

Structure and properties of $(50-x)\text{CaO}-x\text{PbO}-50\text{P}_2\text{O}_5$ metaphosphate glasses

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$(50-x)\text{CaO}-x\text{PbO}-50\text{P}_2\text{O}_5$ glasses ($0 \leq x \leq 50$) were synthesized by quenching technique. They have been characterised by Fourier transform infrared (FT-IR) and Raman spectroscopies. FT-IR and Raman spectral investigations reveal the formation of P–O–Pb bonds which replace P–O–Ca bonds and show that no metaphosphate network depolymerisation occurs when x increases. Thus, PbO acts as the network modifier. Systematic variations of the density and molar volume observed are in agreement with these results. The decrease in T_g with the substitution of PbO for CaO is due the lower energy for one Avogadro's bond between Pb–O than that of Ca–O. The larger polarisability of lead oxide is responsible of the improved chemical durability of these glasses.

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1. Introduction

Over the years, different glass systems of low melting temperatures, high chemical durability and high thermal expansion coefficient have been developed for many applications, which render them useful for a wide range of technical applications. Among conventional oxide glasses, phosphate glasses are interesting amorphous materials that have gained the attention of chemists due to their growing technological importance and desirable applications in several industries [1-6]. However, the addition of metal oxides such as Al_2O_3 , Fe_2O_3 , SnO , PbO , CuO into P_2O_5 glass network are necessary to improve their poor chemical durability [7-11].

The structural role of PbO in many oxide glasses is unique since lead oxide is known to play a dual role both as a network modifier [12] and as a network former [13]. PbO is useful for shielding against high-energy radiations, including nuclear radiation [14] and its addition to phosphate glasses may result in the formation of Pb–O(–P) bonds, which offer them a better chemical durability and reduce the dissolution rate and the melting temperature [15, 16]. While in silicate glasses the coordination number is between 2 and 4, and lead behaves as an intermediate element [17], in phosphate glasses the lead cations are assumed to play a modifier role with higher coordination numbers [18, 19].

In the present work, the structure of glasses with the general composition of $(50-x)\text{CaO}-x\text{PbO}-50\text{P}_2\text{O}_5$ with $0 \text{ mol}\% \leq x \leq 50 \text{ mol}\%$ is investigated using infrared (IR) and Raman spectroscopies in order to elucidate the structural evolution of the glass as a function of

composition. Other properties, such as density, molar volume, glass transition temperature and chemical durability, are investigated and correlated with the structure changes.

2. Experimental

Six compositions of calcium lead phosphate glasses in the $(50-x)\text{CaO}-x\text{PbO}-50\text{P}_2\text{O}_5$ series were prepared in the range of $0 \leq x \leq 50$ by melting analar grade chemicals PbO, CaCO_3 and $(\text{NH}_4)_2\text{HPO}_4$ as the basic reagents in a muffle furnace. The batches were first calcined in platinum crucibles at 500°C for about 2 h for the purpose of excluding H_2O , CO_2 and NH_3 , and then melted at temperature ranging between 900°C and 1100°C , depending on the glass composition. After 30 min under the atmospheric condition in the melting furnace, the glass melts were cast into a preheated graphite mould in air. The glass samples were clear, colourless, and bubble free. All the samples were kept in a desiccator to prevent possible attack by moisture until use.

The amorphous state of all the glass samples was confirmed by the absence of peaks in the XRD patterns.

The glass compositions were chemically analyzed by inductively coupled plasma spectrometry (ICP) with a Jobin Yvon 170, Ultrace spectrometer. The powdered glasses were dissolved in diluted hot nitric acid. The nominal and experimental compositions of the glasses prepared are shown in Table 1.

Table 1.

Data for (50-x)CaO-xPbO-50P₂O₅ glasses, compositions (mol%), molar ratio from analyzed compositions of oxygen to phosphorus (O/P), density ρ (g/cm³), molar volume V_m (cm³/mol), glass transition temperature T_g (°C) and dissolution rate DR (g/cm³ x min) of the studies samples.

