UNIVERSITY OF PARDUBICE

FACULTY OF CHEMICAL TECHNOLOGY

Department of General and Inorganic Chemistry

Chemical model of phosphate glasses with calcium and molybdenum

Monika Chládková

Theses of the Doctoral Dissertation

Pardubice 2022

Study program: **Chemistry and Technology of Materials**

Study field: **Chemistry and Technology of Inorganic Materials**

Author: Monika Chládková

Supervisor: doc. RNDr. Jana Holubová, Ph.D.

Year of the defense: 2022

References

CHLÁDKOVÁ, Monika. Chemical model of phosphate glasses with calcium and molybdenum. Pardubice, 2022. 114 pages. Doctoral thesis (PhD.). University of Pardubice, Faculty of Chemical Technology, Department of General and Inorganic Chemistry. Supervisor doc. RNDr. Jana Holubová, Ph.D.

Abstract

The aim of this work was to study the behavior of molybdenum, a transition metal with the possibility of forming oxo-cations with variable oxidation states, in various structures of the phosphate glass network. The effect of molybdenum was described using a chemical model, i.e. through the composition dependences of the molar concentrations of the actual chemical compounds forming glasses. The work was divided into two parts, in the first part binary phosphate glasses with molybdenum were prepared to determine whether all glasses of selected compositions can be prepared. The structure of the phosphate network passed from so-called ultraphosphates, through metaphosphates and further through glass with an equimolar content of meta- and pyrophosphates, to glass formed only by pyrophosphates. For this reason, a complete structural analysis was performed for all glasses and relevant chemical models were subsequently used to explain the compositional dependences of thermoanalytical properties, glass transition temperature T_g and coefficient of thermal expansion, α. In the second part, three series of ternary molybdenyl-phosphate glasses with calcium were studied, so the cation of a non-transition metal was chosen as another cation. The effect of increasing concentration of molybdenyls, replaced calcium, on the overall chemical composition of glasses was studied. The chemical models were further correlated with the compositional dependences of thermoanalytical properties, and mutual relations influencing the character of the compositional dependences were found.

Keywords

phosphate glasses, molybdenyl, ^{31}P MAS NMR, EPR spectroscopy, Raman spectroscopy, chemical model

Abstrakt

Cílem práce bylo studovat chování molybdenu, tedy přechodného kovu s možností vytvářet oxo-kationty s proměnlivými oxidačními stavy, v různých strukturách fosforečnanové skelné sítě. Vliv molybdenu byl popsán pomocí chemického modelu, tj. prostřednictvím kompozičních závislostí molárních koncentrací skutečných chemických sloučenin vytvářející daná skla. Práce byla rozdělena do dvou částí, kde v první části byla připravena binární fosforečnanová skla s molybdenem s cílem zjistit, zda lze všechna skla o vybraném složení připravit. Složení skel bylo zvoleno tak, aby

struktura fosforečnanové sítě přecházela od tzv. ultrafosforečnanů, přes metafosforečnany a dále přes sklo s ekvimolárním obsahem meta- a difosforečnanů, až po sklo tvořené pouze difosforečnany. Z tohoto důvodu byla u všech skel provedena kompletní strukturní analýza a následně byly použity příslušné chemické modely pro vysvětlení závislostí termoanalytických vlastností na složení, teploty skelného přechodu T_g a koeficientu teplotní roztažnosti α. V druhé části byly studovány tři řady ternárních molybdenyl-fosforečnanových skel s vápníkem, jako další kation byl tedy vybrán nepřechodný kov. Byl sledován vliv zvyšující se koncentrace molybdenylů, nahrazujících vápník, na celkové chemické složení skel. Podobně jako u binárních skel byla provedena celková analýza složení skel, na jejímž základě byl pro každou řadu stanoven chemický model, které byly dále korelovány s kompozičními závislostmi termoanalytických vlastností a byly nalezeny vzájemné vztahy ovlivňující charakter kompozičních závislostí.

Klíčová slova

fosforečnanová skla, molybdenyl, ^{31}P MAS NMR, EPR spektroskopie, Ramanova spektroskopie, chemický model

Table of contents

1. Introduction

Phosphate glasses represent an interesting and promising group of bulk oxide glasses. Compared to silicate glasses, phosphate glasses have a lower melting temperature and a lower glass transition temperature, thus their synthesis is relatively more accessible [1,2]. Compared to silicate glasses, phosphate glasses with alkaline earth metals have excellent UV transmittance, whereas glasses with rare earth metals have a large effective cross-section and low thermo-optic coefficient, and thus have important applications in the field of optics and solid-state lasers [1]. Phosphate glasses can also be completely dissolved in aqueous solution, unlike silicate glasses, and thus can be used as bioglasses with medical applications. However, by using suitable modifying oxides, they can be stabilized and the solubility can be significantly reduced [2]. In contrast, the addition of alkali or transition metals makes phosphate glasses ionic or electron semiconducting to conductive [3,4].

Many works focused on phosphate glass systems, their melts or glass forming regions have been described in the literature. Although many phosphate glasses with main group metals and also with transition metals have been synthesized and described, the behavior of transition metals as cations has not been studied in detail. The behavior of s- and p-metals in the phosphate network can be predicted with high probability, but in the case of transition metals, the d-elements, the situation is more complicated. Transition metals form multiple stable oxidation states and they can also be divided into two groups, transition metals that themselves act as cations and transition metals that form oxo-cations. Molybdenum is a typical representative of the second group and was therefore chosen for a more detailed study of its behavior in phosphate glasses. On this basis, the goals of doctoral thesis were formulated.

1.1 Goals of doctoral thesis

To prepare four binary molybdenum-phosphate glasses, with compositions from the so-called ultraphosphates, metaphosphates, equimolar mixture of metaphosphates and pyrophosphates. However, since phosphate glasses are not a mixture of oxides, as is usually used to describe them, and their properties cannot be described as additive properties of oxides, the basic aim of this work is to obtain all available information on the cationic and anionic part of the glasses and on their basis to propose actual chemical compounds and their molar concentrations, i.e. a chemical model of the glasses.

The aim of the next part of the work is to study the behavior of molybdenum substituted by a non-transition metal. Based on the obtained results, we then prepare four series of ternary glasses of the MoO_3-CaO-P_2O_5 system, starting from calcium metaphosphate and ending with the individual studied glasses of the MoO3-P2O5 system. For all the prepared series of glasses, obtain all the necessary data on the cationic and anionic part and on the basis of these data design and discuss the chemical models.

Furthermore, the aim was to characterize all the prepared glasses in this work by glass transition temperature, T_g, thermal expansion coefficient, α, and correlate the compositional dependence of these properties with the chemical composition of the glasses.

2. Experimental

A total of four compositional series of homogeneous phosphate glasses were prepared. The series of binary system $xMoO_3$-$(100-x)P_2O_5$, x = 33.3, 50, 57.14, 66.7 and three series of ternary calcium phosphate glasses with MoO_3:

1. series: $xMoO_3$-$(50-0.875x)CaO$-$(50-0.125x)P_2O_5$, x = 0, 1, 10, 20, 30, 40, 45, 50, and 57.14,
2. series: $xMoO_3$-$(50-0.75x)CaO$-$(50-0.25x)P_2O_5$, x = 0, 5, 10, 20, 30, 40, 50, 60, and 66.7,
3. series: $xMoO_3$-$(50-x)CaO$-$50P_2O_5$, x = 0, 5, 10, 20, 30, 40 and 50.

All glasses were prepared in a corundum crucible. Concentrated phosphoric acid, MoO_3 and $CaCO_3$ were used as precursors for the synthesis of studied glasses. The weight of the starting materials was calculated for a total glass weight of 10 g. The homogenized mixture was placed in a calcination furnace preheated to approximately 200 °C and slowly heated to 750 °C. Calcination was terminated at approximately 800 °C after 3-8 hours, depending on the glass composition. The crucible was then placed in a synthesis furnace preheated to a temperature of 1150 to 1200 °C depending on the glass composition. At this temperature, the mixture was melted for approximately 10-15 minutes and then poured onto a graphite plate preheated to 350 °C, Fig. 1, and the glass was slowly cooled to room temperature. Subsequently the glasses were labelled and placed in a desiccator due to the hygroscopic properties of phosphate glasses.

Depending on the molybdenum content, the glasses changed color from green to very dark blue, while the calcium phosphate glass without molybdenum was clear and colorless. Glasses with higher molybdenum content ($x \geq 40$) formed fibers during casting, Fig. 2. The greyish smoke escaped from binary glass containing 66.7 mol% of MoO_3.

The chemical composition of all glasses was determined by X-ray fluorescence analysis using μ-XRF M4 Tornado (Bruker). The oxygen content that could not be determined by XRF spectrometer, was calculated later based on a combination of ^{31}P MAS NMR and ESR results.

All samples containing MoO_3 were measured by electron spin resonance (ESR) at room temperature. The analysis was performed on cw-ESR EMXmicro spectrometer (Bruker). Microwave radiation at the frequency of ~ 9.83 GHz ($\lambda \sim 3$ cm) and a magnetic field strength of ~ 0.36 T were used for the measurements. The samples were analyzed with Xenon software and the spin concentration was expressed as spin/g.

^{31}P MAS NMR measurements were performed at room temperature on Ascend 500 spectrometer (Bruker) with 11.74 T magnet. The powder samples were placed in a zirconia probe (Ø 3.2 mm) and measured at the magic angle 54.74° with spinning the sample 15 kHz. The pulse length was 2.4 μs, power level 56 W and recycle delay 60 s. $(NH_4)H_2PO_4$ (δ = 0.9 ppm) was used as secondary standard. The obtained spectra were analyzed with TopSpin 3.2 software (Bruker).

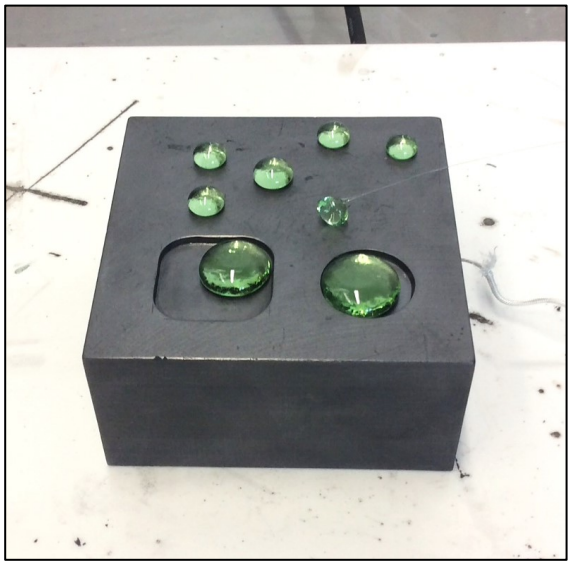

Fig. 1 Glass of a $1MoO_3$-49.125CaO-49.875P_2O_5 system.

