# Behavior of molybdenum in calcium phosphate glasses

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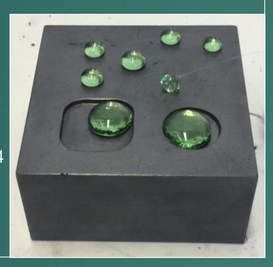
## Introduction

Phosphate glasses with transition metals are frequently studied due to their specific electrical properties, photoconductivity and optical absorption in visible and UV region. However, the chemistry of transition metals in phosphate melts has not been given sufficient attention so far. Transition metals can occur in various oxidation states, form complex ions and increase the stability of phosphate glasses by incorporation to the glass-forming network. One of the transition metals that can be effectively used in phosphate glasses is molybdenum.

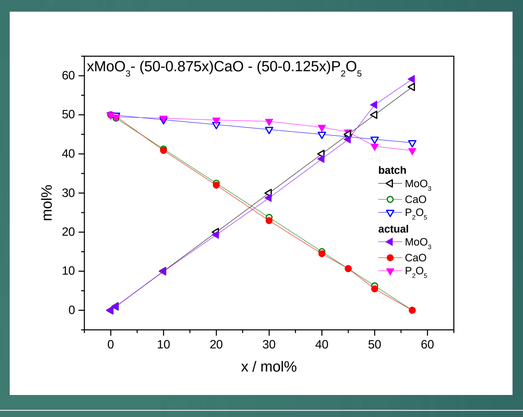
## Calcium phosphate glasses with molybdenum

- molybdenum exists in two oxidation states– $Mo^{VI}$ and $Mo^{V}$
- Mo complex cations – molybdenyls (X = 6 or 5)
  - $(Mo^{X}O_2)^{(X-4)+}$ and $(Mo^{X}O)^{(X-2)+}$
- glass composition of prepared glasses changes from calcium metaphosphate $(Ca(PO_3)_2)$to molybdenyl pyrophosphate $((Mo^{V}O)_4(P_2O_7)_3)$
  - $xMoO_3$-(50-0.875x)CaO-(50-0.125x)$P_2O_5$, x = 0, 1, 10, 20, 30, 40, 45, 50 and 57.14
- glasses were prepared with the conventional melt quenching method from $MoO_3$, $CaCO_3$ and $H_3PO_4$
- the green color of glasses indicates the reduction of Mo(VI) to Mo(V) during synthesis

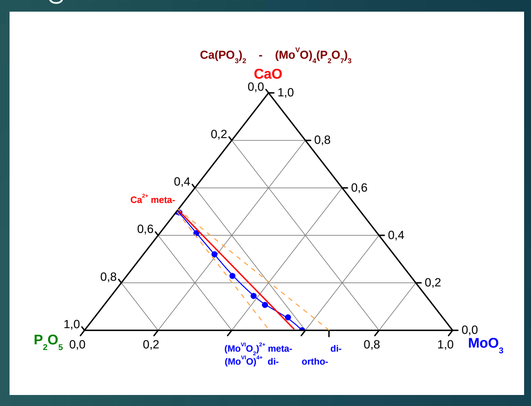


## XRF

The real composition of glasses was determined by XRF. The batch and actual composition has been found close each other. The actual composition is further used for higher correctness.

