in these glasses with an

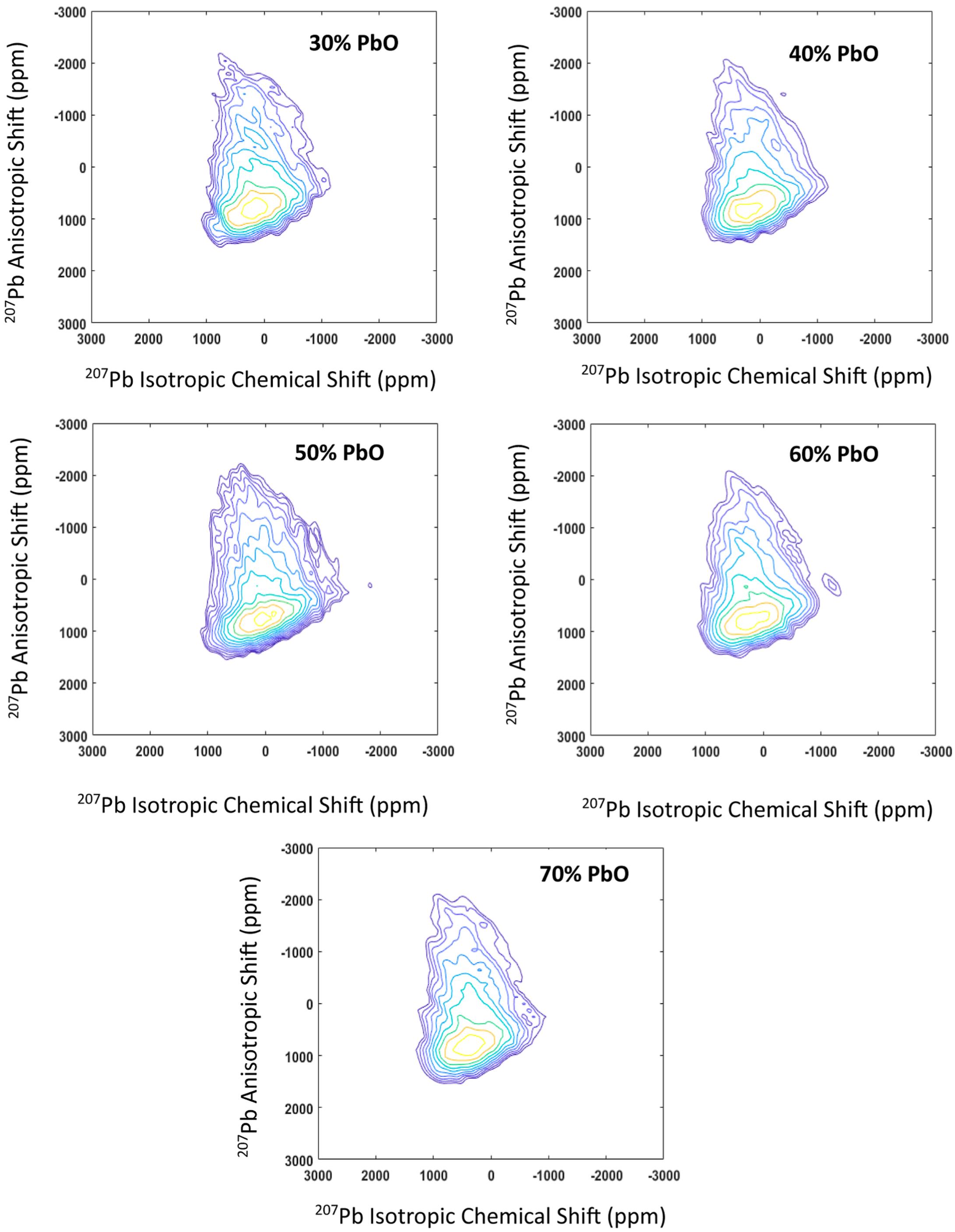

Figure 2. Contour plots of ^{207}Pb MATPASS NMR spectra of $(PbO)_x(SiO_2)_{100-x}$ glasses. Glass composition is denoted in the inset of each spectrum. Ten contours are shown in each spectrum, with the lowest contour starting at 17% of maximum intensity and each successive contour increasing in intensity by 20%.

