



Thermal properties of MnO₂ and SiO₂ containing phosphate glasses

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Abstract Thermal properties of glasses from the P₂O₅–SiO₂–K₂O–MgO–CaO system modified by MnO₂ addition was studied by DSC, XRD and FTIR methods. It has been found that the replacement of MgO and CaO modifiers by MnO₂ in the structural network of phosphate glasses results in decrease in the glass transition temperature (T_g) and thermal stability parameter (ΔT). The identified crystallization products proved to be diversified, including different type of polyphosphates and silicates. It was determined that the type of the crystallizing phosphate phases is consistent with the classification of phosphate glasses, based on the O/P ratio. During the crystallization in higher temperature ranges and with the content of MnO₂ over 25 mol%, a change of crystallization products was noted, including the transition of the diopside type silicate (CaMgSi₂O₆) into the akermanite type silicate (Ca₂MgSi₂O₇). Simultaneously, the nature of transitions taking place during heating of the analyzed glasses was explained on the basis of crystallochemical factors (strengths of bonds) and chemical affinity of the glass components (ΔG of formation).

Introduction

Phosphate glasses have been extensively studied in recent years because of their interesting applications such as containment of radioactive waste [1], bio-implants [2], magnetic information storage [3], solid-state batteries [4]

and agricultural fertilizers with controlled solubility [5]. Manganese ions have been frequently used for exploring the structure and properties of various kinds of glasses, not only phosphate but also borate [6] and silicate ones [7]. It is known that manganese ions exist in various valence states with a different local symmetry in the glass structure. Thus, the manganese ions appear as Mn²⁺ with both tetrahedral and octahedral coordination and/or as Mn³⁺ with octahedral coordination [8]. It is known that the color of manganese compounds—manganese belonging to transition metals—is the result of the absorption of light by ions not fully filled orbitals “*d*”. Hence the violet color of the glasses is caused by the presence of Mn³⁺ ions with the 3*d*⁴4*s*² electron configuration in their structure, and the yellow tint results from the presence of Mn²⁺ ions with the 3*d*⁵4*s*² electron configuration [9]. Literature data report on the structural role of manganese ions in zinc phosphate [10] or fluorophosphates glasses [11]. Thermal characteristics of phosphate–silicate glasses modified by manganese ions are rarely found in the literature. The literature indicates that phosphate glasses may contain in their matrix up to 40 mol% MnO [12–14].

The available data show that the general trend in phosphate glasses [15] is that the glass transition temperature value decreases with a gradual increase in MnO₂ which can be explained by increasing homogeneity of tested glasses and their very good ability to form. The effect of thermal treatment conditions on the crystallization of phosphate glasses modified with manganese ions is practically not discussed in contemporary literature.

Accordingly, the authors have undertaken detailed studies using DSC, XRD and FTIR techniques to examine the effect of MnO₂ addition into the thermal parameters of phosphate–silicate glasses. In order to determine the role of manganese ions in thermal properties of these glasses, a

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detailed study of glass transition and crystallization was conducted.

Experimental

Phosphate glasses from a P_2O_5 – SiO_2 – K_2O – MgO – CaO system modified by the addition of MnO_2 were prepared. In all glasses, constant quantities of P_2O_5 , K_2O , and SiO_2 were kept, and the increasing amount of MnO_2 was introduced at the expense of the decreasing amount of MgO and CaO , with the constant MgO/CaO ratio. The glasses were produced by traditional melting of a mixture of raw materials, i.e., $(NH_4)_2HPO_4$, SiO_2 , K_2CO_3 , MgO , $CaCO_3$ and MnO_2 at 1100 °C. All glasses were ground to grain size of 0.1–0.3 mm.

The chemical composition of glasses was controlled by X-ray fluorescence spectroscopy using an ARL Advant 'XP spectrometer. The homogeneity of the prepared glasses was checked by X-ray mapping.

