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Structure and properties of $(25 - x/2)Li_2O \cdot (25 - x/2)Na_2O \cdot xPbO \cdot 50P_2O_5$ metaphosphate glasses

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Abstract

The structure of $(25 - x/2)Li_2O \cdot (25 - x/2)Na_2O \cdot xPbO \cdot 50P_2O_5$ phosphate glasses ($0 \leqslant x \leqslant 50$ mol%) has been investigated by Raman spectroscopy, and ^{31}P-MAS and ^{207}Pb-VOCS nuclear magnetic resonance. An increase in lead content affects the PO_4 tetrahedra network by weakening bonds between phosphorus and non-bridging oxygens. At low concentration, lead behaves as a modifier cation, with large coordination number. For higher PbO contents, a decrease in the coordination number of the Pb^{2+} cations and an increase in the covalent character of the Pb–O bonds is observed. The changes in density and thermal properties of the glasses are explained through the structural evolution. The non-linear increase of the glass transition and dilatometric softening temperatures with PbO content is related to the non-linear variation of the PbO molar volume. This behavior is discussed in terms of the change in lead coordination when PbO is introduced in a mixed-alkali metaphosphate glass composition.

1. Introduction

Phosphate glasses have specific properties such as low glass transition (T_g) and dilatometric softening (T_s) temperatures, high coefficients of thermal expansion (CTE) or high UV transparency. These properties make them interesting materials for applications in low-temperature sealing [1–6], vitrification of nuclear wastes [7,8], as well as laser host matrices after doping with rare-earth elements [9–12]. The low durability of phosphate glasses can be improved by the substitution of nitrogen for oxygen, which leads to a higher cross-linking density of the glass network [13,14]. Most of the studies reported on phosphate oxynitride glasses have dealt with alkali phosphates (Na,Li) [15,16], mostly because the nitridation under ammonia atmosphere must be carried out at low temperature in order to avoid reduction reactions. However, we have been able to prepare lead oxynitride phosphate glasses [17], because lead can be introduced in phosphate glasses without increasing the temperature at which the melt viscosity is low enough to enable nitridation.

Indeed, the high ionic field strength (IFS) and polarizability of Pb^{2+} cations give lead phosphate glasses low T_s as well as high CTE values and a relatively high chemical durability. Moreover, lead can be incorporated in a phosphate glass network up to proportions as large as 66 mol%, consequently lead phosphate glasses have been widely studied as low-temperature sealing materi-

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Table 1
Nominal and analyzed $(25 - x/2)Li_2O \cdot (25 - x/2)Na_2O \cdot xPbO \cdot 50P_2O_5$ glass compositions

Mol% PbO	Li_2O nominal	Li_2O analyzed (±0.1%)	Na_2O nominal	Na_2O analyzed (±0.1%)	PbO nominal	PbO analyzed (±0.2%)	P_2O_5 nominal	P_2O_5 analyzed (±0.5%)
0	25	22.7	25	25.3	–	–	50	51.9
10	20	17.8	20	20.3	10	9.9	50	52
20	15	13.6	15	15.6	20	20.6	50	50.1
25	12.5	10.5	12.5	12.2	25	26.1	50	51.2
30	10	9.3	10	10.6	30	31	50	49.1
40	5	4.5	5	5.3	40	40.2	50	49.9
50	–	–	–	–	50	50.2	50	49.8

als [5]. Depending on the studied system, the Pb^{2+} ions show an intermediate character between former and modifier. While in silicate glasses the coordination number is between 2 and 4, and lead behaves as an intermediate element [18], in phosphate glasses the lead cations are assumed to play a modifier role with higher coordination numbers [19,20].