average distance of ∼0.235−0.239 nm, consistent with previous diffraction-based findings.[10,11,14]

Besides the isotropic spectra, the 2D ^{207}Pb MATPASS NMR spectra in Figure 2 also allow for the determination of the CSA from the anisotropic line shape and its evolution with ^{207}Pb δ_{iso}. It may be noted here that the chemical shift δ of a nuclide is a second rank tensor that can be described using principal components δ_{11}, δ_{22}, and δ_{33}. The isotropic chemical shift δ_{iso} is the average of these three components

$$\delta_{iso} = \frac{1}{3}(\delta_{11} + \delta_{22} + \delta_{33}) \tag{2}$$

Following the standard convention, these principal components are arranged in such a way that

$$\delta_{11} \geq \delta_{22} \geq \delta_{33} \tag{3}$$

More commonly, however, the symmetry of the tensor is reported in terms of the span Ω and the skew κ, which characterize the CSA and are related to the principal components as

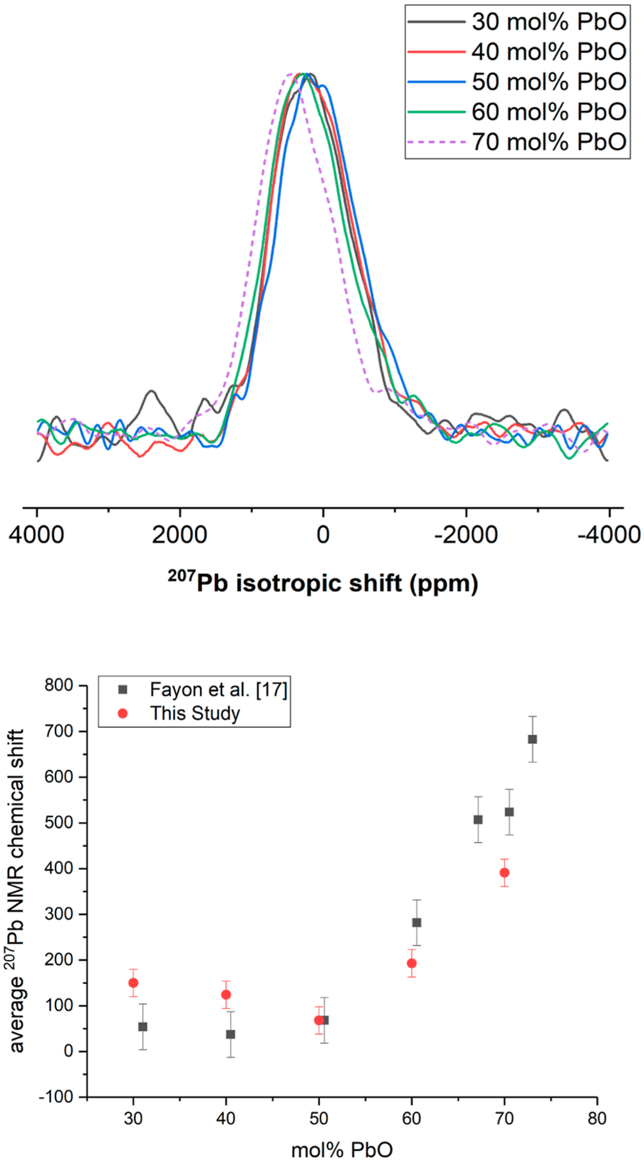

Figure 3. Top: Isotropic projections of ^{207}Pb MATPASS NMR spectra of $(PbO)_x(SiO_2)_{100-x}$ glasses. Solid black, red, blue, and green lines correspond to spectra for glasses with 30, 40, 50, and 60 mol % PbO, respectively. The dashed purple line denotes the spectrum for the glass with 70 mol % PbO. Bottom: Compositional variation of average ^{207}Pb NMR chemical shift obtained from isotropic spectra shown above (red circles) and those obtained in a previous study (black squares) from static ^{207}Pb NMR spectra.[17]

$$\Omega = \delta_{11} - \delta_{33} (\Omega \geq 0) \tag{4}$$

$$\kappa = \frac{3(\delta_{22} - \delta_{\text{iso}})}{\Omega} (+1 \geq \kappa \geq -1) \tag{5}$$