The thermal activity of analyzed glasses was determined by the differential scanning calorimetry (DSC) measurements conducted on an STA 449 F1 Jupiter (Netzsch) apparatus, operating in the heat flux DSC mode. Five reference substances, i.e., indium, tin, bismuth, aluminum and gold were used for temperature and heat flow calibration. Samples weighing approx. 40 mg which contained particles of the size of 0.1–0.3 mm were heated to 900 °C in platinum crucibles at the rate of 10 °C/min in a dry nitrogen atmosphere. A good reproducibility of the DSC measurements was confirmed by repeated measurements; reproducibility of the T_g and T_c values was approx. ± 0.5 °C.

The glass transition temperature (T_g) was determined from the midpoint on the enthalpy curve and the crystallization temperature was determined as the onset of the first crystallization peak ($T_{c\text{ onset}}$). According to information contained in manuals [16–19], the beginning of the crystallization temperature is the value which depends to a lesser extent on measurement parameters, such as the rate of heating or the size of the sample than the crystallization temperature determined at the point of the maximum deflection of the crystallization effect. Hence, this temperature was selected to determine the value of thermal stability ΔT . All thermal parameters were calculated using the Proteus Analysis Program (Netzsch).

The ability of glasses to crystallize was evaluated from the values of the thermal stability parameter of glasses $\Delta T = T_{c\text{ onset}} - T_g$. X-ray diffraction method (X'Pert PRO Diffractometer) was applied to identify the crystalline phases created in the isothermal process (5 h) of glass heating at temperatures (T_c) determined from the DSC measurements. The temperature stability was better than ± 5 °C.

Middle infrared (MIR) spectroscopic measurements of devitrificates were taken on a Bruker Vertex 70v spectrometer using the transmission mode. The samples had the form of pellets made of glasses mixed with KBr. Spectra were collected after 124 scans with 4 cm^{-1} resolution. Positions of bands on the MIR spectra were determined automatically by Win-IR software.

Results and discussion

As a result of the melting process, transparent glasses without defects or inclusions were obtained. The conducted chemical analysis of all produced glasses confirmed their nominal chemical composition. The chemical composition of the examined glasses was presented in Table 1. The amorphous state of the analyzed phosphate glasses was confirmed by the X-ray diffraction method (Fig. 1), and their yellow tint indicates that their structure contains mostly Mn^{2+} ions. The results of the thermal analyses show that when the analyzed phosphate glasses are heated, they undergo transitions, i.e., transformation of vitreous state and crystallization.

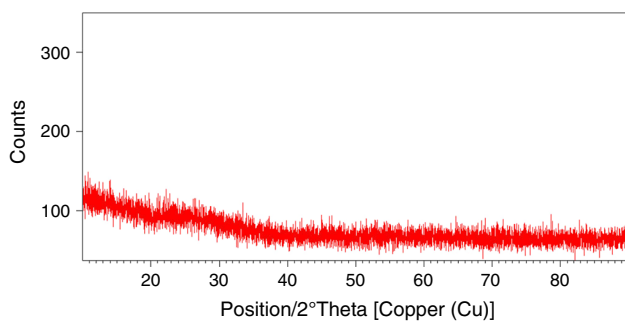
Glass transition effect

The obtained thermal curves are shown in Fig. 2. It was determined that gradual introduction of manganese ions into the structure of the analyzed phosphate glasses at the expense of the decreasing content of calcium and magnesium causes a gradual decrease in the transition temperature (T_g). The values of change of molar heat capacity (Δc_p) which accompanies the transformation of vitreous state did not show any regular changes (Table 2). According to the literature [15], the behavior of T_g can be explained on the basis of crystallochemical factors related to the strength of chemical bonds between oxygen atoms and modifier components. It is known that the ionicity value of bonds between component atoms and oxygen (i_G) [20] is a parameter characterizing strength of the bonds which increases with decreasing ionicity.