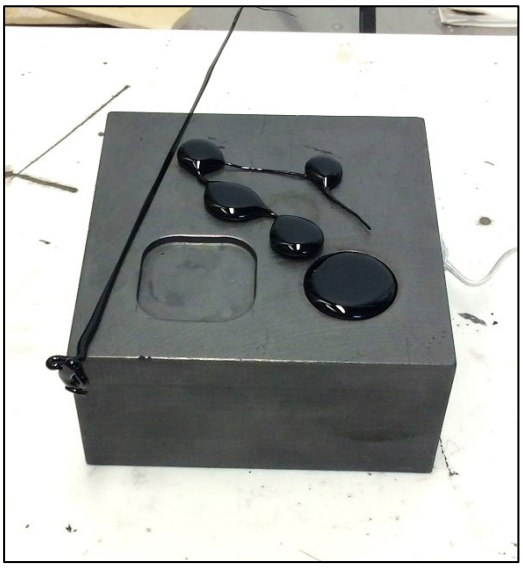

Fig. 2 Glass of a 57.14MoO_3 – 42.86P_2O_5 system.

The thermomechanical analysis of the prepared glasses was performed on TMA Q400 (TA Instruments). The samples were heated at 10°C/min in a nitrogen atmosphere with a flow rate of 20 ml/min. An expansion probe with a preload force 0.050 N was used for all measurements. The dilatometric glass transition temperature, T_g, and the coefficient of thermal expansion, α, were subsequently determined from the dilatation curves using Universal Analysis 2000.

3. Results and discussion

3.1 Chemical model – principle

Based on the obtained experimental results it can be determined the actual composition of the prepared glasses, i.e. the real chemical compounds that were formed in the mixture during the synthesis and define the final structure of the glasses – chemical model. This issue has not received much attention in the literature. The basic work in this field of study of phosphate glasses is represented by the results of Prof. Liška's group [5-10], which are based on thermodynamic modelling of the chemical composition of glasses.

In order to determine the chemical model of the studied binary and ternary glasses, it is first necessary to explain several rules. First, two types of cations are present in this work. Calcium, a non-transition metal that does not form complex cations with oxygen and molybdenum, a transition metal that forms complex cations with oxygen and may be reduced during synthesis. Molybdenum binds one or two oxygen atoms and forms complex cations molybdenyls with different charges, $(Mo{=}O)^{4+}$ or $(Mo{=}O)^{3+}$ and/or $(O{=}Mo{=}O)^{2+}$ or $(O{=}Mo{=}O)^{+}$. Thus, the variability of the glass forming compounds formed during the synthesis increases.

In the first step, the most important thing is to perform a quantitative analysis of the elements by XRF method. In this way, the atomic amount of all elements except oxygen can be determined. Since molybdenum glasses are colored, which means that at least part of the molybdenum has been reduced from Mo(VI) to Mo(V), the degree of molybdenum reduction must also be determined. Molybdenum Mo(V) is a d^1 system and therefore a quantitative analysis of the reduced molybdenum can be performed using EPR spectroscopy. The total amount of molybdenum can then be quantitatively divided according to the corresponding oxidation states. At this point it is already possible to determine the atomic concentration of oxygen in the glass, because there is 1 oxygen atom per 1 Ca atom (CaO), 2.5 oxygen atoms per P atom (P_2O_5), 3 oxygen atoms per Mo(VI) atom (MoO_3) and 2.5 oxygen atoms per Mo(V) atom (Mo_2O_5). In fact, the molybdenum oxide Mo_2O_5 corresponds to the reduction of MoO_3 and is an equivalent expression of the oxygen loss expressed by the reaction $2MoO_3 \rightarrow Mo_2O_5 + 1/2O_2$. In the next step, from the results obtained by ^{31}P MAS NMR spectroscopy the total phosphorus content can be divided into individual phosphate anions (meta-, pyro- and orthophosphates). This allows to determine the amount of oxygen attributable to the anionic part of the glasses, as well as the total negative charge that must be compensated by the charge of the cations. Thus, the remaining oxygen must be bound in the molybdenum, even in the case of ternary glasses with calcium because Ca does not form complex cations with oxygen.

After subtracting the negative charge compensated by the calcium ion, it is possible to assign oxygen to the molybdenum and use Solver (Excel) to determine the individual molybdenyls and determine their molar concentration. At this point, all this information about cations and anions makes it possible to calculate the molar concentrations of the actual chemical compounds that form the individual glasses, i.e. chemical model is created. The calculation of chemical compositions is also performed using Solver (Excel), of course with human assisted calculation, for the reason that there

may be situations where multiple numerically solutions are acceptable. It is necessary to eliminate unrealistic results that are either not possible for a given series of glasses or do not correspond to the stoichiometry of the possible compounds formed. Once the chemical model is established and the molar concentrations of the glass forming compounds are known, the actual molecular weights of the glasses can be calculated and their actual molar volumes determined.

It is important to note that the chemical model describes also the equilibrium composition of the individual glass forming melts, and therefore the glasses, which is often neglected. The preparation of phosphate glasses is usually based on the cooling of the equilibrium melt, i.e. the mixture of chemical compounds formed during calcination and subsequent melting of the mixture of precursors. The chemical equilibria can be described by equations (1 and 2), where the (formal) anion O^{2-} represents the reaction water. At a temperature of ~ 230 °C, orthophosphates are converted to pyrophosphates (2) and these gradually polymerize with increasing temperature and form metaphosphates:

$$2PO_4^{3-} \leftrightarrow P_2O_7^{4-} + O^{2-} \quad (1)$$

$$nP_2O_7^{4-} \leftrightarrow (PO_3^-)_{2n} + nO^2 \quad (2)$$

These equilibria, expressed in the simplified notation $2Q^0 \leftrightarrow Q^1\text{-}Q^1 \leftrightarrow 2Q^2$, are a general process in glasses with constant phosphorus content. At lower melting temperatures, orthophosphates in addition to pyrophosphates will be present in the glasses, although when temperature increases, metaphosphates begin to predominate at the expense of pyrophosphates, and thus the concentration of orthophosphates decreases to the limit of detectability. If the formal P_2O_5 content corresponds to metaphosphates, then the resulting equilibrium melt and thus the glass, will be significantly dominated by Q^2 structural units accompanied by a low concentration of Q^1 structural units. The Q^0 units are detected at most in traces. If the phosphorus content shifts into the composition range between meta- and pyrophosphates, then the concentration of Q^2 units decreases and a significant concentration of Q^1 units and non-negligible concentration of Q^0 units must generally appear in the glass. In addition to the concentration of phosphorus, the above processes in the anionic network are to some extent influenced by the cationic part of the glasses. The situation is even more diverse if the cations are transition metals, especially those which form complex oxo-cations with different oxidation states of transition metals, such as molybdenyls, i.e. molybdenum oxo-cations.

First, the formal binary glasses of the MoO_3-P_2O_5 system will be discussed in this work, on the basis of which the chemical compositions of the formal ternary series of glasses of the CaO-MoO_3-P_2O_5 system were formulated. The results of their study form the second part of this chapter.

Regarding the results presented graphically, it should be emphasized that the connecting lines of the experimental points are given only for the guidance of the eyes. In the text, the composition of the glasses, denoted as batch or as formal, corresponds to the weighed oxides, the real composition, determined by XRF, is referred to as actual.

3.2 Binary phosphate glasses with molybdenum

The binary glass series was composed of four glasses with a MoO_3/P_2O_5 ratio: 1:2, 1:1, 1.33:1 a 2:1, e.j. 33.3:66.7; 50:50; 57.14:42.86 a 66.7:33.3. These formal compositions, expressed in oxides, correspond to the following possible chemical compounds $(MoO)(PO_3)_4$, $(MoO_2)(PO_3)_2$, $(MoO)_4(P_2O_7)_3$ and $(MoO_2)_2P_2O_7$. The glasses were prepared according to Chap. 2., primarily to see if predetermined glasses could be synthesized and glasses of MoO_3-CaO-P_2O_5 system could be subsequently prepared. The idea was to prepare glasses containing compounds with molybdenyls MoO or MoO_2 as cations.

Considering the fact that all the prepared glasses were dark blue, at least a small part of molybdenum Mo(VI) was reduced to Mo(V) during the synthesis with electron orbital configuration d^1. It is therefore more than obvious that the actual composition of the prepared glasses must have shifted from the batch composition and therefore the chemical composition of the glasses is first analyzed.

3.2.1 X-ray fluorescence (XRF)

The relative content of molybdenum and phosphorus in the studied glasses was determined using the X-ray fluorescence. It was found that for all prepared samples the real composition differs significantly from the batch composition. The higher the original content of P_2O_5 was compared to the amount of MoO_3, the more the actual composition of the given glass shifted during the synthesis, Fig. 3.

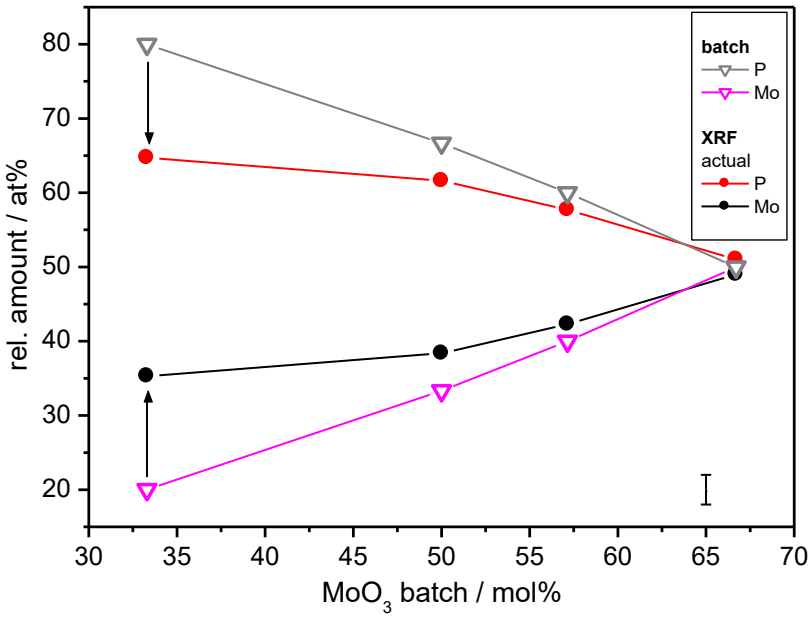

Fig. 3 Relative amounts of molybdenum and phosphorus before (batch) and after synthesis (actual).

The changes in the composition of the glasses correspond to the fact that during synthesis, especially for the glass with x = 33.3, greyish smoke escaped, see Chap. 2. The release of excess phosphorus in the form of P_2O5 is possible because this oxide sublimates at 359 °C. Another reason for this is the possible release of P_2O_5 and water after the decomposition of metaphosphoric acid, which in the case of the substoichiometry of the metal cation remains in the reaction mixture.

3.2.2 Electron spin resonance (ESR)

The intense dark blue coloration of prepared glasses indicates that at least part of the molybdenum was reduced during synthesis to Mo(V), d^1 system, that is suitable for electron spin resonance (ESR). In addition to information on the molybdenum coordination polyhedron, quantitative information on the extent of molybdenum reduction can also be obtained by ESR in combination with the XRF results.

The EPR spectra of studied glasses are shown in Fig. 4. It can be seen that the glass with the highest MoO_3 content (x = 66.7) shows a well finer characteristics in the spectrum. Therefore, it can be concluded that the lowest degree of reduction occurs in this glass, i.e. the content of Mo(V) is the lowest. Conversely, as the MoO_3 content decreases, the spectra broaden, indicating a higher degree of molybdenum reduction.

