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Structure – properties study of Na₂O-CaO-PbO-P₂O₅ metaphosphate glasses

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Abstract

Sodium-calcium-lead phosphate glasses having a mol.% composition $(25-z/2)\text{Na}_2\text{O}-(25-z/2)\text{CaO}-z\text{PbO}-50\text{P}_2\text{O}_5$ ($0 \leq z \leq 50$) were prepared by using the melt-quench technique. Some physical properties have been measured and their structure has been studied by IR and Raman spectroscopies. Density of the glass increases linearly with the substitution of Na₂O and CaO by PbO. Glass molar volume vary slightly with the substitution, and a non-linear increase of PbO molar volume and a non-linear decrease of P₂O₅, Na₂O and CaO ones is observed. Glass transition temperature increases non-linearly with PbO substitution. FTIR and Raman spectra reveal the formation of P–O–Pb bonds, which replace P–O–Na and P–O–Ca bonds, and no modification of the network polymerization is observed with substitution by PbO. However, Raman spectra exhibit shoulder's peak due to (PO₃)²⁻ terminal groups, which seemingly results from disproportionation of species in the glass melts. PbO is

assumed to play a network modifier role like Na_2O and CaO , but it reticulates the phosphate network, which causes an increase of T_g and a slight effect on molar volume.

Keywords

Phosphate glasses; Density; Molar volume; FTIR; Raman

1. Introduction

The specific physical properties of phosphate glasses such as low glass transition (T_g) and low melting temperature (compared with silicate glass), high coefficients of thermal expansion makes them suitable for some specific applications: low-temperature sealing [1-4], vitrification of particular nuclear wastes [5, 6], as well as laser host matrices after doping with rare-earth elements [7-9]. However, pure phosphorus pentoxide (P_2O_5), is known as one of the glass forming oxides having a poor chemical durability, a high hygroscopic nature with regard to hydrolysis of the P–O–P bonding by atmospheric moisture, which restricted their use in replacing silicate glasses to a limited range of technological applications [10, 11]. Nonetheless, the solubility of phosphate glasses can be used to create bioactive materials [12-15]. A mixture of oxides including network modifiers and network intermediates can be added to phosphate glass to stabilize the glass network because P–O–M (where M = metal cation) bond is generally more stable toward atmospheric hydrolysis or solution attack [16-18]. The original properties and applications of phosphate glasses depend on their structure. Their network is made of corner-sharing PO_4 tetrahedral units that can be classified according to their mutual connectivity, using the Q^n terminology, where n being the number of bridging oxygen (BO) per tetrahedron. In this formalism, the pure P_2O_5 glass is formed by Q^3 tetrahedra with three BOs and one double bonded oxygen P=O, forming a three-dimensional cross-linked network. In ultraphosphate glasses both Q^2 and Q^3 structures are present, while in metaphosphate glasses Q^2 tetrahedra prevail, which form chains or rings. Beside these, small phosphate groups like chain-ends or pyro- Q^1 and orthophosphate Q^0 can also be present in the glass structure [19]. For instance, the addition of CaO to P_2O_5 to the point where the O/P ratio is equal to 3 should theoretically produce a metaphosphate (PO_3 ; Q^2) network. In this case the tetrahedral units have a tendency to form long chains and rings and the loose non-bridging oxygen (NBO) can coordinate with the modifying cations (Ca^{2+}) since they have a net negative charge.

It was reported that calcium-sodium phosphate glasses from P_2O_5 -CaO- Na_2O system exhibit low melting temperature, low glass transition temperature and low crystallization temperature, depending on the glass compositions [20-23]. Calcium oxide has a strong effect on reduction of the dissolution rate in water because the Ca^{2+} cation serves as ionic crosslinks between the NBOs of two different phosphate chains, and accordingly increase glass durability [24].