In this connection, the more covalent character of Mn^{2+} –O bonds ($i_G = 0.663$) replacing the more ionic bonds such as Ca–O bonds ($i_G = 0.707$) and Mg–O bonds ($i_G = 0.670$) caused the glass structure to become more rigid, while relaxation is easier and requires little energy input. The more rigid the structure is, the less energy-consuming the corresponding transition from the state of rigid body to the viscoelectric state is, in this way glass transition occurs at lower temperatures. This kind of behavior is consistent with previous research carried out by the authors of this publication which analyzed the influence

Table 1 The nominal chemical composition of analyzed glasses and determined by the X-ray fluorescence spectrometry (XRF) (in brackets)

No.	Content of components/mol%					
	SiO ₂	P ₂ O ₅	K ₂ O	MgO	CaO	MnO ₂
1Mn41P	8 (7.7)	41 (40.3)	6 (6.1)	26 (26.4)	18 (18.6)	1 (0.8)
3Mn41P	8 (7.9)	41 (41.1)	6 (5.9)	25 (24.7)	17 (17.1)	3 (3.1)
6Mn41P	8 (7.6)	41 (41.2)	6 (6.1)	23 (22.5)	16 (16.1)	6 (6.4)
12Mn41P	8 (7.5)	41 (42.2)	6 (5.9)	19.5 (19.1)	13.5 (13.3)	12 (11.9)
25Mn41P	8 (8.4)	41 (42.1)	6 (5.8)	11.8 (10.7)	8.2 (7.6)	25 (25.3)
41Mn41P	8 (7.8)	41 (43.0)	6 (6.0)	2.2 (1.8)	1.8 (1.3)	41 (40.0)

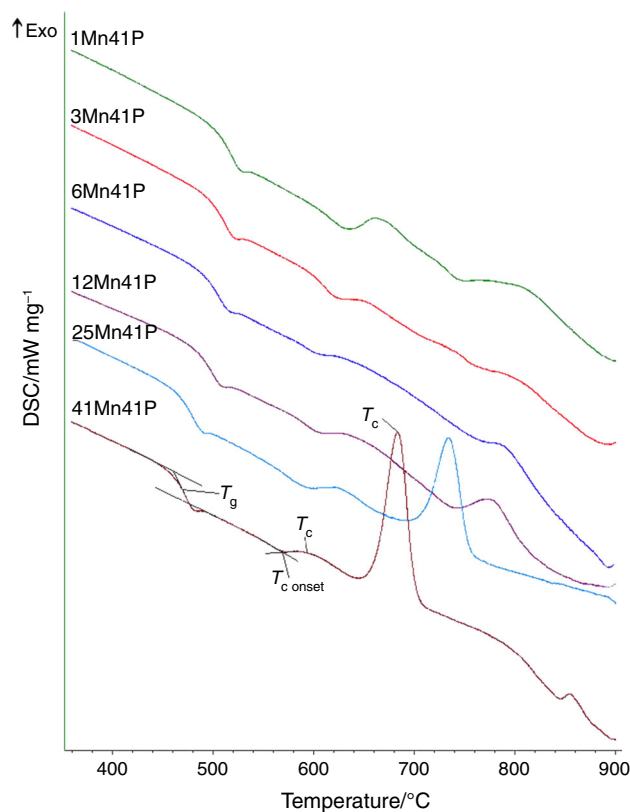
**Fig. 1** XRD pattern of 41Mn41P glass

of added MnO₂ on the structure of silicate glasses from the SiO₂-P₂O₅-K₂O-MgO-CaO system [21].

Crystallization effects

Thermal tests which were carried out enabled us to investigate the influence of the changes in the content of MnO₂ in the chemical composition of the phosphate glasses on their thermal activity (ΔT) and the type of crystallizing phases. Based on the test results, it was determined that the parameter ΔT , which expresses the ability of the glasses to crystallize, shows gradually decreasing values, which indicates that the ability of the glasses to crystallize grows at the same time (Table 3).

