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## Structure and Properties of Lead Silicate Glasses

Daniel Caurant<sup>(1)</sup>, Gilles Wallez<sup>(1)</sup>, Odile Majérus<sup>(1)</sup>,

Gauthier Roisine<sup>(2)</sup>, Thibault Charpentier<sup>(3)</sup>

<sup>(1)</sup> *Chimie ParisTech, Université PSL, CNRS, Institut de Recherche de Chimie Paris (IRCP),*

*UMR 8247, 11 rue P. et M. Curie, 75005 Paris, France*

<sup>(2)</sup> *BUCT-Paris Curie Engineering School, Beijing, China*

<sup>(3)</sup> *NIMBE, CNRS, CEA, Université Paris-Saclay, Gif-sur-Yvette, France*

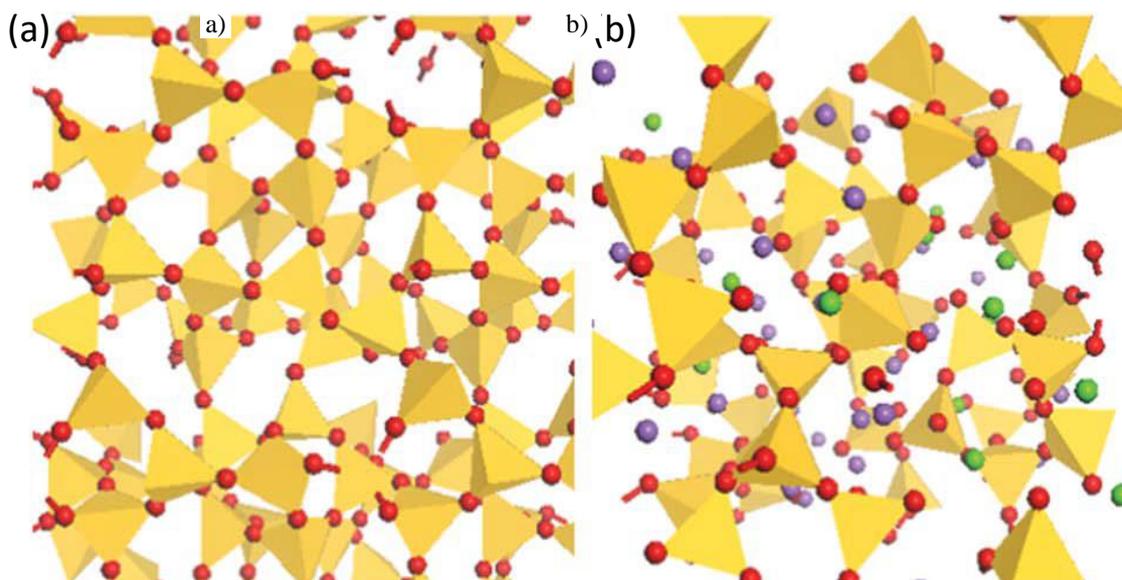
### 3.1. Introduction

As already noted in chapter 1, given their specific properties, glasses containing lead oxide have a very broad field of application. This extends from crystal glasses, enamels and glazes, to optical glasses with high refractive index, passing through glasses absorbing ionizing radiation and glasses for low-temperature welding of metals, ceramics or glasses (Frieser 1975; Rabinovich 1976; Takamori 1979; Volf 1984). For these various applications, glass composition must certainly be adapted in terms of its elaboration and forming (viscosity, expansion coefficient, glass transition temperature  $T_g$ ) as well as in terms of its properties under the conditions of use (refractive index, transparency, color, chemical durability, electrical resistivity, etc.). These various properties, which concern both the liquid during its melting, forming and cooling (quenching), and the final glass, i.e. the amorphous solid resulting from the quenching of the supercooled liquid below  $T_g$ , are closely related to its structure. In the case of oxide glasses that are of interest here, this corresponds to the way in which the polyhedrons associated with the various present cationic species surrounded by oxygen  $O^{2-}$  anions are arranged with respect to one another inside the network that constitutes the glass structure. Unlike crystals, this network has no long-range order (figure 3.1). In the case of glasses containing lead, it is therefore particularly important to understand the way in which  $Pb^{2+}$  ions are inserted in the structure of this network depending on the lead oxide content and on the glass composition (nature of the forming oxide ( $SiO_2$ ,  $B_2O_3$ ,  $P_2O_5$ ), effect of the presence of modifier oxides (alkaline and alkaline-earth oxides) and intermediate oxides ( $Al_2O_3$ ))<sup>1</sup> and to evaluate

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1. A glass former oxide can be defined as an oxide that only by melting + more or less rapid cooling (quenching) readily yields a glass particularly due to the high viscosity of the corresponding liquid in the vicinity of the melting temperature  $T_f$  and in its supercooled state ( $T < T_f$ ). A glass can be defined as a solid that has no long-range order ( $\geq 10\text{\AA}$ ) at the level of its atomic organization (unlike crystallized materials) but has a glass transition temperature  $T_g$  (range of temperature for which the liquid solidifies when cooled and the glass tends to soften when heated). A glass can be considered a supercooled liquid that freezes during quenching. Compared to crystallized materials, glasses have therefore an excess of free energy and are in a nonequilibrium state from the perspective of thermodynamics (when heated above  $T_g$  they tend to crystallize). The main glass former oxides are  $SiO_2$ ,  $B_2O_3$ ,  $P_2O_5$  and  $GeO_2$  which readily lead to glasses and whose structure is a random continuous network of tetrahedrons ( $SiO_4$ ,  $PO_4$ ,  $GeO_4$ ) or triangles ( $BO_3$ ) connected only by the vertices (small surplus of free energy

their impact on the structure of this network, and also on the environment, and the distribution of specific species that may be present, such as transition metal ions used for coloration (see chapter 4).



**Figure 3.1.** Examples of three-dimensional representation of pure silica glass (a) and of a soda-lime silica glass (b) showing the  $\text{SiO}_4$  tetrahedrons (in yellow), the bridging and non-bridging oxygen atoms (in red), and the modifier ions  $\text{Na}^+$  (in purple) and  $\text{Ca}^{2+}$  (in green). Reproduced from (Charpentier et al. 2013) with the permission of The Royal Society of Chemistry.

COMMENT RELATED TO FIGURE 3.1.— Representation a) of the pure silica glass showing the  $\text{SiO}_4$  tetrahedrons all interconnected by bridging oxygen atoms and b) of a soda-lime silica glass ( $\text{SiO}_2\text{-Na}_2\text{O-CaO}$ ) showing the breaking of the silicate network with the formation of non-bridging oxygen atoms connected to a single  $\text{SiO}_4$  tetrahedron. The modifier ions  $\text{Na}^+$  and  $\text{Ca}^{2+}$  compensate the negative charge of the non-bridging oxygen atoms.

This chapter focuses first of all on the chemistry of lead, and more specifically on the properties and stereochemistry of the  $\text{Pb}^{2+}$  ion (species under which lead is present in oxide glasses), the nature of the Pb-O chemical bond and the crystalline structure of pure PbO oxide (stereochemistry and mode of connection of the polyhedrons). Then, since the lead-based oxide glasses of interest are overwhelmingly silicate glasses, the focus is on how the  $\text{Pb}^{2+}$  ions get inserted in the glassy network of silica and modify its structure, first of all in the case of the simple binary  $\text{SiO}_2\text{-PbO}$  system (for which the evolution of the structure of the binary crystalline phases will also be approached depending on their PbO content compared to glasses), then in the case of more complex systems such as the ternary  $\text{SiO}_2\text{-PbO-R}_2\text{O}$  (R: alkaline) and  $\text{SiO}_2\text{-PbO-Al}_2\text{O}_3$  systems. The effect of these structural evolutions on certain properties of the glass or liquid will also be discussed, with the exception of optical properties (transmission, coloration) that are presented in chapter 4.

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compared to the crystallized ordered state), by means of directional bonds of ionic-covalent type (Zachariasen model (Zachariasen 1932)) (figure 3.1a). As for a glass modifier oxide, it can be defined as an oxide that by itself it never leads to a glass by (even extremely rapid) melting + quenching of the melting liquid, particularly due to the very low viscosity of the liquid and to the structural organization of polyhedrons with respect to one another which is difficult to maintain in a disordered state (excess of free energy between the disordered and ordered state much larger than for the glass former oxides). Higher or lower quantities of modifier oxides (particularly alkaline and alkaline-earth oxides) are however added to glass former oxides in the glasses to facilitate the melting of the mixture (role of fluxing agent), fining of the liquid (elimination of microbubbles and homogenization) and forming of objects (role of fluidizing agent), and also to act on the properties of the final glass. At the structural level, modifier oxides (present in the form of cations) by means of non-directional ionic bonds play the role of compensator in the vicinity of negative charges present in the structure, such as those resulting from breaking the ionic-covalent bonds such as Si-O-Si bonds (formation of non-bridging oxygen atoms, Si-O<sup>-</sup>) (figure 3.1b) or those due to the presence of negatively charged species, such as  $\text{AlO}_4^-$  or  $\text{BO}_4^-$ . Like modifier oxides, intermediate oxides – such as  $\text{Al}_2\text{O}_3$  – never lead by themselves to glasses by melting + quenching, but at structural level they generally play a different role from that of modifiers and can enter the structure of the glass formers network. It is important to note however that in the absence of glass former oxide and in the presence of one or several modifier oxides, intermediate oxides can also lead in certain cases to glasses, as it is the case of aluminate glasses (Pye 1988).

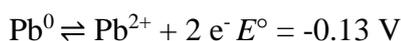
## 3.2. Lead and lead oxides

This section focuses on the key elements facilitating the comprehension of lead chemistry in both crystallized and glassy oxides, with a particular highlight of the importance and consequences (physical and structural properties) of the existence of the free  $6s^2$  electron pair of the  $Pb^{2+}$  ion.

### 3.2.1. Elementary lead and its specific properties

#### 3.2.1.1. Lead oxidation states and $Pb^{2+}$ ion

Lead (atomic number 82) is the heaviest stable element of column 14 of the periodic table. Due to its electron configuration ( $[Xe] 4f^{14} 5d^{10} 6s^2 6p^2$ ), it has three common oxidation states:  $Pb^0$ ,  $Pb^{2+}$  and  $Pb^{4+}$  whose stability domains can be evaluated by the standard potentials of the ionization reactions in aqueous solution:



According to these two equations, bivalent lead is therefore stable within a large potential range, which includes particularly that of the  $O_2/O^{2-}$  pair (1.12 V). It is present in this oxidation state in the vast majority of lead-bearing minerals such as litharge, massicot ( $PbO$ ) and galena ( $PbS$ ) which is the main ore, as well as in various carbonates, silicates, phosphates or sulfates and in oxide glasses (silicates, borates). Tetravalent lead, much rarer, can be found in minium ( $Pb_3O_4$ , or  $Pb^{IV} Pb^{II}_2 O_4$ ) and plattnerite ( $PbO_2$ ), especially known as the material of the positive electrode of lead-acid batteries. Even rarer is metallic (or native) lead. It is therefore logical that following the example of nature, the arts of fire practiced under an oxidizing potential close to that of the atmosphere can be used for the elaboration of solids containing exclusively  $Pb^{2+}$  ions, as in the case of oxide-based glasses.

With a coordination number of 8,  $Pb^{2+}$  ion has a radius of 1.43 Å, comparable to that of strontium  $Sr^{2+}$  (1.40 Å) (Shannon 1976). Similar to the heavy alkaline-earth ions  $Ca^{2+}$ ,  $Sr^{2+}$  and  $Ba^{2+}$  – large and lightly charged –, its oxides have a basic behavior that renders them reactive in relation with acidic oxides ( $B_2O_3$ ,  $CO_2$ ,  $SiO_2$ ,  $P_2O_5$ ,  $SO_3$ , etc.) or amphoteric oxides ( $H_2O$ ,  $Al_2O_3$ ,  $Fe_2O_3$ , etc.) and leads to the formation of many mixed oxides. Lead oxide-based glasses, though they have no defined compositions, are part of this context. However, the outer electron configuration of  $Pb^{2+}$  ion ( $[Xe] 4f^{14} 5d^{10} 6s^2$ ) is radically different from the saturated one of the ions of the 2<sup>nd</sup> column (alkaline-earth). It can be graphically represented as a sphere comprising  $4f$  and  $5d$  orbitals and whose radius corresponds to the one of  $Pb^{4+}$  ion (1.08 Å) (Shannon 1976), the external residual volume (nearly 60 %) being filled by the single  $6s^2$  pair. Strongly screened by the inner orbitals, these two  $6s$  electrons are both labile and very sensitive to the local electric field.

#### 3.2.1.2. Polarizability of $Pb^{2+}$ ion

Polarizability ( $\alpha$ ), which measures the capacity of a particle to polarize under the action of an electric field  $E$  ( $P = \alpha \cdot E$ ,  $P$  being the induced polarization), is generally proportional to the volume, for same charge ions belonging to a same column. As shown in figure 3.2, this relation is strictly followed in the alkaline-earth series, but the  $Pb^{2+}$  ion stands out very clearly due to the contribution of the  $6s^2$  pair. This high polarizability proves to be a key parameter of the physical, chemical and structural properties of the  $Pb^{2+}$  ion, and more generally of the ions of elements of block  $p$  having an  $ns^2np^0$  outer electron configuration, such as  $Tl^+$ ,  $Bi^{3+}$  and  $Te^{4+}$ , isoelectronic with  $Pb^{2+}$ .

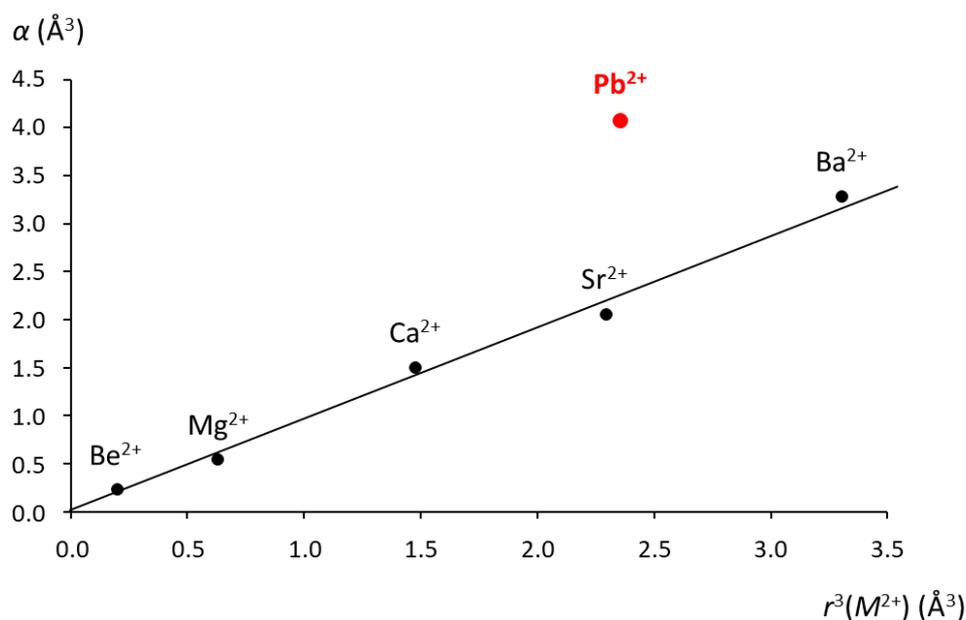
Polarizability determines particularly the relative permittivity  $\epsilon_r$  as shown by the Clausius-Mosotti relation:

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{N\alpha}{3\epsilon_0}$$

which yields:

$$\epsilon_r = \frac{3\epsilon_0 + 2N\alpha}{3\epsilon_0 - N\alpha}$$

$N$  being the number of particles per unit volume and  $\epsilon_0$  the vacuum permittivity.



**Figure 3.2.** Representation of polarizability  $\alpha$  of  $Pb^{2+}$  ion and of alkaline-earth ions (Shannon and Fischer 2016) as a function of the cube of radius with a coordination number of 6

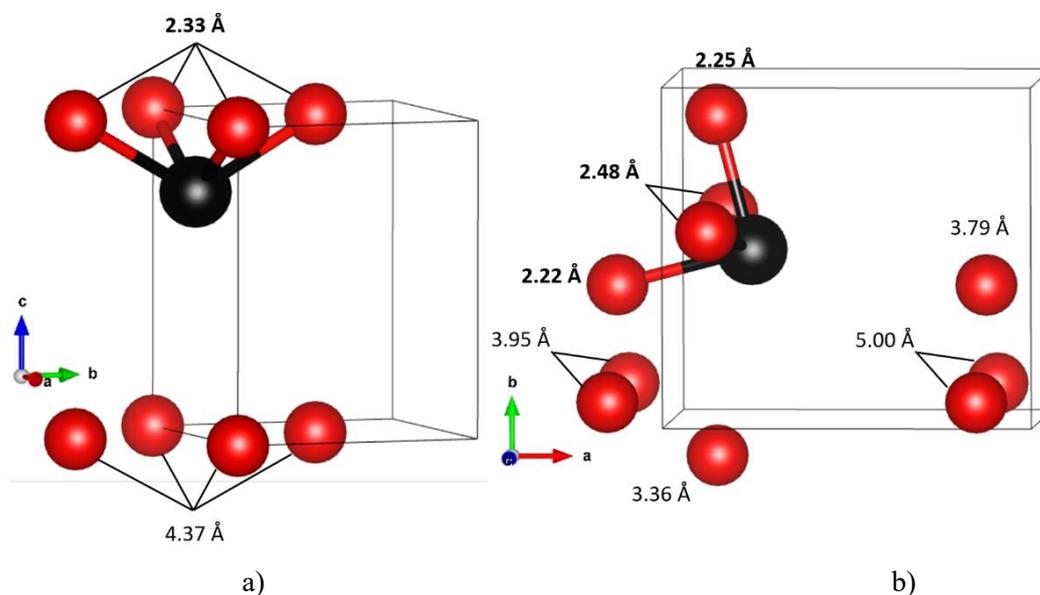
One of the main technological applications of lead oxide-based ceramics is logically found in the industry of dielectric, piezoelectric, pyroelectric and ferroelectric components, whose properties are directly linked to polarizability and where  $Pb^{2+}$  has gradually replaced  $Ba^{2+}$  in their composition. In the range of optical frequencies, polarizability is expressed through the refractive index  $n$  ( $= \sqrt{\epsilon_r}$ ). The predominantly positive effect of lead II can be illustrated by the series of crystal compounds  $M^{II}CO_3$  with aragonite (orthorhombic, biaxial) structure, whose average refractive index, quasi-identical (1.62) for  $M = Ca, Sr$  and  $Ba$ , reaches 1.98 for cerussite  $PbCO_3$ . The shine and covering power of a pulverulent material being directly related to its refractive index, it can be readily understood why white lead (mixture of cerussite and hydrocerussite  $Pb_3(CO_3)_2(OH)_2$ ) has been considered through the ages as top white pigment (Welcomme *et al.* 2007; Stols-Witlox 2011). Likewise, a specific effect of the introduction of lead in the composition of glasses and glazes is to increase the refractive index (chapter 1, figure 1.3).

### 3.2.2. Lead stereochemistry in oxides

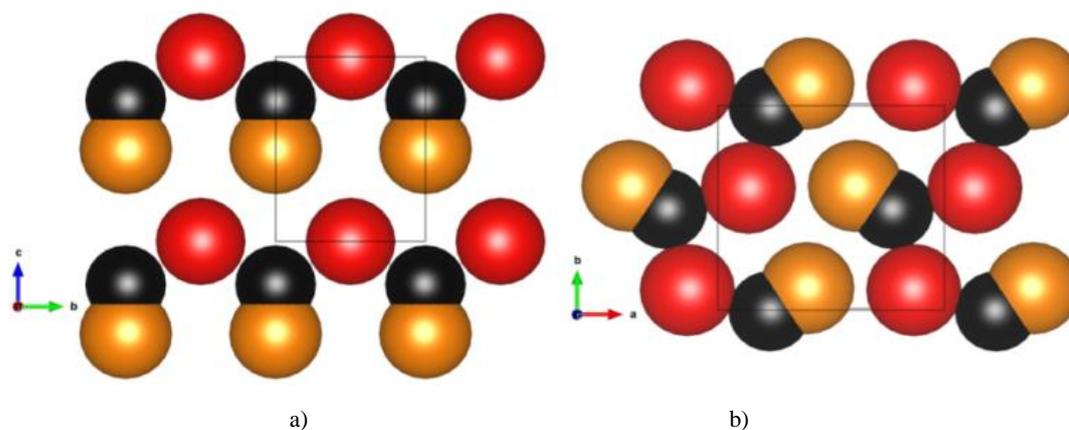
The Valence Shell Electron Pair Repulsion theory (VSEPR) is particularly helpful in understanding the distortions induced by non-bonding doublets of light elements of  $p$  block and explaining the geometry of distorted molecules such as water and ammonia. A similar phenomenon can be observed in coordination complexes and crystalline structures containing heavy ions with the  $ns^2np^0$  configuration, whose two common crystal arrangements of  $PbO$  (litharge and massicot) are typical examples.

