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# Effect of molybdenum addition on the thermal properties of silicate–phosphate glasses

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Bretsznajder Special Chapter

**Abstract** Aim of the study was analysis of two groups of glasses: silicate–phosphate (41 mol.% $SiO_2$–6 mol.% $P_2O_5$) and with inverse phosphate–silicate matrix (41 mol.% $P_2O_5$–6 mol.% $SiO_2$) modified by the addition of molybdenum ions. Their effect on glass forming ability, glass transition effect, crystallization process, and kind of crystallizing phases was examined using such methods as DSC, XRD, and SEM. It was found that the solubility limit of $MoO_3$ in silicate–phosphate glasses is $4.4 < [MoO_3] < 5.7$ mol.%, whereas in phosphate–silicate glasses $MoO_3$ is fully dissolved. It was found that in the case of both matrixes addition of molybdenum ions decreases the glass transition temperature ($T_g$), as well as the value of specific heat change ($\Delta c_p$) accompanying the glass transformation. The presence of molybdenum caused reduced the thermal stability of the studied glasses and a multi-step crystallization of silicate–phosphate glasses. It was found that the crystallizing phases were silicates and phosphates in both groups of glasses. Only in the case of silicate–phosphate glasses containing $MoO_3$ in an amount $\geq 3.3$ mol.% one of the crystallization product was powellite ($CaMoO_4$). The nature of transitions taking place during heating of the analyzed glasses was in accordance with crystallochemical factors (strengths of bonds) and chemical affinity of the glass components ($\Delta G$ formation).

**Keywords** Silicate–phosphate glasses · $MoO_3$ · Thermal stability · Glass transition · Crystallization effect

## Introduction

Molybdenum is a chemical element from the group *d* of transition metals. The free element, which is a silvery metal, has the sixth highest melting point of any element. It readily forms hard, stable carbides and for this reason it is often used in high-strength steel alloys. Industrially, molybdenum compounds are used in high pressure and high temperature applications, as pigments and catalysts. Molybdenum complexes are used as catalysts in the petroleum industry, particularly in removing sulfur from petroleum products. Molybdenum is also known as a nucleating agent in the glass–ceramics industry for its ability to control the phase separation of glasses or as a crystallization catalyst to produce glass–ceramics. The behavior of molybdenum ions in aluminosilicate and borosilicate glasses is of interest because of its nucleating properties, especially in glass compositions selected for nuclear waste containment. Incorporation of molybdenum ions in silicate glasses is a potential route for immobilizing bioavailable molybdenum from polluted sediments, soils, and chemical and medical wastes [1, 2].

Molybdenum is an element occurring in various degrees of oxidation and in glasses it may exist at different oxidation states: $Mo^{6+}$, $Mo^{5+}$, $Mo^{3+}$ and $Mo^{4+}$ or a mix of some of them [3, 4]. Literature data [5, 6] reports, that $MoO_3$ and $P_2O_5$ form stable glasses over a wide range of compositions from 0 to 83 mol.% $MoO_3$ content. Because of molybdenum high field strength, $Mo^{6+}$ cation has a limited solubility in silicate glasses and crystallization of alkali or alkaline-earth molybdates may occur during melt cooling or heat treatment of glasses [7–10].

Thermal characteristics of glasses modified by molybdenum ions are rarely found in the literature. Information covering a range of glass transition and crystallization process mainly concerns phosphate glasses. The available

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data shows, that phosphate glasses belonging to binary $MoO_3$–$P_2O_5$ and ternary $K_2O$–$MoO_3$–$P_2O_5$ systems generally have low melting temperature, high thermal expansion coefficient, low glass transition temperature but their chemical durability is poor in comparison with commercial silicate glasses [11–13]. In the case of phosphate glasses from $Na_2O$–$MoO_3$–$P_2O_5$ system or $Na_2O$–$Li_2O$–$MoO_3$–$P_2O_5$ [14, 15] the $T_g$ decreases with increase in $MoO_3$ content. This kind of $T_g$ characteristic was also reported for other vitreous systems e.g., $Li_2O$–$Na_2O$–$Al_2O_3$–$P_2O_5$ [16] and $Li_2O$–(Na, K, Rb)$_2$O–$B_2O_3$ [17]. The effect of $MoO_3$ addition on the thermal characteristics of silicate glasses has not been found in the literature. The same situation applies to silicate–phosphate glasses belonging to $SiO_2$–$P_2O_5$–$K_2O$–MgO–CaO system modified with $MoO_3$. This kind of glasses acting as glassy fertilizers may contain a complete set of macro- (P, K, Mg, Ca) and microelements needed for the growth of plants [18–20]. In this case molybdenum can have unconventional application. It is a microelement necessary for proper development of plants. Influence of molybdenum on plants growth process is mainly related to its important role in their metabolism, finding use in glassy fertilizers as one of their components.