Batched			Analyzed			O/P	ρ	V_m	T_g	DR
PbO	CaO	P ₂ O ₅	PbO	CaO	P ₂ O ₅					
0	50	50	0	52.51	47.48	3.01	2.65	37.23	549	2.30×10^{-7}
10	40	50	10.65	42.70	46.64	3.05	3.05	37.88	494	1.08×10^{-7}
20	30	50	20.23	33.092	46.66	3.00	3.45	38.39	459	9.92×10^{-8}
30	20	50	29.55	0.55	49.88	3.07	3.83	38.86	423	4.18×10^{-8}
40	10	50	41.75	10.45	47.78	3.07	4.24	39.07	374	1.71×10^{-8}
50	0	50	50.70	0	49.29	3.05	4.58	39.82	361	1.17×10^{-8}

The density of the glasses was determined at room temperature using the Archimedes method with diethyl orthophthalate as an immersion liquid. A random error in the density measurements was found as ± 0.02 g/cm³. The molar volume (V_m) was calculated from the experimentally determined density (ρ) according to the relation:

$$V_M = \frac{M}{\rho}$$

Where M is the molar weight of the glass.

Glass transition temperatures were determined by differential scanning calorimetry (DSC, SETARAM 121) at a heating rate of 10 °C/min.

The infrared spectra of the samples were recorded with a Bruker Tenseur 27 FTIR Spectrometer in frequency range 400–1400 cm⁻¹ at room temperature. The glass samples were ground in a clean mortar as fine powder. Small quantities of glass powder were mixed and ground with spectroscopic grade dry KBr powder in the ratio 1/25. KBr pellets of thickness 1 mm were obtained by pressing the mixture at 15 tons for a few minutes. All measurements were run at 4 cm⁻¹ resolution.

Raman spectra were collected by LABRAM Raman microspectrometer (Jobin-Yvon) equipped with an internal He-Ne laser source ($k = 632.8$ nm) for the excitation and a liquid nitrogen-cooled CCD detector in the region 200–1400 cm⁻¹. A long working distance Olympus objective 80) was used to perform the measurements. The mean spectral resolution and the band position accuracy were 4 and ± 1 cm⁻¹, respectively.

The chemical durability was estimated by measuring the weight loss of a polished glass block in static regime by samples immersion in deionized water at 30 °C for 48 h. All samples were polished to 2000 grit finish prior to test. The samples were measured before and after different immersion times, by using an analytic balance sensitive to 0.1 mg then were dried at 80 °C. The dissolution rate (DR) was calculated as

$$DR = \frac{\Delta w}{S \times t},$$

Where Δw is the weight loss (g), S is the sample area (cm²) before the dissolution test and t is the dissolution time (min).

3. Results and discussion

Nominal and analyzed compositions, O/P molar ratio, density, molar volume, glass transition temperature and dissolution rate of studied glasses are listed in Table 1.

3.1. Density and molar volume

Fig. 1 represents the change of density, ρ and molar volume, V_m of the studied glasses with PbO. The figure shows a monotonic change in density and molar volume with lead content. Such monotonic behavior indicates that the structure of the glass does not change with composition [20, 21]. A gradual replacement of calcium ion with lead ion causes a linear increase in density and molar volume. The increase in density is related to the replacement of a lighter molecular weight M_{CaO} (56.08 g.mol⁻¹) by a heavier one M_{PbO} (223.22 g.mol⁻¹). The increase in molar volume could be explained by considering the fact that de small molecular volume of CaO (16.9 cm³.mol⁻¹) is replaced by the large molecular volume of PbO (23.5 cm³.mol⁻¹) [22].

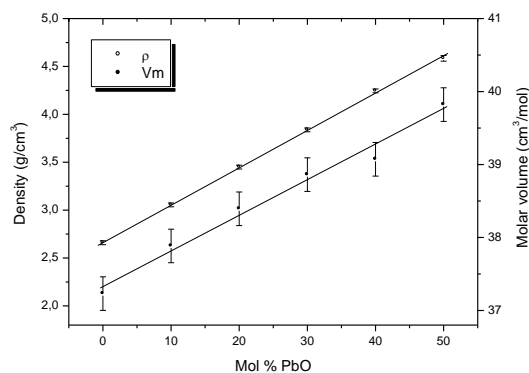


Fig. 1. Composition dependence of density, ρ and molar volume, V_m for the (50-x)CaO-xPbO-50P₂O₅ glasses.