In litharge (tetragonal symmetry,  $P4/nmm$ ,  $a = 4.004$  Å and  $c = 5.071$  Å), stable phase at ambient temperature,  $Pb^{2+}$  ion is surrounded by eight  $O^{2-}$  anions like in a  $CsCl$  structure. But here, instead of a cube, the polyhedron is shaped as a very elongated parallelepiped with a square base, in which lead occupies a highly off-centered position (figure 3.3).  $Pb-O$  distances, extremely disparate ( $4 \times 2.33$  Å

and  $4 \times 4.37 \text{ \AA}$ ), reflect an imbalance in the distribution of bonding forces (Brown and Altermatt 1985), 99 % of which are directed towards the closest four anions. Therefore, the actual coordination number is here only 4, with a hemispherical distribution (known as “umbrella”) specific to cations with  $ns^2np^0$  configuration, lead thus occupying the apex of a square-based pyramid. Short bonds have here the same length as a  $\text{Pb}^{4+}\text{-O}^{2-}$  bond ( $2.33 \text{ \AA}$ ), which shows that the four close oxygen atoms are in contact with the sphere formed by the  $4f$  and  $5d$  orbitals of lead. In massicot (figure 3.3), a  $\text{PbO}$  form that is stable above  $490 \text{ }^\circ\text{C}$ , metastable at ambient temperature, the hemispherical coordination number of lead is 4, though less regular due to the orthorhombic symmetry ( $Pbcm$ ,  $a = 5.893 \text{ \AA}$ ,  $b = 5.490 \text{ \AA}$  and  $c = 4.753 \text{ \AA}$ ).



**Figure 3.3.** Oxygenated environment of the  $\text{Pb}^{2+}$  ion and  $\text{Pb-O}$  distances in two varieties of  $\text{PbO}$ : litharge (a) and massicot (b).  $\text{Pb}$  (in black) and  $\text{O}$  (in red)

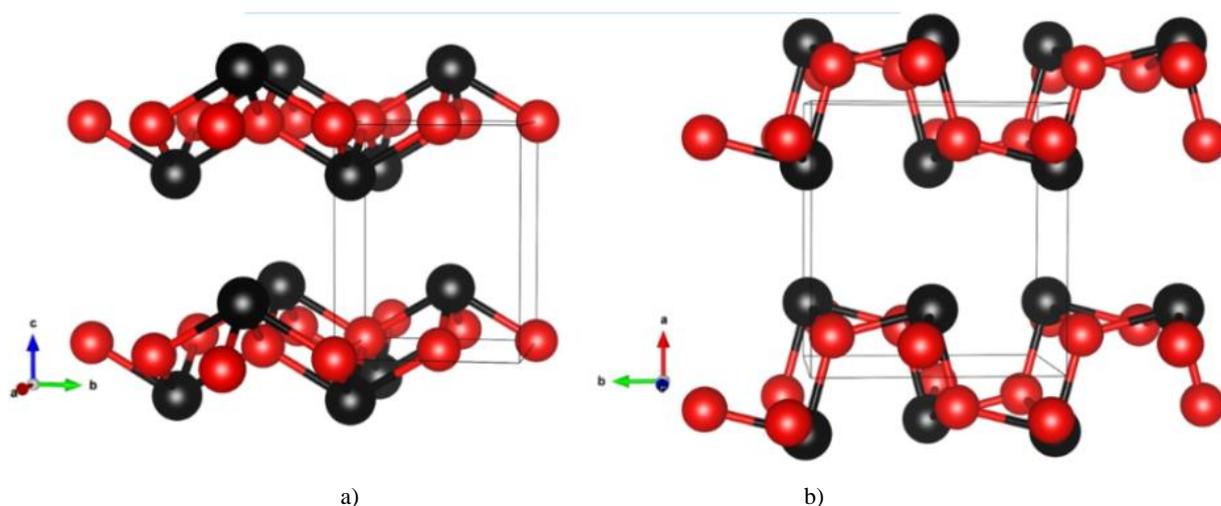


**Figure 3.4.** Representation in actual proportions of lead ions (in black) and of the  $6s^2$  pair (in orange) in the atomic planes of litharge (a) and massicot (b). It is worth noticing the quasi-hexagonal structure built by the  $\text{O}^{2-}$  anions (in red) and the  $6s^2$  pairs.

In both cases, the  $6s^2$  pair is repelled to the opposite of short bonds due to the high polarizability of  $\text{Pb}^{2+}$  ion, in the apparently unoccupied part of the oxygen polyhedron (“apparently” because these two electrons, which are a far less charged and coherent source of scattering than the 78 electrons of the lead core orbitals grouped in a small volume, are difficult to observe by X-ray diffraction, and even more difficult by neutron diffraction, for which only the nuclei are “visible”). From an electrostatic perspective, the  $6s^2$  pair however plays an essential role, like that of a nonbonding pair in VSEPR, as its negative charge strongly repels the anions on the opposite side of strong bonds, hence the strong increase in  $\text{Pb-O}$  distance ( $4.37 \text{ \AA}$ ) on this side of the polyhedron (figure 3.3). The dipole moment of  $\text{Pb}^{2+}$  ion thus influences the geometry of its environment. The representation of ions in actual proportions in the two  $\text{PbO}$  varieties

(figure 3.4) shows that it is off-centered by approximately 1 Å with respect to the nucleus and that it occupies roughly the same volume as an anion. Its presence in the apparently empty volumes of the structures makes it actually possible, with oxygen anions, to obtain pseudo-hexagonal layouts close to the ideal packing density contributing to the stability of these oxides.

Let us now focus on how the  $\text{PbO}_4$  polyhedrons are connected in the two crystal varieties of  $\text{PbO}$ . In the case of litharge, these polyhedrons are interconnected by the edges and arranged head-to-tail to minimize the electron repulsions between non-bonding doublets of the lead atoms (figure 3.5). In massicot, the pyramids are interconnected by the edges, and once more the arrangement makes it possible to minimize the electron repulsions between non-bonding doublets of  $\text{Pb}^{2+}$  ions. Litharge is the most stable form, as it is stabilized by the interactions between non-bonding doublets, with an antiparallel orientation between near-neighbors of the same plane (001). This orientation is partly lost in massicot due to the distortion of polyhedrons, which leads globally to the weakening of this interaction at the crystal scale; massicot is therefore less stable.



**Figure 3.5.** Crystal structures of two  $\text{PbO}$  polymorphs: litharge (a) and massicot (b).  $\text{Pb}$  (in black) and  $\text{O}$  (in red)

The origin of the shift of  $6s$  orbital – normally spherical and nucleus-centered – in ions with  $ns^2np^0$  configuration was the subject of many experimental and theoretical works following those of Gillespie and Nyholm in the 1950s (Gillespie and Nyholm 1957). The widespread model is that of a simple hybridization of  $6s$  and  $6p$  orbitals of  $\text{Pb}^{2+}$  allowing the doublet to take the shape of a protuberant lobe; however recent studies tend to prove the involvement of  $2p$  levels of neighboring  $\text{O}^{2-}$  anions (Watson *et al.* 1999; Waghmare *et al.* 2003). Whatever the mechanism, the structural distortion of a crystalline solid by a stereochemical effect of “free pair” ultimately follows a simple law: minimizing the network energy. In litharge for example, the shift of the  $6s^2$  pair “vacates” the opposite  $4f$  and  $5d$  orbitals, allowing the formation of four short  $\text{Pb}^{4+}\text{-O}^{2-}$  bonds, which are highly covalent and directional, globally more stable than the eight bonds with high ionicity rate that would form in a symmetric structure of  $\text{CsCl}$  type. Adding that its electronegativity (1.87 on Pauling scale) is significantly higher than that of alkaline and alkaline-earth elements ( $\chi_{\text{Na}} = 0.93$ ;  $\chi_{\text{K}} = 0.82$ ;  $\chi_{\text{Mg}} = 1.31$ ;  $\chi_{\text{Ca}} = 1.00$ ), it is clear that the structural role of lead in glasses is much closer to that of glass former or intermediate elements ( $\chi_{\text{Si}} = 1.9$ ;  $\chi_{\text{Al}} = 1.61$ ), although closer to the former due to its size. As it will be noted further on in this chapter (section 3.3.3), in oxide glasses such as silicates, the free pair of  $\text{Pb}^{2+}$  ions contributes also to their incorporation in the form of polyhedrons of low coordination number (3 or 4) with the oxygen anions anisotropically distributed around lead (Fayon *et al.* 1999; Rybicki *et al.* 2001; Alderman *et al.* 2013).

The same energy contingency is however applicable sometimes to the stereochemical activity, when a stable structural form adapted to the composition makes it possible to host the cation in a steady environment. The already mentioned series of  $\text{MCO}_3$  carbonates with aragonite structure offers an example. Metastable for  $\text{Ca}^{2+}$  that more often crystallizes as calcite, it is in fact perfectly adapted to larger

cations, such as  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$  for which it is the stable form. However, the structure of cerussite  $\text{PbCO}_3$  (Chevrier *et al.* 1992) is quasi-identical with that of  $\text{SrCO}_3$  (Pannhorst and Lohn 1970), with an environment of  $\text{Pb}^{2+}$  whose regularity ( $2.65 < \text{Pb-O} < 2.76 \text{ \AA}$ ) proves the absence of stereochemical activity of the  $6s^2$  pair. However, the absence of permanent polarization of  $\text{Pb}^{2+}$  ion does not impede the previously mentioned strong polarizability. Moreover, it is important to note that the stereochemical activity of the free pair of  $\text{Pb}^{2+}$  ion depends also on the nature of neighboring anions. Hence, unlike in  $\text{PbO}$ , the free pair of  $\text{Pb}^{2+}$  ions is stereochemically inactive in  $\text{PbS}$  due to the anion-cation orbital interactions that differ for the two phases (Walsh and Watson 2005). The stereochemical activity of the  $6s^2$  pair is therefore not systematic in the crystal structures containing lead II, but it is however frequent (it is the case of crystallized lead silicates, as it will be seen in section 3.2), though sometimes less marked than in the two varieties of  $\text{PbO}$ .  $\text{Pb}^{2+}$  has for this reason an intermediate behavior between those of its isoelectronic neighbors, the stereochemical activity being rarer and less marked for  $\text{Tl}^+$  and quasi-systematic and strong for  $\text{Bi}^{3+}$ , undoubtedly for reasons of size and charge.

In the biological domain, the effect of the free pair widely contributes to lead toxicity, as it replaces cations that are essential to the metabolic functioning, such as  $\text{Ca}^{2+}$ ,  $\text{Zn}^{2+}$  or  $\text{Fe}^{2+}$  inside the structures of enzymes and complexes. This substitution is on the one hand easy and almost irreversible, as the stereochemical activity of the  $6s^2$  pair allows the formation of strong bonds with the ligands, and on the other hand it is harmful, as it modifies the symmetry to the point of disrupting the functioning (Gourlaouen and Parisel 2007), which renders lead ingestion particularly toxic (lead poisoning, chapters 13 and 14) (Patrick 2006).

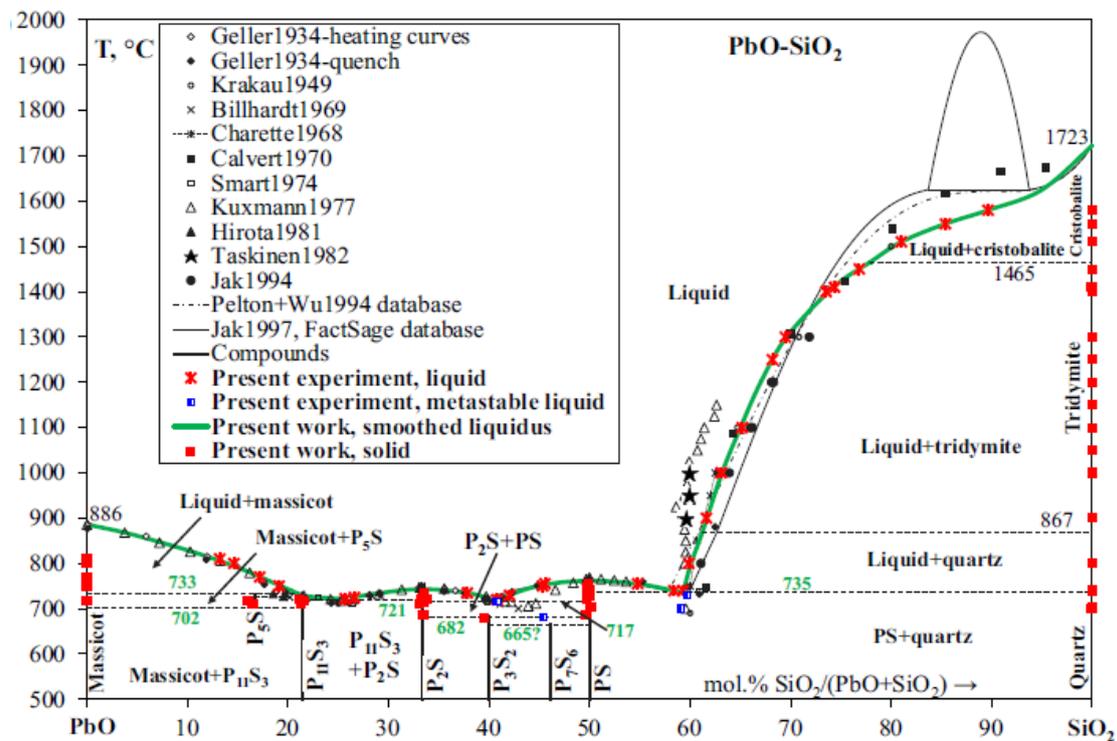
### 3.3. Crystal phases and glasses of the $\text{SiO}_2$ - $\text{PbO}$ system

In lead oxide-based silicate glasses used both in the industry and in the crafts and art (massive glasses, glazes, enamels),  $\text{SiO}_2$  and  $\text{PbO}$  are the majority of oxides forming the glass structure. Hence in the crystal glass, the sum  $\text{SiO}_2 + \text{PbO}$  is generally about 85 % of its mass (the rest being mainly alkaline oxides  $\text{K}_2\text{O}$  and  $\text{Na}_2\text{O}$ ) while in transparent lead glazes deposited on the surface of ceramics, this sum commonly reaches over 90 % in mass (the rest being then mainly constituted of alumina most of the time (Tite *et al.* 1998) (chapter 10). Though the binary glasses of the  $\text{SiO}_2$ - $\text{PbO}$  system have actually no practical use as there is almost always an addition to their composition of other glass former, modifier or intermediate oxides (boron oxide, alkaline oxides, alumina, etc.) depending on the considered applications (Rabinovich 1976), it appears particularly important to properly understand the structure of these simple glasses depending on their  $\text{PbO}$  content and especially the manner in which the  $\text{Pb}^{2+}$  ion is inserted in the structure of the silicate glassy network for both low and highest  $\text{PbO}$  contents, if the objective is to apprehend the structure of more complex lead silicate glasses. This explains the rich literature related to the structural study of glasses of the  $\text{SiO}_2$ - $\text{PbO}$  system published for nearly 85 years (Bair 1936)! Despite the increasingly advanced and various methods of investigation and simulation implemented in order to explore the environment of lead, silicon and oxygen in these simple glasses, there are still many questions related to the way the  $\text{Pb}^{2+}$  ions are incorporated in these glasses and particularly for the highest  $\text{PbO}$  contents, as it will be seen here. But before focusing on the glassy system (the supercooled liquid frozen during quenching, which is in a nonequilibrium state), let us first examine the binary system at thermodynamic equilibrium depending on temperature and its composition, and also on the structure of mixed crystal phases existing in this system and more specifically on the manner in which the  $\text{Pb}^{2+}$  ions are incorporated in their crystal network.

#### 3.3.1. The binary $\text{SiO}_2$ - $\text{PbO}$ system at equilibrium

Given the importance of this system, phase diagrams were proposed for the binary  $\text{SiO}_2$ - $\text{PbO}$  system since the 1930s (Geller *et al.* 1934), which were subsequently completed and refined using new experimental results and calculations. To our knowledge, the most recent one belongs to Shevchenko and Jak (Shevchenko and Jak 2018), combining calculations and experimental results (figure 3.6).

As indicated in chapter 1, this diagram shows the very clear fluxing effect of PbO when added to SiO<sub>2</sub> (strong decrease of the green curve corresponding to the liquidus of the system). However, it can be noted that for PbO contents ranging between 40 and 80 mol%, the liquidus temperature ( $T_{\text{liquidus}}$ ) does not change much and ranges between 730 and 750 °C, but it has a small increase when getting close to the pure PbO phase (massicot,  $T_{\text{melting}} = 886$  °C).



**Figure 3.6.** Phase diagram of the PbO-SiO<sub>2</sub> system (mol%) above 500 °C (Shevchenko and Jak 2018).  
*Massicot: PbO phase stable at high temperature, for mixed crystal phases: P = PbO and S = SiO<sub>2</sub>*

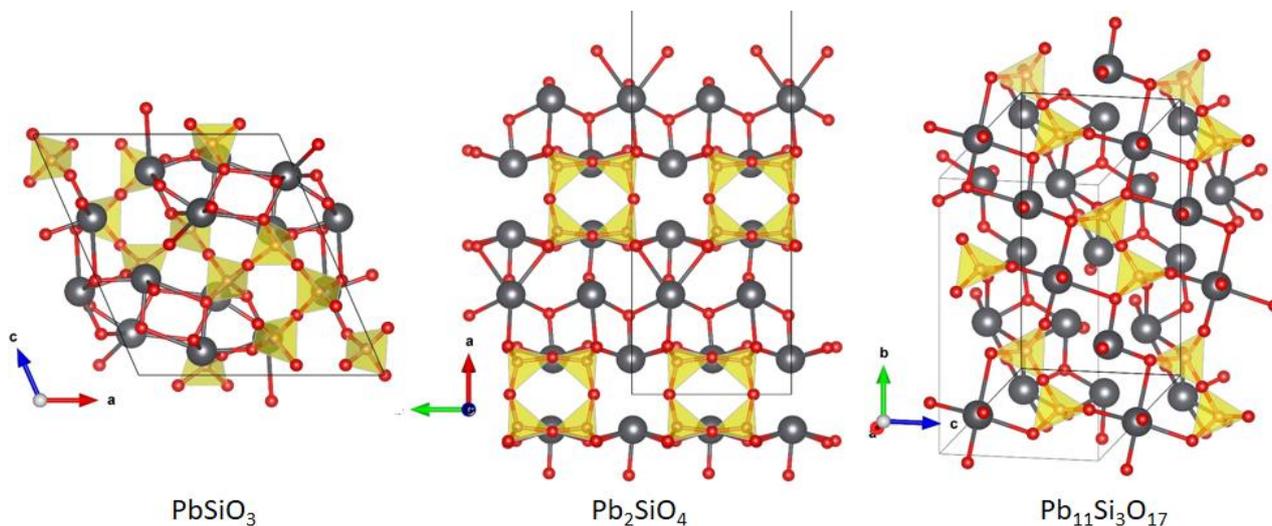
COMMENT ON FIGURE 3.6.– Diagram combining several experimental and calculated results from sources in the literature with recent experimental results (red and blue dots correspond to compositions and temperatures explored by the authors of the study and the green liquidus curve is a smoothing result achieved in this same study). This diagram also contains in full line the phase diagram calculated by the same team in a previous study (Jak et al. 1997).

As long as the PbO content is below 50 mol%, the only stable crystal phases susceptible to form inside the system are the various crystal varieties of silica (cristobalite, tridymite, quartz) and lead metasilicate PbSiO<sub>3</sub> (alamosite) with congruent melting. Therefore, there is no stable mixed crystal phase with less than 50 mol% of PbO. It is important to note that contrary to the predictions of the calculations of Jak *et al.* (Jak *et al.* 1997) (black curve, figure 3.6), the experimental curve of liquidus exhibits no stable demixing dome indicating the existence of phase separation phenomena inside the liquid ( $T > T_{\text{liquidus}}$ ). However, the specific S-shape of the liquidus curve (green curve, figure 3.6) suggests that a metastable demixing may occur in the supercooled liquid ( $T < T_{\text{liquidus}}$ ) (Calvert and Shaw 1970) as in the SiO<sub>2</sub>-BaO system (Seward *et al.* 1968). The diagram shows that several mixed crystal phases may form in this system besides PbSiO<sub>3</sub> for PbO contents above 50 mol%:

- at high temperature, near the liquidus curve: Pb<sub>2</sub>SiO<sub>4</sub> (lead cyclosilicate, with congruent melting), Pb<sub>11</sub>Si<sub>3</sub>O<sub>17</sub> (with congruent melting) and Pb<sub>5</sub>SiO<sub>7</sub> (with incongruent melting). The Pb<sub>4</sub>SiO<sub>6</sub> phase shown in older phase diagrams (Smart and Gasser 1974) would not be stable (Hirota and Hasegawa 1981);
- at lower temperature, in the solidus domain: Pb<sub>7</sub>Si<sub>6</sub>O<sub>19</sub> and Pb<sub>3</sub>Si<sub>2</sub>O<sub>7</sub> (these two phases decompose before melting).