Among various divalent oxides (MO such as CaO, BaO, MgO, etc.) that play the role of glass modifiers for the phosphate glass network, the effect of lead oxide (PbO) is particular since lead oxide is known to play a dual role as a modifier and a former network. Some studies have been reported on PbO- P_2O_5 glasses using Raman, FTIR, NMR and X-ray diffraction techniques [25-34], which confirmed that lead oxide (PbO) takes the role of both glass former and modifier. As a glass former, PbO shares the corners of phosphate network with P-O-Pb linkages. When PbO acts as a network modifier, Pb-atom has a high coordination number like most of conventional modifier oxides [30, 32].

It is of interest to investigate the role of PbO in Na_2O -CaO- P_2O_5 glasses, since PbO may behave as a network former or modifier, in the latter case in competition with Na_2O and CaO. The consequence on glass properties is thus worth to be investigated. The aim of the present work is to analyse the effect of PbO on the structure and properties of phosphate glasses with the formula $(25-z/2)Na_2O$ - $(25-z/2)CaO$ - $zPbO$ - $50P_2O_5$ with ($0 \leq z \leq 50$ mol.% PbO). PbO is introduced in substitution of both Na_2O and CaO in order to observe the competing effect of these oxides in the glass formula. Moreover, we emphasize that the glass formula enables to keep a metaphosphate composition with a constant O/P ratio of 3 for all the glasses investigated here, such as the effect of PbO substitution for Na_2O and CaO should remain distinct from any polymerization effect of the phosphate network. Structural investigations were performed by Infrared and Raman spectroscopies in order to observe if any modification of the network polymerization occurs. The measured properties are density, molar volume, glass transition temperature because these properties may also reveal some structural

modification induced by the introduction of PbO. The evolution of properties with composition will be thus discussed according to structural data.

2. Experimental procedure

Six compositions of sodium calcium lead metaphosphate glasses in the $(25-z/2)\text{Na}_2\text{O}-(25-z/2)\text{CaO}-z\text{PbO}-50\text{P}_2\text{O}_5$ series were prepared in the range of $0 \leq z \leq 50$ by mixing the appropriate amounts of sodium carbonate (Na_2CO_3), calcium carbonate (CaCO_3), lead oxide (PbO) and diammonium hydrogen phosphate ($(\text{NH}_4)_2\text{HPO}_4$). These precursors were weighted, mixed, and calcined at 400°C and then melted in a 90Pt-10Rh crucible at 1000°C for 15 minutes. The glasses were obtained by pouring the melt onto a stainless-steel plate. Weight losses during synthesis were carefully measured and volatilization was found to be insignificant, hence actual compositions are considered to be very close to the nominal compositions. Nevertheless, as will be discussed later, the presence of some Q^1 sites suggest that a few P_2O_5 loss occurred during melting.

Differential scanning calorimetry of powder samples was made at a heating rate of $10 \text{ K}\cdot\text{min}^{-1}$ using the DSC- SETRAM 121 type apparatus to determine the glass transition temperature (T_g); the estimated error is $\pm 5^\circ\text{C}$. Density measurements were carried out at room temperature, using Archimedes' method with diethyl orthophthalate as the immersion fluid. The relative error in these measurements was about $\pm 0.02 \text{ g}\cdot\text{cm}^{-3}$.

The Fourier transform infrared (FTIR) spectroscopy measurements were made on glass powders dispersed in KBr pellets (3 wt.%). The infrared spectra of the powder glass samples were recorded at room temperature in the range $400\text{-}1400 \text{ cm}^{-1}$ using a FTIR Perkin-Elmer spectrometer.

The Raman spectra were recorded on powder of glasses dispersed on a glass slide by means of a LABRAM Raman micro-spectrometer (Jobin-Yvon) equipped with an internal He-Ne laser source ($\lambda = 632.8 \text{ nm}$) for the excitation and a liquid nitrogen-cooled CCD detector in the region $200\text{-}1400 \text{ cm}^{-1}$. A

long working distance Olympus objective ($\times 80$) was used to perform the measurements. The mean spectral resolution and the band position accuracy were 4 and $\pm 1 \text{ cm}^{-1}$, respectively.