The present work is part of a study mainly devoted to phosphorus oxynitride glasses. Such glass compositions result from a progressive nitrogen/oxygen substitution within the phosphate glass network, with formation of P–N bonds at the expense of P–O bonds when an oxide glass precursor is melted in flowing ammonia. We have described previously the preparation conditions as well as the main characteristics of 'LiNaPbPON' glasses as a function of the nitrogen enrichment [17,21]. We have also performed a structural study of the $Li_{0.25}Na_{0.25}Pb_{0.25}PO_{3-3x/2}N_x$ glass series ($0 < x \leqslant 0.69$), and the structural role of lead has been interpreted from a comparison with similar 'LiNaPON' glasses [22]. It has been shown that the presence of Pb^{2+} ions affects the nitridation mechanism, and, moreover, that their network former character increases with nitridation [21]. The role of lead in oxide phosphate glasses has been studied in many phosphate glass compositions [23–25], however, we could not find any data on the introduction of lead in a mixed Li–Na metaphosphate composition. The aim of the present study is thus an investigation of 'LiNaPb' metaphosphate glasses. The effect of increasing amounts of lead is reported for $(25 - x/2)Li_2O \cdot (25 - x/2)Na_2O \cdot xPbO \cdot 50P_2O_5$ glass compositions with $0 \leqslant x \leqslant 50$ mol%. Structural data from Raman and nuclear magnetic resonance spectroscopies are given, and they are completed with density and thermal properties measurements.

2. Experimental

Metaphosphate glass compositions $(25 - x/2)Li_2O \cdot (25 - x/2)Na_2O \cdot xPbO \cdot 50P_2O_5$ ($0 \leqslant x \leqslant 50$ mol%) were prepared by melting reagent grade Li_2CO_3, Na_2CO_3, Pb_3O_4 and H_3PO_4 (85 wt%, $d = 1.7\,g\,cm^{-3}$) in a gas furnace. The batches were first calcined in porcelain crucibles up to 450 °C for a week, then melted at 1100 °C for 1 h. The melts were poured on brass plates in air, then the glasses were annealed for 30 min at temperatures close to T_g. The glass samples were clear, colorless, and bubble free.

The glass compositions were chemically analyzed by inductively coupled plasma-emission spectrometry (ICP) with a *Thermo Jarrel Ash IRIS ADVANTAGE* spectrometer, and flame photometry (FP) with a *Perkin Elmer 2100* spectrometer. The powdered glasses were dissolved in diluted hot hydrochloric acid. The PbO and P_2O_5 contents were measured by ICP while alkali oxides were determined by FP. The nominal and experimental compositions of the glasses prepared are shown in Table 1.

The Raman spectra of the phosphate glasses were obtained with a *Renishaw Ramascope 2000* spectrometer. The calibration was made using the 520.0 cm^{-1} Raman peak of a Si(0 0 1) single crystal. An Ar^+ laser at 514.5 nm wavelength was used, with a 5 mW power and a spot diameter of 1 μm on the sample. The spectral resolution and frequency accuracy were 4 cm^{-1} and 0.5 cm^{-1}, respectively, and the acquisition time 100 s per point. The spectra were recorded at 300 K.

^{31}P-MAS NMR spectra were recorded on a *Bruker ASX 100* spectrometer operating at 40.48 MHz (2.34 T). The pulse length was 1.3 μs (π/4) and 120 s delay time was used. The spinning rate was 12 kHz. The ^{31}P spectra were fitted to Gaussian-type functions, in accordance with the chemical shift distribution of the amorphous state. All NMR vertical scales in this paper are signal amplitude, normalized to the highest peak.

^{207}Pb NMR spectra were obtained on a *Bruker ASX 400* spectrometer. The large electronic shield around the lead nuclei results in a large chemical shift anisotropy (CSA). Hence, the free induction decays have to be recorded from echoes measured at two frequency offsets. Then, two echoes are summed to obtain the whole spectrum. This method, called VOCS (variable offsets cumulative spectrum) was developed for nuclei with large CSA [19]. The ^{207}Pb frequency is 83.69 MHz at 9.4 T. Static echoes were obtained with a $[\pi/2 - \tau - \pi]$ pulse sequence, with $\pi/2 = 3\,\mu s$ and $\tau = 30\,\mu s$. The delay time was 30 s, sufficient to avoid signal saturation, and the

number of scans was 240. A 0.5 M $Pb(NO_3)_2$ solution was used as a secondary reference for ^{207}Pb ($\delta = -2941$ ppm vs. $Pb(CH_3)_4$ at 0 ppm).