Therefore, aim of the work was analysis of two groups of glasses from $SiO_2$–$P_2O_5$–$K_2O$–MgO–CaO system differing in $SiO_2$ and $P_2O_5$ content modified by addition of molybdenum ions. Its effect on glass forming ability, glass transition, crystallization process, and kind of crystallizing phases was examined.

## Experimental

Two groups of glasses from $P_2O_5$–$SiO_2$–$K_2O$–CaO–MgO (denoted in the text as the P group glass) and $SiO_2$–$P_2O_5$–$K_2O$–CaO–MgO (the Si group glass) system modified by $MoO_3$ addition were prepared. In each group of glasses constant quantities of $P_2O_5$, $K_2O$ and $SiO_2$ were kept and increasing amount of $MoO_3$ was introduced at the cost of decreasing amount of MgO and CaO, with the constant MgO/CaO ratio. The glasses were produced by melting of raw materials mixture i.e., $SiO_2$, $H_3PO_4$, $K_2CO_3$, MgO, $CaCO_3$, and $MoO_3$ in platinum crucibles at 1,200 °C (the P group glass) and at 1450 °C (the Si group glass). Then the batch-free glasses were fritted in water (rapidly quenched). All glasses were ground to grain size of 0.1–0.3 mm. The chemical composition of some glasses was controlled by X-ray fluorescence spectroscopy using ARL Advant 'XP spectrometer. Chemical composition of the examined glasses was presented in Tables 1 and 2. Amorphous state of the analyzed glasses was confirmed by X-ray diffraction method.

Thermal stability of the obtained glasses was determined by DSC measurements conducted on STA 449 *F3 Jupiter*®7 (Netzsch) operating in the heat flux DSC mode. The temperature and heat calibrations of the instrument were performed using the melting temperatures and melting enthalpies of high purity aluminum, tin, zinc, silver and gold. The samples (~40 mg) were heated in platinum crucibles at 10 °C $min^{-1}$ in dry nitrogen atmosphere up to 1,100 °C. The glass transition temperature ($T_g$) was registered in a half of the endothermal inflection on DSC curve and changes of the specific heat $\Delta c_p$ accompanying the glass transformation were calculated using Proteus Analysis Program (Netzsch). The ability of glasses to crystallize was evaluated from the values of crystallization temperature $T_c$, registered as a maximum temperature of the crystallization effect and $T_g$ temperature as the thermal stability parameter of glasses $\Delta T = T_c – T_g$. X-ray diffraction method (X'Pert PRO Diffractometer) was applied to

**Table 1** Assumed chemical composition of the P group glasses and results determined by X-ray fluorescence spectrometry method (test)

| No | Content of components/mol.% | | | | | |
|---|---|---|---|---|---|---|
| | $SiO_2$ | $P_2O_5$ | $K_2O$ | MgO | CaO | $MoO_3$ |
| 0Mo41P | 6 | 41 | 6 | 28 | 19 | 0.0 |
| 0Mo41P$_{test}$ | 6.5 | 40.7 | 5.7 | 28.8 | 18.2 | 0.0 |
| 2Mo41P | 6 | 41 | 6 | 27 | 18 | 2 |
| 2Mo41P$_{test}$ | 6.0 | 40.8 | 5.7 | 27.8 | 17.8 | 1.9 |
| 4Mo41P | 6 | 41 | 6 | 26 | 17 | 4 |
| 4Mo41P$_{test}$ | 5.2 | 41.9 | 6.9 | 25.5 | 16.6 | 3.9 |
| 8Mo41P | 6 | 41 | 6 | 23 | 16 | 8 |
| 8Mo41P$_{test}$ | 5.7 | 40.8 | 6.2 | 22.9 | 16.4 | 8.0 |
| 15Mo41P | 6 | 41 | 6 | 19 | 13 | 15 |
| 15Mo41P$_{test}$ | 6.2 | 40.6 | 6.2 | 19.1 | 12.8 | 15.1 |
| 30Mo41P | 6 | 41 | 6 | 10 | 7 | 30 |
| 30Mo41P$_{test}$ | 5.8 | 41.2 | 6.3 | 10.0 | 7.2 | 29.5 |