In combination with XRF results, it was possible to determine the ratio of reduced to non-reduced molybdenum in the individual glasses, see Fig. 5. The EPR results thus confirm the XRF results, with the most significant deviation from the formal composition and the highest degree of reduction occurring in the glass with x = 33.3, i.e. the glass with the lowest molybdenum content.

From the shape of the spectra, it is quite clear that the coordination polyhedron of molybdenum is axially symmetric. This is in good agreement with the fact that molybdenum forms molybdenyls with oxygen in the z-axis $(O = M = O)^{(n-4)+}$ or $(M = O)^{(n-2)+}$, n = 6 or 5. In the latter case, i.e. for n = 5, molybdenyl is active in the ESR. Both molybdenyls are coordination four times in the xy-plane by the non-bridging oxygen of the phosphate anions and thus the former forming a tetragonal bipyramid (D_{4h} symmetry) and the latter one a tetragonal pyramid (C_{4v} symmetry). It should be noted that the reduction of the molybdenum does not change the geometry and binding possibilities of the complex cation, because the unpaired electron of Mo(V) is non-bonding and fully localized on molybdenum. Thus, the structure of the analogous diamagnetic molybdenyls, n = 6, will most likely be the same.

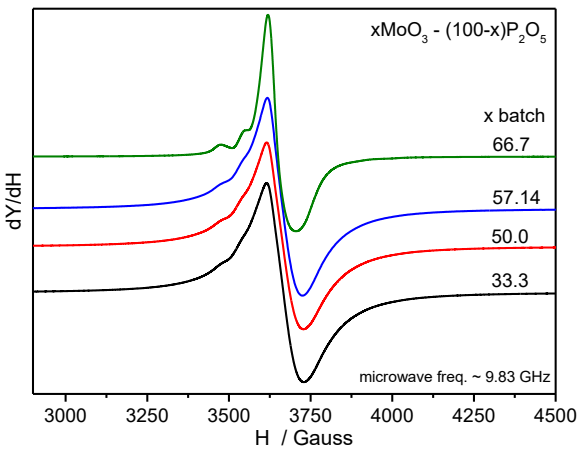

Fig. 4 ESR spectra of studied MoO_3-P_2O_5 glasses.

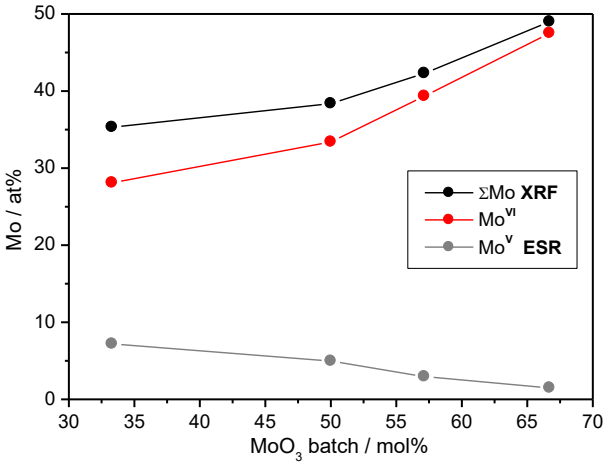

Fig. 5 The relative concentration of Mo, and its division into Mo(VI) and Mo(V).

3.2.3 ^{31}P MAS NMR

The structure of the prepared glasses was further studied by ^{31}P MAS NMR spectroscopy, that can be used to qualitatively and quantitatively determination of concentration of meta-, pyro- and orthophosphates. It is evident from Fig. 6 that as the MoO_3 content increases, and thus the phosphorus content decreases, the spectra shift to the region of lower magnetic fields. The structure of the binary glasses partially passed from metaphosphate structure (~ -33 ppm) to pyrophosphate structure (~ -18 ppm) with increasing molybdenum content, while a band characteristic of orthophosphates (~ -7 ppm) can also be found in the spectra of glasses with a formal content of 66.7 mol% MoO_3. The shift of the entire resonance area to higher magnetic fields is due to the electron shielding associated with molybdenum.

The quantitative analysis of the phosphate structural units was performed by computer simulation, Fig. 7. The anionic glass network with the highest P_2O_5 content is practically composed only of metaphosphates. As the P_2O_5 content decreases, the content of pyrophosphate structural units increases, and in the glass with the lowest P_2O_5 content the structure is already composed mainly of pyrophosphates and orthophosphates begin to appear. At the same time, it is important to note that no resonance of Q^3 structural units was observed (~ -50 ppm and more), the presence of which would indicate the presence of ultraphosphates, which would be expected in the glass with the highest P_2O_5 content [11,12].

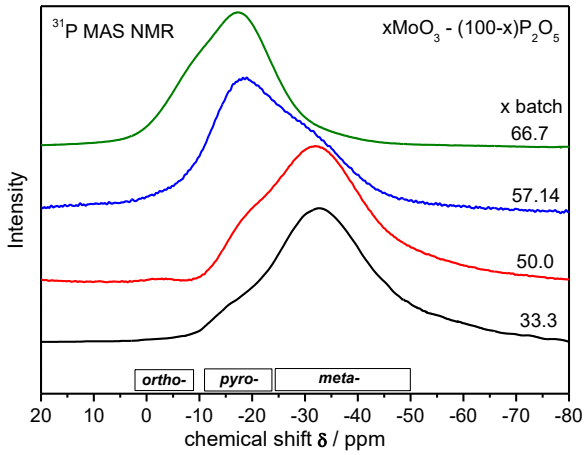

Fig. 6 ^{31}P MAS NMR spectra of studied MoO_3-P_2O_5 glasses.

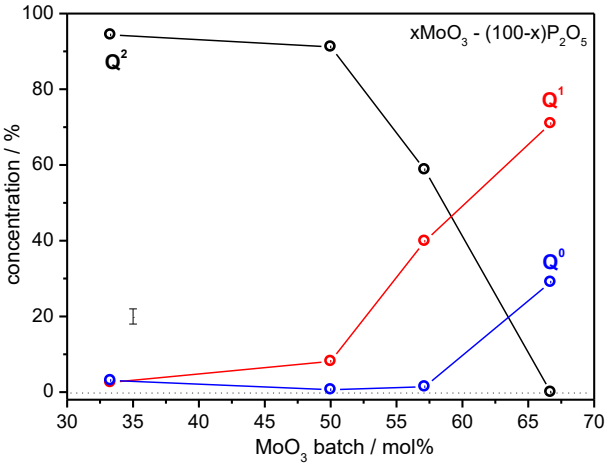

Fig. 7 Compositional dependence of the relative abundance of Q^n units on the batch composition.

3.2.4 Chemical model

In order to determine the real chemical compounds, present in all glasses, it is possible to combine the results from XRF, ESR and ^{31}P MAS NMR spectroscopies, see Chap. 3.1. Due to the low degree of molybdenum reduction (< 10 at%) and thus the low content of Mo_2O_5, the chemical composition of the glasses is for practical reasons expressed only as the formal molar concentration of MoO_3. From the results on Fig. 8 and 9, it is evident that during the synthesis all the glasses changed their chemical composition. The actual formal composition expressed in oxides of all glasses is shown in Table 1.

The most significant change in composition occurred in the glass with 33.3 mol% MoO_3, that corresponds in its batch composition to the ultraphosphates. It should be emphasized that the chemical composition of all the glasses is in the area of the glass-forming region of phosphate glasses, either with real or formally divalent cations, i.e., with cations with a charge of 2+.

From the results of ^{31}P MAS NMR spectroscopy, the relative ratio of structural units Q^2, Q^1 and Q^0 was known. It was therefore possible to determine the oxygen content attributable to the electronegative part of the glasses and thus to determine its negative charge, which must be compensated for by the electropositive part. The oxygen content, the amount of reduced and non-reduced molybdenum, and an indication of the total charge of the electropositive part were then used to determine the concentration and type of each molybdenyl, Fig. 10.

The result shows that the chemical composition of the glasses changes during the synthesis in a way that leads to the optimal chemical composition. The only starting component whose content can be changed (decreased) during the synthesis is volatile P_2O_5, whose sublimation temperature is 359 °C. The P_2O_5 content of the glass system is in fact reduced during preparation by thermal decomposition of the excess of metaphosphoric acid, $(HPO_3)_n$, to water and phosphorus pentoxide.

Table 1 The batch and actual composition of prepared glasses expressed in oxides.

chemical composition	x(MoO_3)	Mo_2O_5	MoO_3	P_2O_5
	mol% (±1 mol%)			
batch	33.30	-	33.30	66.70
	50.00		50.00	50.00
	57.14		57.14	42.86
	66.70		66.70	33.30
actual	52.20	5.62	43.87	50.51
	55.50	3.73	50.08	46.19
	59.40	2.12	56.46	41.42
	65.80	1.02	64.40	34.58

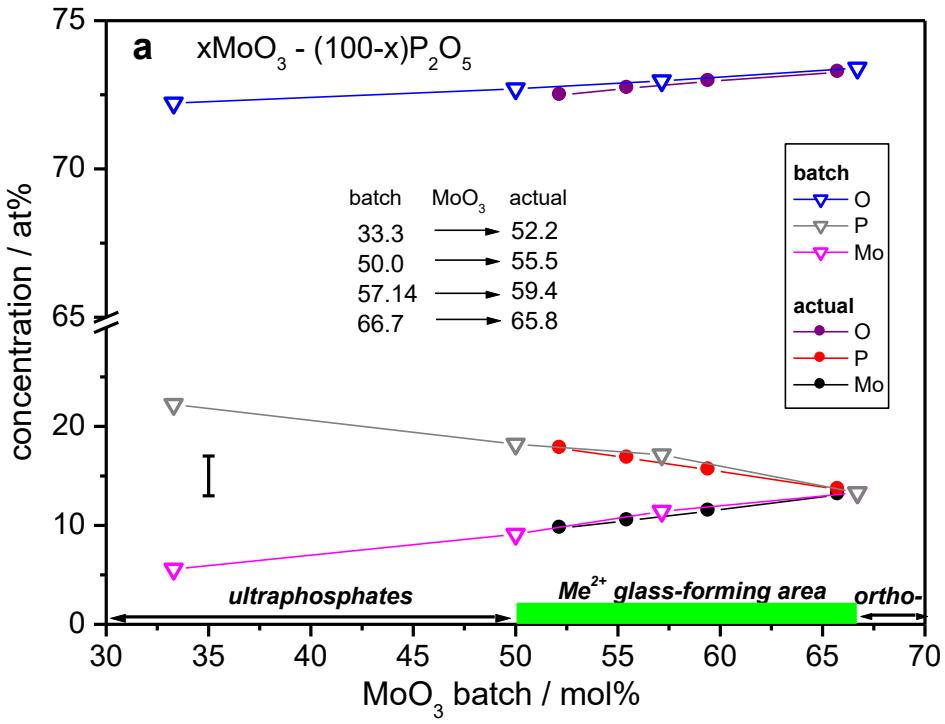

Fig. 8 Changes in chemical compositions during synthesis from batch to actual composition expressed in at%.