3. Results and discussion

3.1. Density and molar volume

The measured density and calculated molar volume (V_m) of $(25-z/2)\text{Na}_2\text{O}-(25-z/2)\text{CaO}-z\text{PbO}-50\text{P}_2\text{O}_5$ $0 \leq z \leq 50$ mol.% glasses are presented in Table 1. The molar volume V_m of glass was calculated from its density (ρ) and the P_2O_5 and PbO amounts by the following relation (Equation 1) where M_{glass} corresponds to the glass molecular weight [35].

$$V_m = M_{\text{glass}} \times (\rho \times \text{mol.}\%_{(\text{glass})}) \quad \text{Eq.1}$$

Table 1: Nominal composition (mol.%), density ρ (g/cm^3), molar volume V_m (cm^3/mol) and glass transition temperature T_g ($^\circ\text{C}$) of $(25-z/2)\text{Na}_2\text{O}-(25-z/2)\text{CaO}-z\text{PbO}-50\text{P}_2\text{O}_5$ ($0 \leq z \leq 50$) metaphosphate glasses.

Composition (mol.%)				$\rho \pm 0.02$ (g/cm^3)	$V_m \pm 0.1$ (cm^3/mol)	$T_g \pm 5$ ($^\circ\text{C}$)
Na_2O	CaO	PbO	P_2O_5			
25	25	0	50	2.58	38.95	367
20	20	10	50	3.00	38.96	371
15	15	20	50	3.44	38.75	377
10	10	30	50	3.86	38.79	381
5	5	40	50	4.24	39.19	387
0	0	50	50	4.68	39.01	397

As expected, the glass density (Figure 1) is found to increase with PbO content. Indeed, when a lower molecular weight substance ($M_{\text{Na}_2\text{O}} + M_{\text{CaO}} = 118.05 \text{ g}\cdot\text{mol}^{-1}$) is substituted by a higher molecular

weight substance ($2 \times M_{\text{PbO}} = 446.40 \text{ g.mol}^{-1}$), the net molecular weight will increase, resulting in an increase in density.

Replacing 25 mol.% Na_2O with 25 mol.% CaO in the $50\text{Na}_2\text{O}-50\text{P}_2\text{O}_5$ glass results in a decrease in molar volume from $42 \text{ cm}^3.\text{mol}^{-1}$ to $38.95 \text{ cm}^3.\text{mol}^{-1}$ [36]. This could be explained by considering that the ionic molar volume of Na^+ (4.45 \AA^3) is replaced by a lower ion molar volume of Ca^{2+} (4.19 \AA^3) [37].

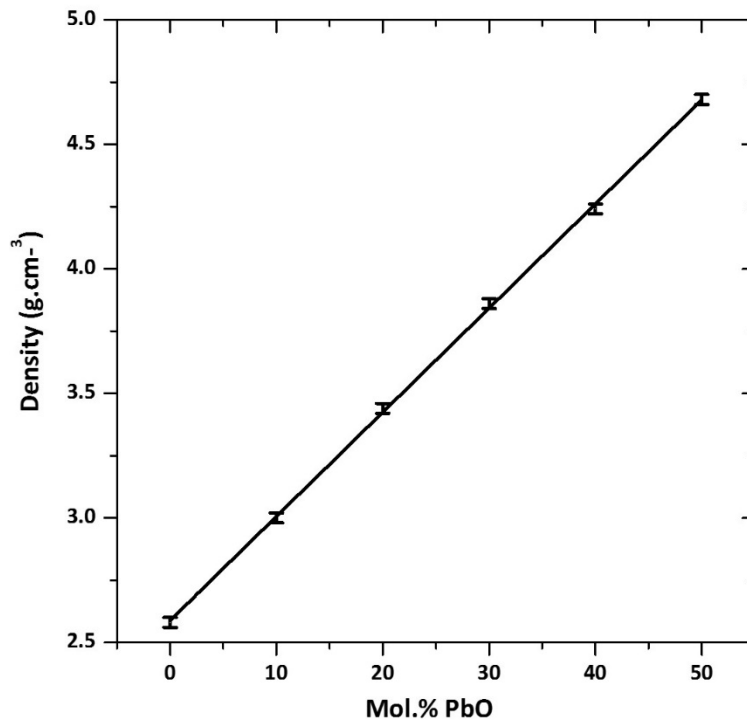


Figure 1. Compositional dependence of density of $(25-z/2)\text{Na}_2\text{O}-(25-z/2)\text{CaO}-z\text{PbO}-50\text{P}_2\text{O}_5$ glasses.