In all analyzed glasses, the crystallization process was a multi-stage process that showed two effects of crystallization on DSC curves in the lower and higher temperature ranges (Fig. 2). The first range was observed at temperatures ranging from 660 to 580 °C, and the second range at temperatures ranging from 810 to 680 °C. In both temperature ranges, the gradual introduction of increasing amounts of MnO₂ into the chemical composition of the glasses facilitated the shift of those thermal effects ($T_{c\text{ onset}}$) toward lower temperatures (Fig. 2).

**Fig. 2** DSC curves of analyzed phosphate-silicate glasses modified with the addition of MnO₂

The crystallization products proved to be diversified and included mostly various types of phosphates and silicates. The types of crystallizing phases are fully identified in Table 4, and some chosen diffractograms are shown in Figs. 3 and 4.

Based on X-ray data, it was determined that in the lower temperature range (660–580 °C) and the lowest content of MnO₂ (1Mn41P) in the composition of the tested glasses, there appeared polyphosphates, i.e., CaK₂(P₂O₇),

Table 2 Thermal characteristics of glass transition region of MnO₂-doped phosphate–silicate glasses

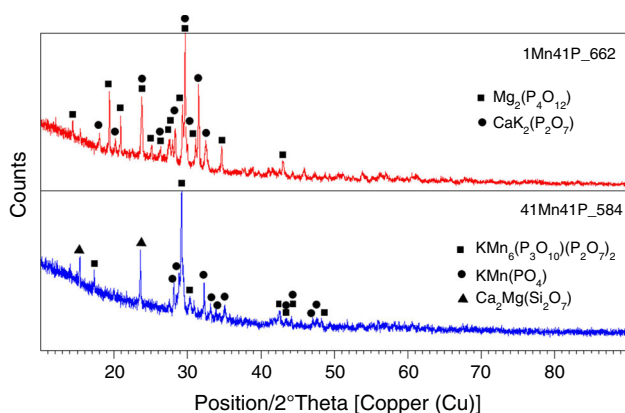
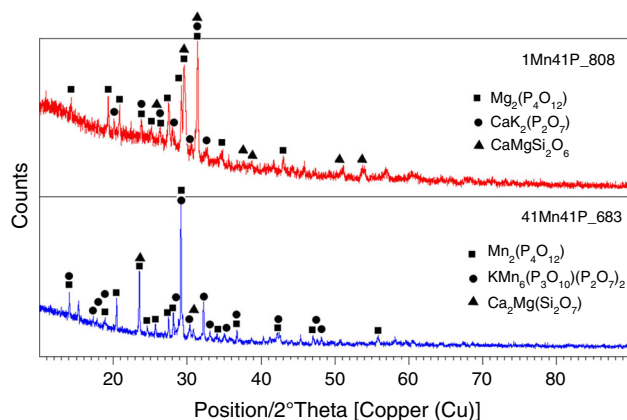
	1Mn41P	3Mn41P	6Mn41P	12Mn41P	25Mn41P	41Mn41P
$T_g/^\circ\text{C}$	511	505	499	492	474	467
$\Delta c_p/J\text{ g}^{-1}\text{ K}^{-1}$	0.25	0.24	0.25	0.25	0.26	0.25

Table 3 Values of ΔT parameter of MnO₂-doped phosphate glasses

	1Mn41P	3Mn41P	6Mn41P	12Mn41P	25Mn41P	41Mn41P
$\Delta T = T_{c\text{ onset}} - T_g$	120	116	107	111	116	101

Table 4 XRD characteristics of crystallization process of analyzed phosphate–silicate glasses

