Molybdenum-phosphate Glass with High MoO_3 Content

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Due to the essential role played by the molybdenum ions in the electrical conduction process, this paper investigate the molybdenum rich part of the binary system: xMoO_3*-(100-x)*P_2O_5 *(with x = 90-70 mol %). The effect of the composition upon glass transition temperature, density and* Mo^{5+} *ion concentration was studied.*

Keywords: semiconducting glass; glass structure

Extensive studies have been carried out on oxide glass containing transition metal ions due to the interests in their conduction mechanism and glass structure. Properties are those depending mainly on the structural particularities, which can be revealed by differential thermal analysis, density value, infrared spectroscopy. [1]

The aim of the study was to investigate the structural changes that occur in the MoO_3-P_2O_5 binary system at high MoO_3 concentrations, in order to make further correlations with their electrical properties.

Experimental part

Glasses under investigation of the forms: x MoO_3 – (100-x) P_2O_5, (x = 90, 85, 80, 75 and 70 mole %) were prepared using reagent grade $MoO_3 \times H_2O$ and $NH_4H_2PO_4$ as starting materials. The raw materials weighed to the desired compositions were mixed and ground in a porcelain mortar. The mixture was melted at 950° C for 40 min in closed porcelain crucibles using an electric furnace and then rapidly quenched between two stainless steel plates. By this quenching technique we fabricated bulk glass samples of about 1 mm thick.

Results and discussions

The differential thermal analysis (DTA) measurements were recorded on a MOM thermal analyzer with a standard heating rate of 10°C min^{-1}. A typical DTA curve for the $80MoO_3$-$20P_2O_5$ glass is presented in figure 1.

The glass transition temperatures range from 730 K down to 623 K as illustrated in figure 2.

A quasilinear decrease of T_g with the MoO_3 addition can be observed, indicating a depolimerization of the phosphate structure of the glass.

The density, d of the glass at 293 K was measured using the displacement method, using isopropanol as working fluid. The influence of the MoO_3 amount over the glass density is shown in figure 3.

The addition of MoO_3 (d = 4.7 kg/dm^3), a much heavier oxide than P_2O_5 (d = 2.3 kg/dm^3) increases the glass densities in the investigated system.

The cantitative method used for the determination of the pentavalent molybdenum ions was based on the indirect complexonometric titration with complexon (III) [2].

The results for the 5 investigated glasses in the MoO_3 – P_2O_5 system are presented in table 1 and illustrated in figure 4.

Even if the dependence between the amount of MoO_3 and the value of the C raport is cvasilinear it can be observed a small increase at 80 mol % MoO_3.

Vibration infrared spectroscopy is used as an analytical probe to elucidate the structural elements of the glass network. The infrared spectra illustrated in figure 5 for the xMoO_3-(100-x)P_2O_5 glass were recorded using a Perkin-Elmer IR spectro-photometer using KBr pellets.