Figure 2 shows that the glass molar volume vary slightly with the substitution of Na_2O and CaO by PbO . This is an unexpected result because of the larger relative ionic radius of Pb^{2+} (1.19 \AA) $>$ Na^+ (1.02 \AA) $>$ Ca^{2+} (1.00 \AA), and correspondingly the ionic molar volume $2 \times V_{\text{Pb}^{2+}}$ (14.12 \AA^3) is larger than $(2 \times V_{\text{Na}^+} + V_{\text{Ca}^{2+}})$ (13.09 \AA^3). Theoretically, replacing an ion of low molar volume with another with high molar volume leads to an increase in the molar volume of the glass [37]. However, the obtained results show a slight variation of the glass molar volume with the addition of PbO . This behaviour could be due to the conversion of the structure formed by metaphosphate chains.

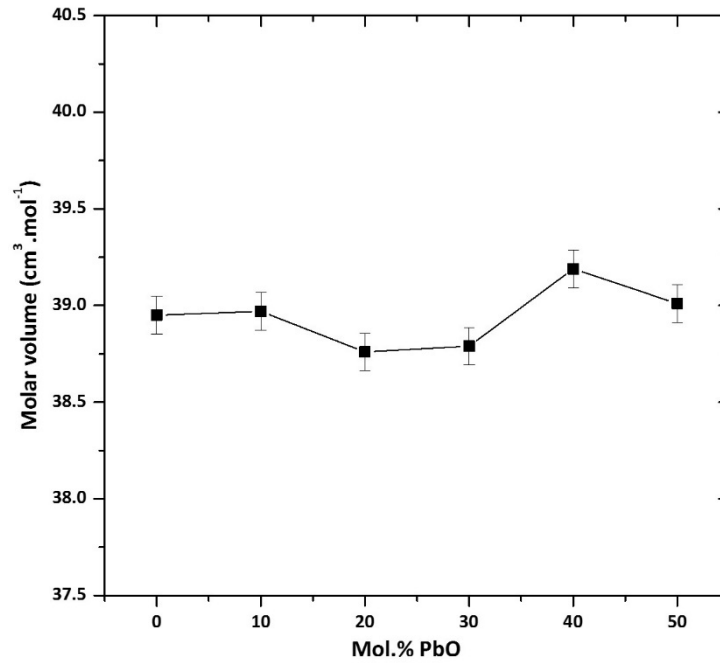


Figure 2. Molar volume variations as a function of the PbO content in $(25-z/2)\text{Na}_2\text{O}-(25-z/2)\text{CaO}-z\text{PbO}-50\text{P}_2\text{O}_5$ glasses.

3.2. Glass transition temperature

The glass transition temperatures (T_g) data for $(25-z/2)\text{Na}_2\text{O}-(25-z/2)\text{CaO}-z\text{PbO}-50\text{P}_2\text{O}_5$ $0 \leq z \leq 50$ mol.% glasses are reported in Table 1. As shown in Figure 3, we note that T_g increases with increasing PbO content from 367°C for $25\text{Na}_2\text{O}-25\text{CaO}-50\text{P}_2\text{O}_5$ ($z=0$) up to 397°C for $50\text{PbO}-50\text{P}_2\text{O}_5$ ($z = 50$ mol.%). The main factor influencing the glass transition temperature, is assumed to be the cross-link of the glass network as Pb^{2+} ions are introduced. Indeed, the calculated values of field strength of the cation ($\text{FS} = Z/a^2$ where Z is the valence of the cation and a is the ion–oxygen bond distance) are in order Ca^{2+} (35 nm^{-2}) > Pb^{2+} (31 nm^{-2}) > Na^+ (18 nm^{-2}) [38]. Thus, substitution PbO for Na_2O and CaO increases T_g , which is related to the larger FS of Pb^{2+} than the average value of Na^+ and Ca^{2+} .