The degrees of departure of Ω from zero and of $|\kappa|$ from 1 represent the deviation of the tensor from spherical and axial symmetry, respectively. As noted earlier, the CSA provides unique information about the symmetry of the bonding environment of a nuclide. A detailed characterization of the CSA tensor of Pb-based oxide compounds was carried out in a previous study by Fayon et al.[30] The results of this study indicated an intriguing correlation between the degree of covalency of Pb−O bonding and the ^{207}Pb δ_{iso} and Ω in these compounds. Ionic compounds with Pb−O coordination number ≥6 are found to be characterized by highly negative ^{207}Pb $\delta_{\text{iso}} \leq -1500$ ppm and a symmetric bonding environment with $\Omega \leq 800$ ppm. In contrast, covalently bonded PbO_3 and PbO_4 environments with sterically active lone pairs are characterized by a larger ^{207}Pb δ_{iso} ranging between −1500 and 2000 ppm and a significantly larger Ω that increases with increasing δ_{iso}, until the former reaches a value of ~3500 to 3900 ppm.[30] Such large values of Ω are consistent with the sterically active lone pair preventing symmetric disposition of the nearest-neighbor oxygen atoms around the central Pb atom, resulting in the pyramidal PbO_3 and PbO_4 coordination geometry with relatively short Pb−O bonds. Moreover, the $|\kappa|$ for these covalent environments always stays close to ~1, implying a nearly uniaxial symmetry with the unique axis likely being oriented along the direction of the lone pair.[30]

An inspection of the 2D ^{207}Pb MATPASS NMR spectra of $(PbO)_x(SiO_2)_{100-x}$ glasses with $30 \leq x \leq 70$ in Figure 2 indicates a relatively large Ω varying between ~2000 and 3000 ppm that increases with increasing ^{207}Pb δ_{iso}. The representative values of Ω and κ of the ^{207}Pb NMR line shapes in these glasses are extracted by simulating anisotropic projections of the MATPASS spectra at three δ_{iso} ranges: (i) 800 ± 200, (ii) 0 ± 200, and (iii) −700 ± 200 ppm using the Dmfit software.[37] Nearly identical results were obtained for all glass compositions within the limits of experimental resolution, indicating that the local symmetry of the Pb−O coordination environments in these glasses is not sensitive to the PbO concentration, at least up to 70 mol % PbO. Representative simulations of the anisotropic ^{207}Pb line shapes are shown in Figure 4 for the glass with 50 mol % PbO. These simulations yield values of $\Omega \sim 3450$, 3070, and 1970 ppm, respectively, for regions (i), (ii), and (iii), implying a relatively small (~10%) decrease in Ω with decreasing δ_{iso} from 1000 ppm down to −200 ppm, followed by a more rapid decrease in Ω (~40%) with further lowering of δ_{iso} to −900 ppm (Figures 2 and 4). On the other hand, the CSA symmetry parameter $|\kappa|$ varies between 0.8 and 1, implying the existence of a strong axial symmetry for all Pb−O coordination environments in these glasses. As noted above, this symmetry is consistent with the covalently bonded pyramidal PbO_3 and PbO_4 units in the structure, with the unique axis of symmetry aligned along the lone pair electrons on Pb.