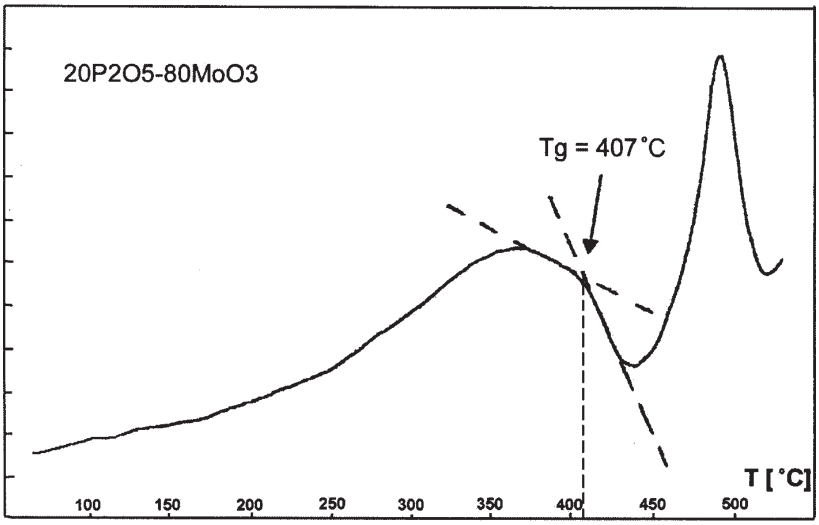

Fig. 1. DTA curve of the $80MoO_3$-$20P_2O_5$ glass

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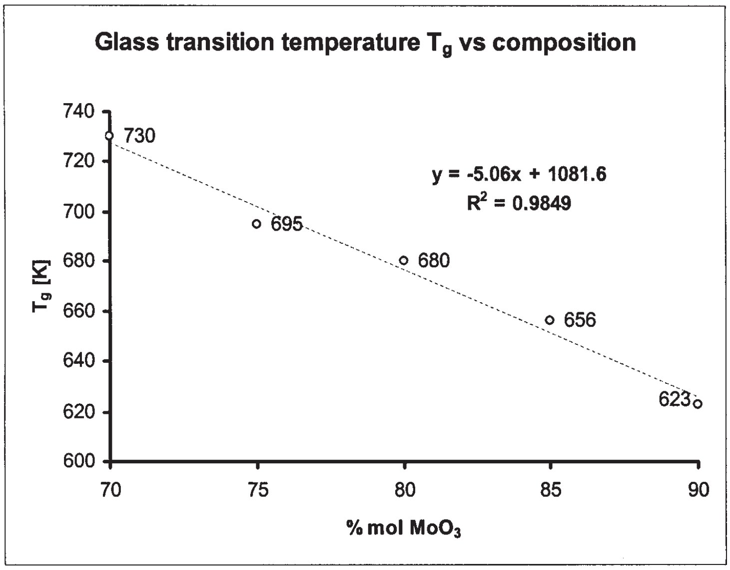


Fig. 2. Composition dependence of the glass transition temperatures for the $xMoO_3$-(100-x)P_2O_5 glass

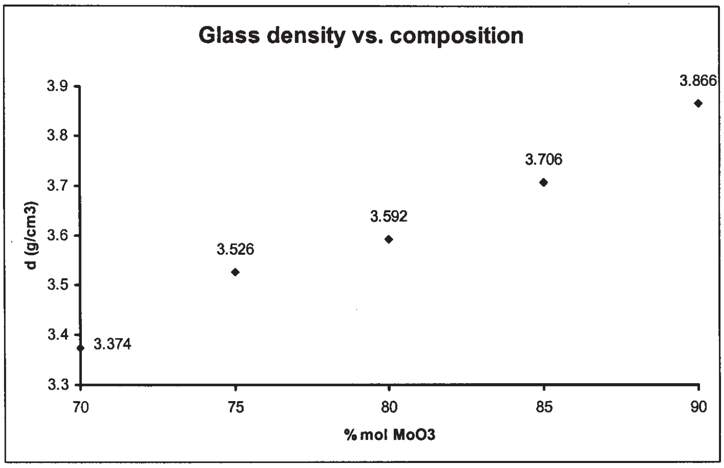


Fig. 3. Composition dependence of the glass densities for the $xMoO_3$-(100-x)P_2O_5 glass

Table 1

VALUES FOR THE Mo^{5+} ION CONCENTRATION, TOTAL MOLYBDENUM CONCENTRATION AND THE RATIO $C = \frac{N_{Mo^{5+}}}{N_{Mo_{total}}}$ FOR THE INVESTIGATED GLASS

% M MoO3	$N_{Mo^{5+}}$ [1/m³]	$N_{Mo_{total}}$ [1/m³]	$C = \frac{N_{Mo^{5+}}}{N_{Mo_{total}}}$
90	$3.24 \cdot 10^{27}$	$2.19 \cdot 10^{28}$	0.148
85	$2.61 \cdot 10^{27}$	$1.98 \cdot 10^{28}$	0.132
80	$2.48 \cdot 10^{27}$	$1.81 \cdot 10^{28}$	0.137
75	$1.60 \cdot 10^{27}$	$1.66 \cdot 10^{28}$	0.096
70	$1.18 \cdot 10^{27}$	$1.49 \cdot 10^{28}$	0.079

The maximum for the absorption peaks and the corresponding vibration bonds are summarized in table 2.

