J Therm Anal Calorim (2012) 108:583–588
DOI 10.1007/s10973-011-1941-7

Thermal study of Mn-containing silicate–phosphate glasses

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MEDICTA 2011 Conference Special Chapter

Abstract Silicate-phosphate glasses of SiO_2–P_2O_5–K_2O–MgO–CaO system containing manganese cations were investigated to obtain information about the influence of manganese ions on the thermal behavior of such glasses. Amorphous state of glasses and the course of phase transformation and crystallization taking place during their heating were investigated by DSC, XRD, and FTIR methods. It was shown that an increasing content of manganese replacing calcium and magnesium in the structure of analyzed glasses causes decrease of glass transition temperature (T_g) and heat capacity change (Δc_p) accompanying the glass transformation. Simultaneously, thermal stability of the glasses increased. Products of multistage crystallization of glasses containing up to 8 mol% of MnO_2 were: marokite ($CaMn_2O_4$), phosphate of $Ca_9MgK(PO_4)_7$ type, and diopside ($CaMgSi_2O_6$). Product of crystallization of glasses containing higher amount of manganese was braunite ($Mn_7O_8SiO_4$). This was accompanied by change of structure of magnesium calcium silicates from diopside-type structure to akermanite-type silicates ($Ca_2MgSi_2O_7$). The data interpretation was based on bonds and chemical interactions of the individual components forming the glass structure.

Keywords Silicate–phosphate glasses · Thermal stability · Crystallization effect · Structure

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Introduction

One of the interesting glass structure modifier is manganese, which is also applicable in metallurgy, as a component and alloy addition increasing their hardness and resistance to abrasion, but also in the form of chemicals for the manufacture of disinfectants or chemical analysis [1]. Manganese compounds, as well as iron and copper are among the most frequently used coloring agent of glasses, giving them shade of blue or red. The most commonly and widely used is natural manganese dioxide—MnO_2 [2].

In the view of the wide possibilities of application of this element literature data report on its addition to the structure of silicate, phosphate, fluorine–phosphate,and fluorine–borate glasses. Manganese ions, as well as iron ions, have the ability of taking different oxidation states depending on the type of vitreous matrix in which they are. Manganese in borate glasses may be in octahedral coordination as Mn^{3+}, whereas in silicate and germanium glasses in the form of Mn^{2+} both in octahedral and tetrahedral coordination [3, 4].

The literature reports that the amount of manganese in different oxidation states in the glassy structure depends for example on a quantitative comparison of modifiers to glass former components, as well as their size and field strength [3]. Manganese ions (Mn^{2+}, Mn^{3+}) are characterized by paramagnetic properties, and therefore, are often referred to as luminescent activators [5] and hence, many publications are concentrated on effect of manganese ions on optical and thermoluminescence properties of glasses [3, 5–7].

Manganese-containing glasses have also unconventional application. It turned out, that biologically active silicate–phosphate glasses may be a carrier of manganese fulfilling the role of microelement necessary for proper development of plants [8, 9]. Influence of manganese on plants growth process is mainly related to regulation of ox–redox reactions and activation of some enzymes in metabolic processes of plants.

Thermal characteristics of glasses modified by manganese ions are rarely found taken in the literature. Information covering a range of glass transition and crystallization process mainly concerns phosphate or borate glasses. The available data shows that in the case of phosphate [10] or borate glasses [3] a gradual increase of MnO (0.1–0.4 mol%) increases the transformation temperature which can be explained by increasing homogeneity of tested glasses and their very good ability to forming [5]. In the case of alumino-phosphate glasses with increase of MnO_2 in their composition (10–50 mol%) their transition temperature gradually decreases and their ability to crystallization increases [7]. However, in the case of sodium–phosphate doped with 1, 5, and 10% mol $MnCl_2$ [11] it was found that with increasing amount of Mn, T_g temperature gradually decreases. According to the authors [11, 12], thermal behavior of the phosphate glasses may be associated with increasing cross-linking density of the vitreous structure which is also a sign of improved chemical resistance of the glasses.

