Journal of Thermal Analysis and Calorimetry, Vol. 90 (2007) 2, 453–458

CHEMICAL DURABILITY OF MoO_3–P_2O_5 AND K_2O–MoO_3–P_2O_5 GLASSES

L. Abbas[1], *L. Bih*[1*], *A. Nadiri*[2], *Y. El Amraoui*[3], *H. Khemakhem*[4] *and D. Mezzane*[5]

[1]UFR, PCMI, Céramiques et Verres, Faculté des Sciences et Techniques Errachidia, B.P 509, Boutalamine, Errachidia, Maroc
[2]UFR-SMI, Faculté des Sciences de Meknes, Maroc
[3]LPSMS, FST-Errachidia, Maroc
[4]LPA, Faculté des Sciences de Sfax, Tunisie
[5]LESEO, FST-Guéliz, Marrakech, Maroc

Thermal and chemical durability studies of the phosphate glasses belonging to the binary MoO_3–P_2O_5 and the ternary K_2O–MoO_3–P_2O_5 systems are reported. The chemical resistant attack tests carried out on the free alkaline MoO_3–P_2O_5 glasses show that the glass associated with the P/Mo ratio 2 has the high chemical durability. It shows also a high glass transition temperature value. The above findings are interpreted in terms of the cross-link density of the glasses and the strength of the M–O bonds (*M*=P, Mo).

The influence of K_2O addition on the properties (density, T_g, durability) of this binary high water resistant glass is studied. It is found that the chemical durability along with the other physical properties are reduced by the incorporation of K_2O in the glass matrix. The results were explained by assuming the formation of non-bridging oxygens and weak bonds. The mechanism of the dissolution of these glasses is proposed.

Keywords: *chemical durability, glasses, molybdenum, phosphate*

Introduction

Phosphate glasses frequently have poor chemical durability in aqueous solutions [1–4]. The molybdenum is potentially of greater interest as it can occupy both octahedral and tetrahedral sites, and is susceptible to exhibit different oxidation states. MoO_3 oxide is able to participate to the formation of material's network either in crystalline or vitreous states. The solid–solid interactions of MoO_3 with different oxides [5] and thermal stability of compounds formed by the adsorption of copper(II) ion on MoO_3 [6] have been published recently. In the present work, the interest in molybdophosphate glasses ensues since it forms water soluble, but otherwise stable, glasses over a wide and continuous compositional range. Although work on phosphate glasses has been reported in recent years, specific information pertaining to the mechanism of glass dissolution and other glass properties are lacking. Among the numerous previous investigations of molybdophosphate glasses we may cite the study of molybdenum phosphate glasses containing Ag_2O or K_2O [7]. Potassium molybdophosphate glasses have been investigated but only for one series of glasses with a constant K_2O content 8 mol%. The resistivity of these vitreous materials was the most physical property studied. In a recent paper [8], iron or alumina molybdophosphate glassy samples have been prepared, namely in the Al_2O_3–(or Fe_2O_3)–MoO_3–P_2O_5 systems. The physical and chemical properties such as glass transition temperature T_g, viscosity and solubility in water have been measured. The aim of the present work is to report on the thermal and chemical properties of binary MoO_3–P_2O_5 and ternary K_2O–MoO_3–P_2O_5 glasses. The choice of the glasses to be studied inside the later diagram is conducted based on the obtained results from the binary system.

Experimental

The synthesis process of the $xMoO_3$–$(1–x)P_2O_5$ and yK_2O–$(1–y)[0.5MoO_3$–$0.5P_2O_5]$ glasses has been described elsewhere [9]. Glass samples of a given composition were prepared from mixtures of reagent grade MoO_3, K_2CO_3 and $NH_4H_2PO_4$. The mixtures were thoroughly ground and heated in a platinum crucible at 520 K for several hours in order to minimise losses by evaporation. The product was melted in air at 1200 K for approximately 1 h and stirred in between in order to ensure the homogeneity of the melt. Each melt was poured on a stainless steel plate preheated at 450 K to avoid shattering of the quenched samples due to thermal stress. Finally, the vitreous samples were annealed for 6 h at 550 K to relieve residual internal stress and slowly cooled to room temperature.