The density of the glasses was measured by helium pycnometry in a *Quantachrome Corp.* multipycnometer by using bulk samples.

The thermal expansion coefficients, glass transition temperatures and dilatometric softening points were determined from thermal expansion curves obtained in air with a *Netzsch Gerätebau* dilatometer, model 402 EP, at a heating rate of 2 K min^{-1}. Prismatic samples of around 10 mm in length were used for measurements.

3. Results

3.1. Raman spectroscopy

The Raman spectra of $(25 - x/2)Li_2O \cdot (25 - x/2)Na_2O \cdot xPbO \cdot 50P_2O_5$ glass compositions are given in Fig. 1 for $x = 0$, 10, 25, 40 and 50 mol%. The spectrum of the lead-free glass ($x = 0$) shows three main peaks corresponding to the vibration modes of the Q^2-type PO_4 tetrahedra: the asymmetric stretching mode of the non-bridging oxygens, $v_{as}(PO_2)$, at $\sim$1250 cm^{-1}, the symmetric stretching mode of the non-bridging oxygens, $v_s(PO_2)$, at $\sim$1165 cm^{-1}, and the symmetric stretching mode of the P–O–P bonds, $v_s(POP)$, at $\sim$690 cm^{-1}. In addition, a weak contribution appears at $\sim$1090 cm^{-1} which is assigned to the symmetric stretching mode of the non-bridging oxygens in Q^1-type PO_4 terminal tetrahedra, $v_s(PO_3^{2-})$ [26–29].

Progressive addition of PbO to the phosphate glass composition induces essentially in the Raman spectra a shift towards lower wave numbers of the $v_{as}(PO_2)$, $v_s(PO_2)$ and $v_s(PO_3^{2-})$ mode stretching vibrations, whereas the $v_s(POP)$ peak remains at approximately the same Raman shift.

3.2. ^{31}P-MAS NMR

The ^{31}P-MAS NMR spectra are gathered in Fig. 2. The spectrum of the 10 mol% PbO composition shows a main resonance centered on -22.0 ppm, which is attributed to Q^2-type sites according to results obtained by Sato et al. in alkali metaphosphate glasses [30]. An additional weak resonance band centered at -8.8 ppm is assigned to a small amount of Q^1-type sites (or pyrophosphate groups), in accordance with Brow et al. [31]. The presence of such groups is attributed to a small excess of cations compared to a metaphosphate composition. Higher PbO contents result in a shift of the resonance frequencies of both Q^2- and Q^1-type sites towards more negative δ values, which is due to an increased shielding effect of the Pb^{2+} cations.

3.3. ^{207}Pb NMR

^{207}Pb VOCS NMR spectra are shown in Fig. 3. The resonance corresponding to 10 mol% PbO is centered approximately on -2800 ppm. As the PbO content increases, the frequency value for the highest intensity is shifted towards higher δ values. As reported in binary lead phosphate glasses, and stated in our previous paper dealing with alkali lead oxynitride phosphate glasses containing 25 mol% PbO [21], the observed δ values and resonance width correspond to typical chemical