### 3.3.2. Crystal phases of the binary SiO<sub>2</sub>-PbO system

This section presents the evolution of the structure of mixed crystal phases mentioned in the previous section depending on the lead oxide content according to the data in the literature<sup>2</sup> (mol% PbO): *alamosite* PbSiO<sub>3</sub> (50 %) (Boucher and Peacor 1968), Pb<sub>7</sub>Si<sub>6</sub>O<sub>19</sub> (53.8 %) (Siidra *et al.* 2014), Pb<sub>3</sub>Si<sub>2</sub>O<sub>7</sub> (60 %) (Petter and Harnik 1971), Pb<sub>2</sub>SiO<sub>4</sub> (66.6 %) (Dent Glasser *et al.* 1981), Pb<sub>11</sub>Si<sub>3</sub>O<sub>17</sub> (78.6 %) (Hirota and Hasegawa 1981; Kato 1982). Three of these structures are represented in figure 3.7. Pb<sub>5</sub>SiO<sub>7</sub> (83.3 %), which is stable only at high temperature (Hirota and Hasegawa 1981), is the only one whose structure remains unsolved. The focus is here on the effect of PbO addition to the silicate network and on the manner in which Pb<sup>2+</sup> ions are incorporated in this structure (type of occupied sites, existence of connections between them and with the silicate units). The absence of mixed crystallized oxides with a PbO content below 50 mol% (or 79 mass%) is a tendency found among the known complex silicates (exception: margarosanite PbCa<sub>2</sub>Si<sub>3</sub>O<sub>9</sub> has a 43 mol% PbO rate). Therefore, the estimation of the structural behavior of crystal glasses and lead glazes (with PbO contents of the order of 10 and 30 mol%, respectively) based on the crystal phases will only be possible by extrapolation, or interpolation with the pure SiO<sub>2</sub> pole. However, as it will be seen in section 3.3.3.1, binary glasses of the SiO<sub>2</sub>-PbO system with up to 83 mol% PbO content can be obtained, therefore for PbO contents that are as high as those of crystal phases (figure 3.7). An examination of the crystal structures shows that the 6s<sup>2</sup> pair of Pb<sup>2+</sup> is systematically active from stereochemical perspective, thus the average number of short bonds ( $d_{\text{Pb-O}} < 2.5 \text{ \AA}$ , with a bond valence above 0.35 v.u.<sup>3</sup>) varies only from 2.3 to 3.0 per Pb<sup>2+</sup> ion, no correlation with the PbO rate being noted.



**Figure 3.7.** Crystal structures of three lead silicates (in-depth representation of 1/2 unit cell) in ascending order of PbO content from left to right (50, 66.6 and 78.6 mol%) showing the various modes of connection between SiO<sub>4</sub> tetrahedrons (in yellow) as well as the asymmetry of the coordination polyhedron for PbO<sub>n</sub>. Pb (in black) and O (in red).

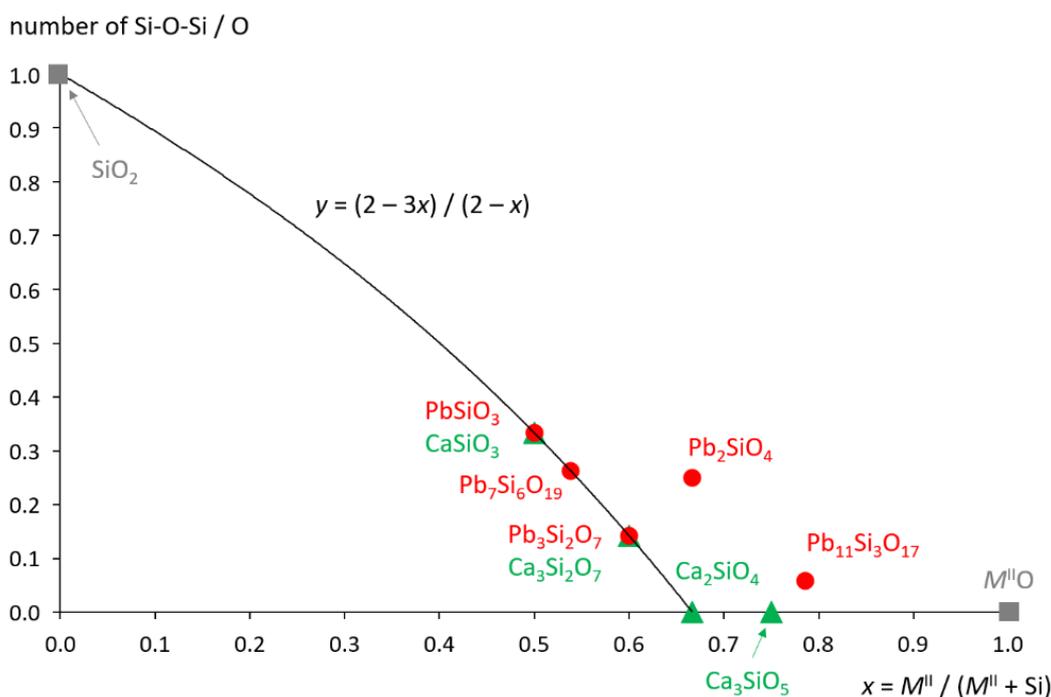
As it disperses SiO<sub>4</sub> tetrahedrons, PbO addition is expected to mechanically reduce their cross-linking. Hence the silicate network, formed of infinite *meta* chains in PbSiO<sub>3</sub> evolves towards *disilicate* units in Pb<sub>3</sub>Si<sub>2</sub>O<sub>7</sub>, following the same tendency as for the addition of CaO. For these two families, the rate of bridging oxygen atoms (involved in the Si-O-Si bonds) evolves in line with the theoretical model following a law in  $(2 - 3x)/(2 - x)$ , with  $x = M^{\text{II}}/(M^{\text{II}} + \text{Si})$  which explains the depolymerization of the silicate network (figure 3.8). The same is applicable to Pb<sub>7</sub>Si<sub>6</sub>O<sub>19</sub>, whose more complex structure expands in Pb<sub>21</sub>(Si<sub>7</sub>O<sub>22</sub>)<sub>2</sub>(Si<sub>4</sub>O<sub>13</sub>). The analysis of crystal structures suggests that in lead glasses and glazes ( $0.1 < x < 0.3$ ), lead oxide has a depolymerizing effect similar to that of a standard modifier. For  $x = 2/3$ , theoretical threshold of total depolymerization (figure 3.8), silicate tetrahedrons become effectively

2. Though most of the structural studies conducted on the binary crystal phases of SiO<sub>2</sub>-PbO system involved X-ray diffraction, NMR studies conducted on <sup>29</sup>Si and <sup>207</sup>Pb nuclei allowed the correlation of the chemical shift changes to the evolution of the environment of silicon and lead in the structure of crystals, thus providing very useful data for understanding the evolution of the environment of these same species in glasses (Bessada *et al.* 1994; Fayon *et al.* 1997).

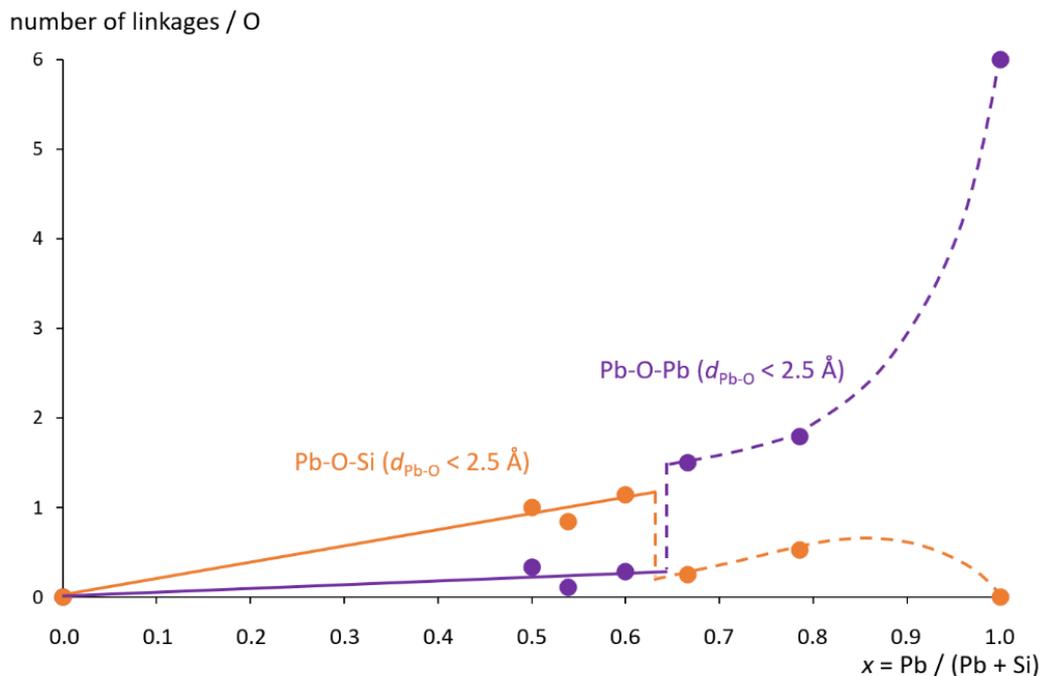
3. v.u.: unit of bond valence.

independent in  $\text{Ca}_2\text{SiO}_4$  (calcium *orthosilicate*), but its lead homologue has a radically different structure, of *oxy-cyclosilicate* type ( $\text{Pb}_2\text{OSiO}_3$ , figure 3.7) due to which Si-O-Si cross-linkages (cycles of 4 tetrahedrons) persist. The same is valid for  $\text{Pb}_{11}\text{Si}_3\text{O}_{17}$  ( $\text{Pb}_{11}\text{O}_6(\text{Si}_2\text{O}_7)(\text{SiO}_4)$ ), which has an even higher lead rate and contains silicate dimers (figure 3.7). This singularity is very likely explained by the stereochemistry of the  $6s^2$  pair, which allows the establishment of strong bonds in the opposite direction of silicate units, certain anions being thus grabbed by three or four  $\text{Pb}^{2+}$  cations and isolated from the silicate network (figure 3.7); the latter can therefore maintain a certain degree of polymerization, for example in the form of cycles or dimers (figure 3.7).

The strong Pb-O bonds (with  $\text{O}^{2-}$  ions that are not bound to silicon) are at the origin of a second form of cross-linking, which does not exist with alkaline or alkaline-earth modifiers. It is however more difficult to define than that of silicate network, due to the irregularity of the lead environment. Taking into account only the Pb-O bonds whose length is below 2.5 Å, the formation of Pb-O-Si and Pb-O-Pb cross-linkages can be noted, their evolutions being represented in figure 3.9. The separation of lead, which occurs beyond  $x = 0.66$  generates a significant decrease of the former, to the benefit of the latter. In the domain of glasses and glazes ( $0.1 < x < 0.3$ ), the interpolation between  $\text{SiO}_2$  and the nearest crystallized lead silicates suggests the existence of a significant primary cross-linking, of about 0.2 to 0.7 “strong” Pb-O-Si cross-linkages per oxygen. On the other hand, the Pb-O-Pb cross-linkages are of about three to four times rarer (figure 3.9). Within the lead-rich crystal phases of  $\text{SiO}_2$ -PbO system ( $\geq 50$  mol% PbO, figure 3.6), the connection between the polyhedrons occupied by  $\text{Pb}^{2+}$  ions is generally done by the edges (figure 3.7).



**Figure 3.8.** Evolution of Si-O-Si cross-linkage rate per oxygen atom depending on the molar ratio  $M^{II}/(M^{II} + \text{Si})$  for  $M = \text{Pb}$  and  $\text{Ca}$  in crystallized lead silicates (●) or calcium silicates (▲)



**Figure 3.9.** Evolution of the rate of Pb-O-Si and Pb-O-Pb cross-linkage per oxygen atom depending on the molar ratio Pb/(Pb + Si) in the crystal phases of lead silicates

This approach based on the comparison with known crystal structures, though weakened by their high PbO rates ( $\geq 50$  mol%) for the crystal glasses and lead glazes ( $\leq 30$  mol% PbO), but more realistic for PbO-rich glasses having contents within the same range as crystal phases (section 3.3.3.1), therefore suggests that lead contributes to the depolymerization of the silicate network similarly to calcium. However, thanks to the stereochemical activity of the  $6s^2$  pair, it allows the formation of Pb-O-Si cross-linkages based on strong Pb-O bonds. The strong Pb-O-Pb cross-linkages would be marginal for crystal glasses and lead glazes but would have a significant and increasing contribution for glasses with much higher PbO contents (figure 3.9).

### 3.3.3. Glasses of the binary $\text{SiO}_2$ -PbO system

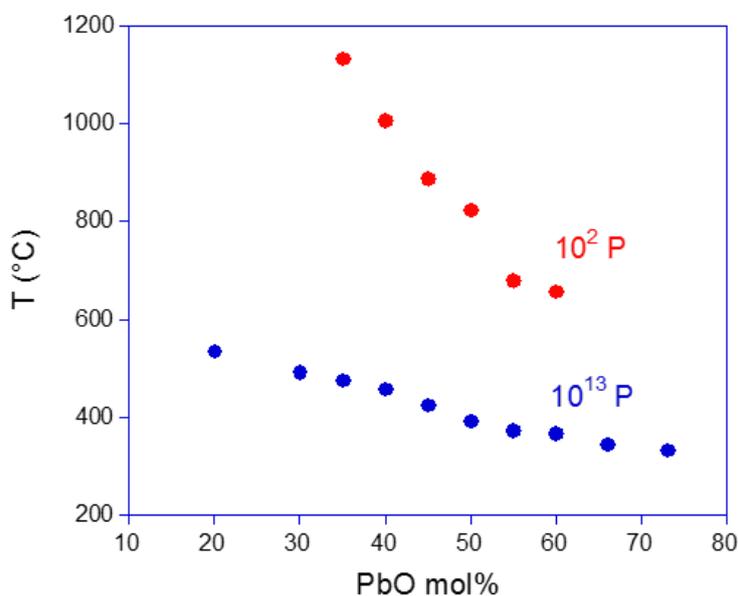
#### 3.3.3.1. Overview of glasses of the binary $\text{SiO}_2$ -PbO system

After the crystal phases of lead silicates, let us now focus on the impact of adding increasing quantities of PbO to the well-known glass former oxide which is vitreous silica  $\text{SiO}_2$  and more particularly on its structure and the manner in which  $\text{Pb}^{2+}$  ions are incorporated in it<sup>4</sup> and also on the evolution of certain physical properties. The study of the structure of these glasses and of the structure-properties relations is particularly important from both fundamental and applied perspectives, as  $\text{SiO}_2$  and PbO are the two predominant oxides in most of the lead oxide-based silicate glasses (crystal glass industry, glazes and enamels, optics, etc.). Moreover, the very wide domain of vitrifiable composition in this system compared to other binary systems, such as alkaline or alkaline-earth silicates is still the subject of many questions in terms of their structure and the role of lead particularly for the PbO-richest compositions. Indeed, it is possible to obtain binary  $\text{SiO}_2$ -PbO glasses by melting- -quenching up to PbO contents of over 83 mol%<sup>5</sup> (95 mass%) (Feller *et al.* 2010) while for the  $\text{SiO}_2$ - $\text{R}_2\text{O}$  systems (R: alkaline) it is increasingly difficult to obtain glasses above 55 mol%  $\text{R}_2\text{O}$  (Imaoka and Yamazaki 1963) due to the very strong tendency to

4. As mentioned above (section 3.2.1.1), lead is overwhelmingly present in the form of  $\text{Pb}^{2+}$  ions in oxide glasses. The presence of  $\text{Pb}^{4+}$  ions would only step in for highly lead-rich glass compositions melted under highly oxidizing atmosphere. This is in line with the evolution of the stability of lead oxides with temperature ( $\text{PbO}_2 < \text{Pb}_3\text{O}_4 < \text{PbO}$ ).

5. Binary glasses with PbO contents above 90 mol% were sometimes mentioned in the literature (Ellis *et al.* 1979), but due to the lacking results of chemical analysis, such data must be carefully considered given the strong evaporation tendency of PbO for lead-rich compositions ( $> 70$ -80 mass% PbO) (Andersen 1919; Volf 1984). Moreover, melting liquids that are very rich in PbO ( $> 90$  mass%) have a very strong crystallization tendency (Faivre and Weiss 1963, p. 587).

crystallize of the corresponding supercooled liquids during cooling, associated both with a decrease in their viscosity and with the very strong depolymerization of the silicate network<sup>6</sup>. In the lead system, for compositions very rich in PbO, the amorphous structure of the liquid can be stabilized by quenching, even though SiO<sub>2</sub> is in a minority. This implies a different structural behavior of Pb<sup>2+</sup> ions compared to that of alkaline and alkaline-earth ions in these glasses and particularly for high PbO (which is in agreement with the comparison of crystal phases of alkaline-earth and lead silicates, figure 3.8), though, like them, its gradual addition to SiO<sub>2</sub> induces both a strong decrease of the liquidus temperature of the system (figure 3.6) and of the viscosity of the liquid (figure 3.10).



**Figure 3.10.** Evolution as a function of PbO content of the temperature corresponding to viscosities of 10<sup>2</sup> and 10<sup>13</sup> Poise for liquids of the SiO<sub>2</sub>-PbO system (according to Martlew data (Martlew 2005)). It can be noted that the temperature corresponding to a given viscosity decreases with the PbO content, which shows its fluxing effect.

It is important to note that even if the liquid is still homogeneous for  $T > T_{\text{liquidus}}$  (figure 3.6), the compositions rich in SiO<sub>2</sub> (> 65 mol%) have a demixing tendency (metastable, therefore sub-liquidus) during the cooling of the liquid (Calvert and Shaw 1970; Vogel 1994). However, the tendency towards phase separation in these binary glasses is suppressed when K<sub>2</sub>O is added (as it is the case in the crystal glass), which can be explained by the quasi-absence of demixing tendency in the binary SiO<sub>2</sub>-K<sub>2</sub>O (Charles 1966) due to the low field strength<sup>7</sup> of K<sup>+</sup> cation ( $F \sim 0.14 \text{ \AA}^{-2}$ ) compared to Pb<sup>2+</sup> cation ( $F \sim 0.36 \text{ \AA}^{-2}$ ) (Vogel 1994). The substantial tendency of binary glasses SiO<sub>2</sub>-PbO with low PbO content to demixing coupled with their very high liquidus temperature (figure 3.6) requiring melting temperatures of about 1 600-1 700 °C explains the small number of studies in the literature on the compositions of lead silicates very rich in silica (Bair 1936; Calvert and Shaw 1970). A certain number of studies have also been conducted on the crystallization of binary SiO<sub>2</sub>-PbO glasses with or without nucleating agent (such as P<sub>2</sub>O<sub>5</sub>) but will not be developed here (Carr and Subramanian 1982a, 1982b; Lippmaa *et al.* 1982; Neiman *et al.* 1982; Kaur *et al.* 2013; Pena *et al.* 2020). Hence, according to Kaur *et al.* (Kaur *et al.* 2013), as long as the PbO content < 50 mol%, glasses resist well to crystallization at heating, while when the PbO content  $\geq 50$  mol%, the majority crystallization of phases such as PbSiO<sub>3</sub> and Pb<sub>2</sub>SiO<sub>4</sub> was evidenced. Before going further into the structural details and in particular on the manner in which Pb<sup>2+</sup> ions are inserted in the vitreous structure and how they react to the silicate network (section 3.3.3.2), it is interesting to

6. For binary SiO<sub>2</sub>-R<sub>2</sub>O glasses, assuming the gradual formation of SiO<sub>4</sub> Q<sup>n</sup> entities with a decreasing number n of bridging oxygen atoms (figure 3.1b) when R<sub>2</sub>O is added (Q<sup>n</sup> represents the SiO<sub>4</sub> tetrahedrons counting n bridging oxygen atoms), it appears that between 50 and 60 mol% R<sub>2</sub>O there are only highly depolymerized entities Q<sup>2</sup> and Q<sup>1</sup> (binary model). Beyond 66.6 mol% R<sub>2</sub>O, the glass would only be constituted of completely depolymerized Q<sup>0</sup> (SiO<sub>4</sub><sup>4-</sup>) entities. It is therefore possible to obtain binary SiO<sub>2</sub>-PbO glasses quite above this last value. For further details, see section 3.3.3.2.1.

7. The field strength F of a cation M<sup>z+</sup> can be defined as the ratio  $F = z/d(M-O)^2$ , where d(M-O) is the average distance between M and the first neighbor O<sup>2-</sup> anions. The values of the field strength for K<sup>+</sup> and Pb<sup>2+</sup> ions were calculated from the average values of the distance d(M-O) in binary silicate glasses (d(K-O)  $\sim 2.64 \text{ \AA}$  and d(Pb-O)  $\sim 2.40 \text{ \AA}$ ).

present the effect of the gradual addition of PbO to the silica on certain physical properties of the glass and of the liquid (Kaur *et al.* 2013).

Besides the above mentioned effect on the viscosity of the melting liquid (strong decrease with the PbO content, figure 3.10), highlighting the fluxing effect of the lead oxide as it is the case for alkaline oxides and boron oxide, the incorporation of increasing PbO contents to the silica leads to a decrease in the glass transition temperature, of the electrical resistivity of glasses and of the surface tension of associated liquids. Moreover, the molar volume tends also to decrease to 60 mol% PbO, then slightly increases (Shelby 1983; Kaur *et al.* 2013; Ben Kacem 2017). The effect of the lead content on the mechanical properties of binary SiO<sub>2</sub>-PbO glasses has also been studied, showing for example a tendency of their hardness and of their Young's modulus to decrease when PbO concentration increases (Yoshihoto and Soga 1987; Kaur *et al.* 2013). The increase in density and in the refractive index presented in chapter 1 is simply explained by the high atomic mass of lead compared to silicon and oxygen (density) and by the strong polarizability of the Pb<sup>2+</sup> ion and its high atomic mass (refractive index). Furthermore, it is important to note that the coefficient of thermal expansion of binary SiO<sub>2</sub>-PbO glasses increases linearly with their molar content in PbO (Greenough *et al.* 1981; Shelby 1983) but remains below that of binary SiO<sub>2</sub>-Na<sub>2</sub>O glasses (Scholze 1980), this property being important particularly for glazes (crazing problem). The chemical durability in aqueous medium of the glasses containing lead oxide was briefly addressed in chapter 1 (section 1.1.8) and is presented in detail in chapter 13 for industrial glasses containing both lead and alkaline ions (crystal glass), therefore it will not be covered here. However, related to the binary SiO<sub>2</sub>-PbO glasses without alkaline ions, it is important to note the study conducted by El-Shamy and Taki-Eldin (El Shamy and Taki-Eldin 1974) on the chemical durability of glasses depending on pH, which shows a nonmonotonic evolution of their tendency to leaching depending on their PbO content. It is also important to mention the more recent works of Mizuno *et al.* (Mizuno *et al.* 2005) on the durability of binary SiO<sub>2</sub>-PbO glasses conducted in an acid medium, which the authors tried to link to the distribution of lead-based structural units PbO<sub>n</sub> in the vitreous structure as a function of lead concentration.