It is tempting to speculate that the region with $1000 \geq \delta_{\text{iso}} \geq -200$ in isotropic ^{207}Pb NMR spectra characterized by relatively high Ω represents predominantly PbO_3 sites, while the rapid lowering of Ω in the region with $\delta_{\text{iso}} \leq -200$ ppm could be indicative of contribution from more symmetric PbO_4 sites. We therefore carried out simulations of the ^{207}Pb NMR isotropic spectral line shapes (Figure 3) with two Gaussian components (Figure 5). The results of such simulations with Gaussian peak widths constrained between 900 and 1000 ppm are listed in Table 1. It may, however, be noted at the outset that such assignment of spectral regions to PbO_3 and PbO_4 sites is not unique, especially since the ^{207}Pb isotropic shift and CSA are correlated in the ^{207}Pb MATPASS NMR spectra of these glasses (Figure 2). The simulation parameters in Table 1 indicate that the average δ_{iso} of the low-frequency component decreases from approximately −300 to −460 ppm and that of the high-frequency component decreases from approximately 350 to 250 ppm as the PbO content increases from 30 to 50 mol %. A further increase in the PbO content to 60 mol % shows a reversal in this trend with the average δ_{iso} of the low- and high-frequency components increasing to nearly −400 and

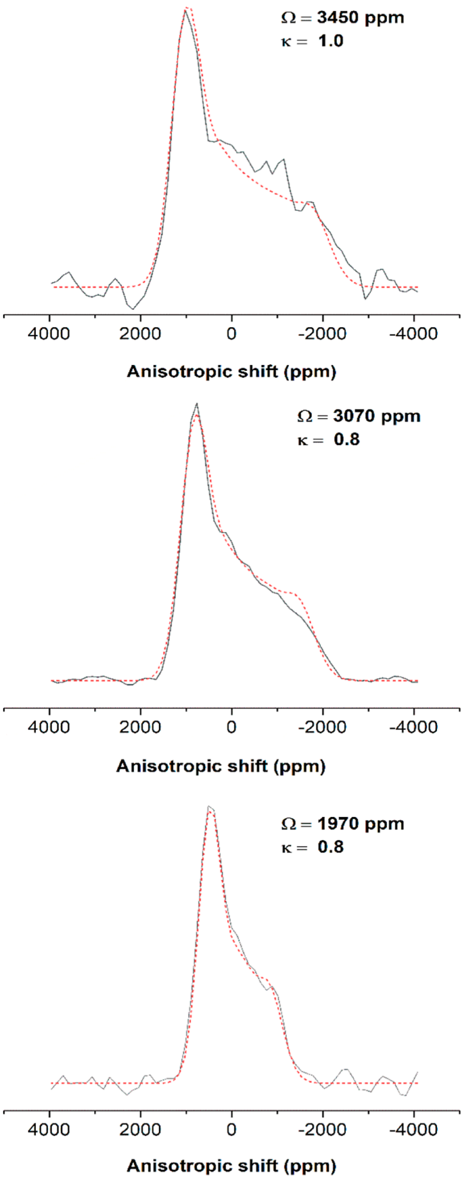

Figure 4. Anisotropic projections of ^{207}Pb MATPASS NMR spectrum of $(PbO)_{50}(SiO_2)_{50}$ glass at three δ_{iso} ranges (from top to bottom): (i) 800 ± 200, (ii) 0 ± 200, and (iii) −700 ± 200 ppm (solid black lines) and corresponding simulations (red dotted lines). The span Ω and skew κ for each simulated line shape are listed alongside the spectrum.