3.2. Glass transition temperature

Fig. 2 shows the glass transition temperature of the glasses with various content of lead oxide. As indicated in the figure, T_g decreases with increasing PbO content. The decrease in glass transition temperature reflects a decrease of cross-link strength of the glass network as Pb^{2+} ions are introduced. This results can be explained by the charge densities (z/a^2) being smaller in the order Pb^{2+} ($z/a^2 = 31 \text{ nm}^{-2}$) < Ca^{2+} ($z/a^2 = 36 \text{ nm}^{-2}$). Furthermore, the energy for one Avogadro's bond (A.b.) between Pb-O (101.2 KJ /Av) is smaller than that of Ca-O (179.3 KJ /Av) [22].

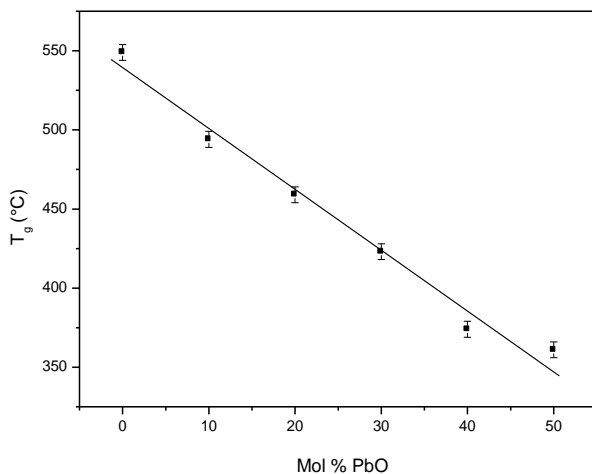


Fig. 2. Composition dependence of glass transition temperature, T_g for the (50-x)CaO-xPbO-50P₂O₅ glasses.

3.3. Spectroscopic studies

Fig. 3 shows the FTIR spectra of (50-x)CaO-xPbO-50P₂O₅ glasses ($0 \leq x \leq 50$), in the frequency range between 400 and 1400 cm^{-1} . The FTIR spectra of these glasses seem to consist of relatively broad bands which may reflect structural disorder of the different phosphate structural groups. Their characteristic features are the PO₂ asymmetric stretching vibration band at 1280-1248 cm^{-1} , the PO₂ symmetric stretching vibration band at 1130 cm^{-1} [23, 24], the ν_{as} of PO₃ groups (chain end) at 1080 cm^{-1} , the ν_s of PO₃ groups at 1037 cm^{-1} [25], the ν_{as} of POP groups at 897-880 cm^{-1} , the ν_s of POP groups at 770 and 725 cm^{-1} [26, 27] and the bending vibration (δ) of P-O bonds at 510 and 480 cm^{-1} [28].

These spectra are identical to those reported in the literature for alkali metaphosphate glasses which have the linear chain structure [29, 30]. This is consistent with the O/P ratio which is close to 3 for all samples (Table 1). The strong band of PO₂ asymmetric stretching mode shifts to lower frequencies from 1280 cm^{-1} in 50CaO-50P₂O₅ glass to 1248 cm^{-1} in 50PbO-50P₂O₅ glass. This shift is expected because the lead-oxygen bonds are less ionic than the calcium-oxygen bonds, and the phosphorus-oxygen bonds linked to lead ions P-O(-Pb²⁺)

are more ionic (hence less covalent) than P-O(-Ca²⁺) bonds.