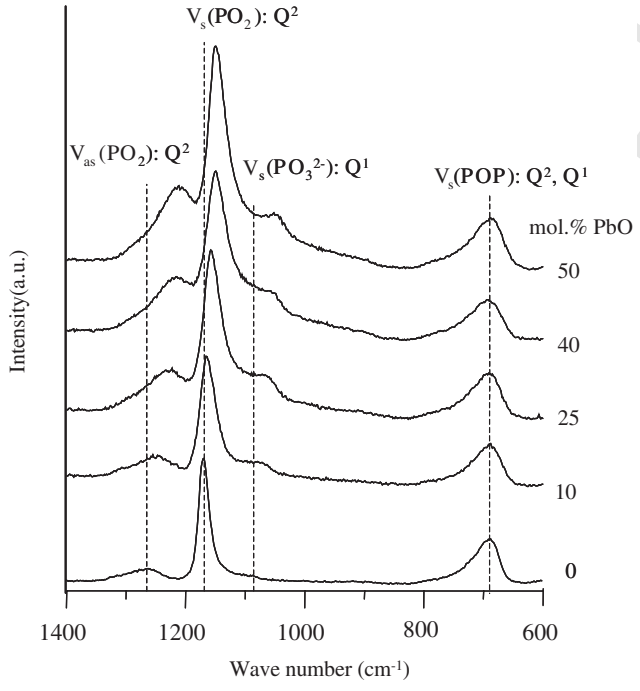

Fig. 1. Raman spectra of $(25 - x/2)Li_2O \cdot (25 - x/2)Na_2O \cdot xPbO \cdot 50P_2O_5$ glasses for $0 \leqslant x \leqslant 50$ mol% PbO.

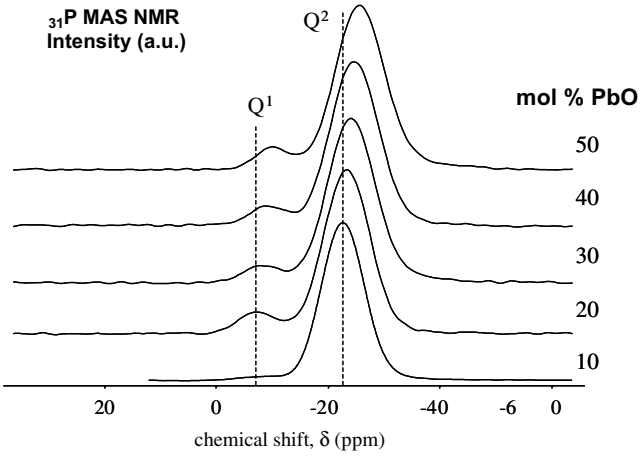

Fig. 2. ^{31}P-MAS NMR spectra of $(25 - x/2)Li_2O \cdot (25 - x/2)Na_2O \cdot xPbO \cdot 50P_2O_5$ glasses for $10 \leqslant x \leqslant 50$ mol% PbO.

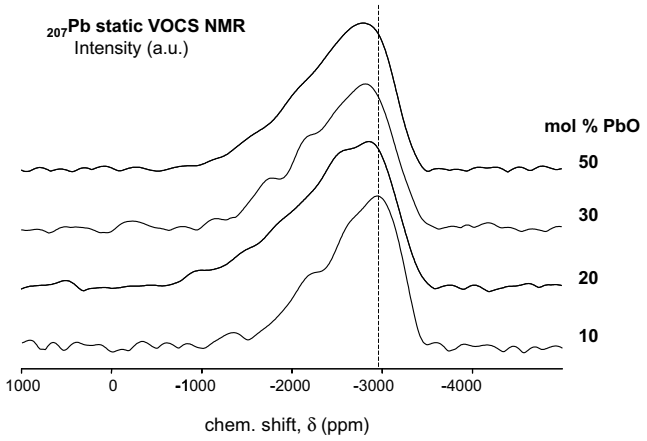

Fig. 3. ^{207}Pb-VOCS NMR spectra of $(25 - x/2)Li_2O \cdot (25 - x/2)Na_2O \cdot xPbO \cdot 50P_2O_5$ glasses for $10 \leqslant x \leqslant 50$ mol% PbO.

shifts of lead cations with a high coordination number, between 7 and 12, and to Pb–O bonds with a predominant ionic character [32]. From X-ray and neutron diffraction results, Hoppe et al. [33,34] also concluded to a large oxygen coordination polyhedron around Pb^{2+} in lead-containing phosphate glasses.