The main reason for undertaking research on effects of manganese on thermal stability and crystallization process of glasses from SiO_2–P_2O_5–K_2O–MgO–CaO system was lack of data concerning thermal characteristics of phosphate-silicate glasses modified by this element.

Table 1 Chemical composition of silicate–phosphate glasses, mol%, determined by X-ray fluorescence spectrometry method

No	Chemical composition of silicate–phosphate glasses/mol%					
	SiO_2	P_2O_5	K_2O	MgO	CaO	MnO_2
0Mn	42.59	6.47	6.74	21.22	22.98	0.00
1.7Mn	43.60	6.17	7.06	19.82	21.65	1.71
3.3Mn	44.17	6.71	7.06	18.44	20.35	3.26
6.8Mn	43.39	6.68	7.00	16.97	19.20	6.77
12.8Mn	43.78	6.52	7.05	14.05	15.76	12.84
25.7Mn	43.79	6.83	7.11	7.79	8.79	25.7

This type of glasses can be used in practice as ecological fertilizers providing a controlled release rate of nutrients such as, phosphorus, potassium, calcium, magnesium, and manganese ions [13, 14].

Experimental

Silicate–phosphate glasses from SiO_2–P_2O_5–K_2O–CaO–MgO system modified by MnO_2 addition 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 cost of the decreasing amount of MgO and CaO, with the constant MgO/CaO ratio. The silicate–phosphate glasses were produced by melting of raw materials mixture, i.e., SiO_2, H_3PO_4, K_2CO_3, MgO, $CaCO_3$, and MnO_2 in platinum crucibles at 1450 °C. Then the obtained amorphous material was fritted in water. 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 ARL Advant 'XP spectrometer. Chemical composition of the examined glasses was presented in Table 1. Amorphous state of the analyzed silicate–phosphate glasses was confirmed by X-ray diffraction method (Fig. 1).

The thermal stability of obtained glasses was determined by DSC measurements conducted on STA 449 *F3 Jupiter*®7 (Netzsch) operating in the heat flux DSC mode. The samples (~40 mg) were heated in platinum crucibles at a rate of 10 °C min^{-1} in dry nitrogen atmosphere up to 1,100 °C. The glass transition temperature (T_g) was determined from the inflection point on the enthalpy curve and all thermal parameters were calculated using the Proteus Analysis Program (Netzsch). The ability of glasses to

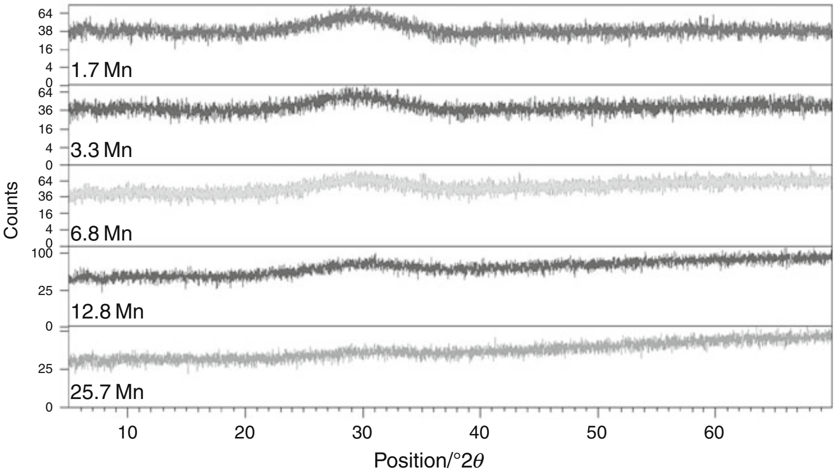

Fig. 1 XRD patterns of analyzed silicate–phosphate glasses

crystallize was evaluated from the values of crystallization temperature T_{cryst} and the thermal stability parameter of glasses $\Delta T = T_{krys} - T_g$. X-ray diffraction method (X'Pert PRO Diffractometer) was applied to identify the crystalline phases created in the isothermal process of glass heating at temperatures determined from the DSC measurements. Fourier transformation infrared spectroscopy (FTIR) studies of crystallized forms of glasses were carried out on FTS 60v (Digilab) spectrometers in MIR range (400–4,000 cm^{-1}). The samples were prepared in the form of KBr pellets.