### 3.3.3.2. Structure of the glasses of the binary SiO<sub>2</sub>-PbO system

According to certain works in the literature (Sorokina *et al.* 1996), the structural role of lead in the binary silicate glasses evolves with the PbO content, passing from modifier to glass former oxide, which might explain the larger expansion of the vitreous field of lead silicates compared to alkaline silicates as mentioned above (section 3.3.3.1). Before presenting more precisely these works and also other studies stating that the structural role of lead would not evolve fundamentally as a function of its concentration (Smets and Lommen 1982; Mizuno *et al.* 2005; Ben Kacem *et al.* 2017) and proposing various structural models, let us focus only on lead oxide PbO and its capacities, or lack thereof, to lead to a glass by melting- quenching.

It is important to note first of all that PbO is not a glass former oxide, since unlike silica, for example, it does not lead by melting + quenching to the formation of a glass. This may be due to several reasons. First of all, the very low viscosity of liquid PbO in the vicinity of its melting temperature ( $\eta \sim 0.01$  Pa.s (0.1 P) (Sinn 1979)) which is higher only by a factor of 10 than that of water at ambient temperature ( $\eta \sim 0.001$  Pa.s (0.01 P) (Korson *et al.* 1969)) and significantly lower than that of melted silica in the vicinity of its melting temperature ( $\eta \sim 10^6$  Pa.s (10<sup>7</sup> P) (Martlew 2005)) explains the ease of PbO crystallization from the liquid by the strong mobility of species and therefore the difficulty to maintain the latter in supercooled state and consequently to obtain a glass by quenching. Moreover, from a structural point of view, according to Zachariasen rules related to glass former oxides M<sub>x</sub>O<sub>y</sub> (Zachariasen 1932), these must be such that on the one hand the MO<sub>n</sub> polyhedrons are loosely coordinated (3 or 4) – which corresponds to small highly charged cations M<sup>+2y/x</sup> such as Si<sup>4+</sup>, B<sup>3+</sup> and P<sup>5+</sup> – and connected with one another only by the vertices (not by the edges or the faces) allowing a significant flexibility in the structural arrangement, without getting a too high increase in the free energy of the system. According to the same rules and for the same reasons, it is stipulated that the oxygen anions should not connect more than 2 MO<sub>n</sub> polyhedrons. The coordination number of Pb<sup>2+</sup> ions being 4 in crystal PbO, as already seen above (figures 3.3 and 3.5), the coordination number of O<sup>2-</sup> ions should also be 4, to have electroneutrality. This

explains why the  $\text{PbO}_4$  units are connected by the edges and not by the vertices, which is contrary to Zachariassen's rules. Being relatively constrained locally, this structure may seem unfavorable to accepting significant disorder at the level of polyhedral layout without this leading to a significant increase in its free energy<sup>8</sup>. From a thermodynamic point of view, this should be in favor of the crystallized state compared to the vitreous state, and could explain structurally why PbO is not a forming oxide. Likewise, according to Dietzel's theory (Dietzel 1948) connecting the cationic field strength  $F$  and the structural role of oxides in glasses, it appears that  $\text{Pb}^{2+}$  ion has a field strength of approximately  $0.36 \text{ \AA}^{-2(9)}$ , which would put PbO in the class of modifier oxides for which  $F$  ranges between 0.1 and  $0.4 \text{ \AA}^{-2}$  ( $F$  ranges between 1.5 and  $2.0 \text{ \AA}^{-2}$  for glass former oxides). However, it is important to recall here that due to its strong polarizability (section 3.2.1.2), from the point of view of its bonds with the nearest neighbor oxygen ions, the  $\text{Pb}^{2+}$  ion can be considered as a  $\text{Pb}^{4+}$  ion with a higher field strength  $F = 0.48 \text{ \AA}^{-2}$ . This would put PbO in the class of intermediate oxides ( $F$  ranging between 0.5 and  $1.0 \text{ \AA}^{-2}$ ) with quite directional Pb-O bonds, which are ionocovalent and asymmetrically arranged in its environment (figures 3.3 and 3.5). This type of Pb-O bond is therefore very different from the one existing between alkaline and alkaline-earth cations and  $\text{O}^{2-}$  anions in the crystallized oxides (ionic bonds distributed quite symmetrically around cations).

It can be then understood that the mode of incorporation of  $\text{Pb}^{2+}$  ions in a silicate glass may be very different<sup>10</sup> from the one of traditional modifier cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , etc.) which are far less polarizable<sup>11</sup> and for which the bonds with the oxygen anions are weaker, ionic and therefore nondirectional. Relying on the crystal structure of PbO and assuming that the environment of  $\text{Pb}^{2+}$  ions in  $\text{SiO}_2$ -PbO glasses was also very asymmetrical with quite strong directional bonds due to their very strong polarization by  $\text{O}^{2-}$  anions, Fajans and Kreidl (Fajans and Kreidl 1948) proposed in the 1940s that this particular type of lead environment was at the origin of the largest stability of the liquids of  $\text{SiO}_2$ -PbO system in terms of crystallization (and therefore of their easier vitrification) compared to alkaline silicate compositions for which the crystallization processes are facilitated by the easier reorganization of species in the corresponding liquids (weaker and non-asymmetric bonds between alkaline cations and  $\text{O}^{2-}$  anions)<sup>12</sup>. However, the study of the structure of binary  $\text{SiO}_2$ -PbO glasses had started about ten years earlier, in 1936, by X-ray scattering (Bair 1936), only one year after the well-known works of Warren and Loring on the X-ray scattering study of the structure of soda silicate glasses (Warren and Loring 1935) and 4 years after the famous Zachariassen's publication on the structure of oxide glasses (Zachariassen 1932). However, the model proposed by Bair for lead silica glasses (Bair 1936), based on his processing of X-ray scattering data, was very close to the structural model of soda silicate glasses of Warren and Loring (random continuous silicate network with homogeneous distribution of  $\text{Pb}^{2+}$  ions near non-bridging oxygen atoms of  $\text{SiO}_4$  tetrahedrons). Since these first works aimed at clarifying the structure of binary  $\text{SiO}_2$ -PbO glasses, many studies have been conducted using various structural investigation methods such as X-ray and neutron scattering, X-ray absorption (EXAFS<sup>13</sup> and XANES<sup>14</sup>), XPS<sup>15</sup>, multinuclear NMR<sup>16</sup> ( $^{207}\text{Pb}$ ,  $^{29}\text{Si}$ ,  $^{17}\text{O}$ ), Raman and IR spectroscopies, as well as molecular dynamics. These studies confirmed the hypothesis of Fajans and Kreidl of a very asymmetric environment of  $\text{Pb}^{2+}$  ions in the

8. It is important to note however that due to the two-dimensional character of the crystalline structure of PbO (litharge and massicot, figure 3.6), it may probably easier accept local constraints due to disorder than three-dimensional crystalline structures such as those of alkaline and alkaline-earth oxides, whose role as modifier oxides is well established.

9. Calculation made according to the crystalline PbO structure and Shannon's ionic radii (Shannon 1976) ( $r_{\text{Pb}^{2+}} = 0.98 \text{ \AA}$ ,  $r_{\text{O}^{2-}} = 1.38 \text{ \AA}$ ).

10. Indeed, as noted in section 3.3.2, for crystallized lead silicates the environment of  $\text{Pb}^{2+}$  ions is also strongly asymmetric.

11. Indeed, according to Kordes, the values of polarizability (in  $\text{Å}^3$ ) are the following:  $\text{Na}^+$  (0.175) <  $\text{Ca}^{2+}$  (0.469) <  $\text{K}^+$  (0.821) <  $\text{Pb}^{2+}$  (3.623) (Dimitrov and Komatsu 2010).

12. It is interesting to signal that according to Vogel (Vogel 1994), the fact that the vitrifiable domain of the  $\text{P}_2\text{O}_5$ -PbO system is less extended than that of  $\text{SiO}_2$ -PbO system (66 mol% compared to 83 mol%) could be explained by the very strong polarization exerted by the  $\text{P}^{5+}$  ions on the  $\text{O}^{2-}$  anions of the phosphate network, which would have a weaker polarizing effect on the  $\text{Pb}^{2+}$  ions than in the case of silicate glasses ( $\text{Si}^{4+}$  ion having a weaker field strength than  $\text{P}^{5+}$  ion), thus leading to weaker Pb-O bonding forces and a higher coordination number for  $\text{Pb}^{2+}$  ions with the oxygen atoms associated with phosphorus (Hoppe *et al.* 2003). For further information on the structure and properties of the glasses of the binary  $\text{P}_2\text{O}_5$ -PbO system, please see the references (Dayanand *et al.* 1996; El-Egili *et al.* 2003; Matori *et al.* 2013).

13. EXAFS : *Extended X-ray Absorption Fine Structure*.

14. XANES : *X-Ray Absorption Near Edge Structure*.

15. XPS : *X-ray Photoelectron Spectroscopy*.

16. NMR: Nuclear Magnetic Resonance (MAS NMR = NMR with magic angle spinning; MQMAS NMR = multi-quantum NMR with magic angle spinning).

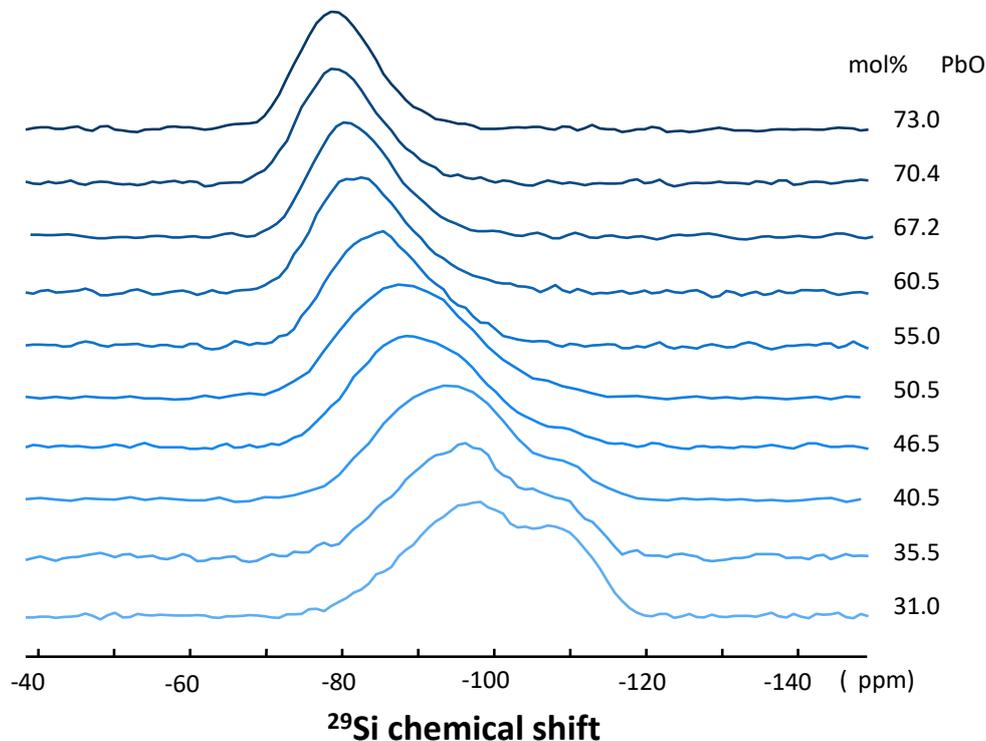
silicate glasses, such as the study of Mydlar *et al.* in 1970 (Mydlar *et al.* 1970). Nowadays all the authors agree that in lead silicate glasses the majority of  $\text{Pb}^{2+}$  ions are found in very asymmetric environments like in the  $\text{PbO}$  and lead silicates crystals (figures 3.3, 3.5 and 3.7) having also a stereochemically ~~their~~ active  $6s^2$  pair  $6s^2$  (sections 3.2.2 and 3.3.2). However, the authors still diverge on the structural role of lead, its type of environment and its evolution as a function of  $\text{PbO}$  content in glass. A part of these structural works on binary  $\text{SiO}_2$ - $\text{PbO}$  glasses was the object of past (Rabinovich 1976) or more recent (Alderman 2013) bibliographic syntheses. Based on some of these studies, and particularly on the more recent ones, the following sections of this chapter focus on the manner in which the silicate vitreous network is affected by the addition of increasing quantities of lead oxide. Then the structural role of  $\text{Pb}^{2+}$  ions and the evolution of their environment and of their distribution in the vitreous network will be examined.

### 3.3.3.2.1. Vitreous silicate network

Prior to any lead oxide addition, the structure of pure silica glass is exclusively formed of  $\text{SiO}_4$  tetrahedrons connected to one another by their vertices forming a continuous network, as seen at the beginning of this chapter (figure 3.1a). In this case each  $\text{SiO}_4$  tetrahedron has four bridging oxygen atoms. In order to introduce the classification of various types of  $\text{SiO}_4$  tetrahedrons present in the glasses composed of silica and one or more other oxides such as  $\text{PbO}$ , let us consider the well-known case of binary  $\text{SiO}_2$ - $\text{Na}_2\text{O}$  glasses. When  $\text{Na}_2\text{O}$  is added to the silica glass,  $\text{Si-O-Si}$  bonds are broken ( $\text{Na}_2\text{O}$  has the role of modifier oxide): the vitreous silicate network becomes partially depolymerized and non-bridging oxygen atoms – whose negative charge is locally compensated by  $\text{Na}^+$  ions – are formed (figure 3.1b). To account for the gradual depolymerization of  $\text{SiO}_4$  tetrahedrons depending on  $\text{Na}_2\text{O}$  content, the notation  $Q^n$  is introduced, representing the  $\text{SiO}_4$  tetrahedrons counting  $n$  bridging oxygen atoms. A pure silica glass thus contains only  $Q^4$  units, and for binary glasses a  $Q^3$  unit corresponds to a  $\text{SiO}_4^-$  tetrahedron, a  $Q^2$  unit to a  $\text{SiO}_4^{2-}$  tetrahedron, a  $Q^1$  unit to a  $\text{SiO}_4^{3-}$  tetrahedron and a  $Q^0$  unit to a  $\text{SiO}_4^{4-}$  tetrahedron that is completely isolated from the rest of the silicate network. The more  $Q^n$  units with low  $n$ , the more difficult it becomes to vitrify the liquid, as it is increasingly fluid and is readily organized in the form of crystals. Using this notation, the chemical equation corresponding to the introduction of  $\text{Na}_2\text{O}$  in a pure silica glass is:  $2Q^4 + \text{Na}_2\text{O} \rightarrow 2Q^3$ . It is in fact an acid-base reaction (in the sense of oxo-acidity (Flood and Förland 1947)) between the basic oxide  $\text{Na}_2\text{O}$  giving  $\text{O}^{2-}$  anions and the acidic oxide  $\text{SiO}_2$  that accepts them. Moreover, in the melting liquid there is an equilibrium (disproportionation reaction) between  $Q^n$  units ( $2Q^n \leftrightarrow Q^{n-1} + Q^{n+1}$ ) that can be found in the glass obtained after quenching (Maekawa *et al.* 1991). The description of the silicate network involves particularly the study of its degree of polymerization, hence following-up the evolution of the proportions of various units  $Q^n$  that compose it. In the case of simple silicate compositions, this can be done, for example, using  $^{29}\text{Si}$  NMR and Raman (Maekawa *et al.* 1991; O'Shaughnessy *et al.* 2020) spectroscopies, while the follow-up of the evolution of the proportions of the various types of oxygen atoms (bridging, non-bridging or not connected to the silicate network) can be achieved by  $^{17}\text{O}$  NMR (after glass enrichment in  $^{17}\text{O}$ )<sup>17</sup> and XPS spectroscopies, for example (Dalby *et al.* 2007; Lee and Kim 2015).

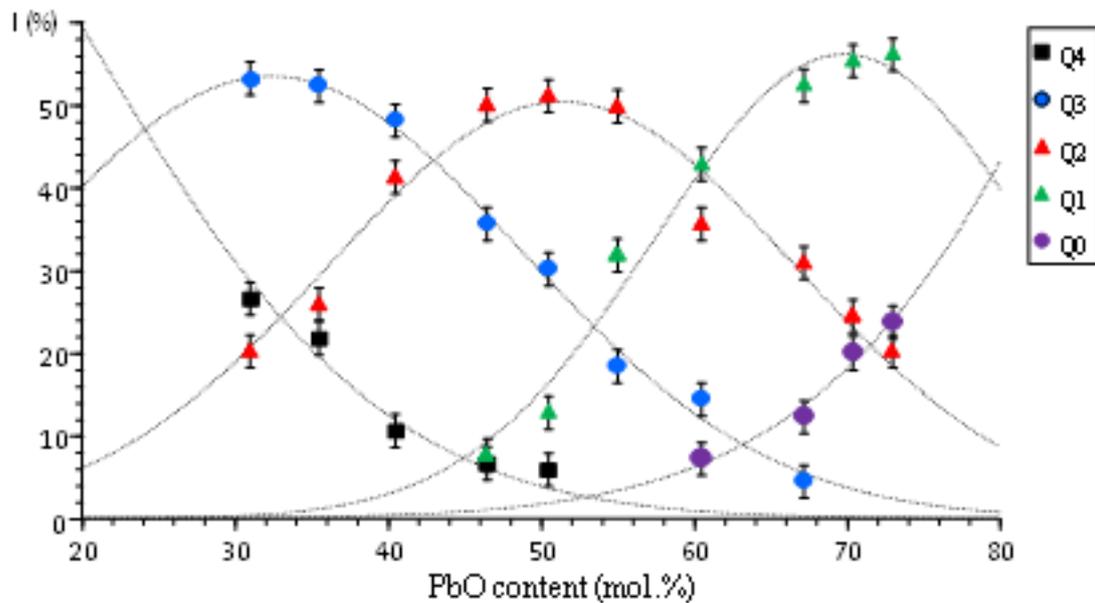
In the case of interest here, several studies focused on the evolution of the structure of the silicate network of lead silicate binary glasses and clearly highlight the fact that the introduction of  $\text{PbO}$  leads to an increasing depolymerization of the silicate network. For example, Bessada *et al.* (Bessada *et al.* 1994), Fayon *et al.* (Fayon *et al.* 1998) and Fayon (Fayon 1998) have used  $^{29}\text{Si}$  NMR to compare the spectra of glasses to those of crystalline phases and to quantify the  $Q^n$  units present in the glasses containing 31 to 73 mol%  $\text{PbO}$  (figures 3.11 and 3.12).

17. Given the very low natural abundance of  $^{17}\text{O}$  isotope (0.038 %) the only one detectable by NMR due to its non-zero nuclear spin  $I$  ( $I = 5/2$ ) compared to the  $^{16}\text{O}$  (99.75 %) isotope, of zero nuclear spin, it is necessary to enrich the glasses in  $^{17}\text{O}$ . In the case of silicate glasses, this is classically done by preparing  $^{17}\text{O}$  enriched silicon oxide  $\text{SiO}_2$ , for example from a mixture of  $\text{SiCl}_4$  and water enriched in  $^{17}\text{O}$ .