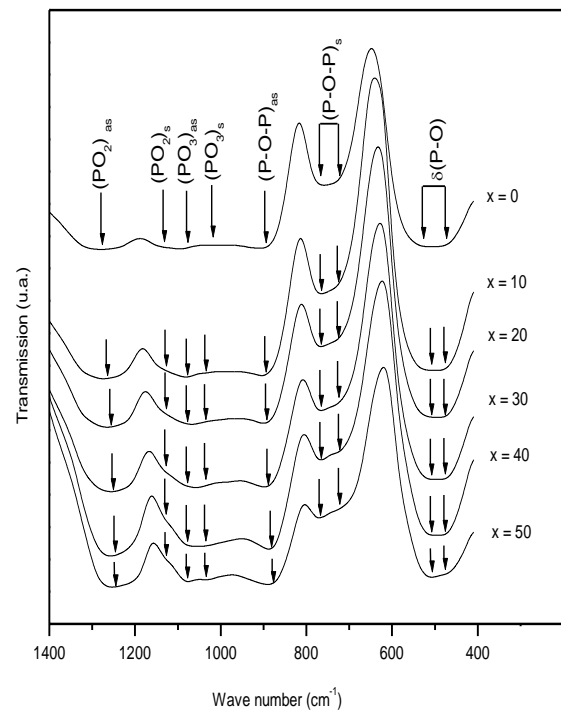


Fig. 3. Infrared spectra of the (50-x)CaO-xPbO-50P₂O₅ glasses.

The asymmetric stretching band of P-O-P shifts to lower frequencies from 896 cm^{-1} in 50CaO-50P₂O₅ glass to 880 cm^{-1} in 50PbO-50P₂O₅ glass. This is because of the decrease in covalent character of P-O-P bonds, indicating that the P-O-P bonds are less strengthened as the Ca²⁺ is replaced by Pb²⁺, which agrees with the decrease of the glass transition temperature.

The Raman spectra of (50-x)CaO-xPbO-50P₂O₅ glasses ($0 \leq x \leq 50$), in the frequency range between 200 and 1400 cm^{-1} , are shown in Fig. 4. All these glasses have similar Raman spectra, the typical five main groups of the stretching vibrations were observed, which are all associated with the metaphosphate structure [31]; the ν_{as} of the O-P-O groups at 1270-1220 cm^{-1} , the ν_s of O-P-O groups at 1174-1154 cm^{-1} , the ν_s of P-O-P groups at 700-690 cm^{-1} , the ν_{as} of PO₃ groups (end groups) at 1120-1060 cm^{-1} , and the bending vibration (δ) of P-O groups at 400-300 cm^{-1} [32-35]. The progressive addition of PbO to phosphate glass composition induces in the Raman spectra a shift towards lower wave numbers. The shifts in band confirm those observed in infrared spectra. Thus, Pb²⁺ ions are substituted into Ca²⁺ sites in metaphosphate glasses.

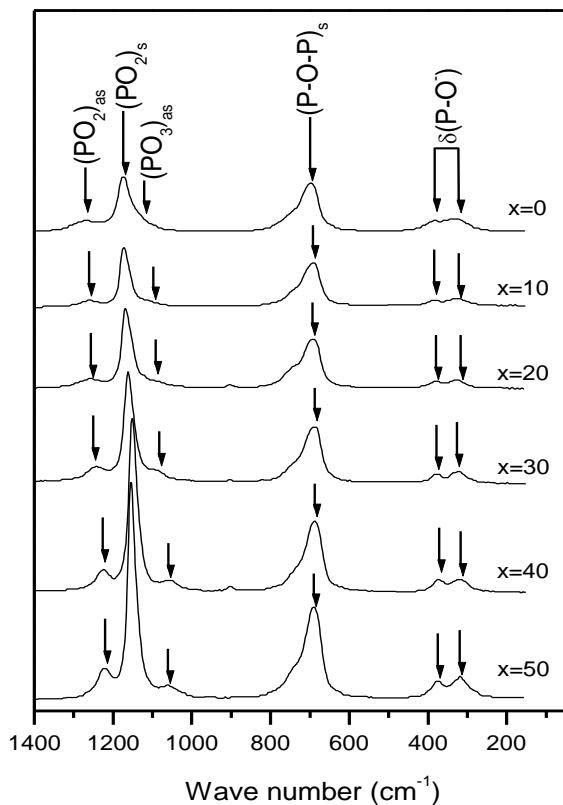


Fig. 4. Raman spectra of the $(50-x)\text{CaO}-x\text{PbO}-50\text{P}_2\text{O}_5$ glasses.