Results and discussion

The thermal studies showed that during the heating process the glasses from SiO_2–P_2O_5–CaO–MgO–K_2O–MnO_2 system underwent typical phase changes, namely glass transformation and crystallization (Fig. 2).

Glassy state transition

Effect of chemical composition of the analyzed glasses on the parameters that describe the transformation of glassy state were placed in Table 2.

Silicate–phosphate glass containing no modifier in the form of manganese cations (0Mn) was characterized by the highest transition temperature (T_g) and highest value of specific heat (Δc_p). The introduction of Mn ions into the structure caused gradual and systematic decrease of values of T_g and Δc_p. This phenomena can be explained on the basis of crystallochemical factors connected with strength of chemical bonds between oxygen atoms and framework-forming components and modifiers [15].

Table 2 Thermal characteristics of glass transformation of MnO_2-doped silicate–phosphate glasses

No	0Mn	1.7Mn	3.3Mn	6.8Mn	12.8Mn	25.7Mn
T_g/°C	697	689	679	667	647	619
Δc_p/J/g K	0.37	0.35	0.35	0.35	0.33	0.33

The characteristics of chemical bonds and interactions of atoms in the structure of silicate–phosphate glasses based on parameters proposed by Görlich [16] was presented in Table 3.

It is known, that the ionicity value of bonds between component atoms and oxygen (i_G) is a parameter characterizing strength of the bonds, which increases with decreasing ionicity. Introduction of increasing amounts of MnO_2 to the structure of the studied silicate-phosphate glasses at the cost of decreasing content of MgO and CaO was associated with an increasing number of Mn^{+2}–O type

Table 3 Characteristics of chemical bonds occurring in structure of the analyzed silicate–phosphate glasses [16]

Chemical bond cation—oxygen type	i_G	Oxygen bridges	Δi_G	Oxygen bridges	Δi_G
K–O	0.823	K–O–P	0.509	K–O–Si	0.395
Ca–O	0.707	Ca–O–P	0.393	Ca–O–Si	0.279
Mg–O	0.670	Mg–O–P	0.356	Mg–O–Si	0.242
Mn^{+2}–O	0.663	Mn^{+2}–O–P	0.349	Mn^{+2}–O–Si	0.235
Mn^{+3}–O	0.505	Mn^{+3}–O–P	0.191	Mn^{+3}–O–Si	0.077
Si–O	0.428	Si–O–P	0.114	Si–O–Si	0.000
P–O	0.314	P–O–P	0.000	P–O–Si	0.114

Fig. 2 DSC curves of analyzed silicate–phosphate glasses modified by MnO2 addition

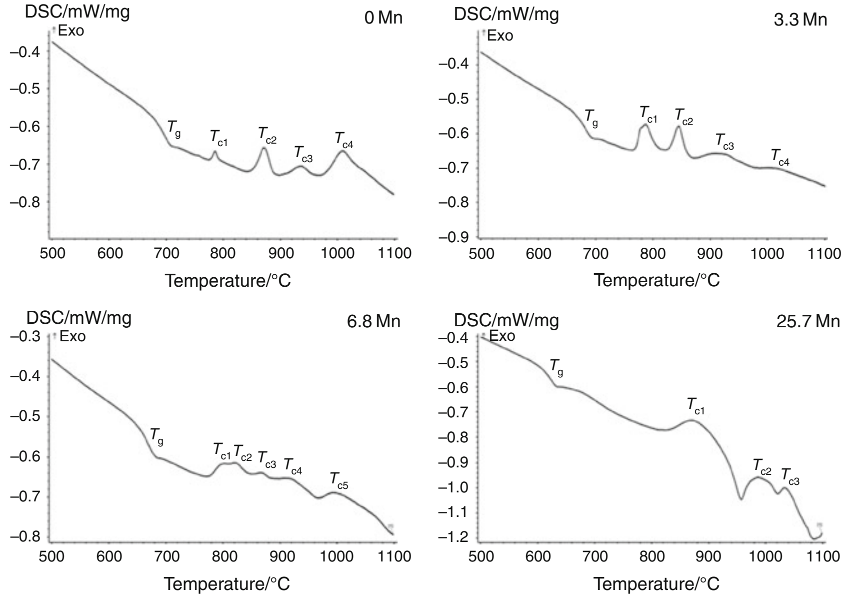

Table 4 Thermal characteristics of crystallization process of MnO_2-doped silicate–phosphate glasses