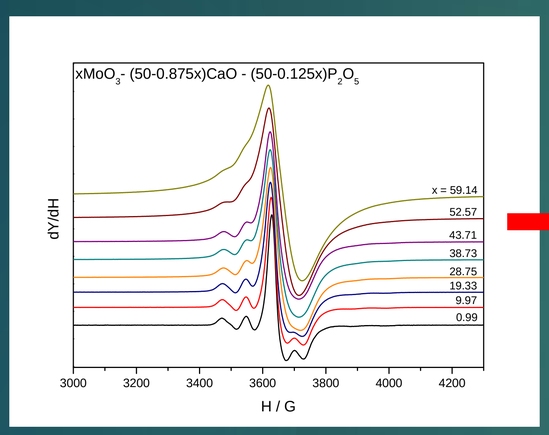


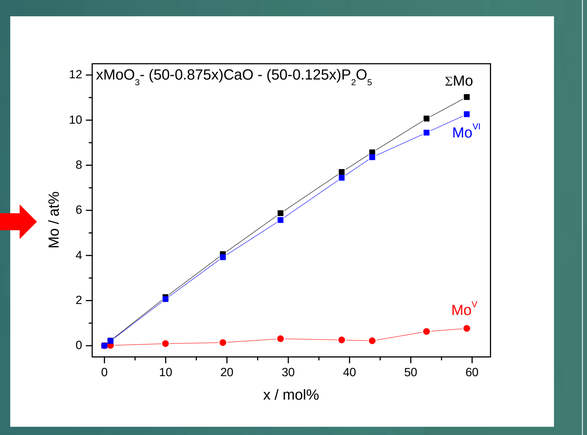

| batch | $MoO_3$ (mol%) | actual |
|---|---|---|
| 1 | → | 0.99 |
| 10 | → | 9.97 |
| 20 | → | 19.33 |
| 30 | → | 28.75 |
| 40 | → | 38.73 |
| 45 | → | 43.71 |
| 50 | → | 52.57 |
| 57.14 | → | 59.14 |




## ESR

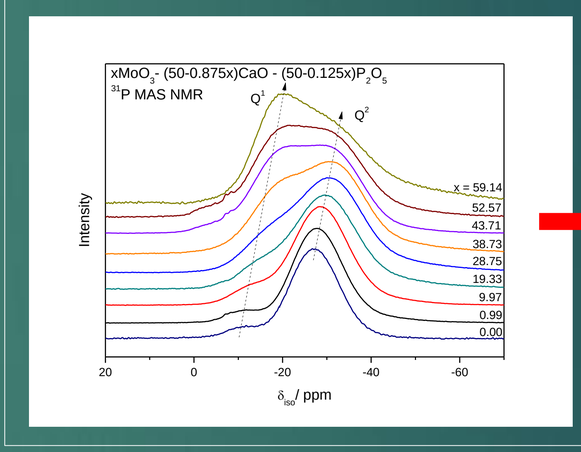
The electron paramagnetic resonance has shown that the coordination polyhedron remained unchanged and due to Jahn-Teller distortion is very probably a tetragonal bipyramid. Quantitative analysis showed that degree of molybdenum reduction is very low, max. 7%.