The result shows that the chemical composition of the glasses changes during the synthesis in a way that leads to the optimal chemical composition. The only starting component whose content can be changed (decreased) during the synthesis is volatile P_2O_5, whose sublimation temperature is 359 °C. The P_2O_5 content of the glass system is in fact reduced during preparation by thermal decomposition of the excess of metaphosphoric acid, $(HPO_3)_n$, to water and phosphorus pentoxide.

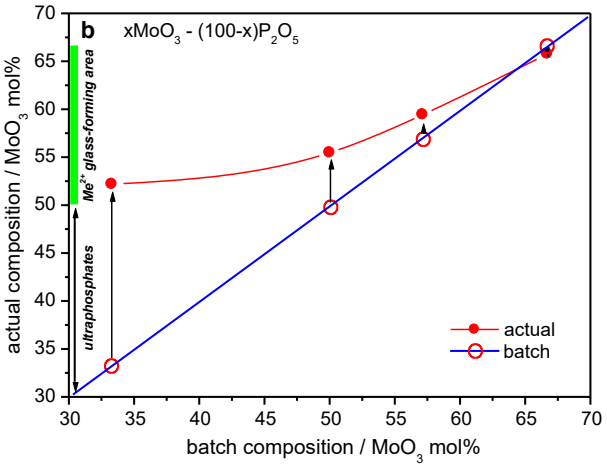

Fig. 9 Changes in chemical compositions from batch to actual composition expressed in mol%.

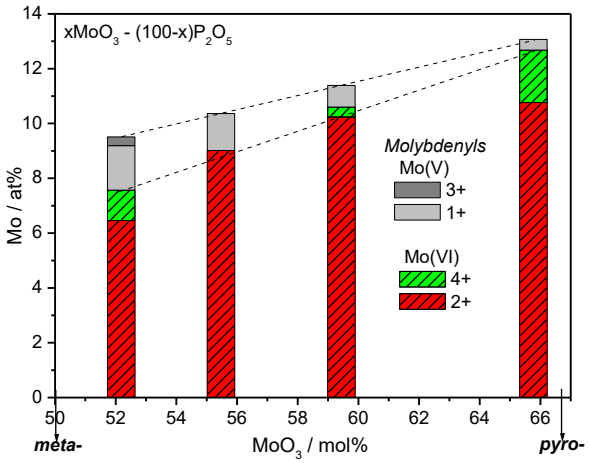

Fig. 10 Compositional dependence of Mo distribution to all possible molybdenyls.

Metaphosphoric acid is formed during calcination from orthophosphoric acid or their hydrogen salts, which are the starting substances predominantly used for the synthesis of phosphate glasses. Its excess depends indirectly on the binding possibilities of the electropositive component. If there is a substoichiometric amount of electropositive component, then this unreacted strongly hygroscopic acid will remain in the synthesis mixture. In this case the metaphosphoric acid easily converted back to orthophosphoric acid by reaction with atmospheric moisture. This may explain the known hygroscopicity of so-called ultraphosphate glasses [12,13].

The loss of P_2O_5 shifts the overall chemical composition of the melt and consequently the glass to higher concentrations of the electropositive component. As a result, the chemical composition of all the glasses that lies in the field of the glass formation with 2+ cations, which is bordered by meta and pyrophosphates. Fig. 10 shows that the molybdenum content varies linearly, the amount of reduced molybdenum decreases linearly with a linearly increasing amount of molybdenum. The glass with batch composition x = 50.0 (actual x = 55.5), as the only one, contains both molybdenyls with two oxygens, i.e. $(MoO_2)^{2+}$ and $(MoO_2)^{+}$. As the molybdenum content increases, the amount of $(MoO_2)^{2+}$ and $(MoO_2)^{+}$ in other glasses gradually decreases at the expense of $(MoO)^{4+}$ molybdenyl, the corresponding molybdenyl of Mo(V), $(MoO)^{3+}$, is not present in these glasses. This molybdenyl only newly appears together with the already mentioned molybdenyl $(MoO)^{4+}$ in the glass with x = 52.2, see Fig. 10.

Another question for explanation is seen from the results provided in Table 2. A glass with a formal composition of x = 50.0, which should be metaphosphate, also contains pyrophosphates and its composition is thus shifted to x = 55.5. This is most often explained as a consequence of the different degree of depolymerization of the phosphate chains [1]. In this case, only the metaphosphates could depolymerize because these are the only phosphate chains in these glasses. There are two problems here, however, on the one hand, after depolymerization, there would be a number of non-stoichiometric thermodynamically unstable phosphate compounds causing an increase in the negative charge of the anions but no other cations to compensate the charge, and

on the other hand, depolymerization is a reaction in which one more oxygen is needed for each chain break and it is unclear what the oxygen source would be. This clearly shows that the idea of depolymerization is somewhat problematic and difficult to explain.

Table 2 Batch and actual composition of studied glasses and proposed chemical model.

MoO_3 mol%	**batch**	**33.30**	**50.00**	**57.14**	**66.70**
	actual	**52.20**	**55.50**	**59.40**	**65.80**
		mol% (±2 mol%)			
chemical model					
$(MoO_2)(PO_3)_2$		72	84	40	-
$(MoO_2)P_2O_7$		5	11	45	69
$(MoO_2)_3(PO_4)_2$		-	1	-	9
$(MoO)(PO_3)_4$		6	-	5	-
$(MoO)P_2O_7$		-	-	5	17
$(MoO)_3(PO_4)_4$		-	-	-	4
$(MoO_2)PO_3$		11	-	3	-
$(MoO_2)_4P_2O_7$		-	4	2	1
$(MoO_2)_3PO_4$		2	-	-	-
$(MoO)PO_4$		4	-	-	-

The explanation of why pyrophosphates not only are, but always must be present in phosphate glasses has been described in Chap. 3.1. As a result, it is practically impossible to prepare an equilibrium melt and thus a glass with only a single type of anion, i.e. with a single structure of the phosphate part. The glass with x = 65.8, which practically corresponds to pyrophosphates, consists mainly of pyrophosphates, but, in accordance with the expected influence of chemical equilibria, a not negligible amount of orthophosphates also appears in the glass.

Based on the observed chemical composition of the glasses, the compositional dependence of the main glass-forming components is shown in Fig. 11, for clarity. The sum of all these four components always makes up more than 86 mol% of the molar composition of the glasses, and it is evident that both metaphosphate and pyrophosphate of the same molybdenyl with a formal charge of 2+ play a major role. It can therefore also be expected that these two compounds will have a significant effect on the properties of the prepared glasses, and this assumption was confirmed by comparing the compositional dependence of the sum of both the molar concentration of the main glass-forming compounds and the glass transition temperature.

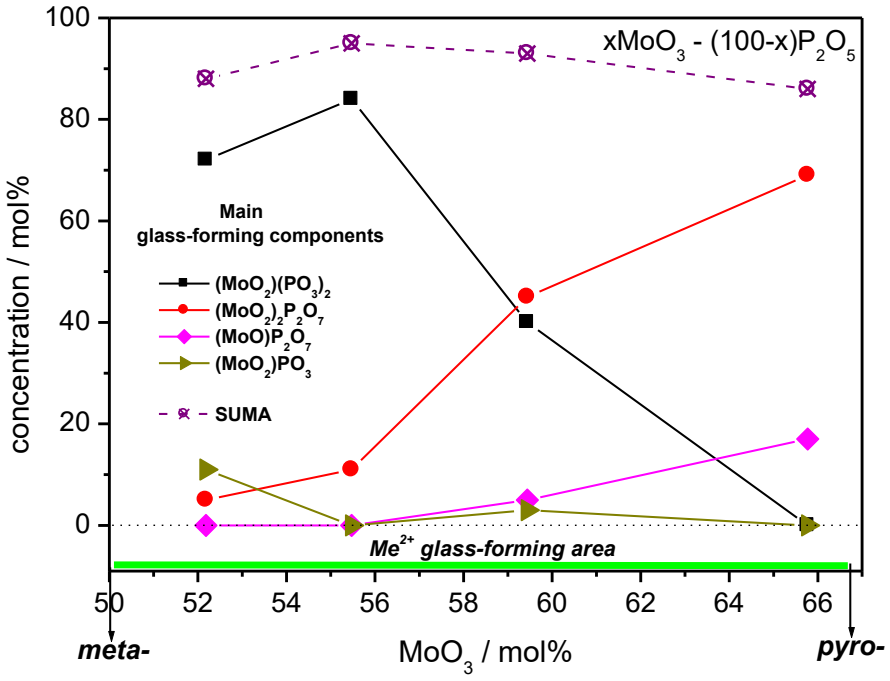

Fig. 11 Compositional dependence of molybdenum distribution to all possible molybdenyls.

3.2.5 Thermal analysis

The glass transition temperature, T_g, and the coefficient of thermal expansion, α, were determined for all glasses. The compositional dependence of the dilatometric T_g and α were obtained by TMA, Fig. 12. If we omit from the evaluation the results of the first glass with x = 33.3 mol%, whose actual composition was significantly shifted from the formal composition, see Fig. 8, it can be seen that with increasing molybdenum content glass transition temperature decreases and thermal expansion increases. This suggests that with increasing MoO_3 content, and therefore decreasing P_2O_5 content, the bonding interactions in the glass structure are weakened. This is reflected in the observed decrease in T_g values and an increase in α values.

In Fig. 13, the compositional dependence of the sum of two glass-forming compounds predominating in all glasses, $(MoO_2)(PO_3)_2$ and $(MoO_2)P_2O_7$, is plotted and for comparison the compositional dependence of the glass transition temperature is added. The almost identical courses of both dependences show that the glass transition temperature is determined by the molar concentration of these two glass-forming compounds. It should be emphasized that only weak bonding interactions can be considered to explain the course of compositional dependence of T_g, because the thermal energy in the glass transition temperature region (~ 500 °C) is less than 0.07 eV, while the energy of covalent bonds is approximately hundred times higher. The gradual decrease in metaphosphates and increase in pyrophosphates causes an overall decrease of these weak interactions, but it is also obvious that the nature of these interactions is similar or at least very close for both of phosphate because the glass transition

temperature of glass with x = 65.8 corresponds to its overall monotonic decrease, although metaphosphates are no longer in this glass.