No.	T_{c1}/°C	T_{c2}/°C	T_{c3}/°C	T_{c4}/°C	T_{c5}/°C
0Mn	786	872	935	1,009	
1.7Mn	828	893	949	973	1,038
3.3Mn	778	786	845	925	1,018
6.8Mn	796	822	866	920	1,007
12.8Mn	892	998	1,043		
25.7Mn	889	987	1,036		

bonds. Violet color of glasses suggested the presence of Mn^{+2} ions in the glass structure [2]. This type of chemical bonds is characterized by lower ionicity ($i_G = 0.663$) in comparison to ionicity of Ca–O (0.707) and Mg–O (0.670) bonds. Simultaneously increasing the amount of structural stresses, the relaxation is easier and requires little energy input. For this reason glass transition occurs in lower temperatures which also correlates with lower values of Δc_p (Table 2).

Crystallization of glasses

Effect of chemical composition of the analyzed glasses on their crystallization temperatures was presented in Table 4.

Based on T_g (Table 2) and T_{c1} (Table 4) values, a thermal stability parameter (ΔT) of the glasses was determined. The DSC studies showed a higher thermal stability of the glasses with increasing amounts of MnO_2 in their structure manifested by higher thermal stability parameter ΔT (Table 5).

Table 5 Thermal and X-ray characteristics of crystallization process of analyzed silicate–phosphate glasses

Glass	$\Delta T = T_c - T_g$/°C	Temperature ranges/°C	Crystallising phases
0Mn	89	750–900	$Ca_9MgK(PO_4)_7$
		900–1,100	$Ca_9MgK(PO_4)_7$, $CaMgSi_2O_6$
1.7Mn	139	800–850	$Ca_9MgK(PO_4)_7$, $CaMn_2O_4$
		850–1,100	$Ca_9MgK(PO_4)_7$, $CaMgSi_2O_6$
3.3Mn	99	750–880	$Ca_9MgK(PO_4)_7$, $CaMn_2O_4$
		880–1,100	$Ca_9MgK(PO_4)_7$, $CaMgSi_2O_6$
6.8Mn	129	770–950	$Ca_9MgK(PO_4)_7$, $CaMn_2O_4$
		950–1,100	$Ca_9MgK(PO_4)_7$, $CaMgSi_2O_6$
12.8Mn	245	820–960	$Ca_9MgK(PO_4)_7$, $Mn_7O_8SiO_4$
		960–1,100	$Ca_9MgK(PO_4)_7$, $CaMgSi_2O_6$, $Mn_7O_8SiO_4$
25.7Mn	270	840–1,000	$Ca_9MgK(PO_4)_7$, $Mn_7O_8SiO_4$
		1,000–1,100	$Ca_9MgK(PO_4)_7$, $Mn_7O_8SiO_4$, $Ca_2MgSi_2O_7$

Thermal curves (Fig. 2) showed that the silicate-phosphate glasses indicated a multistage crystallization. The crystallization of 0Mn glass was multistage process with four well distinguished stages (Fig. 2, Table 4). As a result of introduction of 1.7, 3.3 and 6.8 mol% of MnO_2 into the glass structure the course of crystallization changed into five stages but occurred in wider temperature range and at higher temperatures. The introduction of increasing amount of MnO_2 to the composition of the analyzed glasses (up to 25.7 mol%) changed the character of thermal curves. Thermal effects were overlapping each other and number of thermal effects was reduced from five to three.

XRD study showed that type of crystallizing phases was the same at close crystallization temperatures and thus the XRD results was presented for two temperature ranges (Table 5). In the analyzed temperature ranges the crystallization product in all recrystallized glasses was always phosphate of $Ca_9MgK(PO_4)_7$ type (Fig. 3). The analyzed devitrificates at higher temperature ranges i.e., about 1,000 °C crystallized not only in the form of phosphates but also silicates of diopside type and orthosilicates of $Mn_7O_8SiO_4$ type. In the case of 25.7 Mn sample it was found that the structure of silicate phase changes from a structure of diopside type ($CaMgSi_2O_6$) to a structure corresponding to akermanite type ($Ca_2MgSi_2O_7$) (Fig. 4; Table 5).