Significant changes occur in both intensities and band shapes as a function of composition, from the high molybdenum containing glass (x = 90-80 mol %) to glass with less MoO_3. For the first group, the absorption maxima around 890 cm^{-1} and around 750 cm^{-1} are assigned to ν_1 and ν_3 stretching vibrations of the MoO_4^{2-} anions. The maxima around 980 cm^{-1}, for the glasses containing 90 and 85 mol % MoO_3 is attributed to the Mo=O stretching mode of the [MoO_6] octahedral unit, indicating the existence of strongly deformed [MoO_6] octahedral with a shorter Mo-O bond [3, 4]. The peak around 440 cm^{-1} is assigned to the υ_s(Mo-O-Mo) types of bonds, confirming the presence of the condensed molybdate anions [5]. For the low MoO_3 content glass an additional absorption band at around 630 cm^{-1} can be observed, corresponding to the ν_{as}(Mo-O-Mo) bond. The glass network is formed not only by Mo-O-Mo bridges, but also by P-O-P and Mo – O – P mixed bridges, as it is shown by the presence of the peaks at around 920 cm^{-1} for ν_{as}(P-O-P) and 708 cm^{-1} and around 500 cm^{-1} for ν(Mo-O-P) vibrations. The glass containing 75 and 70 mol% MoO_3 show also a peak at around 1030 cm^{-1} assigned to the ν_s(PO_3) terminal groups [6].

It is well known that the transformation temperature T_g is defined as the temperature corresponding to a glass viscosity of $10^{13.3}$ P. The value of T_g increases as the bond strenght and the mean crosslink density increase. In addition, it seems reasonable to assume that the easiness with which flow can take place in a network depends upon the available free volume into which mobile ions or network fragments can diffuse. So, it has been proposed

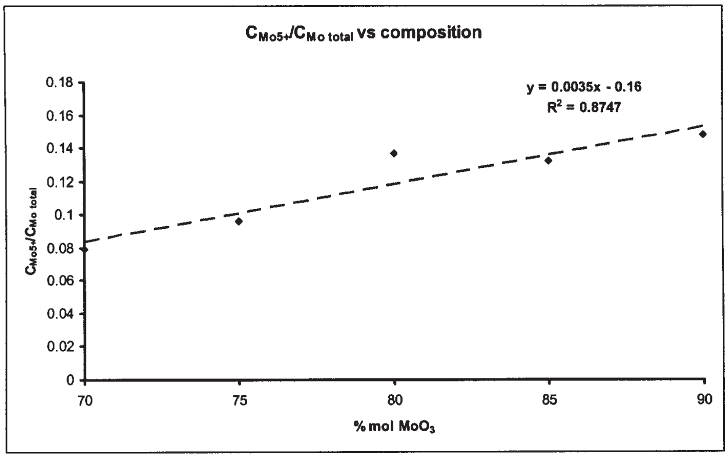


Fig. 4. The influence of the composition upon the $C = \frac{N_{Mo^{5+}}}{N_{Mo_{total}}}$ for the investigated $MoO_3 - P_2O_5$ binary glass