The vitreous state of the samples were analysed through X-ray diffraction (XRD) and differential

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[*] Author for correspondence: bihlahcen@yahoo.fr

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

thermal analysis (DTA) studies. Glass transition temperature was determined on quenched glasses by a Seiko-DTA analyser with a heating rate of 10°C min^{-1} and is accurate to ±5°C. Densities of the glasses were measured by the Archimedes method using xylene as the medium and are accurate to 0.01 g cm^{-3}. Infrared spectra were recorded with a Mattson Genesis series in 1400–400 cm^{-1} range using glass powders dispersed in KBr pellets. The chemical durability of the glasses was estimated in term of the dissolution rate (D_R). This later was calculated from the measured mass loss (ΔW (g)) using the equation [10]:

$$D_R=\Delta W/(At)$$

where A is the surface area (cm^2) of the sample and t is the time (min) that the sample was immersed in the test solution at 32°C. The tests were performed in media having different pH values. The buffer solutions from pH 5.5 to 8.5 were prepared by taking 2.5 vol% glacial acetic acid in water and by adding concentrated ammonia solution until the desired pH value was reached. The pH of the solution was measured using a digital pH-meter (micro pH 2000 Crison). A 0.2 g sample of each glass was put into 1 L Erlenmeyer flasks and shaken with 250 mL of ammonia acetate buffer solution with pH's from 5.5 to 8.5 for different time periods.

The concentration of molybdenum in the leachate solution was determined spectrophotometrically using a iodine monochloride method. The higher valence states of molybdenum (Mo^{6+} and Mo^{5+}) were reduced to the Mo^{3+} state by the use of zinc metal before determination. The concentration of P_2O_5 in the leachate solution is determined as follows: in 20 mL of leachate, an excess amount of standard lanthanum chloride solution was added with constant swirling. Lanthanum phosphate was precipitated quantitatively. The content of the flask were heated at 60–70°C and excess lanthanum chloride was back titrated with standard EDTA solution at pH 5.3 using xylenol orange indicator. A blank titration of the added lanthanum solution was made with the same EDTA solution to obtain the lanthanum equivalent of EDTA. The amount of P_2O_5 was obtained from the difference between the two titer values.

Results and discussion

Binary MoO_3–P_2O_5 and ternary K_2O–MoO_3–P_2O_5 glasses have been elaborated. They are blue in colour. It is realized that the [$x$$MoO_3$–$(1–x)$$P_2O_5$] glass system represents a rather unique system in that it forms stable glasses over a wide and continuous composition range. The upper limit of MoO_3 that permitted formation of a vitreous material, found in this work, was about 78 mol%. Above the 78 mol% of MoO_3, the non-transparent and opalescent materials were obtained for chemical compositions containing more than 78 mol% of MoO_3. This limit lies between 86 and 73 mol% of MoO_3 found by Bridge *et al.* [11] and Provance *et al.* [7], respectively. This range is perhaps the widest for a simple binary mixture of a glass former (P_2O_5) with another oxide that does not form a stable glass itself. The molybdenum ions are multivalent, and exist at least as Mo^{5+} and Mo^{6+} valence states in the MoO_3–P_2O_5 glasses [12, 13]. The Mo^{6+} ions could be located in four-fold and/or six-fold oxygen environments. It is established also that the structure of the vitreous P_2O_5 consists of an assembly of polyhedron PO_4. Each tetrahedron shared three corners with its neighboring tetrahedron while the other oxygen atom is double-bonded to a phosphorus atom [14, 15].

The density of the $x$$MoO_3$–$(1–x)$$P_2O_5$ glasses and its variation with composition (P/Mo ratio) are presented in Fig. 1. The density decreases with increasing P/Mo ratio. This figure shows also the composition dependence of the glass transition temperature T_g. It is found that T_g increases with increase in P/Mo ratio and reaches a maximum value for the composition corresponding to P/Mo=2. Then, it decreases. The dissolution rate (D_R) as a function of P/Mo ratio for the binary $x$$MoO_3$–$(1–x)$$P_2O_5$ glasses at different pH solution values is shown in Fig. 2. Whatever the pH value, the minimum of D_R rate is observed for the glass ($0.5MoO_3$–$0.5P_2O_5$) having the P/Mo ratio equal to 2. According to the above, we can state that the glass with P/Mo=2 is the most aqueous resistant glass in the binary MoO_3–P_2O_5 system. This glass is examined further. In order to assess the effect of K_2O oxide on its chemical durability along with its other physical properties, we have performed measurements on the glasses with increasing K_2O content belonging to the series $y$$K_2O$–$(1–y)$[$0.5MoO_3$–$0.5P_2O_5$]. The dissolution tests of these glasses are carried out in the same experimental conditions to the binary ones. The variation of the D_R of these glasses upon the potassium oxide content is