360 ppm, respectively. The glass with 70 mol % PbO shows a relatively sudden increase in the rate of this change, with the corresponding average δ_{iso} values reaching −160 and 530 ppm, respectively (Table 1). As noted above, we tentatively assigned these two sets of positive and negative ^{207}Pb δ_{iso} values in these glasses to PbO_3 and PbO_4 environments, respectively. Such an assignment is consistent with the ^{207}Pb δ_{iso} values reported in the literature for the PbO_3 (93 ± 5 ppm) and PbO_4 (−166 and −366 ± 5 ppm) pyramidal environments in crystalline $PbSiO_3$ and for the Pb(3) PbO_3 site (329 ± 5 ppm) in crystalline H−Pb_2SiO_4.[30] The Pb(3) PbO_3 site in H−Pb_2SiO_4 and the sole PbO_3 site in $PbSiO_3$ are both characterized by similar average Pb−O distances (0.238−0.239 nm).[38,39] However, the latter has two rather short Pb−O distances at 0.228−0.229 nm and a significantly longer Pb−O distance of 0.260 nm, while the former is characterized by three somewhat equidistant O atoms at 0.234, 0.234, and 0.247 nm, similar to those reported by Alderman et al.[10] on the basis of neutron diffraction results on binary Pb-silicate glasses. On the other hand, the sudden increase in the ^{207}Pb δ_{iso} of the PbO_3 environment in the Pb-silicate glass with 70 mol % PbO (Table 1) to 530 ppm may have a different origin. This value is similar to ^{207}Pb δ_{iso} of the Pb(1) PbO_3 site (634 ± 5 ppm) in H−Pb_2SiO_4, which is characterized by not only relatively short Pb−O bonds (0.218, 0.218, and 0.227 nm) but also by one Pb-FO-Pb linkage.[38] Therefore, we believe the significantly larger ^{207}Pb δ_{iso} of the PbO_3 site in the glass with 70 mol % PbO may arise from a shortening of the average Pb−O distance as well as from the appearance of some Pb-FO-Pb linkages in the structure. The

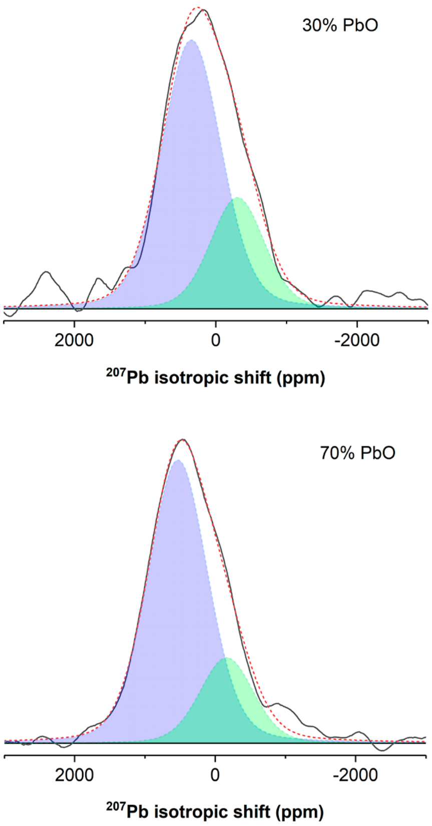

Figure 5. Representative simulations (red dotted line) of experimental ^{207}Pb isotropic NMR spectra (solid black line) of $(PbO)_x(SiO_2)_{100-x}$ glasses with x = 30 (top) and 70 (bottom) using Gaussian components (blue and green filled curves).

Table 1. Parameters Obtained from Simulation of ^{207}Pb Isotropic NMR Spectra of $(PbO)_x(SiO_2)_{100-x}$ Glasses Using Gaussian Components

mol % PbO	component	δ_{iso} (±20 ppm)	width (ppm)	relative area (±5%)
30	1	−305	900	30
	2	346	1000	70
40	1	−418	1000	25
	2	305	900	75
50	1	−460	1000	25
	2	244	900	75
60	1	−410	1000	22
	2	363	900	78
70	1	−163	900	20
	2	530	1000	80

former is corroborated by the neutron diffraction results reported by Alderman et al.[10] and the latter by ^{17}O NMR spectroscopic results reported by Lee and Kim,[19] which indicated the formation of FO species in appreciable quantity in Pb-silicate glasses as the Pb concentration increased to 65 mol % and beyond.