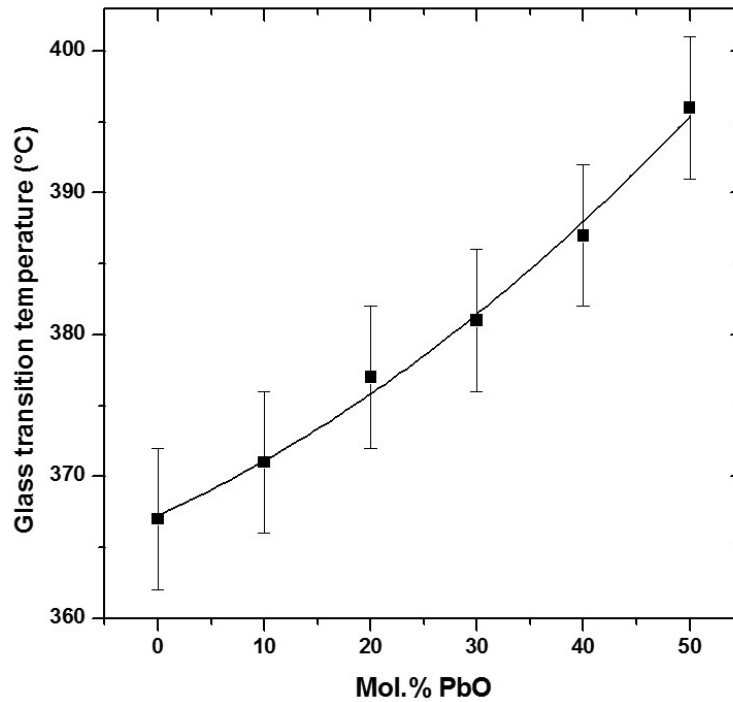


Figure 3. Compositional dependence of glass transition temperature T_g of $(25-z/2)\text{Na}_2\text{O}-(25-z/2)\text{CaO}-z\text{PbO}-50\text{P}_2\text{O}_5$ glasses.

3.3. FT-IR analysis

FT-IR spectra of $(25-z/2)\text{Na}_2\text{O}-(25-z/2)\text{CaO}-z\text{PbO}-50\text{P}_2\text{O}_5$ ($0 \leq x \leq 50$ mol.%) glasses obtained in the wavenumber range between 400 and 1400 cm^{-1} are reported in Figure 4. Their characteristic features are the PO_2 asymmetric (ν_{as}) and symmetric (ν_{s}) stretching vibration band (Q^2 tetrahedra) at 1259-1219 cm^{-1} and 1160-1147 cm^{-1} , respectively. The ν_{as} of PO_3 groups (chain terminator) at 1100-1040 cm^{-1} , the ν_{s} of PO_3 groups at 1010-980 cm^{-1} , the ν_{as} of POP groups (linkages in Q^2 and Q^1 structural unit) at 900-886 cm^{-1} , the ν_{s} of POP groups at 780 and 712 cm^{-1} and the bending vibration (δ) of P-O bonds at 520 and 460 cm^{-1} .