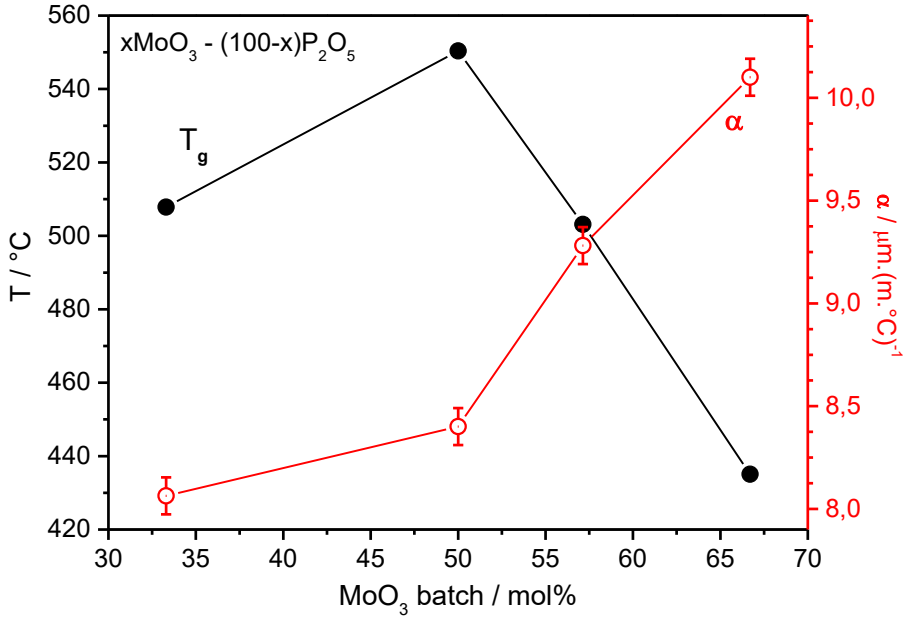

Fig. 12 Compositional dependencies of both the glass transition temperature, Tg, and coefficient of thermal expansion, α.

One possible explanation may be that metaphosphates are inherently polymeric in nature, whereas pyrophosphates are merely dimeric units that are subsequently interconnected by molybdenyls. Thus, it can be expected that the structure of pyrophosphates, at least partially polymerized by molybdenyls, will be less compact than polymeric metaphosphate chains, also interconnected by molybdenyls. Thus, a decrease in the compactness of the glass structure is also reflected in an increase in thermal expansion, Fig. 14. It should be noted that the assumption that a certain degree of polymerization occurs in pyrophosphate glass with molybdenyls(2+) is based on the fact that glass with x = 65.8, practically molybdenyls(2+) pyrophosphate, can be easily prepared when molybdenum is used, while the glassy pyrophosphates of the main group metals are usually difficult to prepare.

Fig. 13 and 14 also show a comparison of the results of the chemical composition calculation, based on the results of several experimental methods (XRF, EPR, NMR) analyzing the composition and structure with the result of a completely independent technique, dilatometry, and demonstrate that the found chemical model of glasses (Table 2) is more than realistic.

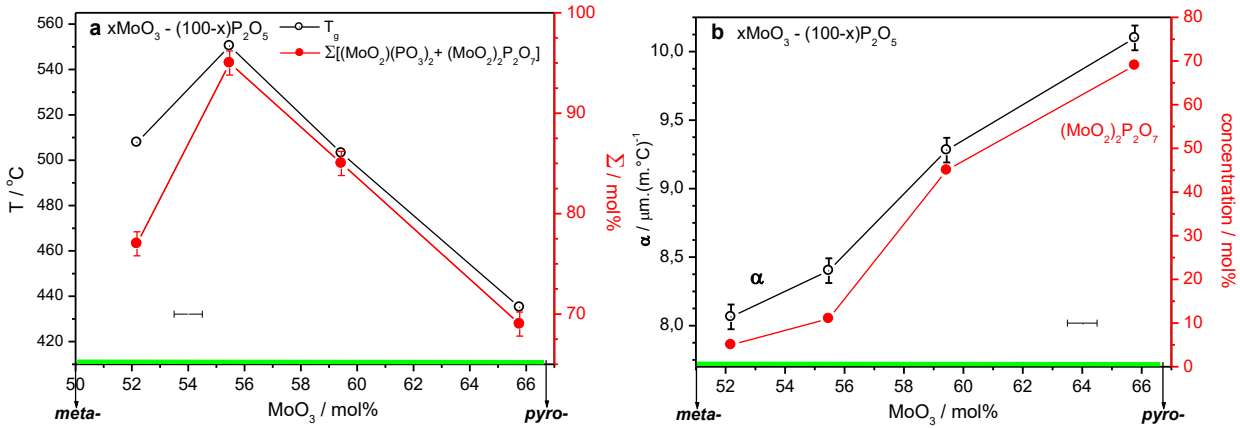

Fig. 13 and 14 Comparison of the courses of the compositional dependencies between dominant glass-forming compounds and glass transition temperature, T_g, (a) and between dominant pyrophosphate and coefficient of thermal expansion, α, (b) of the studied glasses.

3.3 Ternary calcium-phosphate glasses with molybdenum

The glasses of the three series of the $CaO-MoO_3-P_2O_5$ system were prepared according to Chap. 2. The initial glass, i.e. calcium metaphosphate $Ca(PO_3)_2$, gradually changes into a final stable molybdenum-phosphate glasses prepared in Chap. 3.2. Thus, three series of glasses were prepared with the composition (A): $xMoO_3$-(50-0.75x)CaO-(50-0.25x)P_2O_5, (B): $xMoO_3$-(50-0.875x)CaO-(50-0.125x)P_2O_5 and (C): $xMoO_3$-(50-x)CaO-$50P_2O_5$. Unfortunately, the formal notation of the compositions of the prepared series is somewhat complicated for the necessary orientation in the text, and since all three series are based on the same starting glass, $(Ca(PO_3)_2)$, the complicated notation is replaced in the following text by a simple chemical distinction according to the terminal phosphate of final glasses of each series. Thus, series (A) as *pyro* series, series (B) as *meta&pyro*, and series C as *meta* series. It should be noted here that the molybdenum content expressed below as MoO_3 is not actually present in the glasses; it is only a formal expression corresponding to commonly used formal formulas. All three prepared series, including the formal chemical batch composition, are shown in the ternary diagram in Fig. 15.

All glasses with molybdenum gradually passed from light green to dark blue with increasing Mo content, Figs. 1 and 2. This indicates that at least part of the Mo(VI) was reduced to Mo(V), thus the real composition of the glasses changes compared to the batch composition. To obtain the actual composition of each glass, the following analyzes were performed.

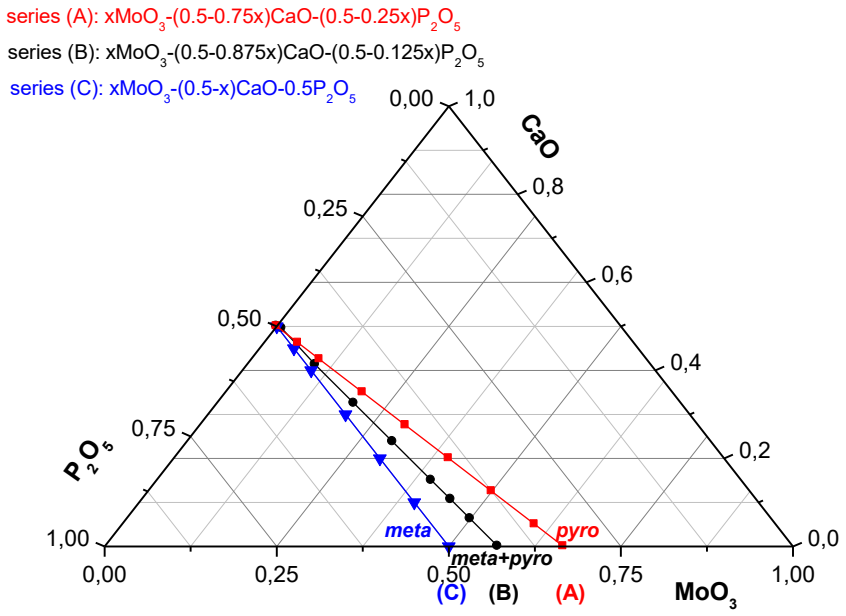

Fig. 15 Ternary diagram of three ternary series of MoO_3-CaO-P_2O_5 system.

3.3.1 X-ray fluorescence (XRF)

The atomic content of elements, except oxygen, was determined by XRF analysis. The actual concentration of the elements, converted to oxides, is given in Table 3. As will be shown below, the largest relative amount of Mo(V) was ~ 13%, which corresponds to ~ 2.5% of the total glass composition, thus the molar concentration of Mo_2O_5 is relatively low. For practical reasons, all compositions of glasses are therefore expressed as formal molar concentration of MoO_3, calculated from actual atomic composition.

Table 3 Batch and actual composition of prepared glasses of all three series.

series (A) *pyro*				**series (B)** *meta&di*				**series (C)** *meta*			
MoO_3 batch	MoO_3	CaO	P_2O_5	MoO_3 batch	MoO_3	CaO	P_2O_5	MoO_3 batch	MoO_3	CaO	P_2O_5
	actual				actual				actual		
mol%											
mean error ± 0.5											
0	0.0	50.3	49.7	0	0.0	50.3	49.7	0	0.0	50.3	49.7
5	5.0	45.8	49.2	1	1.0	49.6	49.4	5	7.6	42.7	49.6
10	9.8	42.4	47.8	10	10.0	40.9	49.1	10	14.1	37.1	48.8
20	19.2	35.1	45.7	20	19.3	32.0	48.7	20	24.6	26.9	48.5
30	29.1	27.2	43.7	30	28.8	23.9	48.3	30	34.8	17.8	47.4
40	39.1	19.2	41.7	40	38.7	14.5	46.8	40	44.9	8.6	46.5
50	49.4	12.2	38.4	45	43.7	10.7	45.6	50	55.5	0.0	44.5
60	60.4	4.6	35.0	50	52.6	5.5	41.9				
66.7	66.9	0.0	33.1	57.1	59.1	0.0	40.9				

3.3.2 Electron spin resonance (ESR)

The amount of reduced molybdenum was determined by ESR spectroscopy and the deviation of the batch composition from the actual one was found to be directly proportional to the amount of molybdenum reduction during the synthesis.

The ESR spectra of the glasses of all studied series are very similar and typical for Mo(V) as for binary glasses, Chap. 3.2.2. The degree of molybdenum reduction was calculated and compared with the total molybdenum content determined by XRF, Fig. 16.

Fig. 16 shows that the lowest reduction during synthesis occurred in the *pyro* series and at the same time the Mo(V) content decreases very slightly with increasing molybdenum content. The deviation of the actual composition is also the smallest for this series. For the *meta&pyro* series, the molybdenum reduction is already slightly larger, except that the reduction increases with increasing molybdenum content. The largest molybdenum reduction was found in series *meta*, where the Mo(V) content increases from 5 to ~ 13 % with increasing molybdenum content. This series shows the most significant deviation from the batch composition of the glasses. These results are of crucial because they allow to determine the amount of oxygen oxidized and released from the reaction mixture during the reduction of molybdenum.