No. of sample	$T_c/^\circ\text{C}$	Crystallizing phase/ICSD code	$T_c/^\circ\text{C}$	Crystallizing phase/ICSD code
1Mn41P	662	Mg ₂ (P ₄ O ₁₂)/98-000-4280	808	Mg ₂ (P ₄ O ₁₂)/98-000-4280
		CaK ₂ (P ₂ O ₇)/98-028-1572		CaK ₂ (P ₂ O ₇)/98-028-1572
3Mn41P	647	KMg(PO ₃) ₃ /98-002-8012	802	CaMn(P ₂ O ₇)/98-008-3580
		CaMn(P ₂ O ₇)/98-008-3580		Mg ₂ (P ₄ O ₁₂)/98-000-4280
		Mg ₂ (P ₄ O ₁₂)/98-000-4280		CaMgSi ₂ O ₆ /98-016-1054
6Mn41P	632	KMg(PO ₃) ₃ /98-002-8012	790	CaMn(P ₂ O ₇)/98-008-3580
		CaMn(P ₂ O ₇)/98-008-3580		Mg ₂ (P ₄ O ₁₂)/98-000-4280
		Mg ₂ (P ₄ O ₁₂)/98-000-4280		CaMgSi ₂ O ₆ /98-016-1051
12Mn41P	627	KMg(PO ₃) ₃ /98-002-8012	773	CaMn(P ₂ O ₇)/98-008-3580
		CaMn(P ₂ O ₇)/98-008-3580		Mg ₂ (P ₄ O ₁₂)/98-000-4280
		Mg ₂ (P ₄ O ₁₂)/98-000-4280		CaMgSi ₂ O ₆ /98-016-1051
25Mn41P	623	KMn ₆ (P ₃ O ₁₀)(P ₂ O ₇) ₂ /98-015-7156	735	KMn ₆ (P ₃ O ₁₀)(P ₂ O ₇) ₂ /98-015-7156
		KMg(PO ₃) ₃ /98-002-8012		Mn ₂ (P ₄ O ₁₂)/98-041-2558
		Mn ₂ P ₄ O ₁₂ /98-041-2558		(Ca _{0.7} Mg _{1.3})(Si ₂ O ₆)/98-015-2226
41Mn41P	584	KMn ₆ (P ₃ O ₁₀)(P ₂ O ₇) ₂ /98-015-7156	683	Mn ₂ (P ₄ O ₁₂)/98-041-2558
		KMn(PO ₄)/98-007-8840		KMn ₆ (P ₃ O ₁₀)(P ₂ O ₇) ₂ /98-015-7156
		Ca ₂ Mg(Si ₂ O ₇)/98-016-0358		Ca ₂ Mg(Si ₂ O ₇)/98-016-0357

**Fig. 3** XRD patterns of selected devitrificates of MnO₂-doped phosphate glasses (lower temperature range)**Fig. 4** XRD patterns of selected devitrificates of MnO₂-doped phosphate glasses (higher temperature range)

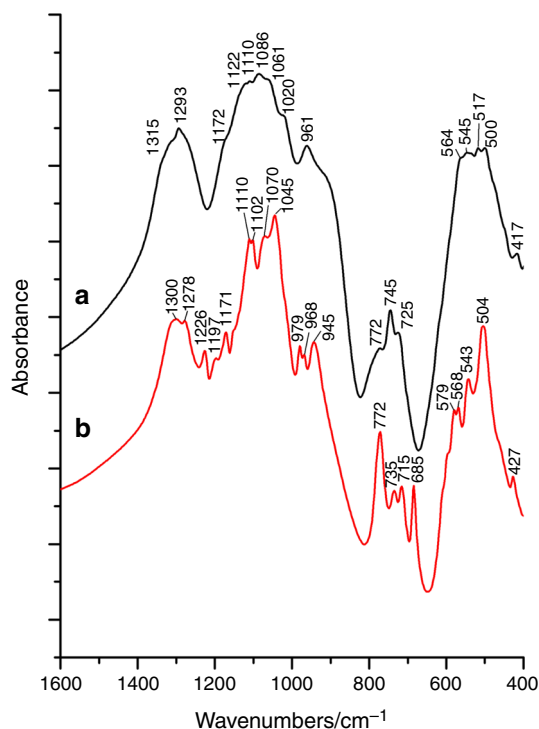


Fig. 5 FTIR spectra of selected recrystallized glasses: a 1Mn41P_808 °C, b 41Mn41P_687 °C