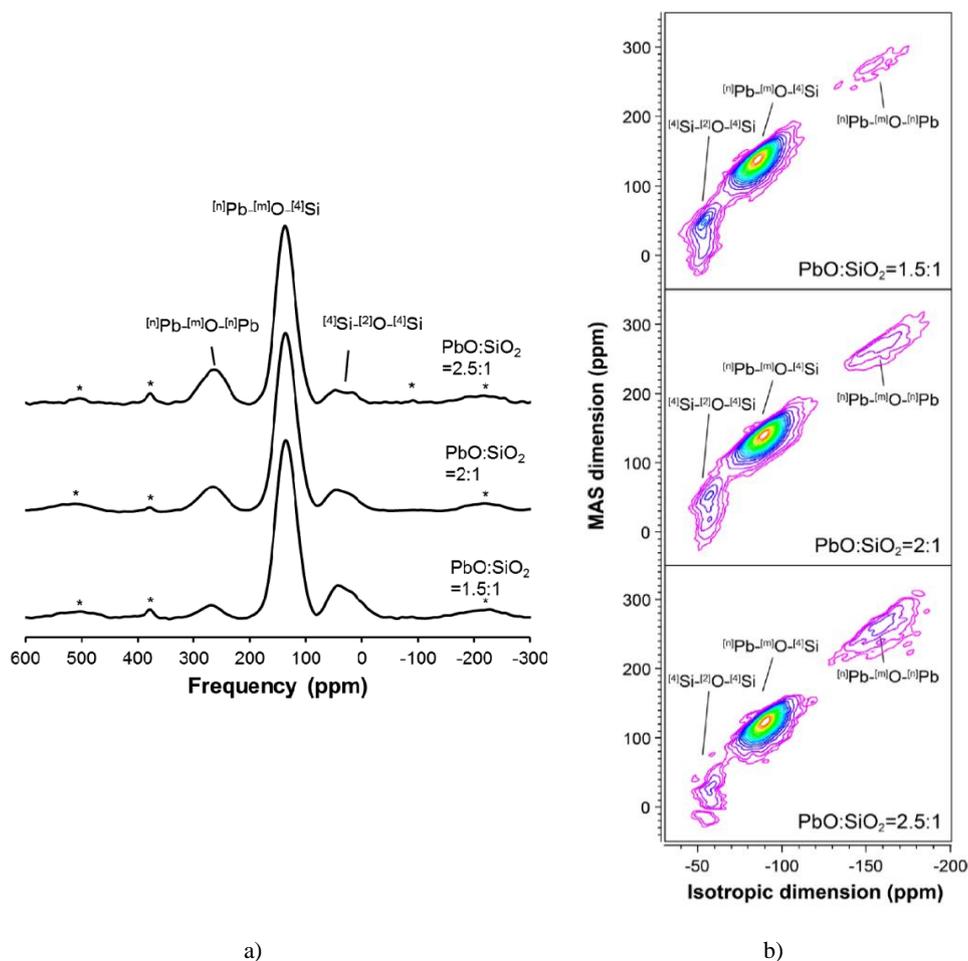


**Figure 3.11.** Evolution of  $^{29}\text{Si}$  MAS NMR spectra of lead silicate glasses depending on their PbO content (Fayon 1998). 7 T magnetic field, 10 kHz rotational frequency (with the kind permission of F. Fayon)

It has thus been shown that from 31 mol% up to approximately 40 mol% PbO, the  $\text{Q}^3$  units were predominant and the proportion of  $\text{Q}^2$  units increased mainly to the detriment of  $\text{Q}^4$  units (Fayon 1998; Fayon *et al.* 1998) (figure 3.12). Then  $\text{Q}^1$  units appear and their proportion increases with the PbO content mainly to the detriment of  $\text{Q}^3$  units and become predominant beyond 60 mol% PbO. Finally, the  $\text{Q}^0$  units appear and are the predominant units with  $\text{Q}^1$  units beyond 72 mol% PbO (figure 3.12). This structural evolution was more recently confirmed over a more extended range of PbO contents (33-83 mol%) by Feller *et al.* (Feller *et al.* 2010) who showed that the glass prepared with 83 mol% PbO contained almost exclusively  $\text{Q}^1$  species (24 %), entities composed of only two  $\text{SiO}_4$  tetrahedrons connected by a vertex, and  $\text{Q}^0$  species (72 %), namely  $\text{SiO}_4$  tetrahedrons with no connection to another  $\text{SiO}_4$  tetrahedron, thus confirming for binary  $\text{SiO}_2$ -PbO compositions the possibility to obtain a vitreous state in the absence of an extended silicate vitreous network. The comparison of  $^{29}\text{Si}$  chemical shifts of  $\text{Q}^n$  units between binary glasses and crystalline phases of the same composition has on the other hand evidenced a number of  $\text{Pb}^{2+}$  ions second nearest neighbors of silicon atoms more significant for the glasses (Bessada *et al.* 1994). Furthermore, it is interesting to note that the equilibrium constants of  $2\text{Q}^n \leftrightarrow \text{Q}^{n-1} + \text{Q}^{n+1}$  reactions (disproportionation) in the overmelted liquid and frozen in the glass during the quenching and which were determined by  $^{29}\text{Si}$  NMR from proportions of various  $\text{Q}^n$  units in the glasses (figure 3.12) have an order of magnitude above that of alkaline silicate glasses (Fayon *et al.* 1998), which tends to show a more significant clustering tendency of  $\text{Pb}^{2+}$  ions compared to alkaline ions. The persistence of  $\text{Q}^2$  and  $\text{Q}^1$  units far beyond 66 mol% PbO (threshold beyond which only  $\text{Q}^0$  units should remain if PbO fully transferred these  $\text{O}^{2-}$  anions to the silicate network by acidic-basic reaction) suggests that an increasing fraction of oxygen atoms in the structure are only connected to  $\text{Pb}^{2+}$  ions, the rest being present in the form of bridging oxygen atoms (Si-O-Si) and non-bridging oxygen atoms (Si-O-Pb). This has been directly confirmed by  $^{17}\text{O}$  NMR for PbO – rich (60-71 mol%) glasses enriched in  $^{17}\text{O}$  (figure 3.13) (Lee and Kim 2015).

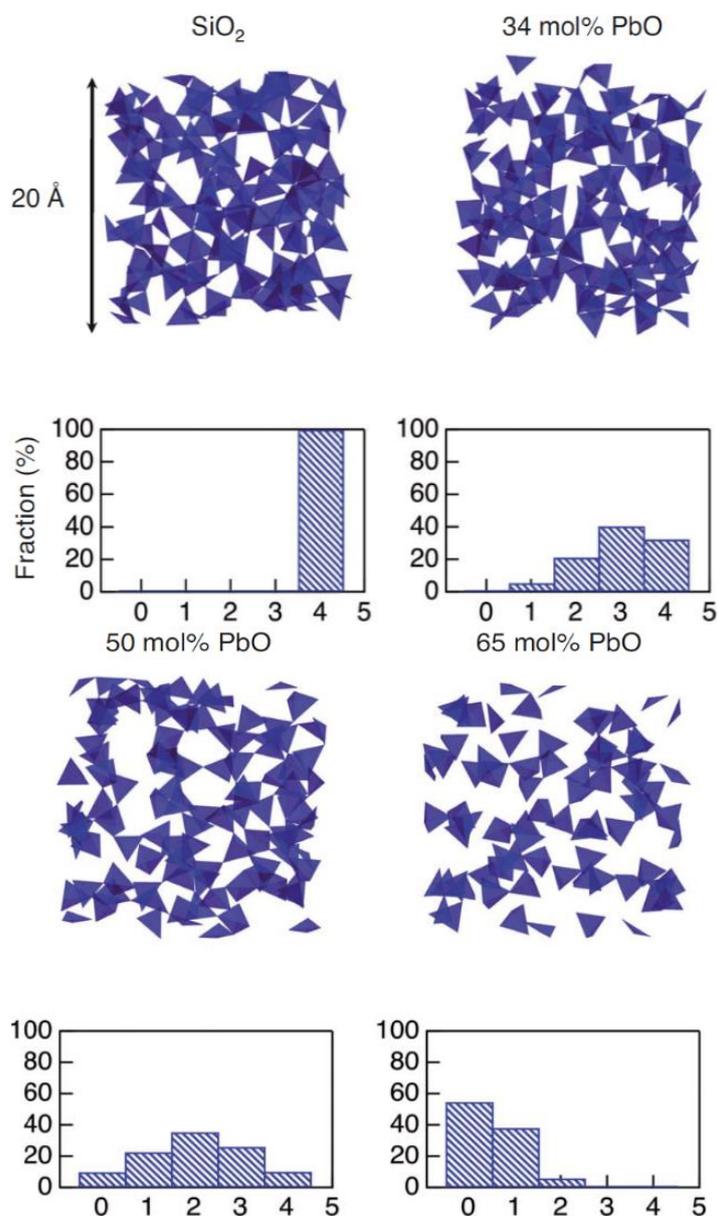


**Figure 3.12.** Evolution of the relative proportions of  $Q^n$  units determined from  $^{29}\text{Si}$  MAS NMR spectra of lead silicate glasses (figure 3.11) as a function of their  $\text{PbO}$  content (the dotted curves serve only as a guide) (Fayon 1998) (with the kind permission of F. Fayon).



**Figure 3.13.** a)  $^{17}\text{O}$  MAS NMR spectra of lead silicate glasses enriched in  $^{17}\text{O}$  and b) 3QMAS NMR spectra of the same lead silicate glasses enriched in  $^{17}\text{O}$  showing the various existing types of oxygen atoms. Reproduced with permission from (Lee, S.K., Kim, E.J., *J. Phys. Chem. C* 119, 748–756, 2015). Copyright (2020) American Chemical Society.

COMMENT ON FIGURE 3.13.— *a) The peaks marked by asterisks are rotational bands. b) The PbO/SiO<sub>2</sub> molar content ratios are indicated in the figures and correspond to 60 (1.5:1), 66 (2:1) and 71 (2,5:1) mol% PbO. The various types of oxygen atoms evidenced are: bridging oxygen atoms (<sup>4</sup>Si-<sup>2</sup>O-<sup>4</sup>Si), non-bridging oxygen atoms (<sup>n</sup>Pb-<sup>m</sup>O-<sup>4</sup>Si) and oxygen atoms bound only to lead (<sup>n</sup>Pb-<sup>m</sup>O-<sup>n</sup>Pb).*



**Figure 3.14.** Evolution of the silicate vitreous network (only SiO<sub>4</sub> tetrahedrons are represented) of lead silicate and pure silica glasses depending on their PbO content. Reproduced with permission from (Kohara, S., Ohno, H., Takata, M., Usuki, T., Morita, H., Suzuya, K., Akola, J., Pusztai, L., *Phys. Rev. B*, 82, 134209, 2010). Copyright (2020) by the American Physical Society.

COMMENT ON FIGURE 3.14.— *The structural models have been obtained by the reverse Monte Carlo method from X-ray and neutron scattering results. The distribution of Q<sup>n</sup> (n = 0, 1, 2, 3, 4) units determined for various glasses from these models is also presented in the form of histograms (Kohara et al. 2010).*

Other authors have used Raman spectroscopy to follow up the evolution of the structure of lead silicate glasses and try to quantify the Q<sup>n</sup> units by sometimes drawing comparisons with the crystalline phases (Furukawa *et al.* 1978; Feller *et al.* 2010; Kaur *et al.* 2013; Ben Kacem *et al.* 2017). Similar to <sup>29</sup>Si NMR, a very strong evolution of Raman spectra with the PbO content was observed in conjunction with an increasing depolymerization of the silicate network. Moreover, in line with the <sup>17</sup>O NMR results (figure 3.13), the joint formation of Pb-O-Pb bonds was evidenced, reflecting an increasing tendency of Pb<sup>2+</sup> ions to bind to one another (clusterization). The studies conducted by XPS (O 1s) on binary SiO<sub>2</sub>-PbO glasses

have also evidenced a strong decrease in the proportion of bridging oxygen atoms with the PbO content, however the resolution of spectra is insufficient to separate the contribution of non-bridging oxygen atoms from that of oxygen atoms that are not bound to silicon (Smets and Lommen 1982; Sorokina *et al.* 1996; Dalby *et al.* 2007). However, some of these studies highlight the persistence of bridging oxygen atoms i.e. Si-O-Si bonds– in the most PbO-rich compositions (Smets and Lommen 1982; Dalby *et al.* 2007) in agreement with the  $^{29}\text{Si}$  NMR studies (figure 3.12). Finally, it is important to mention the studies conducted by X-ray and neutron scattering combined with structural modeling using the reverse Monte Carlo method (Suzuya *et al.* 1999; Kohara *et al.* 2010) which led to a distribution of  $\text{Q}^n$  units as a function of composition (figure 3.14) consistent with  $^{29}\text{Si}$  NMR results (figure 3.12). On the other hand, the structural models obtained by molecular dynamics and which do not take into account the polarizability of  $\text{Pb}^{2+}$  ions that leads to anisotropic local environments yield average results, these works using symmetric interaction potentials (Ribycka *et al.* 1999).

All these results related to the evolution of the silicate network of  $\text{SiO}_2$ -PbO glasses are therefore qualitatively close to at least the evolution of the structure of crystalline phases of lead silicates presented in section 3.2 (figures 3.7 to 3.9). Indeed, both cases show a strong depolymerization of the silicate (vitreous and crystalline) network with the persistence of  $\text{SiO}_4$  tetrahedrons bound to one another for the highest PbO contents (figures 3.7, 3.8 and 3.12):  $\text{Q}^1$  and  $\text{Q}^2$  units for glasses, and  $\text{Si}_4\text{O}_{12}$  rings and  $\text{Q}^1$  units respectively for  $\text{Pb}_2\text{SiO}_4$  (66 mol% PbO) and  $\text{Pb}_{11}\text{Si}_3\text{O}_{17}$  (78 mol% PbO) crystalline phases. In both cases there is a significant proportion of oxygen atoms exclusively bound to lead (Pb-O-Pb bonds) (figures 3.9 and 3.13).

#### 3.3.3.2.2. Environment, distribution and structural role of lead

Various techniques can be used to extract information on the lead environment in glasses. Some of these techniques make it possible to specifically probe the lead, such as NMR<sup>18</sup>, EXAFS and XANES and XPS, while other techniques such as X-ray and neutron scattering, though providing very useful information on the environment of  $\text{Pb}^{2+}$  ions (coordination number, Pb-O distance), probe also other elements that are present in the vitreous network. The studies published in the literature on lead environment and incorporation using these investigation techniques are numerous and sometimes contradictory, so that the structural role of lead in silicate glasses is still under debate. However, the majority of authors agree nowadays that  $\text{Pb}^{2+}$  ions are inserted in the structure of binary silicate glasses with their free pair  $6s^2$  stereochemically active in the form of very asymmetric  $\text{PbO}_n$  polyhedrons with low coordination number ( $n = 3 - 4$ ), of pyramidal type with short Pb-O bonds with strong covalent character: lead would therefore have a local environment close to the one occupied in the crystalline phases of lead silicates and in the pure lead oxide (sections 3.2.2 and 3.3.2). Moreover, for high PbO contents,  $\text{PbO}_n$  units would tend to bind to one another in order to form increasingly larger percolating domains until building the main frame of the vitreous network including increasingly depolymerized silicate units ( $\text{Q}^1$ ,  $\text{Q}^0$ ), similar to crystallized lead silicates (figure 3.7). The existence of such domains is in agreement with  $^{17}\text{O}$  NMR-evidenced increasing proportion of oxygen atoms exclusively bound to lead (Pb-O-Pb bonds, figure 3.13). These conclusions rely, among others, on X-ray absorption (EXAFS, XANES) and X-ray and neutron scattering studies.

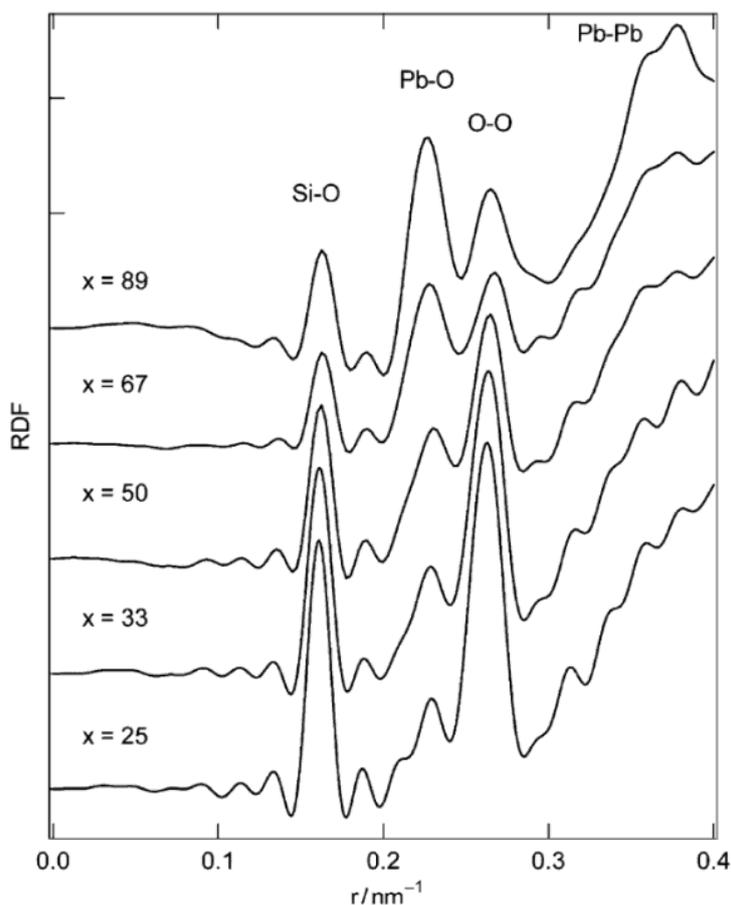
The X-ray and neutron scattering studies allow the extraction of radial distribution functions concerning the various pairs of atoms present in the structure and from which it is possible to find the interatomic distances and coordination numbers (figure 3.15). Hence Hoppe *et al.* (Hoppe *et al.* 2003) and Takaishi *et al.* (Takaishi *et al.* 2005) find the Pb-O distances of the order of 2.30 Å for the nearest oxygen atoms with a coordination number of 3, these distances and coordination numbers varying relatively little with the PbO content in glasses (figure 3.15).

Based on their X-ray and neutron scattering results, and particularly on the Pb-Pb distance that remains quasi-constant (3.83-3.86 Å) for all the studied glasses (25-89 mol%), Takaishi *et al.* proposed a structural

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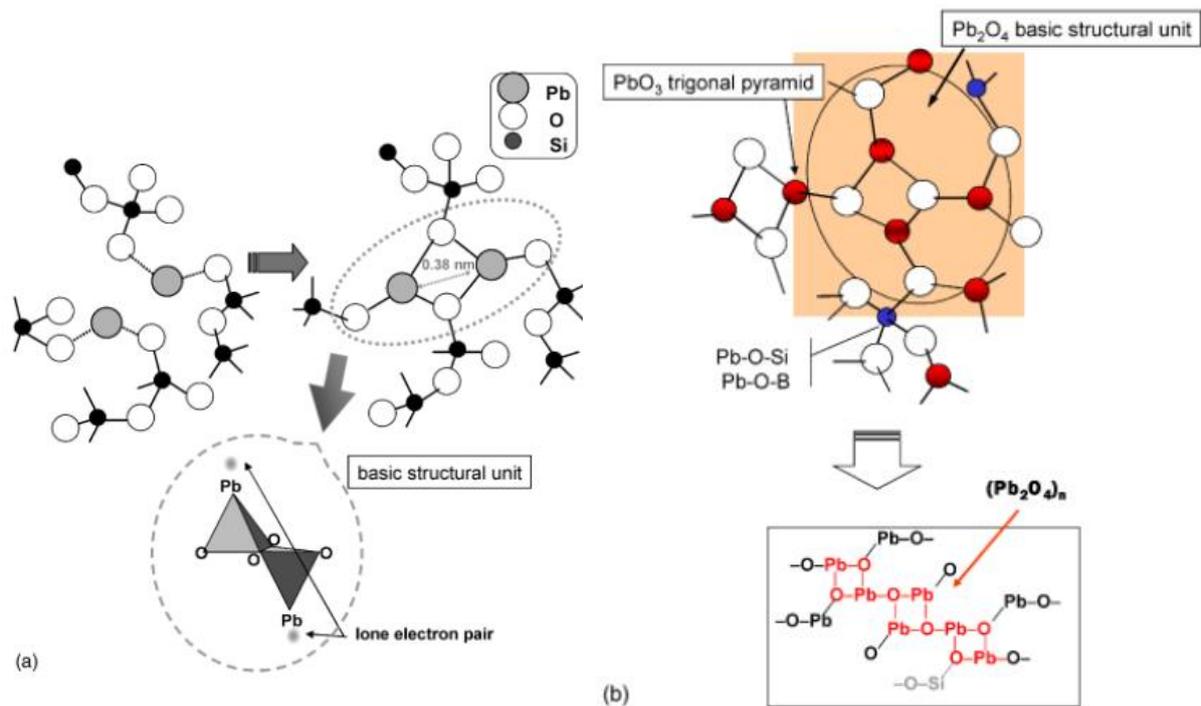
18.  $^{207}\text{Pb}$  is the only stable isotope of lead (natural abundance 22.1 %) having a nonzero nuclear spin ( $I = 1/2$ ), it can therefore be studied by NMR. However, given its high polarizability, the NMR signals obtained are large and poorly resolved.

model of  $\text{SiO}_2\text{-PbO}$  glasses employing  $\text{Pb}_2\text{O}_4$  units constituted of two trigonal pyramidal  $\text{PbO}_3$  connected by an edge and oriented in opposite directions in order to minimize the repulsion between the free pairs  $6s^2$  of the two  $\text{Pb}^{2+}$  ions, these  $\text{Pb}_2\text{O}_4$  units having a zero global charge (figure 3.16) (Mizuno *et al.* 2005; Takaishi *et al.* 2005). These entities would be present starting with the lowest  $\text{PbO}$  contents studied by the authors (25 mol%). According to this model, lead behaves as a forming element starting with the lowest lead concentrations.