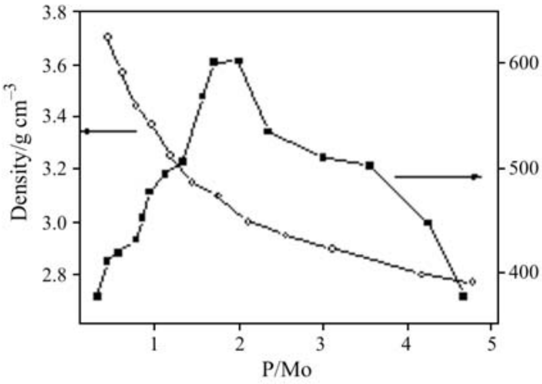

Fig. 1 Variation of the density and the T_g of the MoO_3–P_2O_5 glasses as a function of the P/Mo ratio

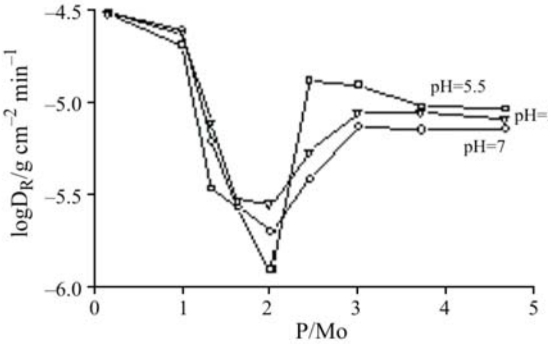

Fig. 2 Variation of the dissolution rate D_R of the MoO_3–P_2O_5 glasses as a function of the P/Mo ratio

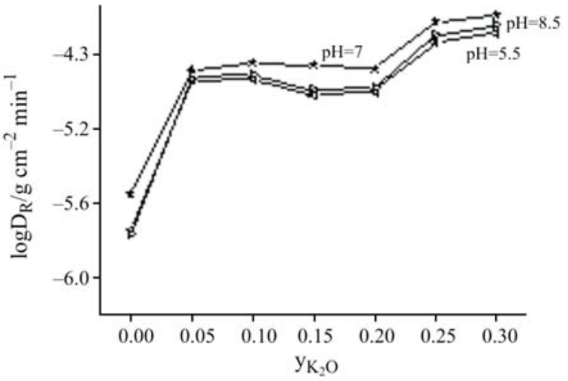

Fig. 3 Variation of the dissolution rate D_R as a function of the K_2O content in yK_2O–$(1–y)[0.5MoO_3$–$0.5P_2O_5]$ glasses

shown in Fig. 3. It is seen that the chemical durability decreases with K_2O content. The decrease is very significant for the first addition of the modifier K_2O oxide. The chemical durability tests are determined for these glasses along with the glass transition temperature which is shown in Fig. 4. This physical parameter is decreasing quantity when the glass matrix is progressively enriched by the modifier K_2O.

Binary MoO_3–P_2O_5 glasses

Glasses elaborated in the binary MoO_3–P_2O_5 system are blue in colour. This blue colour could be explained by the loss of oxygen in the melt owing to the reduction of molybdenum from Mo^{6+} to Mo^{5+} state. Effectively, this statement is confirmed by us recently using the EPR experiments [14]. From Fig. 1 it is seen that the density of the glasses increases with increasing amount of MoO_3. When P_2O_5 replaces MoO_3 in MoO_3–P_2O_5 system, it introduces twice the number of $[PO_4]$ tetrahedral units for each $[MoO_6]$ octahedral group. In addition, the increase in mass for the process of this substitution is 2g. This suggests the direction of density variation as a function of P/Mo ratio.

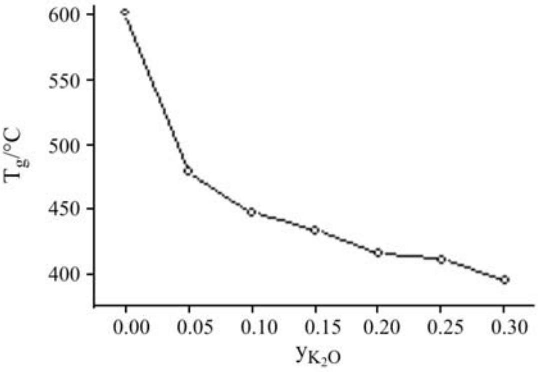

Fig. 4 Variation of the T_g of the yK_2O–$(1–y)[0.5MoO_3$–$0.5P_2O_5]$ glasses as a function of the K_2O content