The simulations of the isotropic ^{207}Pb NMR spectra (Figure 5) indicate a monotonic decrease in the relative fraction of the low-frequency PbO_4 component from ∼30% to ∼20% (±5%) with increasing PbO content from 30 to 70 mol % (Table 1). The corresponding decrease in the average Pb−O coordination number in these glasses is rather small, from ∼3.3 to ∼3.2 (±0.05). This general trend is in approximate agreement with that reported in a previous study by Alderman et al. (Figure 6) based on diffraction measurements.[10] However, the EPSR modeling of the diffraction data of Alderman et al. suggested an increase in the Pb−O coordination number from 3.33 at 35 mol % PbO to 3.55 at 80 mol % PbO for a cutoff distance of 0.27 nm.[10] These authors attributed this result to the transformation of the glass structure at high PbO contents close to 80 mol % toward a layered structure of edge-sharing PbO_4 tetrahedra that is characteristic of crystalline α-PbO and β-PbO.[40,41] Supporting evidence of this hypothesis was provided by a comparison between these crystalline phases and a glass with 80% PbO of their ^{207}Pb δ_{iso} and CSA, as obtained from the static ^{207}Pb NMR spectra.

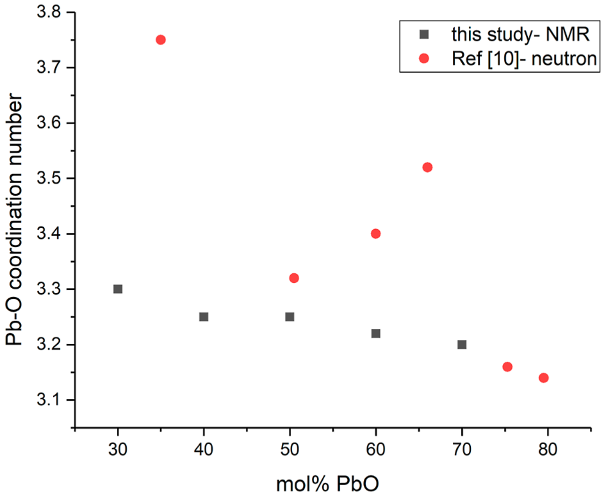

Figure 6. Compositional variation of average Pb−O coordination number of $(PbO)_x(SiO_2)_{100-x}$ glasses obtained in this study (black squares) from simulation of ^{207}Pb isotropic NMR spectra and those obtained from neutron RDF analysis reported in ref 10. The error in the NMR-derived average coordination number is on the order of ±0.05.

It may be noted here that the Pb(2) and Pb(4) PbO_3 sites in $H-Pb_2SiO_4$ are characterized by significantly larger values of ^{207}Pb δ_{iso} of 1344−1382 ppm.[30] Similarly, large ^{207}Pb δ_{iso} values were also reported in the literature for PbO_4 sites in α-PbO and β-PbO (1939 and 1515 ppm, respectively). Fayon et al.[30] have shown that such large ^{207}Pb δ_{iso} values are indicative of decreasing s-hybridization (increased covalent character) of the oxygen ligands, which increases the paramagnetic (positive) contribution to chemical shift. They related the s-hybridization parameter P in crystalline PbO and Pb-silicates to the average Pb−O-X (X = Pb, Si) angle θ and the number N of Si next-nearest neighbors connected to the Pb atom via Pb−O-X linkages as