**Table 2** Assumed chemical composition of the Si group glasses and results determined by X-ray fluorescence spectrometry method (test)

| No | Content of components/mol.% | | | | | |
|---|---|---|---|---|---|---|
| | $SiO_2$ | $P_2O_5$ | $K_2O$ | MgO | CaO | $MoO_3$ |
| 0Mo41Si | 41 | 6 | 6 | 28 | 19 | 0.0 |
| $0Mo41Si_{test}$ | 41.6 | 5.7 | 5.7 | 28.2 | 18.8 | 0.0 |
| 2Mo41Si | 41 | 6 | 6 | 27 | 18 | 2 |
| $2Mo41Si_{test}$ | 38.7 | 7.1 | 5.9 | 27.6 | 18.8 | 1.9 |
| 3Mo41Si | 41 | 6 | 6 | 26 | 18 | 3 |
| $3Mo41Si_{test}$ | 40.6 | 6.1 | 6.3 | 25.6 | 18.1 | 3.3 |
| 4Mo41Si | 41 | 6 | 6 | 26 | 17 | 4 |
| $4Mo41Si_{test}$ | 41.2 | 5.8 | 6.0 | 26.3 | 16.6 | 4.1 |
| 5Mo41Si | 41 | 6 | 6 | 25 | 17 | 5 |
| $5Mo41Si_{test}$ | 39.6 | 7.8 | 6.6 | 24.8 | 16.8 | 4.4 |
| 6Mo41Si | 41 | 6 | 6 | 25 | 16 | 6 |
| $6Mo41Si_{test}$ | 41.9 | 5.6 | 6.2 | 24.8 | 15.8 | 5.7 |
| 7Mo41Si | 41 | 6 | 6 | 24 | 16 | 7 |
| $7Mo41Si_{test}$ | 40.3 | 6.2 | 5.7 | 24.4 | 16.2 | 7.2 |
| 8Mo41Si | 41 | 6 | 6 | 23 | 16 | 8 |
| $8Mo41Si_{test}$ | 41.4 | 5.7 | 5.8 | 22.6 | 16.1 | 8.4 |
| 15Mo41Si | 41 | 6 | 6 | 19 | 13 | 15 |
| $15Mo41Si_{test}$ | 40.6 | 5.8 | 6.3 | 18.7 | 13.3 | 15.3 |
| 30Mo41Si | 41 | 6 | 6 | 10 | 7 | 30 |
| $30Mo41Si_{test}$ | 42.1 | 5.9 | 6.0 | 9.7 | 6.8 | 29.5 |

identify the crystalline phases created during the melt quenching and forming in the isothermal process of glass heating at temperatures determined from the DSC measurements. Microstructure of the analyzed glasses was observed by the Scanning Electron Microscopy (SEM) method.

## Results and discussion

### Glass forming ability

Glasses from the $P_2O_5$–$SiO_2$–$K_2O$–CaO–MgO–$MoO_3$ system with higher $P_2O_5$ content (P group glass) were blue while from the $SiO_2$–$P_2O_5$–$K_2O$–CaO–MgO–$MoO_3$ system (Si group glass) were yellow. Blue color of glasses suggested the presence of $Mo^{3+}$, $Mo^{4+}$, $Mo^{5+}$ and/or $Mo^{6+}$ ions [6] while yellow color suggested the presence of $Mo^{6+}$ ions [7] in the glass structure.