**Figure 3.15.** Radial distribution functions calculated from the neutron scattering data for glasses of composition  $(1-x)\text{SiO}_2 - x\text{PbO}$  ( $x$  in mol%) (Takaishi *et al.* 2005)

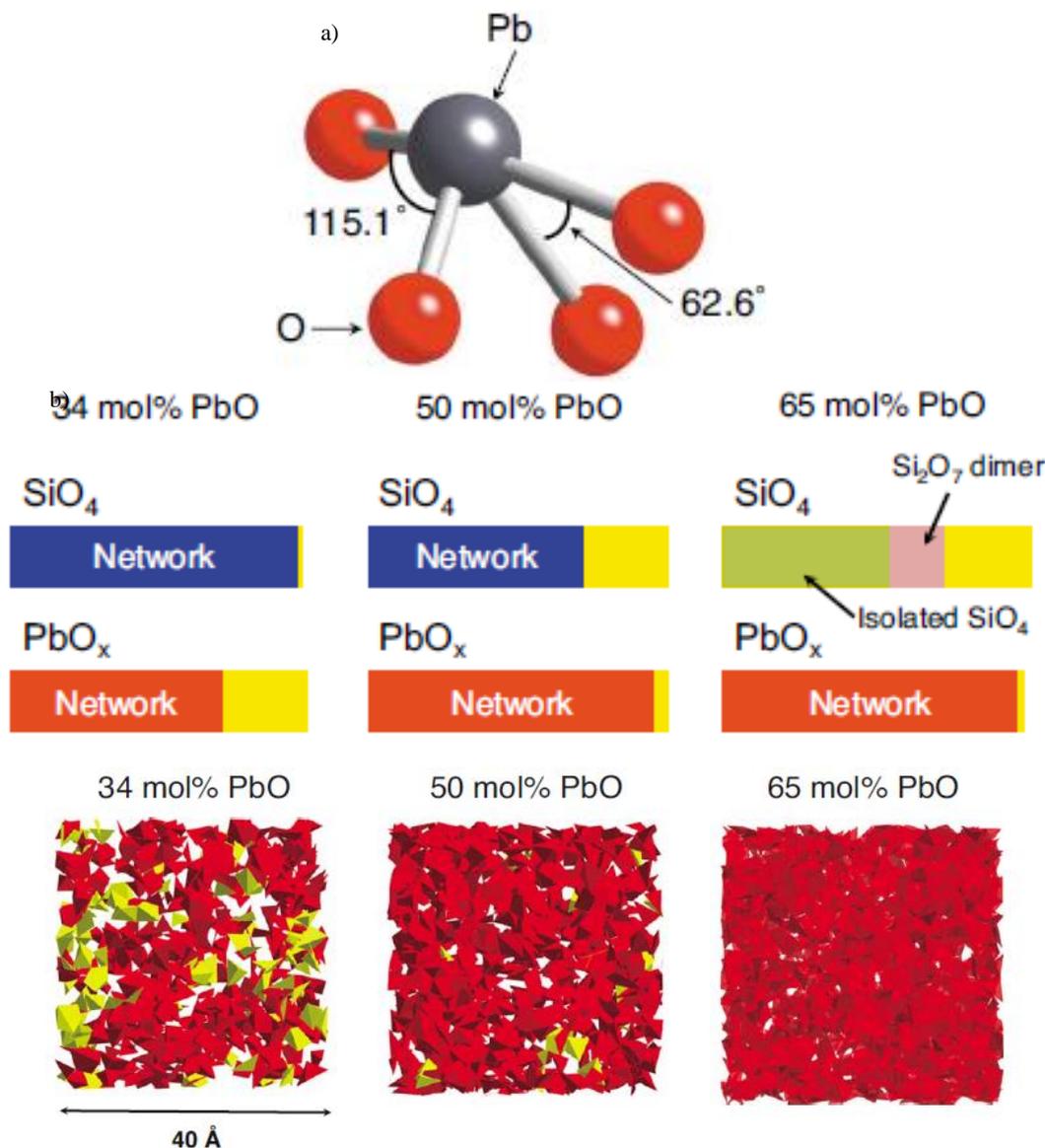
COMMENT ON FIGURE 3.15.— For neutron scattering (shown here), all correlations can be seen, particularly those associated with Si-O and O-O, as in this case lead cannot be distinguished from the other atoms. On the other hand, in the case of X-ray scattering (not shown here) which is largely dominated by lead due to its significantly higher atomic number compared to that of other species present (Si and O), the resulting information are essentially related to Pb-O and Pb-Pb correlations.



**Figure 3.16.** Structural model of lead silicate glasses proposed by Takaishi *et al.* (Takaishi *et al.* 2005) based on the X-ray and neutron scattering results

COMMENT ON FIGURE 3.16.– The  $Pb_2O_4$  basic unit consisting of two  $PbO_3$  pyramids with triangular base connected by an edge and with an opposed layout of the free  $6s^2$  pairs of lead is presented. a) For low  $PbO$  contents,  $Pb_2O_4$  units are incorporated in the silicate network, b) for high  $PbO$  contents there is a connection between the  $Pb_2O_4$  units. The  $3.8 \text{ \AA}$  distance between the  $Pb^{2+}$  ions is indicated.

Based on their scattering results and on a structural model obtained with reverse Monte Carlo simulation method for glasses with  $PbO$  contents between 30 and 65 mol%, Kohara *et al.* (Kohara *et al.* 2010) did not confirm the existence of  $Pb_2O_4$  dimeric units in lead silicate glasses, but a lead environment predominantly in the form of distorted  $PbO_4$  units of square-based pyramidal type (figure 3.17). Such an environment is close to that of lead in the crystalline forms of  $PbO$  (figures 3.3 and 3.5) and in the crystalline phases of lead silicates (figure 3.7). A number of  $PbO_n$  units connected to one another strongly increasing with the lead content were evidenced in the structure of these glasses. The same authors have also presented a compared evolution of the silicate network and of the lead network depending on the lead oxide percentage, which clearly shows the predominance of the lead network starting from at least 50 mol%  $PbO$  (figure 3.17). An equivalent study conducted by Suzuya *et al.* (Suzuya *et al.* 1999) on the 50 mol%  $PbO$  composition also led these authors to propose a lead environment in the form of irregular  $PbO_4$  pyramids; these units are assumed to form rings constituting the lead network. These models employing an increasing connectivity of  $PbO_4$  units to the detriment of the silicate network are close to the one proposed by several other authors (Bessada *et al.* 1994; Wang and Zhang 1996).



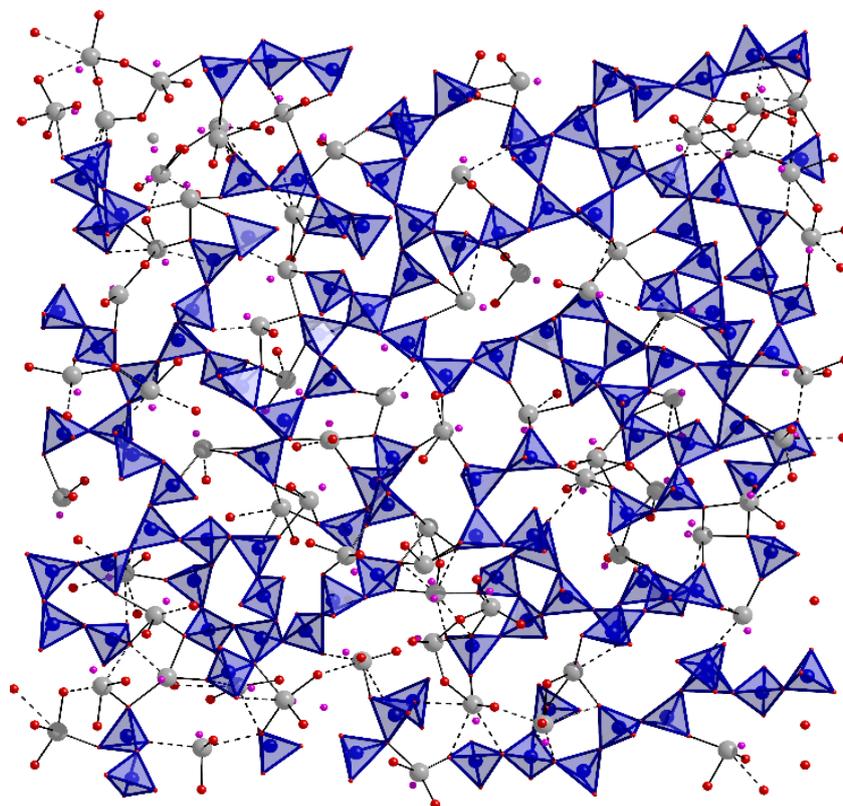
**Figure 3.17.** Local and extended structure of lead silicate glasses (30 – 65 mol% PbO) according to X-ray and neutron scattering results and reverse Monte Carlo simulation method (RMC) (Kohara et al. 2010).

COMMENT ON FIGURE 3.17.— a) Distorted  $\text{PbO}_4$  pyramidal unit resulting from RMC simulations. b) (up) Compared evolution depending on the lead content of silicate networks (blue) and lead networks (red) constituted respectively of  $\text{SiO}_4$  and  $\text{PbO}_x$  interconnected units, the proportion of  $\text{SiO}_4$  and  $\text{PbO}_x$  units that do not participate to these networks is represented in yellow, green and pink. (down) Evolution of the lead network with lead content (The interconnected  $\text{PbO}_x$  units are represented in red, and the rest in yellow, the  $\text{SiO}_4$  tetrahedrons are not represented). Reproduced with permission from (Kohara S., Ohno H., Takata M., Usuki T., Morita H., Suzuya K., Akola J., Pusztai L., Phys. Rev. B, 82, 134209, 2010). Copyright (2020) by the American Physical Society.

Alderman et al. (Alderman 2013; Alderman et al. 2013) have more recently proposed a more convincing structural description of lead silicate glasses (0 – 80 mol% PbO) also based on X-ray and neutron scattering results, but using a structural refinement of their experimental data employing empirical interatomic interaction potentials<sup>19</sup> (figures 3.18 and 3.19). Their modeling was optimized particularly by considering  $\text{Pb}^{2+}$  ions as dipoles to better account for the specific stereochemistry of the sites occupied by these ions, induced by the non-bridging  $6s^2$  doublet of lead. These authors note first of all, as for crystals, an increase with the PbO content of the average Si-O distance ascribed to the evolution of the silicon coordination sphere, and more particularly an increase of the average number of

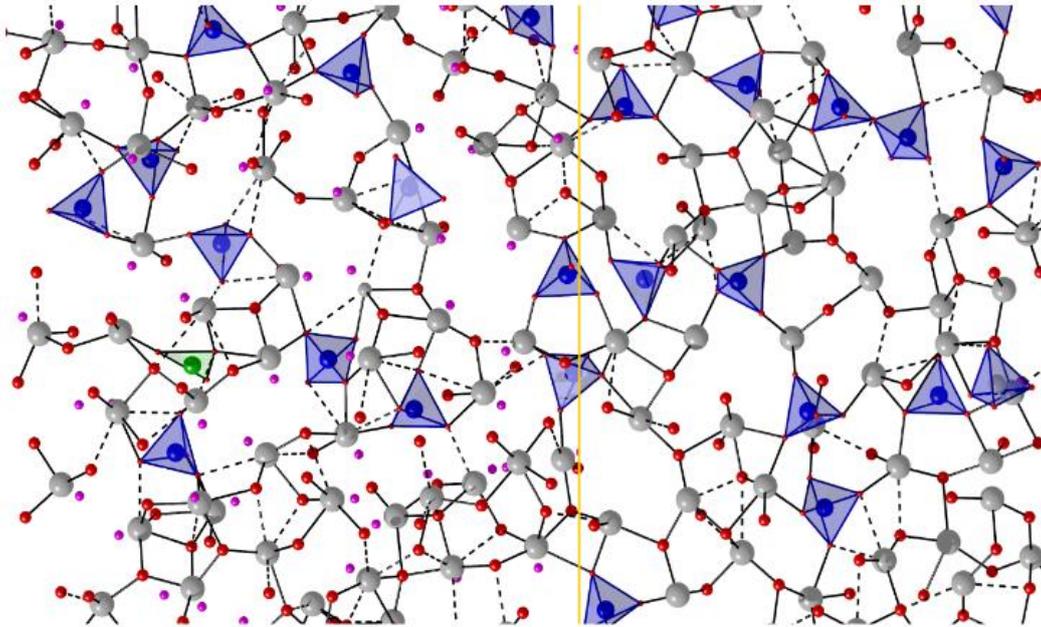
19. This technique referred to as EPSR (Empirical Potential Structure Refinement) was implemented for the study of the local environment around  $\text{Pb}^{2+}$  ions, the way in which  $\text{PbO}_n$  polyhedrons are connected and the layout of free  $6s^2$  pairs. This method, which takes into account the strong polarizability of  $\text{Pb}^{2+}$  ions is therefore more suitable than the simple reverse Monte Carlo method implemented in other studies on lead silicate glasses.

$\text{Pb}^{2+}$  ions around the non-bridging oxygen atoms. The authors also note a slight evolution of the lead environment between 35 and 80 mol%  $\text{PbO}$ : the short  $\text{Pb-O}$  distances ( $\leq 2.7 \text{ \AA}$ ) tend to become shorter and more numerous around the  $\text{Pb}^{2+}$  ions until reaching four bonds. Conversely, the number of long  $\text{Pb-O}$  distances (between 2.7 and 3.27  $\text{ \AA}$ ) tends to decrease. The environment of  $\text{Pb}^{2+}$  ions tends therefore to evolve towards that of litharge (figure 3.5) when the lead oxide rate increases and therefore when the silicon number in the second sphere of coordination of lead decreases. Consequently, the oxygen environment evolves strongly with the lead oxide rate passing from a  $\text{OSi}_2$  environment to an increasingly lead-rich environment as lead oxide is added, tending to a  $\text{OPb}_4$  environment on average, as noted in the crystals. This is reflected by the presence, in all glasses, of  $\text{PbO}_n$  polyhedrons connected by edges, which makes it possible to effectively have several  $\text{Pb}^{2+}$  ions compensating a given non-bridging oxygen atom and to have more than two non-bridging oxygen atoms around a  $\text{Pb}^{2+}$  ion, as it is the case in crystals. However, the presence of the  $\text{Pb}_2\text{O}_4$  unit proposed by Takaishi *et al.* (Takaishi *et al.* 2005) as a basic unit of the lead network independently of the  $\text{PbO}$  content (figure 3.16) was not observed in this study. Finally, an important conclusion of these works is the emphasis of the formation of areas deficient in silicate species in the lead oxide-rich glasses, due to the organization of non-bridging doublets of  $\text{Pb}^{2+}$  ions (figure 3.19). This organization of non-bonding doublets of lead is found in lead-rich crystallized lead silicates such as  $\text{Pb}_{11}\text{Si}_3\text{O}_{17}$  (figure 3.7), litharge and massicot (figure 3.5) that form channels in the crystalline structure. These areas of deficiency (voids) are not present in glasses with low lead oxide content (figure 3.18) whose structure is closer to that of alamosite  $\text{PbSiO}_3$  (figure 3.7).



**Figure 3.18.** Structural model proposed by Alderman for the 35 $\text{PbO}$  – 65 $\text{SiO}_2$  (mol%) glass. Reproduced with the permission of O. Alderman from (Alderman 2013)

COMMENT ON FIGURE 3.18.—  $\text{SiO}_4$  tetrahedrons are represented in blue,  $\text{Pb}^{2+}$  ions by the large grey spheres, and the oxygen atoms by small red spheres. The  $\text{Pb-O}$  bonds whose length is below 2.7 $\text{ \AA}$  are in solid line, those ranging between 2.7 and 3.27 $\text{ \AA}$  are in dotted line. The non-bonding doublets of  $\text{Pb}^{2+}$  ions are represented by small pink spheres.



**Figure 3.19.** Structural model proposed by Alderman for 80PbO – 20SiO<sub>2</sub> glass. To the right of the vertical separation line (yellow), the non-bonding doublets of Pb<sup>2+</sup> ions are omitted, while to the left they are represented (pink spheres). The green triangle is a SiO<sub>3</sub> defect resulting from the calculation. Reproduced with the permission of O. Alderman from (Alderman 2013).

### 3.3.3.3. Summary of the structural evolution of binary SiO<sub>2</sub>-PbO glasses and the role of lead

All the structural results published on the binary SiO<sub>2</sub>-PbO glasses presented in this chapter tend to highlight that the structural role of lead does not change essentially with the PbO content and that it is closer to the role of a glass former oxide. Its short distance environment is very asymmetric, of deformed pyramidal type with triangular or square base (PbO<sub>3</sub>, PbO<sub>4</sub>) with lead at the vertex and in all the cases the free 6s<sup>2</sup> pair of Pb<sup>2+</sup> ions stereochemically active, similar to the PbO crystalline phases (massicot and litharge) and lead silicates (sections 3.2.2 and 3.3.2). The lead environment would therefore slightly evolve as a function of PbO content, with only a light reinforcement of short distance PbO bonds, more tetracoordinated (PbO<sub>4</sub>) environments and the increasing presence of Pb-O-Pb connections with bonds by vertices and edges between the PbO<sub>n</sub> polyhedrons forming an increasingly significant lead network, as in the case of crystalline phases (figures 3.7 and 3.9). Similar to the latter (figures 3.7 and 3.8), a substantial evolution of the silicate network with the PbO content is observed, with gradual depolymerization (Si-O-Si bonds disappear to the benefit of Si-O-Pb bonds, figures 3.12 and 3.14), silicon atoms having an increasing number of Pb<sup>2+</sup> ions as second neighbors. However, for PbO contents above that of lead *oxy-cyclosilicate* (Pb<sub>2</sub>SiO<sub>4</sub>, 60 mol% PbO) from which complete depolymerization of the silicate network was expected – as it is the case for alkaline silicate systems, for example – with only isolated SiO<sub>4</sub> units (Q<sup>0</sup>), small-size units having Si-O-Si bonds are still present even for the lead-richest compositions (figures 3.12, 3.13 and 3.14). The presence of these units in the lead network for lead-rich compositions as well as the existence of an environment distribution for Pb<sup>2+</sup> ions and Pb-O-Pb and Pb-O-Si connections in the structure of glasses (and thus of corresponding liquids at the melting moment and before quenching) must therefore contribute to slowing down the crystallization of the supercooled liquid during quenching and therefore make it easier to obtain a glass. On the other hand, in the case of alkaline and alkaline-earth cations that are bound to O<sup>2-</sup> anions only by ionic and non-directional bonds and that have quite spherical environments in the silicate glasses, it is clear that the reorganization of the liquid leading to crystals is facilitated and therefore it is not possible to vitrify silicate liquids for high alkaline and alkaline-earth oxide contents. All these structural results can be used to explain to a large extent the variation of physical properties of the binary SiO<sub>2</sub>-PbO glasses as a function of PbO content, as mentioned in section 3.3.3.1. Hence the depolymerization of the silicate network, the fact that the average force of the bonds between oxygen and its Si and Pb neighbors decreases with the lead content (Pb-O bonds being weaker than Si-O bonds) and the strong polarizability of Pb<sup>2+</sup> ions (and therefore their strong deformability) explain the decrease with the PbO content of the liquid viscosity, of the vitreous

transition temperature and of the electrical resistivity (figure 3.10). Likewise, the increase of the thermal expansion coefficient of SiO<sub>2</sub>-PbO glasses with the PbO content can be explained by a decrease of the average force of bonds, like for the alkaline silicate glasses; however, the Pb-O bonds having a iono-covalent character, unlike the bonds between alkaline R<sup>+</sup> ions and the O<sup>2-</sup> anions, which are purely ionic, the expansion coefficient of alkaline silicate glasses remains higher than that of lead silicate glasses for the same R<sub>2</sub>O and PbO molar content (Scholze 1980). Finally, the decrease in the molar volume of SiO<sub>2</sub>-PbO glasses when lead concentration increases for the lowest PbO contents (Shelby 1983; Kaur *et al.* 2013; Ben Kacem *et al.* 2017) might be explained by the decrease in the free volume existing in the silicate glasses rich in SiO<sub>2</sub> following the gradual breaking of the Si-O-Si bonds. While the stabilization of the free volume, and even its reincrease from 50 mol% PbO, could be explained by the formation of an increasingly extended lead network and by the presence of an increasing number of free 6s<sup>2</sup> pairs associated with lead creating deficient area (voids) in the structure (figure 3.19). It is important to note that the strong polarizability of Pb<sup>2+</sup> ion and the existence of the free 6s<sup>2</sup> pair stereochemically active may be at the origin of the significantly higher solubility of metallic oxides such as Cr<sub>2</sub>O<sub>3</sub> in silicate glasses containing lead oxide compared to classical silicate glasses containing alkaline and alkaline-earth oxides and in which the chromium oxide is little soluble (Ashour and Shehata 1972; Volf 1984).

### 3.4. Glasses of SiO<sub>2</sub>-PbO-R<sub>2</sub>O system (R= Na, K)

#### 3.4.1. Overview of ternary SiO<sub>2</sub>-PbO-R<sub>2</sub>O glasses

After the binary SiO<sub>2</sub>-PbO glasses, let us focus on the structure and properties of ternary SiO<sub>2</sub>-PbO-R<sub>2</sub>O glasses, where R represents an alkaline element such as Na or K. These ternary glasses have many applications in fields such as luxury glassmaking (crystal glass making), glazes and enamels and glasses absorbing the ionizing radiation, as already mentioned in chapter 1. Hence the crystal glass belongs to the ternary SiO<sub>2</sub>-PbO-K<sub>2</sub>O system with molar contents for example of about 77 % SiO<sub>2</sub>, 11 % K<sub>2</sub>O and 10 % PbO (with, according to productions, a little bit of Na<sub>2</sub>O, Al<sub>2</sub>O<sub>3</sub> and traces of fining agents such as Sb<sub>2</sub>O<sub>3</sub>), which leads to PbO mass contents of about 28 % in this case. While, for example, tin-opacified lead alkaline mixed heritage glazes have mass contents of about 20-40 % PbO and 5-12 % Na<sub>2</sub>O + K<sub>2</sub>O, compared to contents of about 45-60 % PbO and less than 2 % Na<sub>2</sub>O + K<sub>2</sub>O for lead transparent glazes (Tite *et al.* 1998, chapter 10). In the case of crystal glass, there is a multiple interest of adding lead to the binary glass of potassium silicates (melting, forming, machining, optical properties, napping of glazes, see chapter 1). In parallel, the addition of K<sub>2</sub>O to the binary SiO<sub>2</sub>-PbO glass makes it possible to reduce the demixing tendency of lead silicate glasses having low or moderate PbO contents (< 35 mol%) (section 3.3.3.1) (Calvert and Shaw 1970; Vogel 1994) and also facilitates the melting of the vitrifiable mixture. Given the importance both at industrial and heritage levels of the ternary SiO<sub>2</sub>-PbO-R<sub>2</sub>O glasses, many studies related to their hydrolytic resistance in submerged medium or in humid atmosphere were conducted with a twofold purpose: sanitary (Angeli *et al.* 2016) and conservation (Palomar *et al.* 2020). The alteration of this type of glasses is widely dealt with in chapter 13.