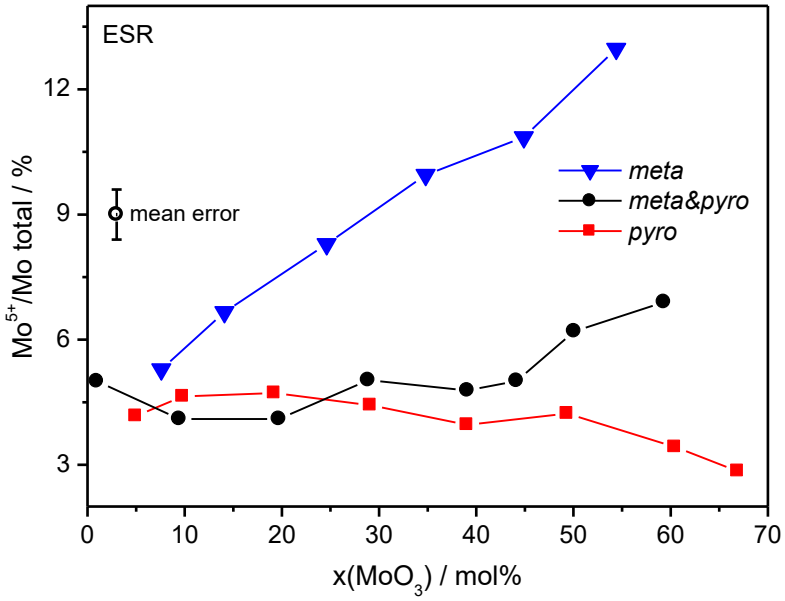

Fig. 16 Relative concentration of Mo(V) for all three series.

In addition to quantitative analysis, the coordination polyhedron of paramagnetic Mo(V) can be determined by ESR spectroscopy. It was obtained by analysis of spectrum with 1 mol% MoO_3 (series *meta&pyro*), which corresponds to 0.22 at% Mo. Computer simulation of the spectrum revealed only one paramagnetic center, which means that Mo(V) forms only one type of complex cation, i.e. one type of molybdenyl.

The values of g and A parameters indicate, to a first approximation, a molybdenum coordination polyhedron with axial symmetry, most likely a tetragonal bipyramid. However, the slightly different values of g and A in the xy-plane indicate

a deformation in that plane and thus a further deformation in the symmetry of coordination polyhedron. In conclusion, Mo(V) in this case occurs as molybdenyl MoO^{2+}, cation in an amount corresponding to reduced portion.

3.3.3 ^{31}P MAS NMR

The ^{31}P MAS NMR spectroscopy was used to determine both qualitative and quantitative analysis of the phosphate structural units of the glasses of all three series. The spectra are shown in Figs. 17, 19 and 21. All spectra were decomposed into individual bands and then the relative concentrations of Q^n structural units were determined, where pyrophosphate is $2.Q^1$. The compositional dependencies of the phosphate anions are shown in Figs. 18, 20 and 22.

The first spectrum in each series is the spectrum of calcium metaphosphate, which has a dominant band at -27 ppm corresponding to the metaphosphate structural units Q^2. The band at -10.5 ppm indicates the presence of small amount of Q^1 structural units (~3%). Compared to the calcium metaphosphate spectrum, the maxima of all bands are shifted to higher magnetic field with increasing molybdenum content, which is caused by higher electron shielding related to electron rich molybdenum.

The spectra of the *pyro* series show a significant change in the structure of phosphate glasses due to the increasing molybdenum content. There is a clear change from a metaphosphate network to a pyrophosphate network, see Fig. 17. With increasing molybdenum content and decreasing phosphorus content, the intensity of metaphosphates decreases, while the intensity of pyrophosphates (-11 ppm) gradually increases. In the spectra of glasses with the highest MoO_3 content, a shoulder at -7 ppm corresponding to structural units of Q^0 appears. Fig. 18 shows the composition dependence of phosphate anions. It can be seen that the concentration of metaphosphates decreases with increasing molybdenum content, whereas the content of pyrophosphate increases up to x ~ 40, from which point it becomes dominant. At the same time, the concentration of orthophosphate increases at the expense of pyrophosphate for the last two glasses of this series.

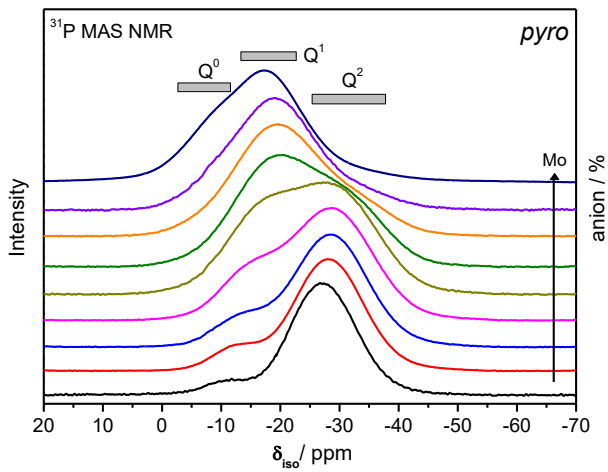

Fig. 17 ^{31}P MAS NMR spectra of series *pyro*.

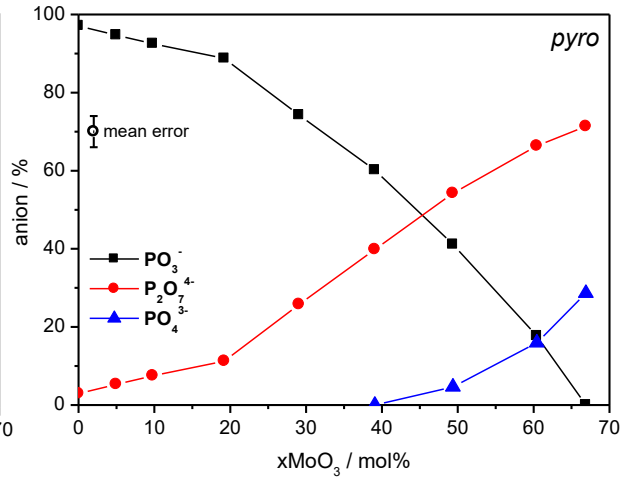

Fig. 18 Compositional dependence of phosphate anions of series *pyro*.

In the series *meta&pyro*, with increasing molybdenum content the maximum of the spectral envelope shifts from -27 ppm to -19 ppm, Fig. 19. However, the compositional dependence of phosphate structures shows that metaphosphates remain as the dominant unit in the entire composition range. The pyrophosphates increase significantly at the expense of metaphosphates from the glass with x = 30, Fig. 20.

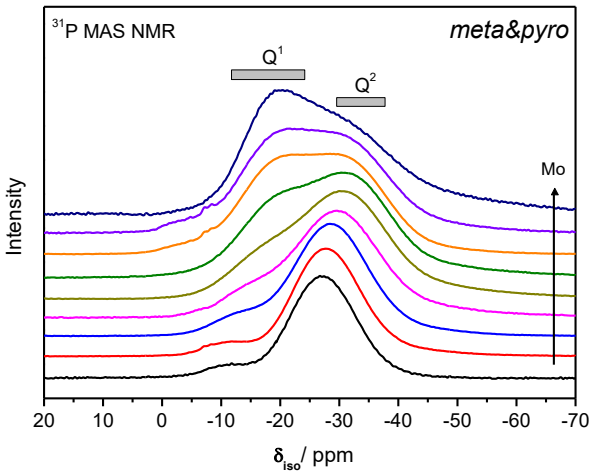

Fig. 19 ^{31}P MAS NMR spectra of series *meta&pyro*.

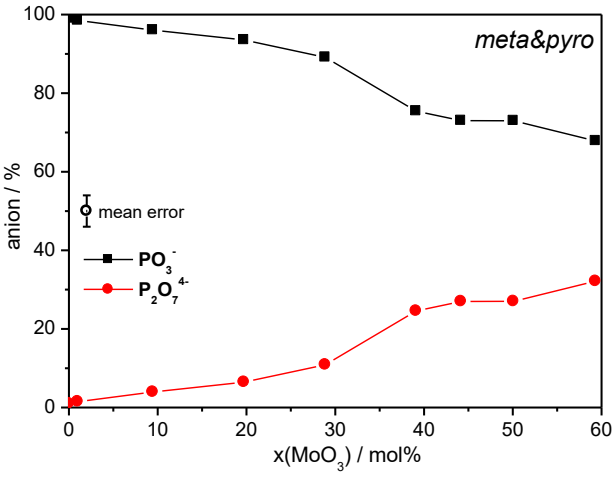

Fig. 20 Compositional dependence of phosphate anions of series *meta&pyro*.

The *meta* series was designed to preserve the metaphosphate structure throughout the compositional range, i.e. $Ca(PO_3)_2 \rightarrow MoO_2(PO_3)_2$. It is evident, Fig. 21, that the metaphosphate structure is significantly dominant in the entire composition range. The content of pyrophosphates increases slightly from x ~ 20 and the metaphosphates decreases proportionally to this, Fig. 22.

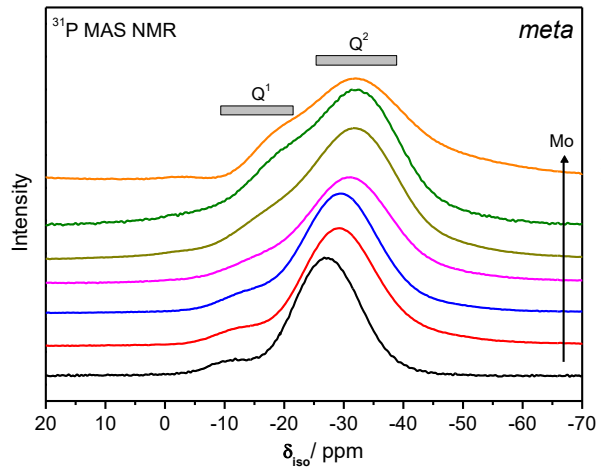

Fig. 21 ^{31}P MAS NMR spectra of series *meta*.

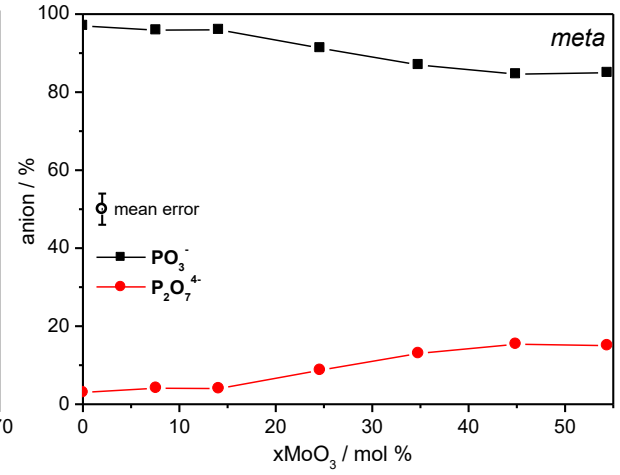

Fig. 22 Compositional dependence of phosphate anions of series *meta*.

3.3.4 Chemical model

From the above results, all data necessary to calculate the chemical models that reflect the changes in the chemical composition of the glasses that occur during synthesis, were obtained. All chemical models were determined according to Chap. 3.1.

It was found that with increasing Mo content, there is a more or less significant increase in the content of structural units Q^1 at the expense of Q^2 units in all series, see Figs. 18, 20 and 22. This increase is most evident in the glasses of *pyro* series, where at the highest molybdenum concentrations the metaphosphates falls to zero and the anionic part of the glass network is then formed of pyro- and orthophosphates. In the case of the *meta&pyro* and *meta* series, the metaphosphate structure predominates throughout the composition.

As already mentioned, molybdenum is incorporated into the structure of the studied glasses only in the form of complex cations, molybdenyls, and cannot form anions, i.e. molybdates. By creating a chemical model, it was possible to determine which of the four molybdenyls are formed in glass of a given composition and it was found that the molybdenyl MoO^{3+} is probably not present in the studied glasses.