3.4. Density and thermal properties

In Table 2 are gathered the densities, glass transition and dilatometric softening temperatures, as well as the thermal expansion coefficients determined within the 30–200 °C temperature range.

4. Discussion

4.1. Structural characterization

The Raman spectra of the $(25 - x/2)Li_2O \cdot (25 - x/2)Na_2O \cdot xPbO \cdot 50P_2O_5$ glass compositions (Fig. 1) show, as the most important change, a shift towards lower frequencies of $\nu_{as}(PO_2)$, $\nu_s(PO_2)$ and $\nu_s(PO_3^{2-})$ when the PbO content increases. This is attributed to a weakening of the P–O bonds which involve oxygen atoms coordinating Pb^{2+} cations. On the other hand, there is no shift of ν_s(POP), so it can be concluded that bridging oxygens of the PO_4 tetrahedra are not directly influenced by lead. In addition, it seems that an increase in intensity of $\nu_s(PO_3^{2-})$ takes place. This fact would mean that the deviation from the metaphosphate composition is more important as the PbO content increases, that is, however, not reflected on the chemical analysis results given in Table 1.

In the ^{31}P-MAS NMR spectra (Fig. 2), the shift towards lower resonance frequencies of both Q^2 and Q^1 contributions which is observed when the PbO content increases is explained by a greater shielding effect of Pb^{2+} cations on the phosphorus atoms: the greater the IFS of the modifier cations, the greater the shielding effect.

Fig. 4 shows the variation of the isotropic chemical shift of the Q^2-type resonance band as a function of the PbO content. The $\delta(^{31}P)$ value for the lead-free glass composition has been taken from [22]. The linear relation found indicates an average bonding of the lead cations with all the non-bridging oxygen atoms of the Q^2 (and Q^1) groups, and also that the phosphorus atoms of the Q^2 (and Q^1) groups have an average shielding by the alkali metal and lead cations.

As can be seen in Fig. 3, an increase in PbO content results in higher chemical shift values of the ^{207}Pb resonance bands. This is interpreted by a lowering of the Pb^{2+} coordination number and an increasing covalent character of the Pb–O bonds. In other words, this corresponds to a progressively greater former character of lead, which is purely modifier at low PbO contents. Such a phenomenon has been previously observed in the corresponding 'LiNaPbPON' oxynitride glass series containing 25 mol% PbO, when the nitrogen content

Table 2
Density values, glass transition temperatures (T_g), dilatometric softening temperatures (T_s) and coefficients of thermal expansion (CTE) of $(25 - x/2)Li_2O \cdot (25 - x/2)Na_2O \cdot xPbO \cdot 50P_2O_5$ glasses

Mol% PbO	Density ($g\,cm^{-3}$) ($\pm 0.1\,g\,cm^{-3}$)	T_g (°C) (±1 °C)	T_s (°C) (±1 °C)	CTE ($\times 10^6\,K^{-1}$)$_{30-200\,°C}$
0	2.5	228	237	20
10	3.0	229	248	22
20	3.4	245	263	20
25	3.7	256	278	18
30	3.9	262	281	19
40	4.3	276	297	17
50	4.9	315	335	16

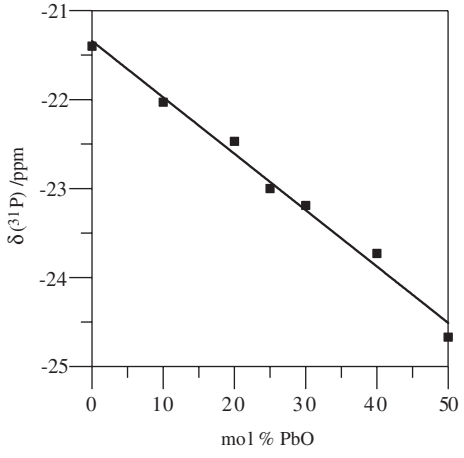

Fig. 4. Chemical shift of the ^{31}P NMR Q^2-type resonance in $(25 - x/2)Li_2O \cdot (25 - x/2)Na_2O \cdot xPbO \cdot 50P_2O_5$ glasses as a function of the PbO content. Line is drawn as a guide for the eyes.