The composition dependence of glass transition temperature (T_g) is shown in Fig. 1 for MoO_3–P_2O_5 system. Similar variations were obtained in the ternary Li_2O–MoO_3–P_2O_5 [16] and A_2O–MoO_3–P_2O_5 (*A*=Li, Na) systems [17]. As shown in this figure, T_g increases with increasing P/Mo ratio and reaches a maximum for a glass with the composition corresponding to P/Mo ratio equal to 2, beyond which it decreases with further increase in P/Mo ratio. The change in T_g is, in general, attributed to the three combined effects: (*i*) change in bond strength, (*ii*) degree of cross-link density and (*iii*) closeness of packing [1]. Defining the cross-link density as the number of bridging oxygen atoms per network-forming atom, one notes that this number is 1 for P_2O_5, whereas it is 3 for MoO_3. The closeness of packing has been defined by Makishima *et al*. [18] in terms of the ionic radii of both cation and anion. Using Makishima equation with the ionic radii data $R^{6+}_{Mo}=0.62$ Å, $R^{5+}_{P}=0.35$ Å and $R^{2-}_{O}=1.32$ Å, we find that the closeness of packing is almost constant for entire vitreous range. It appears then that the variation of T_g could be explained based on the cross-link density and the bond strength parameters. Let us now to identify the effect of the cross-link density. The partial replacement of MoO_3 by P_2O_5, i.e. increases of P/Mo ratio, is expected to decrease the cross-link density for all the compositions of P/Mo ratio unless the nature of structural units formed in the glass matrix are different for the compositions. It is possible that this effect accounts for the decrease in T_g at high P/Mo ratio (Fig. 1). Up to about P/Mo ratio equal to 2, an increase of T_g is observed. This trend of the T_g variation could be emphasized with the variation of the bond strength. Since the P–O thermochemical bond energy is 84 kcal mol^{-1} (in P_4O_{10}) and Mo–O thermochemical bond energy is 29 kcal mol^{-1} (in MoO_3), the mean bond strength must increases with an increase of the P/Mo ratio. The T_g maximum at P/Mo=2 can be envisaged as the competition of the increasing mean bond strength and decreasing cross-link density with increase in P/Mo ratio.

Figure 2 shows the dissolution rate (D_R) result obtained for xMoO$_3$–(1–x)P$_2$O$_5$ glasses. No general trend is established from the variation of dissolution rate with the pH of the solution. The glasses are susceptible to be degraded both in acidic and alkaline medium. The most durable glass is a composition corresponding to P/Mo=2. However, for this glass we can remark that the dissolution rate is higher under basic conditions. From thermal analysis seen above, this vitreous material (P/Mo=2) presents also a maximum value for the glass transition temperature T_g. Therefore, for a composition with P/Mo=2 the glass transition and the chemical durability are strongly coupled. In other words, a minimum of D_R and a maximum of T_g could be issued from the same origin. Hence, the minima of the rate dissolution, and the maxima of T_g can be envisaged as a convolution of the decrease of the cross-link density and the increase of bond strength when P/Mo ratio increases. Moreover, it has been shown that the oxidation state of the transition metal ions in a phosphate glass may affect the chemical durability of the glass [19]. In alkali-molybdenum-phosphate glasses, Bih *et al.* suggested that ratio of Mo^{5+}/Mo$_{total}$ in the glass matrix is chemical composition dependent [16]. Some authors had shown that the Mo^{5+}/Mo$_{total}$ ratio presented a maximum near a composition associated with P/Mo≈2. Therefore, this proposition of the effect of oxidation state on the chemical durability is consistent for the glasses under study. Let us now discuss the effect of pH on glass durability and particularly for a glass with P/Mo=2. Based on the batch chemical composition, this material is associated with the chemical formula of molybdenum metaphosphate MoO$_2$(PO$_3$)$_2$ crystalline phase [20]. In this crystalline phase, the tetrahedral PO$_4$ which have unshared oxygens, share two corners with other tetrahedral to produce infinite wavelike chains. The other two corners of every tetrahedron are shared with MoO$_6$ octahedra. Two adjacent corners of every octahedron share corners with two adjoining tetrahedral in the same chain, two other corners are shared with tetrahedral in different chains, whilst the remaining two corners are unshared. Each octahedron is thus linked to 3 chains of PO$_4$ tetrahedra to form a layer structure but there are no contacts between neighbouring octahedral. In the analogue vitreous phase (0.5MoO$_3$–0.5P$_2$O$_5$), it is obvious to consider that its vitreous network consists of a mixture of the structural groupings that occur in the crystalline phase. It follows that the glass contains mainly bonds of type P–O–P, P–O–Mo and Mo–O. As a matter of fact, the presence of bands at 1100–1300, 900–1000, 720 and 640 cm^{-1} in the infrared spectrum (Fig. 5) of a glass (y=0) confirms this assumption. A general structural study of the glasses by IR spectroscopy is presented in the next section. Since it is accepted that the former P$_2$O$_5$ (equivalent to P–O–P bonds) is an acidic oxide, and the electronegativity of phosphorus and molybdenum ions are comparable, it is reasonable to assume that the P–O–M (M=P, Mo) bonds could easily be disrupted by an alkaline medium. By examining Fig. 2, it then seems logical to conclude that the dissolution rate of the glass with the ratio P/Mo=2 is leached following the sequence pH=8.5>pH=7>pH=5.