Glasses containing up to 6.8 mol% MnO_2 in their composition were characterized by crystallization of calcium dimanganese tetraoxide of $CaMn_2O_4$ type (marokite). When the amount of MnO_2 in the composition of the analyzed glasses was 12.8 mol%, the type of crystallization product was manganese orthosilicate of braunite type ($Mn_7O_8SiO_4$).

In connection with very difficult interpretation of 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 were presented in Fig. 5. FTIR spectrum of devitrificate of 12.8Mn_920 indicated the existence of bands at 522, 478, and 431 cm^{-1} which could be attributed to the symmetric stretching modes of MnO_6 units [17]. This confirms the presence of marokite ($CaMn_2O_4$) in the structure of analyzed devitrificate. Absorption bands occurring in the spectrum of the devitrificate of 12.8Mn_1040 at 475, 512, 970, and 1,080 cm^{-1} corresponded to Si–O bonds characteristic for diopside [18]. In FTIR spectra of devitrificate of 25.7Mn_920 bands at 484, 556, 610, and 1,097 cm^{-1} were presented which corresponded to Si–O bonds characteristic for akermanite [19].

Analysis of the absorption bands of FTIR spectra of glasses containing 8 and 15 mol% MnO_2 in its structure showed the occurrence of bands located at about 555, 591,

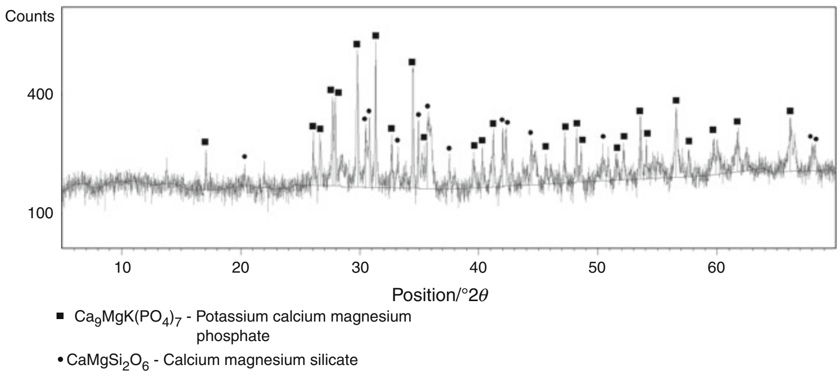

Fig. 3 XRD analyses of 6.8Mn devitrificate of silicate–phosphate glasses

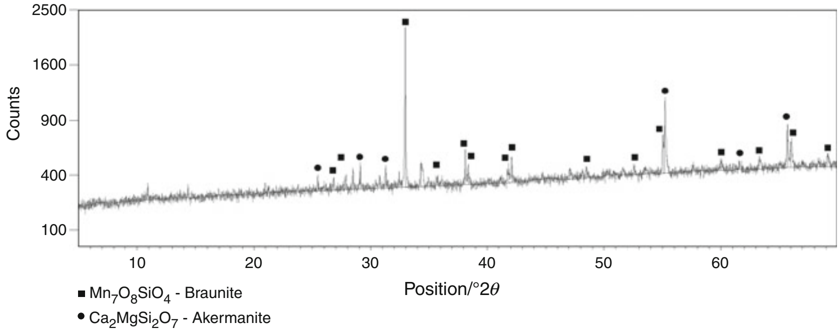

Fig. 4 XRD analyses of 25.7Mn devitrificate of silicate–phosphate glasses

600, and 610 cm^{-1}. Their positions corresponded to PO_4 vibrations (555, 593, 605 and 614 cm^{-1}) occurring in phosphates of whitlockite type ($Ca_7MgK(PO_4)_7$) [20].