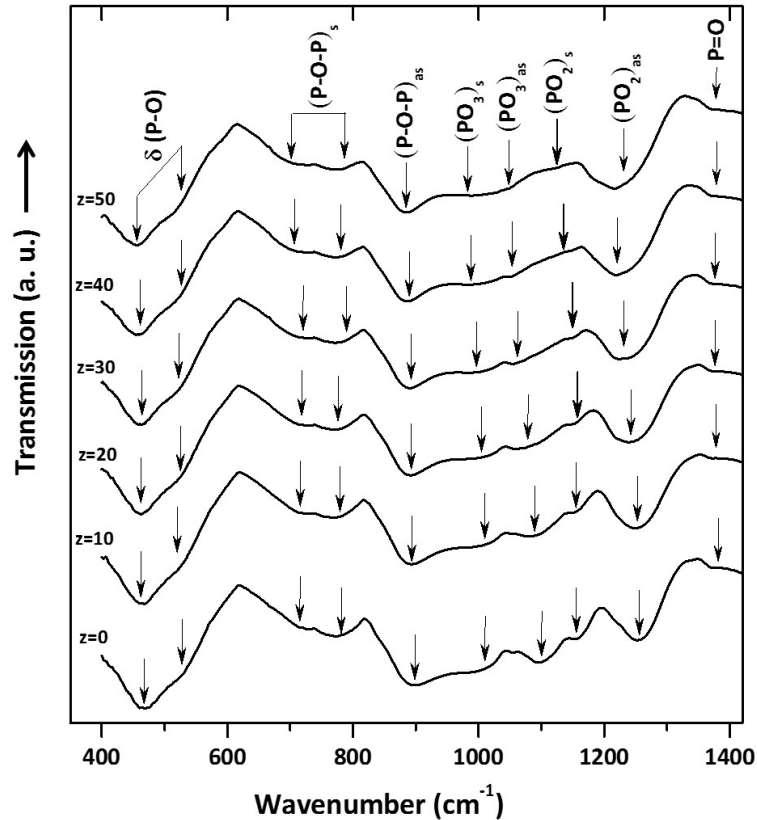


Figure 4. FT-IR spectra of $(25-z/2)\text{Na}_2\text{O}-(25-z/2)\text{CaO}-z\text{PbO}-50\text{P}_2\text{O}_5$ glasses.

The spectra of all these glasses are similar to those of other metaphosphate glasses, which indicates that the metaphosphate structure is preserved with PbO addition [39-41]. Depending on the glass composition, the bands are shifted. Indeed, the ν_{as} of PO_2 (Q^2 tetrahedra) shifts to lower wavenumber from 1259 cm^{-1} in $25\text{Na}_2\text{O}-25\text{CaO}-50\text{P}_2\text{O}_5$ glass to 1219 cm^{-1} in $50\text{PbO}-50\text{P}_2\text{O}_5$ glass (Figure 5) and the ν_{s} of PO_2 shifts from 1160 cm^{-1} in $25\text{Na}_2\text{O}-25\text{CaO}-50\text{P}_2\text{O}_5$ glass to 1124 cm^{-1} in $50\text{PbO}-50\text{P}_2\text{O}_5$ glass. The ν_{as} of PO_3 shifts from 1100 cm^{-1} in $25\text{Na}_2\text{O}-25\text{CaO}-50\text{P}_2\text{O}_5$ glass to 1040 cm^{-1} in $50\text{PbO}-50\text{P}_2\text{O}_5$ glass and the ν_{s} of PO_3 shifts from 1010 cm^{-1} in $25\text{Na}_2\text{O}-25\text{CaO}-50\text{P}_2\text{O}_5$ glass to 980 cm^{-1} in $50\text{PbO}-50\text{P}_2\text{O}_5$ glass. These results are assigned to the change in the terminal P–O bond stretching vibrations caused by the replacement of P–O–Na and P–O–Ca by P–O–Pb linkages. Indeed, the Pb–O bonds are less ionic than the Na–O and Ca–O bonds (because the electronegativity of Pb (2.33) is larger than that of Ca (1) and Na (0.93)), thus P–O(Pb) bonds linked to lead ions are less

covalent (hence more ionic) than P–O(Na) and P–O(Ca) bonds. The band of P–O–P asymmetric stretching mode also shifts to lower wavenumber (Figure 5) [39]. This can be explained by the increase of covalent character (or the electronic density) of P–O–P bonds, indicating that the P–O–P bonds are strengthened as Na⁺ and Ca²⁺ are replaced by Pb²⁺ [42-44].