Ternary K$_2$O–MoO$_3$–P$_2$O$_5$ glasses

A structural investigation of these glasses was realized by infrared spectroscopy in the 1400–400 cm^{-1} range. The obtained spectra for yK$_2$O–(1–y)[xMoO$_3$–(1–x)P$_2$O$_5$] glasses are presented in Fig. 5. A large band constituted of several elementary bands can be observed between 1400 and 400 cm^{-1}. The band at 920–940 cm^{-1} present in all glasses is attributed to the Mo–O stretching frequency of (MoO$_6$) groups which are simultaneously part of (MoO$_6$)(MoO$_6$) and (MoO$_6$)(PO$_4$) structural units [13]. A band with variable intensity located in 1200–1300 cm^{-1} seen in all glasses indicated the presence of metaphosphate groups (ν_{as}PO$_2$) in their structure. A band seen at 1100–1180 cm^{-1} is characteristic of pyrophosphate units (ν_{as}(PO$_3$)^2). The splitting of this later into two shoulders 1100 and 1180 cm^{-1} with increasing K$_2$O content is attributed to the asymmetry of the (PO$_3$)$^{2-}$ groups. Bonding of the (PO$_3$)$^{2-}$ is realized by both K$^+$ and Mo and with a more covalent character for P–O–Mo than P–O–K bonds. A compari-

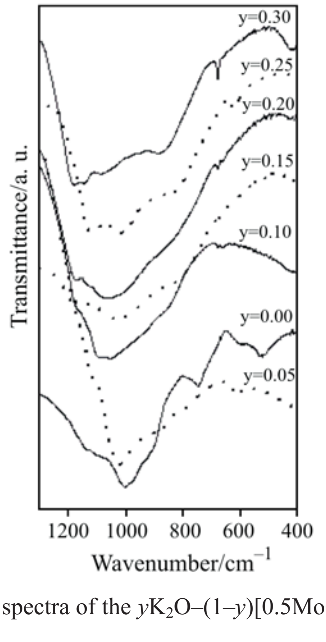

Fig. 5 Infrared spectra of the yK$_2$O–(1–y)[0.5MoO$_3$–0.5P$_2$O$_5$] glasses

son of IR spectra of glasses containing K_2O with that of a glass (y=0) shows that the transmittance of 900 cm^{-1}, ascribed to ($\nu_{as(P-O-P)}$ [13], 730 cm^{-1} ($\nu_{s(P-O-M)}$ (M=P, Mo) and 640 cm^{-1} ($\nu_{as(M-O-Mo)}$) decrease with K_2O content. These results suggest that the linkages P–O–M (M=P, Mo) are disrupted by the presence of K_2O oxide in the glass. These linkages may be modified by K_2O oxide according to the following reactions:

$$K_2O + P{-}O{-}P \leftrightarrow 2P{-}O^{-}\ldots K^{+} \qquad (1)$$

$$K_2O + Mo{-}O{-}Mo \leftrightarrow 2Mo{-}O^{-}\ldots K^{+} \qquad (2)$$

This degradation of the network is accompanied with the formation of weak links such as $K^{+}\ldots O^{-}$ bonds. Based on the above, we associate the decreasing of T_g with increasing K_2O content (Fig. 4) to the formation of weak bonds in the framework.