3.3. Chemical durability

Fig. 5 shows the dissolution rates DR of the glasses with various contents of lead oxide in 30 °C deionized water for 48 h. It indicates that the dissolution rate decreases with increasing PbO content. The dissolution rate varies from 2.30×10^{-7} ($\text{g}/\text{cm}^2 \cdot \text{min}$) for $50\text{CaO}-50\text{P}_2\text{O}_5$ glass to 1.17×10^{-8} ($\text{g}/\text{cm}^2 \cdot \text{min}$) for $50\text{PbO}-50\text{P}_2\text{O}_5$ glass (Table 1).

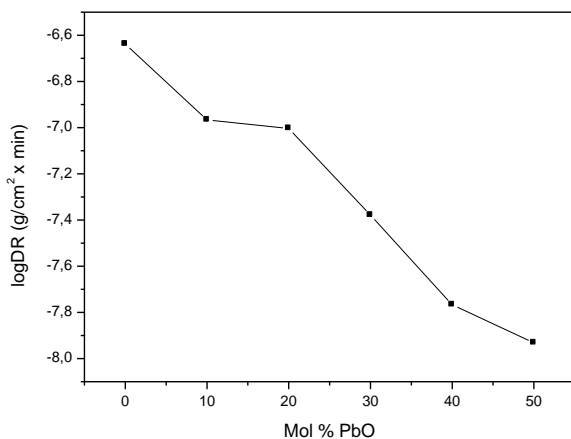


Fig. 5. Composition dependence of dissolution rates (DR) for $(50-x)\text{CaO}-x\text{PbO}-50\text{P}_2\text{O}_5$ glasses after immersion in distilled water at 30 °C for 48 h.

The chemical durability of phosphate glasses is affected by the strength of ionic bonding between cations and phosphate chains, the length of phosphate chains, and whether the H_2O molecules can enter easily into the glass structure between phosphate chains. Apparently, while substituting CaO by PbO in these glasses, the chemical durability should not improve because of the decrease of the glass transition temperature (Fig. 2). The improvement in chemical durability with the substitution of CaO by PbO can be attributed to the replacement of the more resistant P-O-Pb bonds than that of P-O-Ca bonds. Furthermore, as reported by He and Day [36], dissolution rates and the radius of divalent cations are related to an inverse proportion. As for cations of the same valence, the polarisability of oxides is increased with increasing radius of cations. The polarisability of PbO (29.3) is must larger than that of CaO (1.39) [22]. Therefore, the chemical durability of the glass is reinforced with increasing PbO content.

4. Conclusion

In this study, the density, molar volume, glass transition temperature, Infrared and Raman spectroscopies have been investigated for $(50-x)\text{CaO}-x\text{PbO}-50\text{P}_2\text{O}_5$ glasses. IR and Raman spectra reveal the formation of P-O-Pb bonds which replace P-O-Ca bonds and indicate that no depolymerisation is observed. This suggests that PbO acts as the network modifier. System evolution of glass properties confirms these results. The improvement in water durability for the higher PbO content is related to the must larger polarisability of lead compared to calcium.

References

- [1] M. D. Ingram, Phys. Chem. Glasses, **28** (6), 215 (1987).
- [2] Y. He, D. E. Day, Glass Technol., **33** (6), 214 (1992).
- [3] I. W. Donald, B. L. Metcalfe, R. N. J. Taylor, J. Mater. Sci. **32** (22), 5851 (1997).
- [4] M. D. Ingram, Current Opinion in Solid State Mater. Sci. **2** (4), 399 (1997).
- [5] R. M. Wenslow, K. T. Moeller, J. Non-Cryst. Solids, **231**, 78 (1998).
- [6] D. E. Day, Z. Wu, C. S. Ray, P. Hrma, J. Non-Cryst. Solids, **241**, 1 (1998).
- [7] R. K. Brow, L. Kovacic, US Patent **5262364** (1993).
- [8] X. Yu, D. E. Day, G. J. Long, R. K. Brow, J. Non-Cryst. Solids, **215**, 21 (1997).
- [9] A. E. Marino, S. R. Arrasmith, L. L. Gregg, S. D. Jacobs, G. R. Chen, Y. J. Duc, J. Non-Cryst. Solids, **289**, 37 (2001).
- [10] Y. M. Moustafa, A. EL-Adawy, Phys. Status Solidi, **A 179**, 83 (2000).
- [11] A. Chahine, M. Et-tabirou, M. Elbenaissi, M. Haddad, J. L. Pascal, Materials Chemistry and Physics, **84**, 341 (2004).