Mg₂(P₄O₁₂). It was also determined that with the introduction of ever larger amounts of MnO₂ into the chemical composition of the glasses, the manganese ions first replaced potassium ions in the crystallization products, which was accompanied by a change of the crystallization product from

CaK₂(P₂O₇) to CaMn(P₂O₇) and then, with the content of MnO₂ over 25 mol% (25Mn41P and 41Mn41P) created crystallization products in the form of poly- and orthophosphates of KMn₆(P₃O₁₀) (P₂O₇)₂ and KMn(PO₄) type (Table 4; Fig. 3).

The crystallization products identified in the higher temperature range proved to be more diversified, because, apart from products of phosphate types, the crystallization of the silicate matrix was determined. In the glasses containing less than 25 mol% MnO₂, in a way similar to the lower temperature range, the presence of polyphosphates of Mg₂(P₄O₁₂), CaK₂(P₂O₇), CaMn(P₂O₇) types was determined, and in the 25Mn41P and 41Mn41P glasses, apart from KMn₆(P₃O₁₀) (P₂O₇)₂ and Mn₂(P₄O₁₂) phosphate types, there were also crystallization products in the form of silicates (Table 4; Fig. 4). The first identified crystallization product in the higher temperature range was diopside type silicate CaMgSi₂O₆, which only at the content of MnO₂ over 25 mol% transformed into akermanite type silicate Ca₂Mg(Si₂O₇). It should also be emphasized that this silicate was also identified in the lower temperature range in the sample containing 40 mol% MnO₂ (41Mn41P).

As it was very difficult to interpret the XRD results in XRD results related to overlapping of diffraction peaks, it was necessary to confirm the kind of identified crystallizing phases by an alternative method, and thus FTIR method was used. Spectra of selected devitrificates are presented in Fig. 5. The FTIR spectrum of devitrificate of 1Mn41P glass (808 °C) indicated the existence of bands at about 500, 517

Table 5 The O/P ratio of the glasses from analyzed P₂O₅-SiO₂-K₂O-CaO-MgO-MnO₂ system

No	1Mn41P	3Mn41P	6Mn41P	12Mn41P	25Mn41P	41Mn41P
O/P	3.35	3.35	3.38	3.41	3.59	3.72

Table 6 Values of ΔG_f⁰ of the formation of silicates and phosphates crystallizing in analyzed phosphate-silicate glasses

Compound	ΔG _f ⁰ /kJ/mol		
	900/K	1000/K	1100/K
KMn(PO ₄) = 0.5K ₂ O·MnO·½ P ₂ O ₅	-568.8	-582.4	-596.6
CaMg(Si ₂ O ₆) = CaO·MgO·2SiO ₂	-781.8	-791.5	-801.8
Ca ₂ Mg(Si ₂ O ₇) = 2CaO·MgO·2SiO ₂	-946.5	-958.5	-971.2
CaMn(P ₂ O ₇) = CaO·MnO·P ₂ O ₅	-1077.3	-1099.1	-1121.9
CaK ₂ (P ₂ O ₇) = CaO·K ₂ O·P ₂ O ₅	-1083.5	-1107.5	-1132.5
Mn ₂ (P ₄ O ₁₂) = 2MnO·2P ₂ O ₅	-1825.3	-1864.4	-1905.1
Mg ₂ (P ₄ O ₁₂) = 2MgO·2P ₂ O ₅	-1913.7	-1951.0	-1990.0
KMg(PO ₃) ₃ = K ₂ O·2MgO·3P ₂ O ₅	-2832.6	-2891.6	-2953.2
KMn ₆ (P ₃ O ₁₀)(P ₂ O ₇) ₂ = 0.5K ₂ O·6MnO·¾ P ₂ O ₅	-3525.5	-3603.3	-3684.6