The chemical models of all three series are shown in Figs. 23-25. It is clear that with increasing molybdenum content, the content of the initial calcium metaphosphate decreases in the structure of all glasses, and due to the variability of possible molybdenyls, meta- and pyrophosphate molybdenyls with a central Mo(VI) atom gradually begin to predominate. On the other hand, Mo(V) molybdenyls are represented only as a minor part in the structure of the glasses.

A chemical model of the *pyro* series is shown in Fig. 23. The model shows that the compositional dependence can be divided into two regions with the boundary of $x \sim 30$. In the first region, the composition of the glasses is mainly controlled by the content of calcium metaphosphate $Ca(PO_3)_2$, whose concentration decreases with increasing molybdenum content and is gradually replaced by molybdenyl metaphosphate $MoO_2(PO_3)_2$ and calcium pyrophosphate $Ca_2P_2O_7$. In the second region, for $x > 30$, the ability of molybdenum to form multiple oxo-cations is emphasized and the chemical compositions of the glasses become more complicated. The content of calcium phosphate further decreases and molybdenyl pyrophosphate, $(MoO_2)_2P_2O_7$, becomes the predominant compound. For $x > 50$, the concentration of orthophosphate $(MoO_2)_3(PO_4)_2$ increases due to the chemical equilibrium.

The chemical model for the *meta&pyro* glass series is shown in Fig. 24. Calcium is incorporated practically only into metaphosphates, so its concentration decreases almost linearly with increasing Mo content. Decreasing calcium metaphosphate is compensated mainly by $MoO_2(PO_3)_2$ and $(MoO_2)_2(P_2O_7)$, which form practically equimolar mixture of metaphosphate and pyrophosphate in the last glass of the series

The *meta* series is designed so that, the phosphate network remains composed entirely of metaphosphates with the divalent cation. The chemical model of the *meta* series shows that this assumption was achieved, Fig. 25. The presence of small amount of pyrophosphates in these glasses is due to the chemical equilibrium. The compositional dependence of the Q^n units shows that metaphosphates are dominant throughout the compositional range, see Fig. 22. Cations Ca^{2+} are largely replaced by MoO_2^{2+}, which are both predominantly incorporated to metaphosphates. The divalent cation metaphosphates are crucial in the entire compositional range.

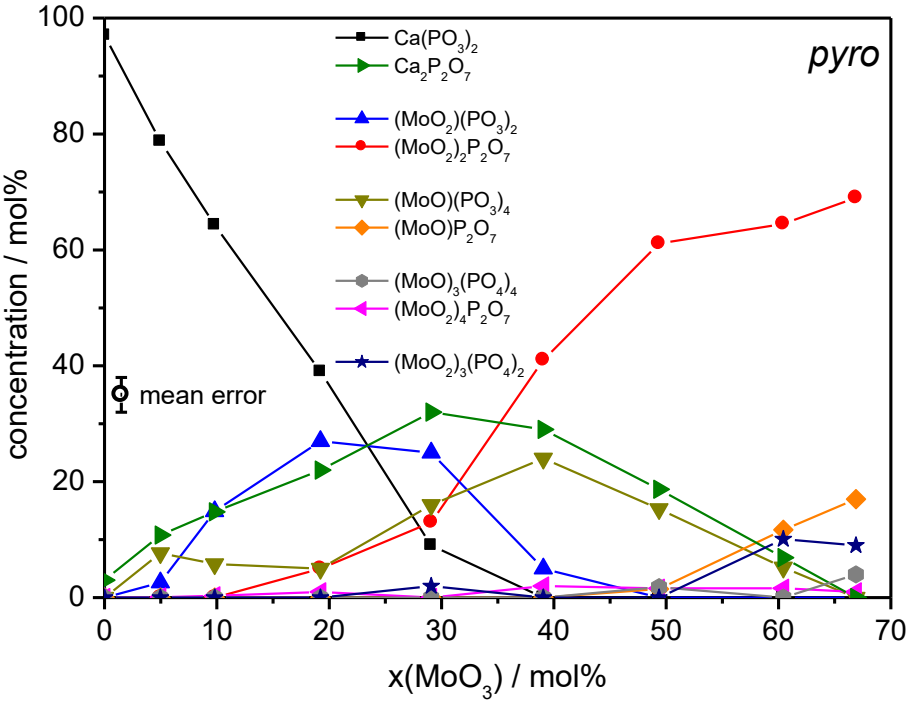

Fig. 23 Chemical model of series *pyro*.

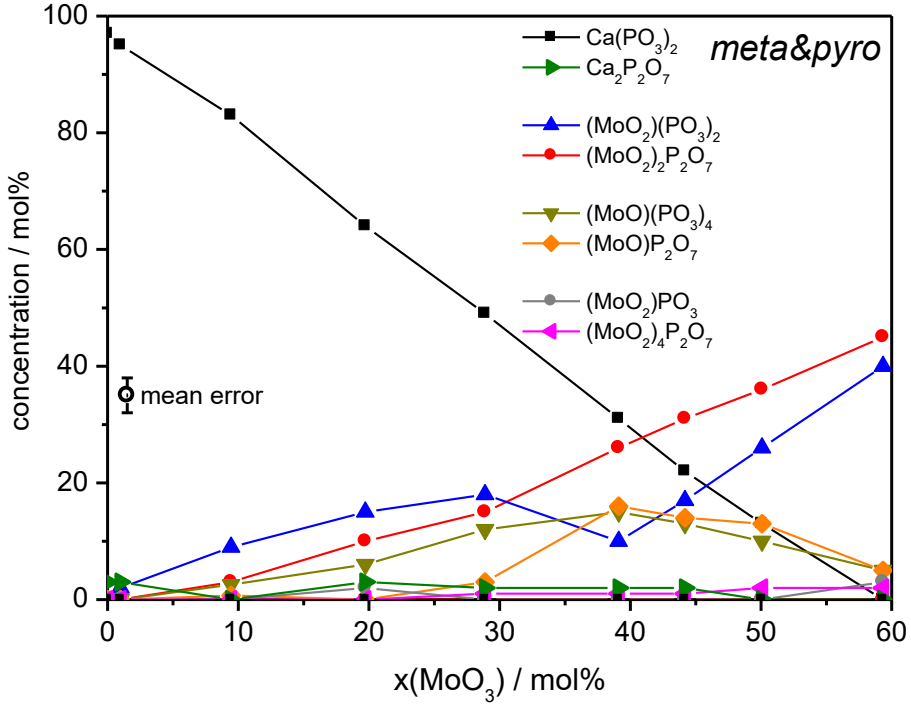

Fig. 24 Chemical model of series *meta&pyro*.

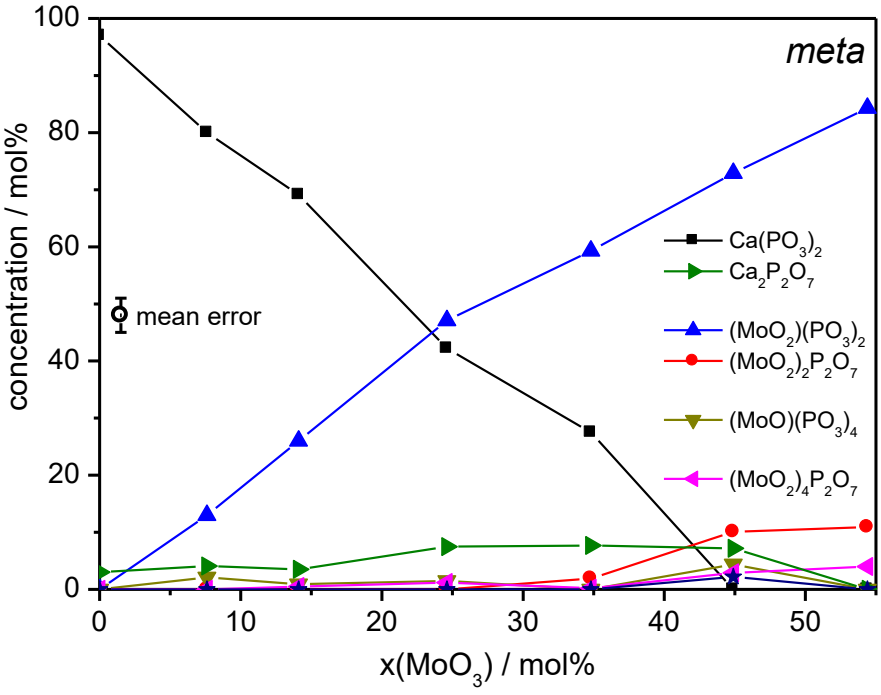

Fig. 25 Chemical model of series *meta*.

3.3.5 Thermal analysis

Two basic thermoanalytical characteristics of glasses, i.e. glass transition temperature, T_g, and coefficient of thermal expansion, α, were measured by TMA and their compositional dependencies are shown Figs. 26 and 27.

It can be seen from Fig. 26 that for the series *pyro*, T_g decreases with increasing molybdenum content in the entire compositional range. In the case of the *meta&pyro* series, there is a break at x ~ 40 on the T_g compositional dependence, and for the *meta* series, there is a decrease in the T_g compositional dependence for the Ca-containing glasses, but a significant increase in the T_g value for the last binary glass. It seems to be very strange, but it was verified by another independent technique, StepScan DSC.

It is evident that in most of the prepared glasses, molybdenum causes a decrease in interactions in the glass structure, which is reflected in a decrease in T_g. The exceptions are glasses with x > 40 in the *meta&pyro* series and the last glass in the series *meta*, where, on the contrary, the structure seems to be more interconnected due to the growth of T_g.

The compositional dependencies of α shown in Fig. 27 are slightly surprising. The α dependence of the *pyro* series shows a break at x ~ 40 compared to the monotonic decrease of T_g. In contrast, the *meta&pyro* series shows a break at T_g dependence, while α decreases with increasing molybdenum concentration, except for the last binary molybdenum phosphate glass. In the case of the series *meta*, the compositional dependence of α decreases with increasing molybdenum content throughout the entire compositional range.