$$P = [(\cos\theta)/(\cos\theta - 1)] + 0.2N \tag{6}$$

and P to ^{207}Pb δ_{iso} as

$$\delta_{iso} = 2076.2 - 2180.2P \tag{7}$$

The empirical correction factor $0.2N$ in eq 6 accounts for the difference between the electronegativities of Pb and Si, which affect the degree of s-hybridization in a Pb−O−Si asymmetric linkage. Moreover, since Pb−O−Si angles are significantly larger than Pb−O−Pb angles in crystalline Pb-silicates, the presence of Si also increases the average θ, and thus, the angular term in square brackets increases (for $90° \leq \theta \leq 180°$) in eq 6. Therefore, replacing Si with Pb in the second neighbor shell of a Pb atom would be expected to increase its ^{207}Pb δ_{iso} (see eq 7). The largest increase in δ_{iso} will be observed for Pb-FO-Pb linkages as the FO atoms are by definition not linked to any Si atoms, as is the case for PbO_4 sites in α-PbO and β-PbO and for Pb(2) and Pb(4) PbO_3 sites in $H-Pb_2SiO_4$.[39,40] These $Pb(FO)_n$ pyramids also share edges in these structures. It is clear from the isotropic ^{207}Pb NMR spectra obtained in this study (Figure 3) that all glasses with up to 70 mol % PbO display negligible intensity in the ^{207}Pb δ_{iso} region characteristic of such Pb sites, and therefore, these glasses do not contain any significant concentration of local structural moieties of edge-sharing $Pb(FO)_n$ pyramids.

3.2. Nature of Intermediate-Range Order. We focus the discussion on the intermediate range order in Pb-silicate glasses from the point of view of the connectivity between PbO_n and SiO_4 coordination polyhedra. The ^{207}Pb isotropic shift range clearly indicates that the mean Pb−O-X angles are in the range expected for the large majority of Pb−O bonds to be associated with Pb−O−Si linkages. The center of gravity of the ^{207}Pb isotropic line shape does not change significantly for glasses with 30 to 60 mol % PbO. A significant deshielding of the center of gravity is observed only as the PbO content increases to 70 mol %, which is consistent with the decrease in the relative fraction of Pb−O−Si linkages and the concomitant appearance of a fraction of oxygen atoms in Pb-FO-Pb linkages. These results are completely consistent with the ^{17}O NMR results of Lee and Kim,[19] which indicated that a significant fraction of FO ions form once the PbO concentration exceeds the 60 mol % mark, and about 20% of the oxygen atoms exist as FO in the glass with 70 mol % FO. The Pb-FO-Pb linkages are typically associated with edge-sharing of PbO_n pyramids in Pb-oxides including PbO and $H-Pb_2SiO_4$ (Pb(2) and Pb(4) sites), which, as discussed above, are characterized by relatively small Pb−O-X angles and consequently, by rather large positive ^{207}Pb δ_{iso} in the range of 1350−1950 ppm.[30] However, these ^{207}Pb δ_{iso} values are outside the range observed for Pb-silicate glasses in the present study. It is worth noting here that the ^{17}O NMR results of Lee and Kim also indicated that the quadrupolar coupling constant of the FO was rather different from that of edge-shared FOs between PbO_4 pyramidal units in α- and β-PbO.[19] Therefore, we argue on the basis of these results that the FOs in Pb-FO-Pb linkages are most likely corner-shared between multiple PbO_n pyramids in glasses with up to 70 mol % PbO. This structural scenario is somewhat similar to that proposed by Imaoka et al., which is characterized by screw chains of corner-shared PbO_n pyramids connected by isolated or partially polymerized silicate units.[13] On the other hand, our proposed model is in contradiction with that proposed by Takaishi et al.,[11] which invokes the formation of a network of predominantly edge-shared PbO_3 pyramids via Pb-FO-Pb linkages, forming Pb_2O_4 units in Pb silicate glasses with high (≥60 mol %) PbO contents. It may be noted that edge-sharing between PbO_4 pyramids forming zigzag chains was also suggested by Morikawa et al. for $2PbO\cdot SiO_2$ glass.[12] Such edge-sharing likely becomes unavoidable with a further increase in PbO content, which ultimately limits the bulk glass formation in the $PbO-SiO_2$ system.