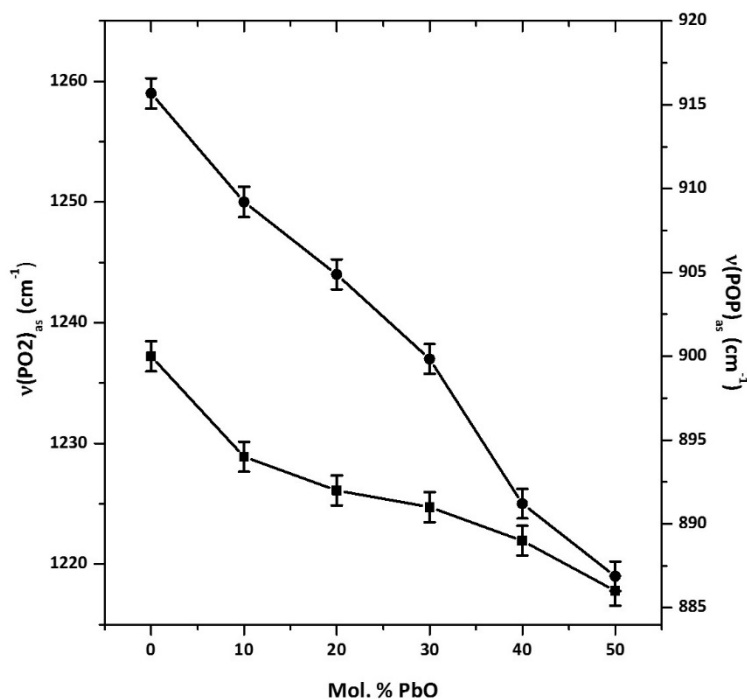


Figure 5. Wavenumber values of $\nu(\text{PO}_2)_{\text{as}}$ (●) and $\nu(\text{POP})_{\text{as}}$ (■) modes versus mol.% PbO in $(25-z/2)\text{Na}_2\text{O}-(25-z/2)\text{CaO}-z\text{PbO}-50\text{P}_2\text{O}_5$ glasses.

3.4. Raman spectroscopy

The Raman spectra of $(25-z/2)\text{Na}_2\text{O}-(25-z/2)\text{CaO}-z\text{PbO}-50\text{P}_2\text{O}_5$ ($0 \leq z \leq 50$ mol.%) glass compositions are shown in Figure 6. The spectrum of the $25\text{Na}_2\text{O}-25\text{CaO}-50\text{P}_2\text{O}_5$ ($z = 0$) shows three main peaks and is similar to the known Raman spectra of other metaphosphate glasses [45-49]. The first most intense band around 1170 cm^{-1} and the second less intense band around 1281 cm^{-1} have been attributed to the symmetric and asymmetric stretching vibrations of PO_2 groups (Q^2 structural units), respectively. The third intense band at 683 cm^{-1} is assigned to the symmetric stretching of P–O–P linkages in Q^2 and Q^1 structural unit [50]. The low wavenumber shoulder bands at 311 cm^{-1} and 308 cm^{-1} are related to bending motions of phosphate polyhedra [51].