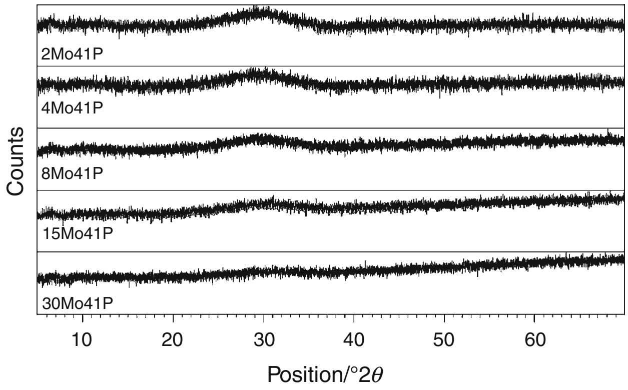

**Fig. 1** XRD patterns of $MoO_3$-doped the P group glasses

XRD study confirmed the amorphous state of the glasses from the P group with 0–29.5 mol.% of $MoO_3$ addition (Fig. 1) and the Si group glasses containing <5.7 mol.% of $MoO_3$ (Fig. 2). The XRD patterns for the glass samples containing ≥5.7 mol.% of $MoO_3$ showed diffraction peaks superimposed on a weak pattern, indicating that partial crystallization occurred as shown in Fig. 2 and the crystallization product of quenched melts was identified as powellite $CaMoO_4$.

On the basis of XRD analysis it was found that solubility limit of $MoO_3$ in the Si group glasses is $4.4 < [MoO_3] < 5.7$ mol.%. The analyzed glasses were characterized by higher solubility limit of $MoO_3$ than soda-lime silicate glasses investigated by Cousi ($3.5 < [MoO_3] < 4$ wt%) [21] and by Caurant ($[MoO_3] < 3.5$ wt%) [22]. It probably results from the fact that the analyzed glasses contain some amount of $P_2O_5$ in their composition. The fact that $Mo^{6+}$ cations are far more soluble in phosphate glasses than in silicate ones could be explained by the fact that

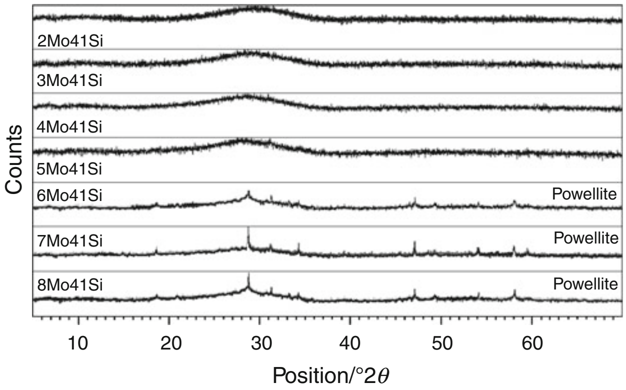

**Fig. 2** XRD patterns of $MoO_3$-doped the Si group glasses

molybdenum cations would be mainly present in six-coordinated environment and would be connected to the phosphate network [23–26]. In silicate glasses molybdenum cations are located in regions enriched in alkali and alkaline-earth cations. Because of high field strength of hexavalent molybdenum cations [22, 27, 28], $Mo^{6+}$ cation exerts a strong ordering effect on the surrounding oxygen ions and may separate easily from the silicate or borosilicate glassy network combining with other elements such as alkali and alkaline-earth to form crystalline molybdates [22, 29–31].

## Thermal characteristics of glasses

DSC curves of P and Si groups glasses containing increasing amount of $MoO_3$ as the modifier of their structure are shown in Figs. 3 and 4. They enabled to estimate the following thermal parameters: glass transformation temperature $T_g$, change of specific heat accompanying $T_g$ transition ($\Delta c_p$), crystallization temperature $T_c$ and thermal stability parameter $\Delta T$. Lower values of the crystallization temperatures and lower values of $\Delta T$ index indicate higher ability of the glasses to crystallize.

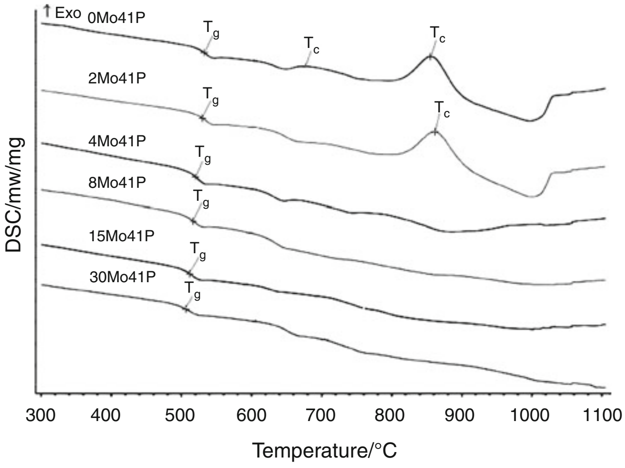

**Fig. 3** DSC curves of glasses from the $P_2O_5$–$SiO_2$–$K_2O$–MgO–CaO system (the P group glass) modified by $MoO_3$ addition