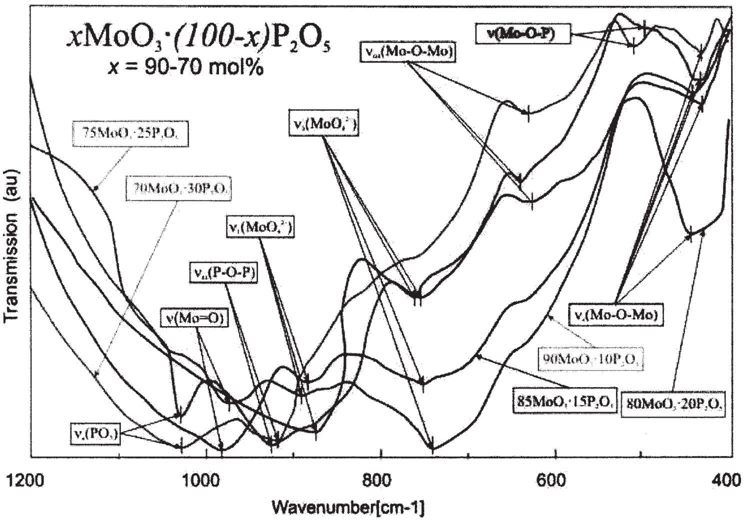


Fig. 5. Infrared spectra of the investigated glass $xMoO_3$-(100-x)P_2O_5

Table 2
THE ABSORPTION MAXIMA AND THE CORRESPONDING VIBRATION BONDS

Sample	Absorption peak [cm^{-1}]	Characteristic vibration bond
$90MoO_3 \cdot 10P_2O_5$	974	ν(Mo=O)
	891	$\nu_1(MoO_4)^{2-}$
	745	$\nu_3(MoO_4)^{2-}$
	443	ν_s(Mo-O-Mo)
$85MoO_3 \cdot 15P_2O_5$	982	ν(Mo=O)
	883	$\nu_1(MoO_4)^{2-}$
	751	$\nu_3(MoO_4)^{2-}$
	432	ν_s(Mo-O-Mo)
$80MoO_3 \cdot 20P_2O_5$	888	$\nu_1(MoO_4)^{2-}$
	753	$\nu_3(MoO_4)^{2-}$
	625	ν_{as}(Mo-O-Mo)
	443	ν_s(Mo-O-Mo)
$75MoO_3 \cdot 25P_2O_5$	1036	$\nu_s(PO_3)^-$
	920	ν_{as}(P-O-P)
	761	$\nu_3(MoO_4)^{2-}$
	630	ν_{as}(Mo-O-Mo)
	497	ν (Mo-O-P)
	444	ν_s(Mo-O-Mo)
$70MoO_3 \cdot 30P_2O_5$	1028	$\nu_s(PO_3)^-$
	918	ν_{as}(P-O-P)
	628	ν_{as}(Mo-O-Mo)
	507	ν (Mo-O-P)
	430	ν_s(Mo-O-Mo)

[7] that T_g will increase with a third variable – the closeness of packing of the network. Quantitatively, this term, associated with the “openness”, the loosening of packing of a vitreous network was defined by the packing density in terms of the ionic radii of both cation and anion. Assuming a tree-dimensional network for the investigated glasses the following relation can be proposed for T_g:

$$T_g = f(n_c,\varepsilon,p) \qquad (1)$$

where:

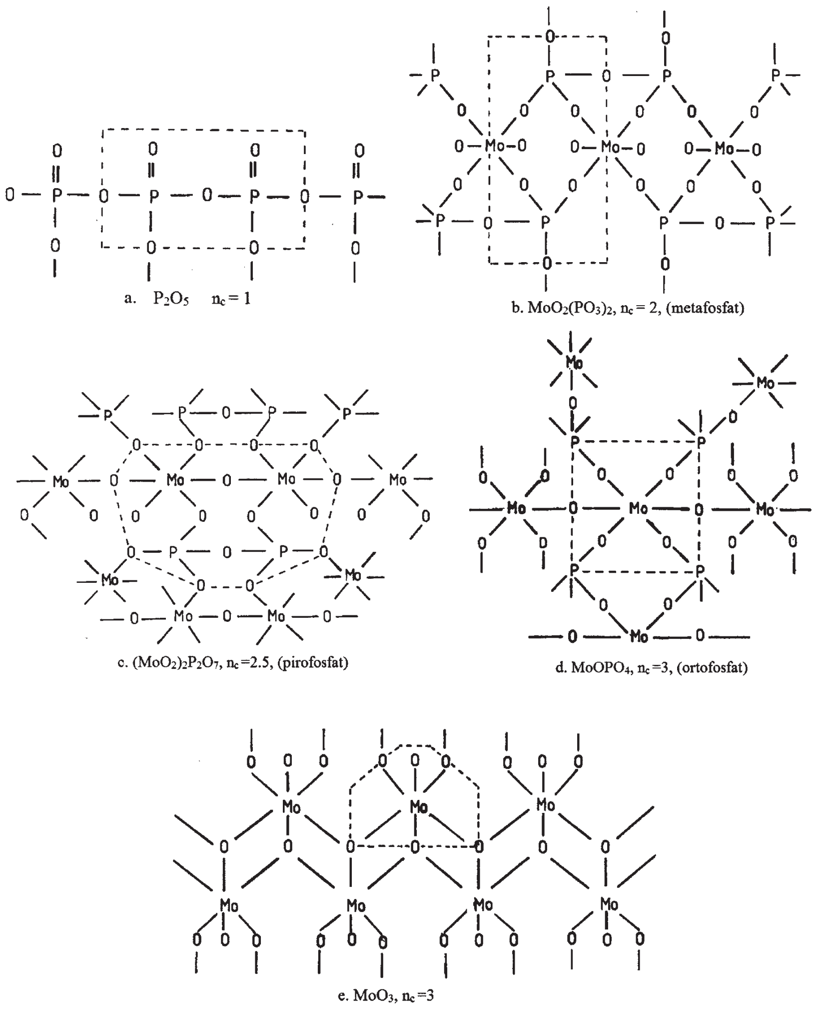
n_c is the mean value of crosslink density (mean number of crosslinks/cation);

ε - the bond strength;

p - the packing density respectively.