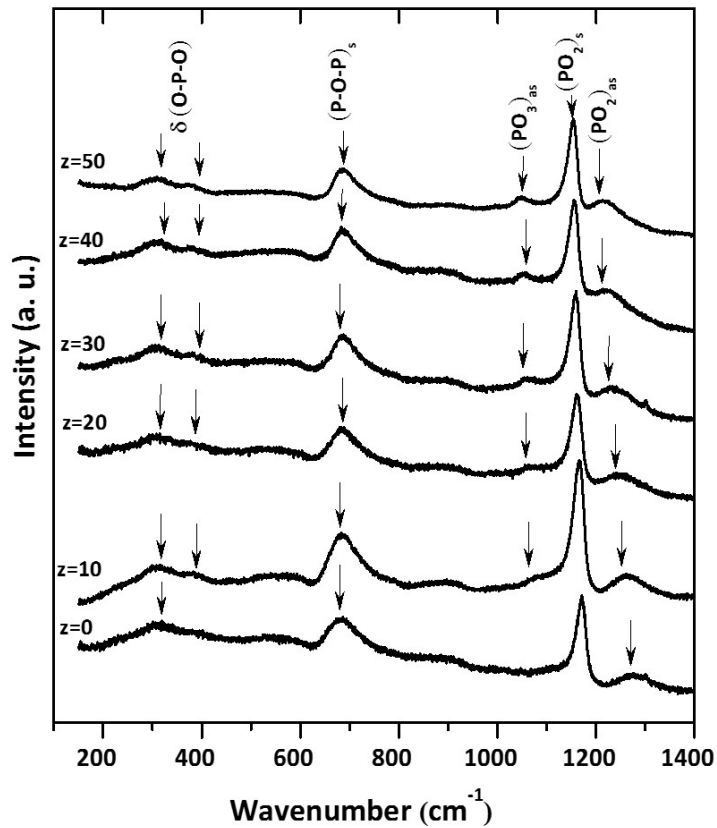


Figure 6. Raman spectra of $(25-z/2)\text{Na}_2\text{O}-(25-z/2)\text{CaO}-z\text{PbO}-50\text{P}_2\text{O}_5$ glasses.

Substitution of PbO for Na_2O and CaO leads to the appearance of a new peak at $1075\text{-}1048\text{ cm}^{-1}$ ($z \geq 10$ mol.%), which is assigned to the asymmetric stretching mode of the non-bridging oxygens in Q^1 -type PO_4 terminal tetrahedra, $\nu_{\text{as}}(\text{PO}_3)^{2-}$. Similar peak appears in mixed Li-Na metaphosphate glasses with PbO content, which may be due to the disproportionation of species in glass melt [52]. Thus, the lowest intensity corresponding to $\nu_{\text{as}}(\text{PO}_3)^{2-}$ (Q^1 tetrahedra), indicates that a small increase in the O/P ratio of the glasses because of P_2O_5 loss ($z \geq 10$ mol.%) [53]. Nevertheless the metaphosphate (PO_3) $^-$ units (Q^2 tetrahedra) remain predominant in the $(25-z/2)\text{Na}_2\text{O}-(25-z/2)\text{CaO}-z\text{PbO}-50\text{P}_2\text{O}_5$ glasses as indicated by the highest intensity at 1170 cm^{-1} in the Raman spectra [53].

The Raman spectra (Figure 6) show a shift towards lower wave numbers of the $\nu_{\text{as}}(\text{PO}_2)$, $\nu_{\text{s}}(\text{PO}_2)$ and $\nu_{\text{as}}(\text{PO}_3)^{2-}$ mode stretching vibrations. The shifts in band wavenumbers is similar to those observed in the infrared spectra. For further discussion of the IR and Raman spectra features, the variations of

symmetric and asymmetric stretching modes of PO_2 units can be attributed to: (a) the larger field strength $FS_{\text{M-O}}$ of Pb^{2+} being larger than the average value of those of Na^+ and Ca^{2+} (b) atomic weight being larger in the order $M(\text{Pb}) = 207.2 \text{ uma} > M(\text{Ca}) = 40.1 \text{ uma} > M(\text{Na}) = 23.0 \text{ uma}$, that affects the metal to non-bridging oxygen bond along phosphate chains. This interpretation agrees with the proposed model of Rouse *et al.* [54] in alkali metal metaphosphate glasses, which suggests that the wavenumber of symmetric and asymmetric PO_2 stretching vibration varies systematically with the mass and field strength of the alkaline ion and O–P–O bond angle.

4. Conclusions

In the present study, the density, molar volume, glass transition temperature, IR and Raman spectroscopies have been investigated for $(25-z/2)\text{Na}_2\text{O}-(25-z/2)\text{CaO}-z\text{PbO}-50\text{P}_2\text{O}_5$ ($0 \leq z \leq 50$) glasses. FTIR and Raman spectra reveal the formation of P–O–Pb bonds, which replaces P–O–Na and P–O–Ca bonds. The predominant structural units in all these glasses are metaphosphate $(\text{PO}_3)^-$ units connected with Pb–O, Ca–O and Na–O bonds. Raman spectra show a small amount of $(\text{PO}_3)^{2-}$ terminal groups exist, which is maybe due to the disproportionation of species in the glass melts. In addition, cross-link strength of the glass network related to Pb^{2+} and Ca^{2+} is responsible for increasing T_g , however, a slight irregular variation of the glass molar volume indicates probably a conversion of the structure formed by metaphosphate chains.

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