and 1010 cm^{-1} which corresponded to Si–O bonds characteristic for diopside [22]. The existence of absorption bands at about 500, 560, 725, 1000 and 1086 cm^{-1} could be attributed to the P–O stretching modes of PO_3 units [23] characteristic for $\text{Ca}_2\text{P}_2\text{O}_7$. This could confirm the presence of $\text{CaK}_2(\text{P}_2\text{O}_7)$ in the structure of analyzed devitrificates. FTIR spectrum of devitrificate of 41Mn41P glass ($687\text{ }^\circ\text{C}$) indicated the existence of bands characteristic of $\text{Mn}_2\text{P}_4\text{O}_{12}$ ($504, 715, 735, 1278, 1300\text{ cm}^{-1}$) [24] and akermanite ($504, 685, 979, 1045\text{ cm}^{-1}$) [22].

From the presented analysis of crystallization products, the consistency of the type of the crystallizing phases can be seen with the well-known classification of phosphate glasses, based on the O/P ratio [25]. The measured values of this parameter for all analyzed phosphate–silicate glasses are presented in Table 5.

Simultaneously, it was observed that during the crystallization process manganese ions tend to incorporate in the phosphate structure but not into the silicates that appear in the higher temperature ranges. The explanation of this phenomenon is the higher affinity of manganese ions to phosphorus ions then to silicon ions. As a measure of the chemical affinity, the difference in the ionicity of cations forming P–O– Mn^{2+} ($i_G = 0.349$) and Si–O– Mn^{2+} ($i_G = 0.235$) bonds was taken [20]. The higher difference in the ionicity of these bonds means the formation of more covalent bonds being the nucleus of crystalline phases, e.g., in the form of $\text{Mn}_2(\text{P}_4\text{O}_{12})$ or $\text{CaMn}(\text{P}_2\text{O}_7)$.

It is also noteworthy that in the tested glasses, the type of the crystallizing compounds is consistent with the enthalpy values of the formation of phosphates and silicates from oxides ΔG , showed in Table 6. From among several reactions which may occur in the given systems, the most probable to occur is the one with the lowest, negative ΔG value. Thus the crystallization of phosphates at the first stage of glass crystallization proceeds, while crystallization of silicates occurs in the higher temperature range. A comparison of ΔG values of the formation of particular phosphates from the oxides with the sequence of their formation at the first stage of crystallization indicates that chemical affinity is also the parameter determining the sequence. For example, from among the crystallized phosphates: $\text{Mg}_2(\text{P}_4\text{O}_{12})$, $\text{CaK}_2(\text{P}_2\text{O}_7)$ and $\text{KMg}(\text{PO}_3)_3$ are the first to crystallize in glasses containing low amounts of manganese. If higher amounts of manganese are introduced into the structure of the glasses under analysis at the expense of calcium and magnesium, phosphates crystallize which contain manganese and are characterized by similar ΔG values of the formation. Only from among the phosphates, KMnPO_4 is the first to crystallize despite its low ΔG value.

Conclusions

Using differential scanning calorimetry, X-ray diffraction analysis and Fourier Transform Infrared spectroscopy, the influence of manganese ions on thermal properties of glasses from the P_2O_5 – SiO_2 – K_2O – CaO – MgO system was evaluated. It was determined that the value of the transition temperature (T_g) decreased gradually and the crystallization ability increased. Diversified crystallization products were identified in the tested glasses, in the form of phosphates and silicates. Furthermore, it was determined that the type of the crystallizing phosphate phases were consistent with the classification of phosphate glasses, based on the O/P ratio. Simultaneously, it was observed that during the crystallization process manganese ions tend to incorporate in the structure of phosphates rather than silicates. Simultaneously, the transitions taking place during heating of the analyzed glasses were explained on the basis of crystallochemical factors (strengths of bonds) and chemical affinity of the glass components (G of formation).

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