It was found that a sequence of the appearance of products of crystallization of the analyzed glasses, which were in the form of silicates or phosphates, was governed by the value of free Gibbs enthalpy of formation of phosphates and silicates from oxides (ΔG), which in turn determines probability of their formation (Table 6). ΔG values shown in Table 6 were based on data found in the literature [21].

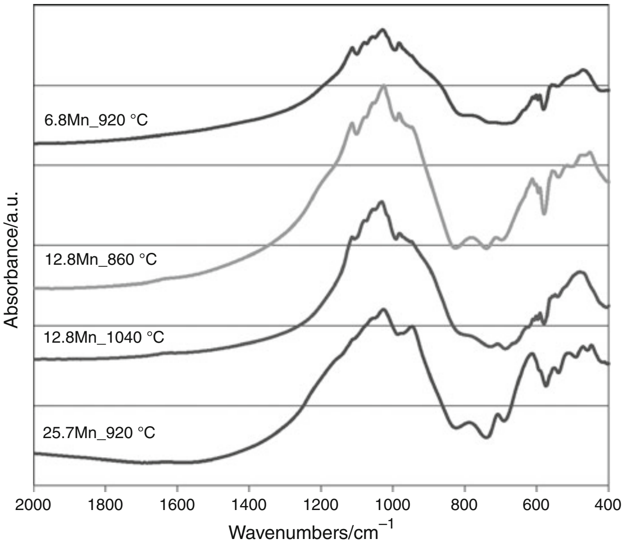

Fig. 5 FTIR spectra of selected recrystallized glasses

The order of appearance of the crystallization products in the form of phosphates and silicates resulted from the value of the Gibbs free enthalpy of the formation of phosphates ($Ca_9MgK(PO_4)_7$: $\Delta G^0_{900} = -18{,}846$ kJ/mol) and silicates ($Mn_7O_8SiO_4$: $\Delta G^0_{1000} = -4598$ kJ/mol) from oxides which determines the probability of their formation.

Because of the low crystallization temperature of marokite ($CaMn_2O_4$) its chemical affinity is thus not the only parameter determining the type of crystallizing phase. According to the conception of multistage crystallization [22, 23], its crystallization was influenced by factors of crystalochemical nature. This refers to the difference of ionicity of bonds in oxygen bridges (Δi_G) which decrease indicated decrease of strength of the bonds. Therefore, as the first crystallized compounds of the modifiers which create the weakest bonds in the silicate–phosphate network (Table 3). Thanks to this manganese was released from the

Table 6 Values of ΔG of the formation of silicates and phosphates crystallizing in analyzed silicate–phosphate glasses

Compounds	ΔG^0_f/kJ/mol		
	900 K	1,000 K	1,100 K
$9CaO\cdots MgO\cdots 0.5K_2O\cdots 3,\ 5P_2O_5$	−18,846	−19,196	−19,563
$7MnO\cdots SiO_2\cdots 1.5O_2$	−4,468	−4,598	−4,732
$2CaO\cdots MgO\cdots 2SiO_2$	−3,960	−4,010	−4,063
$CaO\cdots MgO\cdots 2SiO_2$	−3,271	−3,311	−3,354
$CaO\cdots Mn_2O_3$	−1,789	−1,823	−1,859

silicate–phosphate network as the first forming $CaMn_2O_4$ compound.

Conclusions

Using methods of differential scanning calorimetry (DSC), X-ray diffraction analysis (XRD), and FTIR spectroscopy the influence of manganese ions on thermal behavior of SiO_2–P_2O_5–K_2O–CaO–MgO system was evaluated. It was found that progressively increased amount of MnO_2 in the composition of the analyzed glasses decreased the glass transformation temperature (T_g) and specific heat (Δc_p) accompanying this transition. Simultaneously, introduction of increasing amount of MnO_2 caused the change of the course and type of crystallization products and decreased the ability of glass to crystallization. The nature of transitions taking place during heating of the analyzed glasses was explained on the basis of strengths of oxygen bridges and chemical affinity of the glass components.

Acknowledgements The study was supported by the Grant No. N R08 0010 06 of the Polish Ministry of Science Higher Education and by Faculty of Materials Science and Ceramics AGH – University of Science and Technology (2011) No. 11.11.160.364.

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