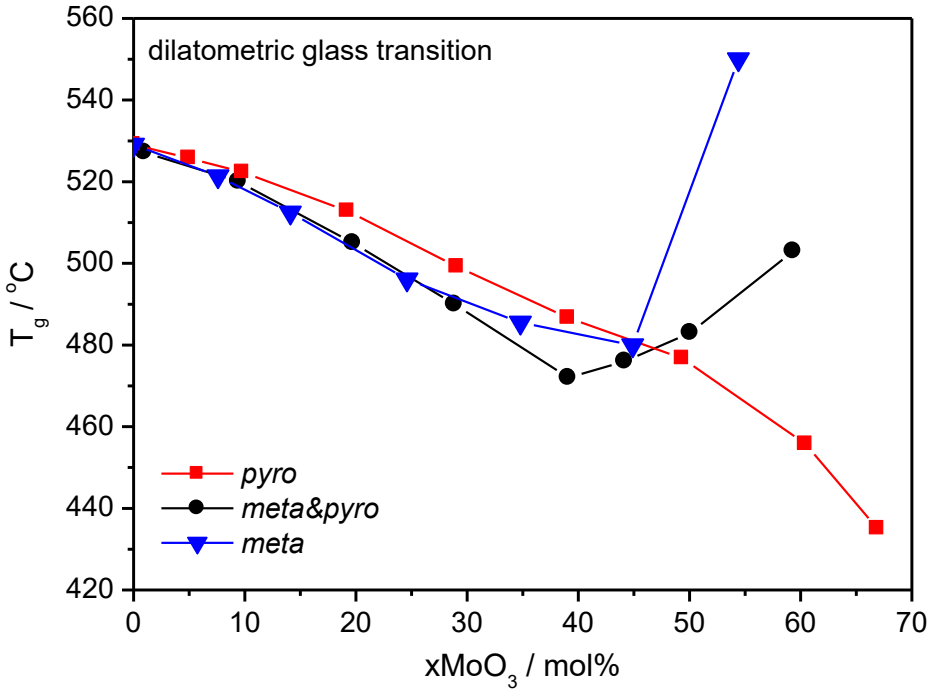

Fig. 26 Compositional dependencies of transition glass temperature, T_g, of all three series.

As discussed in Chap. 3.2.5, only the weak interactions should be considered in explaining the glass transition temperature. It was found that the T_g value increases with increasing metaphosphate content in the glass structure. This can be explained by the above consideration that metaphosphates, as inorganic polymers, can interconnect into larger clusters by weak interactions, which consequently strengthens the glass structure. It can be assumed that higher energy is required to move large clusters. Conversely, if the content of pyrophosphates increased at the expense of metaphosphates, the T_g value decreased. This is due to the fact that the pyrophosphates are only dimers, the structure is therefore less interconnected and less energy is required to convert to melt, which is reflected in lower T_g values. Orthophosphates, that have no bonding potential, require even less energy to release from the structure, causing a further decrease in T_g. In addition, they are small molecules that readily arrange themselves into regular structures, so if they appear in the glass structure in higher concentrations, crystallization occurs.

While the glass transition temperature is associated with weak interactions and disintegration of the glass structure, manifested for example by a decrease in viscosity, the thermal expansion coefficient α reflects the amplitude of vibrations of the structure, which depend mainly on the energies of bonds generally expressed by the Morse potential. The gradual decrease of α in the compositional region with lower molybdenum content is due to the fact that the Ca^{2+} cation of the dominant metaphosphate structure, see Figs. 18, 20 and 22, is gradually replaced by molybdenyl(2+), which through donor-acceptor interactions forms a larger number of significantly covalent bonds. As can be expected, due to the different mechanism of glass transition and thermal expansion, the low concentration of pyrophosphates in this region has no measurable effect on thermal expansion, in contrast to the effect on the

temperature of the glass transition, as mentioned above. On the contrary, the significant increase of pyrophosphates and also orthophosphates result in a weakening of the glass network, so the course of the compositional dependence turns in the opposite direction and α increases.

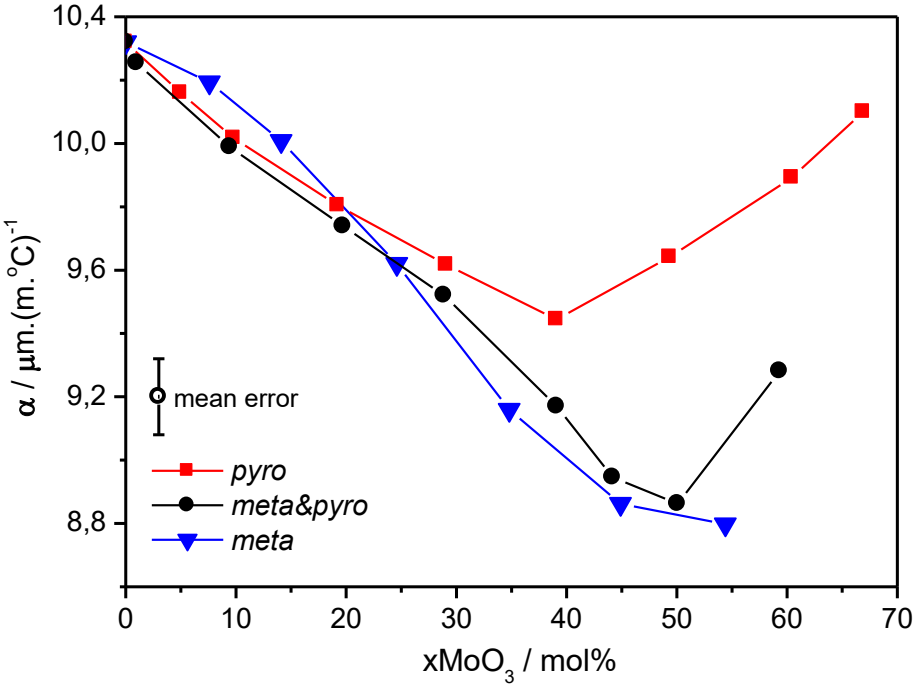

Fig. 27 Compositional dependencies of coefficient of thermal expansion, α, of all three series.

4. Conclusion

The aim of this work was to study the behavior of molybdenum, a transition metal with the possibility of forming oxo-cations with variable oxidation states, in various structures of the phosphate glass network. The effect of molybdenum on phosphate glasses was described using a chemical model, i.e. through the composition dependences of the molar concentrations of the actual chemical compounds forming glasses. Chemical models were subsequently used to explain the compositional dependences of thermoanalytical properties, glass transition temperature T_g and coefficient of thermal expansion α.

The work was divided into two parts, in the first part binary phosphate glasses with molybdenum were prepared in order to determine whether all glasses of selected compositions can be prepared. The composition of the glasses was calculated so that the structure of the phosphate network passed from ultraphosphates, through metaphosphates and further through glass with an equimolar content of meta- and pyrophosphates, to glass formed only by pyrophosphates. For this reason, a complete structural analysis was performed on all glasses. The elemental analysis was performed by XRF spectroscopy and the degree of reduction of molybdenum, i.e. the detailed cationic part of the glasses, was determined by EPR spectroscopy. The anionic part of glasses was characterized by ^{31}P MAS NMR spectroscopy and the overall picture of the structure was correlated with the results of Raman spectroscopy, where the spectra of polarized vibrations were used for a clearer description. At the same time, it was found that ultraphosphate glass is a glass with a lack of metal cation, where the excess of metaphosphoric acid decomposes into phosphorus oxide and water depending on the temperature. This changes the overall composition of this glass. Metaphosphoric acid is the reason for hygroscopicity of ultraphosphate glasses. From the chemical model, it was also possible to determine the actual molecular weight of the glass, because it works with real chemical compounds that make glass.

In the second part, three series of ternary molybdenyl-phosphate glasses with calcium were studied, so the cation of a non-transition metal was chosen as another cation. The effect of increasing concentration of molybdenyls, replacing calcium, on the overall chemical composition of glasses was studied. Each series was based on amorphous calcium metaphosphate and the terminal glass was one of the binary molybdenum phosphate glasses prepared in the first part of the work. Thus, a total of three series of glasses were prepared. The structure of glass network of the first series passed through metaphosphate to pyrophosphate (*pyro* series), the second series had a final composition of meta- and pyrophosphates mixture (*meta&pyro* series) and the third series corresponded to the final composition of metaphosphates (*meta* series). The ultraphosphate series was not prepared due to thermal instability. As with binary glasses, an overall analysis of the glass composition was performed, based on which a chemical model was determined for each series.

The chemical models were further correlated with the compositional dependences of the glass transition temperature, T_g, and with the coefficient of thermal expansion, α, and mutual relations influencing the character of the compositional dependences were found.

5. References

[1] R.K. Brow, Review: the structure of simple phosphate glasses, J. Non-Cryst. Solids 263&264 (2000) 1–28.

[2] J.R. Jones, A.G. Clare, Bio-Glasses: an introduction, Wiley (2012) ISBN 978-0-470-71161-3.

[3] A. Mogus-Milankovic, A. Santic, S.T. Reis, D.E. Day, Electrical properties of phosphate glasses, Mat. Sci. Eng. 2 (2009) 012004.

[4] M.K. Hekmat-Shoar, C.A. Hogarth, G.R. Moridi, A study of the electrical properties of molybdenum phosphate glasses, J. Mat. Science 20 (1985) 889-894.

[5] M. Liška: Studying structure and thermal properties of oxide glasses, (pp. 345-362). V: Some Thermodynamics, Structural and Behavioral Aspects of Materials Accentuating Non-Crystalline States (J. Šesták, M. Holeček, J. Málek, eds.) O.P.S., Nymburk (2009) ISBN 978-80-87269-06-0.

[6] M. Liška, J. Macháček, M. Chromčíková, J. Holubová, Z. Černošek, Thermodynamic model of ZnO-Nb_2O_5-P_2O_5 glasses – parameterization and validation, Int. J. Appl. Glass Sci. 00 (2021) 1–7.

[7] M. Liška, J. Macháček, M. Chromčíková, O. Gedeon, Thermodynamic model and structure of ZnO–MoO_3–P_2O_5 glasses, Phys. Chem. Glasses: Eur. J. Glass Sci. Technol. B 56/2 (2015) 63-66(4).

[8] M. Liška, M. Lissová, A. Plško, M. Chromčíková, T. Gavenda, J. Macháček, Thermodynamic model and Raman spectra of ZnO–P_2O_5 glasses, J. Therm. Anal. Cal. 121 (2015) 85–91.

[9] B. Hruška, R. Dagupati, M. Chromčíková, A. Nowicka, J. Macháček, M. Liška, F. Muñoz, Thermodynamic model and Raman spectra of MgO–P_2O_5 glasses, J. Therm. Anal. Cal. 142 (2020) 2025–2031.

[10] M. Chromčíková, M. Liška, J. Macháček, J. Šulcová, Thermodynamic model and structure of CaO–P_2O_5 glasses, J. Therm. Anal. Cal. 114 (2013) 785–789.

[11] P. Mustarelli, The NMR information on phosphate glasses: A review, Phosphorus Research Bulletin 10 (1999) 25-36.

[12] R.K. Brow, D.R. Tallant, J.J. Hudgens, S.W. Martin, A.D. Irwin, The short-range structure of sodium ultraphosphate glasses, J. Non-Cryst. Solids 177 (1994) 221-228.

[13] G. Palavit, Phosphate glasses and water, Phosphorus Research Bulletin 6 (1996) 85-90.

6. List of published work

[1] Z. Černošek, M. Chládková, J. Holubová, The influence of TiO_2 on the structure and properties of sodium-zinc phosphate glasses, J. Non-Cryst. Solids 531 (2020) 119866. https://doi.org/10.1016/j.jnoncrysol.2019.119866

[2] Z. Černošek, M. Chládková, J. Holubová, Chemical model of binary molybdenum phosphate glasses, J. Solid State Chem. 303 (2021) 122522. https://doi.org/10.1016/j.jssc.2021.122522

[3] Z. Černošek, M. Chládková, J. Holubová, Phosphate glasses, what is the actual chemical composition and structure of these glasses? The view of a chemist, J. Solid State Chem. 314 (2022) 123366. https://doi.org/10.1016/j.jssc.2022.123366