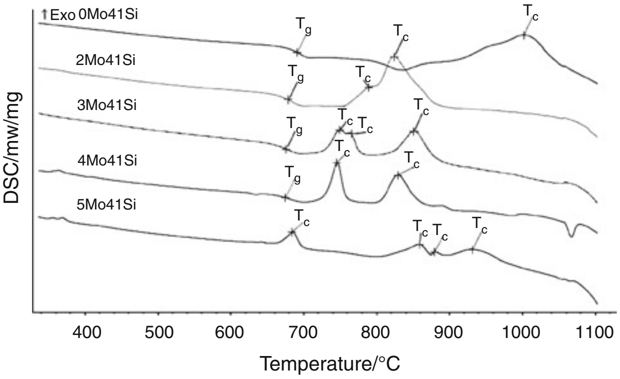

**Fig. 4** DSC curves of glasses from the $SiO_2$–$P_2O_5$–$K_2O$–MgO–CaO system (the Si group glass) modified by $MoO_3$ addition

## Glass transition

The effect of changes in the chemical composition of the analyzed glasses on the parameters characterizing glass transition effect is shown in Table 3.

Both glasses without addition of $MoO_3$ (0Mo41P and 0Mo41Si) were characterized by the highest values of the $T_g$ temperature and a jump-like change of the specific heat ($\Delta c_p$). It should be stated that the $T_g$ temperature was higher for the Si group glass.

The introduction of 1.9 mol.% of $MoO_3$ to the chemical composition of glasses from the P group did not affect the value of transition temperature, whereas in glasses with higher $SiO_2$ content even small addition of $MoO_3$ decreased $T_g$ temperature by 12 °C. In the case of glasses from the P group a gradual increase of its amount at the cost of decreasing content of MgO and CaO resulted in a gradual decrease of $T_g$ temperature and $\Delta c_p$. This behavior can be explained on the basis of crystallochemical factors related to strength of chemical bonds between oxygen atoms and framework-forming components and modifiers [32]. It is known, that the ionicity value of bonds between component atoms and oxygen ($i_G$) [33] is a parameter characterizing strength of the bonds which increases with decreasing ionicity.

The introduction of increasing amounts of MoO3 to the structure of the P group glasses at the cost of decreasing content of MgO and CaO was associated with an increasing number of Mo–O type bonds. This type of chemical bonds is characterized by lower ionicity ($i_{G\ \mathrm{Mo}^{4+}\text{–O}} = 0.421$, $i_{G\ \mathrm{Mo}^{6+}\text{–O}} = 0.303$) in comparison to ionicity of Ca–O (0.707) and Mg–O (0.670) bonds. It increases the amount of structural stresses in the glass structure thus its relaxation is easier and requires little energy input. For this reason glass transition occurs at lower temperatures which also correlates with lower values of $\Delta c_p$ (Table 3).

**Table 3** Thermal characteristics of glass transition of analyzed glasses

| No | 0Mo41P | 2Mo41P | 4Mo41P | 8Mo41P | 15Mo41P | 30Mo41P |
|---|---|---|---|---|---|---|
| $T_g$/°C | 529 | 529 | 520 | 515 | 512 | 508 |
| $\Delta c_p$/J/g/K | 0.35 | 0.34 | 0.33 | 0.27 | 0.26 | 0.25 |

| No | 0Mo41Si | 2Mo41Si | 3Mo41Si | 4Mo41Si | 5Mo41Si | 6Mo41Si | 7Mo41Si | 8Mo41Si |
|---|---|---|---|---|---|---|---|---|
| $T_g$/°C | 690 | 680 | 679 | 679 | – | – | – | – |
| $\Delta c_p$/J/g/K | 0.32 | 0.30 | 0.27 | 0.15 | – | – | – | – |

In the case of glasses with higher $SiO_2$ content the increasing amount of $MoO_3$ in their structure resulted in a very small decrease of the glass transition temperature ($T_g$) and decrease of $\Delta c_p$, which was found when the amount of $MoO_3$ was up to 4.1 mol.%. When the amount of $MoO_3$ increased the glass transition effect was not present. In the case of 5Mo41Si glass this behavior may be due to the nucleation phenomenon. In glasses with higher content of $MoO_3$ the crystallization process during cooling of the melt took place (Table 4).