increases [21]. So, increasing lead or substituting nitrogen for oxygen in Li_2O–Na_2O–PbO–P_2O_5 metaphosphate glass compositions seems to produce a similar effect on the coordination sphere of the Pb^{2+} cations, which, in both cases, is formed exclusively by oxygen [21]. The phenomenon is much more manifest in 'LiNaPbPON' oxynitride glasses, that demonstrates the particular role of nitrogen. In fact, the N/O substitution decreases directly the number of non-bridging oxygens available for the coordination of lead atoms. In the case of 'LiNaPbPO' oxide glasses, as lead substitutes for alkali cations, the decrease in available non-bridging oxygens only results from the higher number of oxygens required by Pb^{2+} compared to Li^+ or Na^+. As more lead is added, this number is progressively reduced.

4.2. Influence of the PbO content on the molar volume. Thermal properties

In Fig. 5, the density values (ρ) and PbO molar volumes (V_m) for the different $(25 - x/2)Li_2O \cdot (25 - x/2)Na_2O \cdot xPbO \cdot 50P_2O_5$ glasses have been plotted as a function of the PbO content x. For each composition the PbO molar volume is calculated using the following equation:

$$V_m(PbO) = (x_i \cdot M)/\rho, \quad (1)$$

where ρ, x_i and M are the density, the PbO molar fraction in the glass composition and the molar weight of PbO, respectively.

While the density increases linearly with x (because it is an additive property), the PbO molar volume does not follow the linear increase simulated by the dashed line in Fig. 5. It increases along the whole composition range, however it deviates all the more as higher is the PbO content. Therefore, an increasing lead content results in a decrease in the volume occupied by the coordination sphere of each Pb^{2+} cation. This is in accordance with the ^{207}Pb NMR results.

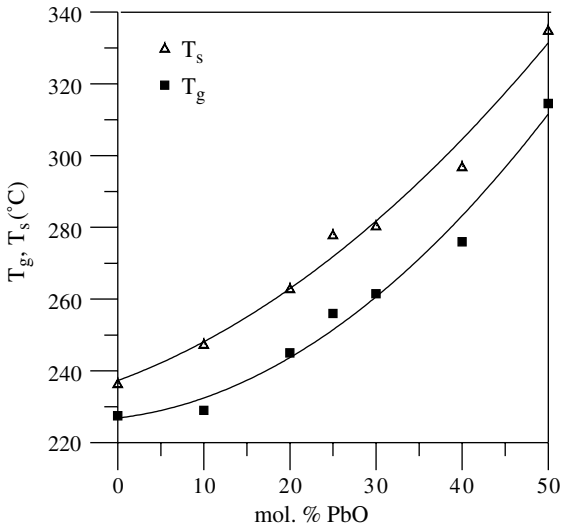

Fig. 6. Glass transition temperature (T_g) and dilatometric softening temperature (T_s) of $(25 - x/2)Li_2O \cdot (25 - x/2)Na_2O \cdot xPbO \cdot 50P_2O_5$ glasses as a function of the PbO content. Lines are drawn as a guide for the eyes.

In Figs. 6 and 7 are shown the variations of T_g and T_s, and CTE, respectively, as a function of the PbO content. In all cases a non-linear variation can be observed, which is more significant from 20 to 25 mol% PbO. T_g and T_s similarly increase while CTE decreases. Such a behavior can be explained through two factors. On one hand, the influence of the mixed alkali effect (MAE) results in lower T_g and T_s, and in higher CTE than those of single alkali compositions. It is greater at high alkali content [35,36]. On the other hand, PbO increases the covalent character of the glass network, that leads to higher T_g and T_s, and lower CTE values. This effect is more important between 25 and 50 mol% of PbO than at lower lead contents, as indicated by the non-linear behavior of the PbO molar volume. The smaller increase in the molar volume at high PbO con-