Figure 6 illustrate the schematic two-dimensional representations of the crystalline phases of the Mo-P-O system (bond lengths and relative orientations are not to be considered) and the corresponding values of n_c [8].

The value of the mean value of crosslink density increases monotonically from 1 (corresponding to the pure P_2O_5 glass) to 2.76 (for the glass containing up to 84 mol% MoO_3) [7], due to the replacement of ruptured P=O bonds by P-O-P and Mo-O-P groups and the fact the crosslink density of Mo in all known configuration with P (ortho-, meta- and pyro- phosphates) is larger that of P in P_2O_5. The bond strength of P-O and Mo-O (560 kJ/mol and 599 kJ/mol [9]) remains approximately constant, so the fall of T_g with the MoO_3 increase can be explained in terms of the


a. P_2O_5 $n_c = 1$

b. $MoO_2(PO_3)_2$, $n_c = 2$, (metafosfat)

c. $(MoO_2)_2P_2O_7$, $n_c = 2.5$, (pirofosfat)

d. $MoOPO_4$, $n_c = 3$, (ortofosfat)

e. MoO_3, $n_c = 3$

Fig. 6. Schematic two-dimensional representations of the crystalline phases of the Mo-P-O system (the dotted regions contain one formula unit)

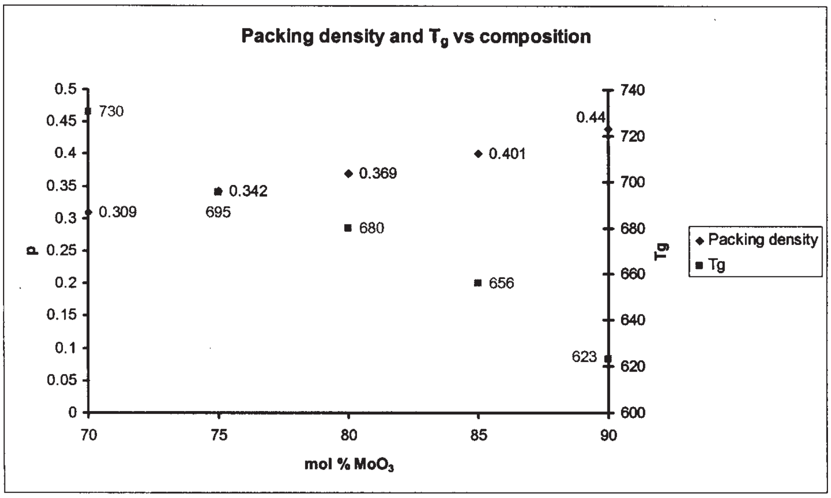


Fig.7. The dependence of the packing density and T_g upon composition for the investigated MoO_3 – P_2O_5 binary glass

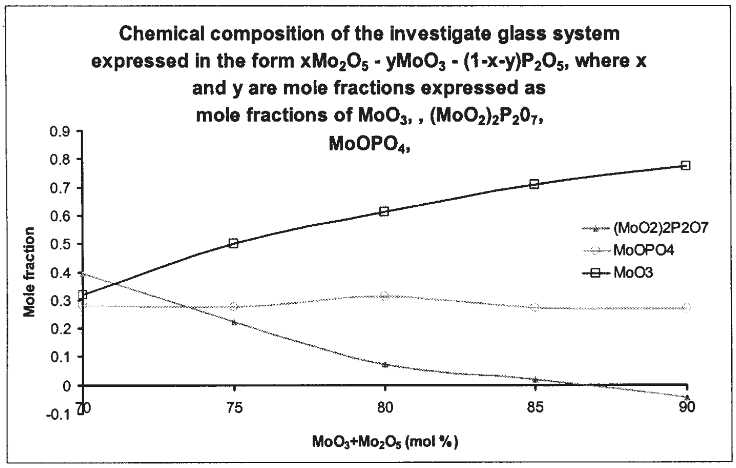


Fig. 8. Composition of the studied glass expressed as mole fractions of $(MoO_2)_2P_2O_7$, MoO_3 and $MoOPO_4$

packing density of those glass. For multicomponent glass, the packing density is described by the equation:

$$p = \frac{\rho}{M}\sum V_i P_i \qquad (2)$$

where:

M is the molecular weight of the glass formula unit,;

ρ - the glass density;

P_i the mole fraction of the *I* oxide and, V_i for an A_xO_y oxide is given by:

$$V_i = \frac{4}{3}\pi N_A\left(xr_A^3 + yr_O^3\right) \qquad (3)$$

where:

N_A is Avogardo's number;

r_A and r_O - the ionic radii of the metallic cation and O^{2-}. For Mo^{6+} (ignoring the small proportion of reduced Mo^{5+}), P^{5+} and O^{2-}, the values of the ionic radii are 0.62Å, 0.34 Å and 1.40 Å respectively [11]. The packing density values calculated using equation 3 and the corresponding T_g values are illustrated in figure 7.

The packing density of the investigated glasses slowly increases with the addition of MoO_3, while T_g decreases in contradiction with equation 1.

A possible explanation of this behaviour, suggested also by the IR data is that the increase of MoO_3 content creates massive changes in the glass structure. An image of those changes can be obtained assuming that the glass consists of the same structural groups that appear in the crystalline phases of the binary MoO_3-P_2O_5 system. Considering a general formula for the investigated glass: xMo_2O_5-$yMoO_3$-$(1\text{-}x\text{-}y)P_2O_5$ where x and y are mole fractions for Mo^{5+} cations (as Mo_2O_5) and Mo^{6+} cations (as MoO_3). Assuming that the entire quantity of Mo^{5+} is contained as $MoOPO_4$, the corresponding quantities of each type of phosphate (pyro and orthophosphate respectively) and the MoO_3 quantity can be calculated (for $60<MoO_3<85$ mol %) as follows [8]:

$$(MoO_2)P_2O_7\text{:}\ \frac{1-2x-y}{4x+2y-1}; \qquad MoOPO_4\text{:}\ \frac{2x}{4x+2y-1};$$

$$MoO_3\text{:}\ \frac{3y+4x-2}{4x+2y-1} \qquad (4)$$

The influence of the glass composition upon the concentration of these species is illustrated in figure 8.

Figure 8 confirms on the one side the composition limitation of these calculation method ($60 < MoO_3 < 85$ mol %), the negative pyrophosphate concentration in the glass containing 90 mole % MoO_3 being physically impossible. On the other side figure 8 offers an image of the structural changes induced in glass with the increase of the MoO_3 quantity. Using the structures corresponding to the crystalline compounds, it can be assumed that the tridimensional structure associated with the molybdenum ortho and pyrophosphate is replaced by a layered structure, similar to the crystalline pure MoO_3. The IR data for glass containing less MoO_3 suggest the presence of the low condensed phosphate anions such as $P_2O_7^{4-}$ and $P_3O_{10}^{5-}$ (confirmed by the ν_{as}(P-O-P) and the $\nu_s(PO_3)^-$ maxima. Together with discrete MoO_4^{2-} tetrahedra units in these glass, suggested by the $\nu_3(MoO_4)^{2-}$ maxima and structural elements containing bridges as Mo-O-Mo and Mo-O-P [6]. The signal for the latest mixed bridges disappear in the high MoO_3 containing glass, with structures based on condensed molybdate anions. In the glasses containing the highest amount of MoO_3 (85 - 90 mol %) it can also be signaled the presence of distorted MoO_6 octahedral units, sugested by the ν(Mo=O) maxima. It is expected that these changes in the glass structure will affect the properties of those glass, as presented in a further paper.

Conclusions

The glass from the binary system: x MoO_3-(100-x) P_2O_5 (x = 70-90 mol %) were investigated. It was proved that both oxides act as glass formers. The existence of $[MoO_4]$, $[MoO_6]$ and $[PO_3]$ units have been proved. The oxygen bridges were established between molybdate units for rich MoO_3 glass and both phosphate and molybdate units for glasses with less MoO_3.

The structure of the investigated glass suffers a depolimerization of the phosphate network by adding MoO_3 as is suggested by the decrease of the transformation temperature T_g.

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