## Crystallization

In the case of glasses with higher $P_2O_5$ content (the P group glass) a smaller tendency toward crystallization can be noticed in comparison to the Si group glasses (Figs. 3, 4) which was confirmed by their much higher thermal stability parameter (Table 4).

In the case of the P group glasses introduction of $MoO_3$ did not change the course of their crystallization (Fig. 3), which showed one-step character. The P group glasses containing ≥3.9 $MoO_3$ mol.% did not crystallize, while the thermal curves (Fig. 4) of the Si group glasses indicated their multistage crystallization. The crystallization effect of 0Mo41Si and 2Mo41Si glasses had one-stage character but the thermal effects were overlapping, while addition of 3.3–4.4 mol.% of $MoO_3$ to its structure changed the course of its crystallization process into three well distinguished stages (5Mo6P).

The X-ray diffraction analysis of 0Mo41P devitrificates (Table 5) showed that, the crystallization product of this glass was a phosphate phase in the form of calcium magnesium potassium phosphate ($Ca_9MgK(PO_4)_7$). The analyzed 0Mo41P and 2Mo41P devitrificates crystallized in higher temperature ranges (800–950 °C) not only in the form of phosphates but also as silicates of forsterite type.

For a silicate devitrificate (the Si group glass) (Fig. 2), which did not contain $MoO_3$ in its composition crystallization occured only in one step at higher temperature and the crystallization products were phosphate of $Ca_9MgK(PO_4)_7$ type and silicate of diopside type ($CaMgSi_2O_6$) (Table 5). The 2Mo41Si glass was also characterized by a single crystallization step, but it took place at significantly lower temperature and XRD analysis of resulting devitrificate showed the presence of $Ca_9MgK(PO_4)_7$ and $CaMgSi_2O_6$.

When the amount of $MoO_3$ in silicate structure was ≥3.3 mol.% in lower range temperature (up to 800 °C) crystallization products were always phosphates of $Ca_9MgK(PO_4)_7$ type and molybdate of $CaMoO_4$ type (powellite). In higher temperature range (800–950 °C) crystallization products were more differentiated, and besides $Ca_9MgK(PO_4)_7$ a new type of silicate i.e., $Ca_2MgSi_2O_7$ type (akermanite) appeared (Table 5). When the amount of $MoO_3$ was 4.1 mol.% the silicate structure changed again from akermanite into merrihueite type ($K_2Mg_5Si_{12}O_{30}$). This type of silicate also occurred when the amount of $MoO_3$ increased to 4.4 mol.%.

It was found that the order of appearance of the crystallization products in the form of phosphates and silicates of the analyzed glasses (Table 5) mainly resulted from the value of the Gibbs free enthalpy of the formation of phosphates and silicates from oxides ($\Delta G$) which determines the probability of their formation (Table 6). It should be noted that in low temperature range compounds of $CaMoO_4$ type crystallized despite the fact that the value of $\Delta G$ of their formation indicates that the crystallization should occur at much higher temperatures.

**Table 4** Thermal stability of analyzed glasses

| No | 0Mo41P | 2Mo41P | 4Mo41P | 8Mo41P | 15Mo41P | 30Mo41P |
|---|---|---|---|---|---|---|
| $\Delta T = T_{c1} - T_g$ | 145 | 331 | – | – | – | – |

| No | 0Mo41Si | 2Mo41Si | 3Mo41Si | 4Mo41Si | 5Mo41Si |
|---|---|---|---|---|---|
| $\Delta T = T_{c1} - T_g$ | 311 | 146 | 71 | 65 | – |