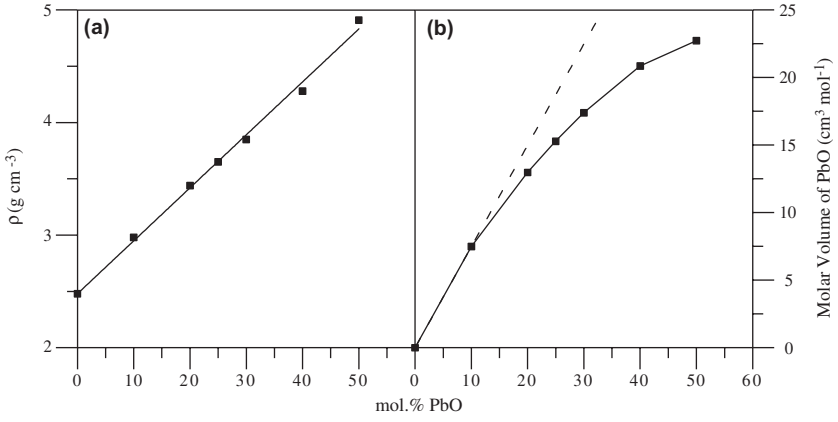

Fig. 5. Density (a) and PbO molar volume (b) variations as a function of the PbO content in $(25 - x/2)Li_2O \cdot (25 - x/2)Na_2O \cdot xPbO \cdot 50P_2O_5$ glasses. The dashed line in (b) is only drawn as a reference for comparison with the experimental values.

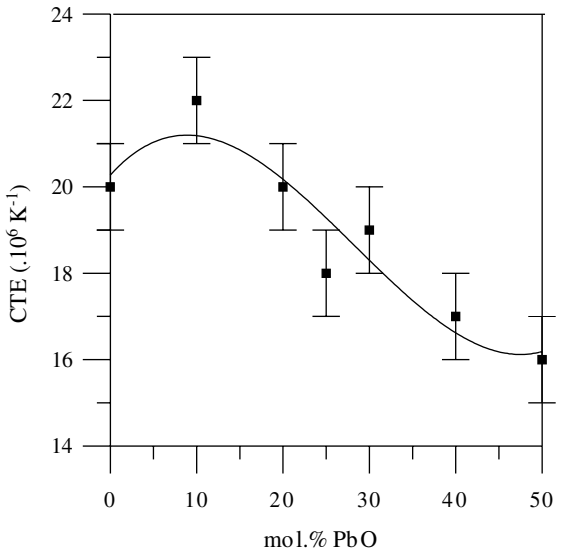

Fig. 7. Coefficient of thermal expansion (CTE) of $(25 - x/2)Li_2O \cdot (25 - x/2)Na_2O \cdot xPbO \cdot 50P_2O_5$ glasses as a function of the PbO content. Line is drawn as a guide for the eyes.

tents gives rise to a larger increase in the characteristic temperatures and a more pronounced decrease in CTE.

5. Conclusions

Raman spectroscopy, ^{31}P-MAS and ^{207}Pb-VOCS NMR of $(25 - x/2)Li_2O \cdot (25 - x/2)Na_2O \cdot xPbO \cdot 50P_2O_5$ glass compositions ($0 \leqslant x \leqslant 50$ mol%) have shown that the Pb^{2+} coordination sphere is large, with coordination numbers about 7–12. An increase in the PbO proportion induces a weakening of P–O bonds of the PO_4 tetrahedra involving the non-bridging oxygens coordinating Pb^{2+}. It results, in addition, in more covalent Pb–O bonds and a lower coordination number of lead.

The variation versus lead content of the PbO molar volume, the glass transition and dilatometric softening temperatures, and the thermal expansion coefficient is consistent with the modification of the lead local environment, and the progressive attenuation of the mixed alkali effect.

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