For the chemical durability of the ternary yK_2O–$(1-y)[xMoO_3$–$(1-x)P_2O_5]$ glasses expressed in term of the dissolution rate shown in Fig. 3, the D_R sharply increases at 10 mol% K_2O, then rises slowly at 20 mol% K_2O and then increases again at an even greater K_2O content. These results indicate that the substitution of K_2O for MoO_3–P_2O_5 glass decreases the water-resistant ability of the glasses. When K_2O was incorporated into the glass matrix of the ($0.5P_2O_5$–$0.5MoO_3$) glass, it would break the network by disrupting the Mo–O–Mo and P–O–P bonds (i.e. Eqs (1) and (2)) and induces the increase of the dissolution rate as observed in (Fig. 3). However, this dissolution trend is not regular. The non-monotone increase of the dissolution rate with K_2O content could possibly due to the existence of structural rearrangement in glass network.

Mechanism of the dissolution of the glasses

From chemical considerations and particularly the chemical composition of the glasses under study, we attempt in the following to propose their mechanism of the dissolution. The main difference between the binary and the ternary glasses is the incorporation of alkaline element in these later. Therefore, one can expect that a mechanism of the dissolution of free-alkaline and alkali-molybdenum phosphate glasses could be different at certain extent. For the ternary K_2O–MoO_3–P_2O_5 glasses, a mechanism proposed here is similar to that describing the corrosion of alkali silicate glasses [21]. The mechanism of the dissolution K_2O–MoO_3–P_2O_5 glasses can be described in a two-stage process: at first, an ion-exchange between the network modifier K^{+} ions in the glass and H^{+}, H_3O^{+} and/or H_2O species from the solution can be observed:

$$M{-}O^{-}\ldots K^{+} + H^{+} \leftrightarrow M{-}O^{-}H^{+} + K^{+}\ (M\text{=P, Mo}) \qquad (3)$$

The ions are diffusing in opposite directions, leading to the formation of a so-called leached or gel layer in the glass, which is depleted in potassium and enriched in hydrogen bearing species. For instance, the formation of P–OH bonds in the surface of some glasses is confirmed by using vibrational spectroscopy [22]. In the second stage of the dissolution process the former network breaks down. From the determination of the concentrations of P_2O_5 and MoO_3 in the leachate solution, it is found that: (*i*) the concentration ratio P/Mo in the acidic solution is lower than that in the bulk glass (P/Mo=2) and (*ii*) the P/Mo ratio in alkaline media is higher than it is in the bulk glass. These results do indicate that leaching of the ternary glasses is selective rather than congruent dissolution. Our main interest in the following is to answer why the dissolution is selective? The Mo–O bond is rather more covalent than the well known network forming Si–O bond, so we suggest that the Mo atoms occupy network forming positions throughout the entire vitreous range of the K_2O–MoO_3–P_2O_5 system. Hence, the glasses which we are interested in are composed with two oxide formers P_2O_5 and MoO_3 rather than a unique phosphate glass-forming. Thus, we envisage these glasses to consist of mainly –P–O–P–, –Mo–O–Mo– and –P–O–Mo– bridging bonds as shown by IR spectroscopy. The ratio of each depends on the composition. Moreover, from the electronegativity considerations [23], P_2O_5 and MoO_3 compounds behave as acidic and basic oxides, respectively. Hence, the modification of the P–O–P units is preferred in alkaline solution, and the disruption of basic Mo–O–Mo bonds is preferred in acidic media:

$$P{-}O{-}P + OH^{-}\ (\text{or } H_2O) \rightarrow P{-}O{-}H + P{-}O^{-} \qquad (4)$$

$$Mo{-}O{-}Mo + H_2O\ (\text{or } H_3O^{+}) \rightarrow 2Mo{-}O{-}H \qquad (5)$$

Therefore, a plausible explanation for the selective dissolution of the glasses must take into account the preferential attacked of some bonds.

Let us now to elucidate the difference between the mechanism of the dissolution rate of the free-alkaline and the alkaline –MoO_3–P_2O_5 glasses. Since the MoO_3–P_2O_5 glasses contain in their glass-matrix only the former cations (P^{5+}, Mo^{6+} and/or Mo^{5+}), one can state that the ion-exchange reaction (Eq. (3)) is not involved in the mechanism of their corrosion, and the most probable reactions that occur in their dissolution are schematised by Eqs (4) and (5).

Conclusions

Some correlations between the physical and the chemical properties of the glasses inside the K_2O–MoO_3–P_2O_5 system have been established. The results obtained clearly indicate that the strengthening of the network increases both the chemical durability and the glass transition temperature. The dissolution of the glasses is selective rather than congruent.

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Received: May 2, 2006
Accepted: January 16, 2007
OnlineFirst: February 26, 2007

DOI: 10.1007/s10973-006-7673-4