**Table 5** X-ray characteristics of crystallization process of analyzed glasses

| No | Temperature ranges/°C | | | | | |
|---|---|---|---|---|---|---|
| | Do 800 °C | | 800–950 °C | | 950–1,100 °C | |
| | Temperature | Crystallizing phases | Temperature | Crystallizing phases | Temperature | Crystallizing phases |
| 0Mo41P | 674 | $Ca_9MgK(PO_4)_7$ | 856 | $Ca_9MgK(PO_4)_7$<br>$Mg_2SiO_4$ | | |
| 2Mo41P | – | – | 824 | $Ca_9MgK(PO_4)_7$<br>$Mg_2SiO_4$ | | |
| 0Mo41Si | | | – | – | 1,001 | $Ca_9MgK(PO_4)_7$<br>$CaMgSi_2O_6$ |
| 2Mo41Si | – | – | 824 | $Ca_9MgK(PO_4)_7$<br>$CaMgSi_2O_6$ | – | – |
| 3Mo41Si | 750 | $Ca_9MgK(PO_4)_7$<br>$CaMoO_4$ | 852 | $Ca_9MgK(PO_4)_7$<br>$Ca_2MgSi_2O_7$ | – | – |
| 4Mo41Si | 746 | $Ca_9MgK(PO_4)_7$<br>$CaMoO_4$ | 829 | $CaMoO_4$<br>$K_2Mg_5Si_{12}O_{30}$<br>$Ca_9MgK(PO_4)_7$ | – | – |
| 5Mo41Si | 685 | $Ca_9MgK(PO_4)_7$<br>$CaMoO_4$ | 858 | $CaMoO_4$<br>$Ca_9MgK(PO_4)_7$ | – | – |
| | | | 932 | $K_2Mg_5Si_{12}O_{30}$<br>$Ca_9MgK(PO_4)_7$ | | |

**Table 6** Values of $\Delta G$ of the formation of silicates and phosphates crystallizing in analysed glasses [34]

| Compound | $\Delta G_f^0$ [kJ/mol] | | |
|---|---|---|---|
| | 900 K | 1,000 K | 1,100 K |
| $Ca_9MgK(PO_4)_7$ | −18,846 | −19,196 | −19,563 |
| $K_2Mg_5Si_{12}O_{30}$ | −15,336 | −15,534 | −3,762 |
| $CaMgSi_2O_6$ | −3,271 | −3,311 | −3,354 |
| $Mg_2SiO_4$ | −2,255 | −2,282 | −2,311 |
| $CaMoO_4$ | −1,537 | −1,565 | −1,596 |

This suggested, that chemical affinity was thus not the only parameter determining the type of crystallizing phases. According to the concept of multistage crystallization [35, 36] their crystallization was influenced by crystallochemical factors related to strength of chemical bonds between oxygen atoms and framework-forming components and modifiers. The oxygen bridges formed as a result of the introduction of modifiers in the form of CaO, MgO or $MoO_3$ into the phosphate/silicate structure were characterized by some specific strength. As it measure the difference in value of ionicity of bonds ($i_G$) between oxygen and the relevant cation was proposed i.e.; $\Delta i_G$ of Ca–O–Si = 0.279; $\Delta i_G$ of Mg–O–Si = 0.242 and $\Delta i_G$ of $Mo^{6+}$–O–Si = 0.125. The smaller the difference in the ionicity of these bonds, the lower is the strength of the oxygen bridges, and hence the easier is breaking of the bonds between them as a result of the crystallization process. Thanks to this molybdenum was released from the silicate network as the first, forming molybdate of $CaMoO_4$ type (powellite).

## Conclusions

The limited solubility of $MoO_3$ ($4.4 < [MoO_3] < 5.7$ -mol.%) in multi-component glasses from the $SiO_2$–$P_2O_5$–$K_2O$–MgO–CaO system containing high amount of $SiO_2$ was established. Progressively, increased amount of $MoO_3$ in the structure of glasses with both phosphate and inverse silicate matrix $T_g$ temperature gradually decreases. Glasses with silicate matrix (the Si group glass) contrary to glasses with phosphate matrix (the P group glass) showed higher tendency to multistage crystallization with increasing amount of $MoO_3$ in their composition. Besides phosphates and silicates, product of their crystallization was powellite ($CaMoO_4$). The nature of transitions taking place during heating of the analyzed glasses was in accordance with crystallochemical factors (strengths of bonds) and chemical affinity of the glass components ($\Delta G$ of formation).

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