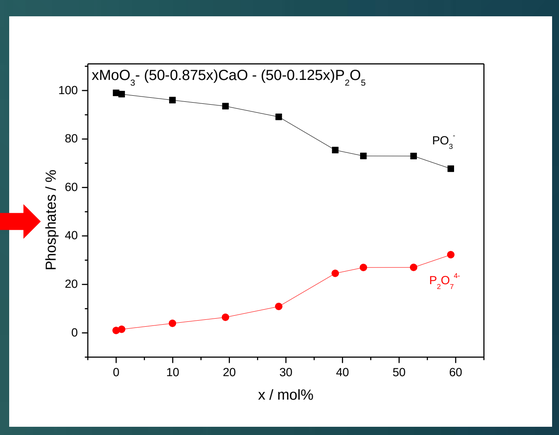



## NMR

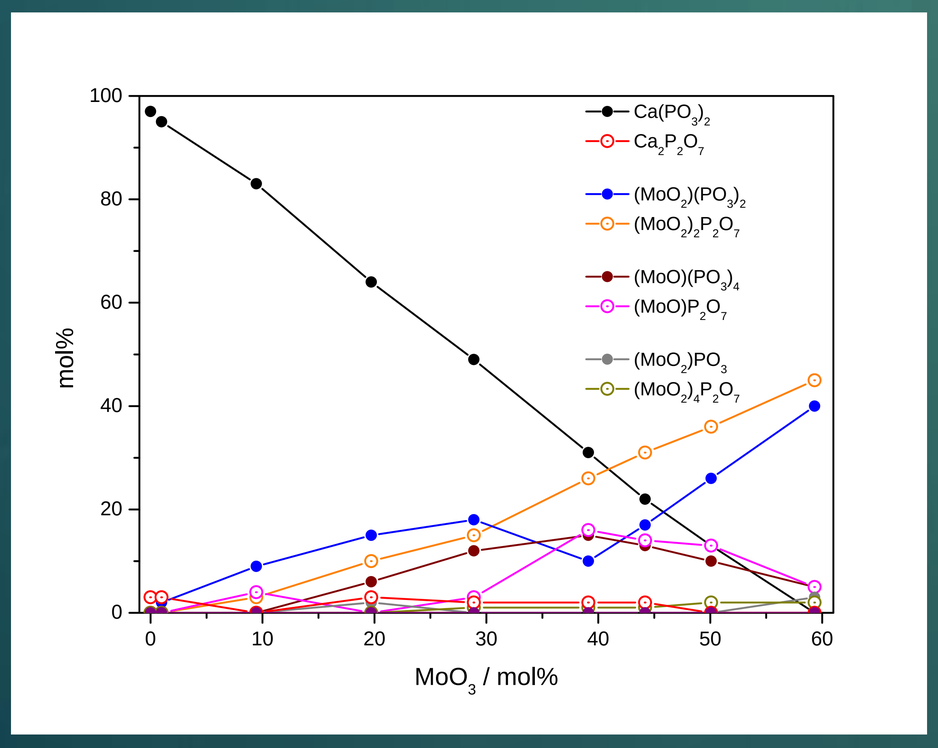
Basic structural units and their relative amount were found by $^{31}P$ MAS NMR. Results show that with increasing amount of $MoO_3$ the metaphosphate structure ($Q^2$ structural units) partially passes into pyrophosphate one ($Q^1$-$Q^1$).



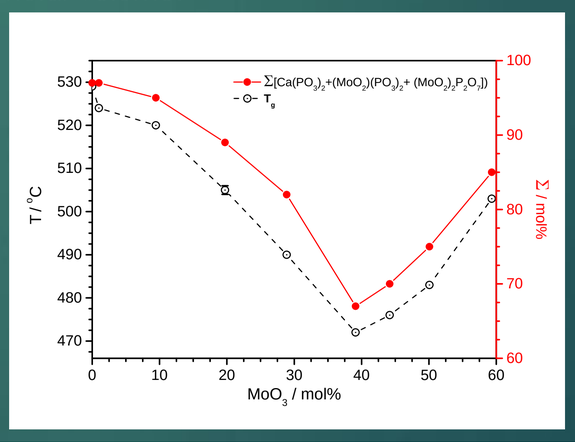

## Chemical model

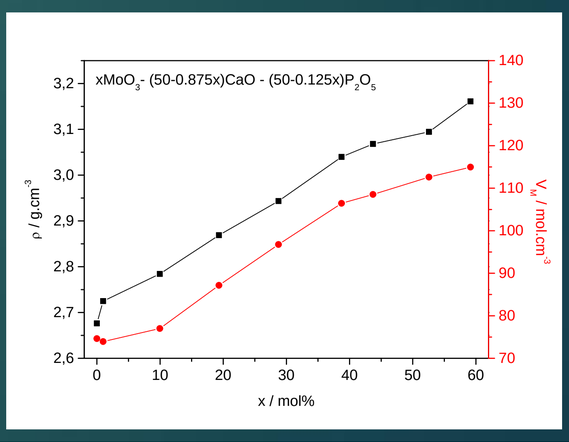
Phosphate glasses are not mixture of oxides, but mixture of chemical compounds formed by chemical reactions of oxides and higher temperatures, a chemical model, i.e. chemical compounds and their molar concentrations, was proposed based on experimental results.




## Glass transition temperature $T_g$, density ρ and molar volume $V_M$

The use of a chemical model shows that the glass transition temperature is crucially dependent on the ratio of the predominant compounds shown in Fig. below. The chemical model makes it possible to determine the correct molecular weight of glass of a given composition, on the basis of which it is possible to calculate real values of e.g. molar volume.




## Conclusion

It has been found that like in aqueous solution, reduction of $Mo^{VI}$ is almost negligible in the glass-forming phosphate melts and that composition of phosphate glassy network is primarily controlled by the presence of divalent cations. Unlike calcium, molybdenyl is incorporated into the glass network structure by four covalent bonds which, in addition to forming a cation-anion network, also allows the involvement of small pyrophosphate dimeric anions in the glass network and thus improves the glass forming ability of the studied system even with complete replacement of calcium by molybdenum.