3.3. Is Pb a Network-Forming Cation? The role of Pb in the silicate glass network has remained rather controversial. The relatively low coordination number with the sterically active lone pair, the strong electronegativity of Pb as well as the covalent nature of the Pb−O bonds, and the extremely wide composition range for glass formation have all been argued to be indicative of the role of Pb^{2+} as a network-forming cation in silicate glasses.[10,14] We argue that this exceptional glass-forming ability of PbO as an additive oxide to SiO_2 is possibly due to the formation of an open and highly interconnected network of PbO_n pyramids and SiO_4 tetrahedra. As has been suggested in the literature, the repulsion between sterically active lone pairs on adjacent Pb likely results in orientational ordering of the PbO_n pyramids in the structure that creates an open and stable network with much larger molar volume compared to those of silicate glasses with comparable silica content containing a modifier cation such as Sr, with similar charge and ionic radius as Pb.[10] The PbO_n and SiO_4 polyhedra can be geometrically/topologically similar and are characterized by strong covalent bonds and the amorphous network remains quite stable up to rather high PbO contents, even when Pb-FO-Pb linkages appear to form a relatively Pb-rich network with the structural moieties of corner-shared $Pb(FO)_n$ pyramids held together by silicate anions. However, we argue that even if Si is a minority species in these glasses, the presence of a small concentration of silicate anions is crucial to the stability of the network. In fact, previous ^{17}O NMR results have indicated that nearly 75% of the oxygen participates in Pb−O−Si linkages in a glass with ~70 mol % PbO.[19] The results presented in this study seem to indicate that the network at this point does not contain any edge-sharing PbO_n pyramids that are characteristic of PbO phases. We hypothesize that the network likely becomes unstable at a point where the PbO concentration becomes high enough that Pb-FO-Pb linkages start to participate in edge-sharing. Therefore, in spite of its unique chemical nature, the role of Pb^{2+} has some strong similarity with that of a network modifying cation in the sense that the addition of PbO to SiO_2 creates NBO on Si atoms that results in a monotonic decrease in the glass transition temperature T_g (Figure 1) and viscosity at a constant rate with increasing PbO content over the entire range of glass formation.[8] The appearance of Pb-FO-Pb linkages in the network at high PbO contents cannot reverse this trend or even slow it down, which is again consistent with its network-modifying character. Nevertheless, one must note that the glass-forming region in the binary $PbO-SiO_2$ system does extend to unusually low SiO_2 contents (~15−20 mol %), at which point large fragments of the structural network must be built exclusively by PbO_n pyramids.[16] Moreover, in binary silicate systems with typical network modifiers, the FO species is expected to appear only for highly modified compositions with $O/Si > 4$, while previous ^{17}O NMR studies[19] have conclusively shown the appearance of FO in Pb-silicate glasses at a significantly lower level of $O/Si \sim 3.5$ (60 mol % PbO). Therefore, we argue that PbO can justifiably be considered as a conditional network-former in oxide glasses.

4. CONCLUSIONS

In summary, 2D ^{207}Pb MATPASS isotropic−anisotropic correlation NMR spectroscopy provides unique and detailed information regarding the coordination environments of Pb atoms in Pb-silicate glasses. The ^{207}Pb δ_{iso} values, in combination with the large Ω varying between ~2000 and 3000 ppm and κ of ~1.0, enable the identification of PbO_3 and PbO_4 pyramidal coordination environments with sterically active lone pairs in Pb-silicate glasses. The relative fraction of these two environments shows rather small change with composition as the PbO content varies between 30 and 70 mol %, with nearly 70 to 80% of the Pb atoms being present as PbO_3 trigonal pyramids. The PbO_n $(3 \leq n \leq 4)$ pyramids are connected to the SiO_4 tetrahedra via Pb-NBO-Si linkages to form an open network. The network weakens with the progressive addition of PbO as the strong Si-BO-Si linkages are replaced by the weaker Pb-NBO-Si linkages. The Pb-FO-Pb linkages appear in the network once the PbO concentration exceeds 60 mol %, where the FO are corner-shared between the PbO_n pyramids. However, the formation of these Pb-rich regions in the network does not impart any additional stability against thermal degradation, as T_g continues to decrease with increasing PbO content. When taken together, these results suggest that PbO behaves as a conditional network-former in silicate glasses.

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Notes

The authors declare no competing financial interest.

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