#### 3.4.2. Structure of ternary SiO<sub>2</sub>-PbO-R<sub>2</sub>O glasses

The structure of binary SiO<sub>2</sub>-PbO glasses as a function of their PbO content was largely presented in section 3.3.2. This section focuses on the effect on the structure of the glass and the lead environment of the simultaneous presence of PbO and an alkaline oxide (such as Na<sub>2</sub>O or K<sub>2</sub>O). The alkaline oxides are well known for their modifier role in the binary SiO<sub>2</sub>-R<sub>2</sub>O silicate glasses, leading to a more or less marked depolymerization of the silicate network as a function of the R<sub>2</sub>O content (Maekawa *et al.* 1991). It is interesting to consider here the way in which the structure of the binary lead silicate glasses is affected when a modifier oxide (here R<sub>2</sub>O) is added to their composition and particularly on the way in which the environment and the distribution of Pb<sup>2+</sup> ions can be modified. However, unlike the structural studies conducted on binary lead silicate glasses, which are particularly abundant in the literature, those related to ternary SiO<sub>2</sub>-PbO-R<sub>2</sub>O glasses are less numerous, despite the important industrial applications of these glasses. Several spectroscopy methods were implemented for the study of these glasses, such as Raman, IR and XPS spectroscopies.

At the same time, while the crystalline phases of the PbO-SiO<sub>2</sub> system were the object of a quasi-systematic structural study (section 3.3.2), very little is known on more complex crystalline compounds, such as those of ternary SiO<sub>2</sub>-PbO-R<sub>2</sub>O systems. Thus, despite the considerable number of possible compositions, crystallized lead silicates containing alkaline or alkaline-earth cations were the object of structural studies only as part of both rare and ancient works related to K<sub>2</sub>Pb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> disilicate (McMurdie 1941) and its isotype K<sub>2</sub>Pb<sub>2</sub>Ge<sub>2</sub>O<sub>7</sub> (Bassi *et al.* 1965), the cyclosilicate PbCa<sub>2</sub>Si<sub>3</sub>O<sub>9</sub> or *margarosanite* (Freed *et al.* 1969) and the oxy-monosilicate Li<sub>10</sub>PbO<sub>2</sub>(SiO<sub>4</sub>)<sub>2</sub> (Brandes *et al.* 1994). Despite different lead contents, these structures show that the depolymerizing effect of alkaline and alkaline-earth oxides – at various degrees depending on their content – support, similarly to binary lead silicates, asymmetric environments for Pb<sup>2+</sup> ions (free 6s<sup>2</sup> pair stereochemically active) and strong Pb-O-Pb cross-linkages. This effect is particularly prominent for the crystalline phase Li<sub>10</sub>PbO<sub>2</sub>(SiO<sub>4</sub>)<sub>2</sub> which has infinite -Pb-O- chains thanks to its exceptionally high rate of alkaline elements that fully depolymerize the silicate network.

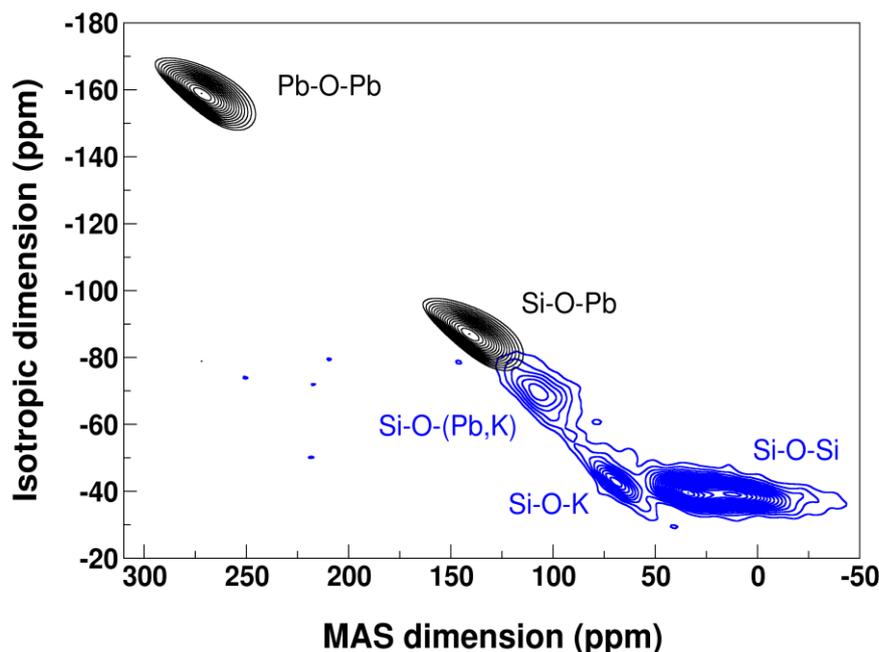
#### 3.4.2.1. *The silicate vitreous network*

There are several studies on ternary SiO<sub>2</sub>-PbO-R<sub>2</sub>O glasses in the literature varying the relative proportions of three oxides. Thus, by adding increasing Na<sub>2</sub>O contents to a glass of composition 50 SiO<sub>2</sub> – 50 PbO (mol%) or increasing PbO contents to a glass of composition 75 SiO<sub>2</sub> – 25 Na<sub>2</sub>O (mol%), studies conducted by <sup>29</sup>Si NMR (Shrikhande *et al.* 2001, 2007) have clearly highlighted a depolymerization of the silicate network, i.e. a decrease of the proportion of bridging oxygen atoms connecting the silicon atoms, as it is the case when increasing PbO contents are added to SiO<sub>2</sub> (figure 3.12). A similar structural evolution has been observed during the gradual substitution of SiO<sub>2</sub> by PbO (up to 50 mol%) in an industrial crystal glass whose composition is close to 77.9 SiO<sub>2</sub> – 10.7 PbO – 11.4 K<sub>2</sub>O (mol%), as presented in figure 13.1. For this latter glass, <sup>29</sup>Si NMR has shown that it was essentially constituted of Q<sup>3</sup> units (59 %) and Q<sup>4</sup> units (41 %), which corresponds to 25.7 % of non-bridging oxygen atoms and is in perfect agreement with what is obtained by calculation from its composition assuming that K<sub>2</sub>O and PbO fully transfer their O<sup>2-</sup> anions to the silicate network (Angeli *et al.* 2016) (complete acid-base reaction). This may suggest that these two oxides have similar effects on the silicate network and a similar structural role. However, for higher PbO contents (> 30 mol%), there is an increasing disagreement between the result of the calculation of the proportion of non-bridging oxygen atoms based on the glass composition and the NMR results (chapter 13). This strongly suggests that for quite high lead contents, a part of the oxygen brought by PbO is in the form of Pb-O-Pb bonds, as it is the case of lead-rich binary SiO<sub>2</sub>-PbO glasses (section 3.3.3.2). A study conducted by XPS (O 1s) on ternary glasses by gradually substituting PbO by Na<sub>2</sub>O also confirms this (Gee *et al.* 2001).

#### 3.4.2.2. *Environment and distribution of lead and alkaline elements in the vitreous network*

To our knowledge, unlike the binary SiO<sub>2</sub>-PbO glasses, there is no EXAFS, XANES, or X-ray or neutron scattering or <sup>207</sup>Pb NMR data available in the literature for the ternary SiO<sub>2</sub>-PbO-R<sub>2</sub>O glasses that may bring direct information on the lead environment in these glasses. The situation is therefore different from the binary SiO<sub>2</sub>-PbO glasses for which it was highlighted by these techniques that lead in the form of Pb<sup>2+</sup> ions (with its stereochemically active free 6s<sup>2</sup> pair) was localized in very asymmetric sites connected to the silicate network by quite strong Si-O-Pb bonds, with the possibility that these sites are also connected to one another for high PbO contents. However, by analogy with the above mentioned ternary crystalline phases of alkaline or alkaline-earth lead silicate, it is highly probable that in the ternary glasses of the same systems the Pb<sup>2+</sup> ions are also located in asymmetric environments with their stereochemically active free 6s<sup>2</sup> pair. Moreover, a recent study conducted by NMR on ternary SiO<sub>2</sub>-PbO-K<sub>2</sub>O glasses enriched in <sup>17</sup>O brought abundant information on the way in which Pb<sup>2+</sup> ions are distributed with respect to K<sup>+</sup> ions in the vitreous network structure depending on the PbO content (substituted for SiO<sub>2</sub>) (figure 3.20) (Angeli *et al.* 2016). This study comes close to the one of Lee *et al.* (Lee *et al.* 2015) conducted on binary SiO<sub>2</sub>-PbO glasses (figure 3.13) and is presented in detail in chapter 13 (figure 13.2). It shows the evolution of the proportion of various types of connections between Si, Pb, O and K in the glass structure depending on its lead content: Si-O-Si, Si-O-K, Si-O-Pb, Si-O-(Pb,K) and Pb-O-Pb. It appears that for the lowest PbO contents such as that of crystal glass (~ 11 mol%), Pb<sup>2+</sup> ions share with a part of the K<sup>+</sup> ions the non-bridging oxygen atoms of the structure in the form of mixed Si-O-(Pb,K) bonds,

a significant part of  $K^+$  ions remaining however connected only to non-bridging oxygen atoms in the form of Si-O-K bonds (figure 3.20).



**Figure 3.20.**  $^{17}O$  MQ-MAS spectrum of a crystal glass (77.1  $SiO_2$  – 10.6  $PbO$  – 11.3  $K_2O$  – 0.8  $Na_2O$  – 0.2  $Sb_2O_3$  mol%) in blue showing the contribution of oxygen atoms of Si-O-Si, Si-O-K and Si-O-(Pb,K) bonds (Angeli *et al.* 2016). The position of the contribution of Si-O-Pb and Pb-O-Pb bonds obtained by Lee *et al.* (Lee *et al.* 2014) for PbO-rich binary  $SiO_2$ -PbO glasses is represented in black.

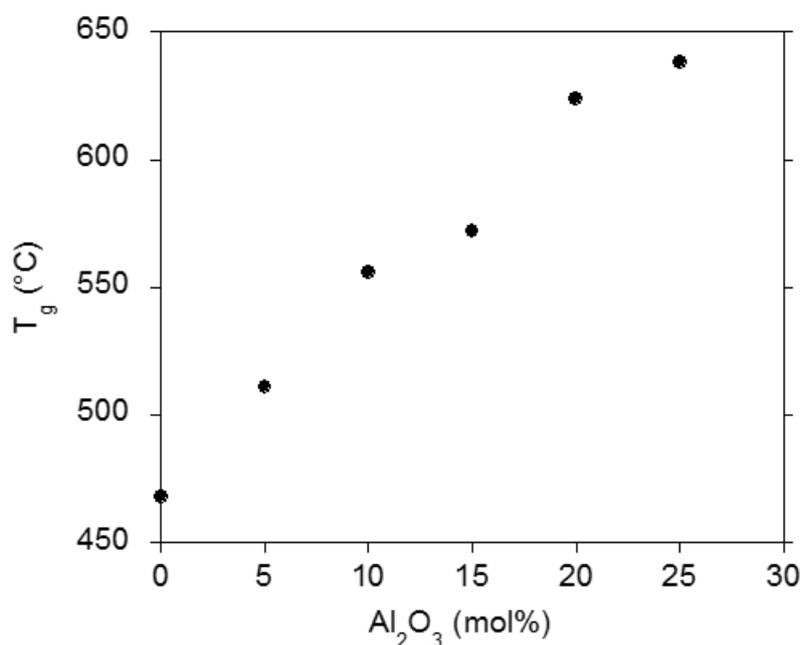
COMMENT ON FIGURE 3.20.— Reproduced with permission from (Angeli, F., Jollivet, P., Charpentier, T., Fournier, M., Gin, S., Environ. Sci. Technol., 50, 11549–11558, 2016). Copyright (2020) American Chemical Society.

It is important to note that for these PbO contents the presence of oxygen atoms isolated from the silicate network in the form of Pb-O-Pb bonds is not observed, which shows that PbO oxide fully reacts with  $SiO_2$ , in agreement with the above mentioned  $^{29}Si$  NMR results. On the other hand, when the PbO content increases up to at least 30 mol%, all the  $K^+$  ions share the non-bridging oxygen atoms with the  $Pb^{2+}$  ions. It is only for higher PbO contents (> 30 mol%) that are highlighted Pb-O-Pb connections, as suggested by  $^{29}Si$  NMR and (O 1s) XPS studies mentioned in section 3.4.2.1. This is consistent with the increasing clusterization of  $PbO_n$  entities and the gradual formation of a lead network as for the binary lead silicate glasses and is in agreement with the structure of the above mentioned ternary crystalline phases of lead-rich alkaline or alkaline-earth silicates. This was confirmed by a molecular dynamic study and adjustment of the NMR results by reverse Monte Carlo method (chapter 13, figure 13.4). Moreover, Si-O-Pb connections without  $K^+$  ions in their nearest neighborhood should be increasingly abundant. The significant change of the environment of potassium ions with the lead content highlighted for these glasses is in agreement with the clear evolution of the (Na 1s) XPS spectrum observed with the lead content for 70  $SiO_2$  – x  $PbO$  – (30-x)  $Na_2O$  (mol%) glasses (Gee *et al.* 2001). These structural evolutions, and particularly the formation of mixed Si-O-(Pb,K) bonds to the detriment of simple Si-O-K bonds, explains the effect of the partial substitution of  $SiO_2$  by PbO on the electrical resistivity (increase) of alkaline silicate glasses (Scholze 1980), the large  $Pb^{2+}$  ions impeding on the mobility of alkaline ions.

### 3.5. Glasses of SiO<sub>2</sub>-PbO-Al<sub>2</sub>O<sub>3</sub> system

#### 3.5.1. Overview of ternary SiO<sub>2</sub>-PbO-Al<sub>2</sub>O<sub>3</sub> glasses

Though the glasses of the ternary SiO<sub>2</sub>-PbO-Al<sub>2</sub>O<sub>3</sub> system have ancient applications, such as glazes deposited on the surface of ceramic objects<sup>20</sup> (Tite *et al.* 1998) and much more recently as materials containing rare earth ions for optics and dosimetry (Bhargavi *et al.* 2012, 2014, 2015; Rao *et al.* 2013, 2014), as well as for the protection against ionizing radiation (Singh *et al.* 2014), only a limited number of works have been published on the glasses of this system. It is particularly the case of studies conducted on their structure and on the impact of the presence of alumina on the environment of Pb<sup>2+</sup> ions in the vitreous network, compared to the extent of the studies conducted on binary SiO<sub>2</sub>-PbO glasses (section 3.3.3). Some examples are essentially the recent studies conducted by Bhargavi *et al.* (Bhargavi *et al.* 2012, 2014, 2015), Rao *et al.* (Rao *et al.* 2013, 2014) and Ben Kacem (Ben Kacem 2017) using vibrational or optical spectroscopies, by Roisine (Roisine 2018) using NMR and Raman spectroscopies and X-ray and neutron scattering, and the more ancient ones of Prabakar and Rao (Prabakar and Rao 1991) using NMR spectroscopy and of Roy (Roy 1990) using infrared spectroscopy. It is important to note however that other structural studies have been conducted on more complex glasses of the SiO<sub>2</sub>-PbO-Al<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub> system containing boron besides aluminum, but they are not covered here (Sawvel *et al.* 2005; Saini *et al.* 2009; Falconeri *et al.* 2012). Though the extension of the vitrifiable domain in the ternary SiO<sub>2</sub>-PbO-Al<sub>2</sub>O<sub>3</sub> system has not been reported in the literature, it can however be stated that the Al<sub>2</sub>O<sub>3</sub> content of the studied glasses never exceeds 30 mol% (Ben Kacem 2017) and that glasses with only 10 mol% SiO<sub>2</sub> (10 SiO<sub>2</sub> – 80 PbO – 10 Al<sub>2</sub>O<sub>3</sub>) could be obtained by classical melting- quenching (Prabakar and Rao 1991). It is interesting to note that hyperquenching can be used to prepare binary Al<sub>2</sub>O<sub>3</sub>-PbO glasses without silicon and with PbO contents ranging between 50 and 95 mol% (Kantor *et al.* 1973; Morikawa *et al.* 1981).



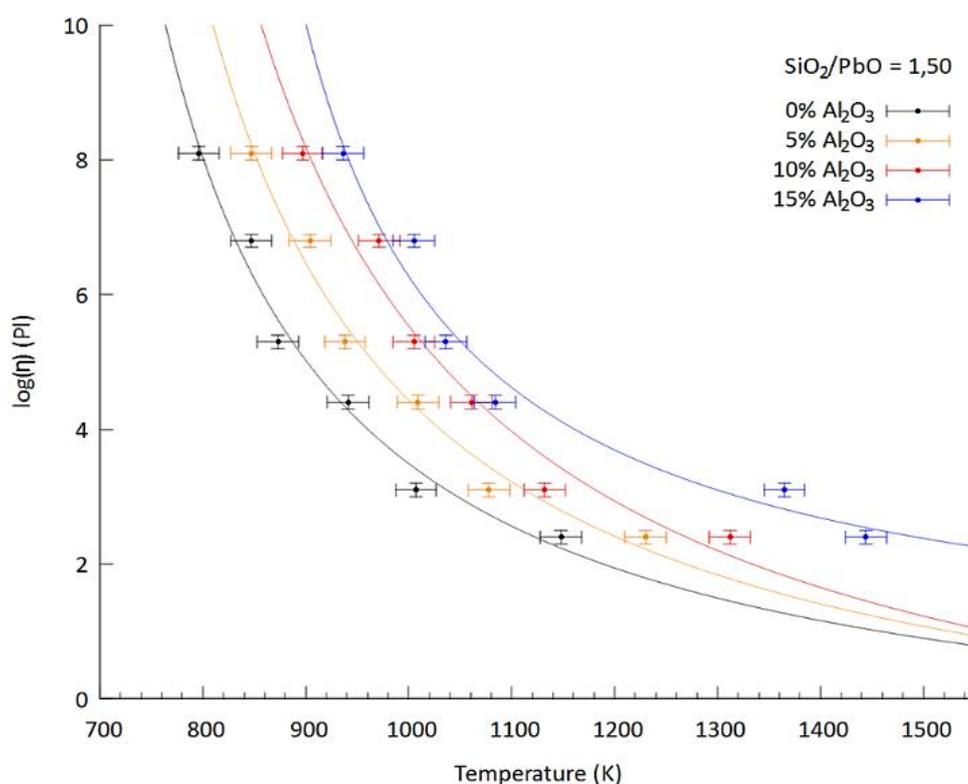
**Figure 3.21.** Evolution of the glass transition temperature  $T_g$  adding increasing Al<sub>2</sub>O<sub>3</sub> contents to the 40SiO<sub>2</sub> – 60PbO (mol%) composition (according to the data of Roisine (Roisine 2018))

There is a multifaceted interest in adding aluminum to the composition of lead silicate glasses due to the significant effect of this element on their properties. Hence, Al<sub>2</sub>O<sub>3</sub> is assumed to increase the mechanical resistance of binary glasses of the SiO<sub>2</sub>-PbO system and to decrease their crystallization tendency

20. In the case of highly lead-rich lead glazes, the origin of the alumina in their composition (< 10 % Al<sub>2</sub>O<sub>3</sub> mass) (Tite *et al.* 1998; Roisine 2018) may be either the raw materials deposited at the surface of ceramic objects before firing, or the partial dissolution in the thin layer of melting liquid rich in SiO<sub>2</sub> and in PbO of a fraction of alumina initially present in the paste constituting the objects.

(Mylyanych *et al.* 1999). Moreover, according to the phase diagram of the  $\text{SiO}_2\text{-PbO-Al}_2\text{O}_3$  system (Chen *et al.* 2001), the introduction of alumina in the binary  $\text{SiO}_2\text{-PbO}$  system would reduce the demixing tendency of the liquid. However, the liquidus temperature tends to significantly increase, particularly for the lead-richest compositions corresponding in particular to the domain of lead glazes, which may pose melting problems and therefore limits the amount of alumina that can be added. Moreover, for this type of  $\text{PbO}$ -rich compositions, the glass transition temperature and the viscosity of the liquid increase rapidly with the alumina rate (figures 3.21 and 3.22).

It is also important to note the existence of a large number of ternary crystalline phases (11 phases according to Chen *et al.* (Chen *et al.* 2001)) in this domain of composition that may contribute, besides the strong increase in viscosity of the melting liquid, to facilitate its vitrification during cooling according to the “frustration” principle (Mysen and Richet 2005). Finally, the positive effect of the presence of aluminum in lead silicate glasses containing rare earth ions is worth mentioning, as it leads to a better dispersion of the latter in the vitreous structure (destruction of clusters) (Rao *et al.* 2013).