- [12] A. J. Bourdillon, F. Khumalo, J. Bordas, *Phil. Mag.*, **B37**, 731 (1978).
- [13] B. G. Rao, K. G. K. Sundar, K. J. Rao, *J. Chem. Soc. Faraday Trans.*, **T80**, 3491 (1984).
- [14] B. C. Sales, L. A. Boatner, *Mater. Lett.*, **2**, 301 (1984).
- [15] K. El-Egili, H. Doweidar, Y. M. Moustafa, I. Abbas, *Physica B*, **339**, 237 (2003).
- [16] P. Y. Shih, *Mater. Chem. Phys.*, **80**, 299 (2003).
- [17] F. Fayon, PhD thesis, university of Orléans, France (1998).
- [18] F. Fayon, C. Landron, K. Sakurai, C. Bessada, D. Massiot, *J. Non-Cryst. Solids*, **243**, 39 (1999).
- [19] U. Hoppe, *J. Non-Cryst. Solids*, **183**, 85 (1995).
- [20] C. F. Drake, J.A. Stephens, B. Ayates, *J. Non-Cryst. Solids*, **28**, 61 (1978).
- [21] M. El Hezzat, M. Et-tabirou, L. Montagne, E. Becaert, G. Palavit, A. Mazzah, P. Dhamelincourt, *Mater. Lett.*, **58**, 60 (2003).
- [22] M. B. Volf, *Chemical Approach to Glass*, *Glass Science and Technology*, **7** (1984), Elsevier.
- [23] R. K. Brow, D. R. Tallant, S. T. Myers, C. C. Phifer, *J. Non-Cryst. Solids*, **191**, 45 (1995).
- [24] J. J. Hudgens, S. W. Martin, *J. Am. Ceram. Soc.*, **76**, 1691 (1993).
- [25] D. E. Corbridge, *J. Appl. Chem.*, **6**, 456 (1956).
- [26] H. S. Liu, T. S. Chin, S. W. Yung, *Mater. Chem. Phys.*, **50**, 1 (1997).
- [27] J. O. Byun, B. H. Kim, K. S. Hong, H. J. Jung, S. W. Lee, A. A. Izyneev, *J. Non-Cryst. Solids*, **190**, 288 (1995).
- [28] L. Montagne, G. Palavit, G. Mairesse, *Phys. Chem. Glasses*, **37** (5), 206 (1996).
- [29] R. F. Bartholomew, *J. Non-Cryst. Solids*, **7**, 221 (1972).
- [30] M. A. Salim, G. D. Khattak, M. S. Hussain, *J. Non-Cryst. Solids*, **185**, 101 (1995).
- [31] B. N. Nelson, G. J. Exarhos, *J. Chem. Phys.*, **71**, 2739 (1979).
- [32] A. Mekki, G. D. Khattak, L. E. Wenger, *J. Non-Cryst. Solids*, **330**, 156 (2003).
- [33] K. Meyer, *J. Non-Cryst. Solids*, **209**, 227 (1997).
- [34] J. Koo, B.-S. Bae, H.-K. Na, *J. Non-Cryst. Solids*, **212**, 173 (1997).
- [35] J. J. Hudgens, R. K. Brow, D. R. Tallant, S. W. Martin, *J. Non-Cryst. Solids*, **223**, 21 (1998).
- [36] Y. He, D. E. Day, *Glass Technol.*, **33** (3), 214 (1992).

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