**Figure 3.22.** Evolution of viscosity  $\eta$  (in poiseuilles  $Pl$ ) as a function of temperature after adding increasing  $\text{Al}_2\text{O}_3$  contents to the  $40\text{SiO}_2 - 60\text{PbO}$  (mol%) composition (Roisine 2018)

### 3.5.2. Structure of ternary $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-PbO}$ glasses

#### 3.5.2.1. Crystalline phases of $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-PbO}$ system

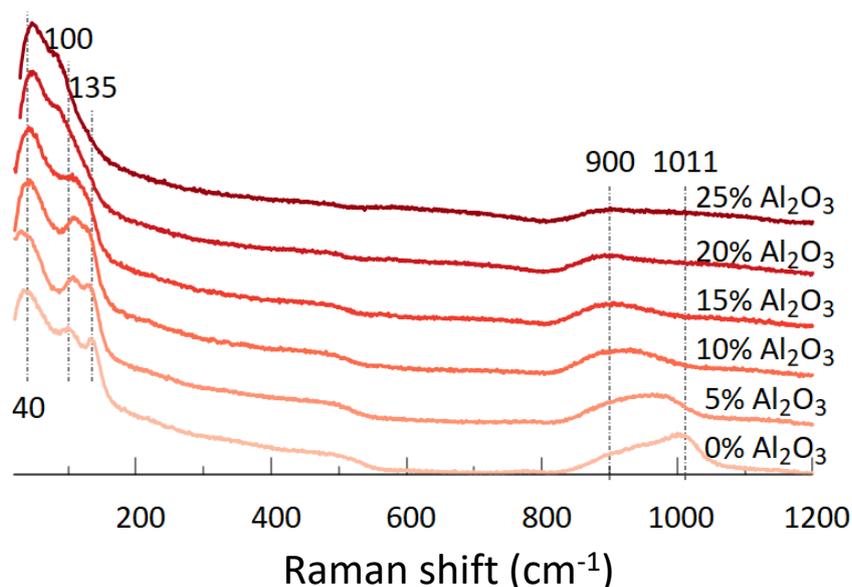
Similar to the above-mentioned ternary systems of alkaline or alkaline-earth lead silicates (section 3.4.2), the known structures of ternary  $\text{Pb-Si-Al-O}$  oxides are very few and come down to lead feldspar  $\text{PbAl}_2\text{Si}_2\text{O}_8$  (Benna *et al.* 1996) and other structures of zeolite type (Ronay and Seff 1985; Yeom *et al.* 1997). However, unlike the crystalline phases of  $\text{SiO}_2\text{-PbO}$ ,  $\text{SiO}_2\text{-PbO-R}_2\text{O}$  and  $\text{SiO}_2\text{-PbO-R}'\text{O}$  (R: alkaline and  $\text{R}'$ : alkaline-earth) systems, in these structures the lengths of  $\text{Pb-O}$  bonds are relatively regular. Their environment in  $\text{PbAl}_2\text{Si}_2\text{O}_8$  is thus very similar to that of  $\text{Sr}^{2+}$  ions in the equivalent feldspar highlighting the absence of stereochemical activity of the lead  $6s^2$  pair in this very aluminum-rich phase. This is likely explained by the force of the aluminosilicate skeleton and its maximal cross-linking.

Bridging two  $\text{SiO}_4$  and  $\text{AlO}_4$  tetrahedrons, an oxide anion has available only about 0.25 u.v. to share with the neighboring  $\text{Pb}^{2+}$  ions, which forbids the formation of strong bonds, and hence the highly structuring Pb-O-Pb cross-linkages observed in the depolymerized silicates of  $\text{SiO}_2$ -PbO,  $\text{SiO}_2$ -PbO- $\text{R}_2\text{O}$  and  $\text{SiO}_2$ -PbO-R'O systems. In this type of aluminum-rich crystalline structure,  $\text{Pb}^{2+}$  ions compensate the charge of the  $\text{AlO}_4^-$  tetrahedral units, unlike the previous systems considered in this chapter.

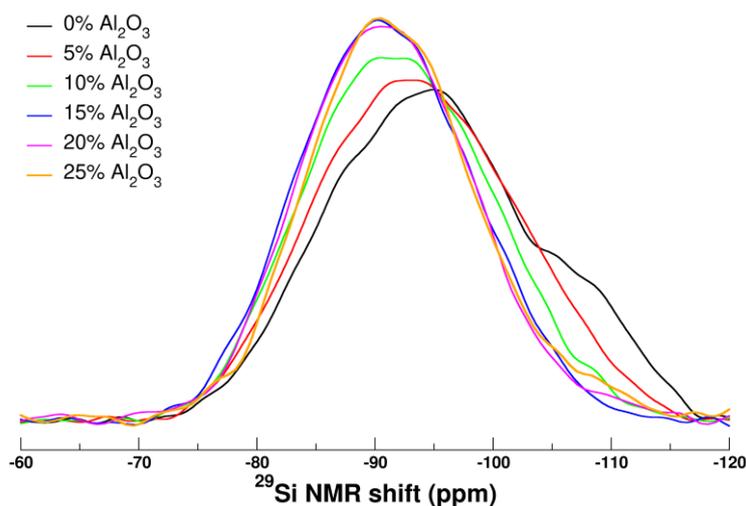
### 3.5.2.2. Aluminosilicate vitreous network and the lead environment

Since the earliest structural studies conducted on ternary  $\text{SiO}_2$ - $\text{Al}_2\text{O}_3$ -PbO glasses (Prabakar et Rao 1991),  $^{27}\text{Al}$  NMR revealed that aluminum was incorporated in their structure essentially in the form of  $\text{AlO}_4^-$  tetrahedral entities and that a part of the  $\text{Pb}^{2+}$  ions present in the structure acted as charge compensators of these entities, for  $\text{Al}_2\text{O}_3$  contents of 10 mol% and PbO contents ranging between 30 and 80 mol%. Concerning the silicate network, the studies conducted more recently on various series of ternary glasses by Raman and  $^{29}\text{Si}$  NMR have shown that the addition of alumina or its partial substitution to PbO in the binary  $\text{SiO}_2$ -PbO glasses led in all cases to a strong evolution of their structure (Ben Kacem 2017; Roisine 2018) (figures 3.23 and 3.24).

It can be observed that, by adding increasing quantities of alumina to lead silicate glasses, there is a shift towards low energies and a change in the shape of Raman band between 800 and 1 200  $\text{cm}^{-1}$  associated with elongation vibrations of T-O bonds of tetrahedral entities  $\text{TO}_4$  (T = Si, Al) (figure 3.23). The evolution of this band can only be explained by the gradual incorporation of aluminum in the form of  $\text{AlO}_4^-$  units in the silicate network and not by a depolymerization of the latter according to  $^{17}\text{O}$  NMR results (figures 3.25 and 3.26) and the evolution of physical properties (strong increase of  $T_g$  and viscosity, figures 3.21 and 3.22).



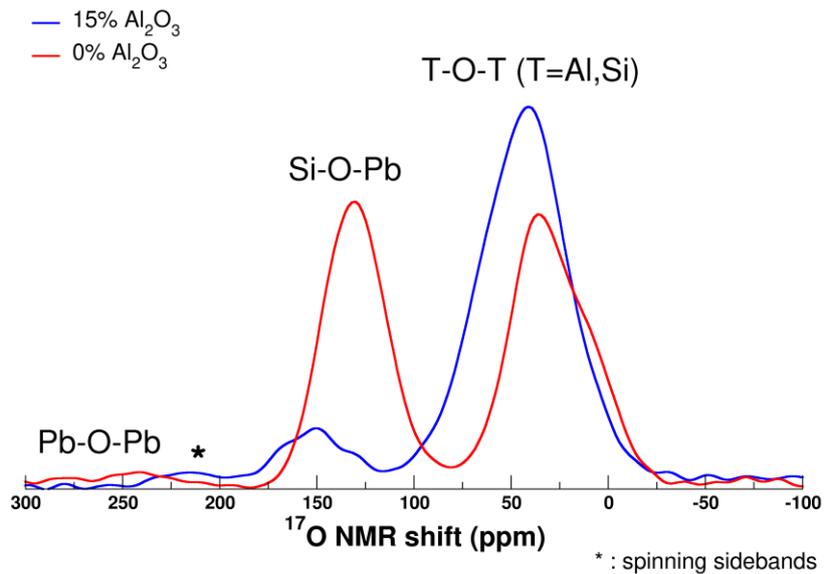
**Figure 3.23.** Evolution of Raman spectra of ternary  $\text{SiO}_2$ - $\text{Al}_2\text{O}_3$ -PbO glasses obtained by adding increasing  $\text{Al}_2\text{O}_3$  contents (0 – 25 mol%) to the binary 60  $\text{SiO}_2$  – 40 PbO (mol%) glass (Roisine 2018)



**Figure 3.24.** Evolution of  $^{29}\text{Si}$  MAS NMR spectra of ternary  $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-PbO}$  glasses obtained by adding increasing  $\text{Al}_2\text{O}_3$  contents (0 – 25 mol%) to the binary 60  $\text{SiO}_2$  – 40  $\text{PbO}$  (mol%) glass. For the glass without  $\text{Al}_2\text{O}_3$ , the contributions towards – 110 and – 95 ppm correspond respectively to  $Q^4$  and  $Q^3$  entities (Roisine 2018).

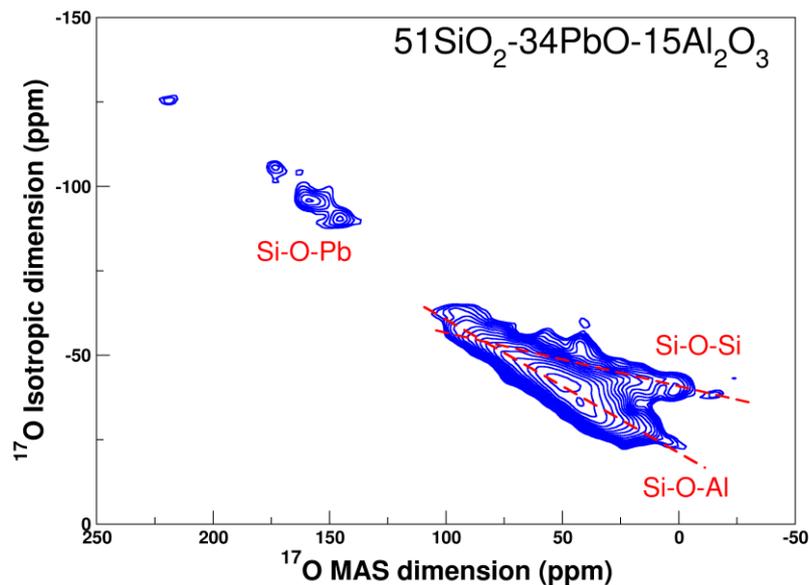
Indeed, it is known for other silicate glasses without lead that the presence of 4-fold coordinated aluminum in the silicon environment (as a second neighbor) leads to a shift of the elongation vibration bands of  $Q^n$  units towards low energies (Rossano and Mysen 2012). The evolution of the  $^{29}\text{Si}$  NMR signal towards the higher values of the chemical shift with the  $\text{Al}_2\text{O}_3$  content (figure 3.24) can be similarly explained, the chemical shift of  $Q^n$  units increasing when a growing number of  $\text{AlO}_4^-$  tetrahedrons are present as second neighbors of  $\text{SiO}_4$  units (Kirkpatrick *et al.* 1985). The low energy region (100-200  $\text{cm}^{-1}$ ) of Raman spectra – corresponding to Pb-O vibrations (Ben Kacem 2017) – has also a strong evolution with the content of alumina added to the binary  $\text{SiO}_2\text{-PbO}$  glasses (figure 3.23). A strong evolution in this region of the spectrum has also been observed if  $\text{PbO}$  is gradually replaced by  $\text{Al}_2\text{O}_3$  with constant  $\text{SiO}_2$  content (Ben Kacem 2017). This shows a significant change of local environment of  $\text{Pb}^{2+}$  ions, which may be explained by the gradual disappearance of quite strong Pb-O-(Pb,Si) bonds to the benefit of weaker Pb-O-Al bonds associated with the role of charge compensator of  $\text{AlO}_4^-$  units played by an increasing number of  $\text{Pb}^{2+}$  ions. Indeed, the direct study of the aluminum environment by  $^{27}\text{Al}$  NMR in these glasses (figure 3.27) shows that it is still predominantly present in the form of  $\text{AlO}_4^-$  (and therefore necessarily locally compensated by  $\text{Pb}^{2+}$  ions, which are the only cations susceptible to play this role in ternary glasses), with the increasing but still minority contribution of  $\text{AlO}_5$  units highlighted by  $^{27}\text{Al}$  MQMAS NMR for the highest alumina contents (> 15 mol%  $\text{Al}_2\text{O}_3$ ) (Roisine 2018).

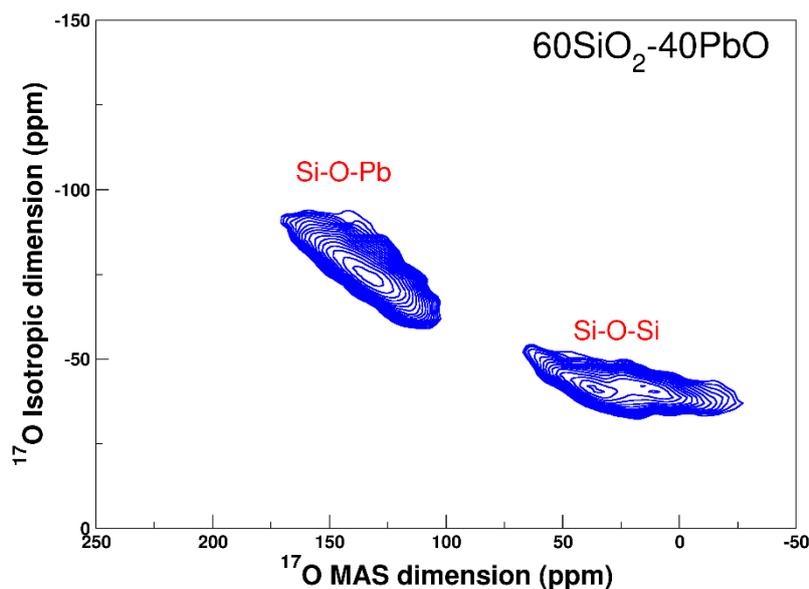
Concerning the oxygen atoms in the structure, the  $^{17}\text{O}$  NMR study of  $^{17}\text{O}$  –enriched ternary glasses also confirms a strong evolution of the lead environment following the addition of alumina in the binary  $\text{SiO}_2\text{-PbO}$  glasses (figures 3.25 and 3.26). Indeed, a strong decrease of the contribution of Si-O-Pb bonds to the benefit of Si-O-Al bonds can be noted, thus showing a strong repolymerization of the vitreous network (strong decrease of the proportion of non-bridging oxygen atoms). Moreover, the small number of Pb-O-Pb bonds present in the binary glass seems to disappear in the ternary glass (figure 3.25), which may suggest a better dispersion of lead in the aluminosilicate network, in agreement with the results obtained by Raman spectroscopy (region of low-frequency spectra).



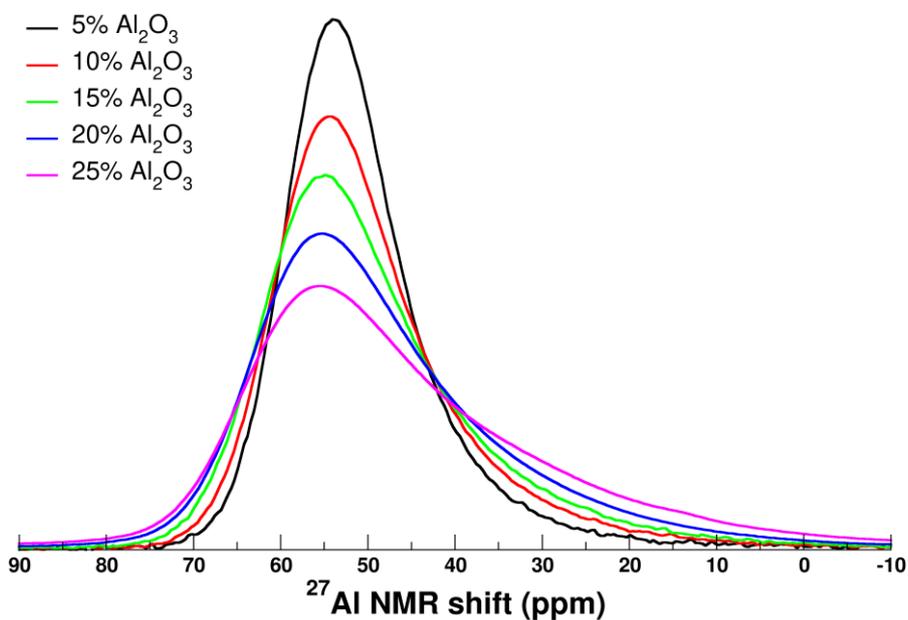
**Figure 3.25.** Comparison of  $^{17}\text{O}$  MAS NMR spectra of  $60 \text{ SiO}_2 - 40 \text{ PbO}$  et  $51 \text{ SiO}_2 - 34 \text{ PbO} - 15 \text{ Al}_2\text{O}_3$  (mol%) glasses enriched in  $^{17}\text{O}$  (\*: rotational band) (Roisine 2018)

However, additional studies conducted on the same glasses by X-ray scattering did not reveal a significant evolution of the average Pb-Pb distance during the addition of alumina to the binary  $\text{SiO}_2$ -PbO glasses (Roisine 2018). According to the structural results concerning the stereochemistry of  $\text{Pb}^{2+}$  ions in  $\text{Al}_2\text{O}_3$ -rich crystalline phases such as  $\text{PbAl}_2\text{Si}_2\text{O}_8$  (section 3.5.2.1) for which the free  $6s^2$  pairs are stereochemically inactive, it may be thought that the same is valid for ternary  $\text{SiO}_2$ - $\text{Al}_2\text{O}_3$ -PbO glasses at least for  $\text{Pb}^{2+}$  ions playing the role of charge compensator of  $\text{AlO}_4^-$  units, excess  $\text{Pb}^{2+}$  ions being likely to preserve their  $6s^2$  pair active, similar to the binary  $\text{SiO}_2$ -PbO glasses.





**Figure 3.26.**  $^{17}\text{O}$  MQMAS NMR spectra of 60  $\text{SiO}_2$ –40  $\text{PbO}$  and 51  $\text{SiO}_2$ –34  $\text{PbO}$ –15  $\text{Al}_2\text{O}_3$  glasses in mol% enriched in  $^{17}\text{O}$  (Roisine 2018)



**Figure 3.27.** Evolution of  $^{27}\text{Al}$  MAS NMR spectra of ternary  $\text{SiO}_2$ - $\text{Al}_2\text{O}_3$ - $\text{PbO}$  glasses obtained by adding increasing  $\text{Al}_2\text{O}_3$  contents (0–25 mol%) to the binary 60  $\text{SiO}_2$ –40  $\text{PbO}$  (mol%) glass (Roisine 2018)

COMMENT ON FIGURE 3.27.— The signal broadening and shift towards higher values of the chemical shift are due respectively to an increase of the quadrupolar coupling constant  $C_Q$  and an increase of the isotropic chemical shift  $\delta_{\text{iso}}$  of  $^{27}\text{Al}$ , reflecting a strong evolution of the distortion of  $\text{AlO}_4^-$  sites when  $\text{Al}_2\text{O}_3$  content increases.

### 3.6. Conclusion

Given its high polarizability and its specific electron configuration (free  $6s^2$  pair),  $Pb^{2+}$  ion has a unique stereochemistry, which leads to obtaining binary  $SiO_2$ - $PbO$  silicate glasses that may contain very high  $PbO$  contents, significantly higher in particular than the quantity of alkaline  $R_2O$  oxides that can be introduced in the binary glasses of alkaline silicates ( $SiO_2$ - $R_2O$ ). Though the first structural studies conducted on binary glasses of lead silicates date back over 80 years, there are still unanswered questions on the structural role of  $PbO$  in silicate glasses and on the evolution of the distribution of  $Pb^{2+}$  ions as a function of the lead concentration. However, the implementation of many investigation methods coupled with numerical simulation methods led to many publications and to an increasingly precise knowledge on the structure of these glasses. Hence, for the binary glasses of the  $SiO_2$ - $PbO$  system, it appears that – as for the  $PbO$  crystalline phases and lead silicates –  $Pb^{2+}$  ions are located in very asymmetrical sites of low coordination (3,4) with their stereochemically active free  $6s^2$  pair. Though the addition of  $PbO$  leads to a depolymerization of the silicate network, the structural role of  $Pb^{2+}$  ions is very different from that of bivalent ions, such as the alkaline-earth ions. Indeed, on the one hand, significantly stronger bonds are established starting with the low  $PbO$  contents between the  $Pb^{2+}$  ions and the non-bridging oxygen atoms of the silicate network, and on the other hand for high  $PbO$  contents an increasing proportion of  $O^{2-}$  ions are found connected only to  $Pb^{2+}$  ions gradually forming an increasingly extended lead network. Nevertheless, even for the strongest  $PbO$  contents, a significant proportion of  $SiO_4$  units remain connected to one another thus contributing to the stabilization of the lead network in relation to crystallization. On the other hand, the structural studies conducted on other lead-rich systems are significantly fewer, but however very instructive. Hence, in the alkaline silicate glasses, for low lead contents  $Pb^{2+}$  ions tend to get incorporated in area containing alkaline ions where they associate with non-bridging oxygen atoms, while for high  $PbO$  contents,  $Pb$ - $O$ - $Pb$  connections appear, as a signature of the formation of an increasingly extended lead network. In these glasses,  $Pb^{2+}$  ions preserve their stereochemically active free  $6s^2$  pair and are located in very asymmetric sites by analogy with crystalline phases. On the other hand, in the case of lead aluminosilicate glasses,  $Pb^{2+}$  ions tend to play the role of charge compensator of the  $AlO_4^-$  units and are likely losing the stereochemical activity of their  $6s^2$  pair. However, questions still remain on the evolution of the lead network as a function of  $Al_2O_3$  content in these glasses.

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